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Flux Enhancement in Ultrafiltration of Bitumen Emulsions Using Tubular Polyvinyldiene Flouride Membranes

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New emulsified bitumen fuels pose an extreme challenge to ultrafiltration (UF) membranes, rapidly depositing and adhering tar solids on membrane surfaces. In this paper, results of pilot tests demonstrating maintenance of permeate flux in such applications are described. Tubular polyvinyldiene fluoride (PVDF) membranes for ultrafiltration were shown to effectively remove Orimulsion®, a bitumen fuel emulsion, from water, resulting in a permeate quality less than 2.0 mg/L as volatile suspended solids, at an average permeate flux on the order of 35–310 Lph/m^2 (21–182 gpd/ft^2). The use of one part bentonite clay to ten parts Orimulsion® solids, by mass, was found to enhance permeate flux and improve membrane cleaning. Although additives were not necessary to obtain suitable flux rates or restore permeate flux, their use was shown to reduce membrane costs considerably. Practical methods for cleaning membranes fouled with bitumen suspensions in water, with and without the presence of filtration additives, are presented. Experimental results revealed that flux regeneration was possible. Further testing included development of an optimal cleaning schedule using a simple mathematical relationship based on pilot data.

Key Words. Ultrafiltration; Fouling; Tubular PVDF membranes; Cleaning; Bitumen emulsions

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INTRODUCTION

Orimulsion® fuel is a surfactant-stabilized emulsion composed of bitumen in water, which is manufactured in Venezuela for use in electric-power-generation facilities as a cost-competitive alternative to conventional fossil fuels. Chemically Orimulsion® is characterized by lower levels of volatiles and low-molecular-weight aromatics than fuel oil no. 6 (1, 2, 3). The Orimulsion® product consists of natural Orinoco bitumen droplets approximately 10–20 μm in diameter (70–71%), water (28–29%), and a stabilizing, water-soluble, nonylphenol ethoxylate surfactant with small trace metal fractions containing nickel, magnesium, and vanadium ($<1\%$) (density = 1.0139 g/mL) (4, 5, 6). Because bitumen is highly viscous and adhesive at room temperatures, emulsification facilitates handling and allows the material to be pumped for transport by tanker or pipeline. Although disapproved in the State of Florida in 1996, the cost-effectiveness of Orimulsion® fuel as well as its use in Europe, Japan, and Canada favors its eventual adoption.

Widespread use of Orimulsion® poses the risk of accidental releases into the environment, and because Orimulsion® is expected to undergo unique transport and dispersion processes (7), conventional cleanup measures may be inadequate. Orimulsion® has dispersive, particulate properties that depend on the salinity of the receiving water and the rapid dilution of the stabilizing surfactant (8, 9). Regardless of salinity, during a spill in a confined low-energy environment, bitumen droplets will tend to resurface and coalesce into films, patches, and tar lumps of agglomerated bitumen at the water surface, because of dilution of the nonylphenyl ethoxylate surfactant (9, 10). It is this sticky, cohesive surface phase of free bitumen at the air–water interface that represents the greatest obstacle for cleaning and filtration treatment, because the droplets adhere at the point of initial contact and leave a solid asphalt-like deposit over time.

In the event of an accidental release, patches from a bitumen spill cloud will likely cling to exposed surfaces, leaving a persistent asphalt coating that is difficult to remove. Many techniques have been tested for cleaning bitumen from stained surfaces. Steam treatment, high-pressure water, chemical dispersants, and degreasing agents are among the methods evaluated that have proved relatively ineffective in removing fresh Orimulsion® from surfaces of equipment and vessels (1, 6).

Conventional oil-spill technology is also inadequate for dealing with spills of Orimulsion® (10). Previous research by Intevep (6) has focused on development of a method of entraining air in spilled Orimulsion® via submersible pumps to take advantage of the floating fraction effect of marine bitumen spills. The method promotes flotation of the spilled bitumen for collection with conventional skimming equipment. In freshwater, recovery of Orimulsion® presents a unique challenge because the material readily disperses throughout the water column; however, UF methods for collecting Orimulsion® have been developed (11).

Ultrafiltration is a pressure-driven membrane treatment process, which among other applications successfully removes particulate material from aqueous media. It has also been used to break oil–water emulsions and concentrate the emulsified product for recovery (12–24). In UF, hydraulic pressure is used to induce clear water flow through a selectively porous, semi-permeable membrane, excluding macromolecules of a preselected molecular size, shape, or charge distribution from the filtrate. Ultrafiltration membranes are capable of rejecting macromolecules or particles in the range larger than approximately 0.001–0.05 μm, or molecular weights from approximately 10^3 to 10^6 daltons (14, 16).

Related applications of UF include separation of water-soluble coolants, cutting/grinding oils, metalworking lubricants, oils in aqueous discharges, and waste oils contaminated with metallic colloids (13, 24). In some cases, retentates generated in this process have been incinerable (25). In addition, tubular membranes similar to those used here have been used to successfully separate latex emulsions stabilized by surfactants as well as spent coolant waste from the manufacture of automobile transmissions (14).

The separation of bitumen fuels from water using UF has not been studied because of the perceived potential for rapid and irreversible membrane fouling as a result of the adhesive nature of Orimulsion® and its resistance to removal. The objective of this paper is to report the development of methods for maintaining permeate flux in UF systems exposed to aqueous suspensions of Orimulsion®. Procedures for regenerating permeate flux and cleaning UF membranes and equipment fouled with bitumen emulsions are reported. Moreover, the use of natural conditioners as filtration aids for the enhancement of filterability is reported. Efficacy of filtration additives, cleaning agents, and specific cleaning methods to deal with staining and membrane fouling is described. A recommended cleaning schedule, derived using a simple mathematical relationship based on pilot data, is also presented.

EXPERIMENTAL

Ultrafiltration Pilot System

Pilot experiments were conducted to determine the feasibility of UF of water contaminated with Orimulsion®. A tubular membrane configuration was selected for testing based on anticipated difficulties in cleaning surfaces fouled with bitumen. Tubular modules have comparatively low surface-area-to-volume ratios and consequently have larger floor-space requirements, which can present practical limits to achievable process flow rates and removal efficiencies. Nevertheless, tubular membranes do not require fine prefiltration, and they resist clogging. They are also particularly well adapted to the treatment of viscous fluids, and they have a wide bore design to facilitate mechanical cleaning and provide the greatest flexibility for recovering permeate flux (16, 25). Pilot experiments were conducted using a tubular polyvinyldiene fluoride (PVDF) membrane configuration. PVDF is a synthetic, non-cellulosic, hydrophobic polymer with a chemical resistance similar to Teflon®. Two 25 mm (1 in) diameter cartridges were tested, including membrane 251 with an initial neutral surface charge (10-HFM-251-FNO, Koch Membrane Systems®) and membrane 276 with an initial negative surface charge (10-HFP-276-FNO, Koch Membrane Systems®). Expected membrane life is reported to be 5–6 yr with proper maintenance and cleaning (26). Additional characteristics of the membrane 251 and 276 are summarized in Appendix 1 (19, 26).

