

Use of Color Removal Membranes on Waste Water Treatment in the Pulp and Paper Industry

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ABSTRACT

Membrane technology has become widely accepted in many seawater and brackish water treatment applications and these days it is more often used also in variety of waste water treatment processes as the final treatment step of water re-use process. In addition to traditional use of membranes for desalination, new requirements have been challenging membrane manufacturers to develop special products for selective removal of hardness, natural organic matter, color, fats, proteins and other macromolecular species. Nanofiltration (NF) membranes are usually used for selective removal of certain species in applications when TDS reduction is not a priority.

Hydranautics has developed a variety of NF membranes for such applications with different characteristics. In the 1980's, HydraCoRe membranes were developed to separate color from soya sauce. Since its first introduction, the HydraCoRe membranes are now manufactured in three varieties with different flow, salt rejection and MWCO. These membranes have already been successfully used on color and organic matter removal applications. One of these applications is the treatment of waste water for the pulp and paper industry. This industry is known as producer of high volumes of waste water with high pH and high color. It is difficult to treat by biological treatment process, as it contains a significant amount of lignin and chlorinated fragments from the bleaching process, high salt and organics content, and fine colloidal material. Pilot tests have been performed by Hydranautics using hollow fiber Ultrafiltration (UF) pretreatment to spiral wound NF membranes to treat this type of water. The HydraCoRe membrane reduced feed color from a dark brown color as high as 12,000 Pt-Co color units (PCU) to < 25 PCU in the permeate which was < than the 50 PCU required to allow discharge to the local river. This paper will present results of pilot tests and discuss future potential of using HydraCoRe membranes in this type of applications.

Keywords: ultrafiltration, nanofiltration, color removal, pulp & paper mill wastewater

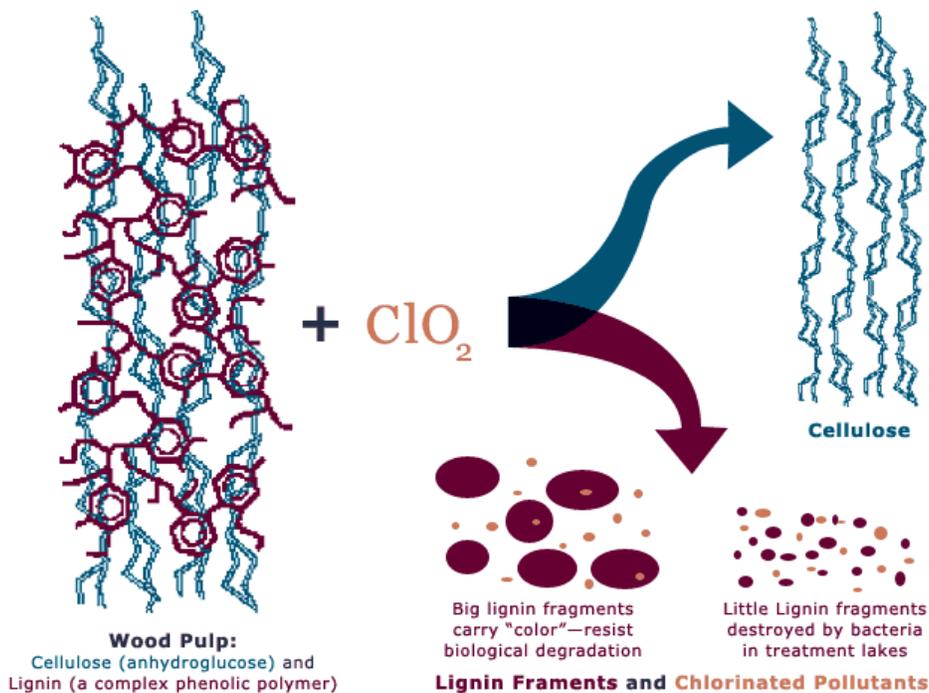
INTRODUCTION

Membrane technology has become widely accepted for the treatment of variety brackish water sources thanks to favorable economics of use low pressure – energy saving membranes together with ability of these membranes selectively remove dissolved species. Over the years, the membrane technology has found its way not only into drinking and industrial water sector, but has also become very frequently part of municipal and industrial waste water treatment process as well as variety of special industrial applications, when membranes are used to recover process chemicals for their further re-use in manufacturing processes. Demands for development of membranes with specific performance continue to increase as water quality requirements tighten and water treatment system designs become more complex. Such demands lead to development of new reverse osmosis (RO) membranes with higher rejection for better dissolved salts and boron removal. In addition to this performance trend, new applications have developed which require selective removal of certain dissolved species, such as hardness, natural organic matter (NOM), pesticides and organic material which causes color. In these applications engineers desire high removal of specific contaminants, but at the same time want to maintain some level of salts in the water so it does not become aggressive, which can cause corrosion problems with piping in the distribution network. A variety of NF membranes are available which successfully soften waters by removal of calcium and magnesium. Such membranes are often characterized by low monovalent ion rejections (80-90%), but high divalent ion rejections (>95%). These NF membranes also have good selectivity for removal of naturally occurring organic compounds as well as iron.

