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DOCUMENT AVAILABILITY

Reports are available free via the U.S. Department of Energy (DOE) Information Bridge Website: http://www.osti.gov/bridge.

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adt:	Air-Dried Ton, unit for mass of pulp, 10% water content
Btu:	British Thermal Unit, unit of energy, 3412 Btu = 1 kWh
DARPA:	Defense Advanced Research Projects Agency
FO:	Forward osmosis
gpm:	Gallons Per Minute
ITP:	Industrial Technologies Program, currently the Advanced Manufacturing Office
kWh:	Kilo Watt Hour, unit of energy
LMH:	Liters per square meter per hour
MF:	Microfiltration
MMBtu:	Million British Thermal Units; M signifies Roman numeral for 1000, so MM is million
MWCO:	Molecular weight cutoff
NF:	Nanofiltration
PS:	Polysulfone
psi:	pounds per square inch
PTFE:	Polytetrafluoroethylene
PVDF:	Polyvinylidenefluoride
RO:	Reverse osmosis
TBtu:	Trillion British Thermal Units
TDS:	Total Dissolved Solids
TOC:	Total organic carbon
TMP:	Transmembrane pressure
TRL:	Technology Readiness Level
TSI:	Teledyne Scientific & Imaging
UF:	Ultrafiltration
WBL:	Weak Black Liquor

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5. EXECUTIVE SUMMARY

In the pulp and paper industry, weak black liquor concentration is carried out using energy intensive evaporators. Briefly, after wood digestion, water is evaporated to concentrate weak black liquor to the point where the black liquor can be burned in a recovery boiler, which ultimately leads to the recovery of digestion chemicals. Because it is less energy intensive than heat-driven separation, pressure-driven separation of water from black liquor using membranes could reduce the energy usage by 55 trillion Btu year^{-1} [1] and carbon dioxide emissions by more than 11 million metric tons CO_2 per year [2] if the first two evaporators are replaced. However, weak black liquor is a hot, corrosive, and highly fouling feed with organic molecules, colloids, and ions that clog membranes within hours of operation. We have shown that membrane-based concentration of weak black liquor is feasible, but only with our antifouling and anti-clogging technology that is based on a sacrificial Bio-inspired Living Skin concept [3]. This concept is based on a conformal coating that is formed at the membrane surface and within the pores. Weak foulant adhesion dramatically decreases membrane fouling while the superhydrophilicity of the coating increases the water permeability. Moreover, the coating can be completely removed during backflushing, which removes foulants that may irreversibly adhere to the coating over long periods of time. The skin shedding completely regenerates the membrane surface and pores, restoring the original flux. This is followed by in-situ recoating, using the existing membrane plumbing and pumps, which essentially creates a brand new membrane surface.

Our coatings resist fouling under hot weak black liquor concentration conditions and can be regenerated in-situ on demand. Weak black liquor permeate flux as well as Fourier-transform infrared spectroscopy results suggest that black liquor foulants adhere very weakly to coated membrane surfaces. We modified the coating process to control the deposition time, which allows us to deposit the coating on large-scale membranes. We tuned the coating chemistry by introducing positive or negative charges to reject divalent ions present in weak black liquor permeate. Therefore, our two-stage membrane system effectively separates high molecular weight organics from weak black liquor using ultrafiltration membranes (Stage 1) and low molecular weight organic molecules and divalent salts from weak black liquor permeate using nanofiltration membranes (Stage 2), while the coating maintains the permeate flux by mitigating fouling.

Coated polymeric ultrafiltration membranes have exhibited up to two-fold increase in permeate flux due to substantially lower fouling when concentrating weak black liquor at 85 °C [4]. Coated tubular ceramic membranes show no observable fouling over a period of 72 hours, compared to uncoated membranes that exhibit a 20% drop in flux in less than 3 hours. Beyond 20% permeate recovery, however, the fouling rate for coated and uncoated membranes approached -0.4 LMH/h due to cake-layer formation. This fouling has been shown to be reversible only with coated membranes; uncoated membranes undergo irreversible fouling and the flux only recovers after chemical cleaning. Continuous surface renewal has been demonstrated using coated membranes that have been stripped and recoated with no loss in performance.

Coated Stage 2 membranes exhibit increased sodium sulfate and sodium hydroxide rejection

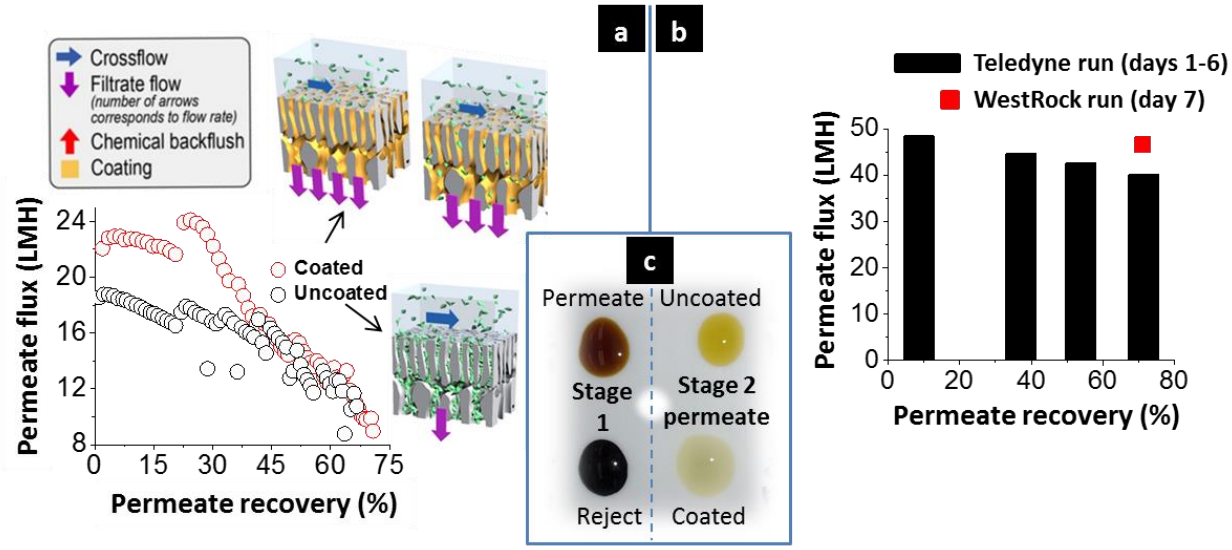


Figure 5.1.1 Teledyne coating performance during Stage 1 (a) and Stage 2 (b) weak black liquor concentration
(**a**) At a transmembrane pressure of 60 psi and a temperature of 85 °C, the permeate flux of the coated membrane decreases by 5.7% (from 22.9 LMH to 21.6 LMH) after concentrating 10 gal weak black liquor to 8 gal (or 20% recovery). Similarly, the uncoated membrane flux decreases by 10.8 % (from 18.8 LMH to 16.5 LMH) at 20% recovery. The flux is significantly lower with the uncoated membrane because foulants adhere to the membrane surface, as shown in the cartoon. After backflushing with weak black liquor permeate, the permeate flux increases to 24.1 LMH as weakly bound foulants and excess coating are removed during the backflushing process. The uncoated membrane flux increases to 17.5 LMH after backflushing; the flux does not recover because irreversible fouling occurs. The coated membrane takes 79% of the time to concentrate weak black liquor to 40% permeate recovery. (**b**) During the 6-day trial at Teledyne, the Stage 2 weak black liquor permeate flux decreases by 17.3% (from 48.5 LMH to 40.1 LMH at 71% permeate recovery) at a transmembrane pressure of 400 psi and a temperature of 70 °C. After transporting the system to WestRock, the flux is 46.5 LMH at 71% recovery (transmembrane pressure, 390 psi; temperature, 67 °C). The coating allows the permeate flux to recover without any cleaning or backflushing. (**c**) Weak black liquor permeate and concentrated reject samples from Stage 1 using weak black liquor as feed (left) and Stage 2 permeate samples from uncoated and coated membrane using Stage 1 permeate as feed (right).

over uncoated membranes. Membranes that are coated with the negatively and positively charged coating exhibit a 7% and 10% increase in sulfate rejection, respectively, over uncoated membranes. Total organic carbon and sodium sulfate analyses of the final Stage 2 permeate and samples from WestRock pulp washers indicate that the permeate may be introduced to the pulp-washing cycle at the first or second washer closest to the digester.

Figure 5.1.1 summarizes the typical performance of coated membranes during weak black liquor concentration. Coated Stage 1 membranes exhibit an average permeate flux of 4.2 LMH/bar when concentrating weak black liquor at 85 °C from 0 to 70% permeate recovery at a transmembrane pressure of 60 psi. Coated Stage 2 membranes exhibit an average permeate flux of 1.6 LMH/bar when concentrating weak black liquor permeate (from Stage 1) at 70 °C from 0 to 70% permeate recovery at a transmembrane pressure of 400 psi. Although the fouling resistance of the coated membranes was impeccable, the Stage 1 permeate flux during the WestRock demonstration was only 0.77 LMH/bar. Based on the results of the demonstration, the calculated annualized capital, operational, and maintenance cost is $8.0M, making the process economically unfeasible. Unfortunately, we ran out of time and resources and we were forced to use an unoptimized coating during the trial. To perform as it has previously, the coating requires a series of conditioning steps that vary with each system geometry. If we tune the conditioning steps to the scaled-up system, then the Stage 1 membrane would perform as it has over the life of the program and the annualized capital, operational, and maintenance cost for Stage 1 would be $2.0M and the payback period for the complete system would be 2.8 years.

6. INTRODUCTION

6.1. Problem

There is a high demand for the reduction of energy usage in the Pulp and Paper industry. In 2002, the U.S. Paper Industry produced 105.6 million tons of pulp and paper products while consuming 2,361 trillion Btu [5]. Among the various manufacturing processes employed, DOE's ITP identified the process of concentration of weak black liquor (WBL), a byproduct during the wood digestion process when producing pulp, in the Forest Products industry as the single largest energy reduction opportunity for separation technologies across all U.S. industries with the potential to save 110 TBtu/year [6]. WBL must be recycled by (I) concentrating to 60-80% solids, (II) burning in a recovery boiler, and (III) causticizing (Figure 6.1.1). Multiple stages of steam-heated evaporators are currently used for the concentration of WBL in the paper pulping process, which leads to large energy consumption due to the high heat of vaporization of water. The concentrated liquor, containing lignin and other organic compounds, is burned in a recovery boiler providing some energy recovery. About 55 TBtu/yr of energy savings could be achieved if the first two evaporator stages are replaced with membrane-based separation, which raises the solids content from ~15% to ~30%. Membranes allow pressure-driven separation based on molecular size, rather than thermal evaporation, and consume less than a third of the energy per unit volume compared to evaporators.

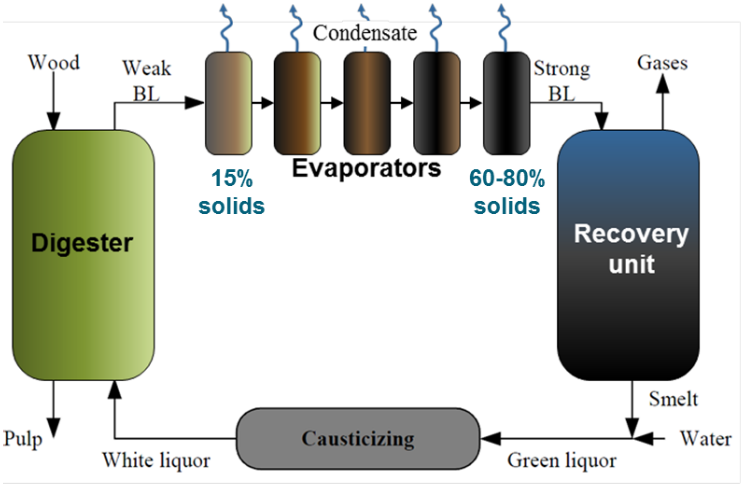


Figure 6.1.1 Schematic of the pulping process
Wood chips, pulping chemicals, and water are added to the digester and the batch is heated under pressure to separate wood fibers by dissolving lignin and other organic compounds to form pulp, which is the main component of paper products. Pulp is separated from the aqueous solution of spent chemicals and organic material, or weak black liquor (BL), and the weak BL is concentrated from about 15% solids to 60-80% solids (strong BL) using several evaporators. The strong BL is burned in a recovery boiler before undergoing causticizing to recover the spent pulping chemicals. The digestion process can then be repeated with fresh wood chips.

High operation and capital cost of membranes is a major challenge in their adoption. Membrane-based separation costs for WBL concentration are dominated by: (I) the need for expensive ceramic membranes since the lower cost polymeric membranes are attacked by high temperature (>80°C) and caustic (pH 13-14) nature of WBL, and (II) higher electricity cost of pressure-driven flow to prevent rapid flux decline due to membrane fouling, which also adds to the maintenance costs. The harsh nature of WBL shortens the lifetime of polymer membranes to about 18 months and necessitates the use of ceramic membranes. The presence of relatively high concentration of salts, organic matter, and particulates with a large particle size distribution leads to diverse fouling phenomena such as scaling, pore blocking, and cake layer formation. The flux, *J*, is represented by equation 6.1:

$$J = \frac{TMP}{\mu \cdot \left(R_m + R_f\right)} \tag{6.1}$$

where *TMP* is the transmembrane pressure, μ is viscosity, and R_m and R_F are resistances to flow due to membrane and fouling, respectively. Thus, fouling results in rapid flux decline and limits the maximum operating flux, making membrane-based WBL concentration unpractical.

6.2. Description of technology

Teledyne Scientific & Imaging (TSI) has developed a pressure-driven membrane-based WBL concentration process that maintains high product flow by mitigating membrane fouling. Our chemically-resistant and antifouling coating can be deposited on ceramic and polymeric membranes to enable economical implementation of the concentration process. The low cost, superhydrophilic, and sacrificial coating can be regenerated in-situ and on demand to combat membrane degradation and fouling from black liquor. Such a coating makes membrane-based WBL concentration feasible since it increases the filtrate flow for longer periods of time. As a result, the overall membrane cost is lower because the membrane lifetime is increased.

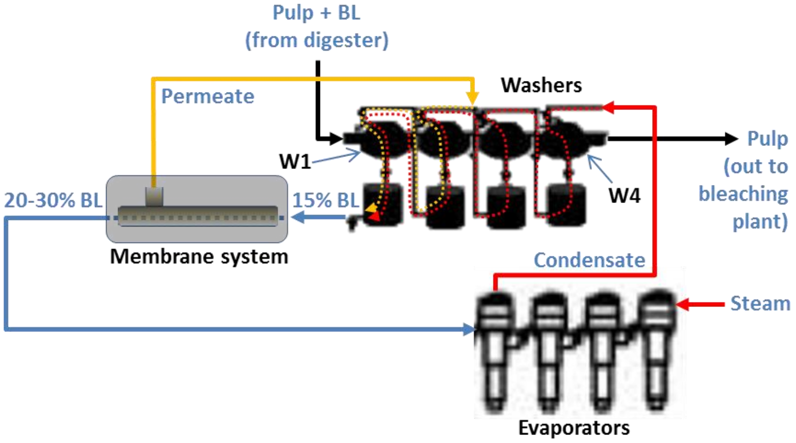


Figure 6.2.1 Membrane system integration

Pulp and black liquor from the digester enter a series of vacuum drum washers where pulp is washed and separated from black liquor. Black liquor with 15% solids is collected from the first washer (W1) and is fed to a membrane filtration system that concentrates the black liquor to 26% solids. Concentrated black liquor is pumped to the evaporators for further concentration. In this example, two of the six evaporators have been removed and replaced with the membrane system. Condensed water (from evaporated black liquor) is added to the fourth washer (W4) to wash the pulp in a counter-current manner. Permeate from the membrane system is added to the second washer for counter-current washing of the pulp. Pulp is cleaned as it travels from W1 to W4 before it is sent to the bleaching plant for paper production.6.3. Potential applications and impacts

Coated membrane systems would be integrated into existing pulping mills between W1 and the evaporators (Figure 6.2.1). Depending on the number of evaporators being replaced, WBL would be concentrated from 15% to 20-30% solids before entering the evaporators. For example, WBL could be concentrated to as high as 30% total dissolved solids in a typical mill if two of the six evaporators are replaced. The permeate would then be used as cooking liquor for wood digestion or for pulp washing.

6.3. Application, impact, and commercialization

Our coating technology could be applied in municipal water treatment, desalination, and chemical and dairy industries in addition to the pulp and paper industry. Since the paper industry is the third largest energy consumer in manufacturing, consuming 2.11 quadrillion Btu [7], implementation of our technology in the WBL concentration process would result in a reduction of greenhouse gases and increase profitability of U.S. paper plants. Assuming a carbon dioxide emission factor of 7.03×10^{-4} metric tons per kilowatt hour of electricity and 100% efficiency during the electric heating of steam, which currently drives the thermal concentration of weak black liquor, replacing the first two evaporators with membranes would decrease the carbon dioxide emissions by more than 11.3 million metric tons CO_2 per year. In addition to increasing the efficiency of paper manufacturing, the cost savings would be around $1.1 billion per year [8]. However, since the technology was matured to TRL 5, commercialization of the technology is in its infancy. To minimize risk, adoption by the pulp and paper industry requires maturation to at least TRL 7 and commercialization would require 3-5 years from the current state of the technology.

7. BACKGROUND

7.1. Objective

The objective of this project was to concentrate weak black liquor (WBL) from ~15-17% solids to 23-29% solids using an economically feasible filtration process comprised of ultrafiltration (UF) followed by nanofiltration (NF) membranes (Figure 7.1.1). In order to recycle the permeate to prepare cooking liquor, the goal was to produce permeate with less than 11% solids. The WBL recovery process would therefore require fewer stages of evaporators and the overall energy required to concentrate WBL would be reduced from 3.5 MMBtu/adt to <2.2 MMBtu/adt [9], resulting in a total energy savings of 55 TBtu per year. Jonsson et al. have demonstrated the potential for membrane separation in the laboratory using a combination of ceramic UF and polymeric NF membranes on hardwood derived black liquors [10]. However, it is not economically feasible, since the payback period is more than 9 years at an energy cost of $0.07 per kWh. We aim to reduce the payback period to <2 years using a transformational coating technology that: 1) enables the use of low cost, high temperature resistant membranes, and 2) reduces the operating energy cost by three times compared to Jonsson's process. Key technical goals are demonstrations of: 1) maintenance of filtrate/permeate quality on coated membranes when subjected to accelerated aging with caustic black liquor feed over a period of at least one week to prove membrane robustness against process conditions, 2) 3X lower energy cost with 15% higher flux during ultrafiltration using coated polymeric membranes, 3) <20% reduction in flux per week with nearly complete flux recovery in weekly cleaning and recoating step, and 4) detailed design and economic model of WBL concentration with a payback period of ~2 years.

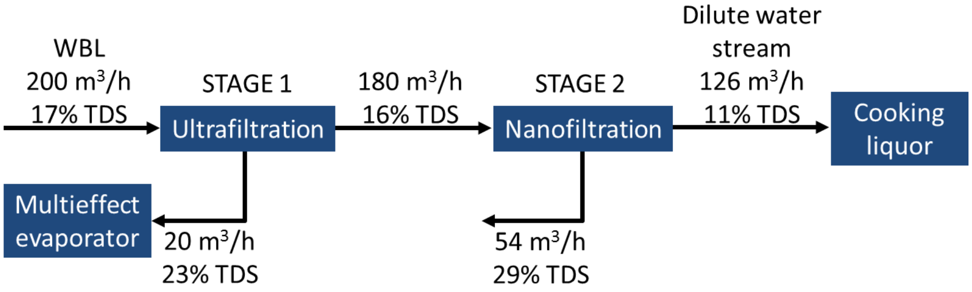


Figure 7.1.1 Proposed membrane-based WBL concentration for a typical plant processing 200 m^3/h

7.2. Approach and innovation

Conventional polymer coating processes typically result in nonuniform coatings on the membrane surface as schematically shown in Figure 7.2.1. This is due to the fact that monomers readily polymerize prior to depositing on membrane surfaces. Our technology controls the reaction kinetics to allow monomer deposition before polymerization is carried out. First, a polymerizable proprietary organic compound (**A**) mixes with the monomer. Presence of **A** slows the diffusion of monomers to surfaces, resulting in a controlled polymerization reaction that forms a conformal and thin adherent layer on all surfaces in the presence of proprietary compound **B**. **A** also enables on-demand removal of the coating with a mixture of existing cleaning solutions that can be used during backflushing. Consequently, the membrane surface, including pore walls, is coated with a uniform film. In addition, the coating can be tuned to reject ions by incorporating either positive or negative charges at the surface.

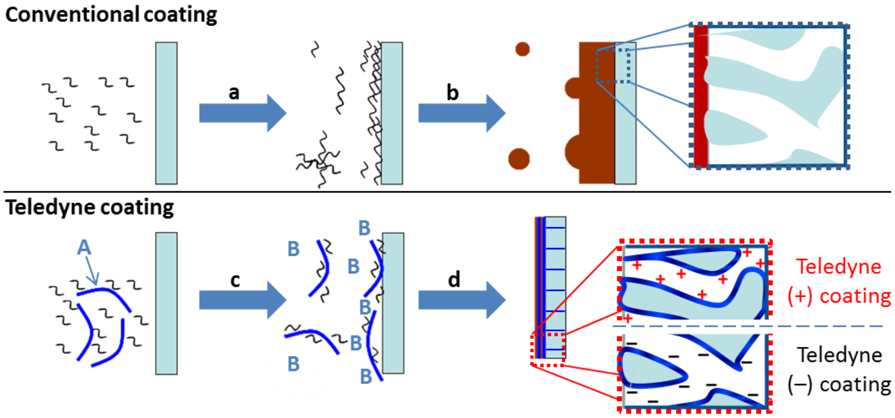


Figure 7.2.1 Conventional (top) and Teledyne (bottom) coating technologies
(**a**) Hydrophilic monomers polymers near the membrane surface. (**b**) Polymer particles deposit on surface forming a 20-100 nm thick nonuniform coating. (**c**) Hydrophilic monomer associates with proprietary compound A, slowing down diffusion to the surface. (**d**) Exposure to compound B induces layered nanostructure, resulting in a 5 nm thick uniform coating.

Our approach to concentrating WBL using membranes is to apply sacrificial protective coatings that resist fouling. The chemical nature and regenerative property of the coating imparts protection from harsh conditions associated with pulp and paper manufacturing, while maintaining high weak black liquor flux. Hydrogen bonding creates tight bonds between water molecules and our coating, resulting in a significant decrease in adhesion of black liquor foulants to the surface since water cannot be easily excluded. Loosely-bound foulants are removed during backflushing, a standard operation in membrane-based separations. Our simple flush-through coating process of a liquid mixture enables a thin 2-5 nm coating both on the membrane surface and within the membrane pores. This is important in preventing fouling from widely variable constituents in weak black liquor and in imparting chemical protection. The coating has no adverse impact on the initial flux rates and the pressure drop across the membrane can be used as a sensor to activate the coating removal and reformation process. The ability to reform the coating in-situ enables membrane regeneration for prolonged lifetime and maintenance of high flux rates that cannot be matched by existing membranes (Figure 7.2.2). We estimate a biweekly recoating process using our low cost coating material, placing a minimal logistical and economic burden on the end-user.

Since the acquisition by Teledyne, Teledyne Scientific & Imaging (TSI) has developed materials and processes for various Teledyne Business Units, including antifouling coatings for commercial marine applications and composite materials for oil and gas exploration that operate under harsh environments. Most relevant among them is our novel antifouling coating that enables significantly superior fouling resistance properties during filtration of organic rich seawater compared to commercially available filters. This DARPA sponsored project followed a prior effort in antifouling surfaces where novel materials were developed that mimic the skin shedding of marine animals to impart foul resistance to surfaces submerged in highly fouling marine environments. During the execution of these projects, we have developed world class capabilities in evaluating membrane surfaces and determining interactions with foulants present in feed streams. Our existing coating technology is at TRL 6 for seawater feed and at TRL 5 for other feed types. Agenda 2020, an industry-led pulp and paper technology innovation consortium, provided membrane-integrated pulp mill models to assist in economic model development. WestRock (formerly MeadWestvaco) is among the largest paper and pulp manufacturers in the US and their willingness to supply black liquor and host the TRL 5 testing provided important end-user perspective and guidance.

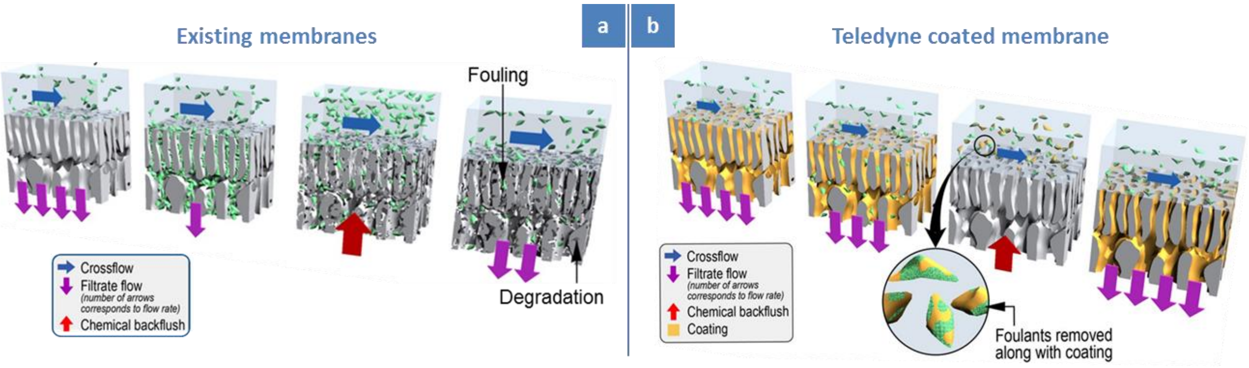


Figure 7.2.2 Schematic of fouling during tangential flow filtration.
(**a**) WBL quickly fouls existing membranes and the resulting increase in membrane resistance decreases the filtrate (or permeate) flow (purple arrows). The filtration process is regularly stopped and backflushing (red arrow) is carried out to release foulants. Because of irreversible fouling the permeate flow does not completely recover. (**b**) A conformal superhydrophilic coating (yellow), deposited on the membrane surface and pore walls, protects the underlying membrane by imparting chemical and fouling resistance. Sacrificial action through coating removal during chemical backflush and subsequent in-place regeneration enables long lifetime.

8. RESULTS AND DISCUSSION

8.1. Small-scale laboratory coupons

8.1.1. Target specifications for membrane-based treatment of black liquor

All weak black liquor (WBL) feed used in this project was obtained from WestRock (formerly MeadWestvaco) pulp and paper mill in Covington, VA. Figure 8.1.1 shows the bench-scale, pressure-controlled WBL flux analyzer used to characterize membrane performance. Several membranes were surveyed (Table 8.1) to determine the possible range of WBL flux. In general, we assembled each membrane in an Amicon stirred cell and installed the stirred cell in the analyzer. Next, water was flushed through the membrane at 25 psi for 30 minutes to rinse the membrane. After flushing, water flux was measured for 30 minutes to ensure the quality and integrity of the membrane. After draining the water, WBL was added to the 316 stainless steel (SS) pressure vessel and the filtrate flux, *J*, was calculated according to equation 8.1:

$$J = \frac{\Delta m}{A \cdot \rho \cdot \Delta t \cdot TMP} \tag{8.1}$$

where *Δm* is the change in mass per unit time (grams), *A* is the membrane area (m^2), ρ is the density (liters/gram), *Δt* is the change in time between measurements (hours), and *TMP* is the transmembrane pressure, which is the pressure difference across the membrane.

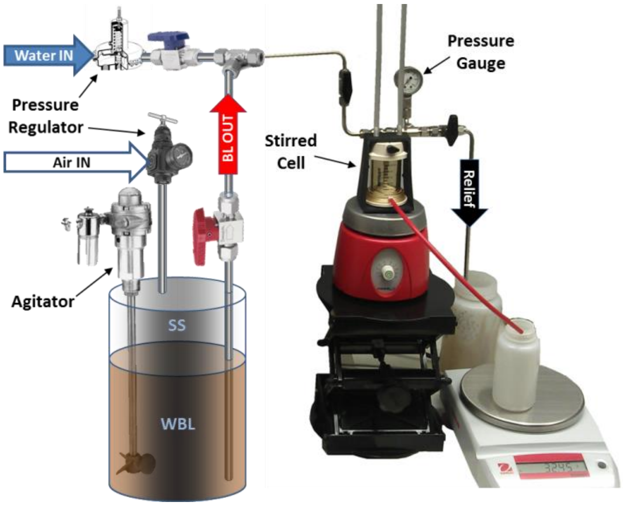


Figure 8.1.1 Weak black liquor flux analyzer
Weak black liquor (WBL) within a stainless steel (SS) pressure vessel is mixed using an air-powered agitator. Compressed air is used to pressurize the SS pressure vessel and force WBL through a given membrane installed in a stirred cell. The filtrate mass is measured using a balance and the flux is calculated using the density of the filtrate.

Preliminary dead-end data suggest that a target flux of 100 L m^{-2} h^{-1} (LMH) for the first stage of filtration is practical Figure 8.1.2). For example, the filtrate flux of WBL using microfiltration (MF) and ultrafiltration (UF) membranes at room temperature is between 20-30 L m^{-2} h^{-1} bar^{-1} (LMH/bar) at 10 psi. Therefore, the target flux would require a pressure difference of 45-75 psi across the membrane, which is very reasonable.