An existing UF pilot plant designed for separating waste oils in bilge water (24) was modified for this research as diagrammed in Fig. 1. The pilot plant consisted of a 200 L (55 gal) circulation tank with a 1725 rpm high-speed turbulent mixer, a multi-stage convertible jet centrifugal pump to produce a constant recirculation rate up to 5.7 m^3/h per tube (25 gpm per tube) at a cross-flow velocity of up to 3.1 m/s (10 ft/s), and a support panel for the clean-in-place system and for the different 3.1 m (10 ft) long membranes, peripheral piping, pressure control, and monitoring equipment. Inlet and outlet module pressures were measured with gauges and controlled by a throttle valve, as shown in Fig. 1. Throughout testing, transmembrane pressures were kept essentially constant (328 $\pm$ 29 kPa).

The pilot plant was operated as a batch process with full recycling of retentate. For several UF runs, the system was operated with a volume concentration ratio of 1 (VCR = 1), meaning that the concentration of the feed solution was held constant throughout the test by returning both the retentate and the permeate to the feed tank. An experiment was also conducted using the system in the concentration mode (VCR = 4), in which the permeate discharged directly to the drain, simulating field operation. Permeate flux was calculated from the time needed to collect 700–1000 mL. Permeate samples were collected from the effluent discharge manifold, and feed/retentate samples were taken from the circulation tank for analysis of volatile suspended solids (VSS), as outlined in Standard Methods 2540 A, D, and E (27), to a detection limit of 0.1 mg/L. Volatile suspended solids measurements were found to be a reliable indicator of Orimulsion® concentrations for dilutions in the range of 1 : 5000 up to 1 : 4, Orimulsion® solids to water, by mass. Alternative measures of Orimulsion® concentration are not available.

Pilot tests were organized as follows. Ultrafiltration *sessions* consisted of 2–4 h of continuous operation prior to shutdown for cooling of feed suspen-

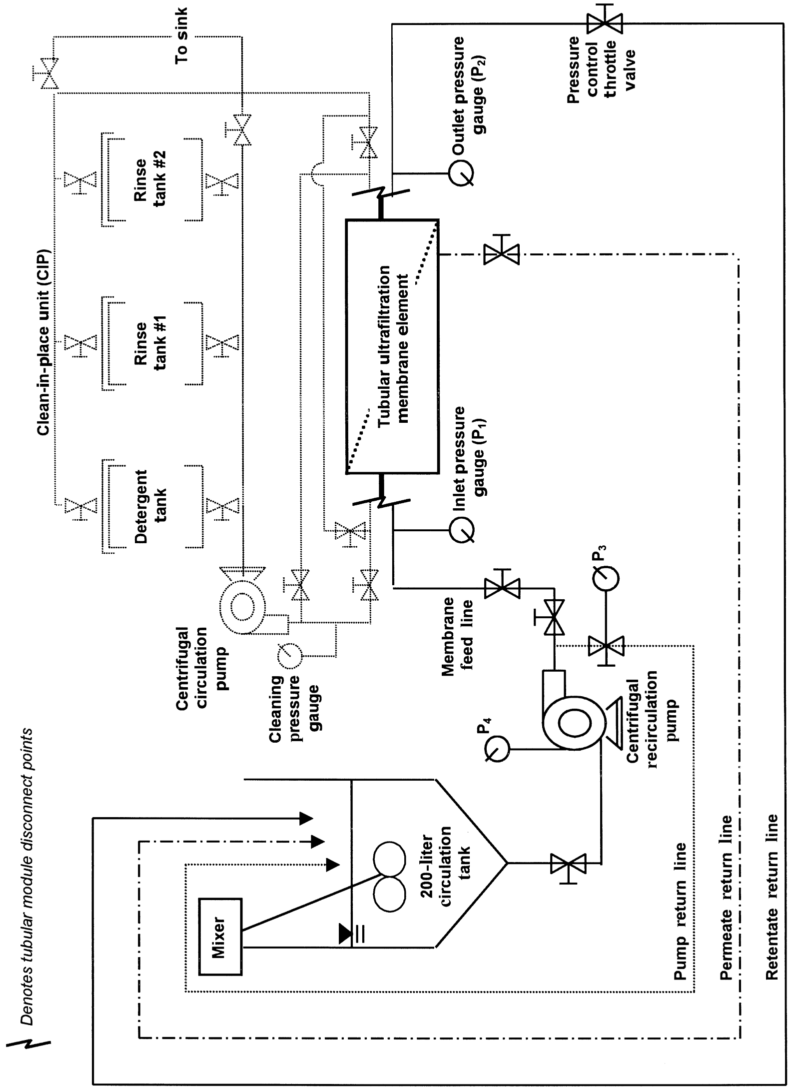


FIG. 1 Schematic diagram of ultrafiltration pilot plant.

sion. Sets of sessions comprised *cycles* during which UF was conducted before taking membranes off-line for cleaning. Sets of sessions performed with the same feed composition comprised *runs*.

Operation of the pilot plant was suspended as needed between sessions to maintain membrane temperature within manufacturer's specifications. Temperature increases were observed during pilot testing as a result of combining relatively high recirculation rates with low wastewater batch volumes. Between sessions, membranes were rinsed with clean tap water until the exit stream appeared clear. To delay premature fouling of the membranes and avoid settling and cooling of bitumen on the surfaces within the unit, the system was purged by returning the remaining liquid back to the circulation tank. This is typically done in UF processes to prevent dry-out and consequent irreversible loss of flux (14). Membranes were taken off-line for cleaning between cycles when the permeate flux fell below the terminal flux of 31–51 Lph/m^2 (18–30 gpd/ft^2) suggested by the manufacturer (26).

Measured permeate flux values were adjusted to a reference temperature of 25°C by using viscosity-based correction factors. Typically, an increase in flux of 35–50% can be expected for a 20°C fluctuation in temperature (25); therefore temperature readings and feed concentrations were used to correct for variations between 24–49°C by estimating a bulk viscosity at the observed temperature. It was assumed that the effective viscosity of the Orimulsion® suspension was equal to the concentration-weighted average of the bitumen viscosity and the dilution-water viscosity. Temperature correction factors consisted of a ratio of the computed concentration-weighted average feed viscosity at the observed temperature, T, to the expected concentration-weighted average viscosity at the reference temperature of 25°C (25). Because of the plastic or pseudoplastic behavior of Orimulsion® and because viscosity measurements often depend on the type of instrument used, bitumen viscosity was estimated based on the empirical method of Puttagunta et al. (28) and calibrated using the fluid properties of water (29) and the reported Orimulsion® viscosity at 30°C, 101.3 kPa provided by the manufacturer (1, 4).

