Novel Low Fouling Nanofiltration Membranes

Craig Bartels, PhD, Hydranautics, Oceanside, CA
Warren Casey, PE, Hydranautics, Houston, TX

Abstract

Nanofiltration (NF) has become a standard process to treat mildly brackish water sources that are high in hardness, iron or organic material which forms disinfection by-products. The goal of the membrane in these processes is to selectively remove certain ions, while passing others. Designing these membranes has become more complex in recent years as regulations on the finished water have become tighter, and there is pressure to reduce operating costs.

Example of such applications are the 10.5 million gallon per day (mgd) Deerfield Beach and the 40 mgd Boca Raton projects in Florida. The permeate from each of these new plants is blended with existing lime softener effluent. To meet the desired hardness of the blended water, the nanofiltration permeate hardness had to fall within a limited range, 25-80 (Deerfield) or 50-80 (Boca Raton) ppm as CaCO3. In each project the nanofiltration membrane must also reduce trihalomethane formation potential (THMFP) below 40 ppb and meet a maximum pressure requirement (90 psi for Deerfield and 80 psi for Boca Raton). In the case of Deerfield, however, there was a requirement to have high iron rejection as well. As a result, a slightly higher rejection NF membrane was required for Deerfield to achieve the iron reduction targets, while a slightly looser NF membrane was required to achieve the hardness passage requirements of the Boca Raton project.

Hydranautics has developed a unique NF membrane which is made by a process that allows the rejection to be tuned to a level that can meet the specific rejection required for these new projects. For the Deerfield project the membrane was made with an average calcium chloride rejection of 86%, while for the Boca Raton project the membrane was made with 80% rejection. As expected, the permeability of the NF membrane for Deerfield is lower, 7500 gallons per day (gpd) compared to the 7800 gpd element for Boca Raton. Information will be reported on the characteristics of these unique membranes, and how they are designed for these unique applications.

In addition to meeting the water quality and initial pressure requirements, these applications also have very high levels of TOC in the water, up to 20 mg/l. The high fouling potential of this water also makes it difficult for the NF membrane to maintain stable performance over the life of the membrane. The unique low fouling feature of the ESNA1-LF nanofiltration membrane makes it ideally suited for difficult organic-laden feedwaters.

The ESNA1-LF membrane has operated at the Deerfield plant since 2003 and has produced product water of 0.13 ppm iron, hardness of 27.3 ppm as CaCO3, THMFP of 27 ppb, and stable operating pressure. The membranes have not required chemical cleaning during this period. The ESNA1-LF2 membrane at Boca Raton plant has been operating since November 2004. The permeate from the NF membranes has an average hardness of 75 ppm as CaCO3 and THMFP of 16 ppb. Meeting these strict water quality requirements has proven that these new low fouling membranes can be tailored, even for very large-scale plants.

