IMPROVEMENTS IN SPIRAL WOUND RO AND NF MEMBRANE & ELEMENT CONSTRUCTION FOR HIGH FOULING FEED WATER APPLICATIONS

Wayne T. Bates Hydranautics Rockton, Illinois
Dr. Craig Bartels Hydranautics Oceanside, Ca.
Rich Franks Hydranautics Oceanside, Ca.

Introduction

This paper will introduce improvements in both reverse osmosis (RO) and nanofiltration (NF) membrane polymer chemistry and in spiral wound RO/NF element construction. These improvements are focused on reducing the rate of fouling in high fouling feed waters while enhancing the quantity and quality of permeate water that can be economically produced.

These improvements have been focused on treating those higher fouling RO/NF feed waters around the industrialized world that at one time were ignored or passed over as being too difficult to treat economically and technically. Historically these water sources were not a water planner's first choice as they were afflicted with some bad actor like high organic, colloidal and biological fouling potential. These difficult water sources can be found in a range of sources from surface water treatment plants to cooling tower blow-downs to industrial waste waters and municipal waste waters. The increasing shortage of inexpensive clean RO/NF feed water sources, coupled with the regulatory difficulties and costs in the disposal of plant wastes, are demanding the reclamation of these feed water sources.

Spiral Wound RO/NF Elements: The Basic Components

Since the 1970's, the spiral wound element configuration has become the most popular and economical form of packaging RO/NF membranes. The reasons for this are:

- The Membrane: A large variety of RO and NF flat sheet membranes have been invented by polymer chemists that can be cast with a significant range of flow and feed pressure requirements along with a significant range of inorganic salt and organic rejection capabilities.
- The Packaging: This configuration offers the highest membrane packing area capability which results in the smallest water plant foot print size while maintaining reasonable anti-fouling characteristics, when compared to other membrane configurations like hollow fiber, tubular or plate-and-frame.
- The Materials of Construction: A wide range of materials offer an optimal blend of low material cost, high quality, chemical stability and physical ruggedness.
- Manufacturability: Offers the highest degree of automatic manufacturing capability, reasonable labor cost, high quality, and high yields.
- Design Flexibility: The modular nature of stacking RO/NF elements into pressure vessels and arrays allow for a wide range of system design features, including hybrid RO designs.

The basic material components of a spiral wound element are:

- The "thin film composite" flat-sheet RO/NF membrane

- The feed-brine spacer
- The permeate carrier
- The permeate water tube
- The membrane leaf adhesives
- The seal carrier (also called the anti-telescoping device or ATD)
- The epoxy fiber-glass outer shell.

Spiral Wound RO/NF Elements: Membrane Improvements

Improvements in polymer chemistry for RO/NF flat sheet membrane has to be considered the most critical requirement in the past and future development of better RO/NF spiral wound elements for the treatment of high fouling waters. Any membrane manufacturing company can make small incremental improvements in the packaging or manufacturing of the spiral wound element to enhance its flow, rejection and anti-fouling capabilities. However, the long term successful treatment of difficult waters has required in the past and will require in the future new and improved flat sheet membranes of different polymer chemistries. The industry needs to recognize this requires a large investment by membrane manufacturers into research & development, and then coupled with the commercialization and implementation costs to bring these new products to market.

Traditionally, membrane improvements focused on RO membranes that needed to have higher rejection for better dissolved salt removal and lower feed pressure and energy requirements for use on relatively low fouling "clean" water sources. High fouling water applications have expanded the requirements to include selective removal of certain dissolved species, such as hardness, iron, natural organic matter (NOM), pesticides, trihalomethane formation potential (THMFP) and organic material which causes color. In many of these cases, engineers desire high removal of specific contaminants, but want to maintain some level of salts in the water so that the water does not become aggressive, which can cause corrosion problems with piping in the distribution network.

Polyamide Based RO: When it comes to the reclamation of a municipally tertiary treated waste water plant, the membrane of choice in this century is a high flux, energy saving polyamide RO membrane with high rejection of inorganic salts and organics. These applications lend them selves to start including MBR or MF/UF pretreatment to the RO. RO biofouling is controlled by maintaining continuous levels of 2 to 4 ppm mg/l of chloramines in the feed source. A controlled level of fouling which results in a gradual decrease in system design flux from around 8 to 12 gfd over a period of months is part of the operational strategy and plant design. Selection of a suitable RO membrane is based not only on the original design flux, but also the ability of the membrane to be chemically cleaned so that it can be continuously restored to a reasonable and repeatable flux. These type of reclamation of plants are being successfully operated all over the world.