In general, flux decline is not comparable between UF experiments, except where testing conditions are similar with respect to operating temperatures, influent composition, membrane type, membrane configuration, transmembrane pressures, recirculation velocities, and perhaps most importantly, cleaning history. Accordingly, a fouling index, k, was defined as the slope of a log–log plot of permeate flux versus time for each session and was used to characterize the extent of fouling. The k values for each session were used to calculate estimated flux values as a function of time for continuous operation at 25°C. This was done by taking the measured flux value at the start of each session and reducing the subsequent flux values at the rate indicated by the experimentally determined k value over that particular session. That is, flux values, F, for a session, and $\log F = \log F_o + k\Delta\log t$, in which F_o is the flux at the start of each session, and $\Delta\log t$ is the difference in the logs of the times between flux measurements. This procedure removed the effect of temporary flux increases due to intersession rinsing and restart.

Filtration Additives

The use of natural conditioning agents for improvement of filterability (30–34) was investigated by selecting inert, inexpensive natural materials commonly used in water-treatment processes. These were bentonite clay, kaolinite clay, lime [solid $Ca(OH)_2$ pellets], and diatomaceous earth filter aid. Samples of Orimulsion® in various dilutions were treated with each of the natural filtration aids at different concentrations to qualitatively observe the effects on resulting bitumen fouling.

Cleaner Testing

Most chemical formulations and many organic solvents, with the exception of chloroform (7), are relatively ineffective and require extended contact time with vigorous wiping and mechanical action to remove bitumen fouling (4, 5, 7). Therefore, prior to pilot testing, several cleaning agents were identified as possible candidates for dealing with Orimulsion®. These were SAC-300 (Omega Supply, Pinellas Park, FL), Citrikleen® HD (West Penetone Corporation, Tenafly, NJ) and Koch® KLD (Kochkleen Liquid Detergent, Koch® Membrane Systems, Inc., Wilmington, MA), all of which are biodegradable, nontoxic, aqueous cleaning agents. SAC-300 is a propriety degreaser. Citrikleen® HD is a blend of citrus-based hydrocarbon degreasers, carbon removers, and surfactant concentrates formulated to dislodge tar-like materials into rinsable particles. Koch® KLD is a concentrated enzymatic alkaline blend of nonionic surfactants and chelating agents specifically formulated to be used in food, beverage, potable water, biotechnological, and wastewater membrane applications. Cleaners were tested on bitumen staining of glass and plastic surfaces contaminated during experimentation. Overall effectiveness in terms of bitumen removal and cleaning requirements was rated considering the degree of mechanical scraping necessary and ease of rinsate disposal.

Cleaning of Membranes

Methods for cleaning UF membranes fouled with Orimulsion® were also developed. Cleaning procedures for permeate flux restoration were tested by connecting the membrane module to a second circulation loop diagrammed in Fig. 1, labeled as the clean-in-place (CIP) equipment. Cleaning agents and tapwater rinses were circulated through the membrane using an attached Grundfos® Type UP 26-96F cast-iron centrifugal pump. Transmembrane pressures (<70 kPa) and recirculation rates (0.4–1.1 m^3/h, or 2–5 gpm) were kept essentially constant throughout cleaning method development. For some cleaning tests, rinse water and cleaning agents were circulated with permeate valves closed. This was done to protect the permeate conduits from mobilized bitumen and prevent contact with solutes containing air, thus minimizing adsorption and clogging within the pores. Opening the permeate valve during circulation allowed concentrated detergent to emulsify trapped bitumen within the pores, and it also allowed for measurement of clean water flux as an estimate of the extent of flux recovery during cleaning. A small amount of foam was present in the permeate in these tests. No effort was made to quantify the effluent detergent concentration through analytical procedures.

Cleaning methods were tested based on the application of cleaning agents, strength and pH of cleaning solution, contact time, flow direction, mechanical cleaning requirements, and duration of rinsing. At the end of each cleaning procedure trial, surfactants or sponge balls, or both, were flushed out of the system, and clean warm tapwater was circulated until rinsate pH returned to neutral. The percentage of flux recovery was calculated by taking the ratio of the clean tapwater flux to the starting flux measured from the beginning of the next cycle after cleaning. The value of the experimentally determined, clean tapwater permeate flux measured at 347 kPa was 1071.5 Lph/m^2.

RESULTS AND DISCUSSION

Operating conditions for each experimental run are summarized in Appendix 2. Linearity in the empirical log-flux-versus-log-time relationship, k, as indicated by the coefficient of determination, r^2, is also listed. These values were later used to generate the curve shown in Fig. 3b.

Membrane Comparison

The two membranes tested (251 and 276) were similar except for initial surface charge and slight differences in reported nominal molecular weight cutoff, as seen in Appendix 1. For comparable feed and operating conditions, the 276 membrane provided a higher initial starting flux. However, as shown in Fig. 2, for similar feed suspensions, the equilibrium flux after the first few hours of operation converged to essentially the same level for both membranes, seemingly indicating rapid bitumen deposition on the membrane surface when subjected to a moderate concentration (1.0–2.5%) of Orimulsion® bitumen in water. Before coating, the 276 membrane shows better rejection of bitumen droplets. This effect was observed for both seawater (Fig. 2) and tapwater suspensions (11).

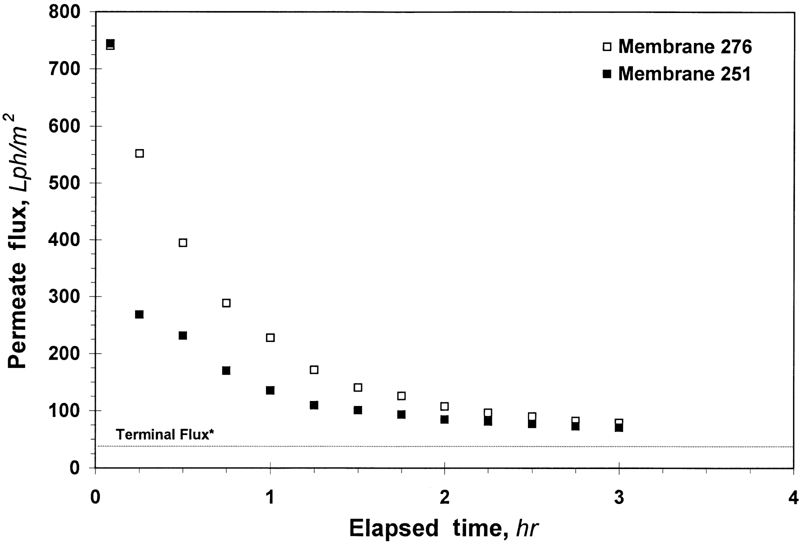


FIG. 2 Comparison of ultrafiltration permeate flux for membrane 251 and 276 using a 2.5 : 100 dilution of Orimulsion® in seawater (Biscayne Bay, Miami, FL) with 0.1 : 1 clay : Orimulsion® solids addition (runs no. 3 and no. 4). *Manufacturer's suggested terminal flux at 25°C.