There are, however, other surface water sources which have fairly low levels of hardness and salinity, but have high levels of organic material which cause color. Organic material can be found in groundwater sources which have surface water intrusion, or groundwater sources which are influenced by decomposing vegetative materials. The contamination of these waters is measured in terms of color units. Different NF membranes are required for the treatment of these colored waters low in salinity in order to keep treated water out of aggressive state. Furthermore, there are also applications, where color must be removed from waste water before it can be discharged to river stream.

One of such application is treatment of waste water produced by pulp and paper industry. [1] This type of industry is a very water-intensive and can consume as high as 60m³ of freshwater per metric ton of paper produced. The generation of wastewater and the characteristics of pulp and paper mill effluent depend upon the type of manufacturing process adopted. Hence, the treatments of the wastewaters from different mills become complicated because no two paper mills discharge identical effluents due to different combination of unit processes involved in the manufacturing of pulp and paper. Wastewater from pulp and paper mills constitutes a major source of aquatic pollution since it contains high organic substances causing high biochemical oxygen demand (BOD), high chemical oxygen demand (COD), extractives (resin acids), chlorinated organics, suspended solids, metals, fatty acids, tannins, lignin and its derivatives causing high brown color, etc.[1]

Picture1: Bleaching Process in Pulp and Paper Industry



A NF pilot plant was operated at a pulp & paper mill in the southeast of United States for the reduction of color from industrial waste stream of extremely dark brown-color of 5,000 to 18,000 PCU prior to discharge into a local river. The plant was also facing mandates from the state to reduce the draw of water from the aquifer wells due to the extensive drought conditions prevalent in 2007 and 2008 in this part of the United States. The immediate urgency to institute a full scale solution was however reduced when heavy rains broke the drought in 2009. The mill continues to shift priorities with the recent economic downturn and the evaluation of spending on projects will be balanced with need to meet environmental guidelines.

The plant process engineering department was presented with a novel HYDRACoRe50 spiral wound nanofiltration (NF) element made of highly charged sulfonated polyethersulfone (SPES) membrane. This membrane had been successfully used in the past in both industrial and municipal applications where the removal of color was desirable. The membrane also had to be more "rugged" than a conventional polyamide membrane in regards to low and high pH tolerance for both service and cleaning modes and had to be resistant to sanitizing oxidants like chlorine.

The feed source was not only high in color but also had a high feed pH at 10.3, up to 600 mg/l TOC (total organic carbon), up to 10 mg/l of TSS (total suspended solids), turbidity up to 6 NTU, up to 2,400 mg/l TDS (total dissolved solids), temperature as high as 49^o C, and there could be residual chlorine levels above 0.1 mg/L from plant operations. The aggressive cleanings would consist of HCl (hydrochloric acid) at pH of 2.0 and Cl₂ (chlorine) concentrations of 100 mg/L.

HYDRACoRe NF MEMBRANE CHARACTERISTIC

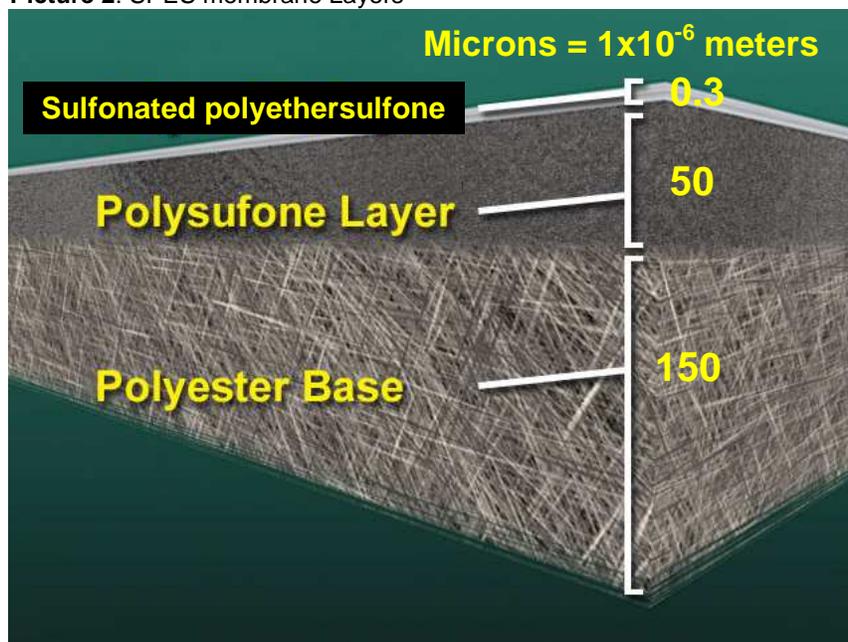
In 1980's, first HydraCoRe NF membrane with MWCO of 1000 Daltons was developed by Nitto Electric Industrial Co. for color separation from soya sauce. This membrane has relatively low rejection of ionic species, especially in the presence of divalent cations, but high rejection of low molecular weight organic compounds [2]. HydraCoRe membranes are now available in three different types with various permeate flow, salt rejection and MWCO.

