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A Membrane Process for Industrial Water Treatment: From Bench to Pilot Demonstration

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Abstract: A rotary membrane filtration system was used to separate die lubricant from a manufacturing wastewater stream consisting of various oils, hydrocarbons, heavy metals, and silicones. The ultrafiltration membranes reduced organics from initial oil and grease contents by factors of 20 to 25, carbon oxygen demand by 1.5 to 2, and total organic carbon by 0.6, while the biological oxygen demand remained constant. The rotary membranes were not fouled as badly as static membranes, and the rotary membrane flux levels were consistently higher and more stable than those of the static membranes tested. Field testing demonstrated that the rotary ultrafilter can concentrate the die lubricant, remove the glycerin component, and produce a die lubricant suitable for in-plant recycling. The recycling system operated for 6 weeks with only seven cleaning cycles and no mechanical or electrical failures. Test data and quality records indicate that when

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recycled die lubricant was used, the die casting scrap was reduced from 8.4 to 7.8%. Rotary ultrafiltration presents significant opportunities that can be evaluated further.

INTRODUCTION

Water treatment is a major separations challenge for all industrial water users. Treating manufacturing wastewater requires simple, rugged, and durable processes. These systems must handle a wide compositional range of wastewater components and consistently provide purified water suitable for reuse. Often they must remove large solids as well as very small organic detergents, other surfactants, and specific organic chemicals. In addition to purifying the wastewater, these systems should concentrate the contaminants to a slurry, either for possible recycling or to minimize the waste. To reduce costs, industrial systems must be energy efficient.

Membranes are energy efficient compared to traditional phase separation processes such as distillation. However, many membrane materials degrade in the harsh thermal and chemical environments frequently encountered in industrial settings. The Idaho National Engineering and Environmental Laboratory (INEEL) has been developing polymeric membranes for industrial separations for 20 yrs (1–9). INEEL recently began working on filtration. This paper presents the results of a collaboration among INEEL, Metaldyne, Inc., and SpinTek Filtration, LLC, to develop a means of separating wastewater solutions generated by the die casting process. Wastewater streams similar to this are common in the metal casting industry, and there are many other applications for a reliable process for treating this type of wastewater.

Die Casting Waste Stream

The die casting plant where the separation process was demonstrated is a state-of-the-art cast/trim/ship facility that produces aluminum castings for automotive transmissions. Molten ASTM A-380 aluminum is auto-ladled into the chamber/sleeve at 643°C. Die lubricant, an oil and water emulsion, is sprayed onto the die to provide cooling and die release. After trimming and inspection, automated handling conveyors process the parts through final finishing, final inspection, basket loading, and loading into delivery trucks. This process generates a complex wastewater stream that contains soaps, detergents, oils, hydrocarbons, heavy metals, and silicones.

The die lubricant ("lube") is purchased as a concentrate and then diluted to suit the process needs. Each casting cycle requires spraying 1.8 to 2.0 L of lube onto the die via nozzles located on a manifold that surrounds the die. The excess die lube drains from the machinery into the plant's drainage system. The drainage system accepts all liquids from the foundry's operations—

detergents from washing operations as well as various oils, greases, and glycol used to maintain the casting machinery. Additionally, some "process cooling" water and cooling tower bleed are piped into the treatment system. Thus, while the primary liquid waste generated from the casting process is die lube, other ingredients also enter the system.

Previously, the waste stream was treated with ultrafiltration followed by reverse osmosis; however, oils and greases fouled the membranes. To prevent fouling, plant personnel installed a gravimetric skimmer and a prefilter to remove particulates and oils and greases from the wastewater solutions as the first step in water treatment. These measures did not remove all of these components from the wastewater stream, so the membrane system's performance was degraded.

Research Objectives

Ideally, the die casting industry would like to process the waste stream into clean water and clean die lube suitable for reuse. In 1999, Metaldyne Incorporated's Twinsburg, Ohio, facility, in cooperation with The North American Die Casting Association, the Department of Energy's Office of Industrial Technology, and INEEL, began investigating the potential to separate solids from wastewater. The goals were to (1) improve discharge quality by lowering the carbon oxygen demand of the wastewater, (2) reduce loading on the plant's treatment system by concentrating the die lube and purifying the water, and (3) recover and reuse both the die lube and water from the wastewater stream. This paper describes our research and results.

TECHNICAL APPROACH

The project began by identifying the problems in the existing die lube dewatering and separations processes, including specific families of materials that caused membrane fouling. Possible methods for controlling fouling were also identified. Then bench-scale experimental studies examined membrane fouling by the feed streams, fouling prevention methods, and the performance of various membrane materials. The next phase of the study demonstrated the ability of a membrane process to concentrate die lube by separating it from the die casting wastewater in the laboratory. Specific goals were to demonstrate 3.3-fold (3.3X), 20-fold (20X), and 50-fold (50X) concentration abilities. The final phase of the project, performed in the die casting facility, focused on concentrating the die lube to 3.3X, as in the laboratory, followed by glycerin removal from the concentrated die lube/glycerin mixture ("cleaning") coupled with reconcentration and reuse of the "cleaned" die lube in casting operations on a full-scale, full-production die casting machine.

EXPERIMENTAL PROCEDURES

Membrane Systems

Initially, three commercial approaches to separating complex wastewater streams were identified. These approaches all used an active porous membrane surface as the primary contactor with the medium to be filtered. Active surface membranes are comprised of either rotary (spinning) or oscillating (vibrating) membrane surfaces. For these studies, the rotary technology was selected. Other competitive technologies may exist; however, they were not identified during deliberate literature reviews.

The rotary membrane system developed by SpinTek Filtration, LLC (SpinTek ST-II/Speedy and ST-IIIL) was selected for this research for several reasons, including the ruggedness of the design, novelty of the technology, history of installed commercial systems (nuclear industry, oil-water separators, mining industry needs) and lower noise levels of the equipment, and overall cost. The rotary membrane system used in these studies can be equipped with one to 25 spinning membrane discs with 929 cm^2 of membrane surface area per disc. The membrane disc consists of a central Ryton™ core that is overlaid with a permeate carrier mesh (Fig. 1). The disc/carrier couple is then overlaid with a selective filtration membrane, and the entire assembly is glued together with urethane adhesives.