Table 8.1 Specifications of membranes used for WBL concentration

Membrane	Type	Pore Size (MWCO)
a	MF - Hydrophobic	0.2 µm
b	MF - Hydrophilic	0.2 µm
c	MF - Hydrophobic	0.1 µm
d	UF - Hydrophilic	0.03 µm
e	UF - Hydrophilic	(100,000 Da)
f	UF - Hydrophobic	(30,000 Da)
g	UF - Hydrophilic	(10,000 Da)
h	NF	(~400 Da)
i	RO	(~100 Da)

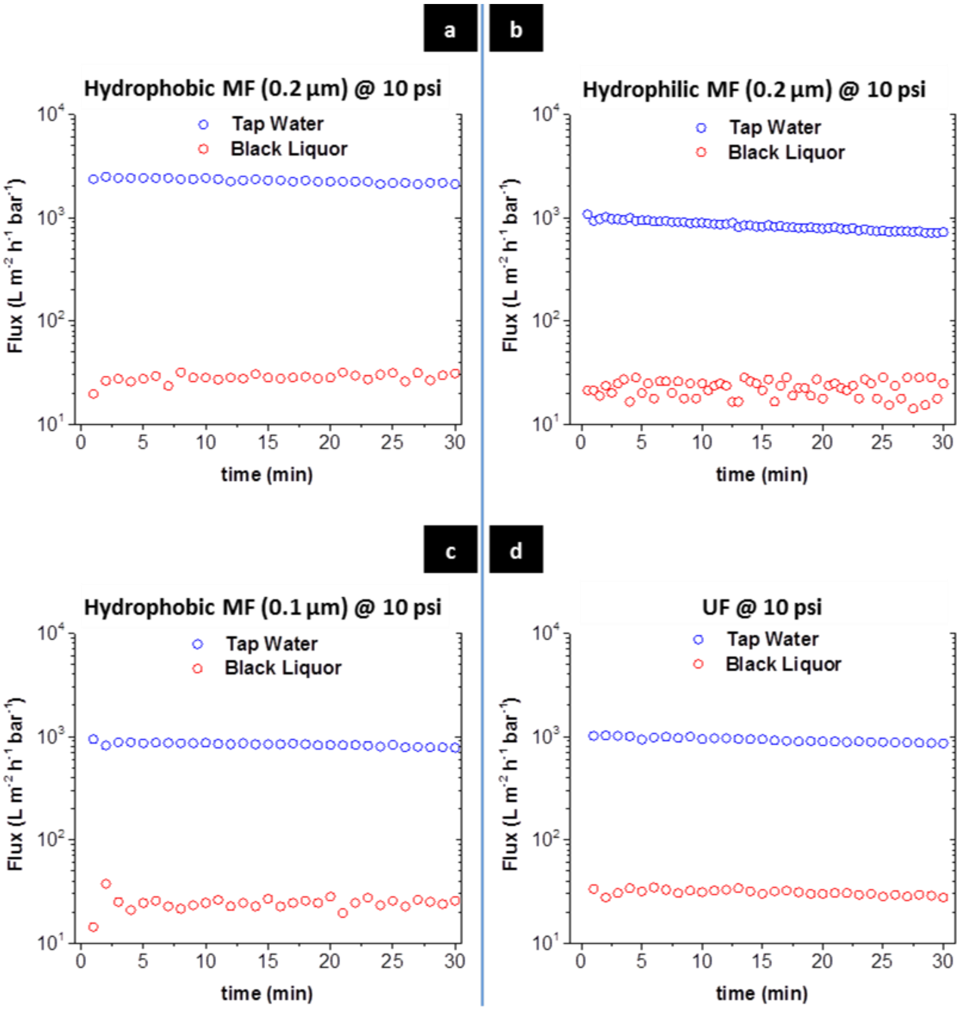


Figure 8.1.2 WBL (○) and water (○) flux @ 10 psi
WBL flux through the tested membranes are anywhere from 30 to 81 times less than the water flux. Filtration of WBL and tap water was carried out at room temperature (21–24°C).

8.1.2. Economic model

We developed a cost model following one prepared by the U.S. Bureau of Reclamation to cost reverse osmosis membranes for desalination [11]. We modified the model to include ultrafiltration and nanofiltration processes. Parameters (units) of the model include: design flow rate (L day^{-1}), plant life span (years), amortization time (years), annual interest rate (%), integrity test frequency (day^{-1}), integrity test duration (min), channel diameter (m), channel length (m), number of channels per module, membrane module area (m^2), membrane module cost ($ m^{-2}), modules per vessel, cost per vessel ($), pump cost index ratio (I), pump material adjustment factor, pump efficiency (%), factor to account for labor costs, membrane lifespan (years), electricity cost ($/kWh), personnel salary ($ year^{-1}), number of personnel, time for air scour (min), offline time (min day^{-1}), chemical cleaning duration (min), backwash duration (min), backwash pressure (kPa), cleaning frequency (year^{-1}), cleaning chemical cost ($ L^{-1}), cleaning cost ($ m^{-3}), cleaning skid ($), and membrane friction constant. Operating conditions (units) of the model include: design flux rate – product basis (L m^{-2} h^{-1}), channel crossflow velocity (m s^{-1}), backwash frequency (year^{-1}), average TMP (kPa), sets of replacement membranes, pressure drop across module (kPa), recirculated volume due to crossflow (L day^{-1}), backwash flux (L m^{-2} h^{-1}), backwash time (min), volume consumed by backwash (L m^{-2}), offline time – backwash / cleaning / integrity test (min day^{-1}), recovery (%), effective flux (L m^{-2} h^{-1}), membrane area (m^2), number of membranes, number of vessels, total membrane cost ($), plumbing and valves ($), instruments and controls ($), tanks and frames ($), miscellaneous ($), feed pump ($), recirculating pump ($), total capital cost ($), annualized capital cost ($ year^{-1}), annualized cost of replacement membranes ($ year^{-1}), energy usage – feed delivery (kWh day^{-1}), energy usage – recirculation (kWh day^{-1}), energy cost for pumping ($ year^{-1}), annual maintenance cost ($ year^{-1}), cleaning cost including disposal ($), chemical cost per cleaning cycle ($), waste disposal cost per cleaning cycle ($), cleaning cycles per year, total cleaning cost including waste disposal ($), total personnel cost ($), total operation and maintenance (O&M) cost ($), total cost ($).

Based on a flow rate of 200 m^3/h, which is typical for a medium-sized paper mill, the Stage 1 and Stage 2 permeate flow rate used in the model are 140 m^3 h^{-1} and 84 m^3 h^{-1}, respectively. Assuming a Stage 1 and Stage 2 permeate flux of 100 LMH and 44 LMH, the required membrane area is 2,820 m^2 and 2,520 m^2, respectively. As a result, the 5-year annualized capital cost and operational and maintenance (O&M) cost are $234K and $1.40M, respectively. Since the 1.2 MMBtu/adst energy savings of concentrating weak black liquor to 30% solids corresponds to an annual saving $5.1M (based on $0.07/kWh) and the annualized cost of the membrane system is $1.63M, the payback period would be less than half of a year.

8.1.3. Commercial membrane material candidates

Figure 8.1.3 shows the average WBL flux over the 30 minute filtration experiments. At a given pore size (i.e. 0.2 µm) and TMP (10 psi), the hydrophobic MF membrane (***a***) exhibits 26% greater WBL flux over the hydrophilic MF membrane (***b***). Even at one half the pore size (i.e. 0.1 µm), the WBL flux is 9.4% greater with the hydrophobic MF membrane (***c***) than with the hydrophilic MF membrane (***b***). Interestingly, the WBL flux through the UF membrane (***d***) is 10% greater than ***a***. There was no observable flux in the case of the nanofiltration (NF) membrane (***h***) up to 25 psi.

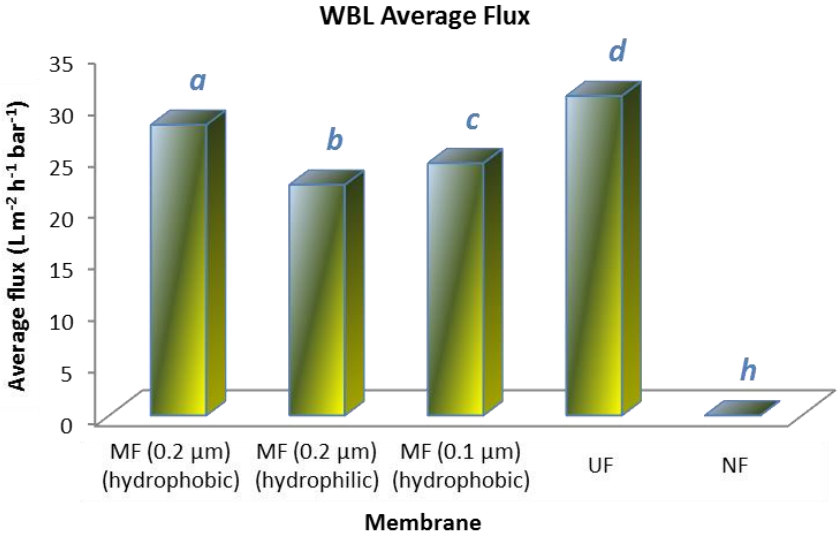


Figure 8.1.3 Average WBL flux
a, 28.1 LMH/bar; **b**, 22.3 LMH/bar; **c**, 24.4 LMH/bar; **d**, 30.9 LMH/bar; **e**, 0 LMH/bar. TMP fixed at 10 psi for MF and UF membranes and at 25 psi for NF membrane. Duration, 30 minutes.

Formation of a cake layer would explain the similarities between the WBL flux of the MF and UF membranes. However, the fact that the UF membrane displays a larger average flux than the MF membranes indicates that the filtration of WBL is complex and membrane stability plays a key role in its concentrating capabilities. For example, the degradation of the UF membrane would explain the flux gains over the MF membranes. As a result, water contact angle measurements were made on membranes after exposure to WBL for 6 days at 80°C.

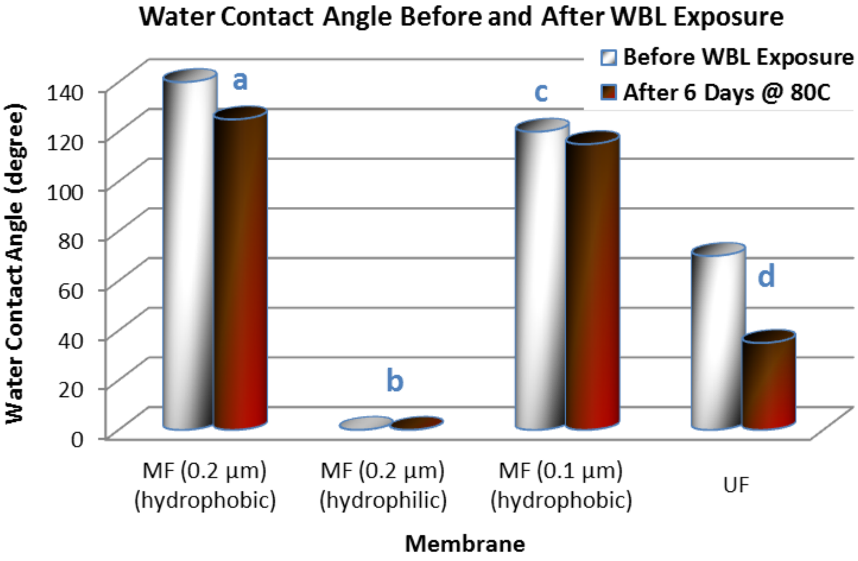


Figure 8.1.4 Water contact angle on membranes before and after WBL exposure at 80C for 6 days
Contact angles on pristine membranes: ***a***, 140°; ***b***, 0°; **c**, 120°; ***d***, 70°. Contact angles after WBL exposure: ***a***, 125°; ***b***, 0°; ***c***, 115°; ***d***, 35°.

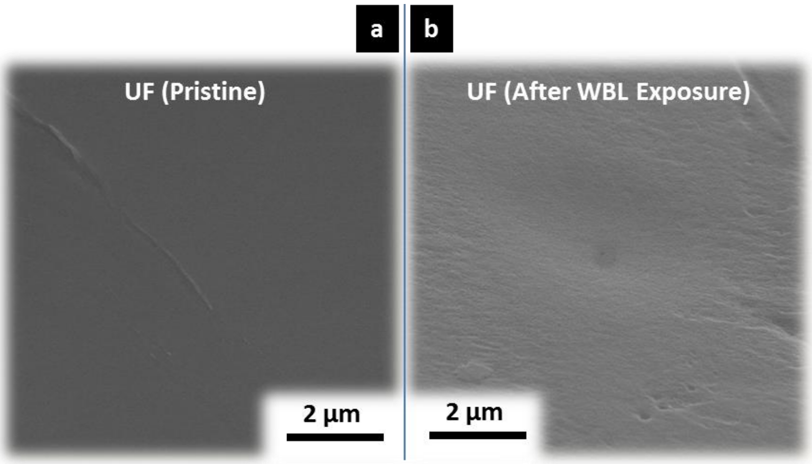


Figure 8.1.5 SEM of UF membrane (a) before and (b) after exposure to WBL at 80°C for 6 days

Figure 8.1.4 shows the water contact angle on membrane surfaces before and after WBL exposure. Membranes ***a*** and ***c*** exhibit a change in water contact angle of 11% and 4%, respectively, after WBL exposure. On the other hand, the water contact angle on the UF membrane (***d***) decreases by 50% after WBL exposure, implying that the surface is essentially changing, either by degradation of the material or by adsorption of foulants. Although the latter is possible, the high WBL flux through the UF membrane suggests that the former is more likely. SEM images (Figure 8.1.5) show pitting on the UF layer after WBL exposure; the features of the underlying support layer are more visible compared to the pristine membrane.

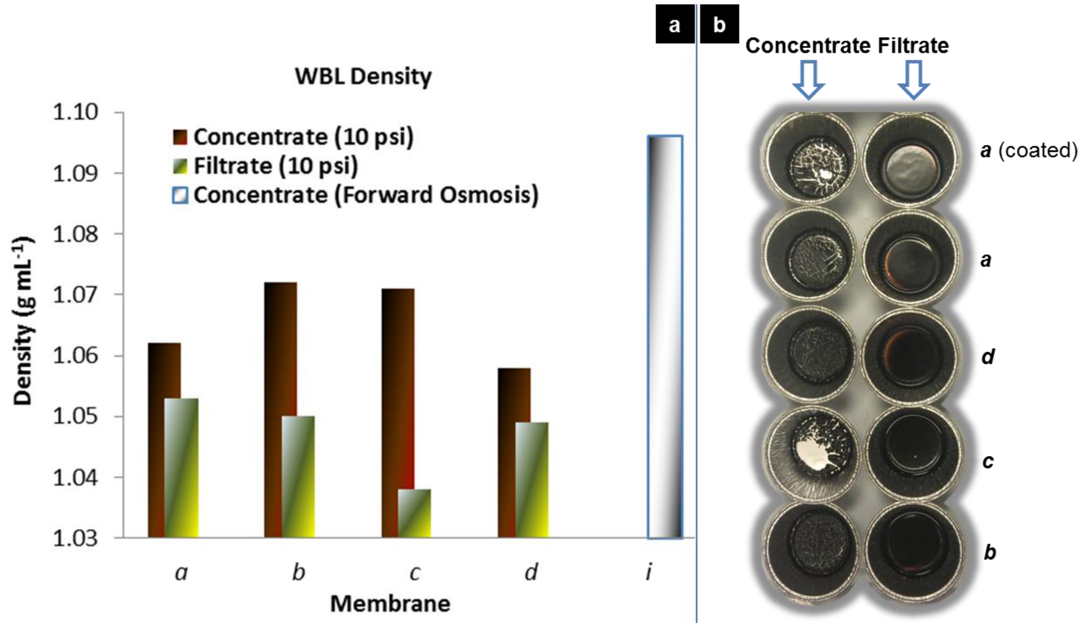


Figure 8.1.6 Density (a) and images (b) of WBL samples

(**a**) WBL filtered at 10 psi using MF, ***a***-***c***, and UF, ***d***, membranes listed in Table 8.1. Density of concentrate (🟫): ***a***, 1.062 g mL^{-1}; ***b***, 1.072 g mL^{-1}; ***c***, 1.071 g mL^{-1}; ***d***, 1.058 g mL^{-1}. Density of filtrate (🟩): ***a***, 1.053 g mL^{-1}; ***b***, 1.050 g mL^{-1}; ***c***, 1.038 g mL^{-1}; ***d***, 1.049 g mL^{-1}. Density of WBL concentrated via forward osmosis using RO membrane, ***i***, and a 50 wt% MgCl draw solution (☐): ***f***, 1.096 g mL^{-1}. (**b**) Concentrate (left) and filtrate (right) samples after heating at 105 °C for 24 hours.

Additionally, the difference in density between WBL concentrate and filtrate is 0.85%, 2.1%, and 3.2% with MF membranes ***a***, ***b***, and ***c***, respectively (Figure 8.1.6a). However, there is only a 0.86% difference in density with the UF membrane (***d***); separation using the UF membrane is less than that using the MF membranes. These data indicate that the UF membrane is degrading in the presence of weak black liquor.

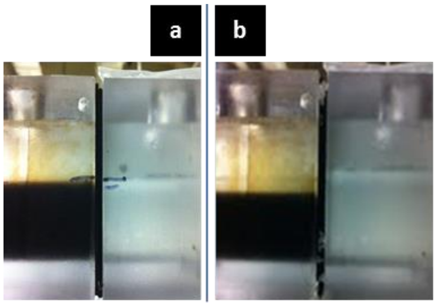


Figure 8.1.7 Room temperature Forward Osmosis WBL concentration using reverse osmosis membrane
(**a**) Initially, equal volumes of weak black liquor (left) and a 50 wt% MgCl draw solution (right), separated by reverse osmosis membrane ***i***, are added to the FO cell. (**b**) With time, water is drawn from black liquor such that the level of the draw solution increases and that of black liquor decreases.

Although forward osmosis (FO) is much slower than filtration, it was investigated because of its potential in further reducing the energy requirements of separating water from WBL. In addition, salts required to create the draw solution are available elsewhere in the Kraft process and are recovered during boiler operations. Therefore, we concentrated WBL via FO using a reverse osmosis (RO) membrane and an aqueous draw solution. As-received WBL and 50 wt% MgCl were added to the FO cell as shown in Figure 8.1.7. At room temperature, the water was drawn from the WBL and the WBL was concentrated. Figure 8.1.6a shows the density of WBL concentrated using filtration (membranes ***a***-***d***) and forward osmosis (membrane ***i***). In our FO experiments, the WBL volume was decreased to less than 2/3 the initial volume. Despite the fact that the WBL density increased by 4.7% after FO-based concentration, the permeate flux was <<0.1 LMH. Interestingly, a coagulated WBL-based gel deposited on the surface of the membrane during each experiment.

Coagulated black liquor films were exploited to increase the FO permeate flux. It turned out that these films were contributing to the separation process, thus, larger molecular weight cutoff membranes were used to increase the flux. For example, when nanofiltration membrane ***h*** (table 8.1) was used for FO-based separation, WBL was concentrated but the draw solution color did not change (Figure 8.1.8a). On the other hand, when the same membrane was used to concentrate WBL via filtration, the pigmented species are not rejected and the permeate is yellow (**b**).

At room temperature the average FO flux of as-received WBL is 0.14 LMH (Figure 8.1.9a), which is rather low. However, when the temperature is increased to 84°C, the initial and average flux increase by more than 22 times and 11 times, respectively. This relatively high flux decreases as the concentration of the draw solution decreases, due to the increase in draw solution volume, which thereby decreases the driving force for diffusion. As a result the average flux of WBL drops to 1.5 LMH, which is still one order of magnitude larger than the flux at room temperature. One way to remedy the decrease in the WBL flux is to maintain a steady concentration of salt in the draw solution. When WBL filtered with membrane ***e*** is added to the FO cell, the average FO permeate flux increases to 0.37 LMH (3.8 times increase over as-received WBL) at room temperature. When the temperature is increased to 84°C, the average FO flux for the 100 kDa filtrate increases to 1.76 LMH, which is 14% higher than that of as-received WBL at 84°C.

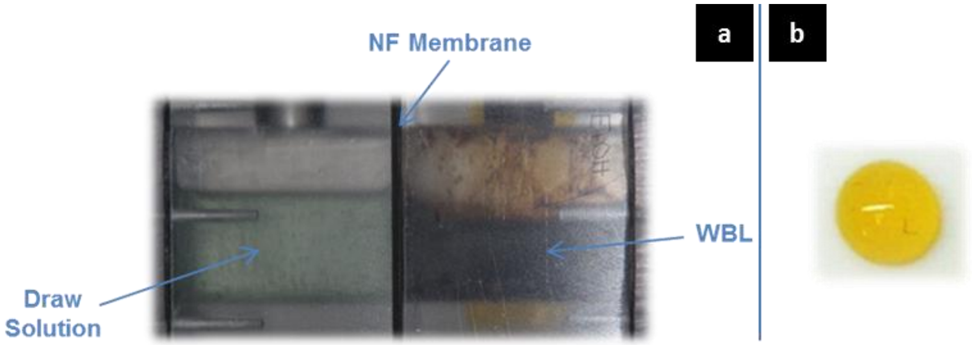


Figure 8.1.8 WBL concentration via nanofiltration membrane
(**a**) Weak black liquor (right) and 50 wt% MgCl draw solution (left), separated by NF membrane ***h*** (Table 8.1), at 84 °C. Water is drawn from black liquor into the draw solution, but the draw solution remains colorless after 8 hours. (**b**) WBL permeate from pressure-driven separation using the same membrane is yellow.

Based on our experiments, polysulfone, polyethersulfone, polytetrafluoroethylene, zirconia, and titania are all promising membrane materials that can withstand the harsh conditions of WBL concentration. RO and FO membrane materials generally include polyamides, which hydrolyze at high temperature in WBL. Although these membranes were stable in WBL at high temperature during the duration of our experiments, they are not recommended for use in a pulp mill. FO was also possible by the formation of a coagulated WBL film on loose NF membranes. Perhaps pulysulfone NF membranes could someday be used for FO-based concentration of WBL.

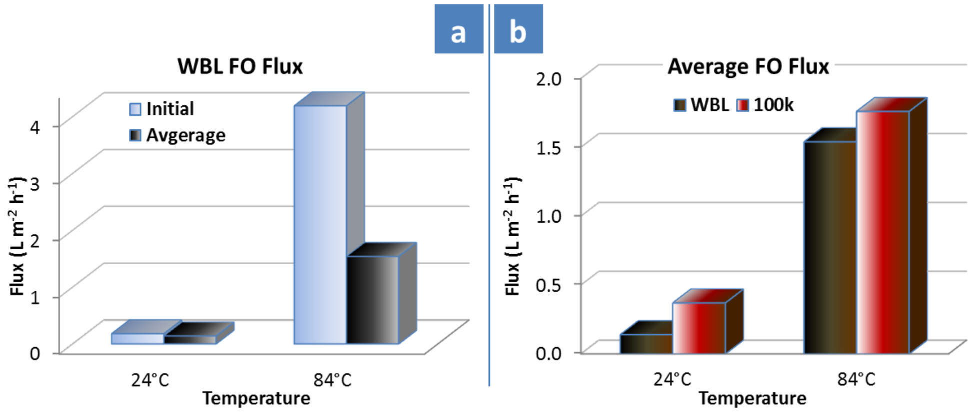


Figure 8.1.9 Forward osmosis flux vs. temperature
(**a**) At room temperature, the initial (☐) and average (■) flux is 0.18 and 0.14 LMH, respectively. At 84°C, the initial and average FO flux is 4.2 and 1.5 LMH, respectively. (**b**) When WBL is prefiltered using a 100 kDa membrane (100k), the average FO permeate flux is 0.37 LMH at room temperature and 1.8 LMH at 84°C.

8.1.4. Weak black liquor foulants

ESM (162B, 101B, 310D) and gas chromatography-mass spectrometry (GC-MS) analyses indicate that black liquor contains a multitude of potential organic foulants, including carbohydrates, lignins, thiols, alcohols, glycols, and carboxylic acids. In addition, WBL flux data suggests that there is some cake formation on large molecular weight cutoff (MF and UF) membranes and the resulting flux may be limited by the cake layer and not necessarily by the pore diameter. We demonstrated the formation of a cake layer and its characteristics using scanning electron microscopy (SEM) (Figure 8.1.10). When WBL was cast on the surface of the MF membrane, the resulting cake layer is thin and the features of the pore are apparent, indicating possible pore penetration. On the other hand, when an identical volume of WBL was cast on the UF membranes, the resulting cake layer was thicker and the underlying membrane features were not apparent. This suggests that more foulants penetrate the pores of the MF membrane, which may explain why a higher flux was observed for certain UF membranes although they have smaller pore diameters.

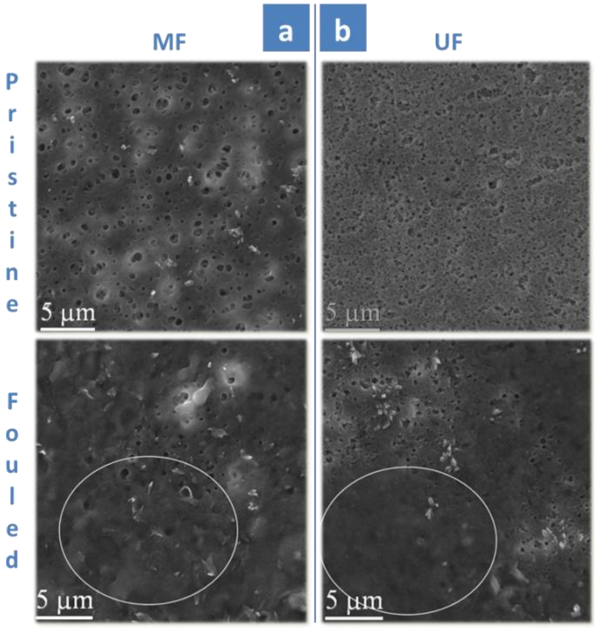


Figure 8.1.10 SEM of hydrophilic microfiltration (a) and ultrafiltration (b) membranes, before (top) and after (bottom) a fixed volume of WBL was cast on each membrane
(**a**) MF (0.2 µm) membranes exposed to WBL show cake layer penetration into the pores (white circle) resulting in decreased flux (22.3 LMH·bar^{-1}) over the UF membrane at room temperature. **b**, UF (0.03 µm) membranes exposed to WBL have a cake layer that is thicker than that of the MF membrane, due to less pore penetration, resulting in a larger flux (27.2 LMH·bar^{-1}) at room temperature.

Attenuated total reflectance (ATR) Fourier-transform infrared spectroscopy (FTIR) was used to identify species in black liquor that are responsible for membrane fouling. Figure 8.1.11 shows the ATR-FTIR results for hydrophobic (***a***) and hydrophilic (***b***) membranes exposed to WBL for 3 days. First, spectra were obtained after soaking pristine membranes in deionized (DI) water (red plots). Then the membranes were immersed in WBL for 3 days to monitor the extent of foulant adsorption in the absence of pressure. After WBL exposure, the membranes were lightly rinsed with DI water and spectra were obtained (blue plots). Adsorption of black liquor contaminants is apparent on the hydrophobic membrane surface, with peaks at 1650, 1550, 1470, and 1100-1000 cm^{-1} after rinsing with water. However, the spectra of the hydrophilic membrane before and after WBL exposure overlap; there is no apparent adsorption of contaminants on the hydrophilic surface after 3 days of WBL exposure. This implies that a hydrophilic surface would be easier to clean and less expensive to maintain. Therefore, the superhydrophilic coating proposed by TSI for fouling mitigation of black liquor should be effective in reducing operational costs of membrane-based WBL concentration.

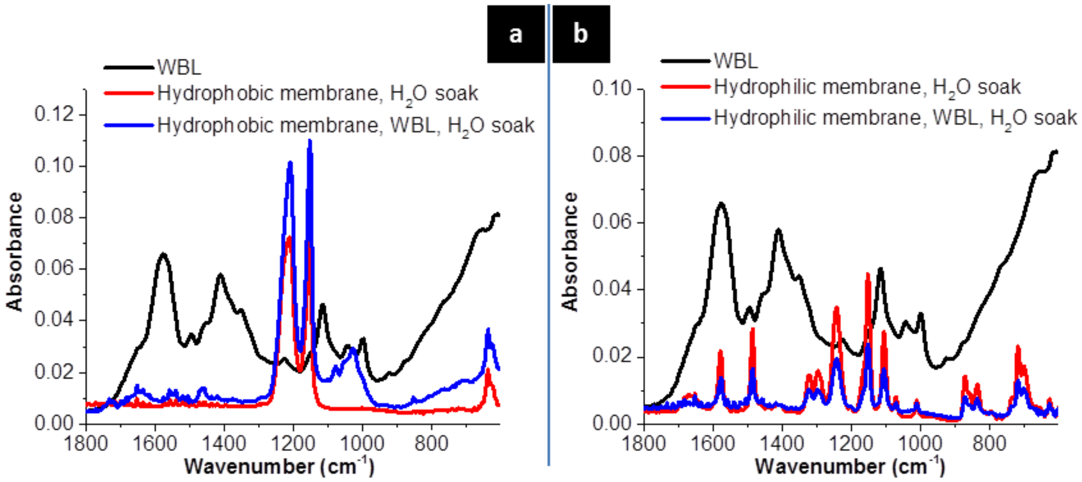


Figure 8.1.11 ATR-FTIR spectra of hydrophobic (a) and hydrophilic (b) membranes before and after WBL exposure (**a**) Spectrum of hydrophobic membrane after soaking in DI water (red line). The membrane was then soaked in WBL for 3 days and a spectrum was obtained after rinsing with water (blue line). (**b**) Spectra of hydrophilic membrane before (red line) and after (blue line) WBL exposure for 3 days.

8.1.5. Coating materials development

Our coating has been formulated specifically for WBL concentration. The reaction kinetics were precisely controlled to tune the working time of the coating. For example, the pure polymer polymerizes in less than 30 minutes (Figure 8.1.12a). However, the polymerization rate was decreased to allow a working time of 2 hours by using composition α. The ability to increase the working time is important since scaled-up systems will require longer deposition times. If polymerization proceeds too quickly, then unreacted monomers may not reach the inner pore walls; polymer chains would be too large to enter pores, which would limit their deposition to exterior membrane surfaces. The working time was increased to greater than 24 hours with composition β.

To test the stability of the coating under typical operating conditions, a polytetrafluoroethylene (PTFE) membrane was coated and boiled in WBL for 3 days. Before WBL exposure, the coated membrane is hydrophilic. After WBL exposure, a drop of water was placed on the membrane surface and the surface remained hydrophilic (Figure 8.1.12b). Even PTFE membranes that are soaked in ethanol, to allow wetting of the surface in aqueous solutions, lose their hydrophilicity after WBL exposure. The data suggest that the coating remains intact when exposed to hot WBL.

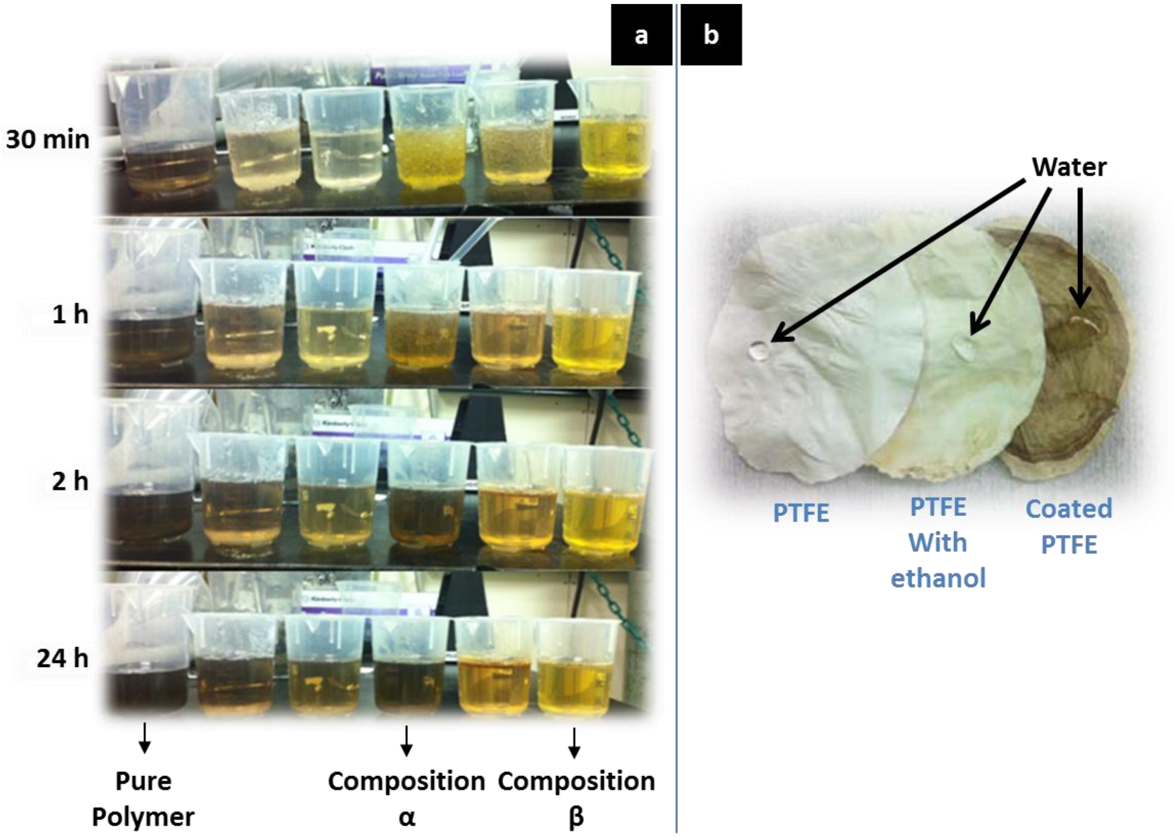


Figure 8.1.12 Coating polymerization time (a) and WBL resistance (b)
(**a**) The pure monomer polymerizes immediately, as indicated by the brown color of the pure polymer. Reaction kinetics can be controlled to decrease the rate of polymerization, thereby increasing the working time to 2 hours (composition α) to 24 hours (composition β). (**b**) The hydrophobic PTFE membrane coating using composition α remains hydrophilic after boiling in WBL. For comparison, the PTFE membrane soaked in ethanol is initially hydrophilic but becomes hydrophobic after WBL exposure. Pristine PTFE is hydrophobic before and after WBL exposure.