Filtration Additives

Colloidal particles, such as bitumen droplets, can remain suspended in the feed and can accelerate membrane fouling because of their size and charge distribution. Material that might otherwise enter the pores and deposit or adsorb within can be aggregated as a pretreatment option for easier rejection at the membrane surface. Aggregation leads to larger effective particle sizes, resulting in less specific resistance and better compressibility of the gel layer. Furthermore, previous research has shown that fine particulates such as silt, sand, and graphite have minimal effects on the membrane surface in UF treatment (15). Operation of UF in a recycling loop to maintain contact between the feed and conditioning agent at a concentration close to the optimum flocculation dose has been demonstrated to decrease the required membrane area, increase permeate flux, extend cleaning frequency, and improve permeate quality (25). Mechanisms reported for these improvements include reduction of foulant penetration into the pores, conditioning of the layer of materials deposited on the membrane surface, and improvement of particle transport characteristics (25).

Orimulsion® can become destabilized by fine particulate matter that may accumulate during storage or transport. Contaminant particles adsorb on the droplets and promote rapid bitumen coalescence and subsequently sedimentation, effectively destroying the emulsion. This behavior was consistently observed for all conditioner additives investigated (Table 1). Qualitatively, it was possible to identify an appropriate conditioner and concentration to use to improve filterability and minimize residuals generation. This corresponded to a concentration of 1 part bentonite clay to 10 parts bitumen solids, by mass. Higher concentration ranges approached a flocculation dose that led to undesirable rapid destabilization and sedimentation.

Pilot experiments showed that destabilized Orimulsion® suspensions in water can be successfully separated using UF without the use of mineral additives, especially from more dilute suspensions (<1.0%). However, membrane throughput decreased by an order of magnitude, necessitating more frequent membrane cleaning or replacement, or alternatively, greater membrane surface area to compensate. As shown in Fig. 3a, ultrafiltration of a concentrated feed without additives intensified fouling, evidenced by an immediate drop of permeate flux from the clean tapwater value of 1071.5 Lph/m^2 (630 gpd/ft^2) to 56 Lph/m^2 (33 gpd/ft^2) and by complete membrane blinding after only 2 h of operation. Without additives, the membrane surface rapidly plugged, and the permeate flux dropped below the manufacturer's terminal flux of 31–51 Lph/m^2 (18–30 gpd/ft^2) after only 30 min of operation. Throughout testing, clay additives increased both filtration flux and cycle length. In Fig. 3a, clay addition resulted in permeate flux values above or near the terminal flux for an extended operating period of 36 h, compared to less than 2 h without. The stepwise appearance of the long-term run with the clay additive shown in Fig. 3a is attributed to the tapwater rinse and storage procedure, performed after each UF session as outlined under "Ultrafiltration Pilot System." The effects of operating with discontinuous sessions in this experiment were removed using a procedure outlined under "Ultrafiltration Pilot System" and shown in Fig. 3b. Although the experiment was conducted using two membranes (251 and 276), it was noted in earlier tests (see "Membrane Comparison") that differences between membranes were minimal after exposure to feed suspensions beyond 3–4 h. This similarity in membrane performance was attributed to rapid bitumen deposition masking the effect of surface charge after the initial period in this and other experimental runs.

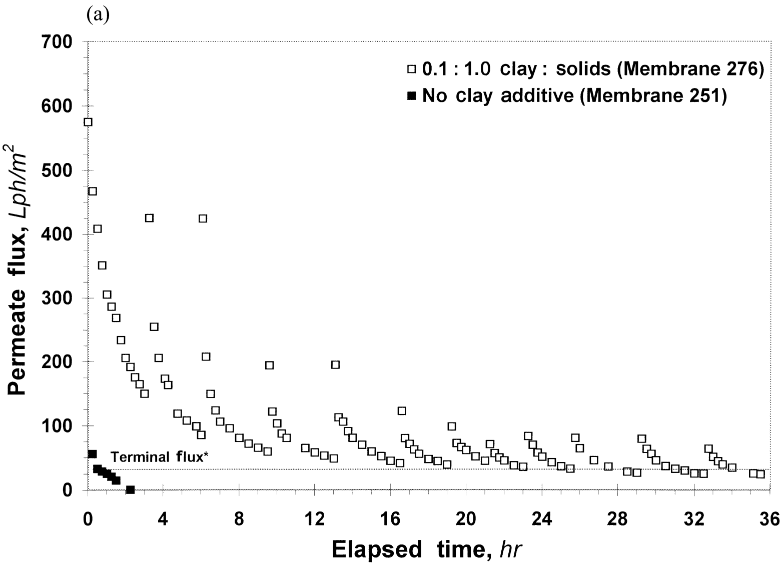
Concentration Testing

Because measured permeate VSS (<2.0 mg/L) was lower than the dilution-water background concentration (VSS = 1.6–7.7), an experiment was conducted with permeate discharge to the sanitary sewer. This experiment (run no. 6) used a concentrated feed suspension comprised of a 1 : 10 dilution of Orimulsion® in tapwater with 0.1 : 1 clay : Orimulsion® solids using the 276 membrane at VCR = 4. After only 6.5 h in this configuration, the bitumen

TABLE 1
Summary of Cleaner Testing Experimentation for Removal of Bitumen

Cleaning product	Result
Pentane (*Baxter*)	Requires working into stain and wiping with high-pressure washing
Hydrochloric acid (*Baxter*)	No effect
Diesel fuel	Requires extended contact time
Kerosene	No effect
Unleaded gasoline	No effect
Coleman® fuel	Minor effect on stained surfaces with vigorous scrubbing
Citrikleen® HD (*West Penetone*)	(Heavy-duty citrus-based biodegradable hydrocarbon solvent degreaser) Diluted and allowed to contact stained surfaces, dislodges bitumen with rinse. Permitted to stand, bitumen separates from the emulsion. Citrus odor.
Citrikleen® (*West Penetone*)	(Regular-strength version of Citrikleen HD) Results similar to Citrikleen HD, but less concentrated and less effective.
Chevron® Pro-Guard	(Proprietary tar-stain remover) Mildly effective. Requires vigorous scrubbing into stained surfaces and washing off. Washings do not separate. Hydrocarbon vapors cause problems if not used in well-ventilated areas.
SAC 300® (*M3, Inc.*)	(Specially formulated hydrocarbon microemulsion cleaning agent) In concentrated form, dislodges bitumen and rinses away clean. Use only in well-ventilated areas because of powerful turpentine-like odors. Washings emulsified and did not separate within a reasonable time.
Thomspson's® Garage Cleaner	Minor effect on stained surfaces with vigorous scrubbing
STP® Carbeurator Cleaner	No effect
Koch® KLD (*Koch Membrane Systems*)	(Biodegradable alkaline membrane-cleaning agent surfactant) Diluted, performs well for dislodging bitumen staining; however, washings take longer to separate from the emulsion. No odor associated with the cleaning agent. Washings are at elevated pH.

