Ceramic Membranes for Environmental Related Applications

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The development of a low cost high performance ceramic membrane technology has been stimulated by the need for submicron filtration of aggressive fluids in harsh environments and/or in cost sensitive environmental applications. Our recent progress in the development of a hollow fiber/tubular potted bundle based ceramic membrane is highlighted in this work. Results are presented from several long-term (>1.5 year) field tests and commercial installations dealing with spent solvent recovery, used oil recycling, and drinking water treatment.

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KEYWORDS

Ceramic membranes; solvent recovery; used oil recycling; drinking water treatment

INTRODUCTION

Although ceramic micro- and ultra-filtration membranes were developed at least half a century ago, they have always been considered a niche product. Due to their high cost (e.g., ≥\$1,000/m^2 versus \$100's/m^2 for polymeric counterparts), their use has been limited primarily to food, beverage and pharmaceutical industry applications traditionally. Recently, most of the development activities have been concentrated in gas separations, particularly as ionic conductors for oxygen transport and as molecular sieve membranes for hydrogen separations. Their use in environmental applications has been very limited due to cost considerations, although they offer several unique advantages in this area, such as chemical and thermal stability and rugged structural stability.

In the past few years Media and Process Technology Inc. (M&P) has focused on the development of low cost high performance ceramic membranes and their use in cost sensitive environmental-related applications. The product that has evolved is based upon single ceramic tubular elements potted into large high surface area bundles as Figure 1 illustrates. In this configuration, the membrane cost is less than 1/3 of that of existing monolithic ceramic membrane technology. However, it still retains the high purity materials of construction and controlled pore size distribution of the more expensive counterparts. Further, the robust nature of the technology has been demonstrated in both field tests and commercial installations for operating times of over 1.5 years with no significant mechanical failure. Finally, to meet the application requirements, the individual tubes as well as the tube bundles can be prepared in various sizes. This flexibility is simply unavailable using conventional monoliths. Numerous industrial streams, both large and small scale, have been identified, which can benefit from this low cost high performance ceramic membrane technology. In this article we will present several examples to illustrate the capabilities of these ceramic membranes to separate colloidal, submicron or micron size suspended particles from a wide range of fluids, including drinking water, industrial solvents and oil (i.e., lubricants) to economically meet current and pending drinking water regulatory treatment objectives or to allow recycle and reuse of these solvents and oil.

The advantages of ceramic membranes for these applications include:

- Narrow and well defined pore size distribution in comparison with their polymeric counterparts; thus, they can achieve a high degree of particulate removal at high flux as demanded by such diverse applications as the removal of viral contamination from drinking water sources or emulsified oils from wastewaters. Figure 2 presents the pore size distribution for our commercial ceramic membranes with various nominal pore sizes covering the micro- and ultra-filtration range.
- Material stability in harsh environments; thus, high temperature deashing of spent lubricants and the removal of submicron suspended/dissolved solids from industrial solvents can be cost effectively practiced.
- Membrane cleaning with harsh chemicals (if necessary); thus, the membrane performance stability can be assured, which is critical in dealing with waste streams that often vary constantly or display a high propensity for membrane fouling.

Tube OD x ID [mm]	Surface Area per Volume [m^2/m^3]	
	ID	OD
3.0 x 1.5	470	940
4.0 x 2.0	400	800
5.5 x 3.5	325	510

Figure 1. M&P ceramic membrane tubes and four-inch commercial element. Also given is the packing density of the various standard tubes based upon the inside and outside surface area.