Novel Low Fouling Nanofiltration Membranes

NAMS '06 Chicago, Ill

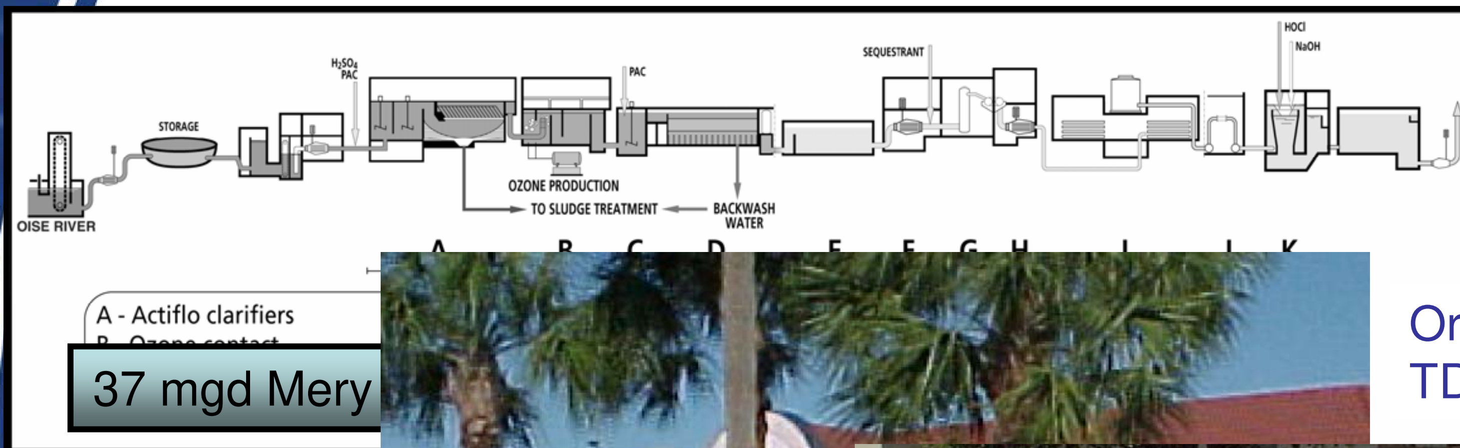
Craig R. Bartels, PhD
Warren Casey

Hydranautics
Oceanside, CA

NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

Commercial Use of Nanofiltration



Organic Removal
TDS Passage

Pesticide R
Partial Ca F

Partial Ca Removal

New Nanofiltration Application Trends

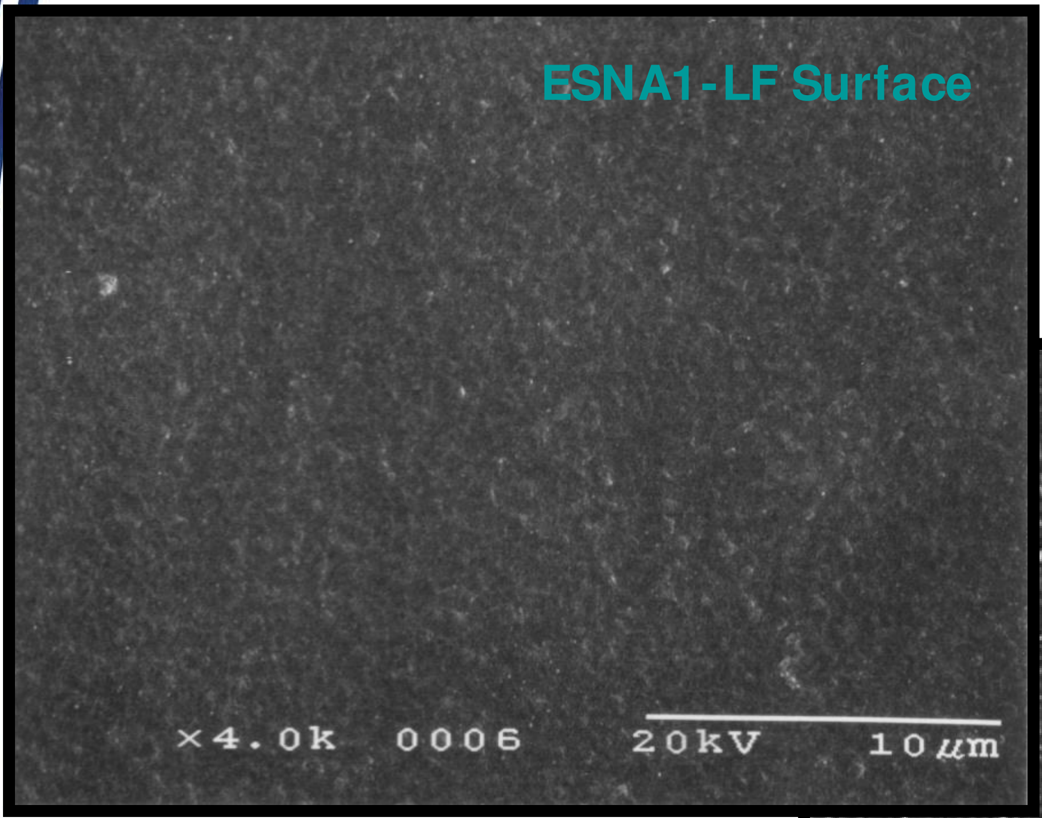
- Larger Plant Sizes: 10 – 40 mgd
- Specific Permeate Hardness Target
- High Organic Levels = High Fouling Potential
- Disinfection By-Products Limits