Table 1 – HydraCoRe Membranes Range

Model	Area, ft2 (m2)	Flow (GPD)			Rejection			MWCO (Dalton)	Standard Test Conditions	
		Nominal	Min	Max	Nominal	Min	Max		Pressure (PSI)	Salinity (mg/L NaCL)
HYDRACoRe 10	385 (36)	17,000	13,600	20,400	20%	5%	40%	1400	50	500
HYDRACoRe 50	385 (36)	9000	7,200	10,800	60%	45%	70%	700	75	500
HYDRACoRe 10-LD	365 (34)	16,000	12,800	19,200	20%	5%	40%	1400	50	500
HYDRACoRe 50-LD	365 (34)	8,500	6,800	10,200	60%	45%	70%	700	75	500
HYDRACoRe 70pHT	385 (36)	9,000	7,200	10,800	20%	5%	40%	720	145	2000

HydraCoRe is a specially formulated sulfonated polyethersulfone (SPES), thin film composite membrane. The properties of the membrane are unique and well-suited to color removal applications. The absence of a typical polyamide barrier layer results in improved fouling resistance, chemical cleanability and disinfection compatibility [2].

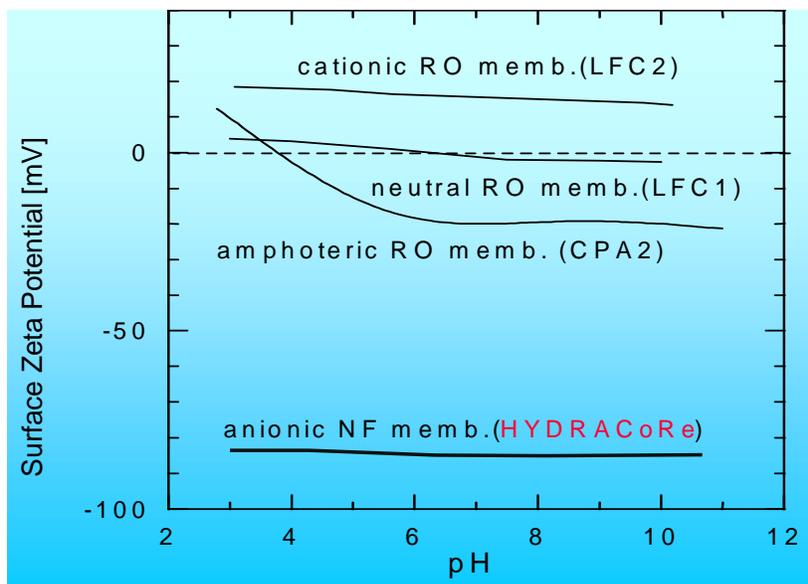
Picture 2: SPES membrane Layers



SURFACE CHARACTERIZATION

The charge on the surface of the HydraCoRe membrane is strongly negative due to the presence of the sulfonate functional groups. Streaming potential measurements for this membrane are given in Figure 1, as well as comparative values for standard and low fouling polyamide thin film composite membranes. This data shows (Chart 1) that the SPES membrane has a surface zeta potential charge of -85 mV over a pH range of 3 to 11. In comparison, a conventional polyamide RO membrane had a zeta potential of $+10$ mV at pH 3 and -20 mV for pH 6 or greater. The large negative charge of the SPES membrane is desired since the NOM in most source waters is composed of humic acids. It is expected that the strong negative charge of the membrane surface will repel the negatively charged humic acid compounds, and thus minimize fouling by organic adsorption [2].