8.1.6. Membrane characterization with and without coating

All data reported in this section are in reference to dead-end filtration experiments, which were carried out in Amicon stirred cells. Figure 8.1.13a shows the filtrate flux of UF membranes of various pore sizes when as-received WBL is concentrated at room temperature. In general, the flux decreases with decreasing pore size. As the molecular weight cutoff (MWCO) is decreased to 10,000 Da, the flux of as-received WBL approaches zero (○). These results underlie the necessity of having a multistage WBL filtration system.

Multistage filtration of WBL was performed in two stages (Figure 8.1.14). First, as-received WBL was filtered through a UF membrane with a MWCO of either 30,000 Da or 100,000 Da. The filtrate was then collected and filtered using a UF membrane with a MWCO of 10,000 Da. Figure 8.1.13b shows the results of multistage filtration of WBL at room temperature. When a loose Stage 1 membrane (100 kDa) is used, the flux through the 10 kDa membrane (○) increases by a factor of 5.4, compared to the direct filtration of as-received WBL (○). When a tight Stage 1 membrane (30 kDa) is used, the Stage 2 flux (○) is 9.5 times greater than the flux of as-received WBL. The increase in the Stage 2 flux is attributed to the decrease in foulants, which is achieved in the first stage.

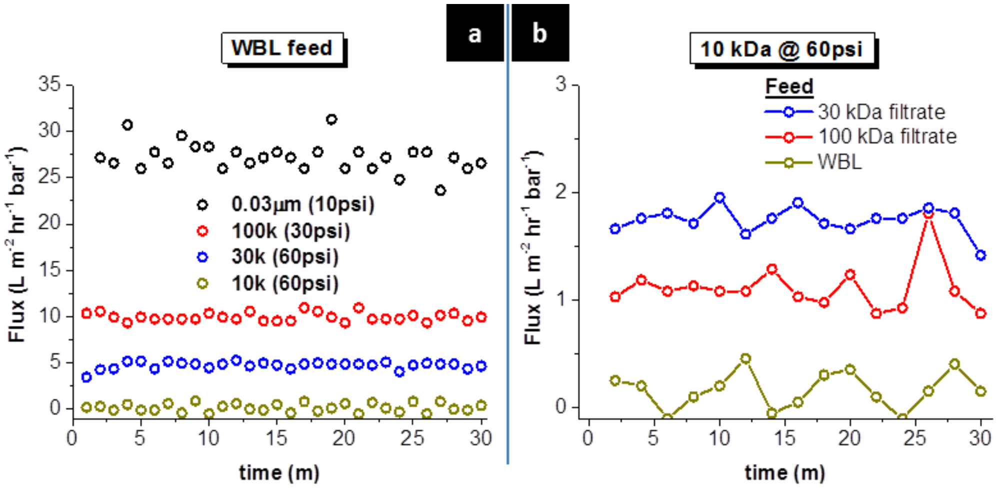


Figure 8.1.13 Room temperature flux vs. time plots for uncoated membranes
(**a**) As-received WBL flux through membrane ***d*** (○) at 10 psi, ***e*** (○) at 30 psi, ***f*** (○) at 60 psi, and ***g*** (○) at 60 psi. The pressure-normalized flux shows a decrease in flux with decreasing pore size. (**b**) Stage 2 membrane ***g*** flux when WBL in is prefiltered with membrane ***f*** (○) and membrane ***e*** (○) during stage 1. When prefiltering the WBL through the 100 kDa (***e***) and 30 kDa (***f***) membranes, the flux through the 10k membrane is increased to 1.07 and 1.74 LMH bar^{-1}, respectively. The direct filtration of as-received WBL through the 10 kDa membrane results in a flux of 0.166 LMH bar^{-1}. Filtration was carried out at room temperature (23°C ±1°C).

Multistage filtration of WBL was also carried out at 84 °C, which is the typical temperature of WBL feed at the pulp mill. The increase in filtrate flux at 84°C is apparent in Figure 8.1.15. For example, the flux of the hydrophobic 0.2 µm membrane (***a***) at 84°C is more than 3 times the flux at room temperature. Similarly, the WBL flux through membranes ***e*** and ***f*** were more than doubled at 84°C. On the other hand, regardless of the Stage 1 filtrate, there was no significant increase the flux through the 10 kDa membrane at elevated temperature.

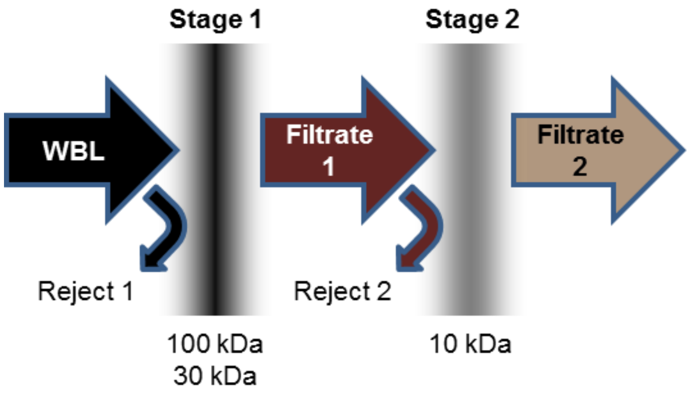


Figure 8.1.14 WBL multistage concentration
Stage 1: WBL is filtered through a large pore diameter UF membrane and the concentrated Stage 1 reject (Reject 1) is collected. *Stage 2:* The filtrate from stage 1 (Filtrate 1) is filtered through a small pore diameter (~10 kDa MWCO) UF membrane and the reject and filtrate are collected.

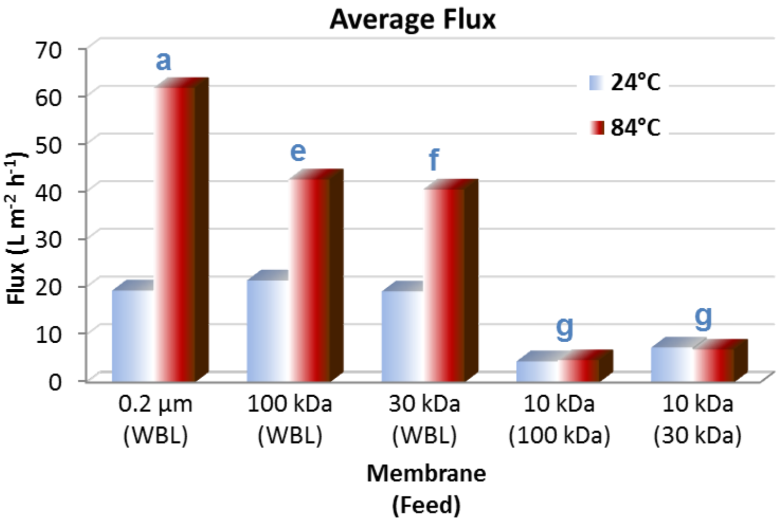


Figure 8.1.15 Average Flux at 24°C (🟦) and 84°C (🟥) for uncoated membranes
a, 19.3 vs. 61.8 LMH; ***e***, 21.4 vs. 42.6 LMH; ***f***, 19.1 vs. 40.5 LMH; ***g*(100k)**, 4.4 vs. 4.7 LMH; ***g*(30k)**, 7.3 vs. 6.9 LMH. TMP: ***a***, 10 psi; ***e***, 30 psi; ***f-g***, 60 psi. Duration, 30 minutes.

Membrane ***e*** was coated and WBL was concentrated at 30 psi (Figure 8.1.16). At both room temperature (blue columns) and elevated temperature (red columns) there was no significant gain in flux with the addition of TSI's superhydrophilic coating to 100 kDa UF membrane. The flux of the uncoated and coated membranes is 9.5 and 7.5 LMH bar^{-1}, respectively, at room temperature. However, at 84°C the filtrate flux through the uncoated and coated membranes increases to 20 and 21 LMH bar^{-1}, respectively. In other words, the flux of the uncoated and coated membranes increases by 110% and 180%, respectively, when the temperature is increased to 84°C. Nonetheless, there is only a 5% increase in flux observed at 84°C when the membrane is coated, suggesting that there is no significant gain in flux when large MWCO membranes are coated with the TSI coating. Rather, at large MWCO (i.e., 100 kDa), temperature is the dominating factor that influences filtrate flux.

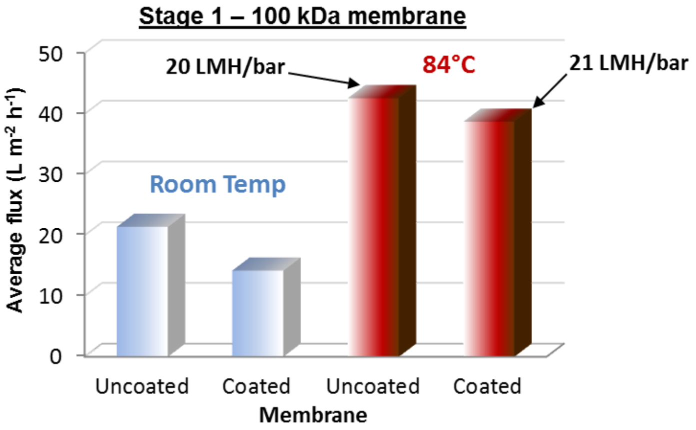


Figure 8.1.16 Average Stage 1 WBL flux through membrane *e* at 22°C (🟦) and 84°C (🟥) @ 30 psi (± 1 psi)
At 22°C the flux of the uncoated and coated membranes are 20 and 15 LMH, respectively. At 84°C the flux of the uncoated membrane is 43 LMH and the coated membrane is 42 LMH.

WBL was pre-filtered (Stage 1) using membrane ***e***. The 100 kDa filtrate was then used as the feed for Stage 2 concentration experiments to study the effects of the coating and temperature on low MWCO (i.e., 10 kDa) UF membranes. Figure 8.1.17 shows the Stage 2 average flux through membrane ***f***. With uncoated membranes, there is no significant increase in WBL filtrate flux when the temperature is increased to 84°C. For example, the average flux of the uncoated membrane at 22°C and 84°C is 4.4 and 4.7 LMH, respectively; the flux increases by 6% when the temperature is increased. On the other hand, the TSI coating increases the 10 kDa membrane flux by over 150% at room temperature and over 110% at 84°C. When compared to Stage 1, the Stage 2 flux indicates that the coating is more effective at mitigating membrane fouling at low MWCO (i.e., 10 kDa), which happens to be the region where WBL fouling significantly hinders the WBL concentration capabilities of multistage concentration. In the case of the larger MWCO (i.e., 100 kDa) membrane, the cake layer, which is formed by foulants that are present in WBL, is more dependent on the temperature and not as much on the coating.

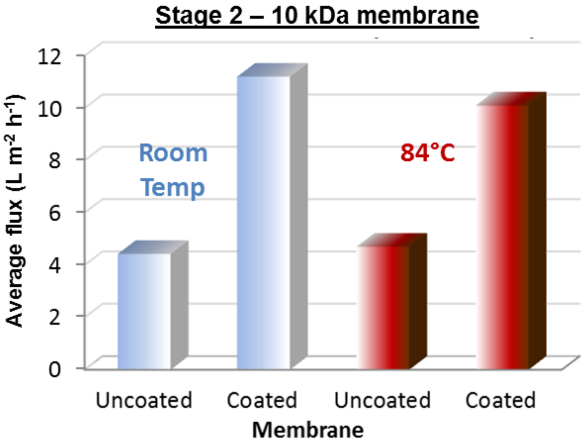


Figure 8.1.17 Stage 2 WBL filtrate flux through membrane *f* at 22°C (🟦) and 84°C (🟥) @ 60 psi using the 100 kDa Stage 1 filtrate

At 22°C the flux of the uncoated and coated membranes are 4.4 and 11.2 L m^{-2} h^{-1}, respectively. At 84°C the flux of the uncoated and coated membranes are 4.7 and 10.1 L m^{-2} h^{-1}.

Commercially available hollow fiber membrane modules (Figure 8.1.18) were integrated into the WBL flux analyzer (Figure 8.1.1) to study the effect of crossflow on membrane fouling. First, coated and uncoated MF membranes (***b***, Table 8.1) in the hollow fiber geometry were used to concentrate WBL at room temperature (Figure 8.1.19). Initially, the flux plateaued at approximately 7.7 LMH/bar and 7.3 LMH/bar with and without the coating, respectively. When the metering valve was closed, dead-end conditions maximized fouling conditions and the flux decreased rapidly to 3.3 LMH/bar and 3.7 LMH/bar with and without the coating, respectively. After increasing the crossflow rate to 90%, the flux of the uncoated membrane increased to 6.2 LMH/bar, which is only 85% of the flux prior to dead-end conditions. On the other hand, the coated membrane filtrate flux increases to 7.5 LMH/bar when crossflow resumes; the flux recovers to 97%. This indicates that even when exposed to dead-end conditions, the cake layer reduces the filtrate flux but our coating is preventing permanent fouling at the WBL/membrane interface.

Figure 8.1.18 Commercial hollow fiber membrane module
Design allows for easy integration into WBL flux analyzer. Crossflow is controlled using a metering valve (concentration side), while vertical ports are used to either collect filtrate or backflush.

Figure 8.1.19a shows the WBL filtrate flux of the coated hollow fiber membrane module at room temperature and at 84°C. At 90% crossflow, the average WBL flux is increased by more than 2.5 times when the temperature is increased to 84°C. However, at elevated temperature the membrane fouling was more problematic during dead-end filtration. For example, prior to dead-end filtration, the flux plateaus at 27.3 LMH/bar. When crossflow is resumed the flux recovers to 59% (16.0 LMH/bar). The data suggest that the cake layer could be penetrating and blocking pores of MF membranes, necessitating the need for backflushing.

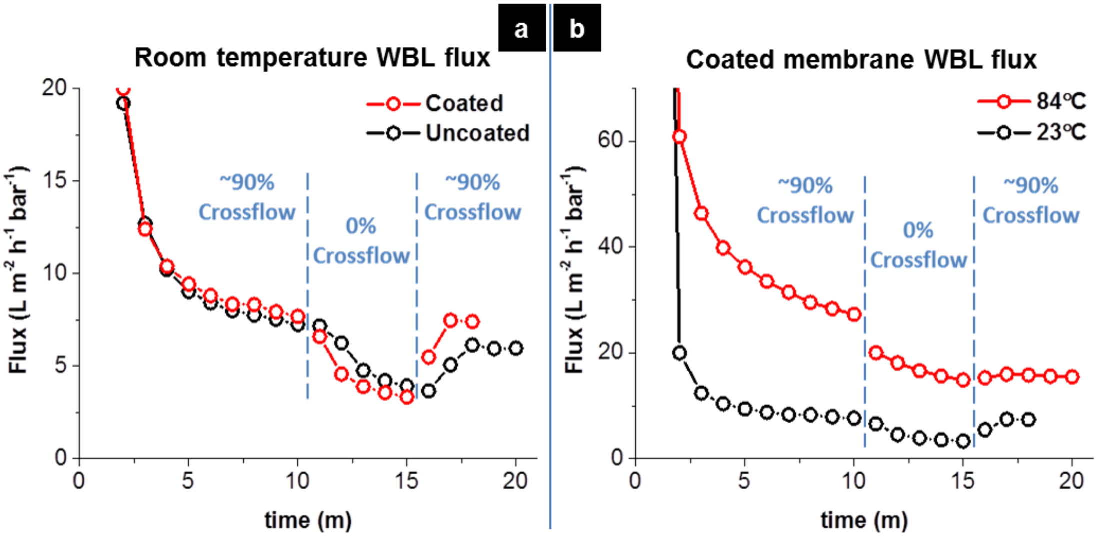


Figure 8.1.19 Filtrate flux of coated and uncoated membranes at room temperature (a) and coated membrane at low and high temperature (b) during crossflow filtration of WBL at a TMP of 10 psi

8.1.7. Characterization of weak black liquor and filtrate streams

Table 8.2 Performance of membranes used to concentrate WBL at room temperature

Membrane / Feed	Avg. Flux (L m^{-2} h^{-1} bar^{-1})	Filtrate TDS (wt%)
a - 0.2µm / **WBL**	28.1	12.8
e - 100k / **WBL**	10.3	10.7
f - 30k / **WBL**	4.5	11.4
g - 10k / **100 kDa filtrate**	1.1	8.7
g - 10k / **30 kDa filtrate**	1.4	9.0

Similar to the room temperature filtrates, TDS values (Figure 8.1.20) of the Stage 2 filtrate samples indicate that the lighter drop (Figure 8.1.21b, 100 kDa feed) contains less dissolved solids than the darker drop (Figure 8.1.21b, 30 kDa feed). At 84°C the TDS of all UF membrane filtrate samples increased slightly, presumably due to faster transport kinetics across the membrane. Nevertheless, the Stage 2 filtrate TDS at 84°C is well below the target TDS of 11% and the lack of pigment is evidence that the 10 kDa membrane is effective at separating organics and, thus, concentrating WBL (Table 8.3).

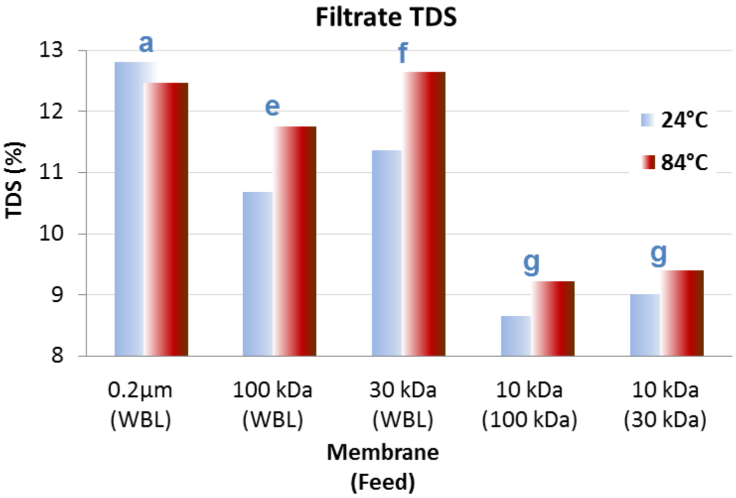


Figure 8.1.20 Total dissolved solids (TDS) of filtrates collected at 24°C (🟦) vs. 84°C (🟥)
a, 12.8% vs. 12.5%; ***e***, 10.7% vs. 11.8%; ***f***, 11.4% vs. 12.6%; ***g*** (100 kDa), 8.7% vs. 9.2%; ***g*** (30 kDa), 9.0% vs. 9.4%.
TMP: ***a***, 10 psi; ***e***, 30 psi; ***f-g***, 60 psi. Duration, 30 minutes.

One key advantage of our coating is the greater than twofold increase in flux observed with low MWCO UF membranes at high temperature. Another advantage is the lower filtrate TDS and total organic carbon (TOC) in the final stage (Table 8.4). When WBL was filtered using the coated 100 kDa Stage 1 membrane, the filtrate TDS was 0.5 wt% higher than that of the uncoated membrane at 84 °C. Flux data suggest that this is because the cake layer is the rate-determining layer at high MWCO and therefore, the flux should have minimal effect on filtrate flux. Yet, the Stage 2 filtrate from the coated membrane was 0.3 wt% lower than that from the

Table 8.3 10 kDa Stage 2 filtrate composition

Analysis	Concentration (%, dry solids basis)	ESM#
Sodium, Na	22.7	327B
Potassium, K	4.39	266B
Potassium carbonate, Na_2CO_3	14.0	132D
Sulfate as SO_4	4.15	074B
Thiosulfate as S_2O_3	7.01	223B
UV Lignin	16.8	162B
Methanol	0.61	105D
Sulfide, Na_2S	2.65	101B
Mercaptan, CH_3SH	1.44	101B
Arabinan, Xylan, Mannan	<0.1	310D
Galactan	0.2	310D
Glucan	0.2	310D
Acid insoluble materials	3.7	310D

uncoated membrane. Since flux data suggests that the UF active layer is the rate-determining layer in low MWCO membranes, the advantages of the coating are apparent; water permeability and dissolved solids rejection at the active layer are enhanced by the presence of the coating.

Attempts were made to further increase the purity of WBL filtrate streams using NF membranes. Previously we have shown that filtration of as-received WBL through NF membranes results in little to no flux (i.e., below detection limit of dead end filtration system) at transmembrane pressures up to 60 psi. When using a 20 kDa Stage 1membrane, the 20 kDa filtrate flux through the NF membrane was also unmeasurable up to 60 psi. Therefore, we investigated the effect of adding an additional stage, such that the MWCO for Stage 1, 2, and 3 was 20,000, 10,000, and 400 Da, respectively. However, the flux was still unmeasurable, indicating that NF membranes are not practical in the dead end system. Figure 8.1.21c shows the filtrate (or permeate) quality of the Stage 3 NF membrane at room temperature. In this

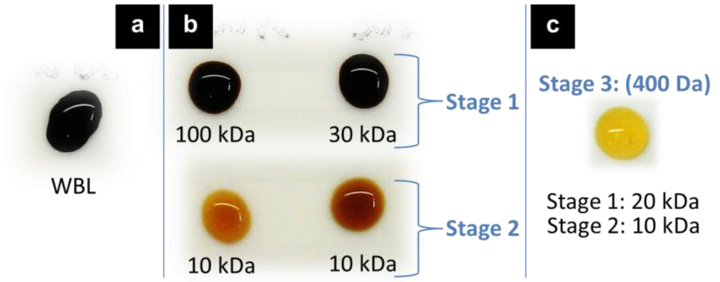


Figure 8.1.21 WBL droplets on a hydrophobic polymer substrate
(**a**) As-received WBL. (**b**) WBL filtered at 84°C. Stage 1 filtrates of 100 kDa and 30 kDa membranes appear dark, yet do not wet the substrate as much as the as-received WBL. Stage 2 filtrates of the 10 kDa membrane are much lighter in color, indicating effective separation of organic compounds from WBL.

case a three-stage dead end filtration system yielded a final permeate with a TOC concentration of 1.7%.

Table 8.4 Coated vs. uncoated membrane performance during multistage concentration of WBL

Membrane (Feed)	Avg. Flux (LMH bar^{-1})		Filtrate TDS		Filtrate TOC	
	22°C	84°C	22°C	84°C	22°C	84°C
e – 100 kDa (WBL)	9.5	20	10.7%	11.8%		
e – Coated 100 kDa (WBL)	7.5	21	11.6%	12.3%		
f – 10 kDa (100 kDa)	1.07	1.13	8.7%	9.2%	2.2%	2.4%
f – Coated 10 kDa (100 kDa)	2.70	2.44	8.2%	8.9%	2.1%	2.2%
h – NF (10 kDa)	~0.1				1.7%	

8.2. Large-scale laboratory membranes

8.2.1. Laboratory test bed development

A first generation room temperature WBL concentrator (R1 unit) capable of concentrating approximately 13 gallons of WBL was developed (Figure 8.2.1). Compatible filter units have surface areas ranging from 1000 cm^2 (>70X increase over the dead-end system) to 3.3 m^2 (>2300X increase) and pore sizes ranging from 0.2 µm to 3,000 Da MWCO. An untreated 1,000 cm^2 hollow fiber membrane module (Table 8.5, ***j***) was installed in the R1 unit and as-received WBL was concentrated at room temperature. Figure 8.2.2a shows the filtrate flux at a crossflow velocity of 2 m s^{-1}. The filtrate flux decreased over 5 hours of concentration. Figure 8.2.2b shows the filtrate flux with respect to filtrate recovery. Here we define the permeate recovery according to:

$$\%\,\mathrm{Recovery} = \frac{\Delta V}{V_i} \times 100 \tag{8.2}$$

where *ΔV* is the volume of filtrate (or permeate) collected and V_i is the initial feed volume. The filtrate flux decreases from an initial flux of 53 LMH/bar to 28 LMH/bar at about 81% recovery, at which the TMP reached a maximum of 14.2 psi.

Table 8.5 Specifications of membranes used for WBL concentration

Membrane	Type	MWCO	Area
j	UF – Hollow fiber, polymer	500 kDa	1,000 cm^2
k	UF – Hollow fiber, polymer	50 kDa	3,100 cm^2
l	UF – Hollow fiber, polymer	10 kDa	1,000 cm^2
m	UF – Tubular, ceramic	15 kDa	0.18-0.50 m^2
n	UF – Tubular, ceramic	1,000 Da	0.18-0.50 m^2
o	NF – Flat sheet, polymer	~700 Da	14-42 cm^2
p	NF – Spiral wound, polymer	~700 Da	0.6-6.4 m^2
q	NF – Flat sheet, polymer	~400 Da	14-42 cm^2
r	NF – Spiral wound, polymer	~400 Da	1.2-1.3 m^2

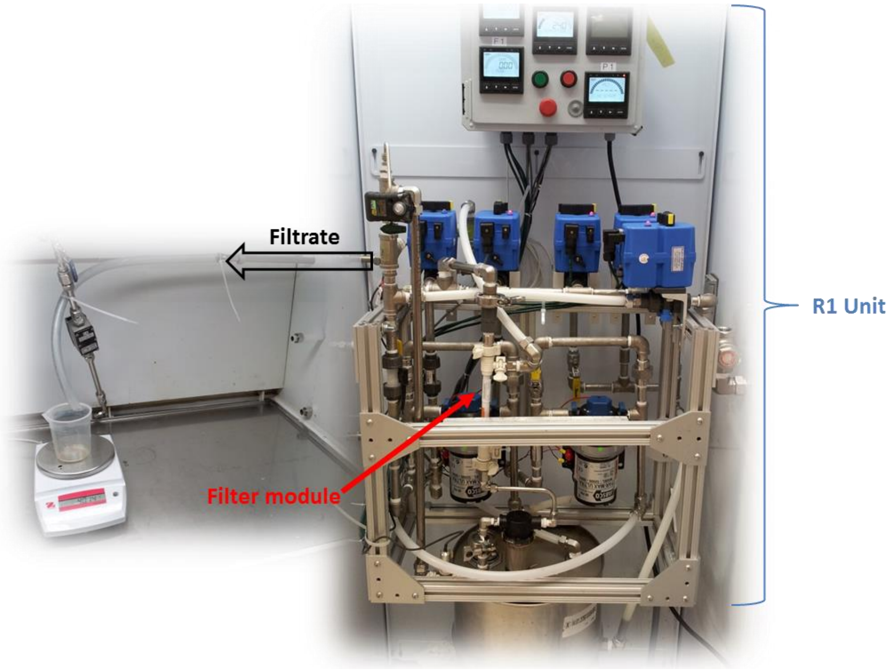


Figure 8.2.1 R1 pilot unit
The first generation room temperature (R1) WBL concentrator unit consists of a series of pumps, valves, and flow meters, all of which are controlled by a digital control box. The feed drum (below the unit) is filled with WBL and filtered through a membrane module at various crossflow velocities. The filtrate mass is measured and the flux is calculated based on the filtrate density and membrane area according to Equation 1.

Here the TMP is defined as:

$$TMP = \frac{(P_{in} + P_{out})}{2} - P_{perm} \tag{8.3}$$

where P_{in}, P_{out}, and P_{perm} are the pressure at the feed, reject, and permeate ports, respectively. It should be noted that the filtration was continuous (i.e., no backflushing or cleaning). With an initial feed volume of 5 gallons, this membrane module exhibited a recovery of 85%.

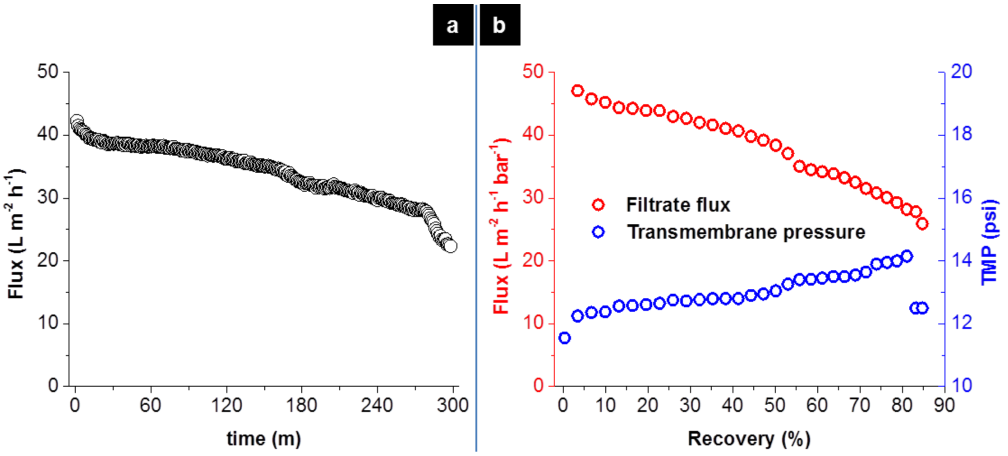


Figure 8.2.2 Room temperature flux vs. time (a) and flux (○) and TMP (○) vs. permeate recovery (b) plots for as-received WBL concentration using membrane *j*
Feed, 5 gal WBL; temperature, 28 °C; crossflow velocity, 2 m s^{-1}; unit, R1.

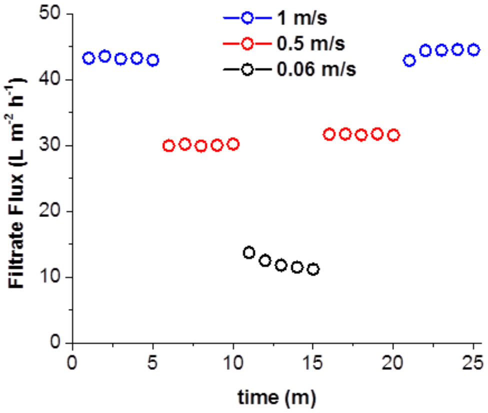


Figure 8.2.3 Influence of crossflow velocity on Stage 1 WBL flux at room temperature using membrane *j*
Feed, 5 gal WBL; TMP, 10.3 psi; temperature, 22°C; crossflow velocity sequence: 1.0 m s^{-1} (**○**), 0.5 m s^{-1} (**○**), 0.06 m s^{-1} (**○**), 0.5 m s^{-1} (**○**), and 1.0 m s^{-1} (**○**); unit. R1.