- Low Pressure Operation
- Timing of Execution

New Low Fouling NF Membranes with Variable Hardness Rejection

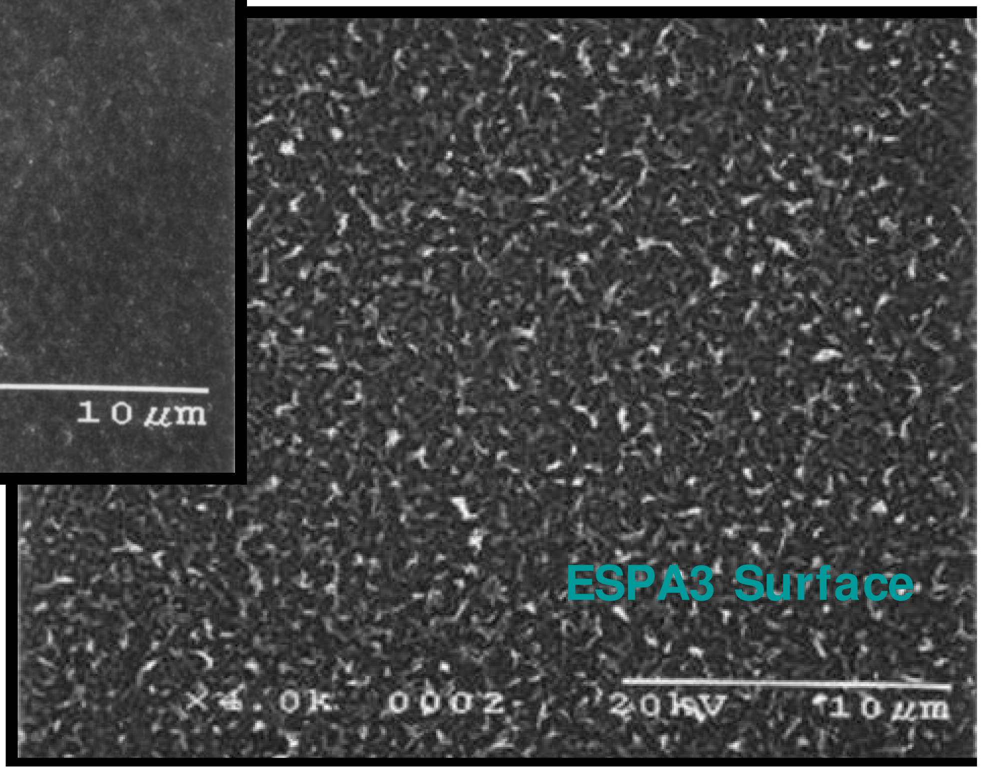
- Controlled hardness removal - eliminating the need for hybrid membrane designs (LF, LF2, LF3 versions)
- Significantly reduces operating costs by lowering power consumption, while providing a non-aggressive low TDS permeate water
- Greatly reduces fouling potential caused from natural organic matter
- Lowest cost per gallon produced – feed pressures of less than 100 psi saves energy cost

