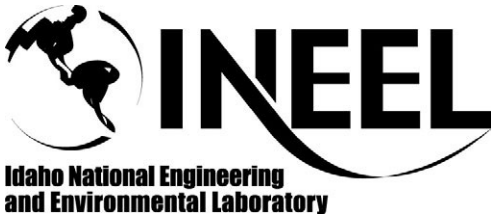

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Development Of The Embedded Membrane Concept

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Recent evaluations in the field of biomass separations have resulted in a novel concept termed the "embedded membrane." Biomass solutions, which typically consist of a sludge-like material, contain a wide range of particle types and concentrations. These highly abusive solutions have the potential to cause reduced flux and even catastrophic failure through erosion mechanisms within the membrane.
The embedded membrane concept relies on embedding finer, filtration inducing particles (e.g. ceramic such as TiO_2) into the interstices of a macroporous support (e.g., sintered metal such as sintered stainless steel). It is believed that the embedded membrane would be resistant to erosion processes, since only the macroporous support material would be subjected to the harsh hydrodynamic properties of the flowing bulk process fluid. Moreover, the finer, filtration inducing embedded particles that provide the necessary filtration efficiency are protected from the bulk process fluid. In an effort to investigate the embedded membrane concept, samples of sintered stainless steel membranes embedded with ceramic particles have been prepared.

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INTRODUCTION

Our interest in UF/MF stems from an ongoing research effort to evaluate the hydrolytic conversion of biomass feed stocks (i.e., waste cellulose such as straw, corn stover, and wood) into the base monomeric sugars, which can, in turn, be processed into chemicals and fuels using a number of innovative fermentation technologies. Biomass feed stocks are typically a sludge containing relatively high quantities of suspended and dissolved solids consisting of fiber, soil, colloidal materials, and other contaminants. Obviously, the head-end unit operation required is an efficient solid – liquid separation system if the downstream chemical separation processes (typically ion exchange and chromatography) are to operate efficiently. High throughput, commercially available roughing or course filtration equipment effectively removes the bulk of suspended solids from the feedstock. However, membrane filtration is necessary to remove the small residual mass of solids (typically on the order of 0.01 to 1 wt % loading) in the size range of ~0.01 to 10 μm which are detrimental to effective operation of downstream chemical separations. Clearly, such a polishing filter relies on the use of UF/MF membranes. Our emphasis lies on the use of UF/MF membranes in characteristic crossflow arrangement (bulk fluid velocity parallel to the membrane surface to minimize or limit the formation of a filter cake layer) due to the obvious advantages associated with continuous, high-volume applications. Note that the anticipated throughput for the filtration and chemical separation systems of an economical, full-scale hydrolysate conversion plant would be on the order of 5,700 L/min (1,500 gpm), representing a substantial capital investment, especially in light of the likely need for redundant systems to facilitate cleaning and/or downtime of the filtration process and to provide the necessary overcapacity.

The large-scale use of crossflow UF/MF systems is limited by the rather low values of achievable permeate flux relative to the necessary throughput of a full size plant. Additionally, the presence of fine solids creates challenges for the operation and durability of commercially available membranes. For example, colloidal and other small particles will tend to foul the membrane, resulting in the need for frequent cleaning cycles, and ultimately replacement, once the filters are depth fouled and cleaning is no longer possible. Additionally, soil particles such as silica will erode the interior membrane surface resulting in either catastrophic failure or reduced performance after extended periods of operation time. The efforts of our research in the arena of crossflow filtration have focused on the bench scale and pilot scale evaluation of numerous commercially available UF/MF membranes, including polymeric, ceramic, and sintered metal products. Both short duration (2-4 hour bench scale tests) and long-term (2 to 3-year pilot scale) evaluations have been performed using a model system of raw beet juice taken as a slip stream from the diffusers in an operating beet sugar plant. Based on the results of our efforts, we believe that sintered metal membranes are currently the best all-around choice for the UF/MF application under consideration.

Looking past the perceived short-term issues of fouling and cleaning (based on our experience that effective cleaning methods and cycles are possible for the CSS membranes), predominate concerns in the biomass application revolves about the expected useful lifetime of the filter elements and the subsequent modes of failure. These issues are integrally tied to the long-term effects of erosion and the subsequent damage to the interior surface of the filter membrane. Consequently, efforts in this project have emphasized defining, in a qualitative fashion, the long-

term effects of erosion. To this end, two potential approaches have been devised: to operate candidate membranes industrially for extended periods of time and evaluate the long-term effects of wear on the membranes; alternatively, development of experimental methods to accelerate and study abrasive wear on candidate membranes. Our approach has been a combination of these two methods. Qualitative operational data has, and continues, to be obtained on filter membranes operated on the pilot scale with the actual raw juice "model" for well over 2200 hours. Additionally, a bench scale unit has been employed with an abrasive (Al_2O_3, common corundum) feed stream to accelerate the processes of abrasive wear. The experimental observations regarding erosion mechanisms of these ultrafiltration membranes have fortuitously resulted in the observation of a phenomenon that lends itself to an "embedded membrane" concept with the potential of resulting in enhanced flux and abrasive resistant filtration media. The embedded membrane relies on incorporating smaller, filtration-inducing particles of ceramic (e.g. TiO_2 or ZrO_2) into the interstices of a macroporous substrate or support, i.e. sintered stainless steel. The resulting composite filter membrane is resilient to abrasive processes since only the substrate material is in contact with the harsh hydrodynamic properties of the flowing bulk process fluid, protecting the layer of finer particles, which provide the necessary filtration efficiency. Furthermore, our observations led to the conclusion that the embedded layer of fine particles results in less resistance to permeate flow (as opposed to discernable layer or coating directly on the surface of the porous substrate), providing enhanced permeate fluxes without loss of filter efficiency.