In order to understand the effect of crossflow on cake layer fouling, the crossflow velocity was varied while maintaining a constant TMP. Figure 8.2.3 shows the filtrate flux of as-received WBL through membrane ***j*** at room temperature. An increase in fouling is apparent when the crossflow velocity decreases. For example the flux decreased from 43 LMH to 30 LMH (30% decrease) when the crossflow velocity was reduced from 1.0 m s^{-1} to 0.5 m s^{-1}. At a crossflow velocity of 0.06 m s^{-1}, the filtrate flux dropped to ~11 LMH, which is a 63% decrease from that at 0.5 m s^{-1}. Also, at 0.06 m s^{-1} the flux appears to be steadily decreasing with time, which is indicative of a growing fouling layer. However, the fact that the flux recovers at velocities ≥0.5 m s^{-1} is a demonstration of effective cake layer removal using crossflow.

10 gallons of WBL was concentrated using membrane ***k***. At a feed temperature of 28 °C and a TMP of 13 psi the filtrate flux is approximately 2.1 LMH at 1.0 m s^{-1} and does not change as the crossflow velocity is varied (Figure 8.2.4a). Figure 8.2.4b shows the filtrate flux versus recovery

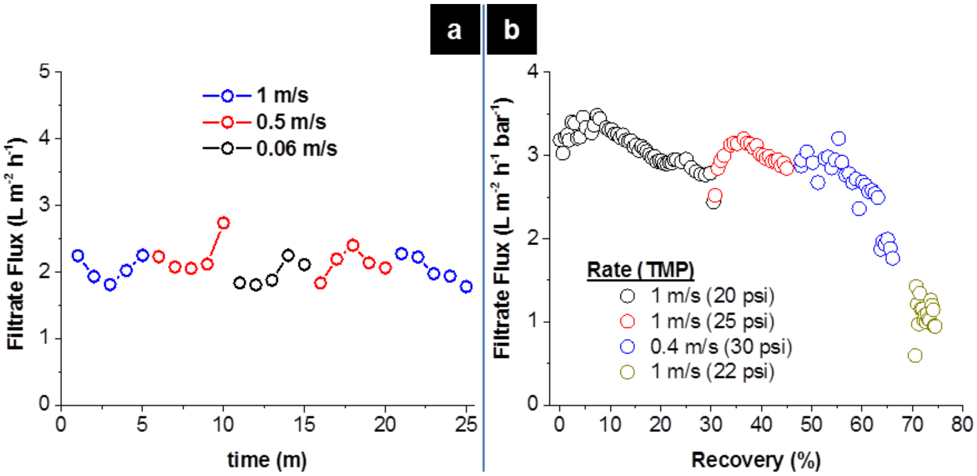


Figure 8.2.4 Stage 1 WBL flux vs. time (a) and flux vs. permeate recovery (b) plots at room temperature using membrane *k*
(**a**) TMP, 13 psi; crossflow velocity: 1.0 m s^{-1} (**○**), 0.5 m s^{-1} (**○**), and 0.06 m s^{-1} (**○**). (**b**) Crossflow velocity / TMP: 1.0 m s^{-1} / 20 psi (**○**), 1 m s^{-1} / 25 psi (**○**), 0.4 m s^{-1} / 30 psi (**○**), and 1 m s^{-1} / 22 psi (**○**). Feed, 10.5 gal WBL; temperature, 28 °C; unit, R1.

at 28°C. With increasing recovery, fouling is apparent in the flux decay at each crossflow velocity. For example, at 1 m s^{-1} and a TMP of 20 psi (○) the flux steadily decreases from a maximum of 3.5 LMH/bar at 7% recovery to about 2.4 LMH/bar at 30% recovery. When the crossflow velocity is unchanged and the TMP is increased to 25 psi (○) the flux increases suddenly to 3.1 LMH/bar at 34% and then decreases steadily to 2.8 LMH/bar at 45% recovery. As the crossflow is decreased to 0.4 m s^{-1} (○) the flux increases to 3.0 LMH/bar at 51%, then decreases steadily to 2.5 LMH/bar at 63%, and decreases abruptly to 1.8 LMH/bar at 66% recovery. Although the crossflow velocity is increased to 1 m s^{-1} (○), the flux decreases to less than 1.0 LMH/bar at 75% recovery. Although the data suggests that the flux may be membrane controlled, another possibility is that removal of the cake layer requires crossflow velocities greater than 1 m s^{-1}.

Compared to the loose UF hollow fiber membrane, ***j***, the tight membrane, ***k***, was more effective at concentrating WBL at lower recovery (Figure 8.2.5). For example, the reject TDS of membrane ***k*** at 50% recovery is very close to that of membrane ***j*** at 85% recovery. However, the filtrate purity of membrane ***k*** decreases with increasing recovery. One interesting observation is that the increase in filtrate TDS appears to coincide with the sudden slope decrease in Figure 8.2.4b. The increase in foulant concentration appears to be contributing to the sudden increase in filtrate TDS. Therefore, the concentration of WBL process should probably be limited to somewhere between 60-70% recovery for membrane ***k*** at low temperature.

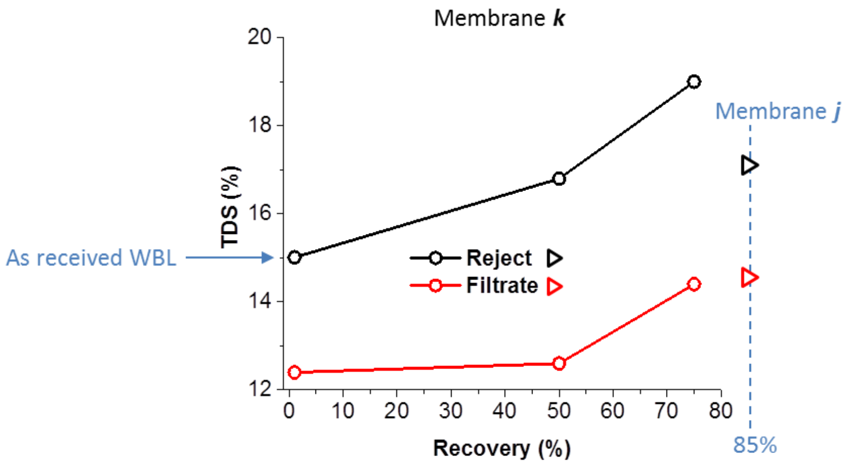


Figure 8.2.5 Stage 1 TDS versus recovery at 28 °C

When WBL is concentrated using membrane ***k***, the TDS of the reject (○) increases steadily from 15.0% to 16.8% (at 50% recovery) and increases abruptly to 19.0% (at 75% recovery). Similarly, the filtrate TDS (○) increases from 12.4% to 12.6% (at 50% recovery) to 14.4% (at 75% recovery). The reject (▷) and filtrate (▷) using membrane ***j*** are 17.1% and 14.6% TDS, respectively, at 85% recovery. Unit, R1.

After Stage 1 filtration of WBL using membrane ***k***, Stage 2 filtration was performed using membrane ***l*** and 5 gallons of Stage 1 filtrate as the feed. Figure 8.2.6 shows the Stage 2 flux at various crossflow velocities at 28°C using. Similar to the Stage 1 process, the flux does not appear to be affected by crossflow velocities from 0.02 m s^{-1} (○) to 1 m s^{-1} (○). Therefore, the flux at low temperature is either membrane-controlled or removal of the cake layer requires crossflow velocities greater than 1 m s^{-1}.

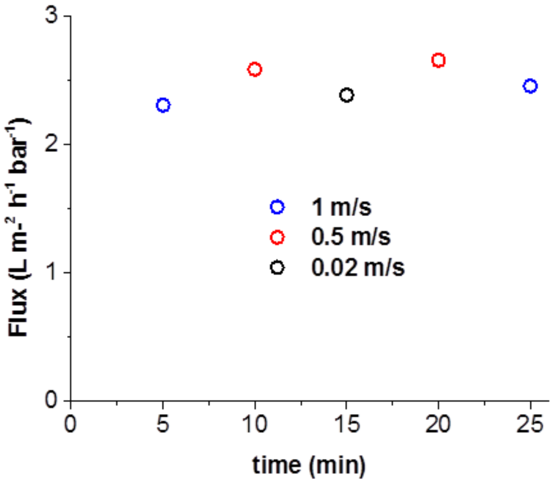


Figure 8.2.6 Influence of crossflow velocity on Stage 2 flux at room temperature using membrane *I*
The filtrate flux at a crossflow velocity of 1 m s^{-1} (○), 0.5 m s^{-1} (○), and 0.02 m s^{-1} (○) is 2.3, 2.6, 2.4, 2.7, and 2.5 LMH bar^{-1} at 5, 10, 15, 20, and 25 minutes, respectively. Feed, 5 gal 50 kDa filtrate; temperature, 28°C; TMP, 27.6 psi; unit, R1.

Figure 8.2.7 shows the influence of crossflow on filtrate TDS. In general, crossflow filtration yields filtrate samples with higher TDS values than dead-end filtration. For example, the Stage 1 filtrate of a WBL feed that is filtered using a 50 kDa hollow fiber membrane has a TDS content of 12.4%. When 5 gallons of 50 kDa filtrate is added to the feed drum and a 10 kDa hollow fiber membrane is used, the Stage 2 filtrate TDS decreases to 11.7%. However, with dead-end filtration, Stage 2 filtrate TDS is 8.7% and 9.0% when using 100 kDa and 30 kDa Stage 1 filtrate as the feed, respectively. The lower TDS in the case of dead-end filtration indicates that the cake layer contributes to the separation process at low temperature.

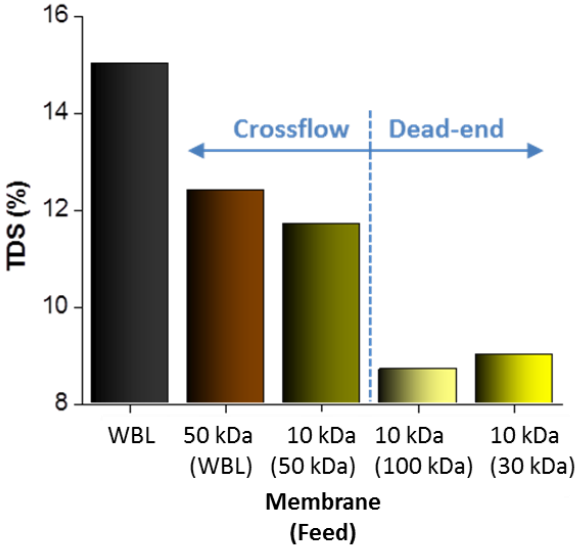


Figure 8.2.7 TDS of filtrate samples from crossflow compared to dead-end filtration at room temperature
TDS of WBL feed is 15.0%. Crossflow filtration of WBL (through 50 kDa Stage 1 hollow fiber membrane) and 50 kDa filtrate (through 10 kDa Stage 2 hollow fiber membrane) yields filtrate streams with 12.4% and 11.7% TDS, respectively. Stage 2 dead-end filtration of 100 kDa and 30 kDa filtrate streams through 10 kDa flat sheet membranes yields TDS of 8.7% and 9.0%, respectively.

Table 8.6 Uncoated membrane *k* performance at 1 m s^{-1} crossflow velocity

Temperature	Transmembrane Pressure (TMP)	Average Flux (LMH)	(LMH·bar^{-1})
28°C	13 psi	2.1	2.3
60°C	**21 psi**	**11.8**	**7.9**

The R1 pilot unit was retrofitted with an inline heater to increase the temperature of the WBL feed to 60°C. At a TMP of 21 psi, the Stage 1 filtrate flux at 60°C is 7.9 LMH/bar. One apparent benefit of a higher temperature feed is the increase in flux (Table 8.6). When the temperature is increased by 32°C the flux increases by 5.6 LMH bar^{-1}. The >240% increase in flux is partially caused by the decrease in pressure drop across the membrane module, *ΔP*, which is represented by equation 8.2:

$$\Delta P = P_{in} - P_{out} \qquad (8.4)$$

where P_{in} and P_{out} are the inlet and outlet (reject) pressures, respectively. As a result, the TMP is higher and the driving force for filtration is distributed more uniformly across the entire membrane. For example, at a crossflow velocity of 1 m s^{-1}, *ΔP* for this membrane is about 13 psi at 28°C compared to about 7.5 psi at 60°C.

WBL was heated to 70°C and the filtrate flux through the 50 kDa membrane was measured as the temperature was decreased to 60°C (Figure 8.2.8). Within the 10 degree window, flux (○) is exponentially dependent on temperature (▷). The model predicts flux values close to 30 LMH/bar at 95°C. Given that polymer membranes typically operate at a TMP of about 2 bar, the model predicts a Stage 1 filtrate flux of around 60 LMH.

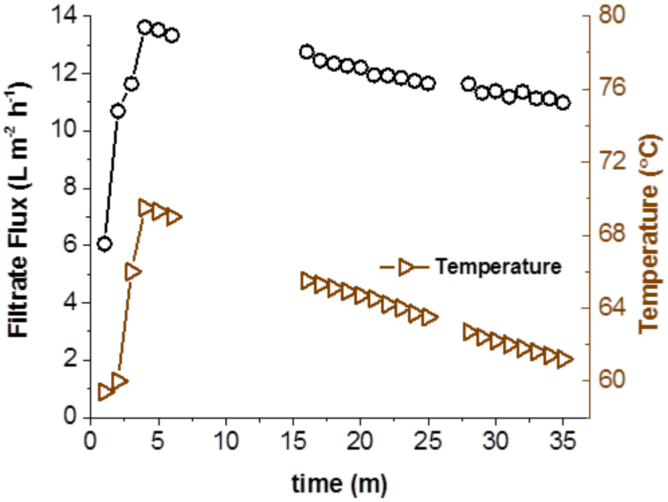


Figure 8.2.8 Stage 1 WBL flux and temperature plots at elevated temperature using membrane *k*
Feed, 10 gal WBL; crossover velocity, 0.5 m s^{-1}; TMP, 18 psi; unit, R1.

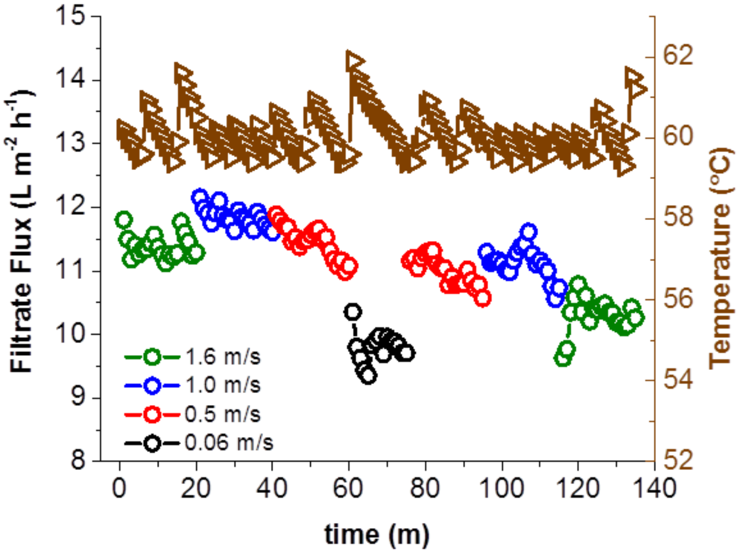


Figure 8.2.9 Influence of crossflow velocity on Stage 1 WBL flux at elevated temperature using membrane *k*
At crossflow velocities of 1.6 m s^{-1} (○), 1.0 m s^{-1} (○), and 0.5 m s^{-1} (○) the flux appears to be steady at about 11.5 LMH. At 0.06 m s^{-1} (○) the flux decreases to below 10 LMH. The filtrate flux recovers when sufficient crossflow velocities are reintroduced. Feed, 10 gal WBL; TMP, 21 psi.

To characterize the fouling mechanism at elevated temperature, WBL was heated to 60°C and the crossflow velocity was varied while the TMP was maintained at 21 psi. It can be seen in Figure 8.2.9 that between of 1.6 m s^{-1} (○) and 0.5 m s^{-1} (○) the WBL filtrate flux seems more dependent on the temperature (▷) fluctuations rather than on crossflow velocity. However, when the crossflow velocity is decreased to 0.06 m s^{-1} (○) there is a sudden drop in flux. The

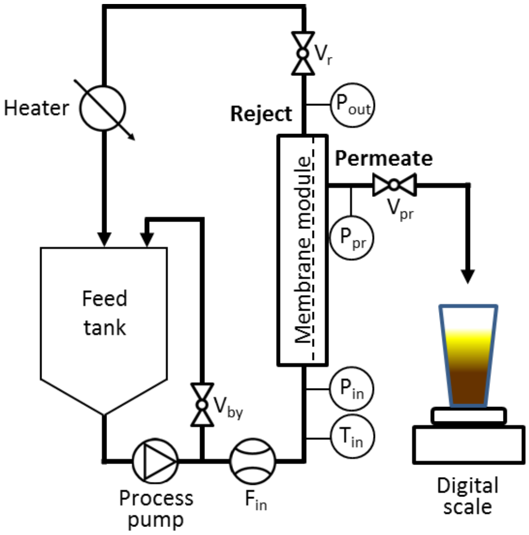


Figure 8.2.10 Schematic of R2 pilot unit
This system consists of high temperature, WBL-resistant materials. The filtrate mass is measured and the flux is calculated based on the filtrate density and membrane area according to Equation 1. F_{in}, inlet flow meter; T_{in}, inlet temperature transducer; P_{in}, inlet pressure transducer; P_{out}, outlet pressure transducer; P_{pr}, permeate (or filtrate) pressure transducer; V_{by}, bypass valve; V_r, reject valve; V_{pr}, permeate (or filtrate) valve.

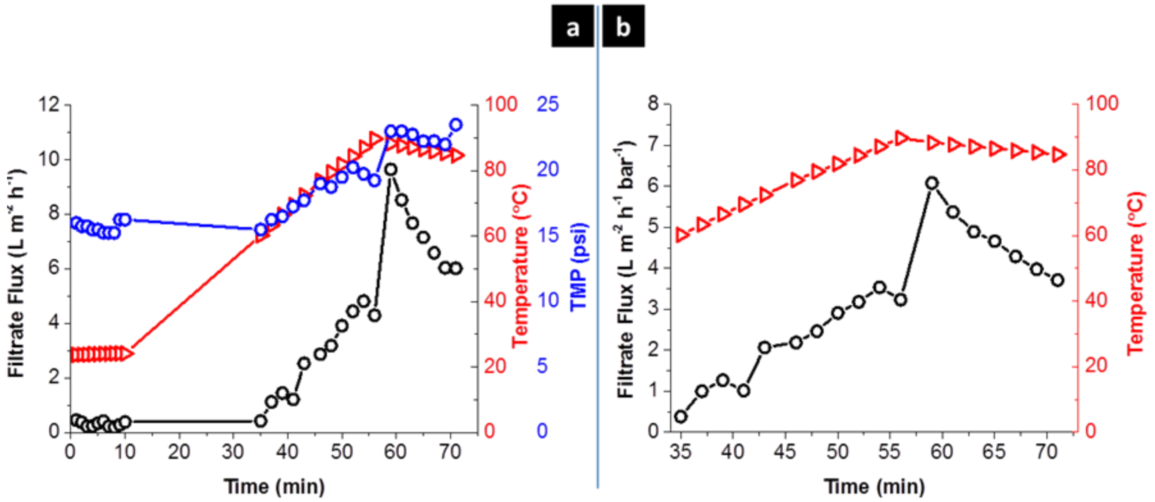


Figure 8.2.11 Stage 1 WBL flux (a) and pressure-normalized flux (b) at elevated temperature using *l*
Feed, 10 gal WBL; crossflow velocity, 1 m s^{-1}; unit, R2.

immediate increase in flux when the crossflow is increased to 0.5 m s^{-1} indicates that the cake layer is formed and removed between crossflow velocities of 0.5 m s^{-1} and 0.06 m s^{-1}. Since this crossflow dependence is not observed with the same membrane at room temperature, it is implied that the increase in thermal energy decreases the cohesive forces within the cake layer. Therefore, cake layer removal should be enhanced further upon deposition of our antifouling coating, which will minimize foulant adhesion to the membrane surface.

An upgraded crossflow filtration system (R2), capable of concentrating WBL at 85 °C, was built mainly out of 316 stainless steel, PTFE, and ethylene propylene diene monomer rubber (EPDM) parts (Figure 8.2.10). While maximum flow is determined by the pump, flow and TMP are fine-tuned using diverging (V_{by}) and restriction (V_r) valves. WBL was added to the feed tank and membrane ***l*** was used to concentrate WBL at temperatures greater than 80°C. Figure 8.2.11a shows the Stage 1 filtrate flux of as-received WBL through membrane ***l***. Initially, the filtrate flux (○) is approximately 0.31 LMH when the temperature (▷) and TMP (○) are 24°C and 16 psi, respectively. When the temperature is increased to 90°C the filtrate flux increases to 9.6 LMH. However, the TMP also increases from 16 psi to 23 psi. It can be seen in Figure 8.2.11b that when the temperature increases from 60°C to 90°C, the filtrate flux increases from 0.4 to 6.1 LMH/bar. This clearly shows that filtrate flux has a strong dependence on the WBL feed temperature.

Membrane ***m*** was used to concentrate WBL at 85 °C (Figure 8.2.12). At a TMP of 34 psi, the permeate flux is 34 LMH/bar at a crossflow velocity of 3.5 m s^{-1}. The filtrate flux continues to decrease as the crossflow is decreased to a minimum of 8 LMH/bar at 0.3 m s^{-1}, which was the lowest crossflow velocity tested. This dependence of permeate flux on crossflow velocity with the 15 kDa ceramic membrane is indicative of cake layer fouling. Cake layer removal is apparent in the filtrate flux increase when the crossflow velocity is increased to 3.5 m s^{-1} at *t* = 52 minutes. It should be noted that the sudden decrease in permeate flux at *t* = 56 minutes was due to a drop in TMP and is not be attributed to membrane fouling. The total dissolved solids (TDS) of the filtrate was approximately 13%. This value is larger than the TDS of

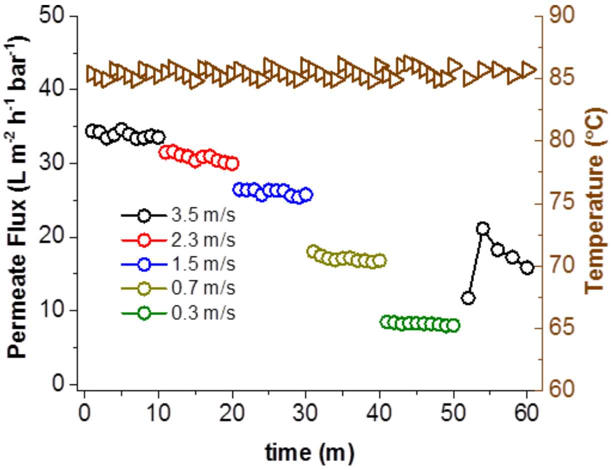


Figure 8.2.12 Influence of crossflow velocity on Stage 1 WBL flux at elevated temperature using membrane *m*
Feed, 10 gal WBL; temperature (▷), 85 °C; TMP, 34 psi; membrane area, 0.18 m^2; unit, R2.

permeate samples from dead end experiments (i.e., 11.8% with membrane ***e***), presumably due to the decrease in cake layer thickness with crossflow. This means that for scale-up, membranes with slightly lower MWCO are required.

Stage 1 permeate was added to the feed tank and concentrated at ~85 °C using membrane ***n*** (Figure 8.2.13). There is no abrupt decrease in permeate flux as the crossflow velocity is incrementally decreased from 3.6 to 0.4 m s^{-1}, implying that the flux is a membrane-controlled process. Rather, a steady decrease in permeate flux at a rate of 0.5 LMH h^{-1} is observed with time due to membrane fouling. The TDS content of the permeate samples are approximately 10%.

Stage 2 permeate was added to the feed tank of a separate NF system and membrane ***r*** was used to purify the feed at room temperature. The NF unit was constructed similarly to the R2 unit (Figure 8.2.10). At a TMP of 200 psi, membrane ***r*** exhibits a permeate flux of about

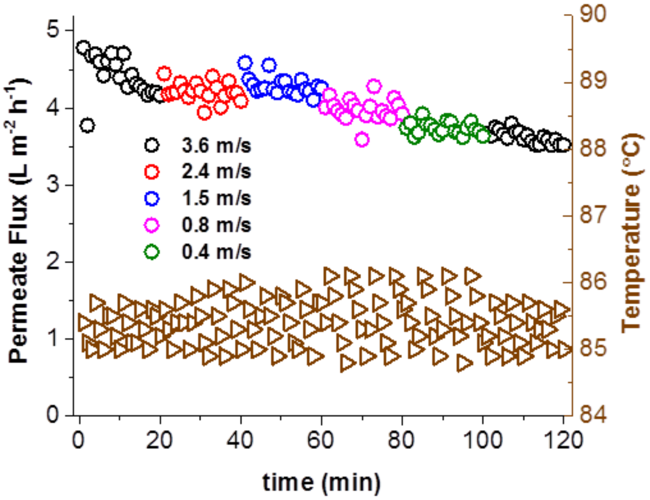


Figure 8.2.13 Influence of crossflow velocity on Stage 2 flux at elevated temperature using membrane *n*
Feed, 10 gal 15 kDa filtrate; temperature (▷), 85 °C; TMP, 33 psi; membrane area, 0.18 m^2; unit, R2.

Figure 8.2.14 Photograph of NF permeate and condensate (from pulp and paper mill evaporator)

1.2 LMH at room temperature. Figure 8.2.14 shows a photo comparing the NF permeate to the condensate collected from the second evaporator. The NF permeate appears to be somewhat lighter in color. However, the TOC concentration is 1.3%, which is about 20 times higher than that of the condensate. Similarly, the sulfate concentration of the NF permeate is 410 mg L^{-1}, which is 13 times higher.

8.2.2. Design tools and coating optimization

Design tools for optimal application of coating materials and process have been developed and a document comprised of proprietary information, not included herein, has been created for the DOE. Briefly, experiments consisting of coating time, coating temperature, degree of coating removal, coating waste, and coating pressure/flow were designed for coating optimization. In the optimized coating process, the coating time needs to be as short as possible to minimize any downtime that would result in decreased paper production. Experiments in minimizing coating time involve varying the coating time, chemical composition, viscosity, and degree of polymerization and measuring the DI water flux, WBL permeate flux, and determining the coating stability and antifouling properties with decreasing coating time.

Coating temperature is the second parameter. Since the membranes will be surrounded by several heat sources, determining whether the high temperature environment affects the coating process is important. Coating temperature experiments involve heating and/or cooling the coating precursors prior to deposition and measuring DI and WBL flux to determine any variability in performance with changing temperatures.

Degree of coating removal is the third parameter. In this report we have shown that the Teledyne coating 1) has been modified for WBL concentration, 2) can be stripped, and 3) can be recoated. However, given that the coating has excellent antifouling properties, it is possible that the coating does not have to be completely stripped. Perhaps the coating could be partially stripped a few times before complete stripping and recoating. This would decrease the maintenance time by allowing the membrane to concentrate WBL for longer periods of time before the recoating process. Determining whether complete stripping is necessary for membrane preservation involves experiments in which the coating is stripped for a given time and the DI and WBL flux are measured.

Minimize coating waste is the fourth parameter. These experiments consist of decreasing the coating solution volumes and measuring the resulting effect on DI water flux and WBL permeate flux to determine coating stability and antifouling properties.

Coating pressure is the fifth parameter. Experiments to determine the resulting effect of coating pressure and flow involve increasing the coating pressure and flow (separately) and measuring the DI water flux and WBL permeate flux to determine the coating stability and antifouling properties.

8.2.3. Membrane characterization

Figure 8.2.15a shows the WBL permeate flux of membrane ***n*** coated with our Stage 1 antifouling coating, G1$_{\mathrm{N}}$, (membrane ***n***-G1$_{\mathrm{N}}$) using the R2 unit. 10 gallons of WBL was heated to 85 °C before filtering at a TMP of 40 psi. There is an apparent dependence of crossflow velocity on flux. At high crossflow velocity (4.4 m s^{-1}) the flux is lower than expected. The flux peaks between 1.9-2.9 m s^{-1} before decreasing with decreasing crossflow. It turns out that ΔP increases significantly above about 3 m s^{-1} (Figure 8.2.15b). For example, ΔP increases from 12 to 21 psi when crossflow is increased from 2.9 to 4.4 m s^{-1}. However, when the crossflow velocity is increased after 120 minutes, the permeate flux increases, indicating that the flux is cake layer limited when ***n***-G1$_{\mathrm{N}}$ is used for Stage 1 WBL concentration.

When continuously filtering (i.e., without backflushing) as-received WBL using the G1$_{\mathrm{N}}$-coated membrane ***n***, the permeate flux decreases from 7.2 L m^{-2} h^{-1} (t = 2.5 h) to 4.0 L m^{-2} h^{-1} (t = 19 h) at ~60 psi (Figure 8.2.16a). The 44% drop in flux is ascribed to continuous cake layer formation at high feed volume reduction. The TOC, lignin, sulfate, and methanol concentrations in the permeate are 18000, 1500, 2500 and 870 mg L^{-1}, respectively. For comparison, the uncoated membrane flux decreases from 9.6 L m^{-2} h^{-1} (t = 4.5 h) to 4.4 L m^{-2} h^{-1} (t = 20 h) at ~60 psi (Figure 8.2.16b), which corresponds to a 54% drop over a shorter period of time. It should be noted that the uncoated membrane was used as a Stage 2 membrane; the feed was less fouling since

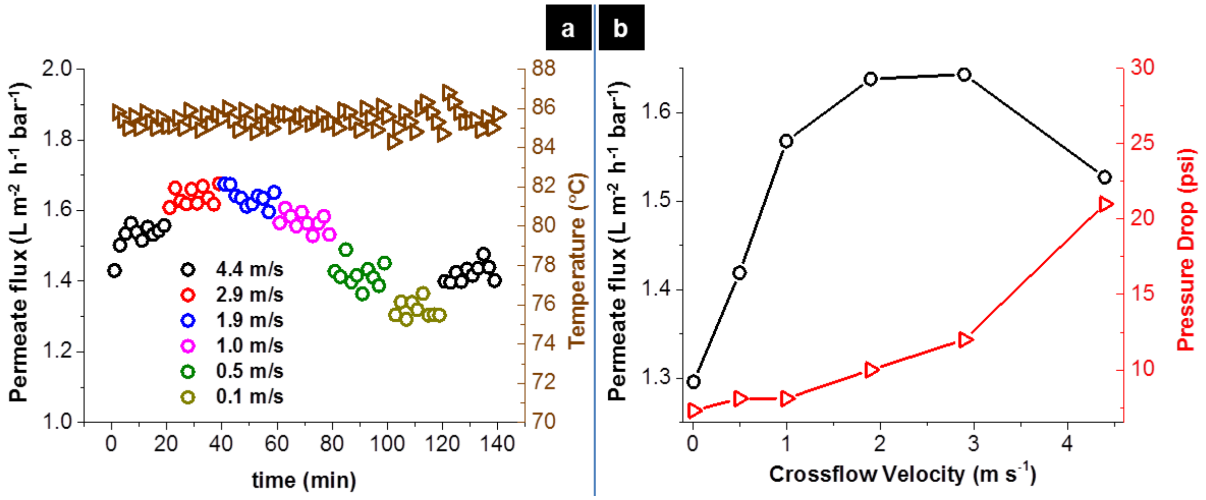


Figure 8.2.15 Influence of crossflow velocity on Stage 1 WBL flux (a) and pressure drop (b) at elevated temperature using G1$_{\mathrm{N}}$-coated membrane *n* (*n*-G1$_{\mathrm{N}}$)

Feed, 10 gal WBL; TMP, 40 psi; membrane area, 0.25 m^2; unit, R2.