Membrane Surface Properties

Smooth Topography

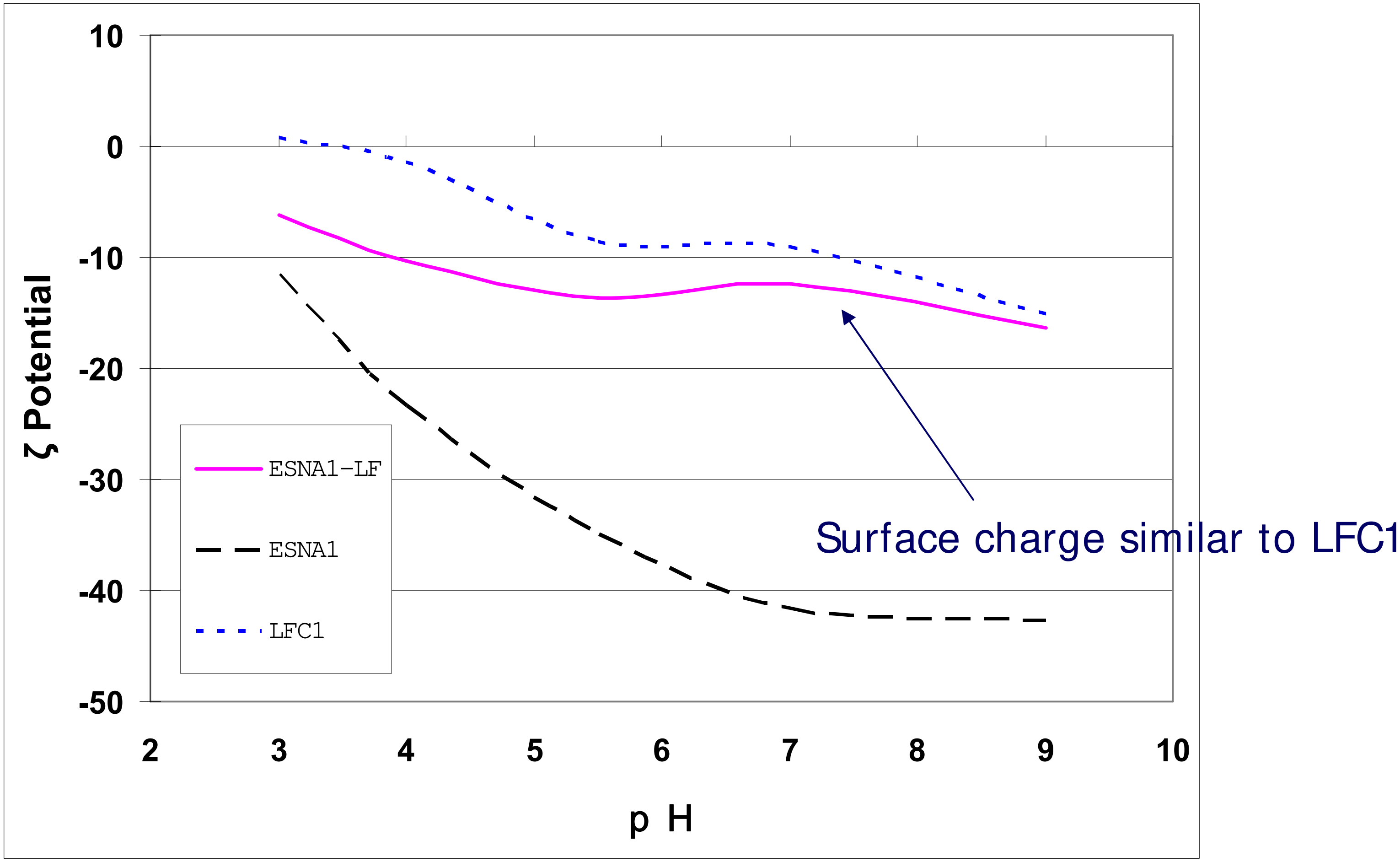


Surface roughness has been decreased to minimize sites for debris trapping



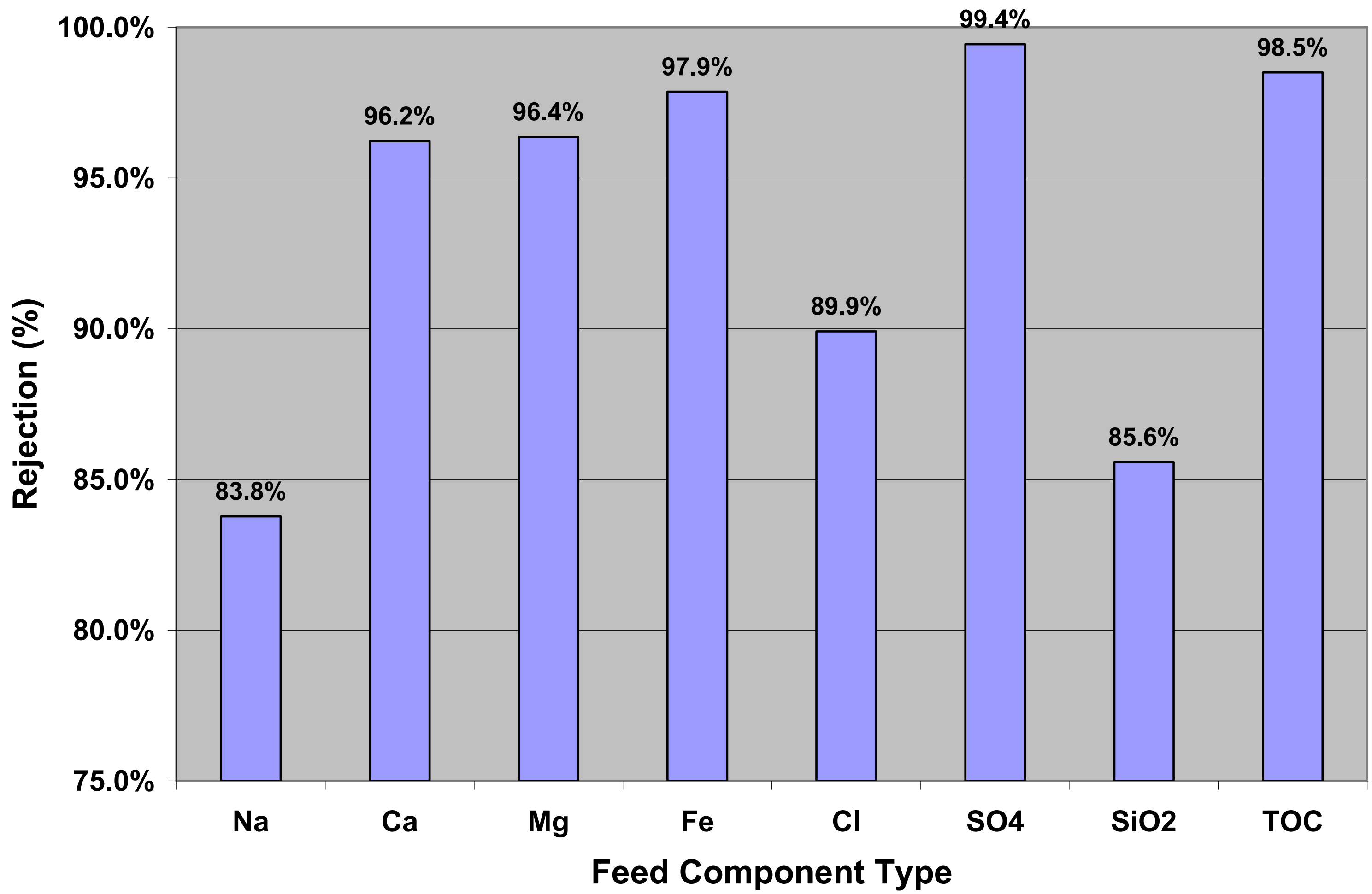
NITTO DENKO