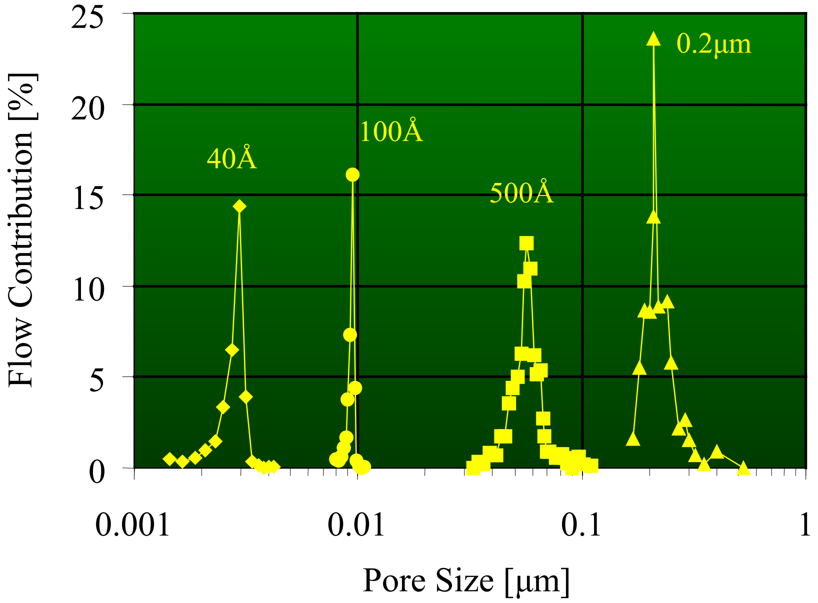

Figure 2. Pore size distributions of various M&P ceramic membranes.

In this article we will present three commercial applications using our ceramic membranes to highlight these advantages.

HIGH FLASH SOLVENT RECOVERY

Background

Throughout the U.S. and around the world, a variety of industries are moving from conventional solvents (toluene, xylene, acetone, mineral spirits, for instance) to high flash solvents including dibasic and other esters, glycol ethers, terpenes (d-limonene isomers), etc. For instance, approximately 65 to 70% of the cleaning solvents used in the screen-printing industry, representing over $50 MM per year in solvent sales, are high flash solvents. Certainly, one of the primary motive forces behind this move has been regulatory pressure. The significantly lower volatility of these solvents yields substantial reductions in both fugitive emissions and exposure of employees to fire/explosion hazards. In addition, these solvents offer several economic advantages. For instance, since explosion proofing is not necessary, the overall facility operation is rendered less complex and the equipment is less expensive. Moreover, health hazards associated with these solvents, which display very low levels of acute oral or inhalation toxicity, are minimal.

The use of high flash solvents in the screen-printing industry, however, presents several undesirable operating disadvantages. First, these materials are very expensive. Virgin high flash solvent prices typically range from $15 to >$30 per gallon versus <$5 per gallon for conventional solvents. Second, although the industry is large, it is highly dispersed, so that spent solvent disposal is expensive, ranging from $1 to >$5 per gallon. Additionally, the spent solvent is contaminated with heavy metals from the pigments, further complicating spent solvent disposal. The above disadvantages associated with the use of high flash solvents can be eliminated if the solvent can be recycled on-site to a near virgin quality for reuse.

Disadvantages of Existing Solvent Recovery Technologies

Although solvent recycling could dramatically reduce these problems, conventional reclamation technologies, such as distillation and standard filtration, suffer significant limitations in terms of technical viability, cost, and user friendliness, as listed in Table 1. These conventional technologies have been evaluated and found incapable of meeting the needs of the screen-printing industry. Hence, as expected, little recycling is practiced presently. A reclamation technology specifically addressing this industry segment is highly desirable. It would not only improve the overall operational economics, but also achieve the national environmental objectives: VOC abatement through the elimination of volatile solvent usage and resource recovery/waste minimization through recycle and reuse.

Ceramic Membrane Filtration Technology

Filtration using ceramic membrane technology developed by Media and Process Technology, Inc. overcomes all of the problems associated with distillation and filtration as listed in Table 1. We have developed a ceramic membrane-based solvent recovery system uniquely suitable for the high flash solvent user (see Figure 3 for a commercial unit). We have successfully installed several systems that have been in operation for over two years. In general, three broad categories of ink systems are used in the screen printing industry, namely, (i) solvent based, (ii) heat set curable, and (iii) UV curable. Numerous bench-top studies have been conducted to confirm the regeneration of spent high flash solvents generated using each of these ink systems. In all cases, we have demonstrated that these spent solvents can be regenerated to near virgin quality. In this section, results from a representative sampling are presented.