concentration in the feed tank increased from 10 to 47 wt%, as determined by VSS measurements, with an average permeate flux of 58 $\pm$ 66 Lph/m^2 (34 $\pm$ 39 gpd/ft^2) and permeate quality $<$2.0 mg/L VSS. Further concentration of the retentate was not investigated because of solids content limitations on the



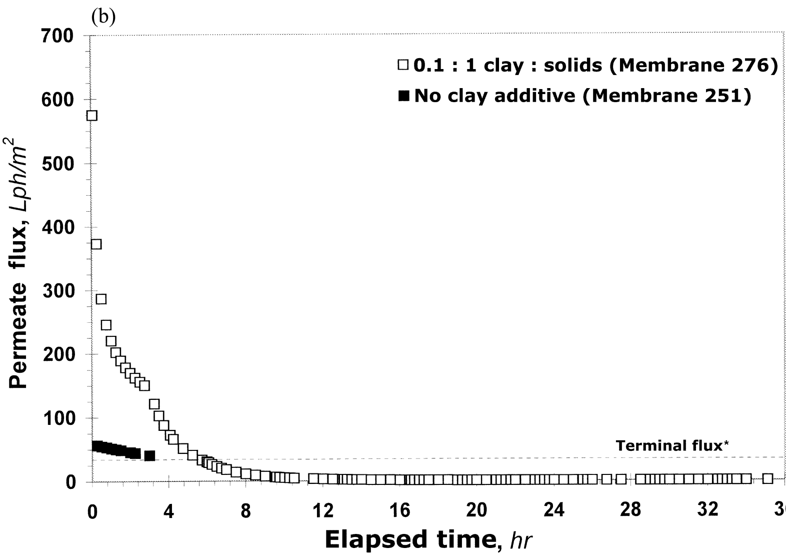


FIG. 3 Comparison of permeate flux versus time for ultrafiltration with and without bentonite clay addition for a 1 : 10 dilution of Orimulsion® (a) in tapwater, (b) in tapwater corrected for intersession rinse and storage (runs no. 2 and no. 5). *Manufacturer's suggested terminal flux at 25°C. Note: Different membranes used, but surface charge differences between membranes were not found to be significant at a steady state (Fig. 2).

centrifugal circulation pump for the pilot plant. For comparison, feed influents containing 1–5% oil have been successfully concentrated up to 30% with permeate fluxes on the order of 60–120 Lph/m^2 (35–70 gpd/ft^2) and permeate quality of 30–100 mg/L oil (25).

Cleaner Testing

Certain chemical agents such as BP Quicksplit, a biodegradable anionic emulsifier, can reportedly remove bitumen staining within 15 min with the bitumen fraction separating from the aqueous phase. Other emulsifiers, such as Jizer Swalve S100, a nonionic emulsifier, are also reported to rinse away bitumen staining; however, washings do not separate out (4). Because these proprietary cleaners are not commonly available, their performance was evaluated, and is summarized in Table 1.

The three commercially available cleaning agents tested did demonstrate sufficient removal of residual contamination when coupled with vigorous manual scrubbing. SAC-300 readily emulsified the bitumen but produced an unpleasant turpentine-type odor. The other cleaners also emulsified the bitumen and generated a floating contaminant fraction that was separable from the spent aqueous cleaner fraction upon settling overnight. Citrikleen® HD removed bitumen patches and fouling when soaked in a 20–50% v/v dilution with warm tapwater for 15 min. When permitted to stand overnight, the bitumen particles in the spent cleaning solution rose to the top and were easily separated. Bitumen staining was also readily removed by immersion in diluted Koch® KLD (0.5–1.0% v/v in warm tapwater), adjusted to pH $>$ 10 with NaOH. Additional scrubbing, if necessary, was sufficient for the stained surface to rinse clean. As with the citrus cleaner, spent washings with emulsified bitumen can be collected and allowed to separate overnight, with the contaminated surface layer skimmed off and the residual cleaner returned to the UF feed tank for further bitumen recovery, if desired. This would be necessary if minimization of hazardous waste generated or disposal costs were an issue.

Cleaning of Membranes

Appropriate UF cleaning strategies typically are dependent on the nature and type of fouling as well as the characteristics of the feed suspension and the retentate stream. Pore plugging from bitumen is particularly difficult to handle, and the problem is confounded because high-molecular-weight cut-off membranes (greater than 5×10^4 daltons), such as those used in this study, are more susceptible to pore plugging and increasing transmembrane-pressure effects (35).

Procedures tested for restoring permeate flux to membranes fouled with bitumen are summarized in Table 2, which lists testing conditions prior to clean-

TABLE 2
Summary of Cleaning Procedure Method Development for Tubular PVDF Membranes Fouled with Bitumen

	Cleaning procedure				
Cleaning characteristics	No. 1	No. 2	No. 3	No. 4	No. 5
Testing conditions					
Membrane name	251	251	251	276	276
Feed concentration (%, by mass)	0.10	0.10	0.10–10	0.10–2.5	1.0
Water type[a]	Tapwater	Tapwater	Tapwater	Tapwater/Seawater	Tapwater
Additives[b]	1 : 1	1 : 1	1 : 1/0.1 : 1/none	none/0.1 : 1	0.1 : 1
Start flux (Lph/m^2, *gpd/ft^2*)	315.8	240.4	282.8	740.3	1056.3
End flux (Lph/m^2, *gpd/ft^2*)[c]	117.4, *69.1**	32.8, *19.3*	0.0, *0.0*	21.9, *12.9*	48.3, *28.4*
Filtration time (hr)	7.25	10	14	5.75	9.25
Cleaning conditions					
Forward flush (min)[d]	30	15	60	10	30
Reverse flush (min)[d]	30	NA	NA	10	30
Forward rinse (min)[e]	15	35	30	5	NA
Reverse rinse (min)[e]	15	5	35	5	NA
Cleaning agent	Koch KLD®	Koch KLD®	Koch KLD®	Koch KLD®	Koch KLD®
Cleaner volume (L/membrane)	10	80	50	50	20
Cleaning strength (%, by volume)	0.5	0.5	0.5	0.5	0.5
Cleaner pH	10.55	10.04	10.23	10.10	10.25
Forward circulation (min)	30	50	45	30	60
Reverse circulation (min)	30	10	60	30	60
Overnight soak	No	Yes	Yes	No	No

Sponge balls	Yes	Yes	Yes	Yes	Yes
Forward direction[f]	2 × 2	2 × 2	1 × 2	2 × 2	NA
Reverse direction[f]	2 × 2	1 × 2	4 × 2	3 × 2	2 × 2
Final forward flush (min)[d]	15	50	10	15	15
Final reverse flush (min)[d]	NA	NA	10	30	NA
Permeate valve	Closed	Open	Open	Closed	Closed
Method performance					
Percent flux recovery[g] (%)	22.4	26.4	69.5	98.6	53.7
Operating : cleaning time ratio	2.4	0.7	0.8	2.1	2.7
Total off-line time (h)	3.08	15.25	16.58	2.75	3.42

[a] Seawater samples were taken from Biscayne Bay, Miami, FL.
[b] Refers to the mass ratio of bentonite clay to bitumen solids in the feed suspension
[c] Measured permeate flux prior to cycle shut-off.
* Denotes that flux readings were not corrected for temperature.
[d] Refers to circulation of tapwater over the membrane surface with return to the feed tank.
NA = Not applicable.
[e] Refers to circulation of tapwater over the membrane surface without return to the feed tank.
[f] (Number of passes) × (Number of sponge balls per mass).
[g] Ratio of the start flux for the next run cycle compared to the measured clean tapwater flux (1071.5 Lph/m^2).

ing, cleaning conditions used, and method performance in terms of flux recovery, operating/cleaning time ratios, and off-line time. The total time requirement for cleaning, listed in Table 2, does not include intersession tap water rinse and storage times; however, it does include the time to empty the system for disassembly each time sponge balls were inserted (2–3 min/sponge ball). In field applications, this part of the procedure may be automated to save time. Furthermore, tap water rinse and storage may not be required because sessions would likely be continuous in field applications.