Membrane Surface Properties: Reduced Surface Charge

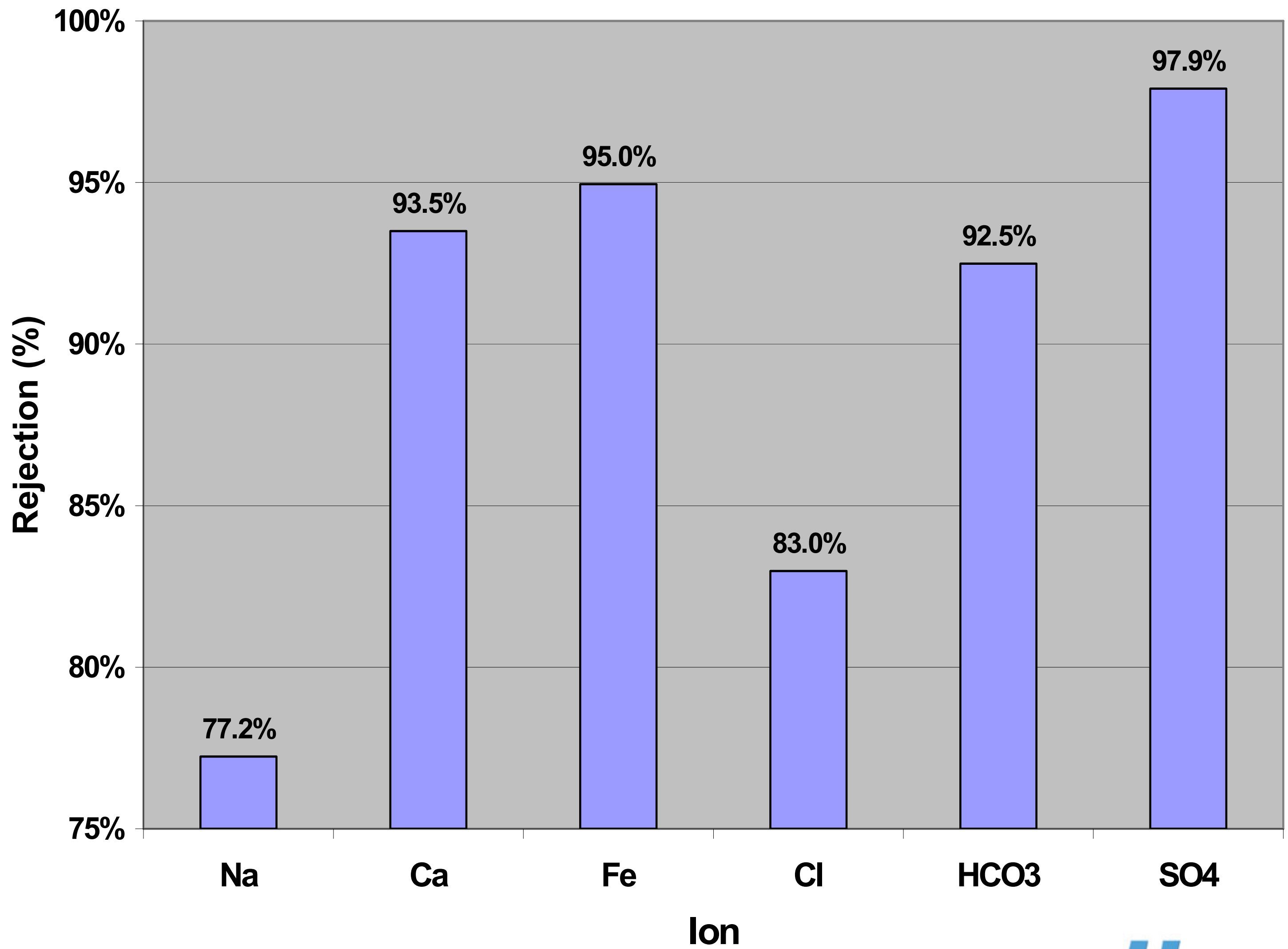


- **Lower surface charge minimizes interaction with surfactants**

ESNA1-LF Salt Rejection (Surface water @ 13 gfd, 25 C)