Polyamide Based NF: A variety of polyamide-based NF membranes have been available which successfully soften waters high in calcium, magnesium and total organic carbon (TOC). Many such plants are operating throughout the world, especially in Florida. Such membranes are often characterized by low feed pressure requirements (< 100 psi), system design fluxes up to 13 to 15 gfd, low monovalent salt rejections (80-90%), but high divalent ion rejections (>95%). Traditionally, these membranes are used in applications where the feedwater has hardness in the range of 200 – 400 mg/L as calcium carbonate and TOC as high as 20 mg/l, and requires a permeate with 70 – 100 mg/L as calcium carbonate and TOC less than 1.0 mg/l. These NF membranes also have good selectivity for NOM, THMFP and HAAFP organic compounds, as well as iron. It is important to note that the design of these NF systems have frequently required for years the use of hybrid membrane designs to achieve optimal permeate quality and flux balancing of lead elements within the pressure vessels of a particular stage of a NF train, or the selection of different elements between stages. They are an ideal membrane technology for producing potable water from a high fouling water source.

Non-Polyamide Based NF: There are “boutique” NF membranes that can fit the needs of treating very difficult highly colored industrial waste waters or highly colored surface water sources. These source waters 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. Natural waters which are high in color may typically have 100 to 400 CU, while an acceptable water would be characterized as having less than 5 CU. At 5 CU, the color in the water is imperceptible to the human eye. Such a membrane was required for a 7.3 mgd treatment project in California that planned to augment their water supply with water from a deep aquifer (1). This well water had an acceptable salinity which ranged from 250 to 500 mg/L of total dissolved solids (TDS) and a calcium level of 13 mg/L, but had high color, ranging from 250-400 color units. A novel NF membrane was selected that resulted in an average system flux of 15 gfd, no major change in permeate and feed TDS and hardness, and a reduction of color to < 5 CU.

This application was ideal for a class of membrane which is based on a highly charged non-polyamide based sulfonated polyethersulfone (SPES) membrane. 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. The properties of the membrane are unique and well-suited to this application. The absence of a typical polyamide barrier layer results in improved fouling resistance, chemical cleanability and disinfection compatibility. The charge on the surface of the membrane is strongly negative due to the presence of the sulfonate functional groups. The large negative charge of the SPES membrane is desired since the NOM in most source waters is composed of humic acids. The strong negative charge of the membrane surface (-50 to -90 mV at pH of 8) will repel the negatively charged humic acid compounds, and thus minimize fouling by organic adsorption. The SPES membrane used here will not significantly alter the ionic composition of the feedwater. The advantage of this membrane when compared to a polyamide based NF is the greater stability toward high pH (up to 13), up to 90 C, continuous chlorine tolerance up to 5 mg/l, and cleaning/disinfecting chlorine tolerance of 100 mg/l.

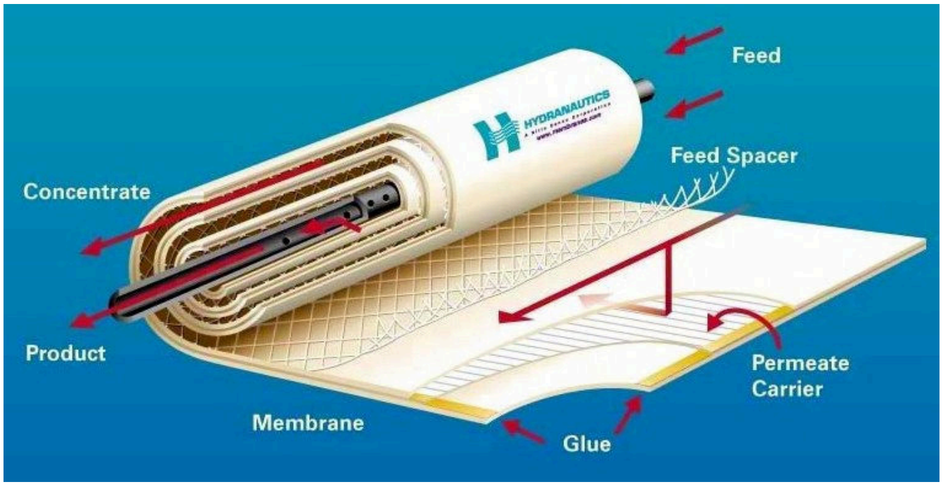
Thus, the SPES membrane is ideally suited to low doses of chlorine to control biofouling, or higher doses of chlorine to improve organic foulant removal, or high pH caustic cleanings. The development of the new SPES membrane has given engineers a unique new membrane which has relatively low salt rejections, but high rejection of naturally occurring organic material. This is an ideal product for color removal in potable water sources or industrial waste waters which are low in TDS.

