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New generation of low fouling nanofiltration membranes

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Abstract

The nanofiltration (NF) membranes and their properties are quite diverse, but can generally be described as having rejection characteristics that range from "loose" RO to "tight" ultrafiltration. The uniqueness of these membranes is highlighted by their ability to selectively reject different dissolved salts, and have high rejection of low molecular weight, dissolved components. Nanofiltration membranes are mainly used to partially soften potable water, allowing some minerals to pass into the product water and thus increase the stability of the water and prevent if from being aggressive to distribution piping material. Additionally, NF membranes are finding increasing use for purifying industrial effluents, and minimizing waste discharge. The key to using NF membranes for particular application is the selection of a membrane with appropriate rejection characteristic and the design of a suitable process. NF membranes are generally characterized by a high charge density and pore sizes in the range of nanometers. The surface charge is most often negative and has the greatest effect on the selective passage nature of these membranes. The design of a NF system can often be more complex than a RO system. Because the required transmembrane pressure is so low, a system design that will result in balanced flux throughout the array is difficult to achieve. One common approach is to design NF systems with multiple element types. Such so called "hybrid" designs can help more finely control flow in the NF system. Also, membrane fouling can cause a change of rejection selectivity and/or reduction of membrane permeability that could affect both the water quality and operating cost due to increased energy requirement and higher consumption of chemicals needed for stabilization of permeate. The rejection characteristics of NF membranes depend on chemistry and surface charges of the separating barrier layer, ionic composition and concentration of feedwater and operating parameters of the NF system: recovery rate and permeate flux. Although, theoretical models have been developed to calculate selective ion rejection of NF membranes, they are mostly adequate only for simple water systems in limited range of water compositions and concentrations. In algorithms applied for projection of permeate composition in commercial NF systems, the theoretical models are augmented by empirical correction coefficients developed from field results. Selection of proper NF membrane type and prediction of performance is further complicated by membrane fouling. In NF projects involving treatment of feedwater with high concentration of dissolved organics the membrane selection process usually include pilot unit operation to evaluate stability of salt rejection and water permeability of candidate membrane elements. The paper will discuss

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present offering of commercial NF membranes, case studies and models applied to calculate their performance. This will also include information on recently developed NF membranes with low fouling characteristic that are successfully applied in the world largest (150,000 m^3/d, 40 mgd) NF plant in Boca Raton, FL. The process of extensive field testing and parallel membrane performance optimization that led to selection of these nanofiltration elements for the Boca Raton plant will be described as well.

Keywords: Nanofiltrtaion; Softening; Membrane fouling

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1. Introduction

The nanofiltration (NF) membranes and their properties are quite diverse, but can generally be described as having rejection characteristics that range from “loose” RO to “tight” ultrafiltration. The uniqueness of these membranes is highlighted by their ability to selectively reject different dissolved salts, and have high rejection of low molecular weight, dissolved components. Nanofiltration membranes are mainly used to partially soften potable water, allowing some minerals to pass into the product water and thus increase the stability of the water and prevent it from being aggressive to distribution piping material. Additionally, NF membranes are finding increasing use for purifying industrial effluents and minimizing waste discharge. The key to using NF membranes for particular applications is the selection of a membrane with the appropriate rejection characteristics and the design of a suitable process. NF membranes are generally characterized by a high charge density and pore sizes in the range of nanometers. The surface charge is most often negative and has the greatest effect on the selective passage nature of these membranes. New membranes have been developed which have unique properties, including a varying range of hardness rejection and fouling resistance. These new membranes have made it possible to meet the more demanding requirements of new nanofiltration plants such as those at Ft Lauderdale, Deerfield Beach and Boca Raton in Florida USA.

The design of a NF system can often be more complex than a RO system. Because the required transmembrane pressure is so low, a system design that will result in balanced flux throughout the array is difficult to achieve. One common approach is to design NF systems with multiple element types. So called “hybrid” designs can help more finely control flow in the NF system. In other cases, plant operators prefer to have one membrane type to more easily manage the membrane inventory. Only if one type suitable membrane cannot be found, will designers use the hybrid design.