Accelerated Membrane Erosion. In an attempt to accelerate abrasive wear on the interior surface of the CSS samples, a 5 wt.% slurry of 20 μm corundum (Al_2O_3) in water was recirculated through short (6" effective length) pieces of tubular membrane samples under true crossflow conditions. Corundum was selected as the abrasive material due to its durability (hardness of 9 on the Mohs scale). The Al_2O_3 slurry was recirculated at 3.5 gpm for 58 hours through a sample of membrane tube which had been previously operated for 2200 hours in the on raw sugar juice. Detailed SEM inspection of the sample indicated no discernable erosion of the ceramic surface coating or steel support and only minor decrease in flux was observed over the course of the abrasion test. During this attempt to accelerate the erosion of the CSS samples, the corundum particles resulted in a far more abrasive effect on the pump than on the filter membrane. The pump failed several times (after as little as 20-30 hours of operation) due to erosion of the pump internals composed a chrome plated steel rotor and rubber stator. As a result of the poor results obtained in these experiments to accelerate the erosion phenomenon, it was apparent that alternative methods of accelerating and characterizing wear effects were required for the CSS samples.

RESULTS AND DISCUSSION

Membrane Samples

The experimental method designed to accelerate erosion and ascertain the long term effects of wear on membrane performance failed for the CSS samples; an alternative approach to accelerating the natural wear process of the membrane inner surface was necessary. A fortuitous turn of events occurred when a colleague provided samples of CSS membranes that were run

industrially, presumably on a similar feed stock to the raw beet juice, for various, but extended periods of time. Three such CSS membranes, identical to those being evaluated at our facilities, were provided. One sample had been run for approximately 1 year of industrial operation, another for approximately 2 years, and a third sample that was extraordinarily abused, under harsh conditions, to filter a solids heavy, very abrasive stream. The unfortunate nuance associated with obtaining these three CSS membrane samples is that quantitative data are unavailable about the feedstock (liquid properties, solids loading, solids rheology, etc.) or operating history (axial velocity, temperature, transmembrane pressure) of these samples. Consequently, all observations and measurements related to their performance are qualitative and cannot be related back to actual operating conditions or history. However, our observations are useful from the standpoint that filter performance can be related to the condition of the interior membrane surface, which indeed varies between the samples available for study. Including the samples of pristine membranes supplied by the manufacturer and the membrane operated for 2200 hours in the pilot skid with raw juice, a range of different membranes, presumably with various degrees of erosion at the interior surface, were available for study. The sample labels and description of the different samples are summarized in Table 1. All samples were provided in tubular form, 2 to 4 feet in length, which were cut and prepared for the visual examinations and use in the CUF system.

Table 1. Summary and labeling of the CSS UF/MF membranes available for study.

Sample Label	Description
New	Pristine membrane - As received from the manufacturer
1P	Operated with raw juice in our pilot installation for ~2200 hours.
2I	Provided by industrial colleague, ~1 year operation w/unknown operating history
3I	Provided by industrial colleague, ~2 years operation w/unknown operating history
4I	Provided by industrial colleague, multi-year operation in a harsh, abusive environment

Visual Inspections

The interior surfaces of the various membrane samples were first characterized and evaluated by visual inspection. Sections of the tubular CSS membranes were cut approximately in half down the length of the membrane (pieces up to several feet in length were cut open). The ceramic material on the interior membrane surface was clearly discernable by its much darker color, readily distinguishable from the shiny, metallic surface of the sintered metal. Visual inspection indicated that the thickness of the interior ceramic layer or coating was noticeably inconsistent, both axially and circumferentially in a specific membrane sample, and also between the different samples. Variations in the thickness of the ceramic layer were most prominent in the new membrane; at points it appeared there were drops or even runs (such as would be observed in an overly thick coat of paint) of excess ceramic material on the interior surface. “Bald” spots, which appeared completely free of ceramic coating, were visually prevalent in the different membranes. The bare areas were even apparent in the new membrane, although these areas were less prevalent than in the other samples. Most notably in the aged samples, the ceramic appeared eroded from the surface of the membrane during normal operations and in places looked as though the ceramic had been scratched from the surface by a dull instrument, exposing the underlying metal substrate. The most striking contrast was of the 4I membrane, which had been

operated extensively under severe conditions. The interior surface showed a very highly polished metallic luster, visually appearing completely free of any traces of ceramic material; the interior surface appeared as though it had been thoroughly polished with fine grit abrasive. Visual inspection qualitatively indicated that the exposed surface area of sintered metal substrate (the total area with the ceramic layer missing) increased in the order:

$$\text{New} < 1P < 2I < 3I < 4I$$

SEM & EDS Analysis

Small pieces (~1 cm^2) were carefully cut from the above samples of the different membranes. These were used to study the interior membrane surface in closer detail using the Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) techniques. In order to examine the subsurface structure of the membranes, samples were carefully prepared by breaking off pieces of the membrane along the length; the cross-section of the membrane thickness could be examined in these samples. Care was taken during the SEM and UDS examination to stay well away from cut edges on the smaller pieces since the metal substrate could be deformed and the ceramic layer damaged during the cutting process. Figures 1 and 2 pictorially indicate a representative summary of several SEM results. Figures 1 and 2 show axial cross-sections of the new and 2I membranes, respectively. The ceramic surface layer on the inner, porous sintered metal support is clearly enunciated in these SEM photographs. The SEM was used to evaluate the thickness of the ceramic coating on those samples where this layer existed and appeared intact. In the new membrane, actual measurements indicated a 10 - 30 μm thick coating of ceramic on the metallic substrate. The inner surface of a bald area from the 1P membrane is shown in Figure 3 and of the 3I membrane in Figure 4. The dark areas indicate the presence of the ceramic coating; the lighter areas indicate the porous sintered metal substrate protruding from the ceramic layer. The composition of the different regions was also verified by chemical analysis using the EDS technique during SEM analyses. The evidence based on SEM, EDS, and visual inspection indicates the ceramic coating on pristine membranes is extremely inconsistent in terms of both thickness and consistency (the inner coating of new membranes was often observed to be cracked and non-homogeneous). Despite these observations, each of the membrane samples typically indicated consistent performances relative to permeate flux and clarity *(vide infra)*.