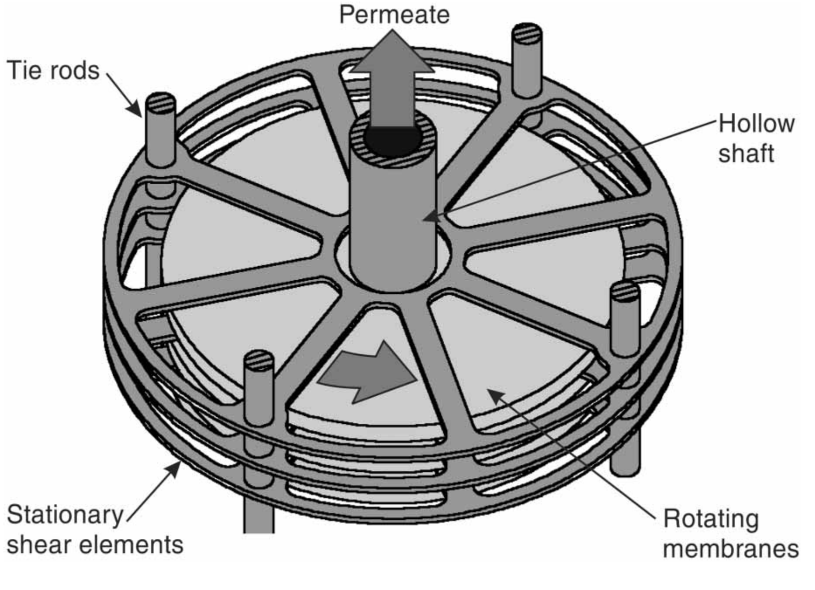

Figure 1. Typical rotary membrane disc assembly, shown with three discs and stationary "wagon wheel" turbulence-inducing elements.

The membranes used in the bench-scale system are the same as those used in the full-scale systems. For these studies, the disc rotation rate was fixed at 1100 rpm on a disc of 30.5-cm diameter. Rotary membrane systems can be fully automated, including feed flow, pressure, temperature, permeate flow, and all appropriate safety instrumentation (Fig. 2). If necessary, the filtrate from the rotary system could be polished by a separate nanofiltration system to remove smaller organic chemicals from the wastewater (Fig. 2).

When screening membrane materials, the rotary ultrafiltration system used one disc with a 0.1-micron composite ceramic–stainless steel or polyvinylidene fluoride (PVDF) membrane. During the concentration tests in the laboratory, two five-disc rotary ultrafilters were used. In the die casting facility, two five-disc rotary ultrafilters were used, both to selectively remove a glycerin/water mixture from the die lube and then to reconcentrate the die lube for recycling.

Bench-Scale Membrane Testing

A static membrane test cell was used to screen flat-sheet membrane samples. Those that had commercially acceptable flux levels with wastewater solutions

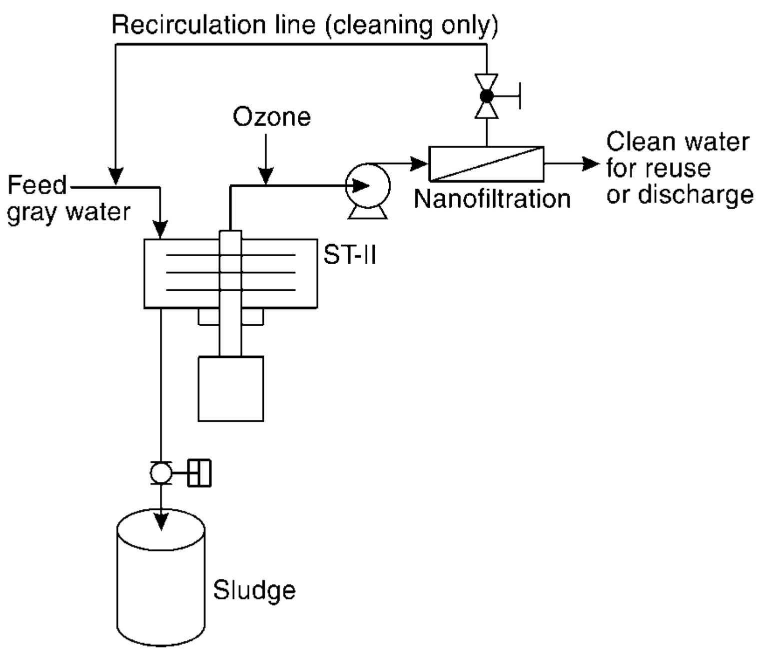

Figure 2. Rotary filtration system process flow.

from the die casting facility were then tested on a single-disc rotary filter. This was a rapid method of membrane screening.

The two bench-scale test platforms consisted of the membrane filtration system and a pumped skid. The static test cell (STC) contained one flat-sheet membrane test sample, while the rotary system had a single membrane filter. The major difference between the two systems was the shear generated at the surface of the membrane. In the rotary system, the membrane disc is 30.5 cm and rotates at 1100 rpm, with an average radial Reynolds Number, $Re_{r(avg)}$, of 2.0×10^5 to 1.2×10^6 (10).

Membranes were tested with wastewater provided by the Twinsburg facility. The wastewater was pumped from 210-L drums into a 2-L feed tank equipped with an agitating stirrer to ensure good mixing of the feed solution prior to its circulation in the membrane testing system. The feed tank was held at constant temperature. The wastewater was pumped from the feed tank to the membrane system. A throttling valve on the feed pump controlled the flow to the system and a back-pressure control valve maintained a constant pressure on the membrane system.

Membrane fluxes are defined as Flux = Filtrate Flow Rate/Area of Membrane} and measured in units of {liters/square meter-day} (L/m^2-day). During testing, data were recorded every 15 min, or as needed.

A nanofiltration polishing step was also evaluated to remove the remaining metal ions from the solution. The assumption was that, under the conditions at the die casting plant (temperature, pH, etc.), the metal ions would be clustered and contained within the larger organic phase globules, as is typically observed with solvent extraction systems. Therefore, one could assume that a nanofilter would remove the metal ions from the stream.

After successful completion of the initial membrane screening, a system consisting of two five-disc rotary ultrafiltration units, a feed pump, storage tank, associated piping and valves, and a fully automatic control panel was assembled. The system was designed to operate continuously and allow high concentrations of the feed. The general layout of this equipment is shown in Fig. 3. The process solutions were pumped from the feed tank into the rotary membrane system. A valve on the concentrate line of the rotary unit was used to maintain a constant pressure on the membrane system. The temperature was controlled using heaters located in the feed tank, along with a heat exchanger on the feed bypass line.

The two five-disc rotary ultrafiltration units were equipped with ceramic–stainless steel composite ultrafiltration membranes with a pore size of 0.1 microns (Trumem, Moscow, Russia). The ceramic composite membrane structures were assembled using stainless steel permeate spacers and Ryton™ discs, as previously described.

Several levels of water removal were investigated, including 3.3X (378 L reduced to 114 L, 378/114 = 3.3), 20X (378 L reduced to 18.9 L, 378/18.9 = 20X), and up to 50X (378 L reduced to 7.6 L, 378/7.6 = 50X).