Also, many NF plants are treating more difficult source waters [1], such as surface waters or ground waters under the influence. These can contain high levels of organic compounds which must be removed to achieve potable water quality targets. In some cases the organic compounds can foul the NF membrane, especially when the system is run at high recovery rates. This adds another complication because membrane fouling can cause a change of rejection selectivity and/or reduction of membrane permeability that could affect both the water quality and operating cost due to increased energy requirement and higher consumption of chemicals needed for stabilization of permeate.

As previously stated, the rejection characteristics of new NF membranes can be tailored to meet a variety of hardness rejection values. Additionally, this new class of NF membranes has properties which make them more resistant to fouling by organic compounds.

2. Membrane properties of new NF membranes

New NF membranes have been developed which can be tailored to have a range of hardness

Table 1
Nanofiltration product performance comparison

Product	Element area		Nominal flow		Nominal rejection (%)
	(ft^2)	(m^2)	(gpd)	(m^3d)	
ESNA1-LF	400	37.2	8200	31.1	89
ESNA1-LF2	400	37.2	10,500	39.8	86
ESNA1-LF3	400	37.2	7200	27.3	90

Test conditions: 500 mg/L of $CaCl_2$, 75 psi, 25°C.

rejection. These membranes are composite polyamide type, similar to existing RO membranes, but are chemically treated to adjust the hardness rejection. This treatment also imparts fouling resistance.

A series of nanofiltration membranes which were prepared with increasing treatments and designated ESNA1-LF, LF2 and LF3. The relative performances of these membranes are listed in Table 1.

As the hardness rejection is parallel to the nominal rejection of the membrane it can be seen, the LF2 has a lower hardness rejection and higher permeability than ESNA1-LF, while ESNA1-LF3 has higher rejection and lower permeability than ESNA1-LF. This trade-off between flux and rejection is typical for membranes, but these membranes are unique due to the fine control of trade-off that can be achieved. Fig. 1 shows the relative rejection of various ions when LF and LF2 are used to treat a low salinity surface water. It can be seen that the actual hardness rejection is 93% versus 83%. This feature is important for many new plants which want a controlled amount of hardness in the water. This requires the hardness rejection to have both a minimum and a maximum value. The other important ion is iron, since many well waters have high values of iron that must be reduced. Again, LF membrane has higher rejection of iron, but lower permeability than LF2.

The other feature of this membrane is the low fouling nature. This can be attributed to two features — the smoothness of the surface and the near neutral surface charge. Fig. 2 shows the scanning electron microscope (SEM) image of the ESNA1-LF membrane compared to the ESPA3 loose polyamide RO membrane.

The lower charge of the ESNA1-LF membrane can be seen in Fig. 3. The figure shows the Zeta Potential of the membrane surface measured as a function of the feed pH. It can be seen that

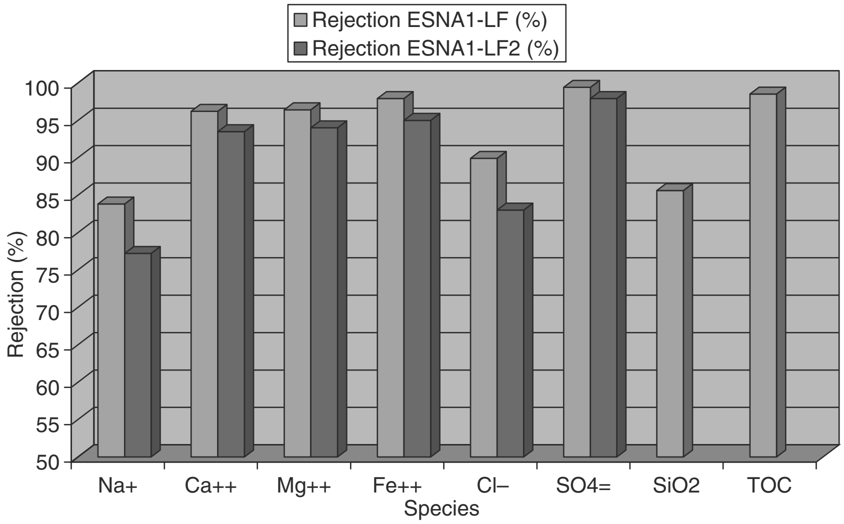

Fig. 1. Comparison of ion rejection values for ESNA1-LF and LF2.