Spiral Wound RO/NF Elements: Improvement in Materials of Construction

Permeate Carriers: Often unheralded and unseen, various advancements have been developed in the weaves of this spongy material and in the materials of construction for the permeate (product) carriers.

The enhancements have aided in the reduction of pressure drop when transmitting permeate to the permeate water tube.

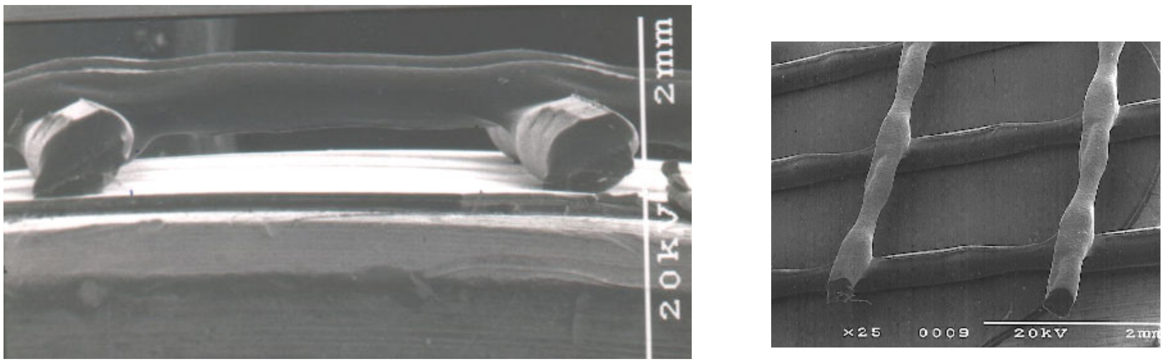
Figure 1: Typical Spiral Wound RO Element Components



Membrane Leaf Adhesives: Improved adhesives have been developed which allow easier processing of the element, automation of the glue lines for improved quality and available active membrane surface area in RO element construction, improved chemical resistance at higher and lower pH, as well as stability at higher temperatures.

Feed/Brine Spacer: This webbed material is responsible for maintaining a feed/concentrate flow channel between the two faces of flat sheet membrane in the spiral wound element. The spacer provides a defined gap for the water to flow through the element and promote mixing of the feed to minimize concentration polarization. The feed/brine spacer must provide a clear path for flow of the water, promote turbulence to keep the feed/brine solution mixed and have minimal pressure drop for water traveling tangentially to the membrane surface. In general, the linear velocity in a feed/brine channel is relatively low with Reynolds numbers which are insufficient to achieve turbulent flow. Typically the flow is in a shearing phase, not turbulent. For a system with good pretreatment, the feed spacer can be quite narrow and function well and this allows for the maximum area in the element. However, for poor quality feedwater, the fouling tendency of the water is much higher and can result in a more rapid plugging of the feed/brine spacer. This results in a higher operating pressure and more frequent cleaning. For high fouling source water applications, there was a need to optimize the feed/brine spacer design for these applications. One performance enhancing improvement is the use of specialized feed/brine spacers that minimize the pressure drop across the RO element by enhancing void volume while improving the flux distribution between the lead and lag elements. The more open spacers also enhance the cleaning effectiveness of the element if it is heavily fouled. These design improvements result in improved physical and chemical cleaning effectiveness, especially for conventionally pre-treated surface source brackish waters with high colloidal and biological fouling potential. Spiral wound RO/NF elements have traditionally used feed spacers that range between 26 mil to 31 mil thick. Figure 1 shows the schematic design of a spiral wound element. Figure 2 shows a magnified scanning electron microscope (SEM) view of a feed/brine spacer. The views show that there is a distinct biplanar design to these spacers that allows feed water or chemical solution to pass through the openings and be partially mixed due to the convoluted path. Traditionally, these spacers are made from polyolefin materials which tolerate both high and low pH extremes that are present during cleaning. Thicker and redesigned feed/brine spacers (up to 34 mil thickness) will provide even lower pressure drop, less rapid plugging and more effective cleaning.