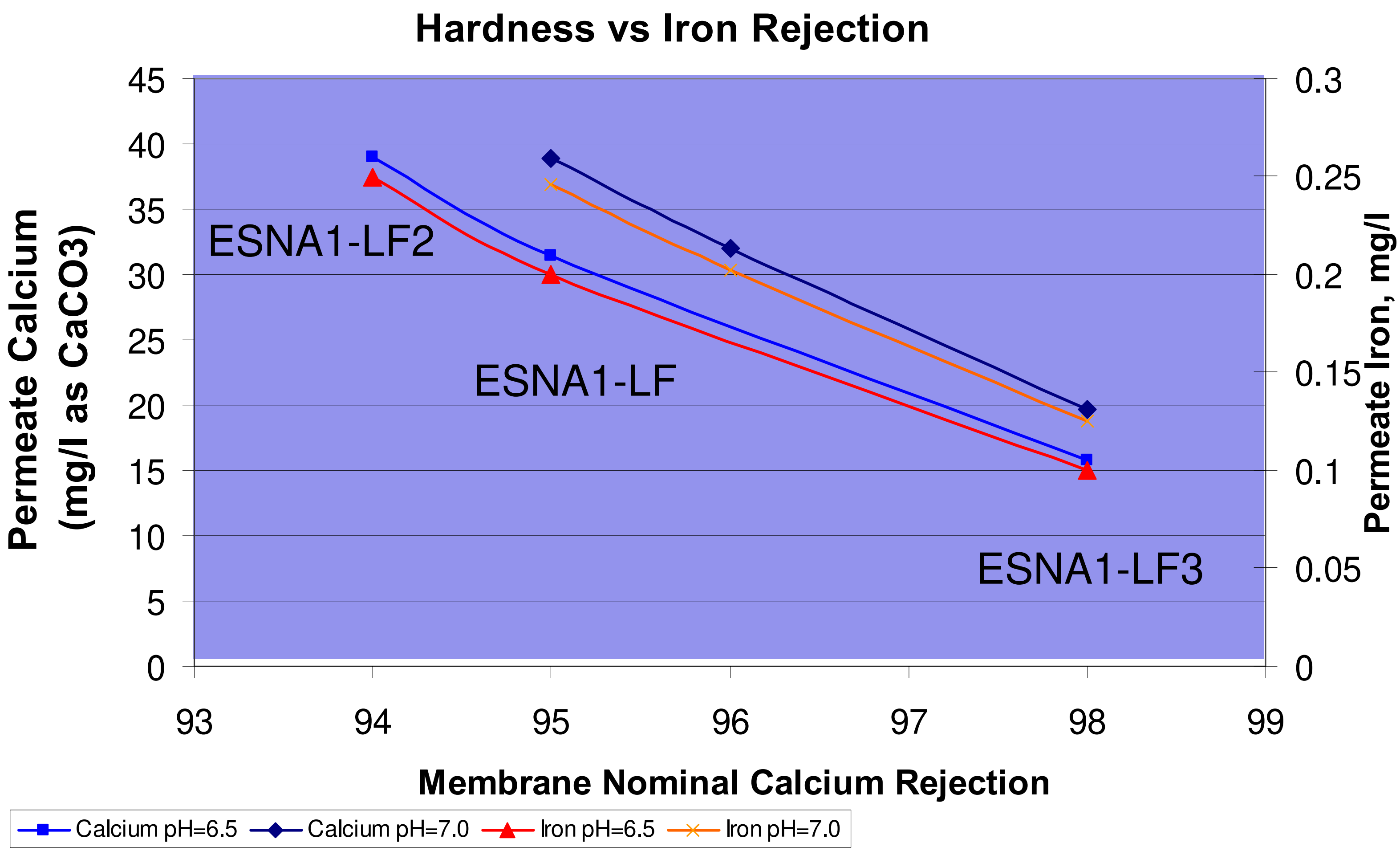
ESNA1-LF2: Salt Rejection (Surface Water @ 13 gfd, 25 C)



NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

Chemistry Modification of ESNA1-LF, LF2 and LF3 to Achieve Desired Permeate Hardness