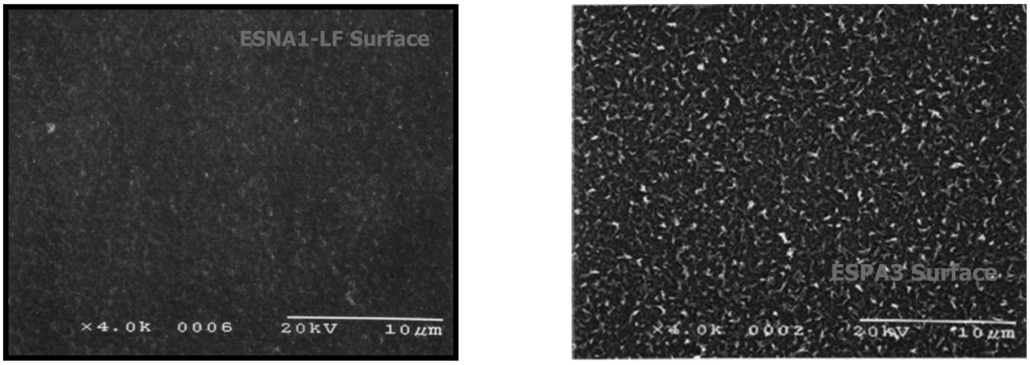

Fig. 2. SEM image of the surface of the ESNA1-LF membrane compared to the ESPA3 membrane.

the traditional nanofiltration membrane has a very strong negative charge at neutral pH values. In contrast the low fouling RO membrane, LFC1, has a slight negative charge at these pH values. Similarly, the ESNA1-LF membrane has a slight, or near neutral surface charge. This minimal surface charge minimizes the interaction with some organic compounds.

3. Nanofiltration system requirements

Due to more complex drinking water requirements, the performance requirements for NF membranes have become more difficult. Examples of this are seen in plants that treat groundwater in Florida, USA. Feedwater and product water requirements for two such plants, Deerfield [2] and Boca Raton [3], are shown in Table 2. Each has a different hardness range target. Because of the high level of iron in the Deerfield water, 1.5 ppm, a higher rejection membrane is needed compared to Boca, which only has 0.3 ppm. The other important requirement is that the membranes should have high rejection of organics that form disinfection by-products. The requirement is that trihalomethane formation potential (THMFP) and haloacetic acid (HAAFP) should be below 42 and 30 ug/L, respectively.

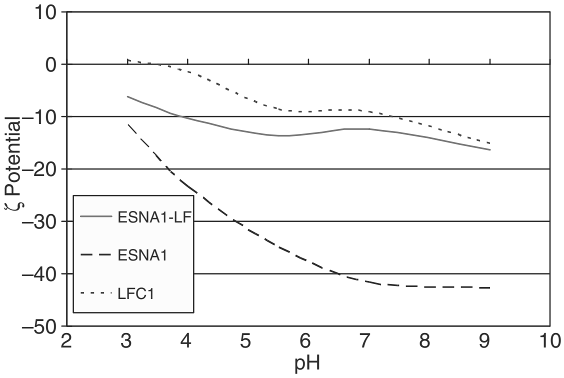

Fig. 3. Surface charge of ESNA1-LF and other membranes.