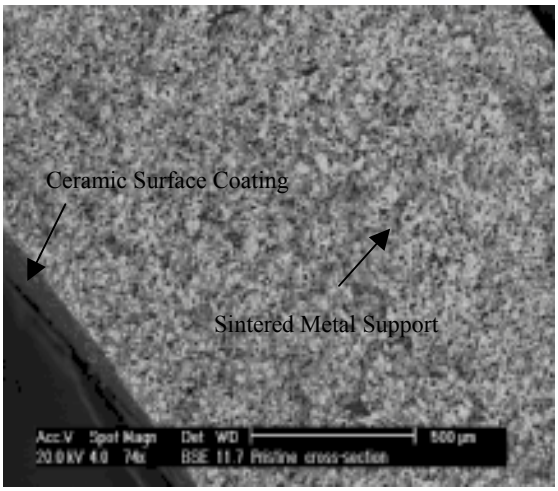

Figure 1. Cross-section of a new membrane.

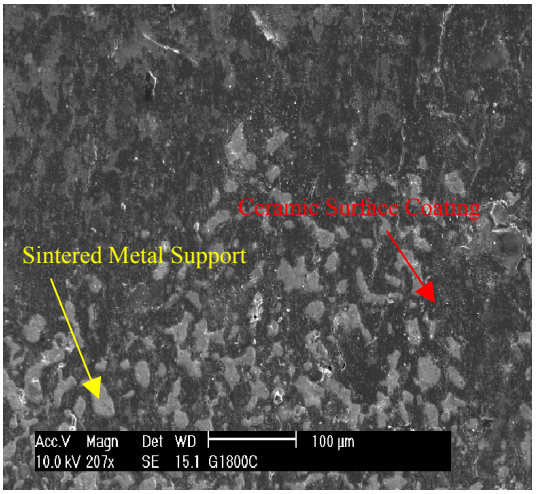

Figure 3. Inner surface of the 1P membrane.

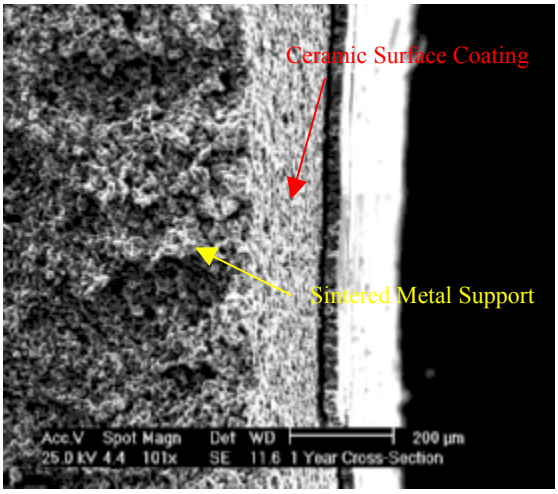

Figure 2. Cross-section of the 2I CSS. membrane.

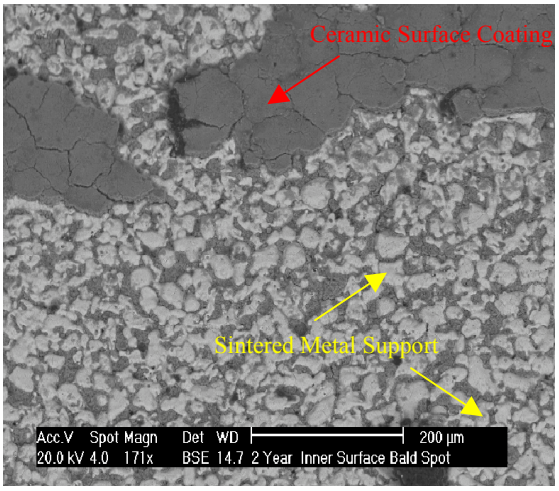

Figure 4. Inner surface of the 3I CSS membrane.

Another very interesting observation was derived from the visual, SEM, and EDS analyses of the 4I sample of the highly eroded membrane, as indicated in the SEM photograph of the interior surface of the membrane indicated in Figures 5 and 6. This photo indicates that the sintered metal substrate was heavily worn and actually "flowed", or was smeared (as in plastic deformation) across the interior surface of the membrane; the individual metal particles observed at the interior surface of the previously examined samples (Figures 3 and 4) are not observed in the 4I sample. The larger pockets of ceramic material embedded in the metallic matrix have also largely disappeared in this sample, and are replaced by much smaller penetrations or imperfections into the predominately metallic surface. Thus, it is postulated that the interior surface of this membrane represents that which would be observed in the advanced stages of

wear by erosive processes, and is indicative of the condition of the interior surface as the membrane as it reaches the end of its useful life.

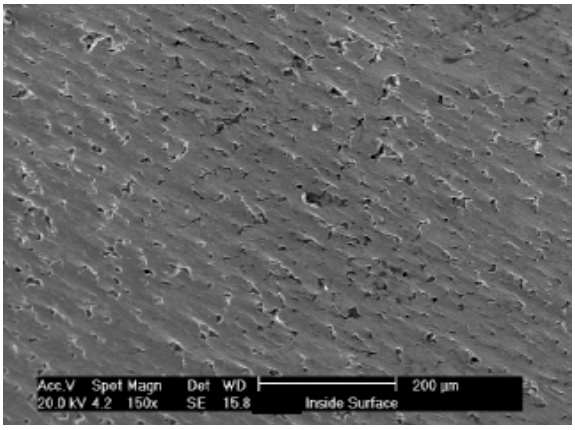

Figure 5. Inner surface of the 4I (150X).