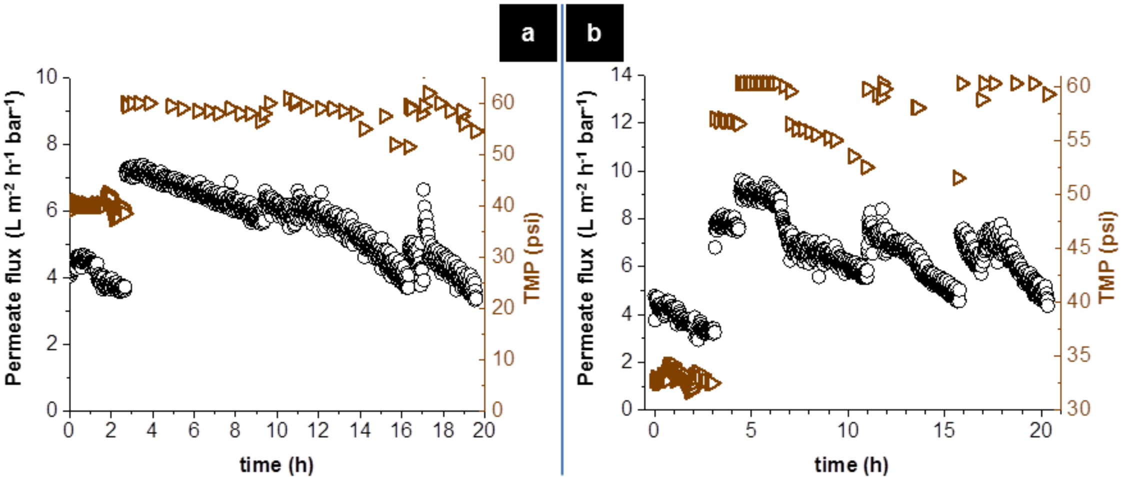


Figure 8.2.16 WBL flux (○) and TMP (▷) vs. time plots for membrane *n* at 85 °C using R2 unit
(**a**) Stage 1 performance of ***n***-G1$_N$ using 10 gal WBL as feed. (**b**) Stage 2 performance of uncoated membrane ***n*** using 10 gal 15 kDa WBL filtrate as feed.

it was first filtered with membrane ***m***. However, the TOC of the Stage 2 permeate using the uncoated membrane was 23,000 mg L^{-1}.

After WBL concentration, membrane ***n***-G1$_N$ was rinsed with DI water and installed in a water flux analyzer. The deionized water flux was 6.9 LMH/bar after WBL concentration (Figure 8.2.17). Since the R2 unit was incapable of backflushing, the coated membrane was installed in a separate system and backflushing was carried out at 80 psi for 10 minutes using a 0.1 M NaOH solution heated to 85 °C. After slowly cooling the membrane to room temperature it was rinsed with DI water and the water flux was measured. After backflushing, the water flux increased to 18 LMH/bar. Since the NaOH solution is similar in pH to the WBL permeate, these results indicate that foulant removal from the coated membrane surface is expected during automated backflushing.

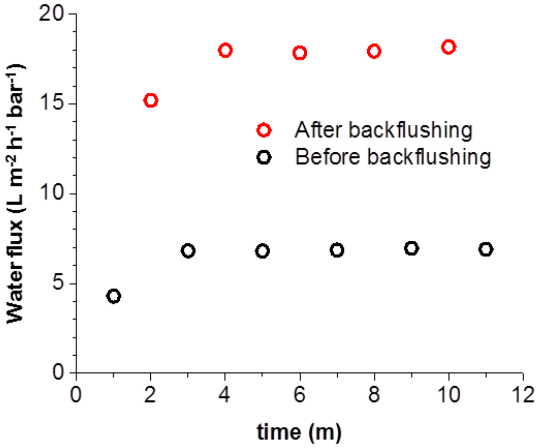


Figure 8.2.17 Water permeate flux of membrane n-G1$_N$ after WBL concentration (○) and after backflushing (○)
Feed, 8 gal DI water; TMP, 30 (±1) psi; temperature, 21 °C; crossflow velocity 1.1 m s^{-1}.

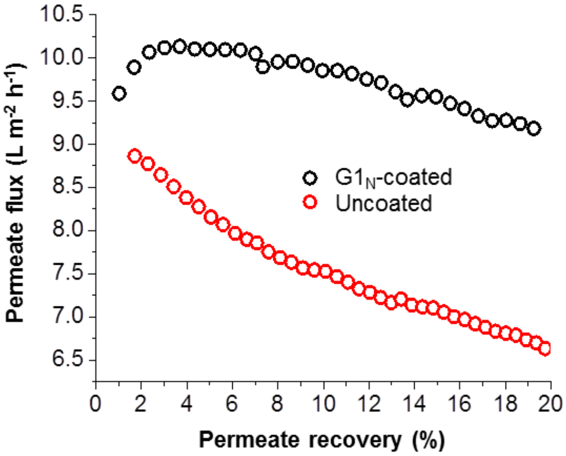


Figure 8.2.18 Stage 1 WBL flux vs. recovery plots for coated (○) and uncoated (○) membrane *n*
Feed, 10 gal WBL; temperature, 85 °C; TMP, 60 psi; crossflow velocity, 3.0 m s^{-1}; membrane area 0.50 m^2; unit, R2.

Our coating was deposited on membrane ***n*** to demonstrate the coating's ability to withstand fouling during WBL concentration. 10 gallons of WBL was added to the feed drum and heated to 85 °C before concentrating the WBL. To avoid any variations in the cake layer, TMP and crossflow velocity were held constant at 60 psi and 3 m s^{-1}, respectively, to minimize any contributions to the permeate flux. Figure 8.2.18 shows the WBL permeate flux of membrane ***n*** with (○) and without (○) the G1$_N$ coating. It can be seen that the uncoated membrane fouls quickly, dropping to 90% at a permeate recovery of 6% (i.e., from a peak flux of 8.9 LMH to 8.0 LMH at 6% recovery). In other words, the permeate flux of the uncoated membrane decreases by 10% after collecting only 0.6 gallons of WBL permeate. On the other hand, the coated membrane exhibits ~1% drop in permeate flux at 6% permeate recovery (i.e., from a peak flux of 10.13 LMH to 10.09 LMH at 6% recovery). The coated membrane is able to produce a permeate recovery of 20% before the flux decreases to 90%.

Figure 8.2.19 shows the WBL permeate flux using the uncoated (**a**-**b**) and coated (**c**-**d**) membrane. After concentrating 10 gallons of WBL to 8 gallons (Run 1), the membranes were removed from the R2 unit and installed in a cleaning station capable of backflushing (Figure 8.2.20). It should be noted that we slowly cooled and heated all solutions during each experiment, i.e., when transferring membranes between systems, to avoid damaging the membranes. Backflushing was carried out in the backflushing system using WBL permeate, heated to 85 °C, at 80 psi for 80 seconds according to the sequences listed in Figure 8.2.20. Fresh WBL was added to the feed tank of the R2 unit after each run. Membrane cleaning was carried out in the cleaning station according the parameters listed in Table 8.7.

Figure 8.2.19a shows the WBL flux for the uncoated membrane (○) after backflushing with WBL permeate (Run 2). Irreversible fouling of the uncoated membrane during WBL concentration is apparent; the initial WBL flux after backflushing is nearly half the initial flux during Run 1. In other words, backflushing is insufficient at removing WBL foulants deposited on uncoated membranes surfaces. After the permeate flux decreased to 4.4 LMH at a permeate recovery of 52%, the membranes were backflushed with WBL permeate at 85 °C. After backflushing, the remaining 4.8 gallons of WBL was concentrated and the permeate flux increased to 5.9 LMH. The fact that the permeate flux is lower than the initial Run 2 flux suggests that the membranes

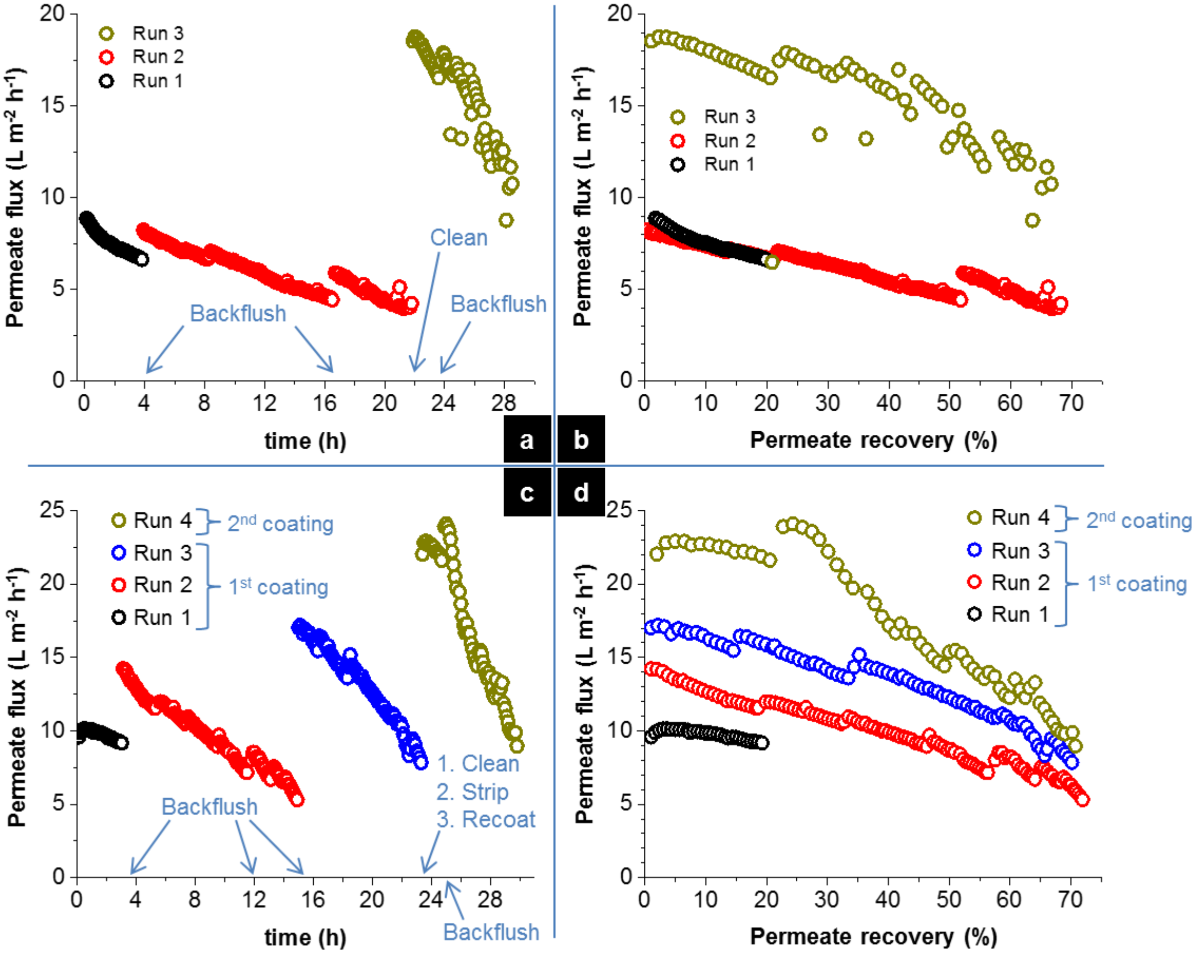
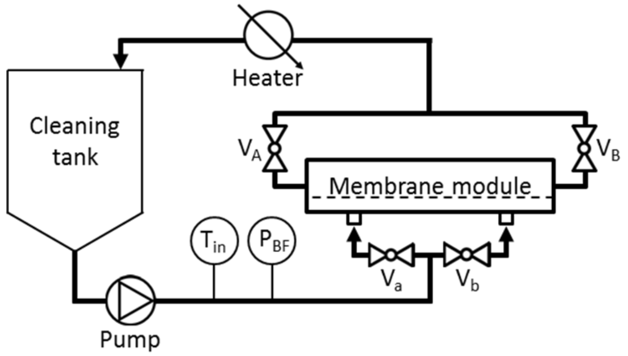


Figure 8.2.19 Stage 1 performance at 85 °C, TMP of 60 psi, and crossflow velocity of 3.0 m s^{-1} using uncoated (a,b) and $G1_N$-coated (c,d) membrane *n*

(**a**-**b**) Two 0.25 m^2 membranes were installed in the R2 unit in parallel, providing a total membrane area of 0.5 m^2. Run 1 (○), 10 gal WBL is concentrated to 20% recovery before backflushing with WBL permeate. Run 2 (○), 10 gal WBL concentrated to 52% recovery, backflushed, and concentrated to 68% recovery. Membrane ***n*** is chemically cleaned. Run 3 (○), 10 gal WBL is concentrated to 21% recovery, backflushed, and concentrated to 70% recovery after chemical cleaning. (**c**-**d**) Two 0.25 m^2 membranes were coated with $G1_N$ and installed in the R2 unit in parallel, providing a total membrane area of 0.5 m^2. Run 1 (○), 10 gal WBL is concentrated to 20% recovery before backflushing. Run 2 (○), 10 gal WBL is concentrated to 56% recovery, backflushed, and concentrated to 72% recovery before backflushing. Run 3 (○), 10 gal WBL is concentrated to 70% recovery. $G1_N^1$-coated membrane is cleaned, stripped, and recoated. $G1_N^2$ Run 1 (○), 10 gal WBL is concentrated to 20% recovery, backflushed, and concentrated to 71% recovery after cleaning/stripping $G1_N^1$ and recoating with $G1_N^2$.

can withstand the temperature fluctuations and process conditions of WBL concentration, since any damage that might have occurred would most likely exist in the form of cracks that would quickly propagate during heating/cooling and filtration/backflushing cycles. The permeate flux then decreases to 4.0 L m^{-2} h^{-1} at 68% recovery. After Run 2, the membranes were transferred to the backflushing station for chemical cleaning.

After chemical cleaning, the initial permeate flux is 18.8 LMH, which is much higher than the initial flux during Run 1 (Figure 8.2.19a). It turns out that there is a protective coating applied by the manufacturer that is removed during the cleaning process. The manufacturer coating is



Short backflush sequence
aA: V_a and V_A open, V_b and V_B closed, 20 sec
bB: V_b and V_B open, V_a and V_A closed, 20 sec

Long backflush sequence
aB: V_a and V_B open, V_b and V_A closed, 20 sec
bA: V_b and V_A open, V_a and V_B closed, 20 sec

Figure 8.2.20 Schematic of backflush/cleaning station
Wetted parts of this system are 316 stainless steel, PTFE, and EPDM. T_{in}, inlet temperature transducer; P_{BF}, backflush pressure transducer; V_a, permeate valve **a**; V_b, permeate valve **b**; V_A, filtration feed valve; V_B, filtration reject valve.

not antifouling in nature, so its absence does not hinder performance. The permeate flux decreases to 16.5 LMH after concentrating the WBL to 8 gallons (Figure 8.2.19b). After backflushing with WBL permeate at 24 hours (20% recovery), the flux only increases to 17.3 LMH, which implies that membrane ***n*** withstands WBL concentration, temperature fluctuations, and the cleaning/stripping protocol, since the permeate flux is lower than the initial flux.

Figure 8.2.19c shows the performance of our $G1_N$ coating on membrane ***n*** with respect to time (**c**) and recovery (**d**). The permeate flux is 14% higher than that of the uncoated membrane (Run 1) and decreases from an initial 10.1 LMH to 9.2 LMH at 20% permeate recovery. After backflushing the initial permeate flux is 14.2 LMH (Run 2), which is approximately 40% higher than that of the previous run. Since previous experiments indicate that the membrane is not damaged by any processes during WBL concentration and/or membrane cleaning, the increase in flux can be explained by the removal of loosely bound $G1_N$ polymer chains from within the pores. It turns out that since the modified coating was not yet optimized, there was excess $G1_N$ within the pores that was being removed during backflushing. When the membrane is backflushed at 56% recovery it increases slightly from 7.2 LMH to 8.5 LMH. The flux drops to 5.5 LMH as the remaining 4.4 gal WBL is concentrated to 2.8 gal (72% recovery).

Instead of cleaning the membrane and stripping the first $G1_N$ coating, the membranes were backflushed with WBL permeate to continue removing excess coating from the pores. After backflushing the initial permeate flux is 17.2 LMH (Run 3), which is approximately 21% higher than that of the previous run, suggesting that less coating has been removed. When continuously concentrating WBL (i.e., without backflushing) the permeate flux decreases to about 8.0 LMH at 70% permeate recovery.

Table 8.7 Cleaning parameters

Chemical	Concentration	Conditions
Sodium hydroxide	380 mM	85 °C, 30 min
Phosphoric acid	15 mM	50 °C, 15 min
Sodium hypochlorite	300 mg L^{-1}	25 °C, pH 11, 30 min

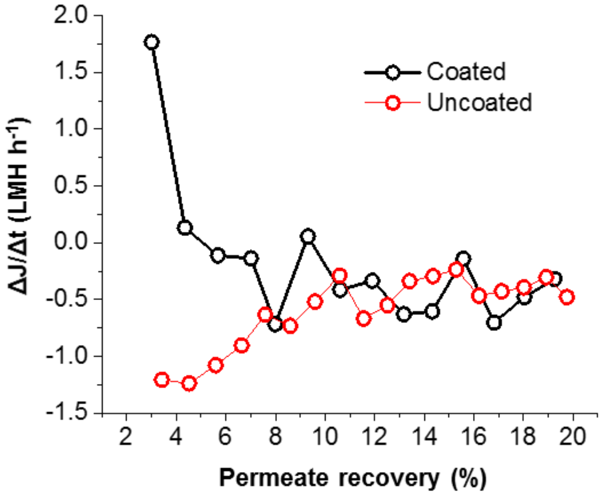


Figure 8.2.21 Fouling rate vs. recovery plot for coated (○) and uncoated (○) membrane *n*
Feed, 10 gal WBL; temperature, 85 °C; TMP, 60 psi; crossflow velocity, 3.0 m s^{-1}; membrane area, 0.5 m^2; unit, R2.

Run 4 (Figure 8.2.19d) shows the WBL flux after stripping and recoating. The initial permeate flux is 22.9 LMH, which is approximately 33% higher than the initial flux of the previous run; the flux increase is expected since the chemical cleaning process removes the manufacturer protective coating. The permeate flux decreases to 21.6 LMH after concentrating the WBL to 8 gal (20% recovery). After backflushing, the permeate flux increases to 24.1 LMH as expected since excess coating is removed during backflushing with hot WBL permeate. At 70% permeate recovery the permeate flux is approximately 9.6 L m^{-2} h^{-1} and the TOC of the final permeate is 52 g/L at 72% permeate recovery. Since the TOC of the permeate from the coated membrane (Figure 8.2.19d, Run 2) is 47 g/L at 72% recovery and the permeate from the uncoated membrane (Figure 8.2.19b, Run 2) is 42 g/L at 68% recovery, we can assume that the process of stripping and recoating does not damage the membrane, since any formed cracks would have propagated throughout the runs and resulted in a significant decrease in TOC rejection.

During fouling experiments, all parameters were precisely controlled to ensure that the environment was identical; the feed volume, temperature, TMP, and crossflow velocity were held constant to avoid any variations in cake layer thickness and fouling potential. Figure 8.2.21 shows the WBL fouling profile for membrane ***n*** with (○) and without (○) the $G1_N$ coating. The rate of change in permeate flux per unit time is plotted with respect to permeate recovery, such that any positive value for ΔJ/Δt represents an increase in flux and a negative value represents a decrease in flux (or fouling). In other words, the more negative the ΔJ/Δt term is the higher the degree of membrane fouling. Contrary to the uncoated membrane performance, ΔJ/Δt is initially positive 1.8 L m^{-2} h^{-2} (or LMH h^{-1}), due to the opening of pores resulting from the removal of excess coating, and steadily decreases to negative 0.4 LMH h^{-1} by 20% permeate recovery. On the other hand, ΔJ/Δt is initially negative 1.2 LMH h^{-1} for the uncoated membrane and increases to 0.4 LMH h^{-1} by 20% permeate recovery. Interestingly, ΔJ/Δt approaches 0.4 LMH h^{-1} at approximately 10% permeate recovery, which implies that that the cake layer could be growing at the same rate beyond 10% permeate recovery. Nevertheless, we demonstrated that the coated membrane outperforms the uncoated membrane.

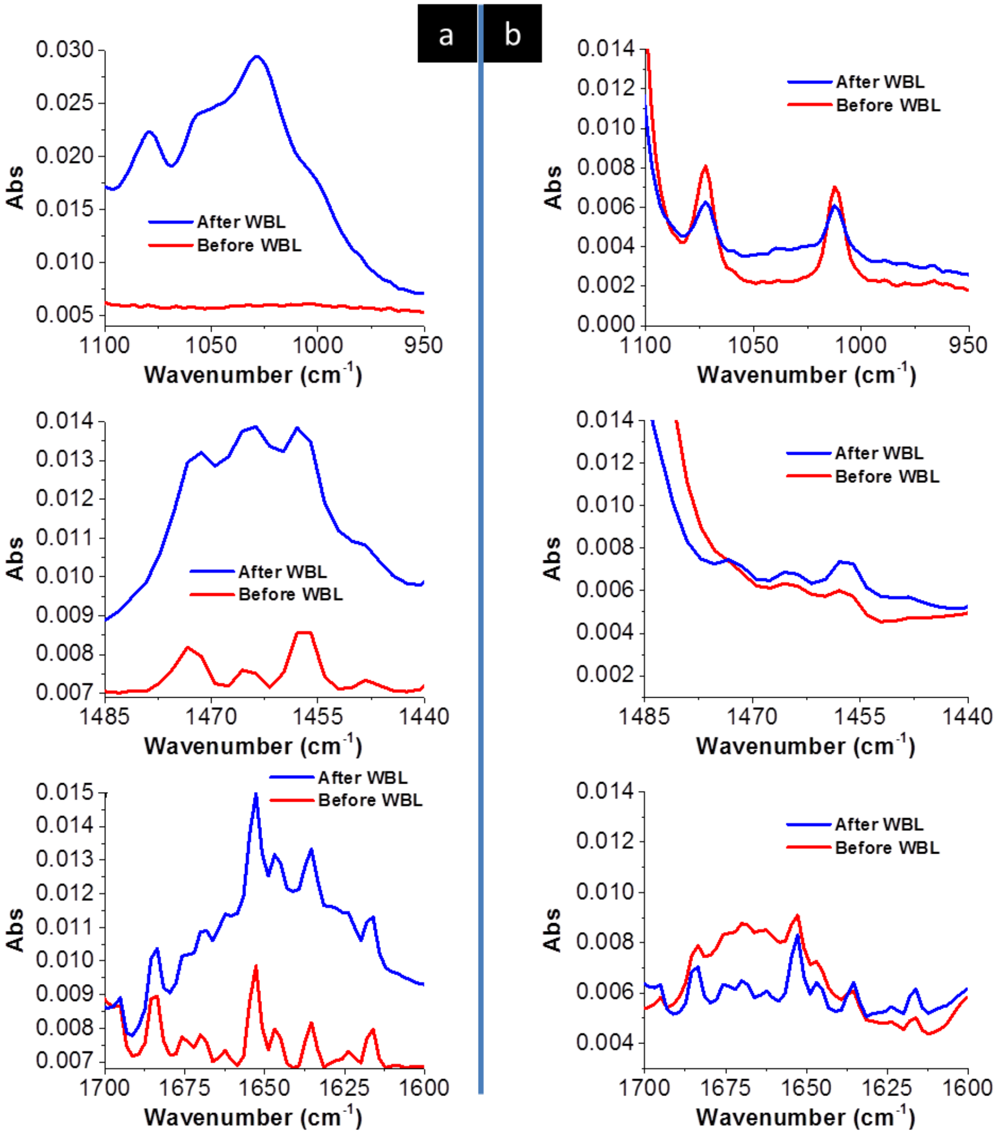


Figure 8.2.22 ATR-FTIR spectra of hydrophobic (a) and hydrophilic (b) membranes before (–) and after (–) WBL exposure

Hydrophobic and hydrophilic membranes were exposed to WBL for 3 days and analyzed using ATR-FTIR to determine the nature of adsorbed foulants on the membrane surface (Figure 8.2.22). Prior to analysis, the membranes were gently rinsed with DI water to remove loosely bound foulants. After WBL exposure (–) the hydrophobic membrane shows signature peaks within the lignin spectrum (Figure 8.2.22a). For example, absorbance at approximately 1025 cm^{-1} and 1080 cm^{-1} are indicative of carbon-oxygen stretching modes of alcohols and aliphatic ethers, respectively, of both guaiacyl and syringyl rings [12]. Similarly, a peak due to carbon-hydrogen deformation of methyl and methylene is observed at 1460 cm^{-1}, while conjugated carbonyl bonds of lignin are detected at 1650 cm^{-1}. These spectra imply that lignin is adsorbed on the hydrophobic surface after WBL exposure.

Hydrophilic membranes show little to no adsorption of WBL foulants (Figure 8.2.22b). For example, after WBL exposure (–) the only detectable peaks observed between 1100 to 950 cm^{-1}

and between 1485 to 1440 cm^{-1} are those of the hydrophilic membrane (–). However, there does seem to be some increase in absorbance at 1670 cm^{-1}, which could be due to a small amount of guaiacly rings present on the surface or in the pores of this membrane. These data suggest that the nature of foulant adhesion is likely a result of hydrophobic interactions between the membrane surface and WBL foulants.

8.2.4. Characterization of weak black liquor and permeate streams

During the first stage, weak black liquor is typically concentrated from 15% to 22.8% total dissolved solids at a permeate recovery of 85%. Stage 1 permeate, which typically contains about 40 $g\ L^{-1}$ total organic carbon and 4 $g\ L^{-1}$ sodium sulfate, is filtered using the Stage 2 membrane at transmembrane pressure of 400 psi. At 63% permeate recovery the second stage permeate contains 9.5% total dissolved solids, 19 $g\ L^{-1}$ total organic carbon, and 2.1 $g\ L^{-1}$ sodium sulfate.

Enhancement in divalent ion rejection from weak black liquor was accomplished by functionalizing our coating with charged functional groups. Sulfate ion rejection is especially important because sodium sulfate, which is a byproduct of wood digestion, is reduced to sodium sulfide in the recovery boiler. Since sodium sulfide is required for wood digestion, sodium sulfate loss must be avoided. The second stage membrane is composed of a polymer that is capable of resisting the environmental conditions at the pulp and paper mill. This nanofiltration membrane exhibits 80-95% sodium sulfate rejection. Weak black liquor typically contains of 3,000 to 5,000 $mg\ L^{-1}$ sodium sulfate. If the membrane rejects 95% of the sodium sulfate in the feed, then the concentration of sodium sulfate in the permeate would be 150 to 250 $mg\ L^{-1}$. However, the high solids content of weak black liquor, i.e., greater than 15 wt% total dissolved solids, makes it difficult maintain a high rejection rate. Thus, it is important to have the ability to tune the pore surface to control the rejection characteristics of the membrane.

Figure 8.2.23a shows the performance of the negatively charged TSI coating using aqueous sodium sulfate as the feed. Sulfate rejection is approximately 98.5% and does not appear to decrease with increasing permeate recovery. At 50% recovery the feed concentration is nearly doubled, yet the coating's ability to separate sodium sulfate from the solution is not compromised. This is a significant improvement over the pristine membrane. For example, prior to depositing the coating, the sodium sulfate rejection decreases from an initial value of ~94% to ~92% at 50% permeate recovery. TSI coatings functionalized with positive charges behave similarly (Figure 8.2.23b). The coating maintains its ability to separate sodium sulfate from water with increasing permeate recovery; the salt rejection increases from 96.8% to 97.7% as the permeate recovery increases from 12.5% to 50.2%. On the other hand, the sodium sulfate rejection decreases from 91% to less than 89% as the permeate recovery increases from 12.5% to 50.7% prior to coating.

Figure 8.2.24 shows weak black liquor samples obtained from Stage 1 and Stage 2 experiments. Weak black liquor was concentrated using the Stage 1 membrane and the reject (top left) and permeate (top right) samples are shown after concentrating to a permeate recovery of 85%.

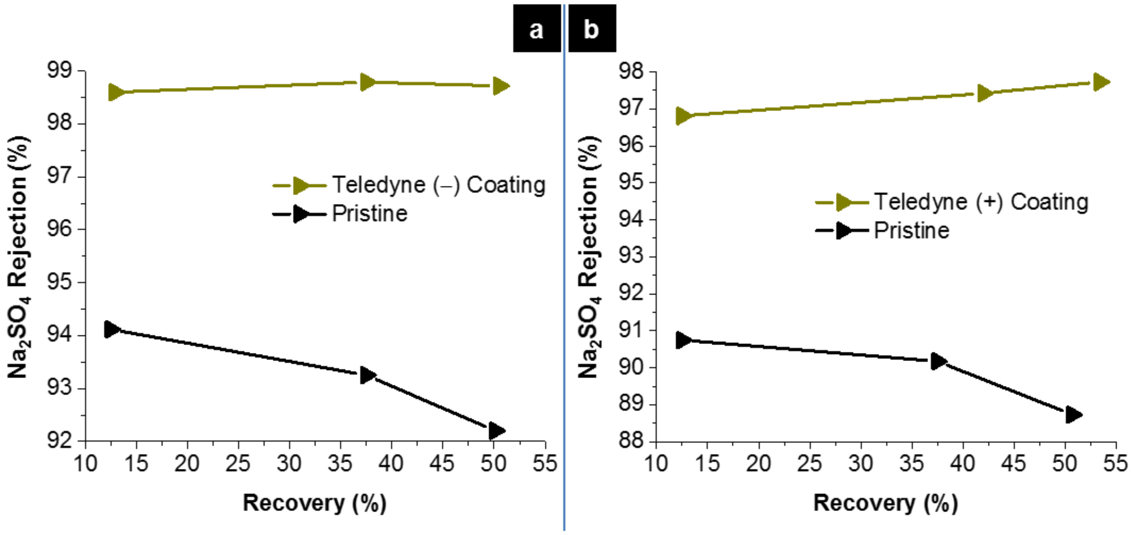


Figure 8.2.23 Sulfate rejection vs. permeate recovery plots for negatively (a) and positively (b) charged coating Membrane, Stage 2 flat sheet NF; filtration mode, dead end; feed, 4,700 mg L^{-1} Na$_2$SO$_4$ in DI water; temperature, 22 °C; TMP, 400 psi; membrane area, 15 cm^2.

When filtering the Stage 1 permeate through the pristine Stage 2 membrane, permeate (bottom right) quality is improved. However, when the Stage 1 permeate is filtered using the positively charged coated Stage 2 membrane, permeate (bottom left) quality is significantly improved. Here, the TSI coating with positive surface charges showed superior separation capabilities over the uncoated membrane.