This water, which is derived from the Biscayne Aquifer, is a shallow aquifer that underlies 4000 square miles in southeast Florida and serves as the primary source of drinking water for Dade, Broward, and southeast Palm Beach counties. Municipal utilities within this region are installing nanofiltration facilities at a record pace to treat the Biscayne Aquifer and provide potable water for the growing population. For most of the area, this source water contains less than 500 mg/L of total dissolved solids (TDS), high levels of hardness and natural organic matter, which imparts color, contributes to the formation of disinfection by-products, and causes membrane fouling. However, variances in the aquifer composition make treatment more challenging. Local concentrations of iron at one location, the presence of nitrate at

Table 2
Feedwater and product water for select Florida NF applications

Species	Units	Feedwater composition			Permeate requirement		
		Deerfield	Boca Raton	Ft Lauderdale	Deerfield	Boca Raton	Ft Lauderdale
Total hardness	mg/L $CaCO_3$	250	265	270	26–82.5	50–80	<30
Iron (dissolved)	mg/L	1.5	0.3	2	<0.2	<0.2	<0.15
HCO_3	mg/L	285	265	269	<175	<175	>15
TDS	mg/L	482	466	500	<250	<300	
TOC	mg/L	20	12	11	<1	<1	<1
THMFP	µg/L				<40	<42	
THAAFP	µg/L				<30	<30	
Color	CU	50	50	90	<1	<2	<3

another location, and the absence of both at a third location, have resulted in different separation objectives for three municipal utilities that are all located within 100 miles of each other.

A system design was developed to meet the required product water quality, minimize energy costs, maximize water recovery, reduce chemical costs and ensure stable operation. Pilot testing was performed [1] for both sites to identify suitable membranes. At both locations, the ESNA1-LF type product proved to operate stable and did not show significant fouling, while conventional

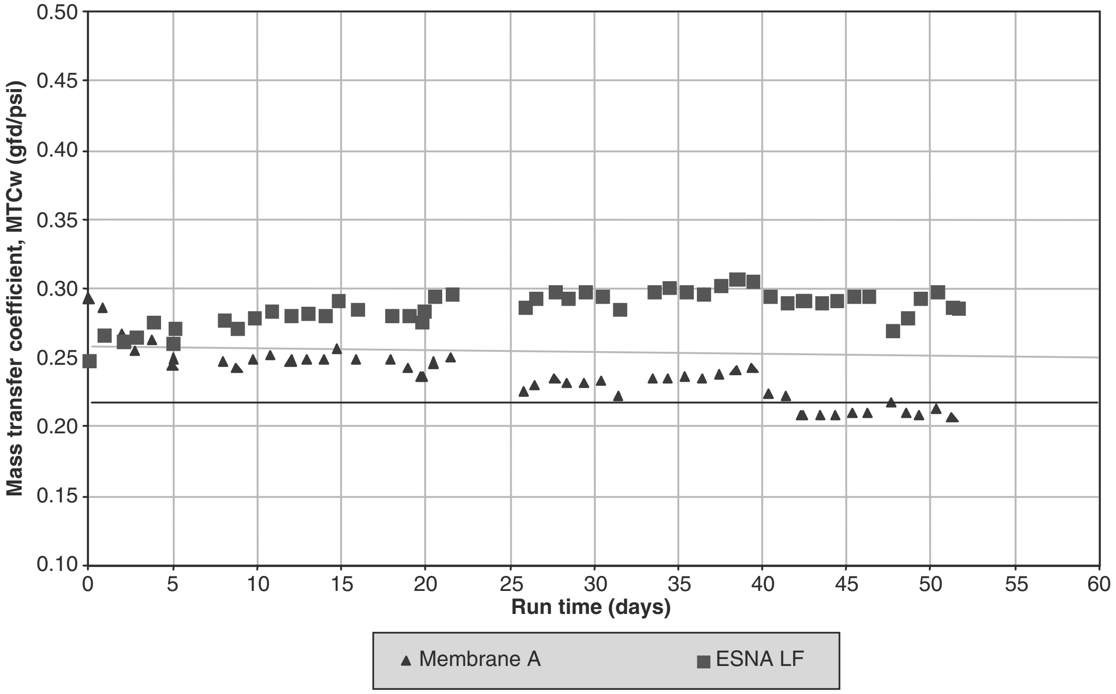

Fig. 4. Normalized membrane permeability at the Boca Raton pilot test.