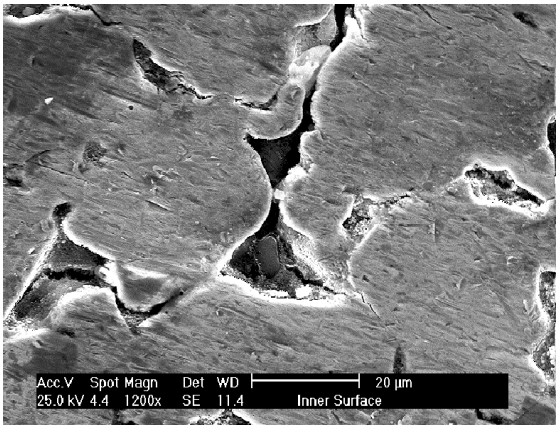

Figure 6. Inner surface of the 4I (1200X).

The above observations for the various membrane samples beg the question: "How are these membranes functioning efficiently in the absence of the ceramic layer, which is attributed the filtration properties of the CSS membranes?" In an attempt to answer this question, the interior surfaces of the membrane samples were probed via EDS analysis. The EDS spectra indicated that in each of the membrane samples, ceramic material was still prevalent in the interstices of the sintered metal support, and in some cases was measured to be present at depths of 20 to 30 µm into the sintered metal support structure. This feature is in fact prevalent in the SEM photographs as indicated in Figures 5 and 6. Furthermore, EDS spectra taken inside the small imperfections of the 4I membrane (right hand photo in Figure 6) indicated that ceramic material was indeed prevalent in the small imperfections or depressions of this membrane.

Flux Measurements

In order to further understand why the membranes were still operating efficiently without the interior ceramic coating, flux measurements were performed with both water and raw beet juice on samples of each CSS membrane using the CUF systems. The objective was to evaluate permeate flux with respect to the condition of the interior membrane surface. Triplicate samples of each different membrane were prepared for the flux measurements, with the exception of the pristine (new) membrane; only sufficient lengths of this material was available to prepare two pieces of sample for testing. Initially, clean water flux for each sample was measured in the CUF system under identical operational conditions. Samples were then cleaned using an aggressive chemical cleaning procedure (in situ) followed by a water rinse and a repeated water flux measurement. The cleaning procedure used was that which had been developed for the most effective cleaning of the membranes in the pilot skid. The samples were placed in a second, identical CUF apparatus and the flux measured as a function of time with raw juice, until semi-steady state flux was achieved.

Permeation rates were measured for raw juice on the samples after cleaning and water flux determinations. These data are shown for the different samples in Figures 7 - 13. The

permeation rates for raw juice were consistently and substantially lower than those measured for clean water. This is attributed to the presence of solids forming a boundary layer at the membrane surface. The rapid, initial formation of the solids boundary layer is indicted by the rapid decline in flux during the first 15 - 30 minutes of the filtration process. The general shape of the raw juice permeation rate is consistent for all samples with the build up of solids at the interior surface and the resulting rapid decrease in flux, followed by the quasi-steady state equilibrium after the boundary layer has formed. There is much less variation in the juice flux for the individual samples with raw juice than was observed with clean water, likely due the formation of the solids boundary layer controlling the flux as the primary resistance to flow across the membrane.

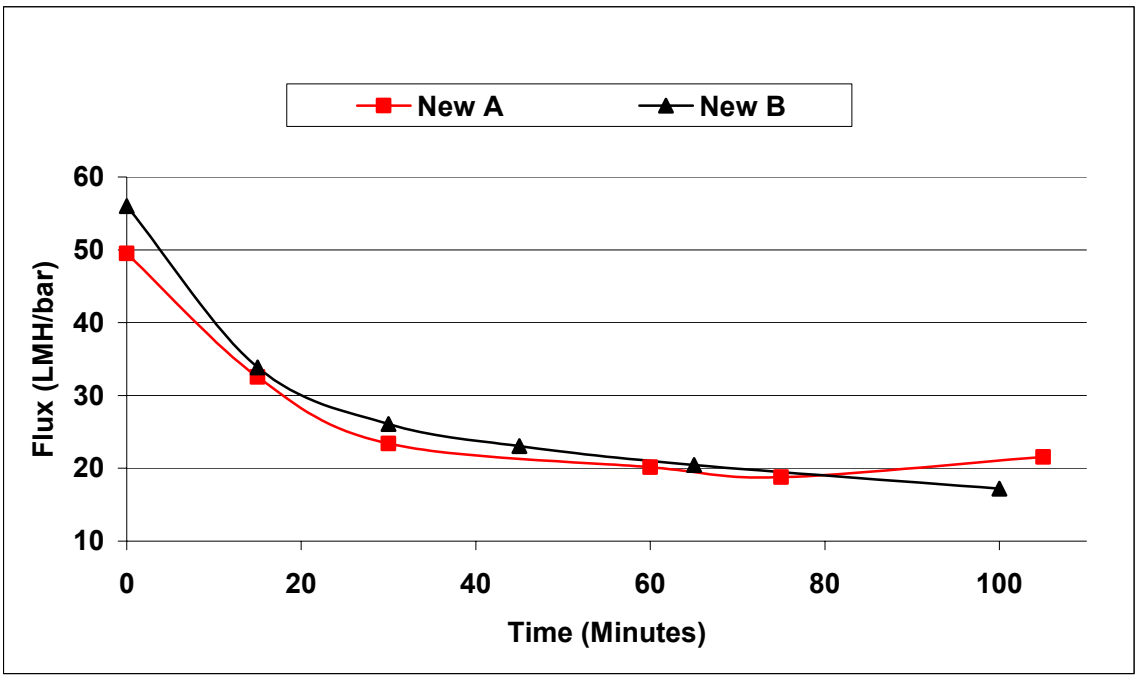

Figure 7. Juice flux vs. time for the new membrane at 30 psig TMP.