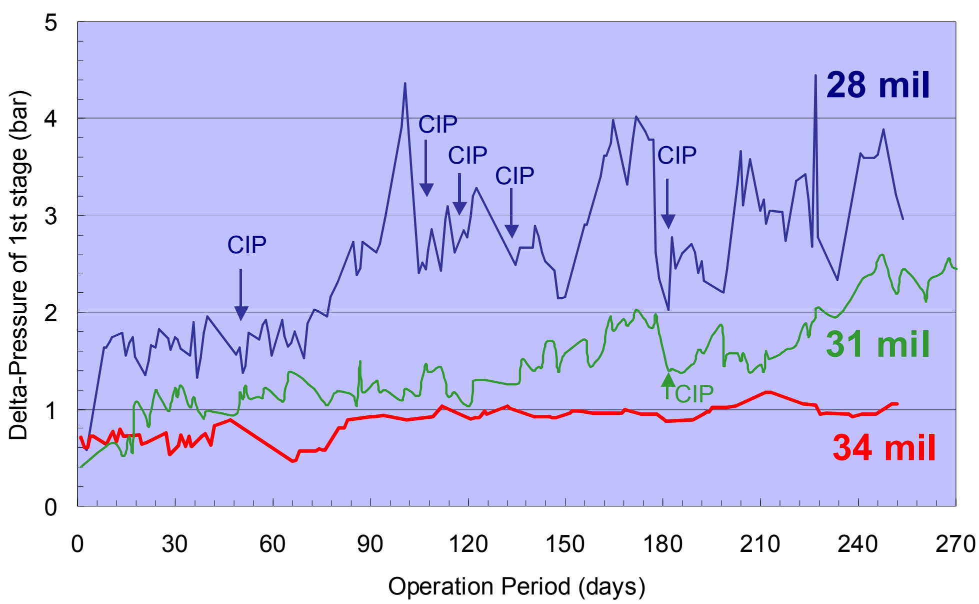
Figure 2: Schematic design of a spiral wound element and SEM view of feed spacer.



Thicker feed spacers are being used in special products for high fouling applications. To overcome the problem of lost area, automation has been utilized to control glue line placement, as well as some other element design changes. These changes have allowed these elements with thicker feed spacers to be made with the standard 37.2 sq m (400 sq ft) membrane area. In addition to using thicker feed spacers, the geometry of the spacer has also been optimized. This has resulted in additional reduction of the pressure drop which improves the energy efficiency of the RO/NF system.

Figure 3 shows the pressure drop measured for a variety of elements using different feed spacers. The operation was done in three phases, first with a standard 28 mil spacer, then a new geometry 31 mil spacer, and finally the new geometry 34 mil spacer. It is also seen that the conventional 28 mil spacer element has numerous clean-in-place (CIP) events to maintain the acceptable pressure drop in the vessel.

Figure 3: Delta P on surface water feed using different feed /brine spacer thicknesses.

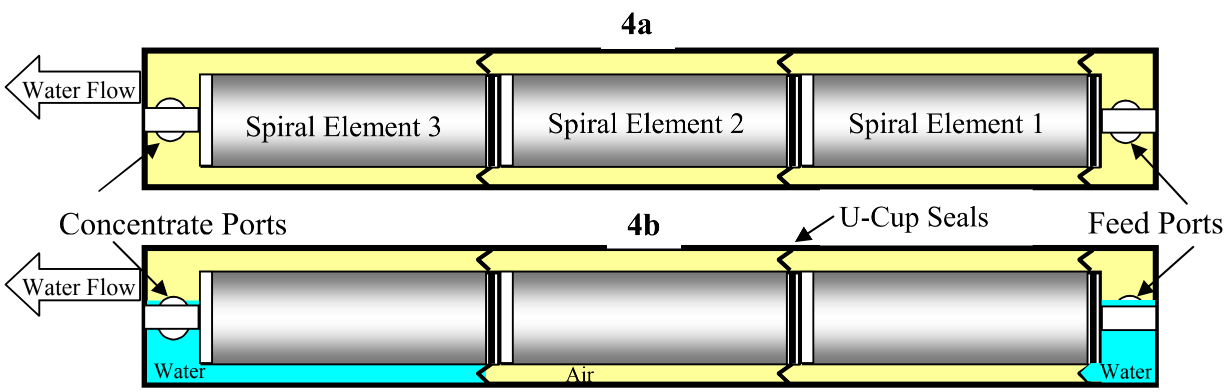


Seal Carrier: This component, which is positioned at both ends of the fiber glass wrapped spiral wound element, has had two functions. One function was to carry the chevron-style u-cup brine seal which prevented the feed water and cleaning solution from by-passing the RO element. The other function was to support the downstream side of the spiral wound flat sheet membrane and feed/brine spacer and prevented the membrane leaves from telescoping due to the pressure differential across the element, which is why it also was called the anti-telescoping device (ATD).

