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Introduction

The nanofiltration (NF) membrane process, has a separation property located between ultrafiltration (UF) and reverse osmosis (RO). Its main application area is in potable water treatment and wastewater reuse. Since late 1980's, mainly in Florida, USA, large scale membrane softening water treatment plants have been installed and operated to remove high levels of hardness, color, iron, and trihalomethane (THM) precursors from well water. These plants (as shown in Table1) have a permeate capacity not less than 1 mgd (3800m³/d), and utilize NF membranes to produce potable water for municipal applications. In 1988 Nitto Denko -Hydranautics started to provide PVD1 softening membrane elements for potable water treatment plants. In September 1996, the new ESNA softening membrane elements were introduced by Nitto Denko-Hydranautics.

Table 1, Representative Membrane Systems Utilizing NF Membranes for Potable Water Production

Client - Location	Date	Description
West Palm Beach, FL	2000	23 mgd, using ESPA3 and ESNA1 membrane elements
Irabu-cho, Okinawa, Japan	2000	1.2 mgd, 80% Recovery, Ultra-low Pressure RO system using ES15-D8 (ESPA Equivalent) membrane elements
Jupiter, FL	1997	3 mgd expansion, using ESPA membrane elements
Hollywood, FL	1996	18 mgd, 90% Recovery, Hybrid system of CPA2 and PVD1 membrane elements
Collier County, FL	1993	12 mgd, 90% Recovery, PVD1 softening membrane elements
Dunedin, FL	1992	9 mgd, 85% Recovery, PVD1 membrane elements
Fort Myers, FL	1990	12 mgd, 90% Recovery, Hybrid system of NCM1 and PVD1 membrane elements, replaced by ESPA and ESNA
St. Lucie West, FL	1988	1 mgd, Originally started in 1988, using PVD1, and then replaced by ESNA in 1996

My presentation will mainly deal with typical examples of NF membrane systems. These includes NF plants at St Lucie West and Fort Myers in USA, and then Irabu-chou in Japan. The paper will describe benefits of using new, improved NF membranes (ESNA) in terms of reduced operating costs, superior removal of both inorganic and organic ions, and reliable, stable operation

Outline of St. Lucie West Plant

Feedwater to the RO plant is pumped from shallow wells (approximately 70 ft deep). As shown in Table 2, the feed water is characterized by high levels of hardness, organics, THM precursors, color, and soluble iron. Due to the need to reduce the high levels of these constituents and the fact that the raw water is characterized by low salinity, membrane softening was chosen as the process of choice.

Being a fairly clean well water source, pretreatment to the RO plant consisted of sulfuric acid injection to control CaCO₃ scale potential, and five micron cartridge filtration.

Table 2: Feedwater Quality and Comparison of Permeate Quality for ESNA and PVD1 Membranes

Constituent	Feed	ESNA	Acid Feed	PVD1
		Permeate) [Permeate*
Ca (ppm)	107	4.7	90	35
Mg (ppm)	6	0.31	7	2.4
Na (ppm)	49.3	11.6	60	34.2
Fe (ppm)	2.6	0.05	3	<0.3
Alkalinity (ppm)	290	25	1.1	1.3
Cl (ppm)	80	12.6	65	78
SO ₄ (ppm)	30	0.8	250	5.3
Silíca (ppm)	23.4	2.9	23	21.4
TDS (ppm)	588	58.0	501	180
THM Potential (μg/l)	80 - 120	13.6	80-120	9.9
Feed Pressure (psi)	80		80	
Feed pH for each system	7.15		4.0	

^{*} projected for start-up at pH 4

The soluble iron concentration in the raw water ranges from 2 - 4 ppm and potable water limits need iron levels below 0.3 ppm. The PVD1 membrane, initially exhibited higher passage to iron. It was later learned that iron passage of the PVD1 membranes was a direct function of the sulfate ion concentration. The conversion of alkalinity to sulfate resulted in an increase of iron rejection in the feedwater. Therefore, the feedwater was acidified with sulfuric acid to increase the sulfate ion concentration so that the permeate iron concentration would fall within the allowable potable water standards. To achieve this level, the RO plant required the injection of more than 1500 lb/day of sulfuric acid, which amounted to an excess of \$45,000 dollars per year; the addition also reduced the feedwater to a pH of 4. Due to the low permeate and concentrate pH, caustic soda (NaOH) injection was necessary to elevate the pH level to a neutral state. The amount of caustic soda used for both permeate and concentrate was in excess of 1000 lb/day, which amounted to over \$80,000 dollars per year.