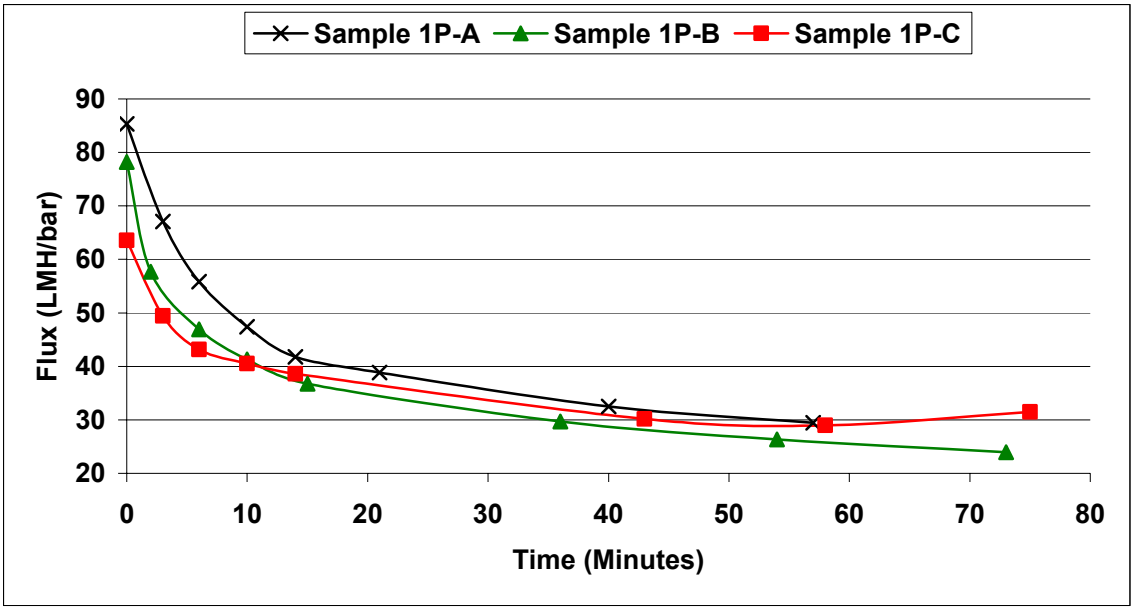

Figure 8. Juice flux vs. time for the 1P membrane at 30 psig TMP.

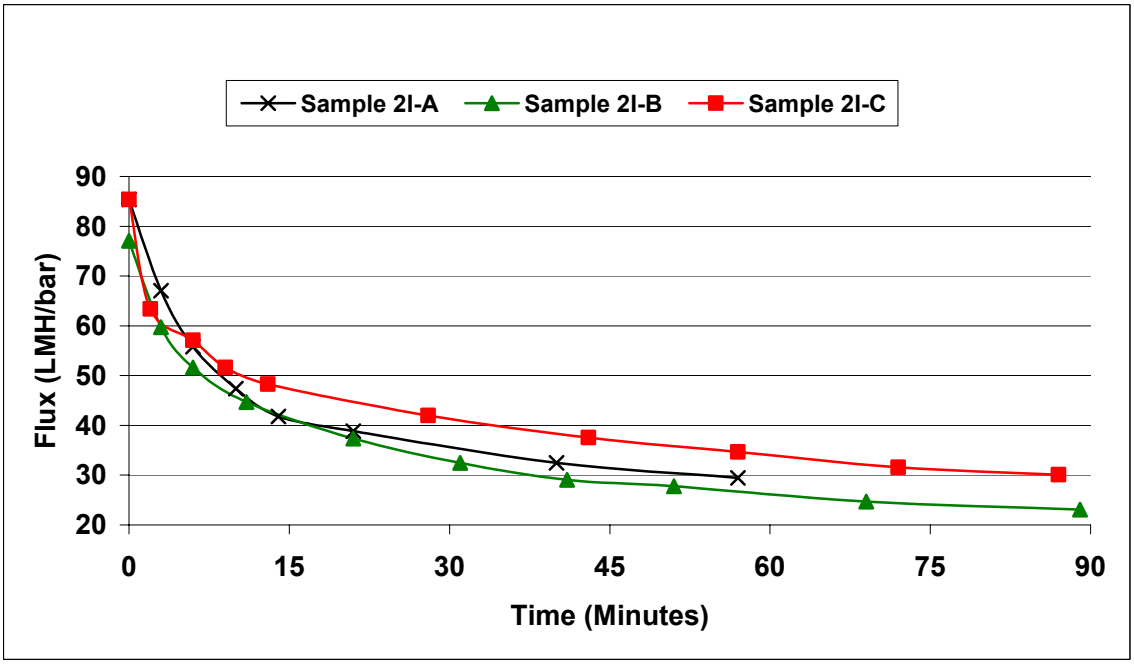

Figure 9. Juice flux vs. time for the 2I membrane at 30 psig TMP.