There had been no real change in the design of the seal carrier until recently. A redesigned seal carrier has been developed that now allows for the venting of the air from the pressure vessel. In a commercial size RO/NF system, there are usually 6-8 elements in a pressure vessel. Due to the presence of the u-cup brine seal, water does not readily flow around the outside of the spiral wound element. During the service and flushing modes, the feed water flows and pressurizes the inside of the element, which can be as high as 60 to 80 bar for seawater applications. In some cases, especially when starting a new system, there can be air on the outside of the element, in the annular gap between the RO/NF element's fiber-glass shell and the inside of the RO/NF pressure vessel. This annular gap can be also be filled with feed water and trapped air during service and flushing modes, which is common if there is some drain down of liquid when an operating plant is stopped. In either case, the air in this gap should be purged from the system. Since there is no flow path for water around the outside of the element, the air must be removed and displaced with water where the two elements contact the face of each other or by-passing the u-cup seal. This venting can be difficult due to the differential pressure across the elements in the vessel which forces the two seal carriers tightly together. For systems that ramp pressure up too quickly, the air in the annular gap may not be quickly removed. This results in a large pressure differential across the epoxy fiberglass shell. In some cases this pressure differential can rupture the fiber-glass shell and irreversibly damage the element.

A detailed analysis of pressures and water flow in a multi-element vessel revealed that there are issues with elements related to purging air from a pressure vessel due to the U-cup seals preventing the natural flushing of the annular gap. Figure 4 shows a schematic diagram of a pressure vessel with RO elements. In Figure 4a, the vessel does not contain any water, while in Figure 4b, the schematic shows water in the vessel immediately after the first addition of water (2).

Figure 4: Schematic of spiral elements in a pressure vessel.
4a: After loading and before water introduced
4b: Just after water first starts to enter the vessel.

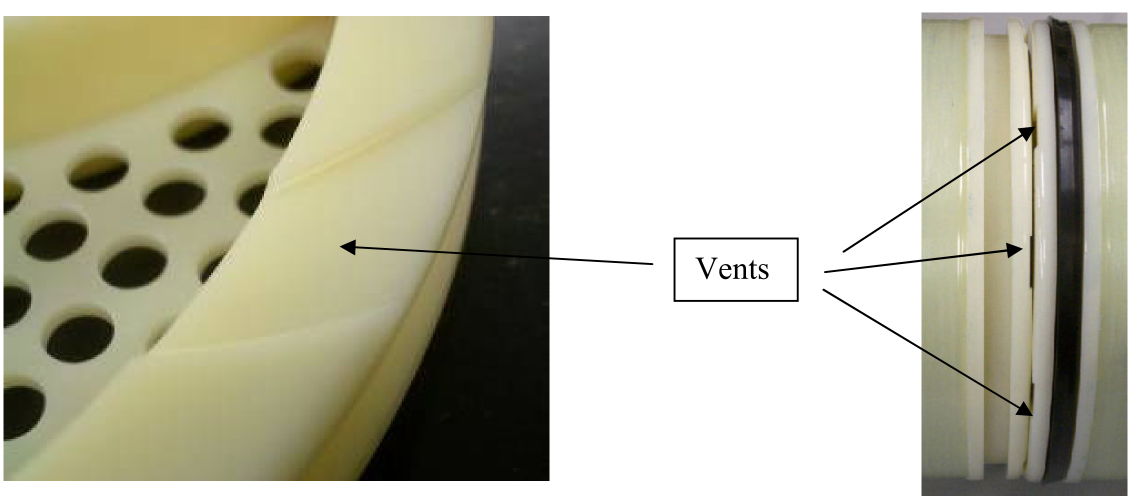


It can be seen that the water easily floods the vessel in front of the first element by displacing the air down through the elements. Also, the water fills the back of the vessel all the way to the U-cup seal of the last element. The air is displaced out of the vessel. However, the U-cup seal prevents the water from going to the next to last element. The only way to get the air out of the annular gap of elements 1 and 2 is to pressurize the water so it will flow past the u-cup seal; however, the air would then have to go against the seal to escape or go forward in the vessel to the next element position. Alternatively, the water may flood the annular gap by pressurizing the feedwater so it will separate the two facing seal carriers between elements 1 and 2 or 2 and 3. This would allow water into the annular gap and air to go out through the element. Either of these mechanisms is not very effective for venting the air from the system.