Membrane Replacement

In May 1996, after 8 year-operation with the PVD1 membranes since their first installtion, St. Lucie West Water District selected ESNA membrane for their replacement based on bidding results for a total evaluated cost of the plant operation. Hydranautics successfully won the membrane replacement by demonstrating to have the lowest total operating cost among three membrane manufacturers, Fluid Systems, Filmtec, and Hydranautics. The ESNA membrane provided the advantages and savings with respect to the original design. **Table 3** shows the comparison between previous and current plant operating costs. The ESNA design resulted in a substantial reduction in the feed operating pressures. Moreover, the need for acid addition was eliminated, thus reducing demand for caustic soda and calcium chloride. Even with the decrease in feed pressure, the permeate flow was increased approximately 15%, with only a 5% addition in membrane area.

Table 3: Chemical Cost Breakdown for ESNA and PVD1

Cost Component (\$per 1000m³)	ESNA	PVD1
Acid	0.0	\$35.0
Caustic Soda	\$0.0	\$62.1
Calcium Chloride	\$32.7	\$27.6
Antiscalant	\$10.3	0.0
Total Chemical Cost per 1000m³	\$43.0	\$124.7

The Advantages Using ESNA

The ESNA membrane is a new ultra-low pressure softening membrane that is characterized by a higher specific flux and higher rejection than the PVD1 membrane. The ESNA membrane is rated at a specific flux of 0.30 gfd/psi which enables the operation at almost 50% of the Net Driving Pressure (NDP) of the PVD1. This translates to significant cost savings with respect to energy consumption and installation cost. Also, the overall sodium chloride rejection of the ESNA has been improved to 90%, as compared to 80% nominal with the PVD1, which provides an overall better permeate quality.

In St. Lucie West, the ESNA membranes currently produce an overall permeate quality that is 68% lower TDS as compared to the operation with the PVD1 membrane. **Table 2** outlines actual permeate quality parameters comparing between the PVD1 and ESNA membranes in the St. Lucie West Plant. The ESNA membrane is also used for the removal of low molecular weight organics, viruses and bacteria. In the St. Lucie West plant, there is a high concentration of TOC, color and THM precursors. The ESNA, like the PVD1, has provided excellent rejection to these constituents. Overall, the rejection of the ESNA membrane for TOC and THM precursors is better than expected. Since the

District is required to comply with potable water quality guidelines, the fact the ESNA exhibited superior field performance was a definite attribute of membrane.

Process Description

The softening plant, as it is designed today, utilizes (252) 8540-UHY-ESNA membrane elements arranged in a 24:12 array using 7 element long pressure vessels. (See figure 3 for a flow diagram). The plant operates at 85% recovery with a rated permeate flow of 694 gpm and a design flux rate of 8.9 gfd. The 8540-UHY-ESNA membrane elements are rated for a permeate flow rate of 9000 gpd at 75 psi of feed pressure.

Due to the increased membrane area (445 ft² with the ESNA, as compared to 425 ft² with the PVD1), the overall flux rate of the system was reduced by 5%. In addition, Hydranautics provided the St. Lucie West Water District with the option to increase the overall permeate flow rate by 15% to 800 gpm. So far, the District has not taken advantage of this option due to permitting considerations, but the option remains a viable one.