Chart 1: Surface Zeta potential measurement for RO and HydraCoRe NF membranes

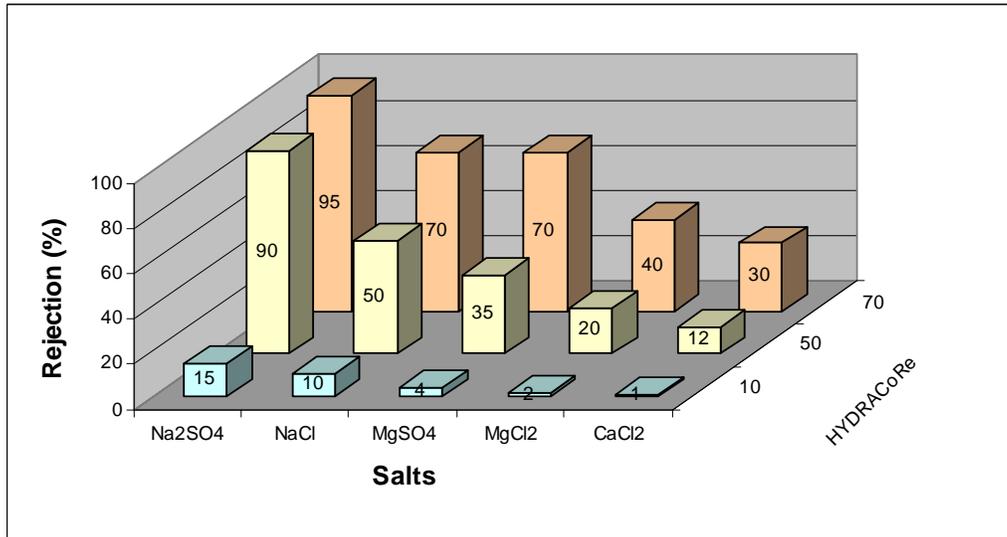


ION SEPARATION PROPERTIES

The SPES membrane is a fairly loose NF membrane, and derives a significant degree of dissolved salt rejection from the charge repulsion mechanism. The presence of various ion species does have a dramatic affect on the actual selectivity of the membrane. This is shown in Chart 2. The rejection of each ionic solution was determined in cell tests with flat sheet pieces of membrane at standard test conditions as described in Table1. The effect of the ion size and charge on the membrane selectivity is clearly seen Chart 2. The rejection for sodium chloride is 10 - 70% while the rejection of sodium sulfate is 15 - 95% depending on membrane type. This can be explained by the strong negative charge of the membrane surface having greater repulsion of the large, divalent sulfate ion, compared to the smaller monovalent chloride ion. In contrast, the rejection of a calcium chloride solution was only 1 - 30% compared to 10-70% rejection for sodium chloride. In this case the larger divalent calcium ion results in a lower membrane rejection compared to the smaller, monovalent sodium. The factor important for causing this effect is the stronger attraction between the membrane surface and the positively

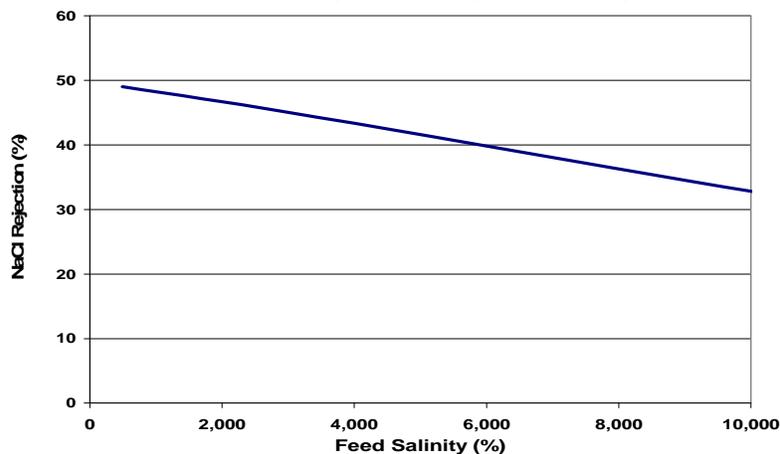
charged calcium ion. In particular, the charge at the membrane surface is thought to be somewhat neutralized by the calcium ions, thus minimizing the rejection due to charge [2].

Chart 2: Rejection characterization of various ionic pair solutions by HydraCoRe membranes



Based on this understanding, another expected effect is the reduction in salt rejection as the feed concentration increases. Various experiments have been done on model and actual surface water mixtures. For example, the membrane HydraCoRe 50 was tested for rejection of a NaCl feed with varying concentration. The result is shown in Chart 3. It can be seen that the rejection drops as the feed concentration increases. It is believed that this is due to the higher charge density of the feedwater reducing the effect of the charge repulsion effect of the negatively charged membrane surface. In another test with natural water, the HydraCoRe 50 had 40% rejection for 500 mg/l TDS surface water, while the rejection dropped to 20% for a 2000 mg/l TDS surface water. In a full-scale system, recovery is generally greater than 80%, which can cause a scaling problem with most RO systems. HydraCoRe systems do not have this problem, because of the high passage rate of the ions. In many cases the permeate TDS will approach the TDS of the initial RO feed. Thus, a full-scale NF system utilizing the HydraCoRe membrane will not significantly change the ion composition of the feedwater, will not cause scaling, and will allow very high recovery rates. For some specific applications with low feed salinity, this is preferred as explained earlier [2].

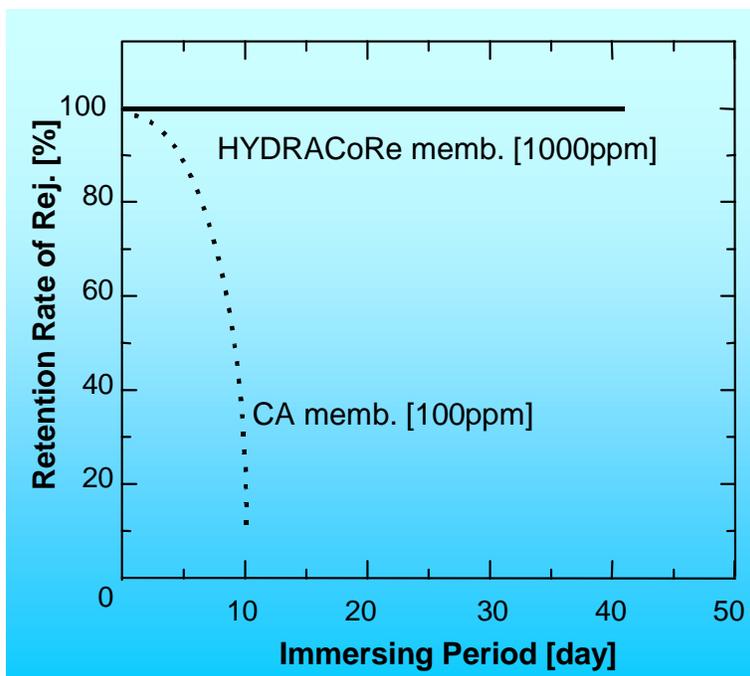
Chart 3 – Feed Salinity effect on HydraCoRe Rejection