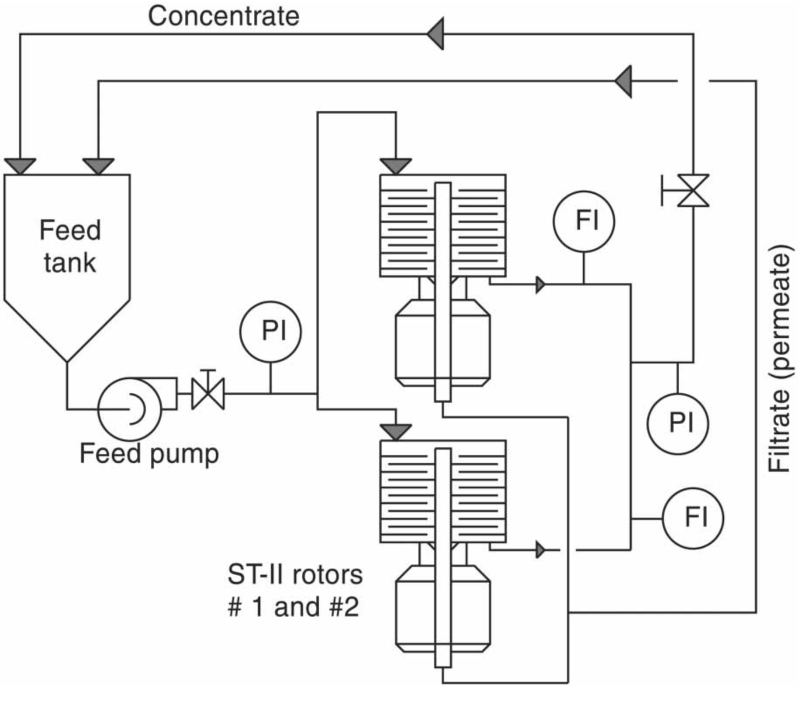

Figure 3. Process flow and instrument diagram for field demonstration system during stabilization. After the membrane fluxes were stable, the filtrate (permeate) line was removed from the feed tank to allow concentration.

To allow testing up to 50X concentration, an 1890-L polyethylene feed tank was used. The system's dead or "hold-up" volume was approximately 7 L, so at the end of the 50X experiment just enough concentrated feed solution remained to operate the rotary unit's feed pump and rotors. During normal operations at the 20X level, about 95 L typically remained, and the membrane rotors and pumps were not threatened with going dry.

Die Lube Concentration Testing Procedure at Twinsburg Facility

The feed tank was filled with 1890 L of fresh die lube wastewater, then the pumps and rotary membrane system were activated. The permeate and concentrate were recycled back to the feed tank until system performance, gauged by membrane fluxes, was stabilized. The permeate line was then withdrawn from the feed tank and placed in the industrial water drain at the plant while the feed solution was concentrated to the target value, typically 20X. The concentration was determined volumetrically.

Stable flux was defined as the flux at which the membrane provided a constant flux with the test solution under operating conditions. So, for example, the initial flux might be $2442\,L/m^2$-day and the stable flux $2035\,L/m^2$-day. With the die casting wastewater, the original or "virgin" clean water flux is never regained, even after the most stringent cleaning protocols. A small amount of oil and grease probably becomes lodged within the porous structure of the membranes and is not fully removed from the membrane structure during cleaning. Membrane cleaning needs were determined at the end of each experiment; cleaning procedures were implemented when the permeation rate fell to approximately $1220\,L/m^2$-day.

Selective Glycerin Removal from Concentrated Die Lube

Glycerin can be removed from the concentrated die lube by diluting the lube with clean water and then reconcentrating it with the rotary membrane—the glycerin passes through the membrane filter while dissolved in the permeating water. This separation was determined by the carbon oxygen demand (COD), which was significantly reduced in the die lube and increased in the permeate by this process. To remove the glycerin, the die lube solution was first concentrated to 20X. Then the rotary system was flushed with fresh water to establish that the membranes were not fouled, the concentrated feed solution was returned to the feed tank, and the balance of the volume made up with clean, softened water. The system was then restarted with the concentrate and permeate lines recycled back into the feed tank until a stable flux was achieved. Upon achieving a stable flux, the permeate line was moved to the industrial drain. After 3 h of concentration, the COD level in the permeate stream was 6700 mg/L; after 5.5 h, it was 4400 mg/L. This 30% reduction in COD suggests that glycerin can be selectively removed from the solution prior to recycling the die lube in the plant, which is desirable from the perspective of closed plant recycling.

Membrane Cleaning Process

During the early stages of these experiments, a cleaning process to remove foulants (primarily greases and oils) from the inorganic membranes, supports, and rotary disc shrouds was developed. Suggested cleaners included 2-butoxy-ethanol at elevated temperatures, hot water, and detergent (specifically, Dawn™ dish detergent, Proctor and Gamble, Cincinnati, OH, and "MC-4," a specialized alkaline membrane cleaner supplied by Zenon Environmental, Inc. Oakville, ON, Canada). We chose to clean the membranes with hot water and Alkanox™ laboratory cleanser as a model for Zenon's MC-4 membrane cleaner. The results of the cleaning efforts are summarized in Table 1.

Table 1. Membrane cleaning procedure developed for inorganic composite membranes

Membrane description	Membrane condition	Feed water temperature (°C)	Feed water pressure (MPa)	Flux (L/m^2-day)
Baseline: Virgin Membrane	Virgin	35		1,062
Used, Supplied by Metaldyne	Fouled	43	0.31	17.5
	Fouled	90	0.31	34
	Fouled, soaked in Alcanox overnight	90	0.31	264.7
Used, Supplied by Metaldyne	Fouled, treated w/Alcanox	40	40.28	294
	Fouled, treated w/Alcanox	50	0.28	360
	Fouled, treated w/Alcanox	70	0.28	459.8
	Fouled, treated w/Alcanox	85	0.28	475.5
	Fouled, treated w/Alcanox	40	0.28	358

Based upon these results, during the experiments the membranes were cleaned as follows. The commercial caustic MC-4 cleaner was combined with 5 wt% Dawn™ detergent and 5% Cellusolve (ethyleneglycol monobutyl ether, Aldrich Chemicals, Inc., Milwaukee, WI) in clean water in the feed tank. The system was run with the membranes spinning (1100 rpm) at 68–71°C without pressure for 30 to 100 min to wash the surfaces of the membranes. Then pressure was applied (0.172 MPa), and the water flux was observed. If the water flux approached the original membrane water flux (±20%), then the membranes were considered clean. The membranes were then rinsed with water, followed by a 5% citric acid rinse for 30 min to neutralize the surfaces of the membranes, followed by rinsing with plain, softened water (Culligan, Inc.) for 20 to 40 min.