Figure 8.2.25 shows the sulfate concentration of the weak black liquor permeate collected using the coated Stage 2 membranes. The permeate from the negatively charged coating (**O**) contains approximately 370 mg L^{-1} and 550 mg L^{-1} sulfate at 19% and 38% permeate recovery, respectively. However, when a positively charged coating (**O**) is deposited on the Stage 2 membrane the sulfate concentration is much lower. For example, at 20% and 35% permeate recovery the sulfate concentration is 240 mg L^{-1} and 380 mg L^{-1}, respectively. This increase in performance is presumably due to the increased rejection of sodium ions with the positively charged surface.

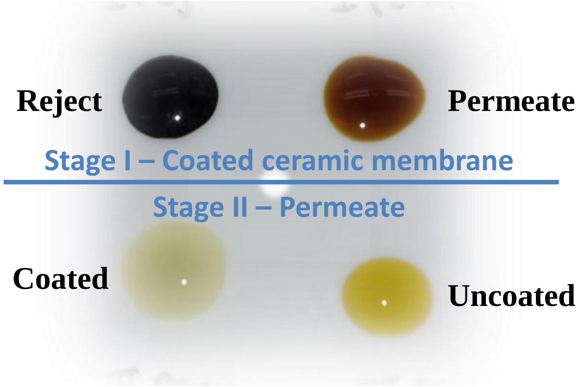


Figure 8.2.24 Weak black liquor samples from Stage 1 (top) and Stage 2 (bottom) experiments Stage 1: feed, WBL; temperature, 85 °C; TMP, 60 psi; permeate recovery, 85%. Stage 2: feed, Stage 1 WBL permeate; temperature, 22 °C; TMP, 400 psi; permeate recovery, 35% (coated), 55% (uncoated).

Organic carbon rejection appears to have minimal dependence on surface charge when weak black liquor permeate is used as feed. For example, the TOC concentration of Stage 2 permeate collected using the negatively charged coated membrane is 16 g L^{-1}. On the other hand, when a positively charged coating is deposited on the Stage 2 membrane, the TOC concentration of the permeate is 15 g L^{-1}. The TOC results suggest that a significant amount of uncharged, low molecular weight organic species may be permeating the membrane with minimal resistance. This is evidenced by gas chromatography-mass spectroscopy (GCMS) analysis, which shows the presence of low molecular weight organic compounds in the Stage 2 permeate. According to GCMS data, the concentration of organic species in weak black liquor permeate generally follows the following trend: [alcohols] > [glycols] > [carboxylic acids].

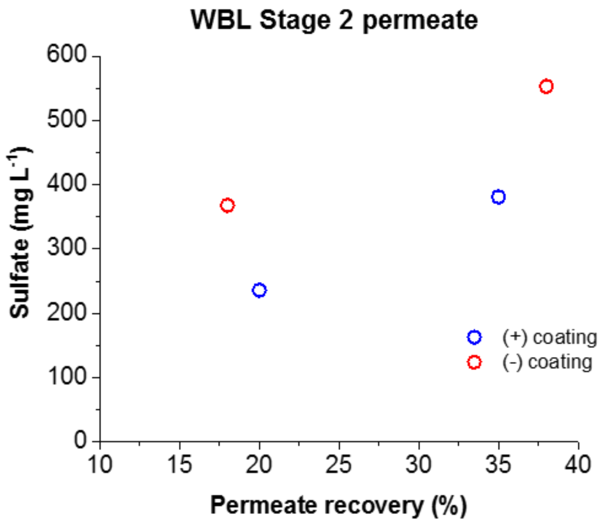


Figure 8.2.25 Sulfate concentration vs. permeate recovery for Stage 2 membranes with charged coating
Feed, Stage 1 WBL permeate; pressure, 400 psi; temperature, 22 °C.

Membrane stability experiments were carried out on spiral wound Stage 2 membranes before and after treatment with cleaning agents. Initially, the sodium sulfate and sodium hydroxide rejection are 93.1% and 29%, respectively (Figure 8.2.26). After concentrating Stage 1 WBL permeate, the sodium sulfate and sodium hydroxide rejection slightly increase to 95.7% and 31%. After cleaning the fouled membrane with an oxidizing agent the sodium sulfate rejection decreases to 93.0% and the sodium hydroxide rejection increases to 33%. It should be noted that using an oxidizing agent alone is not sufficient. When the fouled membrane is cleaned with the oxidizing agent the reject has a light brown tint. During the following sodium sulfate experiment (run 6) the reject is colorless. However, when sodium hydroxide rejection is measured (run 7) a dark brown solution exits the reject port of the membrane module. On the other hand, this is not observed when the steps are reversed. After run 7, the membrane is fouled with weak black liquor permeate and cleaned using the acid solution. The sodium sulfate and sodium hydroxide rejection decrease to 90% and 25%, indicating that acidic cleaners should not be used immediately after weak black liquor concentration. Rather, caustic alkaline cleaners should be used during the first cleaning step. After drying the membrane using compressed nitrogen, the sodium sulfate and sodium hydroxide flux decreases by 14% and 19% respectively. The sodium sulfate and sodium hydroxide rejection recovers to 92.0%

and 30%. After cleaning, the TSI N1 coating was deposited onto the membrane surface and the sulfate and hydroxide rejection increased to 97% and 55%, respectively. The increase in rejection, especially in the case of sodium hydroxide, after cleaning and coating in-place demonstrates the effectiveness of the chosen cleaning agents and the overall stability of the membrane to the cleaning and coating processes.

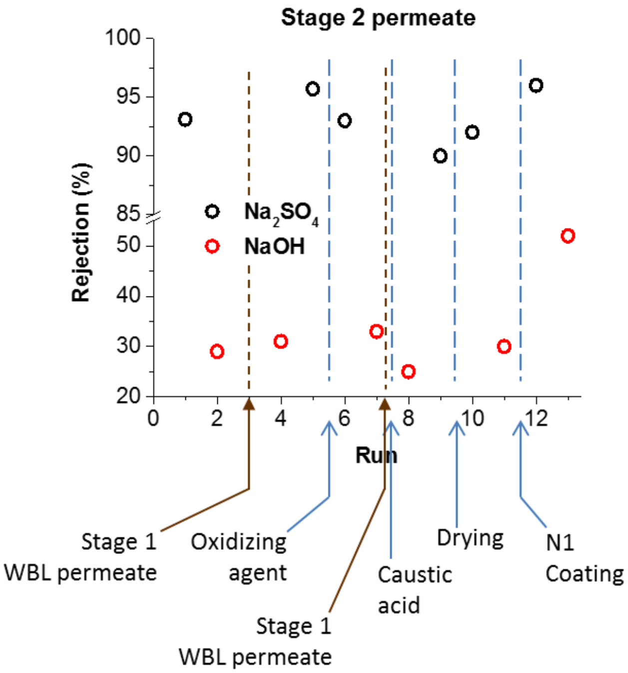


Figure 8.2.26 Stage 2 membrane sodium hydroxide (O) and sulfate (O) rejection
Membrane configuration, spiral wound; membrane diameter/length/area, 2.5"/21"/0.56 m^2; solutions, 4.7 g L^{-1} aqueous sodium sulfate and 4.0 g L^{-1} aqueous sodium hydroxide; temperature, 40 °C (±5 °C); transmembrane pressure, 400 psi; feed flow, 1.8 gal min^{-1}.

Enhancement in sulfate rejection during weak black liquor concentration is observed when our coating is deposited on spiral wound membranes. For example, Stage 2 weak black liquor permeate typically contains 2,100 mg L^{-1} sulfate at 63% recovery. However, the sulfate concentration of the Stage 2 permeate is much less when weak black liquor Stage 1 permeate is concentrated using the coated Stage 2 membrane (Figure 8.2.27). Using the N1-coated membrane, the sulfate concentration is approximately 470 mg L^{-1}, 650 mg L^{-1}, and 770 mg L^{-1} at 12%, 25%, and 48% permeate recovery, respectively.

Permeate produced during membrane-based weak black liquor concentration could be used to wash pulp collected after wood digestion. This process, known as brownstock washing, is usually carried out in a countercurrent manner. Briefly, the mixture of pulp and black liquor is sent to a series of washers in one direction (W1→W2→W3→W4) while condensed water from the evaporators is used to wash the pulp in the opposite direction (W4→W3→W2→W1), where W1 is the washer closest to the digester and W4 is the final washer containing clean pulp. Wash water that is collected from the first washer is the dirtiest of the four washers and is sent

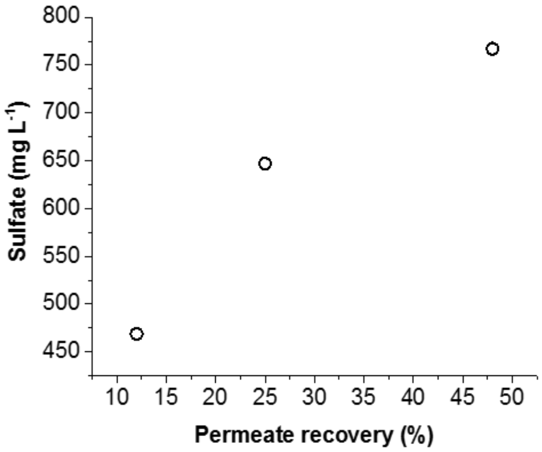


Figure 8.2.27 Sulfate concentration of permeate vs. permeate recovery for N1-coated stage 2 membrane
Membrane configuration, spiral wound; membrane diameter/length/area, 2.5”/21”/0.56 m^2; feed, Stage 1 WBL permeate; temperature, 50 °C; transmembrane pressure, 400 psi; feed flow, 1.8 gal min^{-1}.

to the evaporators to be concentrated to strong black liquor. On the other hand, washed pulp exits the fourth washer and is sent to a separate plant in the mill where it is bleached. It is important for the permeate to be as dilute as possible since any chemicals that are not thoroughly rinsed and collected in the wash water would be lost to the bleaching plant.

Washer samples were collected from WestRock washers W1, W2, W3, and W4 and analyzed. Figure 8.2.28 shows the TOC (🟩) and sulfate (🟦) concentrations of each sample. Analysis of W1 samples shows that the wash water is rather concentrated at the end of the wash cycle. In fact, the TOC concentration of the W1 stream is approximately twice as high as that of the membrane permeate stream (– – –). Similarly, the sulfate concentration of the membrane permeate stream (– – –) is nearly that of the W1, W2, and W3 streams. Therefore, if the alkaline permeate produced by membrane-based separation is added to the wash cycle at W1

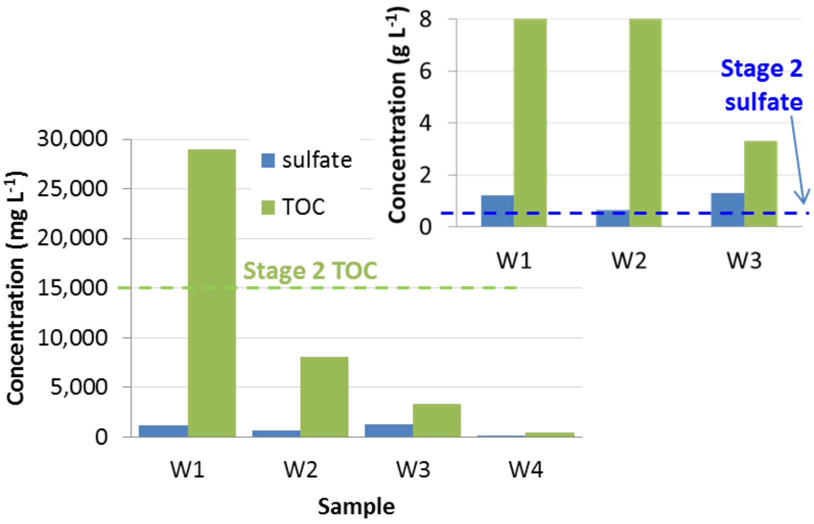


Figure 8.2.28 Concentration of vacuum drum washer samples collected during pulp washing
Samples C1, C2, C3, and C4 are obtained from WestRock washers 1, 2, 3, and 4, respectively. Permeate TOC (– – –) concentration, 15 g L^{-1} at 35% permeate recovery obtained using charged coating; permeate sulfate (– – –) concentration, 770 g L^{-1} obtained at 48% permeate recovery using coated membrane.

or W2, then perhaps the pulp could be sufficiently cleaned. Condensed water from the evaporators would be added to W4, resulting in removal of sodium hydroxide in addition to further removal of residual black liquor from the pulp.

8.2.5. Effects of environment on membranes

Ceramic membranes were coated with the TSI coating and were tested using hardwood and softwood weak black liquor from WestRock Company. Two membranes, each with a membrane area of 0.25 m^2, were coated with the G1 coating. 50 gallons of weak black liquor were added to the feed drum and heated to greater than 80 °C before opening the permeate valve and filtering weak black liquor for more than 3 days. Figure 8.2.29 shows the operating parameters during weak black liquor filtration. The transmembrane pressure (Figure 8.2.29a) is roughly 62.5 psi during the first day of filtration. A slight increase in pressure is observed during a valve adjustment, but beyond this point the transmembrane pressure remains steady at about 61 psi throughout the remaining 2 days of weak black liquor filtration. The pressure drop, which is the difference in pressure between the feed and reject ports, is about 9 psi for this configuration throughout the 3 day run. Since the crossflow velocity is maintained at 3.3 $m\ s^{-1}$, the pressure drop should double if an additional membrane is added in series. However, lowering the crossflow velocity and increasing the transmembrane pressure generally decreases the pressure drop and maximizes the utilized membrane area in the field.

Figure 8.2.30 shows the performance of the coated ceramic membranes. After increasing the temperature of the feed to greater than 80 °C, which took approximately 5.5 hours, the permeate valve was opened and weak black liquor permeate was collected for over 3 days. During this time, approximately 400 liters (~105 gallons) of weak black liquor permeate was collected and recycled back into the feed drum. The antifouling and sacrificial properties of the TSI coating are apparent in the permeate flux data (○). For example, no membrane fouling is observed throughout the entire filtration process (i.e., the permeate flux does not decrease),

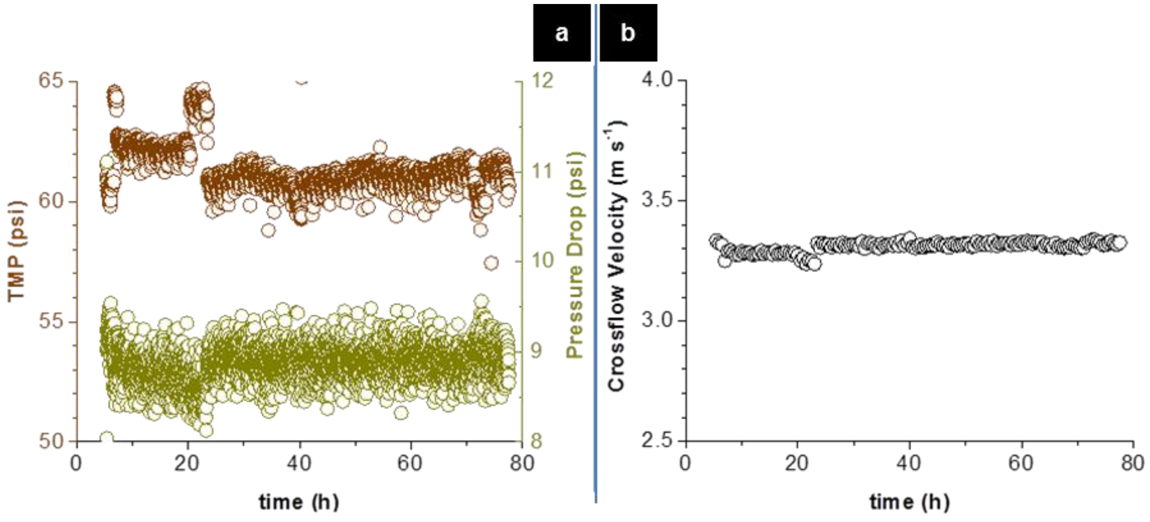


Figure 8.2.29 Transmembrane pressure and pressure drop vs. time (a) and crossflow velocity versus time (b) Membrane configuration, tubular; membrane area, 0.5 m^2; feed, 50 gal WBL; temperature, 83 °C.

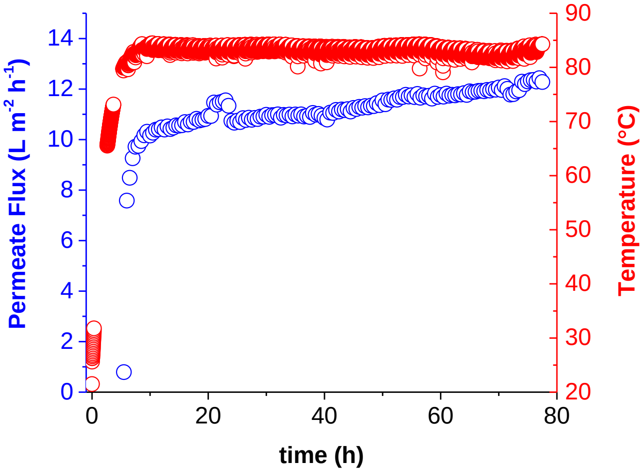


Figure 8.2.30 Permeate flux (○) and feed temperature (○) vs. time plots for ceramic membranes coated with Teledyne G1$_N$ coating

Membrane configuration, tubular; membrane area, 0.5 m^2; feed, 50 gal WBL; temperature, 83 °C; TMP, 61 psi; crossflow velocity, 3.3 m s^{-1}.

which is remarkable considering that no backflushing was necessary. Since the temperature is not increasing during this time, but is constant at ~83 °C, the slightly increasing permeate flux indicates that excess coating material is being stripped away. After 72 hours the permeate flux is 12.3 L m^{-2} h^{-1} for the coated membrane, compared to the permeate flux of the uncoated membrane which decreases from 9.0 L m^{-2} h^{-1} to 8.5 L m^{-2} h^{-1} within 30 minutes.

Figure 8.2.31 shows the weak black liquor fouling profile for the ceramic membrane with (○) and without (○) the TSI coating. Here, the rate of change in flux per unit time is plotted with respect to time, such that any positive value for ΔJ/Δt represents an increase in flux and a negative value represents a decrease in flux (or fouling). In other words, the more negative the ΔJ/Δt term is the higher the degree of membrane fouling. After 72 hours of weak black liquor filtration, ΔJ/Δt is positive 0.2 L m^{-2} h^{-2} (or LMH h^{-1}) for the coated membrane. This is due to the

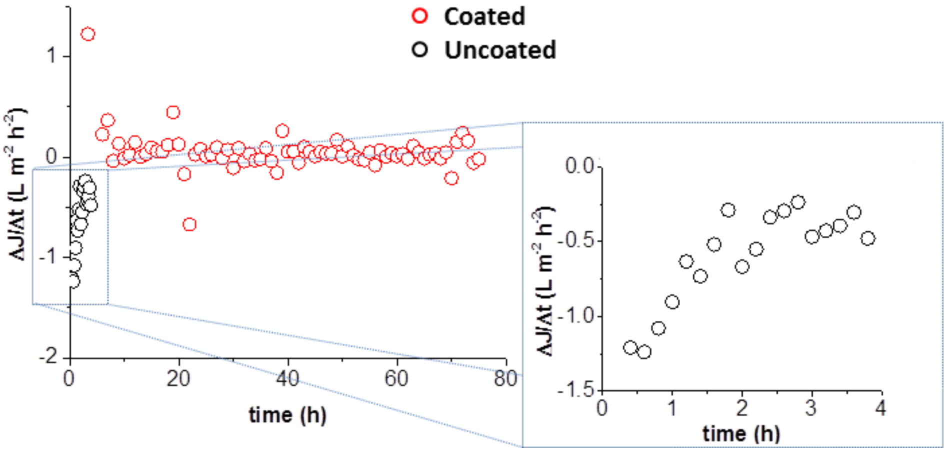


Figure 8.2.31 ΔJ/Δt versus time plot for ceramic membranes

Membrane configuration, tubular; membrane area, 0.5 m^2; feed, 50 gal WBL; temperature, 83 °C; TMP, 61 psi; crossflow velocity, 3.3 m s^{-1}.

opening of pores resulting from the removal of excess coating. On the other hand, $\Delta J/\Delta t$ steadily decreases to negative 0.4 L m^{-2} h^{-2} after only 4 hours without the coating. These data demonstrate the ability of the TSI coating to resist fouling.

8.3. Scaled-up membranes

8.3.1 In-place coating and cleaning development

Figure 8.3.1 shows the layout of the cleaning/coating subsystem. A garden hose is connected to the system and tap water is filtered using a reverse osmosis membrane. Filtered water is collected in the *water tank*. *Tanks A*, *B*, and *C* are filled with concentrated cleaning chemicals, while *tanks D*, *E*, and *G* are filled with concentrated coating chemicals. Solutions are added to the *cleaning/coating tank* using metering pumps. Water is added to the *cleaning/coating tank* and *tank F* to adjust the concentration of the cleaning and coating solutions. An agitator is used to mix the solutions in the *cleaning/coating tank*. After cleaning the membrane, compressed gas is used to purge the *cleaning/coating tank*, membrane module, *tank G*, and *tank F* during the coating process. Cleaning and coating solutions are circulated through the Stage 1 or Stage 2 membrane module using the *process pump* and an inline heater is used to control the temperature. The *waste pump* transfers all waste to either the *acid waste* or *base waste* tank.

Membrane cleaning begins by rinsing with filtered water and draining the weak black liquor wastewater to the base waste tank. An alkaline cleaning agent (mainly sodium hydroxide) is then heated and pumped through the membrane to remove any adsorbed lignin from the membrane surface, as well as a variety of other organic compounds. After draining the alkaline solution into the base waste tank, filtered water is used to rinse the tubing, drum, and membrane and rinsing is repeated until the pH is 7-8. An acidic cleaning agent (mainly phosphoric acid) is then used to remove inorganic compounds from the membrane surface. Similarly, the acid must be heated, pumped through the membrane, and wasted. The system is rinsed several times with filtered water until the pH is 6-7. The final cleaning step consists of an oxidizing agent (mainly sodium hypochlorite), which is used to remove any remaining organic foulants on the membrane surface. In addition to foulants, the oxidizer is used to depolymerize the coating. Typically, the oxidizing agent is pumped through the membrane at room temperature. However, the pH and temperature may be adjusted to tune the coating removal process.

Once the membrane is cleaned and the coating is stripped, the coating is reapplied. In the field, this process can be challenging when considering the possible environmental variations at different locations and during different seasons of the year. For this reason the cleaning/coating system is designed with the capabilities to control the fundamental environmental parameters: temperature, atmospheric composition, and pressure. Temperature is controlled using heating elements. This allows the polymerization reaction and solution viscosity to be similar with each coating attempt. The atmosphere is controlled by using a gas cylinder to purge the plumbing and membrane with a gas of known composition. A pressure regulator is used to control the pressure of the gas over the coating solution. Purging allows the composition of the atmosphere and concentration of dissolved gas in the solution to be similar regardless of where the system is located. After coating deposition, the excess

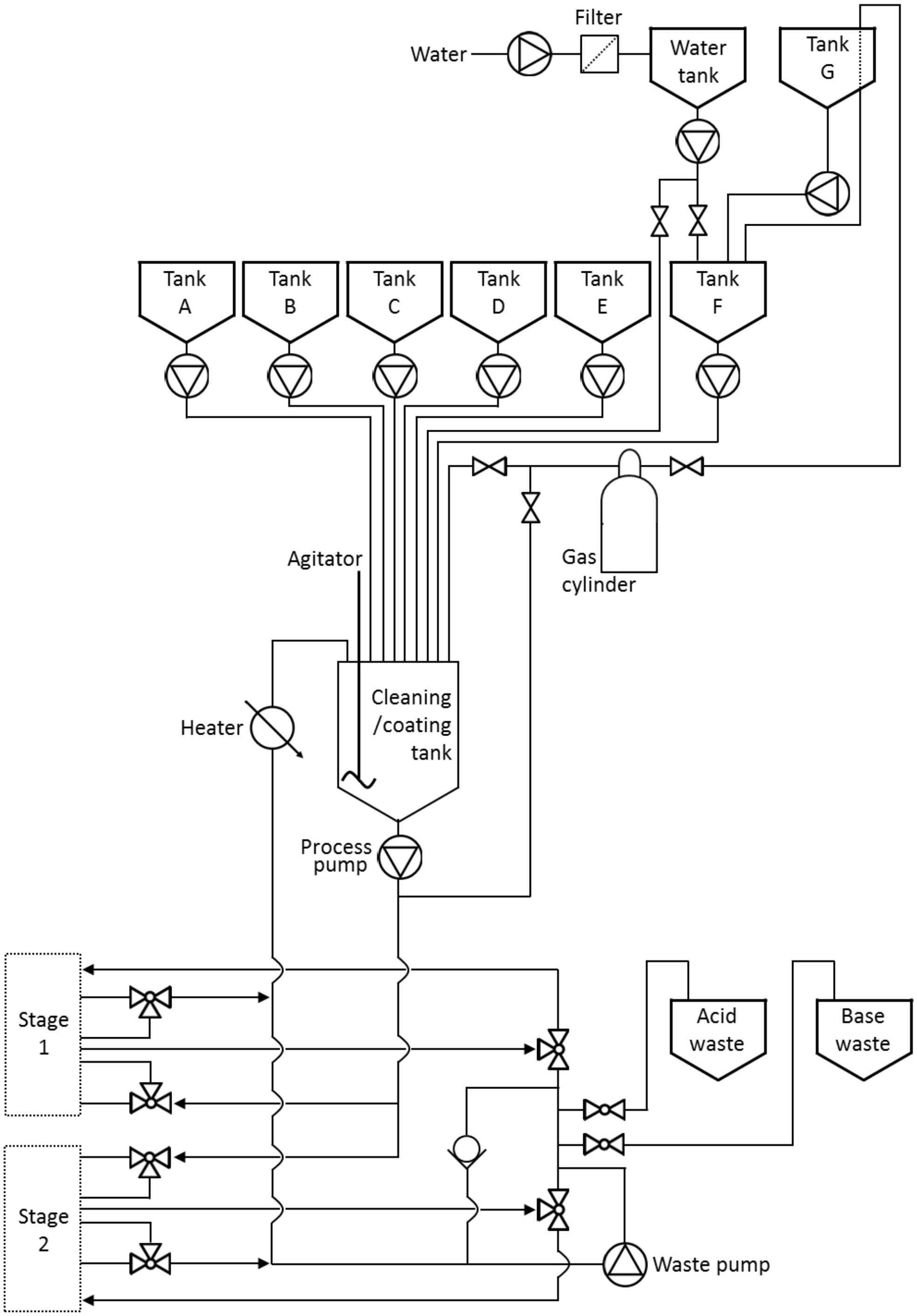


Figure 8.3.1 Diagram of Cleaning/Coating subsystem

polymerized solution is collected in the waste drum. A final rinse removes excess coating materials, to prevent contamination of the weak black liquor, and the 3-way ball valves are returned to their original positions to isolate the coating system from the concentration systems.

8.3.2 TRL 5 demonstration

System configurations of Stage 1 and Stage 2 can be seen in images of the respective touchscreen control panels (Figure 8.3.2). All wetted parts are 316 stainless steel, Incoloy, PTFE, and EPDM to prevent failure from hot weak black liquor. Due to limited resources, Stage 1 was limited to three ultrafiltration membranes providing a total membrane area of 1.5 m^2. Stage 2 consisted of a 4040 nanofiltration membrane (4” diameter, 40” length) with a membrane area of 6.4 m^2. After PLC programming, the two systems were coupled to the cleaning/coating (C/C) system in the demonstration cargo trailer as shown in Figure 8.3.3.

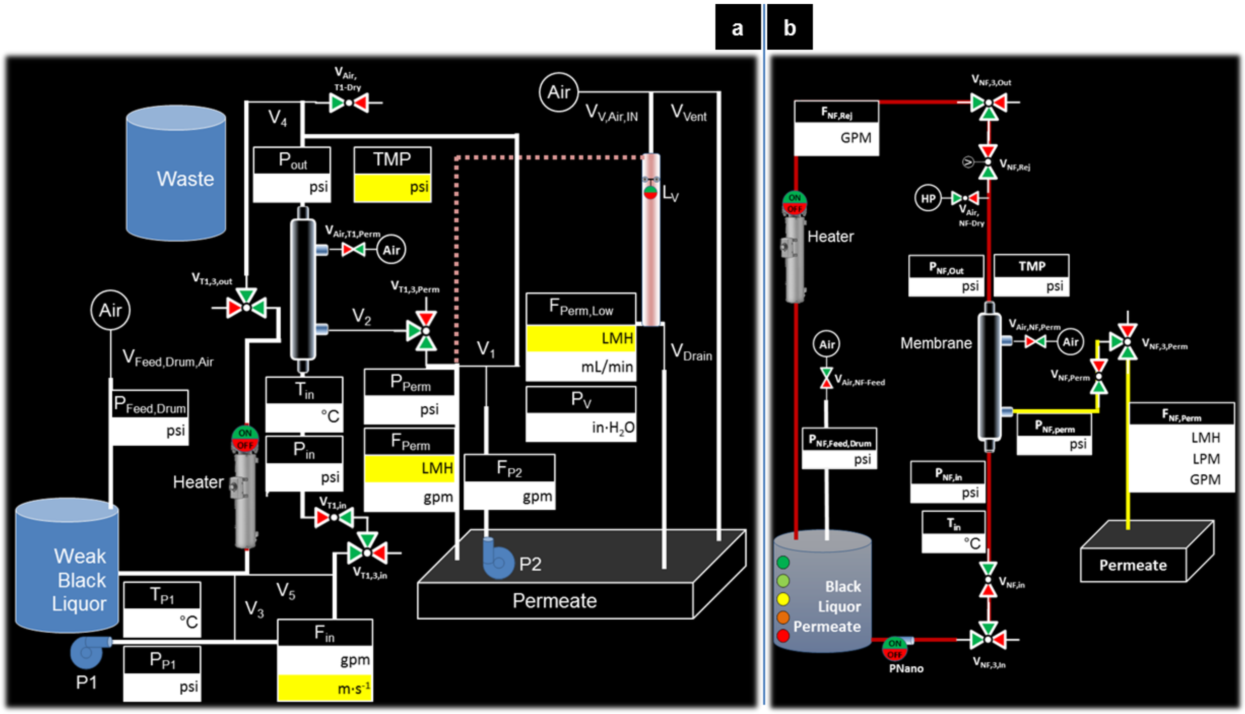


Figure 8.3.2 Diagram of Stage 1 (a) and Stage 2 (b) systems

Figure 8.3.3 shows a schematic of the demonstration trailer (400). Stage 1 (100), Stage 2 (200), and the C/C (300) subsystems are coupled using 316 stainless steel tubing. A bumper hitch (413) allows towing by a full-size truck. Tap water is supplied to the trailer through garden hose fittings 402 and 405. A sink (401) is used for washing and water is drained though a pipe (403). The pilot unit is wired to electrical disconnects (410) inside of the trailer. The disconnects are wired to electrical panels (411) mounted to the front exterior wall of the trailer; 480 VAC (3 phase, 50 A fused), 208 VAC (3 phase, 40 A fused), and 240 VAC (single phase, 30 A) are supplied. Weak black liquor is supplied through a hose that is connected to a sanitary fitting (407), which feeds the Stage 1 feed drum (101). A touchscreen PLC unit (104) is used to control the Stage 1 system. The Stage 1 pump (102) circulates weak black liquor through the coated ceramic membrane (103) and concentrated black liquor is supplied to the mill through a sanitary fitting (406). A small fraction (approximately 3 gallons) of permeate is collected in the Stage 1 permeate tank (106) for backflushing and the rest is pumped to the Stage 2 feed drum (201). A touchscreen PLC unit (204), which controls the Stage 2 and C/C systems, allows the Stage 2 pump (202) to circulate filtered weak black liquor through the coated nanofiltration membrane (203). Concentrated black liquor (reject from Stage 2) is combined with the Stage 1 reject and supplied to the mill through a sanitary fitting (406). Permeate from the pilot unit is supplied to the mill through a sanitary fitting (404).