Warm tap water flushes and rinse cycles moistened the membrane surface and aided in displacement of bulk material and settled solids on the gel layer. Because Orimulsion® fouling is resistant to removal, a significant amount of permanent flux regeneration with simply a tap water rinse was not expected. Nevertheless, a tap water flush did provide a degree of temporary flux increase for the first 15–30 min of UF sessions as evidenced by the stepwise appearance in Fig. 3a.

Membrane cleaners were effective at pH > 10 and were able to dislodge bitumen material trapped within the active surface. An overnight soak in combination with sponge-ball insertion using fresh alkaline cleaner was employed in some tests. This enhanced cleaning by first loosening then dislodging the crustlike, compacted bitumen/clay gel layer of surface deposition. However, this represented a significant source of off-line time. Further testing showed that elimination of the overnight soak step shortened cleaning times by a factor of 6 without negatively affecting flux recovery (Table 2). When the amount of cleaning agent was restricted to less than 0.25 m^3/m^2 (cleaner volume/membrane area), flux recovery decreased, from 98.6% to below 54%.

As shown in Fig. 4, partial permeate flux restoration was possible after the first cleaning cycle. The flux regeneration ratio was increased slightly using cleaning procedure no. 2 with the modification of an overnight soak and an open permeate valve.

Selection of the most appropriate cleaning-method modifications was dependent on both the flux restoration target level and the pre-cleaning filtration conditions. During pilot testing, excellent flux recovery was obtained using cleaning methods ranging from 2–4 h (Table 2). For a wide range of feed concentrations in waters of varying salinity, suitable flux regeneration is possible using a cleaning procedure similar to no. 4, which showed the highest flux recovery, the lowest total off-line time, and an operating : cleaning-time ratio greater than 2. If time considerations are a constraint, it is recommended to reduce or eliminate the flush and rinse cycles because those steps by themselves do not demonstrate significant permanent flux recovery. For this application, an optimal UF membrane-cleaning procedure would likely consist of (a) a brief, warm tap water (27–35°C) rinse of the membrane surface to remove

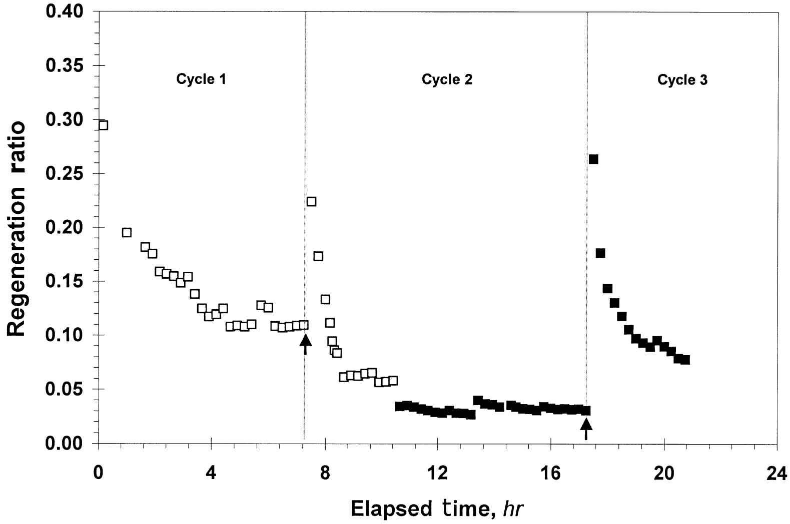


FIG. 4 Regeneration ratio (measured flux/clean water flux) versus time for ultrafiltration run no. 1 (cycles nos. 1–3) using a 1 : 1000 dilution of Orimulsion® in tapwater with 1 : 1 clay : Orimulsion® solids addition on the 251 membrane. Arrows denote cleaning cycle start points. The first arrow from the left corresponds to cleaning procedure no. 1, and the second arrow corresponds to cleaning procedure no. 2. *Manufacturer's suggested terminal flux at 25°C. (□) Temperature corrections not available. (■) Temperature-corrected values.

bulk bitumen, (b) addition of membrane cleaner adjusted to pH $>$ 10 with NaOH, (c) insertion of sponge balls in both flow directions to dislodge and remove bitumen deposits from the membrane surface, and (d) a tap water rinse to return pH to neutral. According to pilot data, UF of highly concentrated feeds ($>$1.0%) without the use of filtration additives is possible but not recommended because complete bitumen plugging is expected to occur rapidly. However, if the resulting permeate flux is reduced to zero, considerable flux restoration can be achieved by employing an overnight soak, as in cleaning procedure no. 3. Shorter cleaning times will result from reduction of one or more steps in the cleaning procedure; however, this will likely be at the expense of lower flux recovery.

Complete flux regeneration was possible in this study by using the scouring action of sponge balls in conjunction with the emulsifying action of the alkaline cleaner. Visible plugs of bitumen were lifted off and removed from the membrane surface by the sponge balls, indicating the extent of bitumen fouling and the ability of the sponge balls to clean the membrane surface. After cleaning, the flux decline for the next run was slightly sharper than before

(Fig. 4), decreasing from $k = -0.23$ to $k = -5.05$ after cleaning procedure no. 1 and decreasing even further to $k = -5.71$ after cleaning procedure no. 2.

PROCESS ECONOMICS

Because of the tendency of Orimulsion® to foul UF membranes and the unique challenges involved with cleaning surfaces fouled with Orimulsion®, a simple optimization was conducted to determine how long a UF process should be run to maximize total permeate throughput before cleaning is initiated. To maximize total permeate output, the trade-off considered was filtration cycle length, or time requirement until the next membrane cleaning or replacement, versus clean membrane flux increase. To do this, actual pilot data from run 5, cycle 5 was used, in which filtration conditions included an extended run length (36 h) and a highly concentrated feed material that consisted of a 1 : 10 dilution of Orimulsion® in tapwater with 0.1 : 1 clay : Orimulsion® solids addition (Figs. 3a and 3b). These conditions would be relevant to an application of bitumen recovery using UF technology.