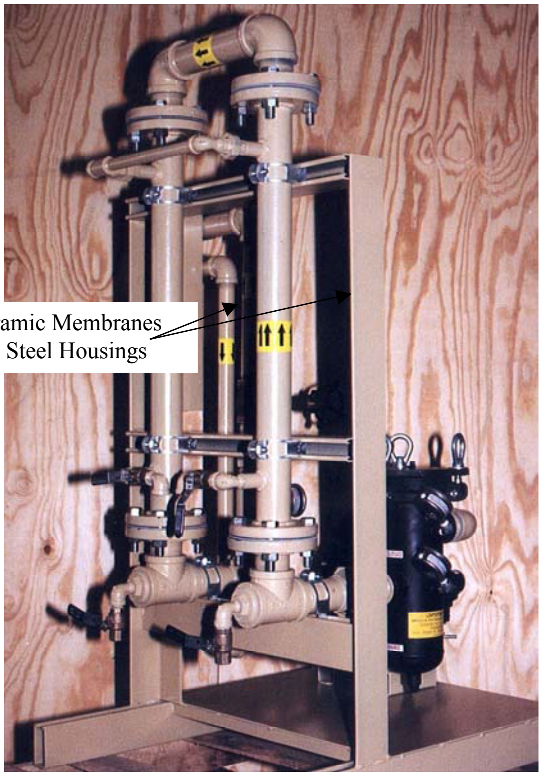

Figure 3. High flash solvent recovery unit featuring M&P ceramic membranes.

Laboratory Evaluation of Spent Solvent Obtained from a Commercial Screen Printer

As an example, a waste solvent sample (contaminant is a "heat set" ink) was obtained from a client. The waste sample was highly turbid due to contamination with screen-

Table 1. Limitations of distillation and commercially available filtration technology and advantages of ceramic membrane technology for the recovery of spent high flash solvents.

Conventional Technologies:

Technology		Limitation
Distillation		1. High temperature/vacuum operation requiring experienced operator. 2. Fugitive emissions and fire/explosion hazard. 3. Thermal degradation of the solvent and/or additives. 4. Many additives (surfactants, detergents, polymers, etc.) do not evaporate rendering distilled solvent essentially useless. 5. Not suitable for small-scale user because of cost and/or complexity.
Filtration	Diatomaceous Earth	1. Recovered product quality is poor. 2. Spent DE disposal problematic. 3. Blinding of media with contaminants yields low flux or productivity.
	Polymeric Membranes	1. No polymeric membrane available with the required submircon pore size and solvent stability.

M&P Ceramic Membrane Technology:

Advantage	Comments
1. Excellent solvent resistance.	Can be used to treat entire range of high flash solvents.
2. Excellent recovered product quality.	Finished product quality similar to virgin material.
3. Low temperature operation.	No thermal degradation of solvent.
4. Good product recovery ratios.	>90% solvent recovery can be achieved.
5. No additional waste disposal problem.	Waste volume necessary for disposal is <10% of original volume.
6. Low tech.	Technology is easily implemented. No special operator training required. Minimal maintenance, etc.
7. Implemented on small scale.	Most high flash solvent waste is highly segmented with numerous small-scale generators of waste solvent.

printing pigments and was considered unusable. This sample was recycled using M&P ceramic membrane technology. The membranes were operated at room temperature at a driving pressure of ca. 35 psi. The permeance at the beginning and the end of the membrane test was ~8 and ~2.5 liter/m^2/hr/bar, respectively, and 76% of the solvent was recovered. At these conditions, it is possible to recover a drum of used solvent in two or three days at a solvent savings of >$1,000 per drum. Hence, the membrane is more than paid for with the first recovered drum of solvent. Further, simply removing the concentrated residue from the system and replacing it with a fresh batch of spent solvent easily and fully reversed the permeance decay. Hence, in general, membrane cleaning is unnecessary in this industry.

The permeate sample was clear and orange in appearance, and no change in solvent visual quality was observed throughout the run. Figure 4 shows the clarity of the membrane-recycled solvent compared with the spent material for this and several other solvents tested by us. The viscosity of the permeate sample was 2.5cSt, approximately 25% higher than the virgin solvent at 2.0cSt. The higher viscosity of the permeate sample results from a loss of low boiling solvent components and contamination of the solvent by polymeric binders used in the inks. The membrane treatment does not alter fundamentally the solvent. In actual screen cleaning tests, the solvent power of the permeate sample was found to be comparable to the virgin solvent.