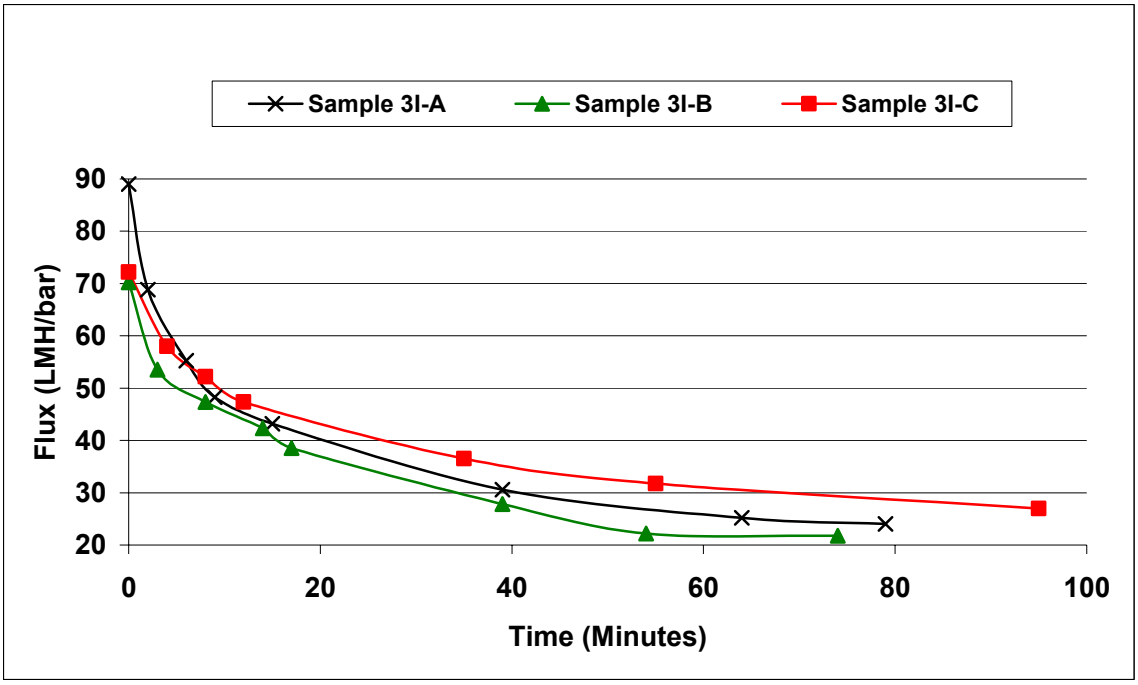

Figure 10. Juice flux vs. time for the 3I membrane at 30 psig TMP.

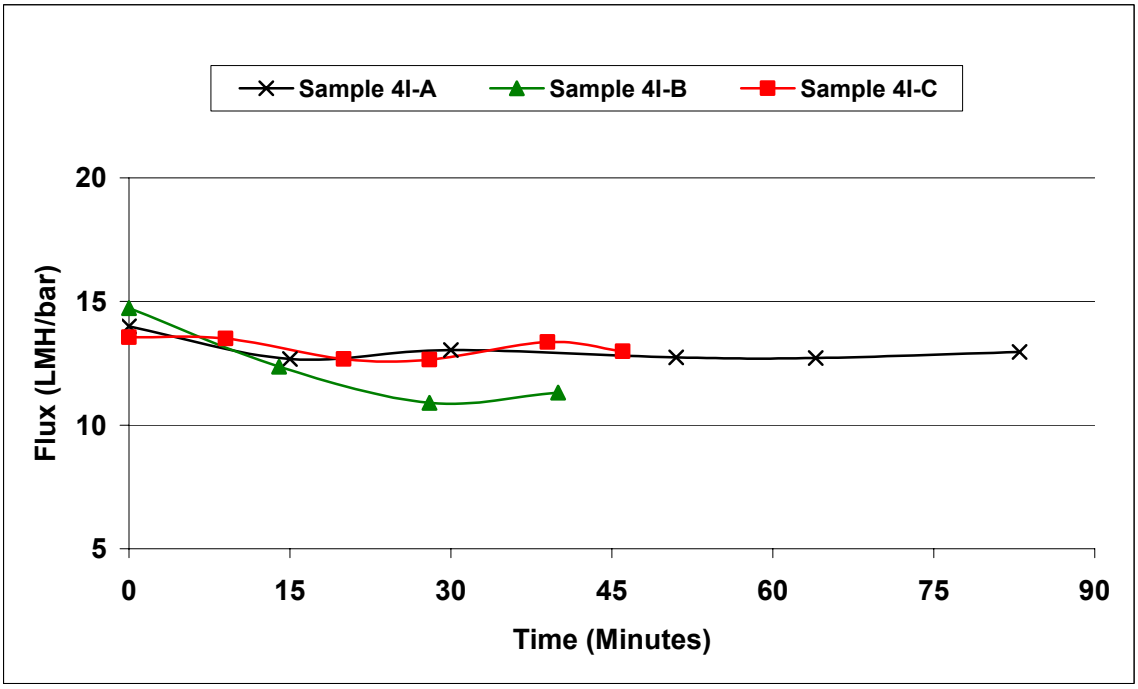

Figure 11. Juice flux vs. time for the 4I membrane at 30 psig TMP.

Comparative graphs shown in Figures 12 and 13 depict the average raw juice flux vs. time for all samples at 30 TMP and the average steady-state raw juice flux. With the exception of the abused sample, all permeate curves are similar, but slight differences in juice flux are observed. Furthermore, if the values of the semi-steady state flux are compared, the abraded membrane samples (with the exception of the abused membrane) all appear to be higher than for the new P1 membrane. This observation lends credibility to the idea that the membrane embedded in the upper surface of the porous support is responsible for the filtration efficiency, while the excess surface coating in the new membranes is actually an unnecessary, added resistance to permeate flux. More importantly, in all cases solids were not detected in the permeate samples indicating that there was no measurable degradation in filter efficiency coinciding with the higher permeation rates. This observation also lends credibility to the idea that the while the surface coating is nonexistent on the 4I membrane, the embedded particles maintain filter efficiency.