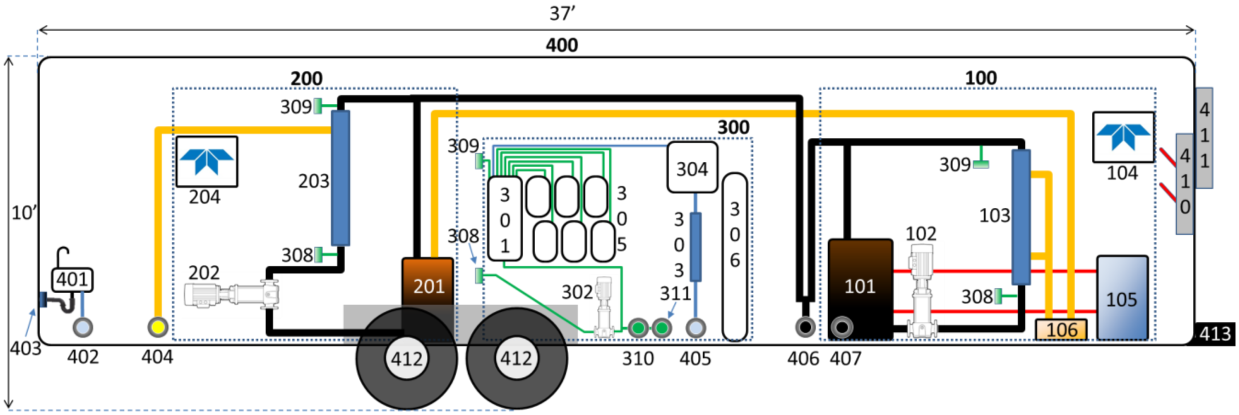


Figure 8.3.3 Schematic of demonstration trailer

The C/C subsystem (300) has a process tank (301) where cleaning and coating chemicals are mixed prior to pumping to the Stage 1 and Stage 2 membranes. First, tap water is added to the trailer at 405 and filtered using a reverse osmosis (RO) membrane (303) before being collected in a RO water tank (304). Concentrated cleaning and coating chemicals that are contained in six tanks (305) are added to the C/C tank (301) and RO water is added to adjust the concentration. A process pump (302) circulates the cleaning and coating chemicals to the Stage 1 and Stage 2 membranes through sanitary fittings (308 and 309). Acid and base wastes are supplied through sanitary fittings 310 and 311. Compressed gas (306) is used to assist in draining, drying, and coating the membranes.

The goal for the trial was to concentrate weak black liquor using coated membranes for 6 days at Teledyne and for 1 day at WestRock, with less than 20% drop in flux over the 7-day trial. First, the Stage 1 and Stage 2 membranes were coated in the trailer with the $G1_N$ and negatively charged N1 formulations, respectively. Prior to weak black liquor concentration, water was used to test the coated membranes. Table 8.8 summarizes the Stage 1 membrane performance using water as feed. The permeate flux of the large-scale demo system (Task 14) is 2.8 times lower than that of the laboratory-scale system developed during Task 12. It should be noted that due to differences in laboratory and trailer environments, it was difficult to control all variables. The primary reason for the difference in permeate flux is the increase in frictional head associated with the large-scale membrane length. For example, the twofold increase in membrane length results in a large pressure drop (ΔP) along the membrane inlet and outlet ports (i.e., $P_{feed} - P_{reject}$).

Table 8.8 $G1_N$-coated Stage 1 membrane performance using water as feed

Task	Membrane length (mm)	Transmembrane pressure (psi)	Temperature (°C)	Water flux (LMH)	(LMH/bar)	Pressure drop (psi)
12	580	50	22	46	13.3	~1
14	1178	61	32	20	4.7	28

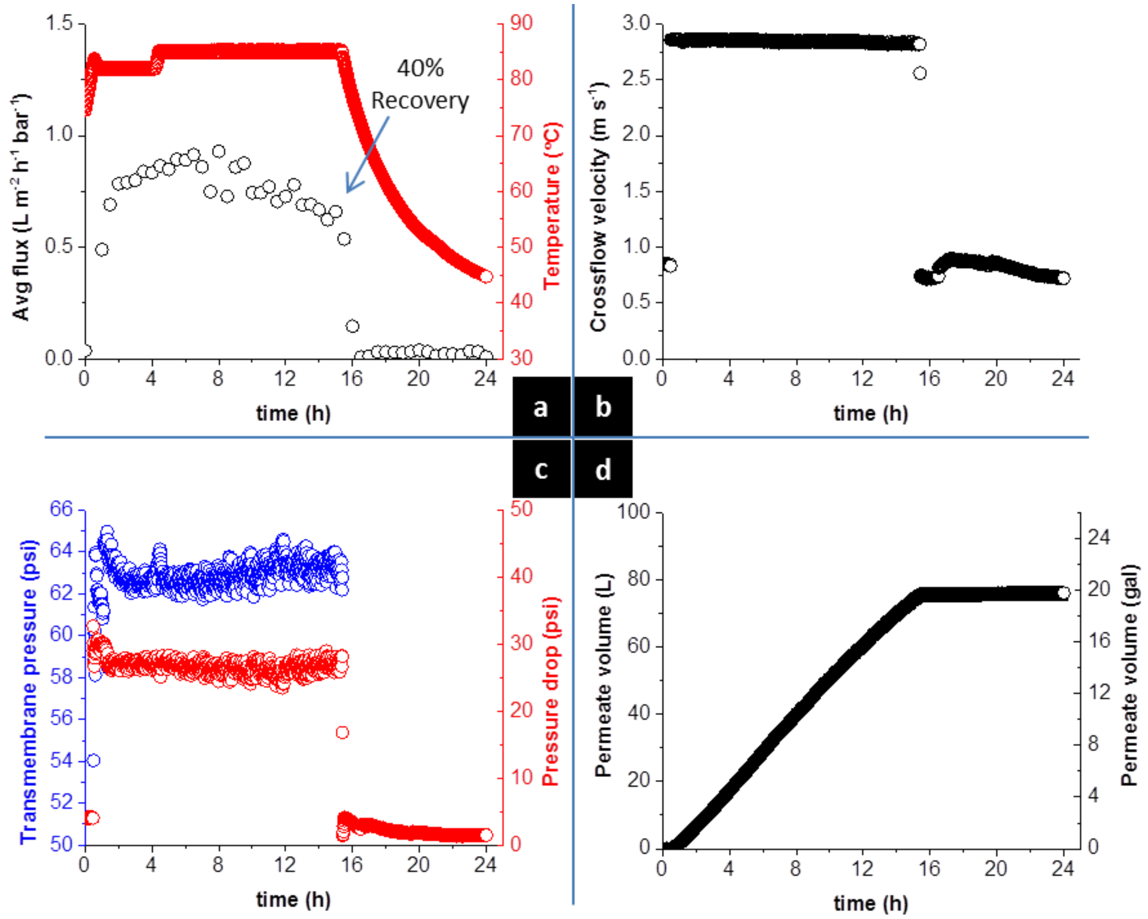


Figure 8.3.4 Stage 1 performance during initial WBL concentration in demo trailer at Teledyne
50 gal of weak black liquor (WBL), supplied by WestRock, was concentrated using the Stage 1 system in the trailer and the Stage 1 permeate was added to the Stage 2 feed drum. (**a**) Temperature was increased to 85 °C during WBL concentration. After WBL concentration the temperature was slowly decreased to prevent membrane damage. The average permeate flux decreases from approximately 0.93 to 0.66 L m^{-2} h^{-1} bar^{-1} (LMH/bar) as the recovery increased to 40% at 15.5 hours. (**b**) Crossflow velocity was held at 2.9 m s^{-1} during WBL concentration and decreased to 0.9 m s^{-1} during cooling. (**c**) The transmembrane pressure and pressure drop were maintained at 63 psi and 28 psi, respectively, during WBL concentration. (**d**) 20 gal of permeate was collected in approximately 15 hours.

Table 8.9 Weak black liquor concentration at various G1$_N$ coating development stages

Stage 1 Coating	Temperature (°C)	TMP (psi)	Pressure drop (psi)	Avg. WBL flux (LMH)	(LMH/bar)	Recovery range (%)
TRL 4	85	61	13	11.7	2.8	0–40
				9.84	2.3	0–70
TRL 4 (Optimized)	85	60	14	21.8	5.3	0–40
				17.2	4.2	0–70
TRL 5	85	63	27	3.4	0.77	0–40

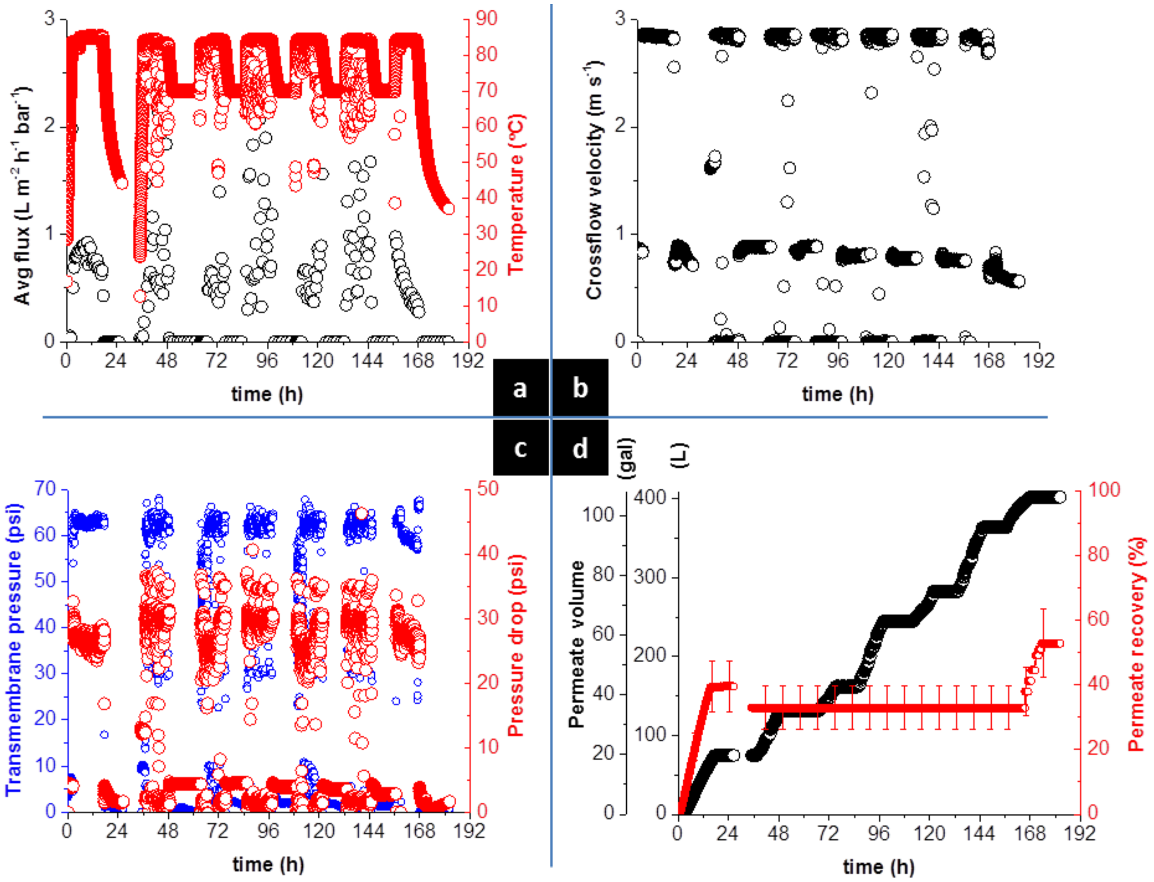


Figure 8.3.5 G1$_N$-coated Stage 1 membrane performance during 6-day Milestone 7 trial at Teledyne

After producing 20 gallons of Stage 1 weak black liquor permeate for Stage 2, 10 gallons of WBL was added to the Stage 1 feed drum. (**a**) Temperature was increased to 85 °C during WBL concentration (daytime) and decreased to 70 °C overnight. After concentrating WBL for 6 additional days the temperature was slowly decreased to prevent membrane damage. (**b**) Crossflow velocity was held at 2.9 m s^{-1} during WBL concentration and decreased to 0.9 m s^{-1} overnight. (**c**) TMP was maintained at 63 psi during the day and 0-5 psi overnight. (**d**) Total permeate volume filtered through Stage 1 membrane and the corresponding permeate recovery during demo run.

At Teledyne, 50 gal of weak black liquor, supplied by WestRock, was added to the Stage 1 feed drum and heated to 85 °C. Before beginning the trial run, Stage 1 permeate had to be produced to feed the Stage 2 system. Figure 8.3.4 shows the performance during the initial weak black liquor run. After reaching the standard operating temperature (i.e., >80 °C) the crossflow velocity (**b**) and transmembrane pressure (**c**) were increased to 2.9 m s^{-1} and 63 psi, respectively, and the permeate valve was opened. At 85 °C the permeate flux (**a**) plateaued at approximately 0.93 L m^{-2} h^{-1} bar^{-1} (LMH/bar) and dropped to about 0.66 LMH/bar at 40% recovery. The average permeate flux (J_{perm}), which was calculated by dividing the permeate volume by the time (Figure 8.3.4d), membrane area, and pressure, was approximately 3.6 to 6.9 times lower than that of laboratory-scale membranes at similar permeate recovery (Table 8.9). Since the decrease in permeate flux is not proportional to the increase in pressure drop (i.e., $J_{perm,TRL4}/J_{perm,TRL5} \neq \Delta P_{TRL5}/\Delta P_{TRL4}$), the coating must also be contributing to the permeate flux. This can be seen with the optimized TRL 4 coating, which displayed a permeate flux that was 1.9 times that of the TRL 4 coating under a similar pressure drop. Therefore, the coating on the large-scale membranes does not appear to be fully optimized.

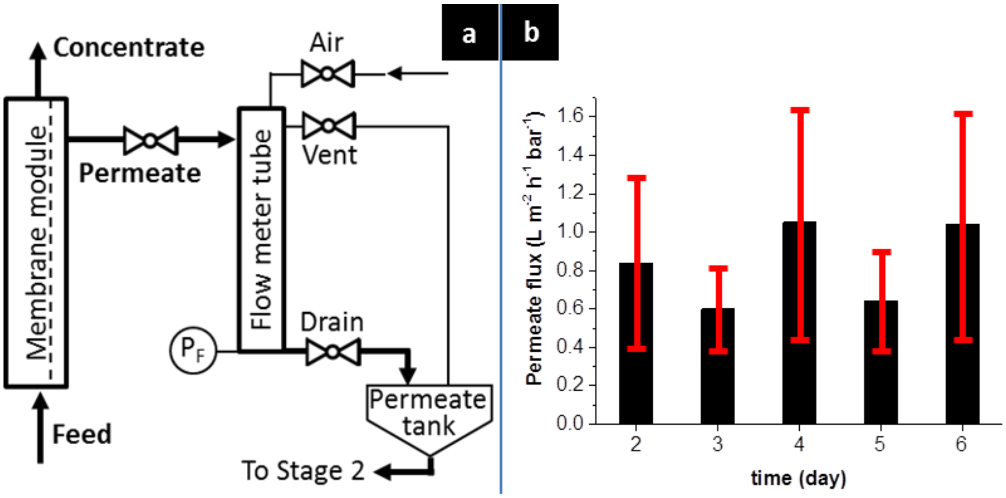


Figure 8.3.6 Stage 1 permeate flow meter (a) and average flux vs. time of G1$_N$-coated membranes (b)
(**a**) Permeate is collected in the flow meter tube (1.18” inner diameter). The pressure above P_F is converted to permeate column height. Permeate volume (product of column height and area) is used to calculate the permeate flux. (**b**) The average permeate flux does not show any sign of membrane fouling over 6 days of weak black liquor concentration at constant recovery. The high standard deviation is a result of large variations in permeate flux during permeate tube draining, backflushing, and flow reverse. Feed, weak black liquor; temperature, 85 °C; TMP, 63 psi; permeate recovery, 33%.

After adding 20 gal of weak black liquor permeate to the Stage 2 feed drum and cooling the Stage 1 feed to 44 °C (Figure 8.3.5a), 10 gal of weak black liquor was added to the Stage 1 feed drum and the weak black liquor concentration trial was continued. Over the following 6 days, permeate was collected for 12 hours each day. For safety reasons, the TMP (**c**) and temperature were decreased to ~2 psi and 70 °C, respectively, and the permeate valve was closed overnight. This allowed us to run the system continuously in order to expose the coating to the harsh, highly fouling black liquor feed for the duration of the run. From 35 to 165 hours, permeate was recycled back into the feed drum (during backflushing) and the permeate flux (**a**) did not appear to change significantly. However, flux variations were significant at constant recovery, presumably due to the system configuration.

Figure 8.3.6a shows a schematic of the Stage 1 permeate flow meter. First, weak black liquor permeate is collected in the flow meter tube, with the air, vent, and permeate valves in the closed, open, and closed positions, respectively. At a column height of 60” the air, vent, and drain valves are switched to the open, closed, and open positions. After air blows the collected permeate into the permeate tank, the valves return to their original position and the process repeats. Drainage alone does not appear to be the cause of the permeate fluctuations, as is seen during Day 1 (Figure 8.3.4a) when Stage 1 permeate is collected to feed Stage 2. When backflushing and flow reverse are introduced during constant recovery (35 to 165 h) the flux fluctuations are large. Figure 8.3.6b shows the average permeate flux during this period. Although the error is large, there is no indication of membrane fouling; there is no apparent decrease in permeate flux with time.

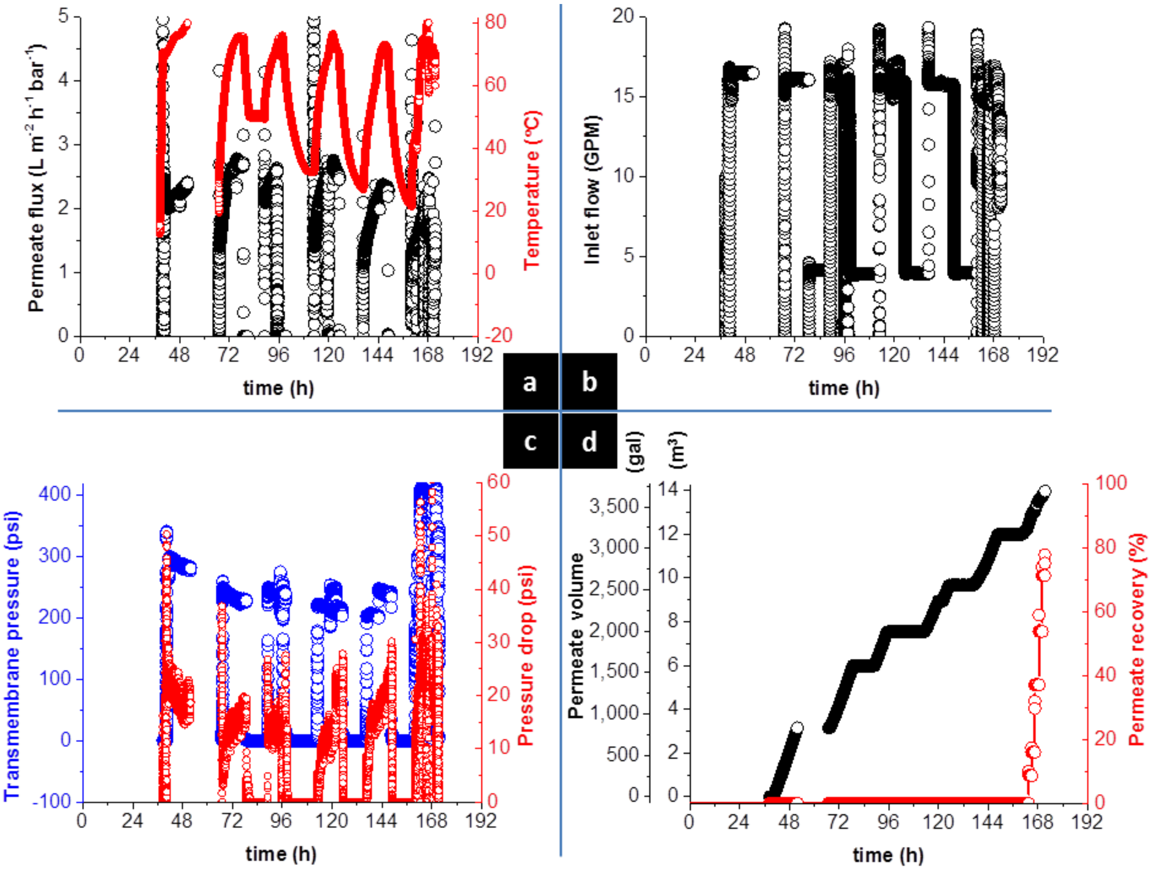


Figure 8.3.7 N1-coated Stage 2 membrane performance during 6-day Milestone 7 trial at Teledyne
Permeate flux and temperature (**a**), feed flow rate (**b**), TMP and pressure drop (**c**), and permeate volume and recovery (**d**) plots using Stage 1 weak black liquor permeate as feed.

Stage 1 coated membranes showed less than 20% drop in flux over the duration of the trial. This was expected since the $G1_N$ coating exhibits excellent fouling resistance during weak black liquor filtration. For example, we have previously shown that high MWCO uncoated membranes undergo irreversible fouling during weak black liquor concentration, while coated membranes exhibit 1) minimal fouling and 2) a permeate flux that is mainly cake layer-dependent. Thus, permeate flux is relatively constant since the permeate recovery (Figure 8.3.5d) is constant at 33% during this time period. However, as permeate was pumped to the Stage 2 feed drum (t = 165–173 hours), the permeate flux decreased to 0.34 LMH/bar as the recovery increased to 53%. It should be noted that there is significant error (~20%) in the permeate recovery due to large leaks that resulted in the loss of reject and permeate streams. Nevertheless, 108 gallons of weak black liquor penetrated the coated pores of the Stage 1 membrane and the permeate flux did not decrease until the permeate recovery increased. Since the permeate flux recovered from batch to batch without cleaning or backflushing, the coating surface is considered antifouling because no permanent fouling occurred.

Figure 8.3.7 shows the performance of the N1-coated Stage 2 membrane. Similar to the Stage 1 system, we concentrated weak black liquor at 70 °C (**a**) for 12 hours each day and we minimized the TMP (**c**) and decreased the temperature to 50 °C overnight. It should be noted

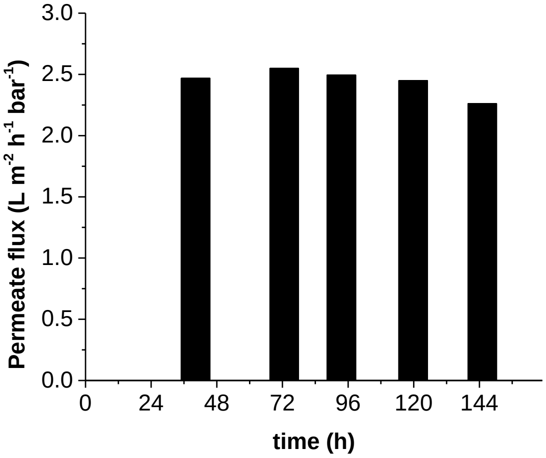


Figure 8.3.8 N1-coated Stage 2 membrane permeate flux vs. time plot at constant recovery
Feed, Stage 1 weak black liquor permeate; temperature, 70 °C; TMP, 227 (±15) psi; permeate recovery, 0%.

that we had to lower the set point temperature and TMP to account for reduced heat dissipation during hot weather (~110 °F). During the 6-day trial run at Teledyne, 14.0 m^3 of permeate penetrated the coated Stage 2 membrane pores (Figure 8.3.7d). From 38 to 163 hours the Stage 2 permeate was recycled back into the Stage 2 feed drum, thus the permeate recovery was constant. During this period, it is difficult to tell whether any membrane fouling is occurring because the permeate flux changes with temperature (**a**) and pressure (**c**). Figure 8.3.8 shows the permeate flux plotted at constant temperature and pressure. At 70 °C and 227 psi, a maximum permeate flux of 2.5 LMH/bar was observed at 73 h and a minimum of 2.3 LMH/bar was observed at 145 h. Thus, there was only an 11% decrease in permeate flux at constant recovery. Because a heat wave made it difficult to control the temperature, we had to run the Stage 2 system with the heater off on the 6th day. Also, since the target TMP was 400 psi, we did not obtain any data at 227 psi and 70 °C on that day.

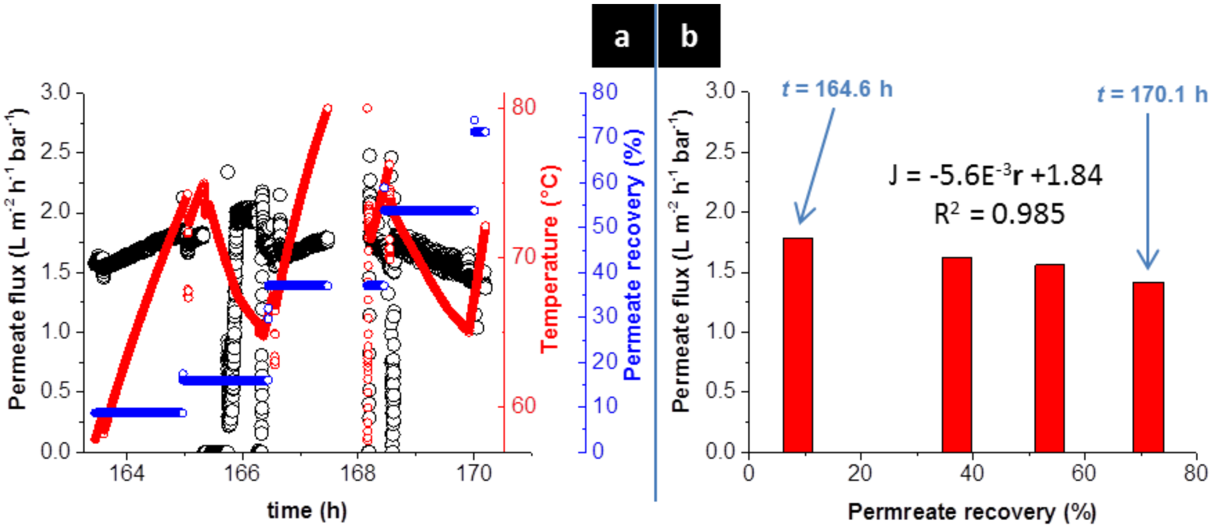


Figure 8.3.9 N1-coated Stage 2 membrane performance (a) and flux vs. recovery plot (b) at 400 psi
Feed, Stage 1 weak black liquor permeate; temperature, 70.0 (±0.1) °C; TMP, 400 (±7) psi.

At 400 psi the permeate flux, which is lower than that at 227 psi because of the increased concentration polarization at the membrane-feed interface, increased with increasing temperature and decreased with time (Figure 8.3.9a). However, the decrease in permeate flux from 164.6 h to 170.1 h was due to increasing permeate recovery, r, (Figure 8.3.9b). If we assume that permeate flux follows the linear fit, then we could approximate the flux at 400 psi ($J_{NF,400}$) to be 1.84 LMH/bar at 0% recovery. Since the flux at 200 psi is 2.26 LMH/bar and $J_{NF,400}/J_{NF,200}$ is 0.814 (at t = 145 h), we could extrapolate $J_{NF,400}$ to an initial value of approximately 2.0 LMH/bar (at t = 40 h). Therefore, the drop in permeate flux would have been close to 8.5% over the 6-day trial.

Table 8.10 Summary of streams obtained from coated Stage 1 and Stage 2 membranes

Stream	TDS (wt%)	Volume (gal) (Meas./Est.)	Recovery (%) (Meas./Est.)
WBL feed	15	60 ±6	
Stage 1 reject	20.62	15.9/18	74/70
Stage 2 reject	15.10	7.0/17	
Stage 2 Permeate	9.17	25/25	78/60

Table 8.10 summarizes the performance of the trial run at Teledyne. The coated Stage 1 membranes concentrated weak black liquor from approximately 15% to 20.62% total dissolved solids (TDS) at a permeate recovery of 70-74%. The permeate from Stage 1 was concentrated by the coated Stage 2 membrane to 15.10% at a permeate recovery of 60-78% and the final permeate had a TDS of 9.17%. The final reject stream, which is the combined black liquor reject from both stages, had a TDS of 18.9%. This concentration was 18% lower than the expected 23.1% TDS. The main reason for this was the low concentration of the Stage 2 reject. In this case the overall permeate recovery was 42-52%.

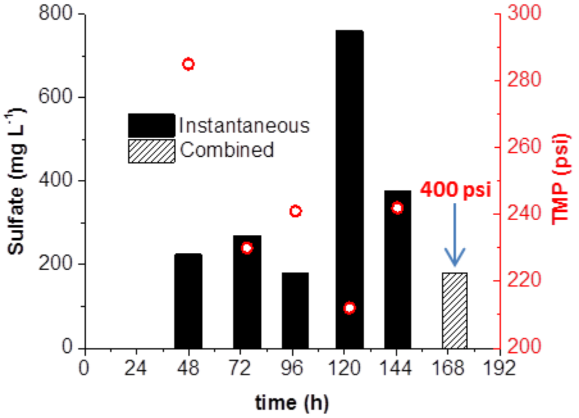


Figure 8.3.10 Sulfate concentration of Stage 2 permeate collected at 75 °C

While recirculating the permeate to the feed drum, instantaneous permeate samples were collected at a TMP of 242 (±24) psi for analysis throughout the trial. On the 6th day, Stage 2 permeate was collected at a TMP of 400 psi (58 °C < T < 68 °C) and added to a 55 gal drum. At the conclusion of the trial, a sample was collected from the combined permeate in the drum for sulfate analysis.

Figure 8.3.10 shows the Stage 2 sulfate concentration of permeate samples collected throughout the trial at Teledyne. Within the TMP range tested, the sulfate concentration generally decreased with increasing TMP. At 122 h there was a significant increase in sulfate concentration, which may have been due to either a lower TMP or a change in membrane-WBL interfacial interactions. However, since the separation efficiency recovered at 145 h, it is safe to assume that the coating remained intact. After 163 h of weak black liquor concentration, the TMP was increased to 400 psi and Stage 2 permeate was collected and added to a 55 gal drum. It should be noted that the starting feed temperature was decreased to 58 °C to account for the excessive heat in Thousand Oaks. After collecting all 25 gal of permeate at 400 psi, a sample of the combined permeate was taken from the 55 gal drum and analyzed. The sulfate concentration of the combined permeate was 180 mg L^{-1}. The apparent fouling mitigation (i.e., <11% drop in flux) and the low sulfate concentration over the course of the trial indicate that the Teledyne coating survived the harsh conditions of weak black liquor concentration.