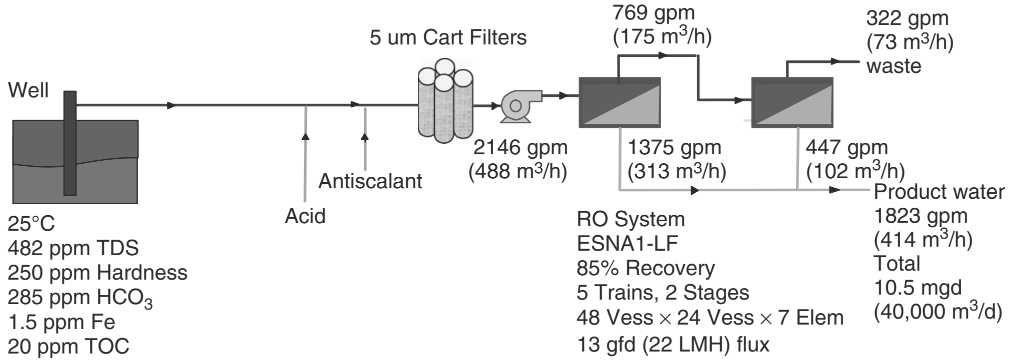

Fig. 5. Deerfield Beach system design.

NF membranes did show significant fouling (Fig. 4).

For the Deerfield Beach project, the ESNA1-LF gave high enough rejection to reduce iron and disinfection by-products to acceptable values, while controlling hardness in the acceptable range. At Boca Raton pilot, the ESNA1-LF2 was selected because the iron rejection requirement was much easier to achieve, while it was required to have less hardness rejection (see Table 2).

The pretreatment to the nanofiltration system at Deerfield (Fig. 5) consists of sulfuric acid addition, scale inhibitor injection, followed by 5 micron cartridge filtration [2]. This is the typical pretreatment to almost all of the reverse osmosis and nanofiltration systems in Florida that operate on un-aerated well water supplies. The permeate is sent to a degassifier for carbon dioxide (and sometimes H_2S) reduction and later blended with lime softened effluent. The nanofiltration concentrate is directed to a pressurized sanitary main.

For the Boca Raton project, the pretreatment included a multimedia filter, and no antiscalant or acid was used [3]. Typically, this would not be possible because of the high scaling potential of the $CaCO_3$. The LSI of the concentrate is expected to be around 1.9. However, pilot testing demonstrated that stable operation could be achieved without acid or antiscalant. Apparently, this is due to the high level of organics in the well water acting as a natural scale inhibitor. The design is shown in Fig. 6.

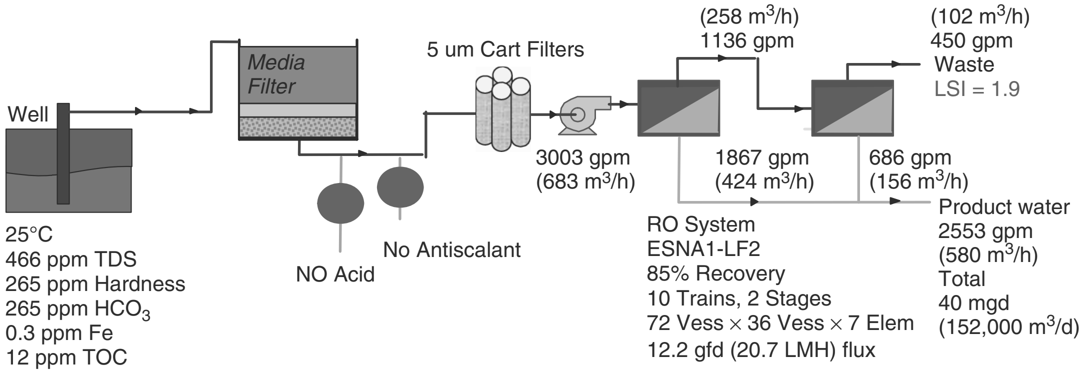

Fig. 6. Boca Raton NF plant system design.