Washing and Recycling Die Lube in Casting Operations

The die lube concentration testing showed good results, so a long-term test was designed and implemented at the Twinsburg facility. The first step in recycling die lube is to collect the mixture of die lube drippings, as well as the wash-down waters used to clean the die and other plant equipment. This was done using the plant drainage system. Concentrating this feed solution by 3.3X (3.3X, 20X, and 50X volume reductions from initial 378 L feed and 50X from 18.9 L) was found to be optimal for subsequent glycerin removal. After concentration to 3.3X, the rotary filter continued to operate, and fresh, soft water was added to the feed tank to selectively remove (diafiltration) the glycerin. After washing and reconcentration, the die lube was transferred to another tank for remixing and reintroduction into the die casting machine.

To begin each batch, 1890 L of fresh die lube wastewater was added to the feed tank of the rotary ultrafilter system. Concentration began, with the clear water filtrate being sent to the drain and the concentrate back to the feed tank. More untreated wastewater was added to the feed tank to replace the filtrate sent to the drain until the feed tank concentration reached 3.3X. At that point, softened tap water was added to the feed tank. The amount of water required to remove the glycerin varied depending on the amount of glycerin in the concentrated feed solution. Once the concentrated die lube was free of glycerin, as determined by COD decrease, it was transferred to another tank for remixing and reuse in the die casting machine. For the final phase of the project, the rotary ultrafilter operated continuously for 6 weeks, producing clean die lubricant for reuse in die casting operations.

Chemical Analyses

Chemical analyses were performed by Truesdail Laboratories, Inc., Tustin, CA, for the bench-scale testing, by Nalco Diversified Technologies, Chagrin Falls, OH, for the pilot-scale research, and by Biosolutions, LLC, Chagrin Falls, OH, for the final segment of the project.

RESULTS AND DISCUSSION

Due to their unique nature, the results for each phase of testing are presented and discussed individually in the following section.

Results of Bench-Scale Tests

Static Test Cell Membrane Screening Tests

During membrane screening in the static test cell, unexpected fouling and flux decline problems were encountered when using the ceramic—stainless steel composite membranes. The results of the initial experiments, shown in Figs. 4 and 5, suggested not pursuing the inorganic composite membranes

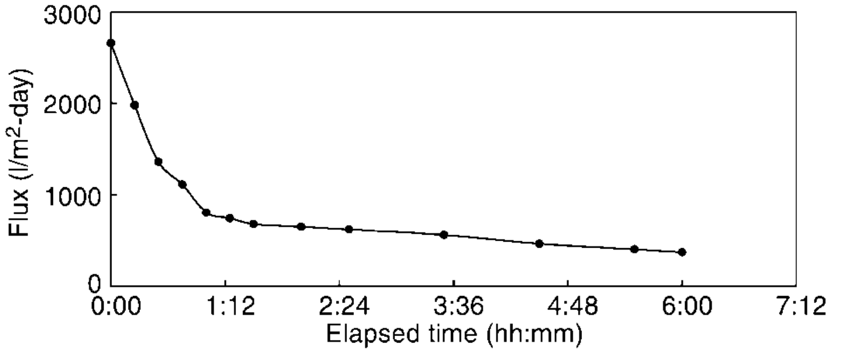

Figure 4. Flux profile for the static test cell with 0.15 micron ceramic membrane. The test was stopped due to low flux.

any further. The results of our experiments with the polymeric (PVDF) membranes, shown in Fig. 6, suggested that we pursue them and their relatives for the die casting water treatment process. Thus, the polymeric membranes were slated for further evaluation on the rotary membrane system.

Bench-scale Rotary Membrane Tests

Two different polymeric (PVDF-based) membranes were tested: an ultrafiltration membrane with a 100,000 molecular weight cut-off (0.05 micron, 400 angstrom mean pore diameter), and a "tighter" ultra/nanofiltration membrane with a 10,000 molecular weight cut-off (0.005 microns, 40 angstrom mean pore diameter). These membranes were made by different manufacturers, and the pore sizes probably are not exactly what they are specified to be in relationship to one another, which likely explains why they had similar

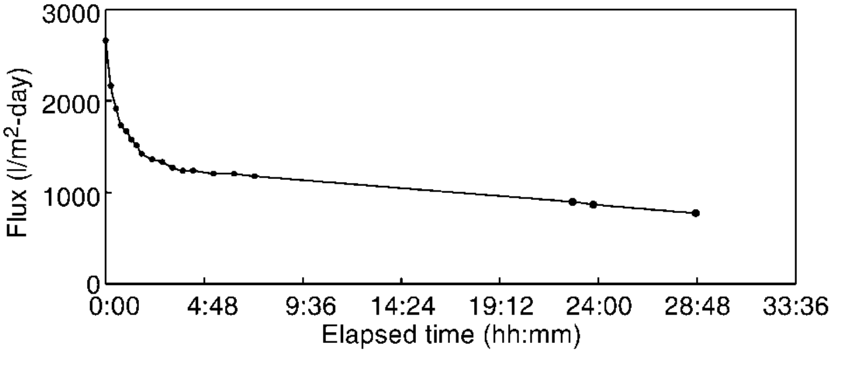

Figure 5. Flux profile for static test cell with 0.007 micron ceramic membrane.

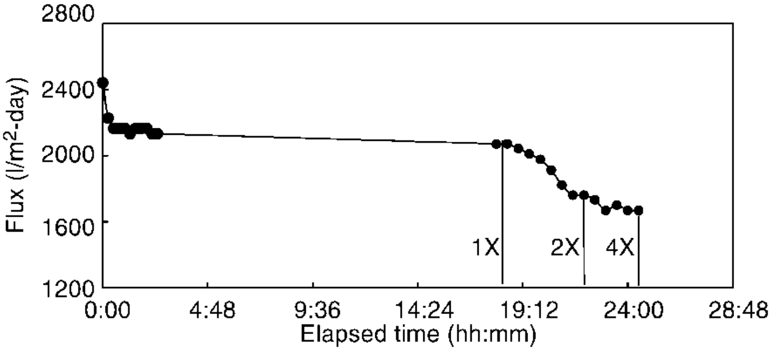

Figure 6. Flux profile for the static test cell with 100,000 molecular weight cut-off (0.05 microns) polymeric membrane.

fluxes even though their nominal pore sizes differed by a factor of 10. Flux and concentration profiles from these tests are shown in Figs. 7 through 10. At the completion of each of these experiments, the permeate solutions were allowed to stand overnight before being delivered to the analytical labs. During this time, significant hydro-gel-like precipitates formed in the permeate solutions. The gels, speculatively, are hydrated aluminum, zinc, and iron oxy-/hydroxy-species (11). The gels are very pH sensitive and dissolve immediately with drop-wise additions of acid to the 1-L samples. Due to the complex nature of the solutions that were evaluated (i.e., high aluminum and zinc contents), all samples were acidified with drop-wise additions of hydrochloric acid, prior to analysis, to ensure that all metal ions were dissolved in the solutions. The analytical data from the screening tests are summarized in Table 2; the concentration factors for each component are summarized in Table 3.