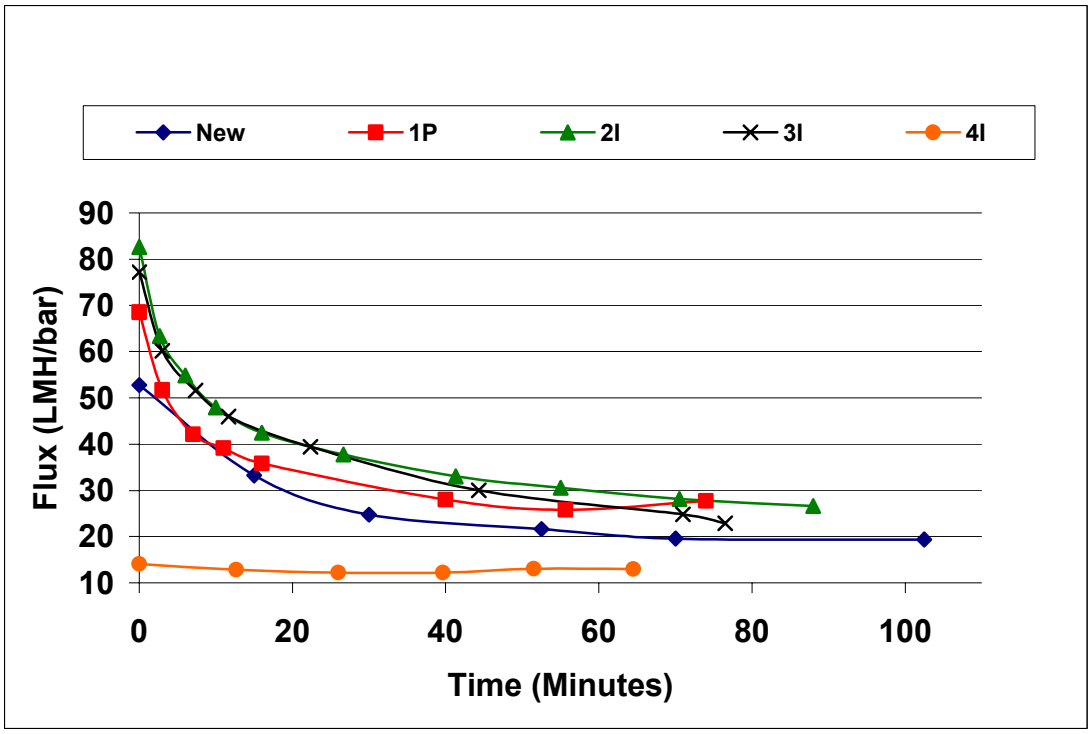

Figure 12. Raw juice flux vs. time for the different membrane samples.

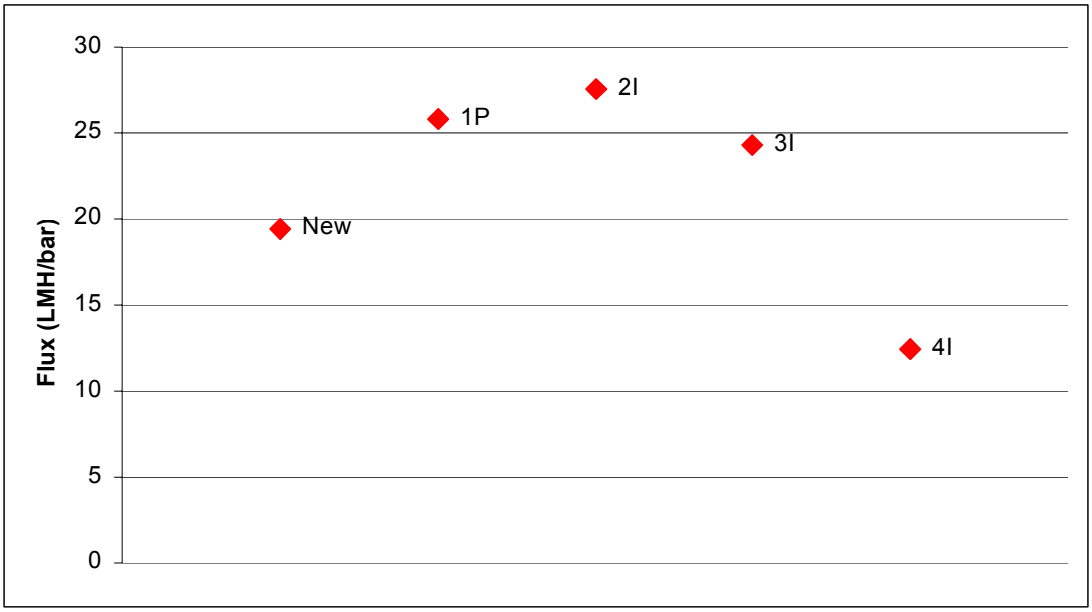

Figure 13. Steady-state fluxes of raw juice for the membrane samples.

In general, the observations associated with the highly abused membrane leads to a general theory regarding the long-term effects of erosion on CSS type membranes in abrasive environments: The long term effect of abrasion at the interior CSS membrane surface is to initially remove the ceramic coating and expose the sintered metal substrate to the abrasive particles in the bulk fluid. The results are pockets of the ceramic embedded in the interstices between the larger metallic substrate particles of the support. The abrasive particles in the bulk fluid then, over time, begin to erode or abrade the exposed metallic surface, which tends to flow or smear across the surface due to the malleable nature of the metal. This effect tends to fill in the ceramic containing pockets resulting in a net reduction in the available porosity at the membrane surface. It is unfortunate that details of the operational history for this membrane are unknown; information regarding the bulk fluid properties, entrained solids loading and rheology, and the operational parameters (axial velocity, transmembrane pressure, temperature, operation time, etc) are unavailable. Without this key information, only general conclusions regarding the effects of erosion on membrane performance (flux and efficiency) can be postulated and it is impractical to estimate membrane life based on actual process conditions. However, it may be postulated that the long term effects of membrane wear would likely not result in a catastrophic failure mode (rupture), rather it would result in a substantial deterioration of filtrate flux, without a decline in filtrate clarity.