To investigate flux over extended times in the field, two corrections were made to the data. First, all permeate flux values were corrected to a reference temperature of 25°C, as previously described. Second, since long-term flux decline was discontinuous (Fig. 3a), k values for each operating session were used as an indicator of the rate of flux decline as a function of time and used to calculate estimated flux values as a function of time for continuous operating conditions at 25°C. That is, flux at the start of each session was set equal to the final flux of the preceding session and reduced at the rate indicated by the experimentally determined value of k for that session. This procedure removed the effect of temporary flux increases resulting from intersession rinsing and restart. These calculated flux values decreased continuously over time as shown in Fig. 3b.

To find an optimum run time, an overall or net rate of permeate production, taking into account off-line cleaning time, for various cycle lengths was defined as

$$R = \frac{1}{t + \tau} \int_0^t F\, dt \qquad (1)$$

In Eq. 1, R is equal to the net rate of permeate output in Lph/m^2 for a given ultrafiltration cycle length between cleanings, t, in hours. F, in Lph/m^2, is the calculated, continuous permeate flux as a function of time, assuming continuous operation at 25°C (Fig. 3b), and τ is time required for cleaning, in hours. The relationship assumes that the flux behavior of subsequent filtration cycles is similar and that cleaning completely restores original starting flux. These assumptions were considered reasonable given the results shown in Fig. 4, and were used to develop a simple optimization of membrane cleaning schedules. The objective function, R, was maximized with respect to ultrafiltration cycle time, t, for values of τ ranging from 0–10 h.

In Fig. 5, the net rate of permeate output, R, was plotted as a function of time-to-cleaning for several assumed cleaning times to determine when it is more economical to shut down filtration, implement cleaning, and return the system to operation. The calculated net flux curve reached a maximum value for UF session lengths from 3 to 4 hours for the filtration conditions studied. This cycle length was remarkably constant for cleaning times ranging from 1 to 10 h, dropping to 2 h for a 0.5 h cleaning time.

Cycle lengths corresponding to maximum throughput for cleaning times up to 10 h are plotted versus cleaning time in Fig. 6. Slight discontinuities before $t = 4$ hours and $t = 7$ hours are artifacts of the numerical integration using $\Delta t = 15$ minutes. Reduction of Δt would introduce an additional uncertainty to the analysis, because permeate flux was measured experimentally at 15 min intervals. According to Fig. 6, optimal filtration cycle lengths varied from 3.25 to 3.5 h for cleaning times of 2–4 h. Other factors to consider in determining the most economical point in the run to begin cleaning include the quantity and quality of residuals produced in the cleaning process, training and safety

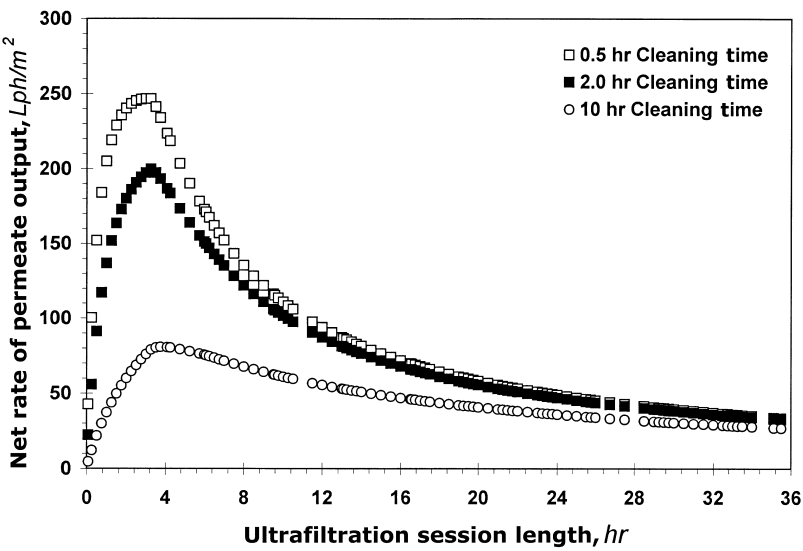


FIG. 5 Net rate of permeate output versus session length for ultrafiltration of a 1 : 10 dilution of Orimulsion® in tapwater with 0.1 : 1.0 clay : Orimulsion® solids addition on the 276 membrane (run no. 5).

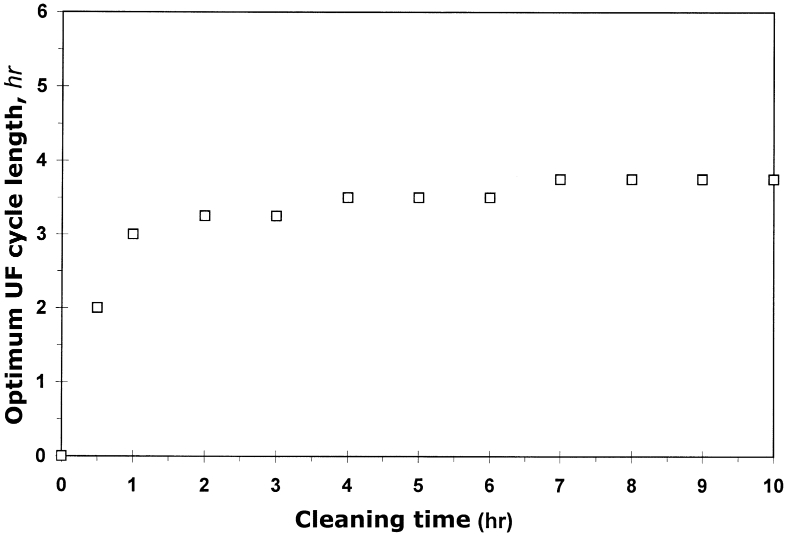


FIG. 6 Session length for maximum throughput versus cleaning time for ultrafiltration of a 1 : 10 dilution of Orimulsion® in tapwater with 0.1 : 1 clay : Orimulsion® solids addition on the 276 membrane (run no. 5).

of operators, and labor costs for maintenance personnel given the complexity of cleaning methods and the level of equipment automation.

The economics of UF with and without the use of additives were also compared. Consideration was given to membrane area costs as a trade-off, because the cost of replacing membranes is generally the single largest component of the operation (25). An average minor-oil-spill volume has been estimated at 1500 L (400 gal) of product (36, 37). A typical application for a UF process would be for concentrating material collected by skimmers employed in a port where spill containment is available. This skimmer waste would likely contain a large fraction of the sticky surface bitumen characteristic of Orimulsion® spills. For such a spill scenario, at a concentration of 1 : 50, by mass, an active membrane area can be predetermined using the estimated permeate flux values calculated in Fig. 3b to compute a net rate of permeate output (Fig. 5) for an optimum 3 h cycle with an automated 2 h cleaning time. Results of this cost analysis show that 290 m^2 (3100 ft^2) would be needed to achieve a 50% solids concentration of residuals within 24 h, without the addition of filtration additives. Capital costs of membrane area would be on the order of \$620,000 or \$415 per liter (\$1550 per gallon) spilled. Cost reduction is possible through the use of filtration additives. Addition of clay at 1 part to 10 parts bitumen will decrease the surface area requirement and allow a longer run time before membrane replacement is necessary. Area requirements when filtration additives were employed decreased to 30 m^2 (320 ft^2), or five times less, for a threefold increase in filtration cycle time before terminal flux was expected. The corresponding cost of membranes would then be approximately $64,000 or $43 per liter ($155 per gallon) spilled. These estimates do not include pumping costs, permanent or auxiliary facilities costs, or disposal costs. However, even for such a concentrated feed, the addition of clay is seen to reduce costs substantially. Differences in membrane costs can escalate further for more dilute waste streams.