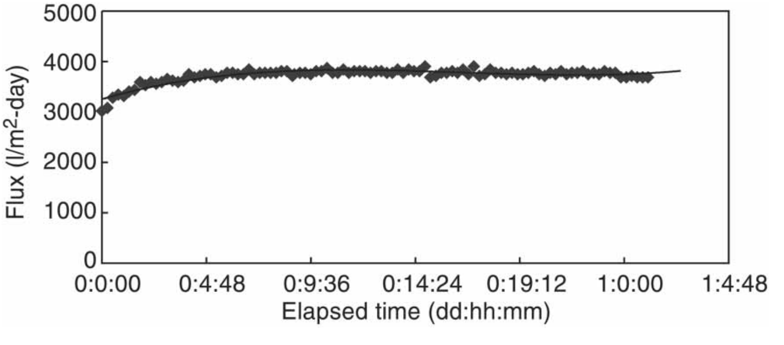

Figure 7. Flux profile for 100,000 molecular weight cut-off polymeric (PVDF) membrane (ST-II-1 Test 2).

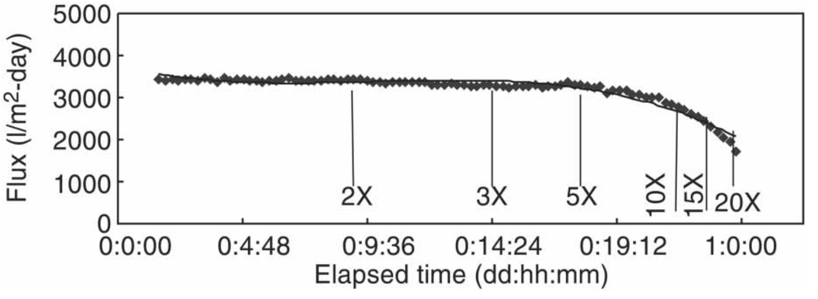

Figure 8. Concentration profile for 100,000 molecular weight cut-off polymeric (PVDF) membrane (ST-II-1 Test 2).

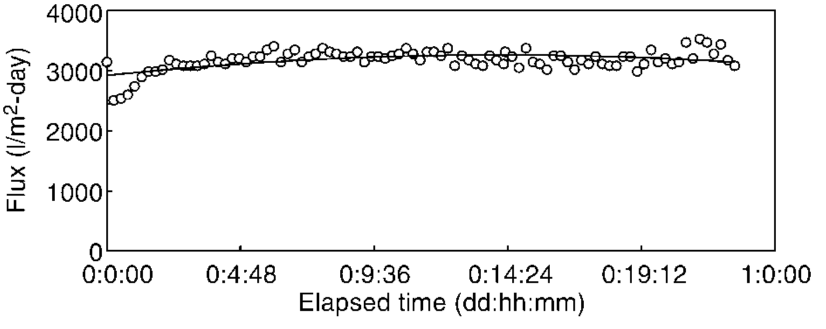

Figure 9. Flux profile for 10,000 molecular weight cut-off polymeric (PVDF) membrane (ST-II-1 Tests).

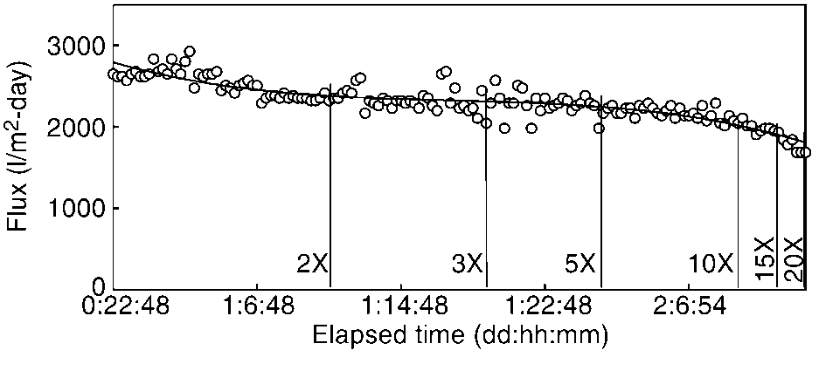

Figure 10. Concentration profile for 10,000 molecular weight cut-off polymeric (PVDF) membrane (ST-II-1 Test 3).

Table 2. Chemical analyses for laboratory tests with polymeric (PVDF) membranes

Sample ID, Description	Total organic carbon mg/L	Biological oxygen demand mg/L	Carbon oxygen demand mg/L	Oil & grease mg/L	Pb mg/L	Cu mg/L	Ni mg/L	Zn mg/L
100,000 MW cut-off polymeric membrane								
1) Initial Perm.	2,108	2,262	6,296	11.2	ND	ND	0.08	0.47
2) Raw Feed	3,463	2,714	12,567	225	ND	0.12	0.08	0.55
3) 1X Final	2,143	2,456	6,174	12.7	ND	ND	ND	0.46
4) 4X Conc.	9,287	6,030	48,230	490	ND	0.70	0.10	0.74
5) 4X Perm.	2,272	2,445	6,456	12.0	ND	ND	0.09	0.47
6) 8X Conc.	19,637	8,072	87,928	634	0.36	1.44	0.15	1.00
7) 8X Perm.	2,683	2,277	6,915	10.5	ND	ND	0.09	0.52
8) 12X Conc.	22,518	3,438	1,17,498	1,078	0.51	2.01	0.19	1.22
9) 12X Perm.	2,488	2,295	7,344	11.6	ND	ND	0.11	0.51
10) 16X Conc.	29,404	11,789	1,63,077	1,538	0.70	2.80	0.22	1.38
11) 16X Perm.	2,839	1,558	8,593	6.5	ND	ND	0.10	0.54
12) 20X Conc.	43,339	12,250	2,06,172		1.04	4.00	0.29	1.72
13) 20X Perm.	2,680	4,014	8,725	12.4	ND	ND	0.09	0.51