Pretreatment to the plant consist of antiscalant injection (to compensate for the acid removal) and one micron cartridge filtration. The need for acid addition, as described earlier, was eliminated. Permeate from the trains is discharged into a degasifier for hydrogen sulfide (H₂S) removal and carbon dioxide (CO₂) stripping. The pH is then adjusted by caustic addition to a pH of 9.0, while total hardness is brought up to the desired level by adding calcium chloride. The concentrate pH is also increased with the addition of caustic soda to a pH of 8.0, and then combined into the irrigation distribution system. St. Lucie West can be viewed as a zero discharge plant because both the permeate and concentrate are consumed for a specific purpose.

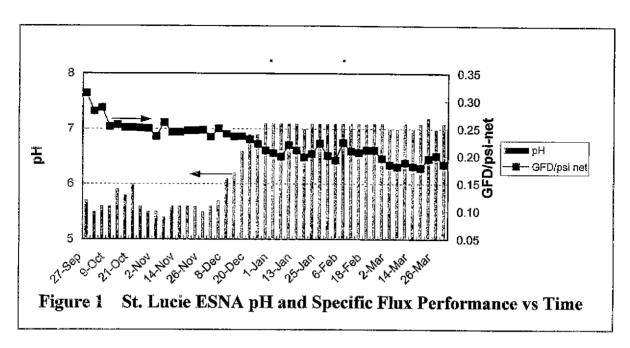
Operating Conditions

The plant with the ESNA membranes commenced operation on September 27, 1996. The feed pressure and salt passage at start-up were both as projected. The initial specific flux rate was 0.30 gfd/psi and salt passage was approximately 6%. Initially, a conservative approach was chosen, and the decision was made to acidify to a pH of 5.8 before gradually adding scale inhibitor and reducing acid concentration. The decision was based on the need to verify that the scale inhibitor would indeed work at elevated feed iron levels. Addition of acid to this pH will control CaCO₃ and/or FeCO₃ scaling while a gradual replacement of the acid with an organic scale inhibitor takes place.

Using the new ESNA membranes, the plant began operation with only 1350 lb/day of acid addition (to pH 5.8) as opposed the previous acid addition of greater than 1500 lb/day (pH 4.0) using the PVD1 membranes. During January 1997, acid addition was removed completely, subsequently increasing the feed water pH from 5.8 to 7.1. Antiscalant addition was set at a rate of 2.0 ppm.

Operational Analysis

The St. Lucie West plant provides an interesting case study for the effects and dependence of membrane flux and rejection on pH and antiscalants in highly fouling feed waters containing a large concentration of organic constituents. The feedwater to the St. Lucie West RO plant contains excessive levels of TOC (23-30 mg/l), which contributes to high levels of THM precursors and color formation (see Table 2). As described previously, the only pretreatment that is currently used is antiscalant addition and one micron cartridge filtration. The high levels of organic constituents have had a direct impact on the flux decline that the ESNA membranes have experienced. Observing Figure 1, we can see a membrane flux decline ten days after start-up and also in January 1997 corresponding to the discontinuation of acid addition and the institution of antiscalant addition. Ten days after start-up, the specific flux of the membranes was reduced to 0.25 gfd/psi, a 15% decline. The flux remained at this level for four months until the beginning of January, when it was reduced to 0.20 gfd/psi, an additional 20% decline. Since January 1997, the flux rate of the membrane elements has remained constant.



In addition, the salt passage has remained constant since the start-up in September 1996 (see Figure 2). The salt passage of individual ions and overall conductivity was lower than the projected performance based on nominal values of the ESNA membrane. From the operating data, it is apparent that a certain degree of fouling has occurred on the membrane surface, therefore forming a thicker layer on the membrane surface subsequently reducing the membrane flux.