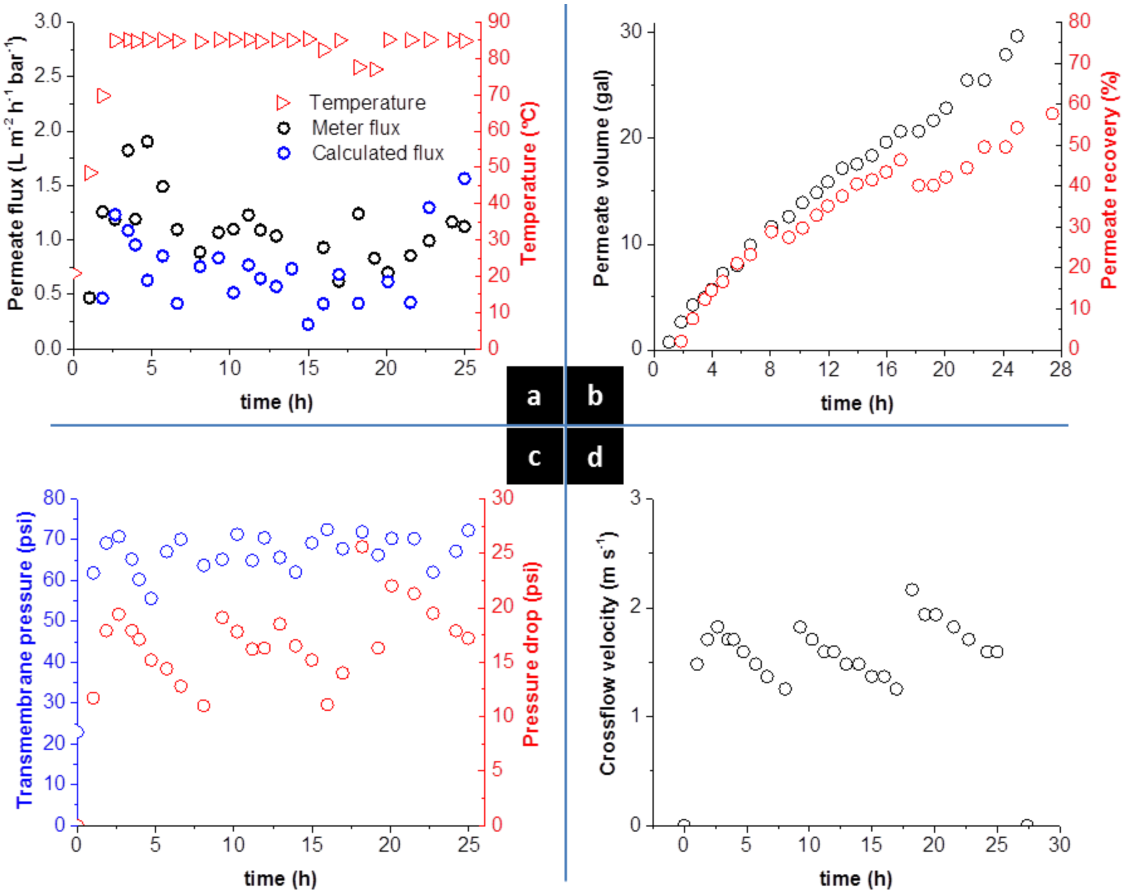


Figure 8.3.11 Stage 1 performance during WBL concentration in demo trailer at WestRock

32 gal of WBL, supplied by Evaporator #4, was concentrated using the Stage 1 system. The Stage 1 permeate was added to the Stage 2 feed drum. (**a**) Temperature was increased to 85 °C during WBL concentration. The permeate flux measured by the flow meter (black circles) was slightly higher than the flux calculated by multiplying the flow rate of the transfer pump (that transferred the Stage 1 permeate to the Stage 2 feed drum) by the time (blue circles). (**b**) The total permeate volume obtained using the meter flux (black) was 45 gal, while the permeate volume obtained from the calculated flux (red) was 30 gal. (**c**) The average transmembrane pressure and pressure drop were maintained at 67 psi and 17 psi, respectively, during WBL concentration. (**d**) Crossflow velocity peaked at 1.8 m s^{-1} and decreased to 1.3 m s^{-1} after 8 h of WBL concentration. The crossflow increased after adding 7.5 gal of WBL at 8 h. The crossflow increased to 2.2 m s^{-1} after adding 8.5 gal of WBL at 18 h, and decreased to 1.6 m s^{-1} at 25 h.

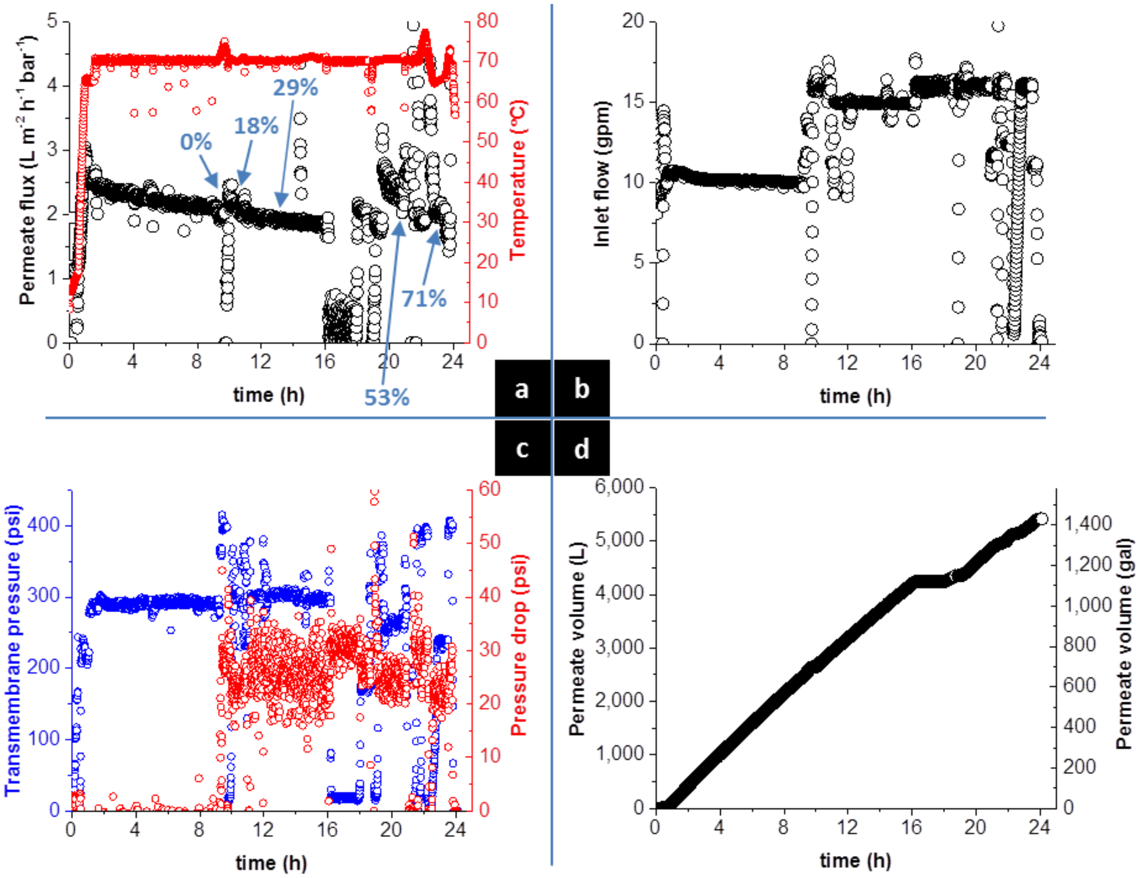


Figure 8.3.12 Stage 2 performance during WBL concentration in demo trailer at WestRock
29 (±3) gal of Stage 1 permeate was concentrated using the Stage 2 system. (**a**) Feed temperature was increased to 70 °C. The permeate flux decreased to 2.04 LMH/bar (300 psi, 70.8 °C) at 18% permeate recovery (blue arrows), 1.88 LMH/bar (309 psi, 70.2 °C) at 29% recovery, 2.16 LMH/bar (312 psi, 71.0 °C) at 53% recovery, and 1.73 LMH/bar (389 psi, 66.7 °C) at 71% recovery. (**b**) Inlet flow increased from 10 gpm (*t* = 0-10 h) to 15 gpm as the feed volume increased. (**c**) Average transmembrane pressure and pressure drop vs. time. Target TMP varied between 200-300 psi during constant recovery and was increased to 400 psi during Stage 2 concentration. (**d**) The total measured permeate volume through the pores was 1,450 gal. The total permeate collected was 19 (±2) gal.

Upon completion of the 6-day trial run at Teledyne, the systems were drained, rinsed with water, and the trailer was towed to WestRock in Covington, VA. A hose supplying weak black liquor (from Evaporator #4) was connected to the Stage 1 feed drum and electrical connections supplying 3 phase 480 VAC (60 A) and single phase 240 VAC (80 A) were made. 10 gal of weak black liquor was cooled in two 5 gal carboys and added to the Stage 1 feed drum. It should be noted that the black liquor was much foamier than what we have seen at Teledyne. We slowly added 22 gal of weak black liquor, while circulating the feed to prevent thermal shock, and increased the temperature to 85 °C at a rate of 0.4 ° min^{-1}.

Figure 8.3.11a shows the permeate flux measured by the meter shown in Figure 8.3.6a. The flux fluctuated significantly and appeared to be higher than the flux that was calculated based on the amount of permeate that was pumped to the Stage 2 feed drum. The foaminess of the permeate is believed be the culprit in the measured flux, but the exact mechanism is unknown. However, the calculated flux is in agreement with the volume of permeate collected (Figure 8.3.11b). At a TMP of 67 psi (**c**) the 5-hour average permeate flux decreased from 0.87 to

0.64 LMH/bar over 25 hours; the flux decreased by 26% as the permeate recovery increased to 58%. The drop in flux was expected since the total membrane resistance increases with increasing permeate recovery. Ideally, if the feed from the 6-day run at Teledyne was the same as the feed supplied by evaporator #4, then the permeate at a given run time and/or recovery could be compared to determine the extent of fouling during the 6-day run. Unfortunately, the WestRock feed was different (i.e., foamier). Nevertheless, after concentrating weak black liquor for more than 6 days at Teledyne, the average permeate flux during the first 5 hours at WestRock was 0.87 LMH/bar (at 17% recovery), which is 94% of the maximum flux measured at Teledyne (t = 8 h). One reason for the 6% drop in flux (compared to t = 8 h) was the lower crossflow velocity (Figure 8.3.11d). The high foam content of the feed made pumping difficult, which resulted in a 34% drop in crossflow velocity; we have previously shown that the permeate flux decreases with decreasing crossflow velocity. The crossflow velocity decreased with decreasing feed volume and increased when weak black liquor was added (t = 8 h and 18 h). Since the flux recovered after the 6-day trial without cleaning or backflushing (i.e., rinsing with water only), it is safe to conclude that permanent membrane fouling on coated surfaces and pores was mitigated.

Figure 8.3.12 shows the performance of the Stage 2 system at WestRock. The permeate flux (**a**) equilibrated around 2.48 LMH/bar within the first hour after the TMP (**c**) reached 300 psi. At constant recovery (t = 0-10 h), the flux decreased at a rate of 0.73 LMH/bar/h to 2.09 LMH/bar. As Stage 1 permeate was added and the Stage 2 feed drum began to foam, Stage 2 permeate was collected thereby increasing the recovery. From 0-29% permeate recovery the permeate flux decreased at a rate of 0.02 LMH/bar/%$_{\text{recovery}}$. No significant increase in flux is apparent when the inlet flow (**b**) is increased (t = 10 h). Thus, the 16% drop in flux is seemingly due to intermediate pore blocking. At 53% recovery the permeate flux was 2.16 LMH/bar. When the TMP was increased to 400 psi and the Stage 2 feed was concentrated during the final hours, the permeate flux dropped to 1.73 LMH/bar at 71% permeate recovery.

Table 8.11 Summary of streams obtained from coated Stage 1 and Stage 2 membranes at WestRock

Stream	Volume (gal) (Meas./Est.)	Recovery (%) (Meas./Est.)
WBL feed	48 ±5	
Stage 1 reject	19.2/21.4	60/55
Stage 2 reject	4.3/6.3	
Stage 2 Permeate	18.3/20.3	78/76

Despite the fact that flux decreases with increasing permeate recovery, the coating displayed extraordinary fouling resistance. Previously we have shown that the performance of uncoated membranes is hindered within hours of concentrating weak black liquor because of excessive fouling. Furthermore, much of the observed fouling has been found to be irreversible; most of the permeate flux does not recover without the use of cleaning chemicals. However, the coated membranes tested throughout the life of this program show little to no permanent fouling. We have demonstrated this during the TRL 5 demonstration at Teledyne and WestRock. When weak black liquor was concentrated for >6 days using the $G1_N$ coating the

Stage 1 permeate flux decreased to a minimum of 0.34 LMH/bar, but only after concentrating the weak black liquor to 53% permeate recovery. However, after rinsing with water and running Stage 1 at WestRock in Covington, VA, the permeate flux recovered to >0.87 LMH/bar. Since no chemical or mechanical cleaning processes were carried out, the results suggest the following: 1) weak interactions between the weak black liquor and the $G1_N$ coating mitigated membrane fouling and 2) the flux drop was due to increased membrane resistance with increasing permeate recovery.

Similarly, the Stage 2 membrane flux peaked at 2.5 LMH/bar during the 6-day run at Teledyne. During the final hours the flux decreased to a minimum of 1.42 LMH/bar at 400 psi TMP and 70% recovery. However, when Stage 2 was rinsed with water and run at WestRock, the permeate flux recovered to 2.5 LMH/bar. Thus, the N1 coating is also antifouling in nature because flux recovery was observed without implementing any cleaning processes. Therefore, the flux drop observed at high permeate recovery was mainly a result of increased osmotic pressure, which decreases the effective pressure differential across the membrane.

8.3.3 Business case for membrane-based weak black liquor concentration

We developed a detailed cost model, following one prepared by the U.S. Bureau of Reclamation to cost reverse osmosis membranes for desalination, that includes ultrafiltration and nanofiltration processes [11]. Appendices A1-A3 summarize the cost based on this model. Based on a flow rate of 200 m^3 h^{-1}, which is typical for a medium-sized paper mill, the Stage 1 and Stage 2 permeate flow rate used in the model are 140 m^3 h^{-1} and 84 m^3 h^{-1}, respectively. TRL 5 results obtained during the trial were used to calculate the required membrane area for each stage. Assuming a weak black liquor permeate flux of 5 LMH at 100 psi TMP, 40,000 m^2 is required for Stage 1. At a permeate flux of 40 LMH at 400 psi TMP, 2,800 m^2 is required for Stage 2. As a result, the 5-year annualized capital cost and O&M cost are much greater than those of Stage 2 (Table 8.11). Since the 1.2 MMBtu/adst energy savings of concentrating weak black liquor to 30% solids corresponds to an annual saving $5.1M (based on $0.07/kWh) and the annualized cost of the membrane system is $8.0M, the membrane-based separation process is not feasible.

Table 8.12 Total capital, 5-year annualized capital, O&M, and annualized cost based on TRL 5 demo

Stage	Capital cost (Total / 5-yr ann.)	O&M Cost	Annualized cost
Stage 1	$13.1M/$2.6M	$4.71M	**$7.33M**
Stage 2	$0.57M/$0.11M	$0.59M	**$0.70M**
Total	**$13.7M/$2.7M**	**$5.3M**	**$8.0M**

Despite the fact that the Stage 1 performance of this single experiment was unsatisfactory, membrane-based concentration of weak black liquor could be economically feasible if the Stage 1 flux increases above the break-even point of 5.9 LMH (Figure 8.3.13). Our optimized TRL 4 coating performance, developed during budget period 2, is well above this point. Although this coating produced an average flux that was slightly less than the expected 20 LMH (Table 8.9), the annualized Stage 1 cost would be $2.0M and the payback period for the total package would be 2.8 years (assuming a Stage 2 flux of 20 LMH) with the optimized coating. Results from unoptimized TRL 4 coatings indicate that the Stage 1 annualized cost and payback period would be $3.0M and 4.7 years, respectively

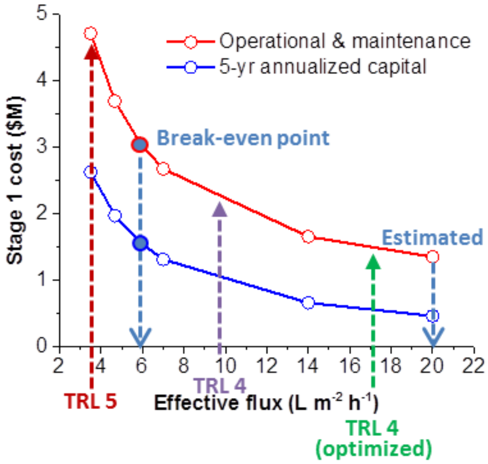


Figure 8.3.13 Stage 1 cost
Break-even point occurs at a Stage 1 flux of 5.9 LMH, assuming that the Stage 2 flux remains at 30 LMH.

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9. BENEFITS ASSESSMENT

According to Agenda 2020 Technology Alliance, which is an industry-led consortium that promotes the development of advanced technologies for the pulp and paper industry, the goal is to double the energy productivity and reduce the manufacturing energy demand from 23 million Btu per ton in 2012 to 11.5 million Btu per ton by 2030 [13]. This will also result in increased profitability at the paper mills due to reduction of energy costs. Since liquor evaporation is the highest energy consuming process in pulp mills, current heat-driven approaches to concentrating black liquor have been deemed inadequate in reducing energy and achieving a sustainable approach for pulp and paper manufacturing [13]. On the other hand, pressure-driven separation of water from black liquor using membranes could reduce energy usage by 55 trillion Btu year^{-1} if the first two evaporators are replaced, which would allow weak black liquor to be concentrated from about 15% solids to 26% solids without the use of thermal evaporation [1]. Assuming a carbon dioxide emission factor of 7.03×10^{-4} metric tons per kilowatt hour of electricity and 100% efficiency during the electric heating of steam, which currently drives the thermal concentration of weak black liquor, replacing the first two evaporators with membranes would decrease the carbon dioxide emissions by more than 11.3 million metric tons CO_2 per year. In addition to increasing the efficiency of paper manufacturing, the cost savings would be greater than $1B per year [8].

10. COMMERCIALIZATION

Teledyne is currently conducting a higher TRL and commercialization effort for municipal water filtration market using the coating technology developed under a prior DARPA program for water treatment. This effort will be leveraged for market penetration strategies to further refine our commercialization approach for this project. Given the size of the paper and pulp market and the relatively simple coating operation, we do not anticipate needing other markets to justify a commercially feasible coating operation. However, data from other markets from our parallel commercialization effort will certainly help to further establish a robust business case. We have built fully automated skids for seawater filtration and are currently undertaking a commercialization effort for filtering highly contaminated ground water for municipal water districts. Based on these efforts, which are similar in scope and size to this project, we estimate that our scope, schedule and budget are commensurate with stated objectives. In addition, we are currently commercializing our coatings for municipal water filtration, which will be leveraged. Teledyne provides additional leverage through: (i) internally funded commercialization efforts focused on municipal water filtration and antifouling of streamer cables used in oil exploration, and (ii) a DARPA funded effort in seawater desalination. Teledyne has built world class capabilities in membrane filtration and coatings through these ongoing efforts.

11. ACCOMPLISHMENTS

We have successfully developed antifouling coatings and demonstrated multistage concentration of weak black liquor. The coatings withstand weak black liquor under the environmental conditions of the pulp and paper mill. Crossflow performance was significantly improved with the coating at pH greater than 13 and temperatures greater than 80 °C. At 84 °C the weak black liquor permeate flux of low molecular weight cutoff polymeric ultrafiltration membranes has been doubled with the addition of the coating.

Laboratory-scaled coated tubular ceramic membranes outperform uncoated membranes. When concentrating 10 gallons of weak black liquor at 85 °C at a transmembrane pressure of 60 psi, the uncoated membrane exhibits a 10% drop in permeate flux after 0.8 hours (or 6% permeate recovery). On the other hand, in addition to displaying higher permeate flux, the membrane coated with our $G1_N$ coating does not exhibit a 10% drop in flux until 3 hours (or 20% recovery). After coating ceramic membranes with our coating, hardwood and softwood weak black liquor from WestRock Company was heated to >80 °C and filtered continuously for 3 days without any observable fouling or need for backflushing. Permeate flux was measured for 72 hours, after processing a total of 100 gallons of weak black liquor permeate, and no drop in flux was observed at constant recovery.

A report of the optimal parameters for field testing using the pilot unit was completed. Optimal parameters for in-place coating and backflushing were documented. A trailer was customized and equipped with the TRL 5 multistage weak black liquor concentration system. A cleaning and coating system was integrated into the trailer and coupled with the multistage system and the membranes were coated in-place. Weak black liquor was concentrated in the TRL 5 system for 6 days at Teledyne with less than 20% drop in flux at constant recovery. The Stage 1 flux drop was negligible and the Stage 2 flux drop was 11% at constant recovery. The system was rinsed with water and the trailer was towed to WestRock in Covington, VA. WestRock electrical connections were made and weak black liquor plumbing was successfully integrated and the paper mill approved the trial run after a safety inspection. The weak black liquor permeate flux recovered after the 6-day run at Teledyne without cleaning, indicating that any observed flux drop was not due to permanent fouling. We successfully demonstrated the antifouling properties of the coating using weak black liquor instantaneously supplied by an operational paper mill.

12. CONCLUSIONS

Weak black liquor has been concentrated using membranes coated with antifouling sacrificial coatings. Without the coating, weak black liquor irreversibly fouls membranes and the flux decreases by 20% in less than three hours. However, our coating mitigates membrane fouling, allowing coated membranes to produce a high permeate flux for longer periods of time. Fouling mitigation has been attributed to strong interactions between water and the coating, which cause weak black liquor foulants to adhere weakly to the coated surface. Any drop in flux observed with coated membranes is reversible; the flux recovers, without the use of cleaning chemicals, upon addition of fresh weak black liquor. The coating can be continuously stripped and recoated in-situ without any drop in performance.

Membrane-based concentration has been demonstrated using a two-stage process. The first stage separates high molecular weight organics from weak black liquor using ultrafiltration membranes, while the second stage separates low molecular weight organic molecules and divalent salts form weak black liquor permeate using nanofiltration membranes. Flux sustainability and rejection capabilities have been significantly enhanced using our coatings. Although these enhancements have been consistent throughout the life of the program, the first stage membrane performed poorly during the WestRock demonstration and the annualized capital, operational, and maintenance cost calculated based on those results make the process economically unfeasible. Unfortunately, we ran out of time and resources and we were forced to use an unoptimized coating during the trial. To perform as it has previously, the coating requires a series of conditioning steps that vary with each system geometry. If we tune the conditioning steps to the scaled-up system, then the Stage 1 membrane would perform as it has over the life of the program and the annualized capital, operational, and maintenance cost for Stage 1 would be \$2.0M and the payback period for the complete system would be 2.8 years.

13. RECOMMENDATIONS

Although significant barriers and challenges have been overcome and resolved to enable pressure-driven weak black liquor concentration, we must first repeat the trial with the optimized TRL 5 Stage 1 coating and confirm the economic gain and energy savings. It should be noted that all of our experiments throughout the program show good performance except the one trial run. Nevertheless, this technology requires a TRL 7 pilot-scale implementation in an operational pulp and paper mill for extended periods (3 to 6 months) to create buy-in from the paper mills because TRL 5, which has been achieved through this program, is too risky for adoption by the pulp and paper industry. A TRL 7 demonstration would enable adoption of weak black liquor membrane-based concentration by addressing critical concerns such as: (i) the durability and longevity of the coating during operation at the pulping mill over a practical period of time (3 to 6 months); (ii) the performance of the membrane system itself under harsh conditions (although the chosen membrane materials are resistant to hot weak black liquor, performance over extended period is unknown); (iii) coating scale-up process for several membrane modules connected in series configuration, each with standard 8 inch diameter spiral-wound membrane modules that contain 25 square meters of membrane area. When scaling up the coating process from a single 4" diameter spiral-wound membrane module to six industrial sized 8" diameter membrane modules in a six-element housing, the effect of weak black liquor filtration through the last few series-connected membranes must be determined since the weak black liquor becomes increasingly concentrated as it travels from one module to the next. Also, the performance, as the type of wood chips added to the digester varies throughout the year, needs to be determined. The quality of membrane permeate must be determined as the type of wood chips vary and from series-connected membrane modules to ensure adequate washing.

Additional concerns from the pulp and paper industry must be addressed. One concern is if membrane-based concentrated black liquor and permeate streams have any effect on upstream and/or downstream processes. Another is how the membrane-based weak black liquor concentration process is affected in worst-case operating conditions at the mill, for example if black liquor from the digester is fed to the membrane system at 95 °C. It is therefore necessary to mature the technology to TRL 7 to address these concerns and to create acceptance of membrane-based weak black liquor concentration by the industry. Therefore, we propose three areas of research to enable the adoption: (i) concentration of weak black liquor using a system comprised of coated industrial-sized membranes with six series connected modules, (ii) demonstrating the black liquor concentration performance and fouling resistance, and (iii) demonstrating effective brownstock washing by using permeate that is produced by the membrane system to wash the pulp using a four-stage belt washer. This project would require two years to achieve TRL 7 and acceptance by the pulp and paper industry.

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Appendices

A.1 Economic model based on WestRock demonstration

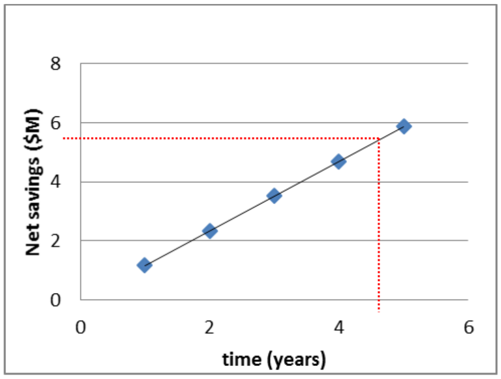
Below is a summarized version of the economic model used to calculate the cost of membrane-based concentration of weak black liquor. The total since the total annualized cost is greater than the energy savings, the process is not economically feasible.

		Stage 1	Stage 2
Backwash frequency	min	20	0
Average TMP	kPa	700	2750
Sets of replacement membranes		1	1
Backwash flux	LMH	10	0
Number of backwash per day		72	0
Total time per backwash	min	3	0
Volume consumed by backwash	L/m^2	0.5	0
Offline time - backwash	min/day	216	0
Offline time - integrity test	min/day	20	0
Offline time - cleaning	min/day	80	80
Total offline time	min/day	316	80
Percent of time offline		0.22	0.22
Recovery	%	70	60
Effective LMH		3.5	30
Membrane area	m^2	40000	2800
Number of membranes		3738	262
Number of vessels		623	44
Total membrane cost	$	5246105.92	227227.41
Total capital cost	$	13115264.80	568068.54
Annualized capital cost (5 yr)	$/yr	2623052.96	113613.71
Membrane replacement cost	$/yr	262305.30	37871.24
Energy usage- feed delivery	KWh/day	400	600
Energy usage-recirculation	KWh/day	250	0
Energy cost for pumping	$/yr	23725	21900
Annual maintenance cost	$/yr	450000	100000
Chemical cost per clean	$	28960	2027.2
Waste disposal cost per clean	$	2811.79	196.83
Number of cleans per year		120	120
Cleaning/waste disposal cost	$/yr	3812614.97	266883.05
Total personnel cost	$/yr	160000	160000
Total O&M cost	$/yr	4708645.26	586654.28
Total cost	$/yr	7331698.22	700267.99
Total annualized cost (5 yr)	$/yr	8,031,966.21	
Energy savings	$/yr	5,100,000	
Payback period	yr	N/A - Net loss	

A.2 Economic model based on TRL 4 coating

Data obtaining using scaled-up TRL 4 coated membranes show an annual net savings of $1.18M per year and a payback period of 4.7 years.

		Stage 1	Stage 2
Backwash frequency	min	20	0
Average TMP	kPa	700	2750
Sets of replacement membranes		1	1
Backwash flux	LMH	10	0
Number of backwash per day		72	0
Total time per backwash	min	3	0
Volume consumed by backwash	L/m^2	0.5	0
Offline time - backwash	min/day	216	0
Offline time - integrity test	min/day	20	0
Offline time - cleaning	min/day	80	80
Total offline time	min/day	316	80
Percent of time offline		0.219	0.219
Recovery	%	70	60
Effective LMH		9.84	20
Membrane area	m^2	14228	4200
Number of membranes		1330	393
Number of vessels		222	65
Total membrane cost	$	1865992.96	340841.12
Total capital cost	$	4664982.40	852102.80
Annualized capital cost (5 yr)	$/yr	932996.48	170420.56
Membrane replacement cost	$/yr	93299.65	56806.85
Energy usage- feed delivery	KWh/day	400	600
Energy usage-recirculation	KWh/day	250	0
Energy cost for pumping	$/yr	23725	21900
Annual maintenance cost	$/yr	450000	100000
Chemical cost per clean	$	10300.81	3040.80
Waste disposal cost per clean	$	1000.13	295.24
Number of cleans per year		120	120
Cleaning/waste disposal cost	$/yr	1356113.05	400324.57
Total personnel cost	$/yr	160000	160000
Total O&M cost	$/yr	2083137.69	739031.43
Total cost	$/yr	3016134.17	909451.99
Total annualized cost (5 yr)	$/yr	3,925,586.16	
Energy savings	$/yr	5,100,000	
Payback period	yr	4.7	



A.3 Economic model based on optimized TRL 4 coating

Data obtaining using scaled-up optimized TRL 4 coated membranes show an annual net savings of $1.57M per year and a payback period of 2.8 years.

		Stage 1	Stage 2
Backwash frequency	min	20	0
Average TMP	kPa	700	2750
Sets of replacement membranes		1	1
Backwash flux	LMH	10	0
Number of backwash per day		72	0
Total time per backwash	min	3	0
Volume consumed by backwash	L/m^2	0.5	0
Offline time - backwash	min/day	216	0
Offline time - integrity test	min/day	20	0
Offline time - cleaning	min/day	80	80
Total offline time	min/day	316	80
Percent of time offline		0.219	0.219
Recovery	%	70	60
Effective LMH		17.2	10
Membrane area	m^2	8140	8400
Number of membranes		761	785
Number of vessels		127	131
Total membrane cost	$	1067521.55	681682.24
Total capital cost	$	2668803.88	1704205.61
Annualized capital cost (5 yr)	$/yr	533760.78	340841.12
Annualized cost of replacement	$/yr	53376.08	113613.71
Energy usage- feed delivery	KWh/day	400	600
Energy usage-recirculation	KWh/day	250	0
Energy cost for pumping	$/yr	23725	21900
Annual maintenance cost	$/yr	450000	100000
Chemical cost per clean	$	5893.02	6081.60
Waste disposal cost per clean	$	572.17	590.48
Number of cleans per year		120	120
Total clean cost including waste	$/yr	775822.81	800649.14
Total personnel cost	$/yr	160000	160000
Total O&M cost	$/yr	1462923.89	1196162.85
Total cost	$/yr	1996684.67	1537003.97
Total annualized cost (5 yr)	$/yr	3,533,688.64	
Energy savings	$/yr	5,100,000	
Payback period	yr	2.8