CHEMICAL STABILITY

The advantage of a SPES membrane is the greater stability toward pH and chlorine, compared to conventional polyamide membrane. Chlorine is especially harmful to polyamide membranes due to the hydrolysis of the polyamide and resulting increase in salt passage. Polyamide RO membranes will typically be limited to an exposure less than 0.01 mg/l chlorine. A general rule is that the salt passage of polyamide membranes doubles for an exposure of 2000 ppm-hours of free chlorine. As a result, low doses of chlorine cannot be used to control biofouling for polyamide membranes, and chlorine cannot be used to clean organic or biologically fouled polyamide membranes. In contrast the SPES membrane is a very chlorine tolerant membrane. A test was done by soaking the SPES membrane in a 1000 mg/l sodium hypochlorite solution. As it can be seen on Chart 4, the membrane retained the same rejection over 50 days of exposure. For comparison, a cellulose acetate membrane was exposed to a 100 mg/l sodium hypochlorite solution, and had a doubling of salt passage in 10 days (24,000 ppm hour tolerance). Thus, the SPES membrane is ideally suited to low doses of chlorine to control biofouling or higher doses of chlorine to improve organic foulant removal. This will greatly enhance the application of this membrane for difficult waters [2].

Chart 4 – HydraCoRe Chemical Stability against free Cl₂ solution



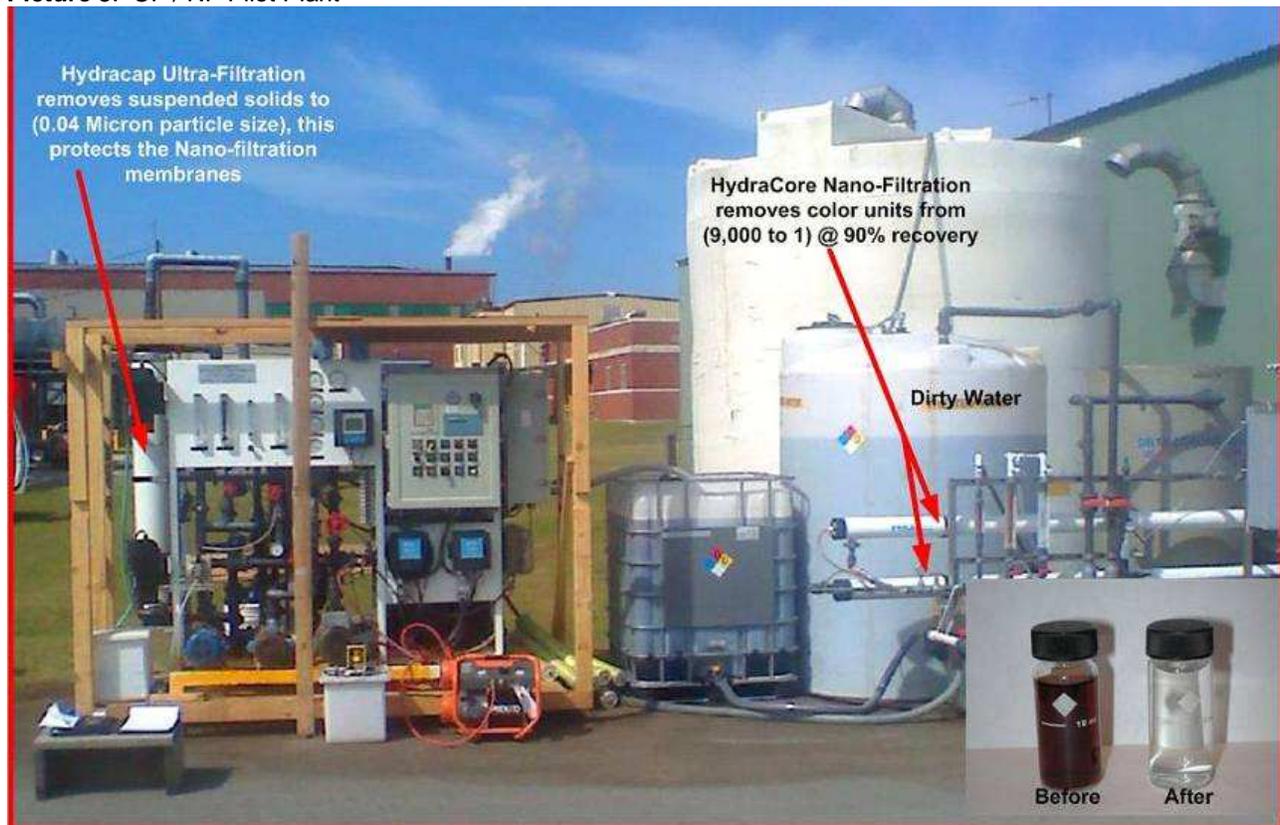
LABORATORY AND PILOT TESTING WITH PULP AND PAPER MILL WASTE WATER

In October 2007 a feed water sample of Pulp and Paper Mill waste water from the southeast of United States was sent to the corporate laboratories for evaluation of the HYDRACoRe50 membrane to produce the required permeate quality with color of less than 50 PCU prior to making a larger commitment to a pilot plant. The cell test results indicated that membrane was capable of producing permeate of 21 PCU with a feed of 2,730 PCU for a 99.2% reduction of color. This membrane also exhibited 55 to 65% mixed ion salt rejecting capability at feed

conductivity of 2,260 uS/cm and 79% rejection of the TOC. Based on these positive results of laboratory test, the decision was made to proceed with the pilot.