EMBEDDED MEMBRANE DEVELOPMENT AND FABRICATION

In order to better understand the embedded membrane concept and its potential benefits, samples of embedded membranes have been fabricated. Using a proprietary embedding process, TiO_2 was embedded within the substrate of tubular sections of sintered metal. Through this process, the surface coating observed with the new CSS membrane was eliminated. TiO_2 is present just below the surface of the membrane exposing the sintered metal substrate. Embedded TiO_2 extends below the surface to a depth of approximately 20 microns. Furthermore, a method is being developed to control the depth of the TiO_2 within the metal substrate. Figure 14 displays the inner surface of the newly fabricated embedded membrane. It should be noted that figure 14 resembles the bald area from the 1P membrane as shown in Figures 3 and of the 3I membrane in Figure 4. The dark areas indicate the presence of the ceramic coating; the lighter areas indicate the porous sintered metal substrate protruding from the ceramic layer.

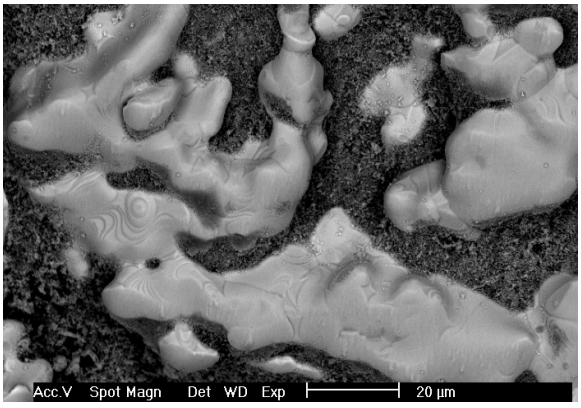

Figure 14. Inner surface of newly fabricated. embedded membrane.

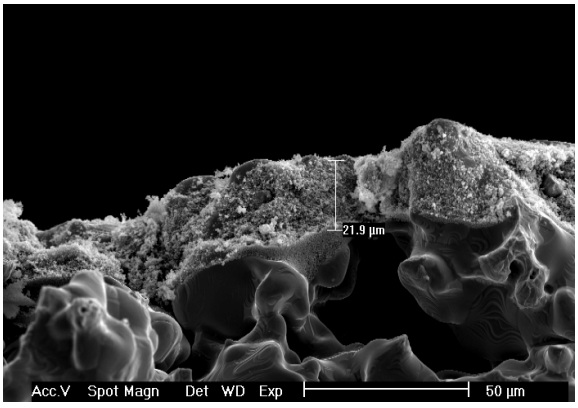

Figure 15. Axial cross-section of newly fabricated embedded membrane.

Figure15 displays the axial cross-section of the newly fabricated embedded membrane. The ceramic surface layer on the inner, porous sintered metal support is clearly enunciated in these SEM photographs. The light areas indicate embedded ceramic material; the darker areas indicate the porous sintered metal substrate.

Testing of the newly fabricated embedded membranes is scheduled to begin soon. Initial testing will compare water-flux and raw juice flux at the bench-scale using previously mentioned CSS membranes (New, 1P, 2I, 3I, 4I) and various models of the newly embedded membrane.

CONCLUSIONS

Observations regarding the permeate flux and filtration efficiency on asymmetric composite ceramic coated sintered metal membranes and the long-term effects of erosive wear on the interior surfaces have qualitatively led to several observations. The postulated sequence of physical changes to the interior of the CSS membranes and the observed effects are as follows:

1) New or as-received membranes have largely intact surface coatings that act as a resistance to permeate flow, resulting in lower fluxes without impacting filter efficiency in terms of particulate removal.
2) During the course of extended industrial operation, the surface coating tends to wear away from the substrate by erosive wear mechanisms. This erosion exposes the substrate to the process fluid and flow properties. The exposed substrate tends to protect or shield a layer of embedded surface material that resides in the substrate as a nuance of the manufacturing process from the flow properties of the bulk fluid. Permeate flux is enhanced as a function of time, coinciding with the resistive surface layer being removed. Solids retention (filter efficiency) is not impacted since the material embedded within the substrate pores serves to reject the bulk solids.
3) With continued, extended operation, wear mechanisms continue to erode the substrate material. In the case of the sintered metal, deformation tends to smooth the rough membrane surface and the substrate begins to fill the interstices containing the effective filter media. As this process occurs, permeate flux decreases with time corresponding to a reduction in porosity at the interior surface. Filter efficiency is therefore not impacted over the course of the useful membrane life due to embedded particles filling the interstices of the macroporous support.

The above series of events results in the eventual failure of the membrane due to a decline the permeate flux. This failure mode is not catastrophic, i.e., a sudden breach of the filter media does not result in contamination of the product fluid with solids. The time frame in which the above series of events occur is currently unknown, but certainly is dependent on two factors, the physical properties of the membrane surface (hardness, roughness) and the properties of the bulk slurry being filtered, primarily the rheology of the solids (hardness, density, size, etc). The observations associated with this work provide a scenario of what may be expected during long-term operation of these types of membranes; however, detailed understanding or modeling of the long term effects of erosive mechanisms on membrane performance is a complicated problem, likely to be better understood only upon examination and data that becomes available following extensive, documented operational history.

Based on our limited, qualitative observations, it is postulated that the newly fabricated embedded membranes, where finer porosity particles are embedded in the surface layers of the porous substrate will result in superior flux rates while still maintaining the properties of excellent particle rejection.

REFERENCES

N. R. Mann, T. A. Todd, "Crossflow Filtration Testing on INEEL Radioactive and Non-Radioactive Waste Slurries", *Chemical Engineering Journal*, 80 (1-3), 2000.

N. R. Mann, R. S. Herbst, J. R. Hess and V. Kochergin, "A Concept for Enhanced Flux, Erosion Resistant Membranes for Biomass Separations", American Filtration and Separation Society 16th Annual Technical Conference and Expo. Reno, Nevada. June 17-20, 2003.