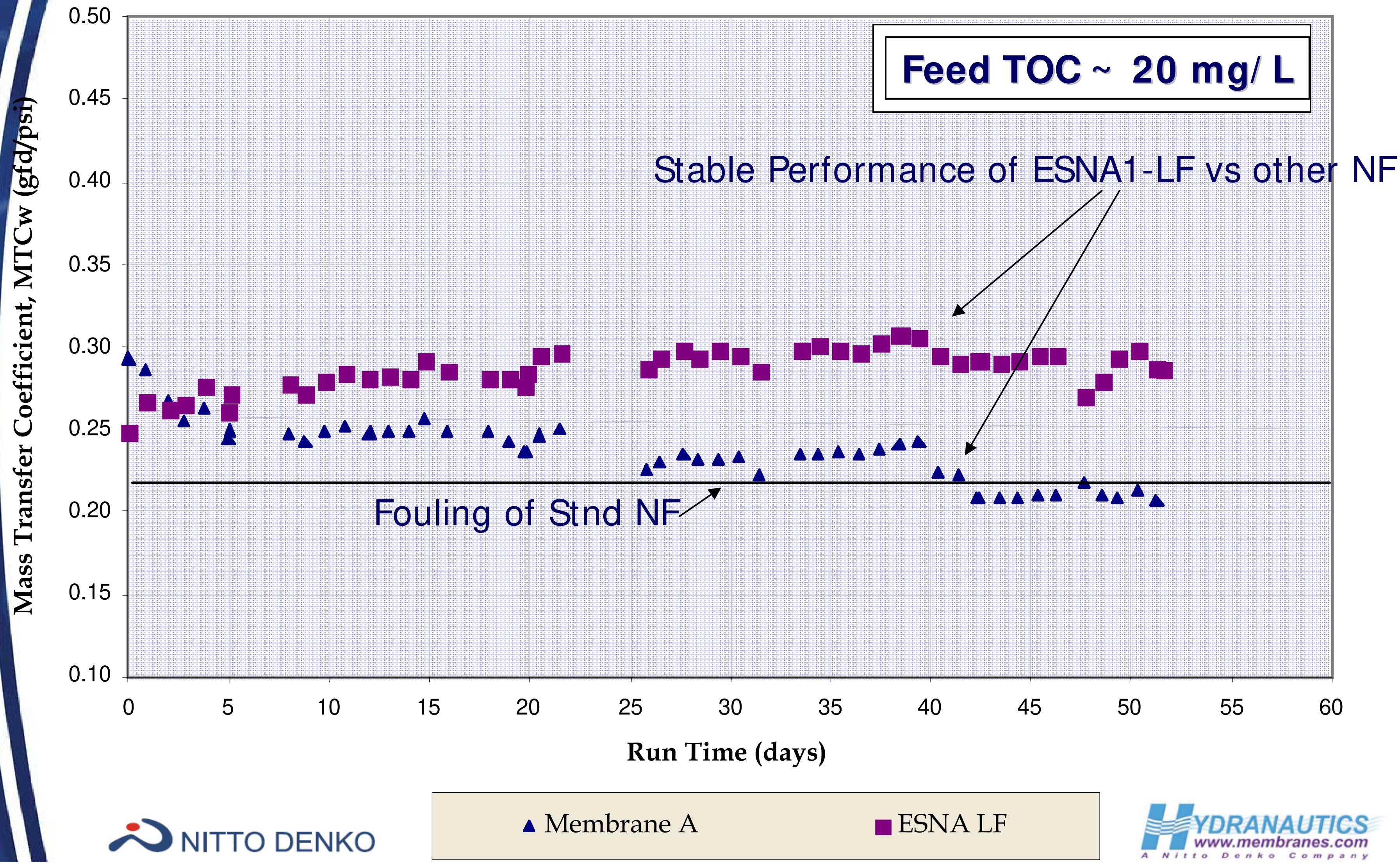


Typical Florida Feed Waters

	Boca Raton	Deerfield Beach	Hollywood
Total Hardness (mg/l $CaCO_3$)	265	250	250
Fe (mg/l ion)	0.3	1.5	1.0
HCO_3 (mg/l as ion)	265	285	266
TDS mg/l (sum of ions)	466	482	468
TOC (mg/l)	12	20	-
Color (CU)	50	50	-
pH	7.0	7.0	-

Boca Raton Water Samples

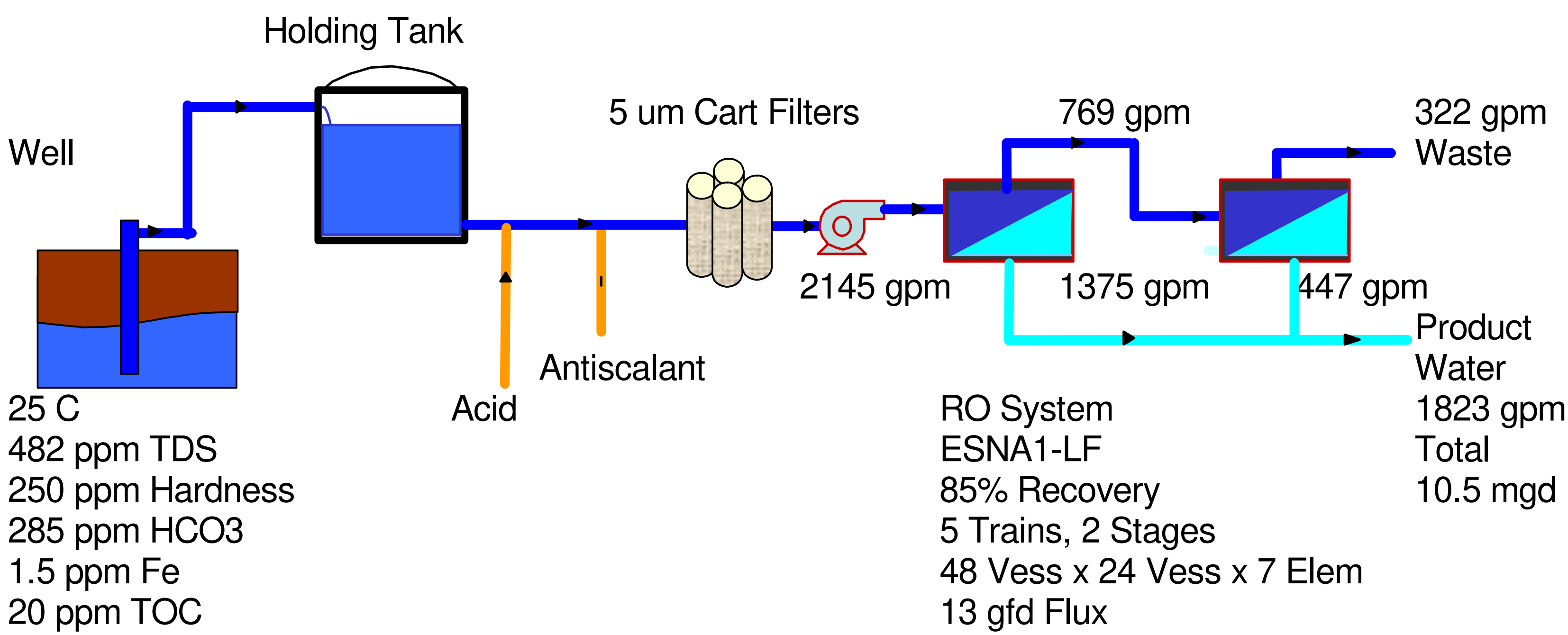
ESNA1-LF2 Pilot Data: Low Fouling Membrane Performance Comparison



NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

Deerfield Treatment Process



City of Deerfield Beach, FL

RO System Design:
10.5 MGD of Permeate
ESNA1-LF Membrane
5 trains
48-24 array of 7M tubes
85% recovery
13.0 gfd.