The NF pilot plant supplied in March 2008 was a small 2-stage array unit which consisted of two pressure vessels in series with three HYDRACoRe50 (4" model with 6.98 m² area) membranes per each pressure vessel. Capacity of pilot plant was 24.5 m³/day of permeate at design flux of 24 l/m²-h (LMH). A concentrate recirculation line was also installed to increase the feed and concentrate cross-flow velocities and simulate flows that would be observed in the full scale system and allow the pilot to increase the system recovery from 50% to 90%. The waste water was trucked over to the pilot and stored in a 3.8 m³ tank and then cooled down on a heat exchanger from 49°C to 40°C in order to comply with the NF membrane operational temperature limit.

Picture 3: UF / NF Pilot Plant



Initially there was no pre-treatment installed before NF membranes and therefore they were fouled quickly by the suspended solids from the waste water feed. A 1-micron media filter was therefore added as pre-treatment to improve NF feed quality but it did not sufficiently reduce the fouling potential and SDI-15 (silt density index at 15-minutes) remained out of measureable levels. Rinses with chlorinated city water were introduced to improve situation, but they were only partially successful in NF membranes fouling reduction. Cleanings with 100 mg/l HCL at pH 2.0 were very efficient, but the fouling quickly reoccurred. After one month of operation, the NF membrane was sent for autopsy to Hydranautics corporate R&D facility. Investigation indicated that a heavy orange-brown organic fouling of the feed spacer and membrane surface was substantial. During the re-test the differential pressure from the feed-to-concentrate was 2.1 bar (30 PSI) which was substantial increase against clean element differential pressure of less than 0.7 bar (10 PSI). The weight of the fouled lead element in the first stage was 5.45 kg while the

weight of new clean element is about 3.6 kg from the factory. It was evident that further pre-treatment would be required.

The decision was made to install an UF pilot pre-treatment system to reduce the suspended solids load, turbidity and fouling potential of NF feed. The UF system that was selected used a single HYDRAcap60 capillary UF module with 46 m² (500 sq. ft.) nominal membrane area. The membrane is a robust hydrophilic polyethersulfone with a nominal MWCO of 150,000 daltons. The fiber dimensions are 0.8 mm ID and 1.3 mm OD. This fiber has a maximum chlorine exposure time of 200,000 ppm-hrs and instantaneous chlorine tolerance of 100 mg/l. The operating pH range is typically 4 to 10 but for this application it was extended to 4 to 11 for warranty purposes. The cleaning pH range is 1.5 to 13 which makes it very suitable for the low pH and high pH cleanings that may be required. The operating mode for this UF is “inside to outside filtration”.

Initial tests were done in the laboratory to see if the HYDRAcap UF membrane could effectively reduce the colloidal material in the raw plant wastewater. The filtered wastewater was also noticeably more clear after passing through the membrane. The feedwater had very little deposit, even after standing for a long period. These results confirmed suspicions that the feedwater was heavily loaded with fine colloidal material which would not be easily removed from the water by conventional separation methods. The decision was then made to implement HYDRAcap pretreatment at the pilot.

The UF pilot was designed to operate at peak flux of 54.4 LMH (32 GFD) and at an average flux of 44.2 LMH (26 GFD). At peak flow conditions, the UF filtrate flow was 2.5 m³/hr (11.1 GPM). A bleed flow to drain of 0.23 m³/hr (1 GPM) was applied to achieve 92% recovery of the filtered raw feed. The pre-treatment to the UF consisted of 45-micron automatic self-cleaning strainer to remove large suspended solids and fibers that can plug the UF.

The UF pilot used a high backwash flow rate to keep the membrane surface clean. Final operating recovery of UF system was 83%. The full scale plant has a backwash recovery system planned to recover the backwash waste water and effectively reduce the volume of UF concentrate for disposal.