This issue is particularly problematic for seawater systems. In a seawater system the feed in the element is being pressurized to 60-80 bar of pressure. Until the water fully floods the annular gap, the pressure in the annular gap will be much lower than in the element. This pressure differential can lead to catastrophic damage. It takes very high pressure differentials to cause this to happen. Such pressure can be generated when feed pressure ramps up too fast and the air cannot be removed fast enough.

This issue has recently been addressed in the development of a new seal carrier which can allow rapid venting of the air from the annular gap. The new design incorporates six recessed areas several millimeters deep in the seal carrier which act as vents (Figure 5). When two opposing seal carriers are face to face, these small gaps provide an opening which allows the water to flow through (usually at the bottom of the seal carrier) and the air to pass through (usually through the top of the seal carrier). Since each element has this feature, the annular gaps can rapidly fill with water and the air can be expelled.

Figure 5: New seal carrier design with recessed vents



The added feature of vents provided in the new seal carrier designs will ensure that air can be readily removed from the annular gap between the outside of the element and the pressure vessel wall. This ensures rapid pressure equalization between the inside and outside of the spiral element. As a result, aggressive operation will be much less likely to cause damage, such as bursting of the FRP shell.

Another significant advantage to the removal of air in the annular gap of RO elements during the service mode is a reduction in the growth of biofilm on the outside of the RO/NF fiber-glass shell at any air/water interfaces that should develop. This can be advantageous in high fouling waters. When a biocide is in the feed water, it allows the continuous slow introduction of biocide. An example where this is useful is the continuous addition of chloramines from the feed water in a municipal waste water system using a polyamide-based RO membrane.

One final advantage is better and more efficient cleaning, disinfection and reduced flushing water volumes. The new seal carrier vents have improved introduction and movement of cleaning chemical, disinfecting biocides and flushing water through the annular space on the fiber-glass side of the RO/NF element. This has to result in improved operations of the RO/NF system in the treatment of high fouling waters.

Conclusion

The improvements in RO/NF membranes and the spiral wound element packaging are important advancements for the continued optimization of RO/NF technology for high fouling feed waters. The introduction of new and better RO/NF membranes for the treatment of difficult feed waters is of critical importance for the long term growth of this industry, as we can only improve the element packaging so much. The use of a chlorine tolerant spiral wound sulfonated polyethersulfone (SPES) UF membrane for the removal of color and organics was presented as an example of new membranes that designers can "pull from the shelf" for NF color removal system designs.

The new thicker brine spacers will allow spiral elements to handle more difficult feed water from a myriad of sources. Although it is always preferred to have properly functioning pretreatment with turbidity less than 0.2 NTU and 15-minute SDIs, the thicker feed spacers give greater flexibility for service and cleaning/disinfection operations. Improvements in manufacturing technologies and component designs still allow the continuance of high membrane areas of 400 ft^2, even with the thicker feed spacers. Due to improved spacer design, it has been shown that the pressure drop across a vessel can be further reduced compared to the use of conventional spacers. Any pressure saved by reduced feed-to-concentrate pressure drops results in lower feed pressure requirements and lower energy costs. Testing at industrial sites has proven the value of these new spacers to reduce pressure drop, slow fouling rates, and improve the cleanability of the RO/NF elements.

Additionally, a new seal carrier design can improve the removal of air from pressure vessels. A new seal carrier design provides vents which allow air to quickly escape between the seal carriers as water floods into the annular gap. This feature prevents damage to the fiber-glass shell in seawater RO systems, it can reduce the rate of biofouling in the RO/NF system, improve the cleaning and disinfection capability, and reduce the amount of flushing water during cleanings.

References

1. Dr. Craig Bartels, Dr. Mark Wilf, (2002), "Selective Color Removal Nanofiltration Membrane for the 7 MGD Irvine Ranch Water Treatment Project", *Hydranautics, Oceanside..*

2. C Bartels, M. Hirose, and H. Fujioka, April 2007 , "Performance advancement in the spiral wound RO/NF element design", *EDS Conference*, Halkidiki, Greece.