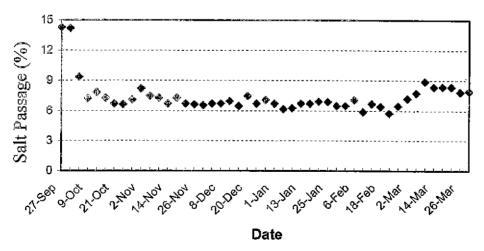


Figure 2 Salt Passage Performance vs. Time Elapsed

To try and evaluate the reason for the flux decline, one has to examine all the possible contributing factors. One hypothesis is the dependence of the membrane performance on the pH value under these conditions. From Figure 1 one can see that there is a certain relationship between increasing the pH level and the flux reduction. The pH level, to a certain degree, could have slightly affected either the charge on the membrane surface or the dissociation rate of the organic constituents. This could have caused the organic constituents to have a higher affinity to the membrane surface, therefore increasing the barrier layer and subsequently reducing the flux.

Another possibility is the effect of the antiscalant on the membrane surface. The antiscalant, combined with the high organic levels, could have changed the morphology of the membrane surface, therefore causing it to be more prone to the adherence of organic matter. The data supports the theory of membrane flux decline due to high concentration of organic constituents, however it is unknown whether these factors alone or as a combination could be attributed to the membrane flux decrease. Also, the City of St. Lucie has yet to perform a membrane cleaning, which in fact could restore, to a certain degree, the initial performance. Therefore, is has yet to be confirmed whether this condition is reversible or not. Further study is required to reach a definite conclusion.

RO Softening Plant at Fort Myers, Florida

The City of Ft. Myers obtained raw water for municipal use from the local river, which contains substantial natural organic material (NOM). NOM inadequately removed by conventional treatment process and remains in the water after treatment, reacts with chlorine applied for disinfection to form haloganated organics (THM) above the federal limit level. City of Ft. Myers decided to expanded capacity of their water supply system and improve potable water quality by constructing of a membrane softening plant. After conduction pilot demonstration test using softening membranes, they found the reduction of THMFP to be a level below 50 ppb was achievable. It has been also established that the softening system should operated at 90 % recovery rate, average flux rate should be set at $0.61 \text{m}^3/\text{m}^2/\text{d}$ (15 gfd) and net driving pressure should be maintained at 7 bar.

As the outline of the membrane softening water plant is shown in Table 4, the river feed water to the plant is pumped from shallow wells and is filtrated with cartridge filters rated at 5 micron. Feed water pretreatment includes addition of organic scale inhibitor and acid. In order to minimize acid consumption acid is added in two points: before cartridge filters and to the concentrate stream after the first stage (feed to the second stage). Pressure vessels are arranged in a three-stage array. Feed pressure is developed by parallel pumps operating to a common first stage feed manifold. Permeate flow from individual stage is controlled by applying permeate backpressure.

Table 4 Outline of Membrane Softening Water Plant in City of Fort Myers

Planning Start:	1987		
Commissioning:	December 1992		
Plant Capacity	12MGD		
Number of RO Trains	3		
Array	48:24:24		
Element Type First Stage: Second Stage: Permeate Recovery	8540-LSY-PVD1 / NCM 8540-USY-ESPA 88%		
Feed Water Type	Shallow Well Water TDS: 480 mg/L T-Hardness: 230 mg/L as CaCO ₃ HCO ₃ : 250 - 300 mg/L H ₂ S: 0.4 - 1.0 mg/L Fe: 0.5 - 3.0 mg/L TOC: 23 - 30 mg/L Color: 75 (deg)		
Product Water Quality	285 mg/L TDS 41 mg/L T-Hardness 4 Color (deg)		
Pretreatment	pH adjustment at 6 with H_2SO_4 as scale inhibitor cartridge filtration (0.5 micron)		
Post-treatment	Degasifier for removing CO ₂ and H ₂ S LSI Adjustment with 50% NaOH, Chemical dosing: CaCL ₂ , HF, ZnPO ₄ , CL ₂		
Design Feed Net Driving Pressure	0.7 MPa (100 psi)		
High Pressure Pump	1MPa (150 psi) 350 HP x 3100gpd x 4		
Power Consumption	Less than 0.4 kWh / m ³		
	1.4 kWh / K-gallon		

Outline of Irabu-cho Okinawa Plant

The RO plant at the town of Irabu-cho on a small island process well water from shallow aquifer of 850mg/L TDS salinity. Flow diagram of the Irabu-cho plant is shown in Fig. 3. The raw well water is also heavily contaminated with high levels of nitrate and nitrite-N originating from agricultural fertilizer drainage and household wastewater. To ultra-low pressure RO plant has been installed to comply with the safe drinking water standards.