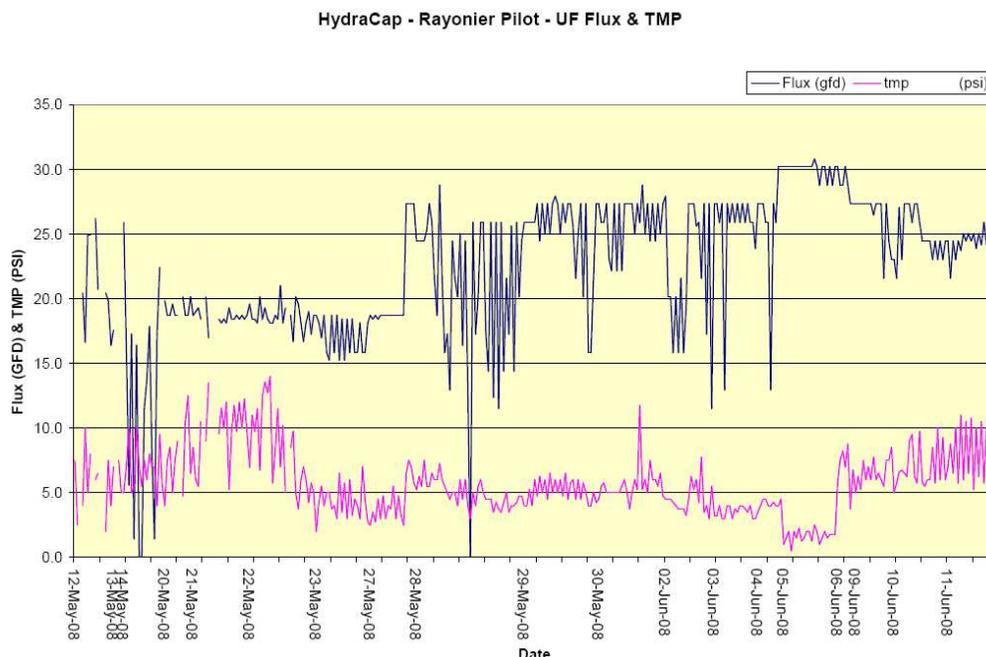
CEBs (chemically enhanced backwashes) were rarely used, mostly when shutting down the pilot for weekends or extended shut-downs. CEBs used NF permeate as the make-up water. HCl solution with pH of 2.0 and the 100 mg/l chlorine solutions were used for CEBs..

The UF System was operated at flux of 40 – 50 LMH (23.5 to 29.4 GFD) since end of May 2008 with TMP (trans-membrane pressure) ranging from 0.3 to 0.8 bar (4 to 11 PSI) depending on temperature which ranged from 21 to 35°C with excursions to 40°C. Short term operational results had shown that the UF was capable of achieving the quantity and quality of filtrate required for the NF system.

Table 2: UF Feed and Filtrate Quality for November 20, 2008

	UF Feed	UF Filtrate/NF Feed
Color CU	12,000	12,000
Turbidity NTU	6.1	0.24
pH	10.2	10.2
TOC mg/L as C	580	530
TSS mg/L	8.7	< 5

Chart 5: UF Pilot Flux and TMP evolution



Operation of the NF pilot was restarted in May 2008 once the UF system was installed and started to produce properly pretreated feed water. The operation of the pilot was intermittent for the remainder of the year as the pilot was operated on as needed basis to gain important design criteria for the full scale plant. As it can be seen on chart below, the NF plant was running at flux of 22 – 29 LMH (13 – 17 GFD) with permeate production of 4 – 5 m³/h at recovery of 80-90%. The NF pilot did not require chemical cleaning once the UF system was in place and differential pressure was stabilized at about 0.4 – 0.5 bar (6 – 7 PSI).

This was a very aggressive design for the pilot, since there were only 6 elements in series. To operate at such high recoveries, it is always preferable to keep flow rates that are around 50-70% lower than the flow rates to the lead elements. In this pilot test, the flow rate in the tail element was only 10-20% of the flow rate in the lead elements. Despite this poor hydraulic condition, the performance of the HydraCoRe was reasonably stable. This also demonstrates that the high passage of ions by the HydraCoRe membrane prevents the formation of scale at the tail end of the system.

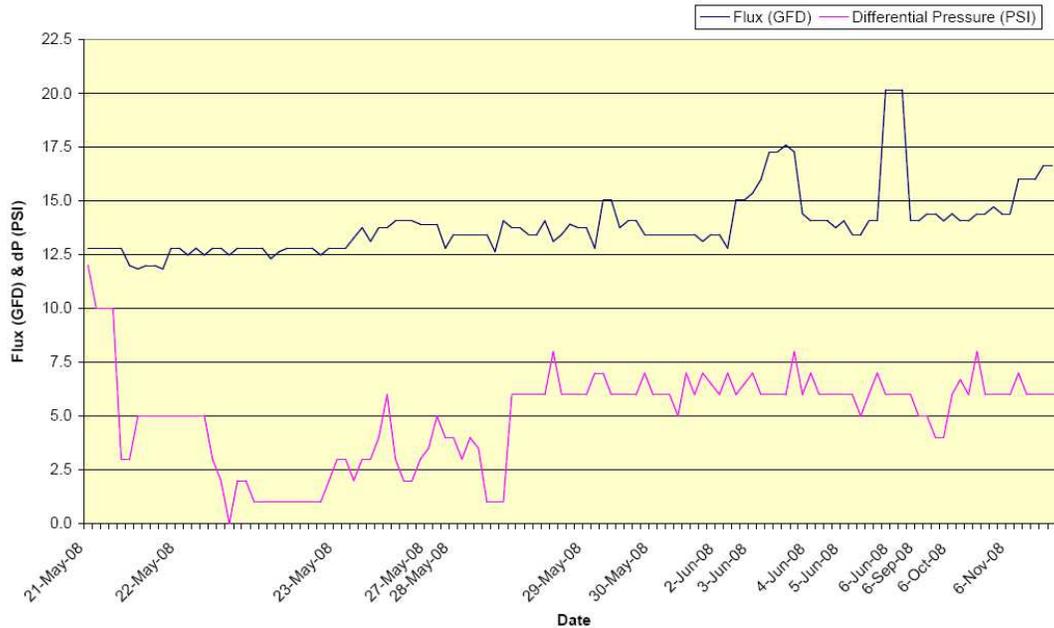
A full water analysis of the UF feed water, the UF filtrate, and the NF permeate was performed in November 2008. For comparison, the softened city water was also sampled. Analytical results are compared in below table. The UF system was operating at flux of 39 LMH (23 GFD) at 26°C and 90% recovery with a 0.23 m³/h (1 GPM) bleed of the concentrate. The NF system was operating at 15.3 LMH (9 GFD) and 86% recovery.