10,000 MW cut-off polymeric membrane								
14) Initial Perm.	2,406	2,219	7,393	11.3	ND	ND	0.08	0.52
15) Raw Feed	3,210	2,416	11,590	274	ND	0.11	0.10	0.54
16) Final Perm.	2,211	1,443	6,758	13.8	ND	ND	0.08	0.51
17) 4X Perm.	2,206	2,049	7,115	5.6	ND	ND	0.08	0.51
18) 4X Conc.	6,504	3,388	26,060	294	ND	0.36	0.09	0.63
19) 8X Perm.	2,388	2,152	7,012	18.4	ND	ND	0.09	0.55
20) 8X Conc.	10,380	3,880	47,890	634	ND	0.72	0.13	0.83
21) 12X Perm.	2,606	2,611	7,408	9.4	ND	ND	0.09	0.57
22) 12X Conc.	10,572	4,699	72,370	713	0.33	1.12	0.16	1.04
23) 16X Perm.	2,764	2,205	8,047	7.9	ND	ND	0.09	0.56
24) 16X Conc.	14,340	5,176	79,200	944	0.35	1.31	0.15	1.01
25) 20X Perm.	2,756	1,979	8,315	11.7	ND	ND	0.09	0.58
26) 20X Conc.	18,614	6,117	1,04,687	1,202	0.40	1.68	0.17	1.11

Table 3. Concentration factors for polymeric (PVDF) membranes in laboratory tests

Sample ID (see Table 2 for description)	Total organic carbon mg/L	Biological oxygen demand mg/L	Carbon oxygen demand mg/L	Oil & grease mg/L	Pb mg/L	Cu mg/L	Ni mg/L	Zn mg/L
100,000 MW								
1, 3/2	1X	1X	2X	18X	ND	R	1X	1X
4/5	4X	2X	7X	41X	ND	R	1X	1X
6/7	7X	3X	13X	60X	R	R	1X	1X
8/9	9X	1.5X	15X	98X	R	R	1X	1X
10/11	10X	8X	19X	220X	R	R	2X	2X
12/13	16X	3X	24X	120X	R	R	3X	3X
10,000 MW								
15/14, 16	1X	1X	2X	25X	ND	R	1X	1X
18/17	3X	1X	3X	50X	ND	R	1X	1X
20/19	4X	1X	2X	34X	R	1X	1X	1X
22/21	4X	2X	9X	75X	R	R	2X	2X
24/23	5X	2X	10X	120X	R	R	2X	2X
26/25	6X	3X	13X	100X	R	R	2X	2X

Rotary Nanofiltration Membrane Tests

The experimental results, presented in Figs. 11 and 12, show that a nanofilter (either ceramic composite or polymeric) is not adequate to remove oils and greases from water at the industrial scale because fouling of the membrane results in large losses of membrane flux. Furthermore, chemical analysis showed, to our surprise, that metal ions are not removed from the stream. The chemical analysis data are summarized in Table 4.

Discussion of Bench-Scale Tests

Polymer membranes in the rotary system provided surprisingly high fluxes and high-quality separations. The rotary membranes exhibited less fouling

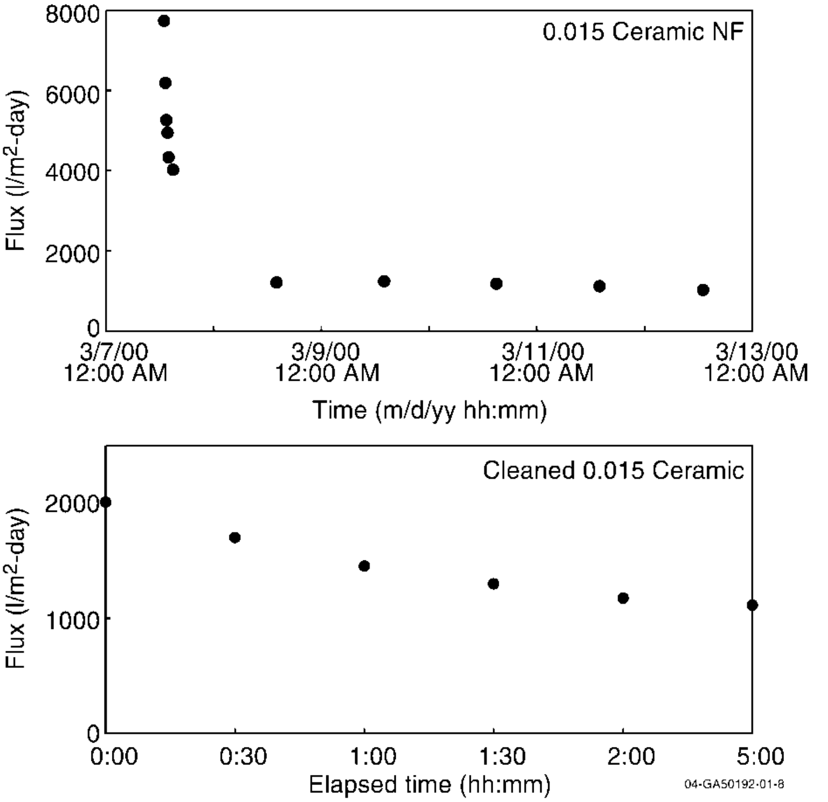

Figure 11. Performance of ceramic rotary membrane nanofiltration membrane (nominal 0.015 micron mean pore diameter) shows flux decline (top), probably due to fouling, and improvement after cleaning (bottom).

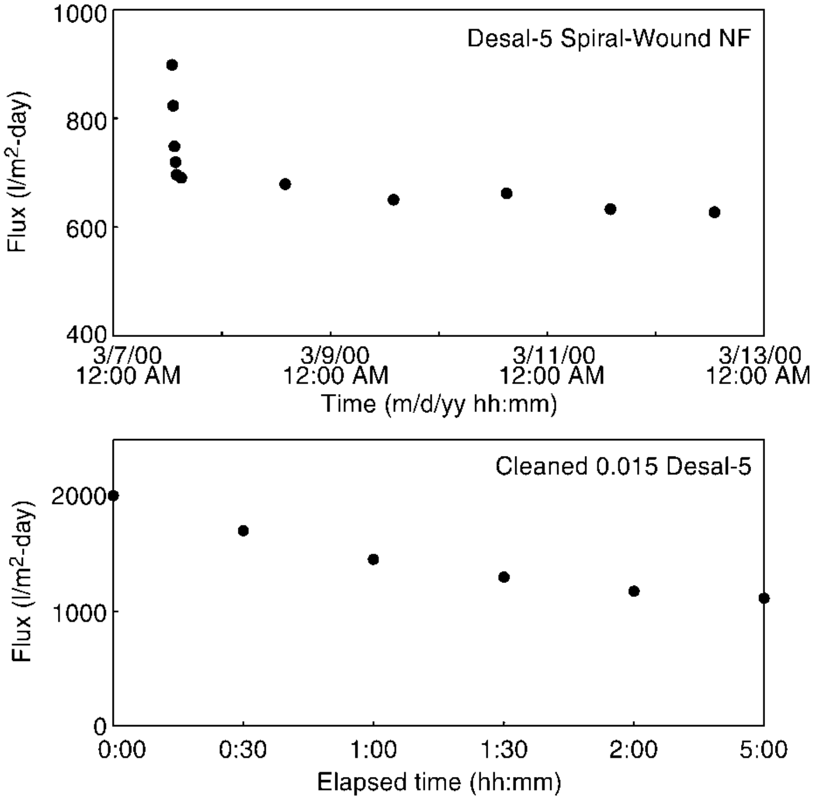

Figure 12. Performance of Desal-5 spiral-wound, static polymeric nanofiltration membrane shows flux decline (top), probably due to fouling, and improvement after cleaning (bottom).