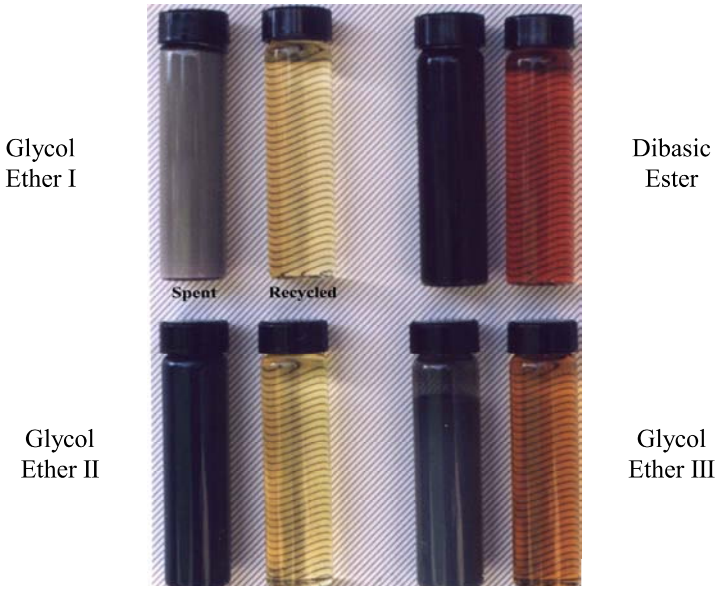

Figure 4. Spent and recycled samples of solvent reclaimed using M&P ceramic membranes. The spent samples were obtained from various clients and were unusable. The recycled solvent is turbidity free and is comparable in quality, in terms of solvent cutting power, to the virgin solvent.

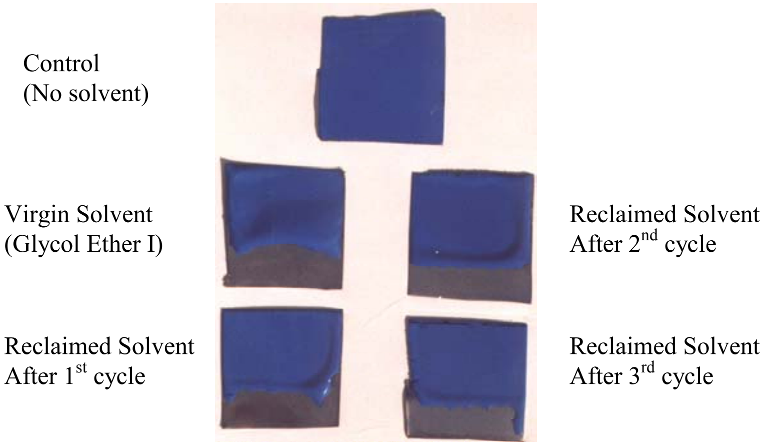

Figure 5. Paint test coupons showing the stripping power of a solvent reclaimed and reused three times with M&P ceramic membranes. Even after three cycles, the reclaimed solvent is as effective as the virgin material at removing paint from the test coupons.

Number of Regeneration Cycles

The number of times a spent solvent sample can be regenerated is of interest to the end user. Three simulated reuses of a spent screen printing solvent were conducted using our bench membrane test systems. Samples from each cycle as well as the virgin solvent were tested for solvent power in a simulated paint-stripping test. In this test, 2" square coupons coated with a fully cured sample of Rustoleum 9100 System High Performance Epoxy Paint were immersed to about 1/3 their height in each of the solvent samples and left to stand covered. Within two hours all of the paint coupons showed signs of blistering and peeling. Left to stand overnight, the paint was completely removed from the exposed portion of the coupon as shown in the photos in Figure 5. Overall, no difference in solvent stripping power was noted for any of the samples at either two hours or overnight. Although this test does not cover all possible solvent and ink combinations, the results demonstrate that the solvent can be recycled and reused many times. Finally, all of our customers, some of whom have been using systems based upon M&P ceramic membranes for over two years, report virgin solvent requirement reductions of over 80% via recycling of spent material, indicating that the solvent maintains its cleaning efficiency on a long term basis over a number of reclaim/reuse cycles.

DRINKING WATER TREATMENT

Background

Disinfection of public drinking water supplies continues to be the focus of governmental attention and regulation. For instance, under Stage I and II of the Disinfection/Disinfection By-Production (D/DBP) Rule, increased removal of THM precursors is proposed while the Interim Enhanced Surface Water Treatment Rule (ESWTR) will require improved microorganism control (Giardia, Cryptosporidium). Although large water utilities will be able to absorb the cost of meeting the (to be) established criteria, many of the smaller authorities will struggle to conform due to the lack of a simple, low cost yet effective treatment technology. The focus of our technology development was to demonstrate the use of our innovative, low cost ceramic membrane technology as a cost effective single step treatment option for small community drinking water treatment.