CONCLUSIONS

Pilot tests indicated that UF can be an effective unit process for removal of Orimulsion® from relatively concentrated waste aqueous streams, even after exposure to severe bitumen fouling conditions. The addition of approximately one part by mass of clay to ten parts destabilized, diluted Orimulsion® suspension was found to increase UF run times from just 2 h without clay to at least 36 h with the additive, thereby enhancing recovery and reducing membrane fouling, cleaning, and replacement costs.

Initially, it was thought that the adhesive nature of the destabilized bitumen emulsion would immediately blind and irreversibly foul a UF membrane. However, within most run lengths tested, the reported lower limit of flux decline was breached only without clay addition. In practical applications, filtration additives may be necessary to obtain realistic filtration cycles and lower membrane area requirements. Moreover, the use of additives might allow the use of UF cartridge configurations having greater membrane area per element, minimizing the process footprint.

Regardless of whether clay additives are used, flux restoration after fouling can be achieved using the cleaning methods reported. Cleaning procedure development tests indicated that a tubular PVDF membrane completely blocked with Orimulsion® can be cleaned and restored to its original clean water flux rating using biodegradable, membrane-safe cleaning agents. Complete recovery can be time-consuming and generates a volume of spent cleaner tainted with bitumen that must be disposed of as a hazardous waste. However, nearly complete flux regeneration is possible with only slight modifications of the recommended cleaning procedure, including elimination of the overnight soak step. This modification greatly reduces the time required for cleaning and allows for practical off-line cleaning times of 2–4 h with 54–99% expected flux recovery.

APPENDICES

APPENDIX 1
Summary of Ultrafiltration Membrane Characteristics

Initial surface charge (Membrane 251, *Membrane 276*)	Neutral, *Negative*
Molecular weight cut-off*, kD (Membrane 251, *Membrane 276*)	80–100, *100–125*
Configuration	Tubular
Membrane material	PVDF
Length, m/tube (*ft/tube*)	3.0 (*10*)
Diameter, cm (in.)	2.5 (*1.0*)
Surface area, m^2/tube (*ft^2/tube*)	0.20 (*2.2*)
Max. operating temperature, °C	49
Max. permeate pressure, kPa (*psig*)	35 (*5*)
Max. transmembrane pressure, kPa (*psig*)	595 (*85*)
Avg. expected permeate flux, Lph/m^2 (*gpd/ft^2*)	51 (*30*)
Short-term pH range @49°C	1.5–10.5
Continuous pH range @49°C	2.0–10.0

* Nominal molecular weight cut-off values correspond to apparent pore diameters on the order of ~10 nm.

APPENDIX 2
Summary of Ultrafiltration Pilot Testing and Operating Conditions

Run no.	Cycle no.	Session no.	Membrane type	Dilution rate[a]	Clay ratio[b]	Avg TMP (kPa)	Avg VSS[c] (mg/L)	Fouling index	
								k	r^2
1	1	1	251	1 : 1000	1 : 1	320.1 ± 4.9	0.35	*−0.23*	*0.98*
1	1	2	251	1 : 1000	1 : 1	323.4 ± 7.7	1.05	*−1.00*	*0.89*
1	1	3	251	1 : 1000	1 : 1	270.2 ± 62.6*	1.10	*−0.50*	*0.44*
1	1	4	251	1 : 1000	1 : 1	320.2 ± 8.8	<0.10	*−0.71*	*0.60*
1	2	1	251	1 : 1000	1 : 1	297.0 ± 64.8*	NA	*−5.05*	*0.81*
1	2	2	251	1 : 1000	1 : 1	319.2 ± 0.0	0.35	*−0.12*	*0.35*
1	2	3	251	1 : 1000	1 : 1	314.6 ± 6.6	<0.10	−0.76	0.69
1	3	1	251	1 : 1000	1 : 1	314.5 ± 5.9	0.11	−5.71	0.82
2	3	1	251	1 : 10	None	324.7 ± 5.5	NA	−1.26	0.68
3	4	1	251	1 : 40[D]	0.1 : 1	348.5 ± 6.5	0.22	−0.64	0.98
4	5	1	276	1 : 40[D]	0.1 : 1	347.5 ± 6.7	<0.10	−0.69	0.95
5	6	1	276	1 : 10	0.1 : 1	331.0 ± 4.6	1.89	−0.38	0.90
5	6	2	276	1 : 10	0.1 : 1	328.9 ± 6.8	1.33	−2.28	0.92
5	6	3	276	1 : 10	0.1 : 1	337.8 ± 3.4	0.22	−3.45	0.81
5	6	4	276	1 : 10	0.1 : 1	337.5 ± 4.7	0.76	−3.64	0.86
5	6	5	276	1 : 10	0.1 : 1	333.9 ± 11.3	0.94	−5.58	0.90
5	6	6	276	1 : 10	0.1 : 1	328.8 ± 8.2	0.59	−7.08	0.85
5	6	7	276	1 : 10	0.1 : 1	335.5 ± 3.5	<0.10	−8.20	0.92
5	6	8	276	1 : 10	0.1 : 1	329.7 ± 4.4	0.80	−8.47	0.92
5	6	9	276	1 : 10	0.1 : 1	330.7 ± 3.4	0.24	−9.86	0.96
5	6	10	276	1 : 10	0.1 : 1	337.3 ± 15.6	0.69	−9.19	0.96
5	6	1	276	1 : 10	0.1 : 1	336.7 ± 3.5	1.16	−10.71	0.94
5	6	2	276	1 : 10	0.1 : 1	330.7± 5.3	0.70	−11.22	0.94
6	6	1	276	1 : 10	0.1 : 1	334.5 ± 9.9	1.21	*−0.38*	*0.98*
6	6	2	276	1 : 10	0.1 : 1	330.5 ± 9.1	1.86	−2.15	0.72

[a] Mass ratio of bitumen solids to tapwater.
[b] Mass ratio of bentonite clay to bitumen solids.
[c] Mean value of multiple volatile suspended solids measurements.
[d] Seawater dilutions (Biscayne Bay, Miami, FL).
* Denotes that pressure fluctuations were experienced because of valve failure.
Values in italics indicate that temperature corrections were not available.

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