Table 3: UF and NF Pilot Water Analyses in November 2008

		UF Feed	UF Filtrate and NF Feed	NF Permeate	Softened City
TDS	mg/l	2,345	1,928	973	338
Color	PCU	12,000	12,000	20	10
Turbidity	NTU	6.1	0.24	< 0.1	< 0.1
TOC	mg/l	580	530	53	< 1
TSS	mg/l	8.7	< 5	< 5	< 5

Chart 6: NF Pilot differential pressure evolution

HydraCoRe50 - Rayonier Pilot - Flux & Differential Pressure



The following table compares actual NF operational versus projected performance.

Table 4: NF Pilot Actual vs Projected Operation in November 2008

	Actual	Projected
Feed Pressure	84-98 psid (5.8-6.8 bar)	90 psi (6.2 bar)
Delta P	5 psid (0.35 bar)	6 psid (0.41 bar)
Feed temperature	30-35 C	33 C
Flux	9 gfd (15.3 lmh)	9 gfd (15.3 lmh)
Permeate quality as mg/L:		
Ca	< 0.5	4
Mg	< 0.5	2
Na	340	374
CO ₃	310	550
SO ₄	13	1
CL	250	268
Silica	59	53
TDS	973	1253

FULL SCALE SYSTEM DESIGN

A full scale UF/NF waste water treatment system was considered. For any type of wastewater of this type, the process would likely consist of an equalization tank, heat exchanger, self-cleaning strainer and finally the UF pre-treatment followed by NF plant.

A full scale system UF system should also have at least four trains (4 x 33 of HYDRAcap60 modules. This allows only train to be off-line for backwashing or cleaning, while the remaining three trains run at 33% higher flux and keep the total processed volume constant. A separate Backwash Recovery UF system should be considered to treat backflush waste water. It is expected that this system could recover 80-85% of the backwash water from the primary HYDRAcap system. In this design, the total net UF system recovery of 96% can be achieved. UF filtrate will be collected in a tank, which will feed the NF system and also be used as backwash water source for the UF system.

The Primary NF system should consist of at least three trains (3 x 50%), each configured as two stage array with 2 x 1 array pressure vessels in each stage. Each pressure vessel will contain seven of HydraCoRe50 elements. Trains would likely operate at a conservative 80% recovery and flux of 20 LMH (11.8 GFD) in order to reduce the rate of fouling.

Concentrates from Primary NF system could then be treated on two (2 x 100%) Brine Recovery NF trains, each designed as two stage array. The Brine Recovery NF would use again HydraCoRe50 membranes with a design flux of 19.6 LMH (11.5 GFD). The purpose of the brine recovery trains is to recover up to 75% of the Primary NF concentrate and thereby increase the net NF system recovery to 90% or greater.

It is recommended that the backwash waste water from the UF system and concentrates from the Brine Recovery NF system be sent to other process in the plant for potential use or further processing before discharge. This step is very important to ensure that the plant is environmentally friendly with its discharge, while ensuring an economical design. This selection of the final treatment will depend on the particular design of the pulp and paper plant.

The waste water remediation treatment goals can be further expanded to include production of re-usable permeate of sufficient quality to be re-used in bleaching process. This would require maintaining minimum chloride levels in the concentrates. Therefore HydraCoRe10 membranes are being considered for this purpose as they have lower salt rejection and can produce permeate with minimum color but higher chlorides concentration.

CONCLUSION

The development of HydraCoRe NF membranes has opened the door for new membrane applications which require high rejection of organic molecules with MW larger than 1000 Daltons but do not need high salt rejection. The unique properties make this membrane ideal solution for color removal from potable or waste water sources as well as for recovery of chemicals used in some manufacturing processes. However, it is still critically important to provide a low turbidity feedwater to the these NF membranes. UF membrane pretreatment can play an important role to meet this need.

Results of pilot tests performed on Pulp & Paper Mill waste water confirmed, that HydraCoRe NF and HYDRAcap UF membranes can be successfully used for removal of color from waste water produced by this industry. Color reduction of 99.83% was achieved during pilot test with permeate color value of ~ 20 PCU being much lower than limiting value of 50 PCU required for disposal into local river stream. Reduction of color not only improved the aesthetic quality of the water, but it also would minimize polyphenol discharge to the river, which was an undesirable contaminant for a mussel indigenous to the region. Besides the color removal, the NF plant also reduced TOC concentration by 90%.

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