Membrane-based filtration, such as micro filtration (MF), ultra filtration (UF), nanofiltration (NF) and reverse osmosis (RO), has been investigated as a potential alternative to conventional water treatment options for small communities. Membrane installations are compact and easily automated. Tight UF, NF and RO have been demonstrated to remove significant levels of THM precursors from drinking water supplies and deliver excellent microorganism control. Hence, membrane filtration can potentially provide turbidity removal, THM precursor reduction, and disinfection in a single step. Furthermore, because of the high levels of microorganism removal that can be achieved, chlorination for residual disinfection can be significantly reduced. Thus, lower levels of residual chlorine combined with substantially lower THM precursor levels (due to filtration) can lead to much lower overall THM contamination. For these reasons, a membrane-based filtration process could be an ideal single step disinfection option for a small water utility.

Disadvantages of Existing Membrane-based Technology

To date membrane based processes, although widely accepted as a possible treatment strategy, have not been broadly employed in drinking water applications due to operational related difficulties, primarily flux loss due to fouling and biofilm formation. Fouling problems have handicapped the use of tight UF polymeric membranes for the proposed one-step drinking water disinfection. Although negatively charged tight UF membranes have shown some fouling resistance to colloids and humic materials, these membranes are particularly susceptible to chlorine and other oxidant attack. Therefore, a dichotomy apparently exists concerning the development of commercially viable fouling resistant polymeric membranes that can achieve one-step disinfection without the need for chemical pretreatment to control membrane fouling. Chemically inert and easily cleaned ceramic membranes offer a new direction and promising solution.

Advantages of Ceramic Membrane Technology

The primary advantage of using ceramic membranes is the ability to accomplish the current and pending regulatory treatment objectives in a single step with no chemical pretreatment. Turbidity, bacteria, virus, and THM precursor removal has been demonstrated in an extensive laboratory study and then confirmed in a field test using a surface water source. Key performance parameters are discussed below:

Removal Efficiency

Turbidity and THM precursor removal efficiency has been confirmed in a large-scale field test (>1,000 hours total) using Allegheny River water as the source as shown in Figure 6. Turbidity was consistently reduced to <0.2 NTU in the permeate from ca. 5 to 15 NTU in the feed water. About 50 to 70% THM precursor removal was consistently demonstrated in this field study as shown in Figure 6. Along with the >3 to 4-log removal of virus (MS2 bacteriophage) separately demonstrated in the lab (see Figure 7), the ceramic membrane product/technology fulfills the current and pending regulatory objectives for drinking water treatment.

Permeance Stability

In addition to the excellent removal efficiency, good steady state permeance was also obtained during the long term (i.e., ~1,000 hours) field-test as Figure 6 shows. Much higher steady state permeances on the order of 150 to 200 lmhb are obtained using ground water as a source. Part of our study program also focused on membrane cleaning. The production of drinking water, particularly from surface water, is complicated by the wide spectrum of contaminants that can be potentially present. Further, geographic region, season, and other factors can have a tremendous influence on feed water quality. To be a viable product with consistent performance, we have developed several alternative membrane cleaning methods. Chemical cleaning has been demonstrated to ensure consistent performance in the field as shown Figure 6.

Economics

A significant part of our effort has been devoted to membrane and module development, specifically for the small-scale drinking water treatment. Ceramic elements have been fabricated with packing densities as high as 940 m^2/m^3 (see Figure 1). This high packing density reduces the capital cost of the treatment system. The ceramic membrane made with high purity α-Al_2O_3 demonstrated