The NF product water specifications were selected to be able to blend with water from the lime softeners already operating at these sites. The resulting blend is designed to meet the product water quality requirements. In particular, the NF membrane system will greatly reduce TOC in the finished water compared to lime softeners. Normally, the municipalities may use up to 30 ppm of chlorine to reduce the color. With the use of NF membranes, the chlorine demand of the water is significantly less. Also, the lower TOC and chlorine concentration will produce much less disinfection by-products, which is the goal of the hybrid design.

4. Commercial plant operation

The 40,000 m^3/d (10.5 mgd) Deerfield Beach nanofiltration system consists of five units, each with a capacity of 9900 m^3/d (2.625 mgd). Only four units are required to meet the total demand with the fifth unit in a standby mode. Each unit operates at 85% recovery and is a 48–24 two-stage array of pressure vessels. Each pressure vessel contains seven spiral wound nanofiltration elements for a total of 504 each ESNA1-LF nanofiltration elements per unit. A total of 2520 elements were supplied for the project. The units operate at an average flux of 22 LMH (13 GFD).

At Deerfield Beach all five units started operation in November and December of 2003 [2]. All five units were within the specified ranges at startup and continue to meet specifications 3 years after startup. As can be seen in Table 3, the permeate quality has easily made the specification for iron, producing 0.1 ppm Fe in the product. The system hardness rejection averages 95% and the total trihalomethane and haloacetic formation potentials of the permeate are well below limits. The average flux decline of all 5 units is approximately 10% after 1½ years of service (Fig. 7). As of late 2006, no unit has required a cleaning based on flux decline even though the feed TOC levels in feedwater have been measured as high as 36 mg/L. Only the normalized trans-element pressure drop has increased and indications are that cleaning will soon be needed.

The NF membrane plant has achieved its objectives by greatly lowering THM and HAA values in the product water. THM values had typically been 25–90 ug/L and THAA values were in the range of 60–90 ug/L. The regulatory

Table 3
Florida feedwater examples and NF permeate values

Species	Units	Feedwater composition			Actual NF permeate		
		Deerfield	Boca Raton	Ft Lauderdale	Deerfield	Boca Raton	Ft Lauderdale pilot
Total hardness	mg/L $CaCO_3$	250	266	270	27.5	50–80	15
Iron (Dissolved)	mg/L	1.5	0.3	2	0.14	0.04	0.1
HCO_3	mg/L	285	265	269	26	74	20
TDS	mg/L	482	466	500	61	137	
TOC	mg/L	20	11.7	11	<1	<1	
THMFP	µg/L				27	16.2	
THAAFP	µg/L				26	14.6	
Color	CU	50	50	90	<1	<1	

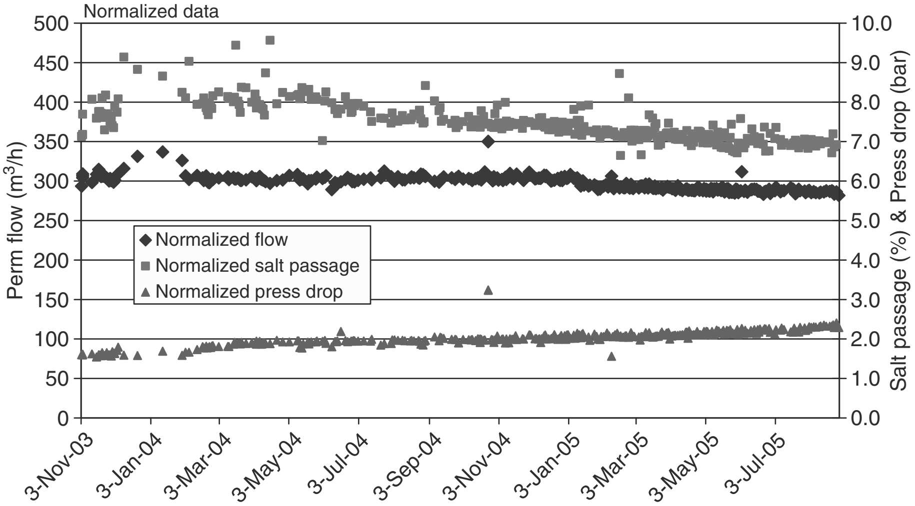

Fig. 7. Performance of the Deerfield ESNA1-LF NF plant.