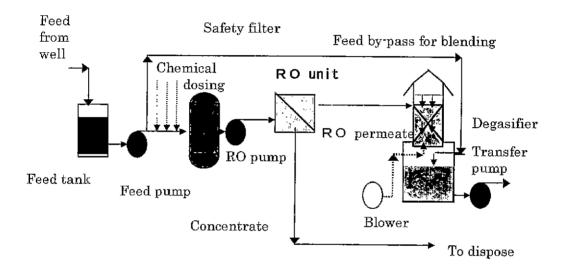


Figure 3. RO System Flow Schematic of Irabu-cho Water Plant

Feed water pretreatment consists of scale inhibitor and acid addition followed by cartridge filtration: 10 micron-PP wound type. The plant commenced operation just as of March 2000, at the recovery rate of 80%. An ultra-low pressure ES15 (ESPA) membrane which has been introduced commercially in 1995 has specific flux twice as high as of conventional polyamide composite (NTR-759HR or CPA2) membrane and therefore had a potential to significantly reduce pressure requirements of desalting process.

The flow diagram of the RO drinking water treatment is outlined in Figure 3. The RO permeate is blended with about 10% feed water by passing the RO process to adjust the dissolved ions content of the final purified water in this plant. Accordingly, the over all

water recovery rate of the plant is 90 - 92%. The outline of Irabu-cho RO system is shown in the next Table 5.

Table 5 Outline of Irabu-cho, Okinawa RO Membrane Treatment Plant Data

Planning Start:	1996
Commissioning:	March 2000
Plant Capacity	1.2MGD
Number of RO Trains	4
Array per Train	6:4 (6elements / Vessel)
Element Type	ES15-D8 (Equivalent to ESPA)
Permeate Recovery	80%
Feed Water Type	Well Water
	842 mg/L TDS 354 mg/L T-Hardness as CaCO ₃ 132 mg/L Na+ 260 mg/L CL- 10 mg/L as NO ₃ * -N / NO ₂ *-N
RO Product Water Quality	50 mg/L TDS 1.6 mg/L T-Hardness as CaCO ₃ 10 mg/L Na ⁺ 8 mg/L CL ⁻ ~2 mg/L as NO ⁻ ₃ -N / NO ⁻ ₂ -N
Pretreatment	pH adjustment at 6 with H₂SO₄ and SHMP as scale inhibitor cartridge filtration (10 micron-m)
Post-treatment	Degasifier for removing CO ₂ LSI Adjustment with 50% NaOH, By-passing 10 - 15 % Feed Water to blend with RO product
Design Feed Net Driving Pressure	0.75 MPa (107 psi)
High Pressure Pump	1.4MPa (200 psi)
Electricity for Water Production	0.5 kWh / m³ (Estimated)

Closing Remarks

The NF and RO technology for water production is widely used for improving quality of potable water. The largest number of membrane plant installations is located in Florida and California, USA.

Now it is becoming more popular to construct integrated membrane systems with ultrafiltration and NF membranes operating in one system. Examples of such installations are large integrated membrane plants in France and Netherlands, which are combining two kinds of membrane types to maximize efficiency of a treatment process to treat a variety of feed water to conform to the safety drinking water standard.

In Japan, a research and development project applying membrane as a core technology for public water supply is conducted as "ACT 21" (Advanced Aqua Clean Technology for the 21st Century) Project. The aim of this study is to develop new technology for upgrading water treatment, in order to get consistently excellent water quality with minimal use of chemicals as well as with compact footprint equipment and easy maintenances.

We would like to contribute potable water production through continuous further improvement of membrane technology and supplying all kinds of membrane products for pretreatment, desalting brackish and seawater, softening applications and waste water reclamation all over the world.

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