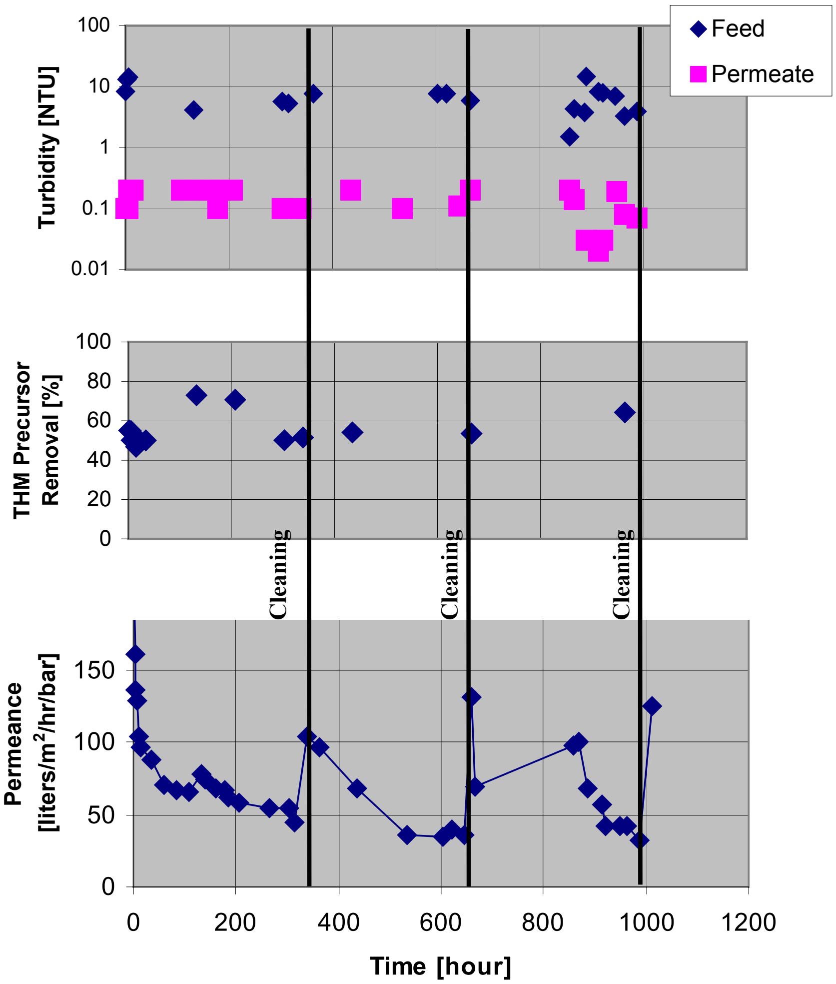

Figure 6. Permeance, THM precursor rejection, and feed and permeate turbidities obtained using an M&P ceramic membrane element in the treatment of Allegheny River water. No pre-treatment was performed. As indicated, three cleaning cycles were conducted throughout the test period. The original flux was restored after each cleaning.

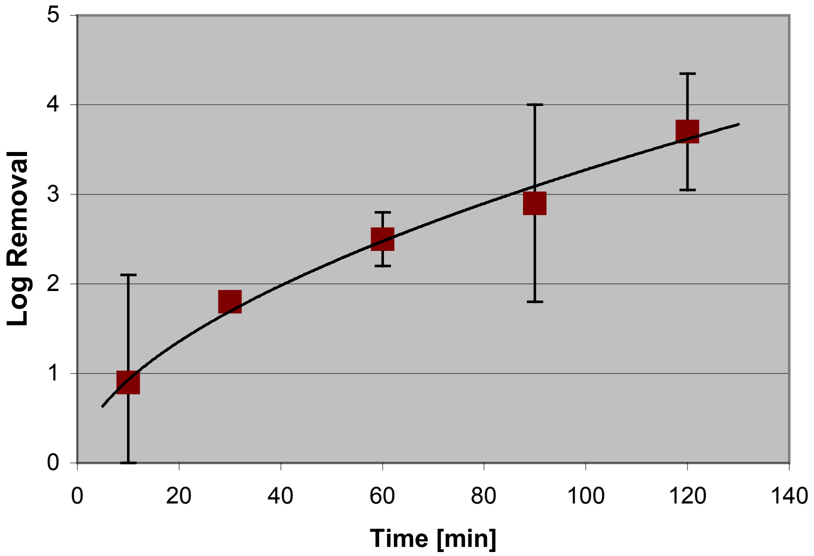

Figure 7. Virus removal efficiency of M&P ceramic membranes. Feed is distilled water spiked with MS2 bacteriophage. Much higher removal levels are expected in actual water treatment since significant viral loading is found on micron and submircon size, suspended solids, which are readily removed using M&P ceramic membranes.

excellent chemical stability in the presence of oxidants and at extreme pH in lab and field tests. Thus, long service life and a high degree of permeance recovery after fouling can be expected. With these advantages, the total production cost of treating surface waters to yield high quality drinking water that exceeds current and proposed regulatory standards is relatively low at <$1.00/1,000 gallons (1 million gallons per day; year 2000 dollars).