limits for both of these were 80 and 60 ug/L respectively. With a membrane to softener blend of 60:40, the product water easily met the regulatory limits.

In regards to cost, the use of the low foul NF membranes allowed the plant to operate at pH 6.5 instead of the original design of 6.2. In addition the plant has saved money by not performing any chemical cleanings to date.

The 151,000 m^3/d (40 mgd) Boca Raton plant was designed at 20.7 LMH (12.2 GFD) with a 72:36 two stage array of 7 element vessels. Train 1 started operation in August 2004. The other trains were started sequentially after they were proven to meet the performance requirements [3]. The final train came on-line in April 2005. This plant utilizes ESNA1-LF2 membrane, a looser nanofiltration membrane tailored for higher hardness passage than the LF. Some adjustments were made to one train to meet the target values. Another problem occurred shortly after start-up when some media form the filters inadvertently passed into some of the NF trains. This resulted in high pressure drop when the sand plugged the feed channels of the lead elements. The elements which were affected were eventually flushed and installed in a single train.

Since that event, the plant has operated stably. As noted above, the system design for Boca was different from Deerfield because there was no use of acid addition or antiscalant. This resulted in significant cost savings. In addition the transmembrane pressure (feed minus permeate) was 5 bar (73 psi), which was less than the specified 5.5 bar (80 psi). The plant also met all the permeate water requirements (Table 3).

The performance of one train from the Boca plant is given in Fig. 8. It shows that this plant has reasonable performance over the past two years, meeting all water quality requirements and running at a pressure of less than 90 psi as required. However, there has been some fouling. The normalized permeate flow has dropped 34% and the dP has increased 50%. Some high pH cleanings have been performed to remove organic material, but these have not significantly restored original values. Initial analysis indicated the presence of calcium phosphate deposits. Acid cleaning was effective to remove this and restore flow to a test element.

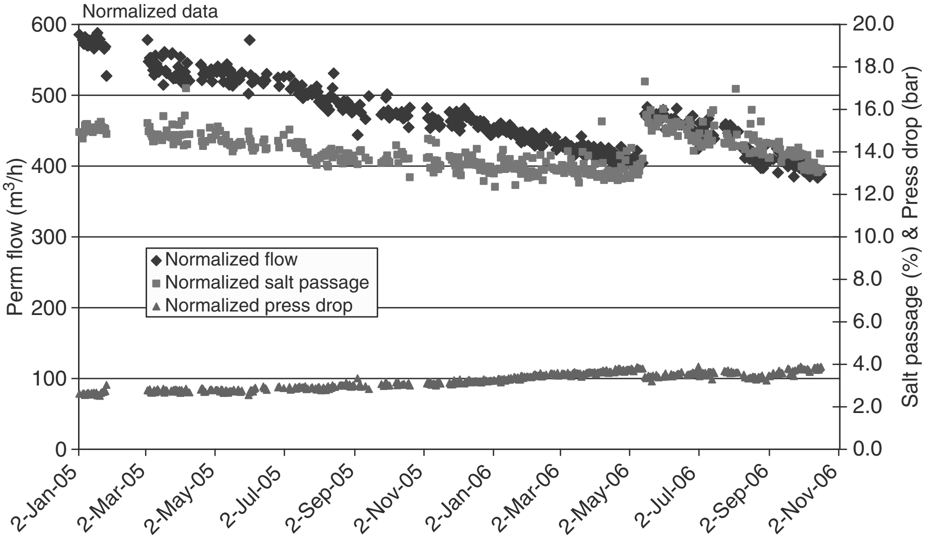

Fig. 8. Performance of one train at the Boca Raton plant.