than the static systems, and they consistently exhibited larger and more stable fluxes than the static membranes. The rotary ultrafiltration membranes significantly reduced total metals in the permeate (water); however, after a period of time, several metals (notably lead and copper) were detectable in the retentate as the organic concentration of the feed solutions increased. This result suggests that the metals prefer to stay with the organic components of the die casting solutions. Although the metals content was reduced significantly using tight ultrafiltration rotary membranes, significant hydro-gel-like precipitates formed in the permeate solutions upon standing. The gels were probably hydrated aluminum and iron oxy-/hydroxy-species. These gels are very pH sensitive and dissolved immediately with drop-wise additions of hydrochloric acid to the samples. Nanofiltration to polish the effluent showed only small concentration increases of the metal ions (Table 4, Desal-5 spiral wound cartridge),

Table 4. Chemical analyses for ceramic and polymeric nanofilter tests

Sample ID	Total organic carbon mg/L	Biological oxygen demand mg/L	Carbon oxygen demand mg/L	Oil & grease mg/L	Pb mg/L	Cu mg/L	Ni mg/L	Zn mg/L
Desal-5 spiral wound cartridge								
Permeate	1,510	1,160	3,931	ND	ND	0.09	0.24	0.63
Raw feed	3,463	2,714	12,567	225	ND	0.12	0.08	0.55
0.015 micron ceramic membrane								
Permeate	1,894	2,418	4,885	ND	ND	0.05	0.23	0.42
Raw feed	3,463	2,714	12,567	225	ND	0.12	0.08	0.55

in the retentates. The results of the experiments, however, were encouraging because permeates from the nanofiltration system were clear and colorless with no significant gel precipitation upon standing. A true reverse osmosis membrane, such as those already installed at the die casting plant, would be most appropriate for a polishing step should it be needed.

The bench-scale tests demonstrated that rotary membrane technology was a good candidate for field testing at the die casting plant. These results provided the basis for proceeding further with the project.

Discussion of Pilot-Scale Rotary Membrane Testing

The first membranes mounted on the rotary systems were commercial polymeric (PVDF) ultrafiltration (100,000 molecular weight cut-off) membranes. These membranes worked well for the bench-scale single-disc tests. However, in the pilot-scale system, when the membranes were motionless for even a few minutes in clean or dirty water they tended to "pucker" on the discs. Then, when the membranes began rotating, they rubbed on the wagon wheel-shaped spacers (Fig. 1). Rubbing on the spacers marked and tore the membranes' surfaces, causing them to become nonselective. All measures to mitigate membrane rubbing failed (including attempts to increase membrane-shear element distance and tightening of the membrane on the rotating disc). Therefore, stainless steel–ceramic composite membranes with 0.1-micron pores were chosen for use in the pilot-scale tests. The performance of these membranes exceeded our expectations. However, membrane fouling remained a problem, so we used the cleaning protocols described previously to remove oils, greases, and other foulants.

During testing at the die casting plant, we concentrated the die lube solution to the expected 3.3X and 20X levels, and even 50X. However, at the 50X level, process reliability was difficult to maintain, membrane life was limited due to fouling, and permeate quality was poor. We concluded that the 50X level was impractical for commercial use. At the 20X level, the equipment was reliable, the quality of permeate was acceptable for discharge to the drain, and solids removal supported reuse of the die lube.

Application of Recycled Die Lube for Die Casting

The principal goal of this final phase of the project was to test the ability of the membrane system to both concentrate and purify the die lube for closed-plant recycling. Therefore, it was necessary to test the die lube that was recovered in a production casting process. The die casting machine used in this test makes aluminum castings for the automotive industry. The casting process for this product exemplifies the most extreme demands on the die lubricant. In this process, die cooling, mold release characteristics, and resistance to metal adhesion (or soldering) are the most critical parameters that must be monitored. The castings made in this study are roughly 26.7×26.7 cm. They are predominantly 2.75-cm thick, with one large feature that has a thickness of 3.18 cm. Because of the features and details of this part, its surface area is great compared to its overall length and width.

For this test, the wastewater from the casting operation was pretreated in the plant's system for removing free oils and greases using rope skimmers and dissolved air flotation. Then the wastewater was processed in the rotary membrane ultrafilter system, which separated the unwanted pollutants and water from the die lubricant. Over time, membrane fouling diminished the fluxes. However, membrane cleaning removed the oils and greases; the fluxes returned nearly to the manufacturer's original clean water flux specifications. After concentration to the 3.3X level, the die lubricant was rediluted to the specified total solids content, reconcentrated to remove glycerin, and rediluted with water to the specified solids level for use in the casting process. Batches mixed from 50% recycled lubricant and 50% new lubricant were delivered to the casting machine each day. The carbon oxygen demand (COD) of the wastewater solution, after concentration to the 3.3X level, varied between 12,000 and 15,000 mg/L. After washing with soft water, the COD was reduced to 1,500 to 2,000 mg/L. This reduction was attributed to removal of small, soluble, organic chemicals, primarily glycerin that came from other plant operations.

Comparison of the test data and quality records before and after the recycled die lube was introduced to the system indicates that the scrap was reduced from 8.4% to 7.8%. No statistical analysis has been conducted to evaluate the significance of this change. A slight increase in tooling costs (measured in cost per unit of production) was observed. However, the increase in costs was influenced significantly by tool breakage that occurred during this test. The increase in tooling costs was evaluated and cannot be related directly or indirectly to the recycled die lubricant. The operational cost analysis for a rotary membrane system in the die casting water treatment application is summarized in Table 5.

SUMMARY

Based upon our laboratory-scale experiments, we asserted that the rotary ultrafiltration membranes could substantially reduce organics found in the die casting solutions. The initial oil and grease were reduced by 20–25X, carbon oxygen demand (COD) by 1.5–2X, and total organic carbon by 0.6, while biological oxygen demand remained the same. As the organic concentrations of die lube increased in the retentate, the permeate concentrations of the organics remained remarkably similar to their original concentrations. This speaks for an equilibrium being reached and the membrane pore size being very stable.