The above testing results demonstrate the process viability of a one-step drinking water treatment with no feed water chemical pre-treatment. In addition, our ceramic membrane technology can be used in RO pretreatment to replace existing chemical pretreatment for the production of industrial process water.

DEASHING/DEMINERALIZATION OF USED OILS

Background

Compared with the above two applications, deashing/demineralization of used oils represents one of the more challenging industrial fluid/particle separations due to the presence of micron and submicron particles in viscous hydrocarbon fluids. Deashing/demineralization involves the removal of fine wear metals, soot generated from combustion, and by-products from additive degradation. Globally, over four billion gallons of spent lubricants are generated annually. Although this oil can be considered a valuable renewable resource, less than 10% of the worldwide supply is actually re-refined into high quality lubricant basestocks or high quality fuel. The remainder is typically burned as low value fuel.

Disadvantages of Existing Recycling Technologies

Since conventional filters are not effective in treating this type of fluid, traditional re-refining technologies rely on distillation to accomplish the deashing objective as a first processing step. The major disadvantages of distillation, however, include (i) high energy costs since the lubricant must be vaporized, (ii) unfavorable economy of scale, and (iii) significant quality degradation in terms of odor and color. As a result of the economy of scale requirement, waste oil generated at dispersed locations around the country must be trucked to a centralized facility for processing. However, the transportation cost alone is a significant cost factor, so that only a small fraction of the used oil generated in the US today is actually re-refined. To overcome this problem, small-scale decentralized facilities would be preferred and would take better advantage of the current used oil collection infrastructure. Up until now such re-refining facilities have simply been unavailable.

Advantages of Ceramic Membrane Filtration

The oil re-refining process in general consists of two steps, a deashing step to remove particulate matter and a decolorization step as a polishing step to remove color bodies. Here, we limit our discussion to the use of ceramic membranes for deashing of spent passenger car motor oils and synthetic oils. Following deashing, spent oil can be sold as low ash high quality burner fuel or further processed by decolorization and returned to the original or secondary markets. Table 2 presents a typical metals profile for used passenger car motor oils before and after ceramic membrane filtration. Typically, over 80 to 85% of the ash is removed. The primary ash contributing components that remain are generally associated with soluble additives in the oil (eg: zinc, phosphorous, and others) and are not easily removed via filtration.

Table 2. Metal/ash contaminant removal from a sample of waste motor oil using M&P ceramic membranes.

Contaminant	Contaminant Concentration As Received [ppm]	Contaminant Concentration After Membrane [ppm]	Contaminant Removal Ratio [%]
Iron via ICP	205ppm	39ppm	81.0%
Chromium	5	2	60.0
Lead	67	12	82.1
Copper	202	18	90.1
Sodium	103	4	96.1
Magnesium	244	13	94.7
Calcium	726	15	97.9
Phosphorous	495	155	68.7
Zinc	860	165	80.8
Ash Content (ASTM D-482)	0.602wt%	0.097wt%	83.9