A more detailed study has been done at the Boca Raton plant using a single element test unit. A variety of chemicals are being tested to select the most effective cleaning regime. When elements were removed from the system, it was evident that the tail of the system had signs of salt crystals. This is a sign of scale formation. Testing of individual elements revealed that the last two elements of the second stage had lost a significant amount of flow (Table 4). Acid cleaning was shown to restore the original flow and rejection of the element. This further supports the analysis that scaling has occurred. Cleaning of the entire plant is planned next.

Despite these issues, the plant has performed extremely well. An early analysis was done which indicated that the avoidance of acid and antiscalant addition, as well as the caustic that would be need for post-treatment results in a savings of \$927,000 per year. The lower than expected feed pressure also resulted in a \$48,000 per year savings compared to the original design.

The analysis of the plant performance and the presence of scale on the tail elements indicates

Table 4
Effect of element cleaning study at Boca Raton plant

Vessel	Stg 2 vessel position	Serial #	Element flow at a normalized TMP of 4.69 bar			
			Factory test (m^3/h)	Preclean (m^3/h)	Post low pH clean (m^3/h)	Post high pH clean (m^3/h)
108	7	A916827	1957	914	2111	2235
99	1	A913466	2193	0	1787	2269
99	3	A917052	2108	0	2303	2535
99	4	A915286	1576	0	1433	1899
99	7	A916885	1951	0	2203	2493

that the natural organics present in the water are not sufficient to fully control scaling. However, the fact that the plant ran this long without acid cleaning indicates that the natural organics have controlled scaling to some degree, but will need to be augmented with acid or antiscalant addition similar to the Deerfield plant.

Finally, pilot testing was recently carried out for the 45,500 m^3/d (12 mgd) Ft Lauderdale plant. As seen in Table 2, the permeate quality targets for this project were slightly different than the other plants in that the iron was projected to be even higher and there was a minimum value of alkalinity that was allowed. Initially, ESPA4 RO membrane was selected to meet the requirements; however, the permeate alkalinity was below the 15 ppm limit. Ultimately, designers elected to use ESPA4 in the first stage, while the second stage 7 element vessel had 4 ESPA4 in the front position and 3 ESNA1-LF2 elements in the back position. This hybrid design met the permeate water quality targets, as shown in Table 3.

5. Conclusion

The operation of these NF plants indicates that the new series of low fouling NF membranes are able to treat these high organic laden feedwaters with stable performance. Due to the more stringent water quality requirements and the hybrid design with existing softener technology, membranes with variable hardness rejection are required. The ESNA1-LF series of membranes can be tailored to a fine degree to meet these requirements. These NF membranes also give high rejection of organic compounds to allow the plants to meet the disinfection by-product reduction requirements. For complex waters like these, it is important to pilot test to select the optimum membrane and system design. The results at the Boca Raton plant show the surprising ability to run with very high LSI, without using antiscalant. This is believed to be due to the antiscalant properties of the natural organic matter. Although the performance of this plant has not equaled the stable results of the one that does add acid and antiscalant, the performance is reasonable, and can be further optimized to find the lowest cost operating point.

References

[1] C. Keifer and H.E. Jackson, Advantages of New Low Fouling Nanofiltration Membranes versus a Hybrid Membrane Design for Deerfield Beach, Proc. AWWA National Meeting in New Orleans, LA, June 16–20, 2002.

[2] C.A. Kiefer, W.M. Miller, J.L. Leone and W.B. Suratt, Optimizing New Low Fouling Nanofiltration membrane performance for Deerfield Beach, AWWA Membrane Technology Conference, Atlanta, GA, 2003

[3] F. Brinson, C.A. Kiefer, W.B. Suratt, C. Helfrich, W. Casey and H. Said, Process optimization during the first year of operation of a 40-mgd nanofiltration plant, AWWA Annual Meeting, San Francisco, CA, 2005.