During testing on a larger scale in the die casting plant, we successfully concentrated the die lube solution to 3.3X and 20X levels, and even as high as 50X. However, at 50X process reliability was difficult to maintain, membrane lifetime was limited, and permeate quality was poor. We concluded that 50X is impractical for commercial use. At 20X, the equipment was reliable, the quality of permeate was acceptable, and solids removal supported recycling of the die lube.

The final step for this project was a continuous 6-week test that demonstrated the rotary membrane system's ability to concentrate, wash, and recycle the die lube solution at the die casting plant. Die lube was continually concentrated and the COD reduced by a factor of 8 to 10, which is attributed to successfully removing glycerin from the die lube. The cleaned die lube was then recycled in a production die casting machine. Test data and quality records indicate that scrap from the die casting operation was reduced from 8.4% to 7.8% while using the recycled die lubricant.

The two rotary filters operated continuously for 6 weeks without any downtime due to mechanical or electrical failure. The inorganic composite membranes showed no apparent damage due to abrasion or to the effects of the die lube solution. Only seven cleaning cycles were required to maintain filtrate throughput. Several experimental runs were conducted without prior membrane cleaning, which demonstrated that it would not be necessary to clean the membranes between campaigns in full-scale implementation of the system. This is desirable because cleaning increases costs and generates waste.

Table 5. Rotary membrane system cost analysis

Costs		
Capital		
Rotating membrane system	$750,000	
Commissioning	$24,000	
	Total capital cost	$774,000
Operating		
Power cost	$0.06/kW-hr	
Cost per cleaning	$25.00	
Membrane replacement	$96,000	
Cost per kL		
Membrane replacement	$3.93	
Membrane cleaning	$0.08	
Power	$2.74	
Misc. operating cost	$0.17	
	Total operating cost per kL	$6.92
	Total daily operating cost	$457.40

Assumptions			
System		Operation	
Feed water volume	75,600 L/day	Operating days/month	30 days
System output	71,820 L/day	Operating pressure	0.28 MPa
Percentage recovery	95%	Recycle flow/disc pack	3.78 L
Membrane		Total recycle flow	1,210 L/min.
Type	0.1 micron	Recycle pressure drop	0.221 MPa
Performance	2,442 L/m^2-day	Pump efficiency	80%
Diameter	11 in./disc pack	Motor efficiency	94%
Surface area	929 cm^2/disc pack	Brake HP—Recycle pump	5.0 BHP
Disc packs/system	320	Brake HP—Rotors	200 BHP
		Brake HP—Total required	160.0 BHP
		Total system power consumption	119.4 kW-h
		Membrane	
		Cleaning interval	5 days
		Lifetime (conservatively)	1 yr

CONCLUSIONS

The oil and water mixtures produced by a die casting plant can be cleaned up using rotary membrane technology—field testing showed very promising results. The wastewater solution was concentrated to the targets of 3.3X and 20X in seven separate tests, and one test further concentrated it to 50X. (However, throughput from 20X to 50X is too low for commercial use.) During all of these tests, the filtrates were clear and colorless, indicating nearly complete removal of the die casting lubricant material from the wastewater. The rotary filter system also removed glycerin from the concentrated die lube. At the completion of these tests, the membranes were cleaned and flux recovered.

This project successfully demonstrated that a rotary ultrafilter system can concentrate the die lube components from the waste stream of a die casting operation, thereby improving discharge quality by lowering the carbon oxygen demand of the wastewater and recovering both the die lube and water from the wastewater stream for reuse. Manufacturing records indicate that the scrap was reduced from 8.4% to 7.8% after the recycled die lube was introduced into the system. The recycling system operated continuously for 6 weeks; only seven membrane-cleaning cycles were required, and the system experienced no down time due to mechanical or electrical failure.

The studies described in this paper yielded tremendous results. They proved that die lubricant can be recycled. Although further evaluation is needed to determine if it is cost effective for the die lube to be recycled, these studies have shown significant opportunities for further evaluation by the die casting industry, and other industries with similar waste streams.

REFERENCES

1. McCaffrey, R.R. and Cummings, D.G. (1988) Gas Separation Properties of Phosphazene Polymer Membranes, Fifth Symposium on Separation Science and Technology for Energy Applications, Knoxville, Tennessee, October 26–29, 1987, Sep. *Sci. Technol.*, 23: 1627–1643.
2. Allen, C.A., McAtee, R.E., Cummings, D.G., Grey, A.E., and McCaffrey, R.R. (1987) Separation of Cr Ions from Co and Mn Ions by Poly(bis(phenoxy)phosphazene) Membranes. *J. Membr. Sci.*, 33: 181–189.
3. McCaffrey, R.R., McAtee, R.E., Cummings, D.G., Grey, A.E., Allen, C.A., and Appelhans, A.D. (1986) Synthesis, Casting, and Diffusion Testing of Poly[bis(trifluorethoxy)phosphazene] Membranes. *J. Membr. Sci.*, 28: 47–67.
4. Femec, D.A. and McCaffrey, R.R. (1994) Solvent Replacement in the Synthesis of Persubstituted Phosphonitrilic Hydroquinine Prepolymer Materials. *J. Polym. Sci.*, 52: 501–505.
5. Peterson, E.S., Stone, M.L., Bauer, W.F., and Gianotto, A.K. (1992) The Removal of Organics from Waste Streams Using Polyphosphazene Membranes,

Proceedings of the International Conference on Effective Industrial Membrane Processes, Benefits and Opportunities, Euromembrane 92-Paris, Paris, France, 1992, 6 (21): 381–387.

6. Peterson, E.S., Stone, M.L., McCaffrey, R.R., and Cummings, D.G. (1993) Mixed Gas Separation Properties of Phosphazene Polymer Membranes. *Sep. Sci. Technol.*, 28 (1–3): 423–440.
7. Peterson, E.S. and Stone, M.L. (1994) Helium Separation Properties of Polymer Membranes. *J. Membr. Sci.*, 86: 57–58.
8. Peterson, E.S., Stone, M.L., Orme, C.J., and Reavill, D.A., III (1995) Chemical Separations Using Shell and Tube Composite Polyphosphazene Membranes. *Sep. Sci. Technol.*, 30 (7–9): 1573–1587.
9. Peterson, E.S., Stone, M.L., and Orme, C.J. Method for Preparing Membranes with Dynamic Separation Performance. US Patent 5,385,672.
10. Viadero, R.C., Baughn, R.L., and Reed, B.E. (1999) Study of Series Resistances in High-Shear Rotary Ultrafiltration. *J. Membr. Sci.*, 162: 199.
11. Cotton, F.A. and Wilkinson, G. (1988) *Advanced Inorganic Chemistry*, 5th Ed.; Wiley Science Publishers: New York; 711.