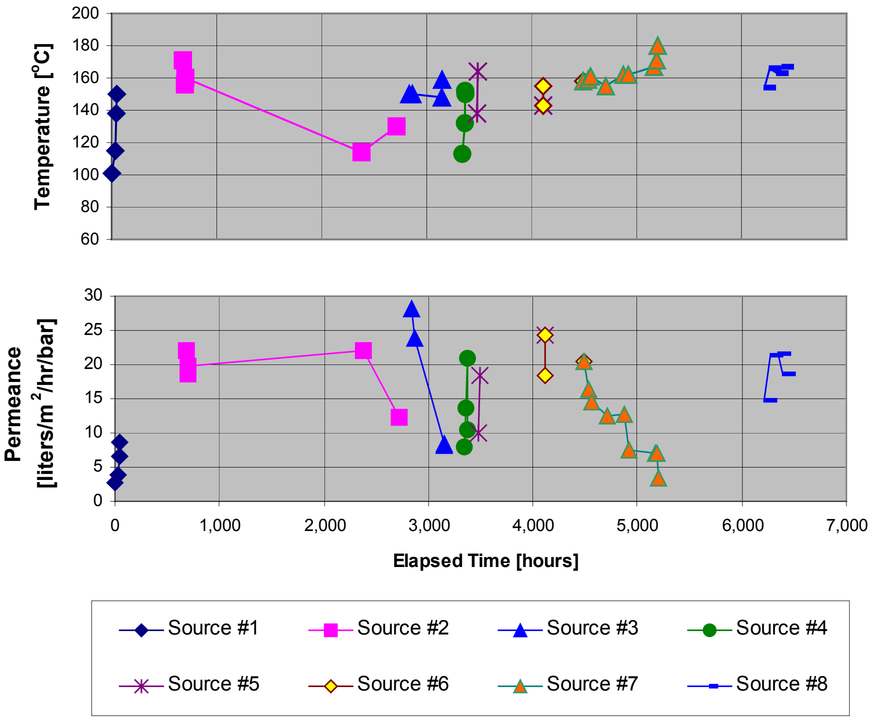

Figure 8. **Permeance of various used oils processed at M&P's production facility in a continuous long-term membrane performance test. Also shown is the operating temperature. Recycle or concentration indicates the mode of operation. The permeance is primarily a function of the used oil viscosity and extent the sample has been concentrated. No membrane cleaning was necessary throughout the test run.**

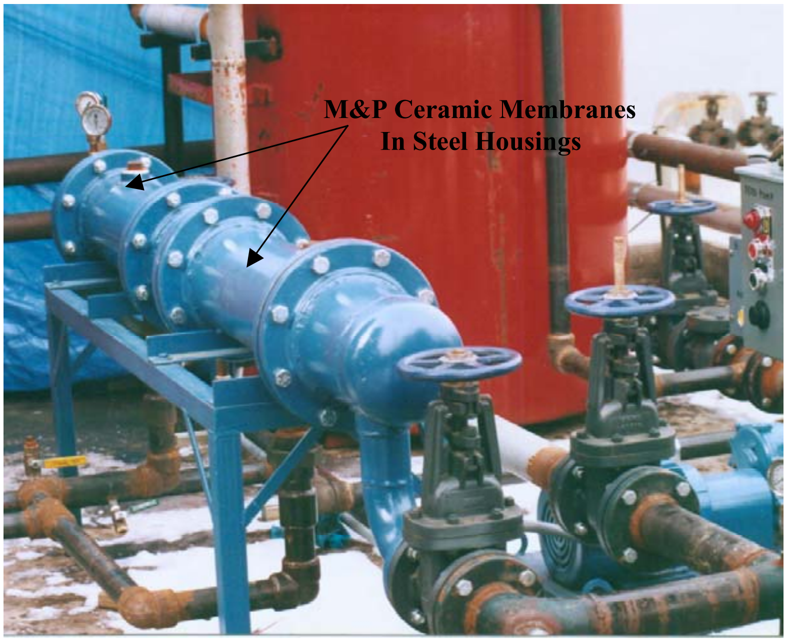

Figure 9. **Used oil deashing unit featuring M&P ceramic membranes.**

Figure 8 shows the permeance of M&P ceramic membranes over an extended operating time frame. Operating temperatures range from ca. 120 to 170ºC. As can be seen, good permeance stability is maintained. Further, in general membrane cleaning is unnecessary in waste oil processing. Permeance decay results primarily from increased feed viscosity as the solids content is progressively increased (concentrated) during membrane treatment. The permeance is typically fully recovered when a new batch of spent oil is charged to the feed tank as Figure 8 demonstrates. Finally, the treatment cost to generate high quality deashed oil from spent motor oil is less than 5¢/gallon.

Presently, we maintain a used oil processing demonstration facility employing our ceramic membranes for deashing/demetalization and a proprietary process for decolorization. This production scale facility has been in operation for over two years (see Figure 9). Both petroleum based (mineral) and synthetic oils have been recycled and sold to a number of lubricant packagers/blenders for reuse.

SUMMARY AND CONCLUSIONS

Although ceramic membranes offer unique material and performance advantages, in the past their high cost has prohibited their use in cost sensitive areas, for instance in environmental related applications. Cost reductions in the membrane and housing would lead to wide acceptance in these areas. In addition, high packing density is a critically important factor in large-scale applications. However, conventional ceramic membrane technology offers low packing density at high cost. In the past few years, we have made significant progress in overcoming both of these limitations. Today, our ceramic membranes are competitive with polymeric membranes, making them a standard instead of niche product.

ACKNOWLEDGEMENTS

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NOMENCLATURE

lmhb:	permeance in liters/meter^2/hour/bar
THM:	trihalomethane