Pretreatment:
Acid
Antiscalant
Cartridge filtration.

Operation:
Start-up November 2003
Steady Performance
No cleaning in two years

Deerfield Beach Separation Objective

		Feed	Permeate
Total Hardness	(mg/l $CaCO_3$)	250	26 – 82.5
Iron (Dissolved)	(mg/l as ion)	1.5	< 0.2
HCO_3	(mg/l as ion)	285	< 175
TDS	(mg/l as ions)	482	< 250
TOC	(mg/l)	20	< 1.0 (THMFP < 40 ppb) THAAFP < 30 ppb)
Color	(CU)	50	< 1
Recovery			85%
TMP @ 25C	(psi)		90 psi
Average Flux	(GFD)	-	13.0

NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

Deerfield Plant Data

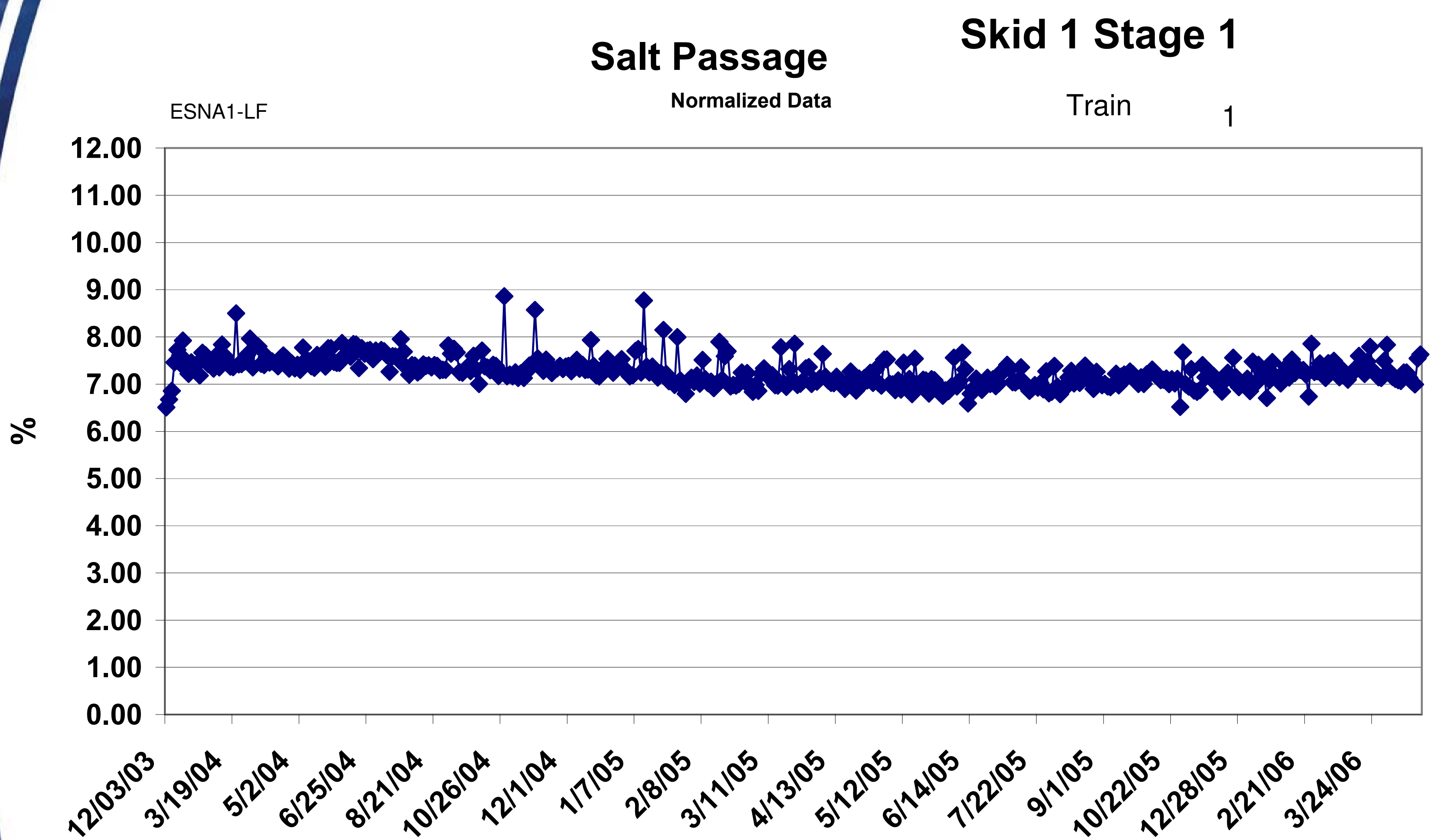
ESNA1-LF Performance Trend

Custom Element Settings	TMP (26.2C, 9psi permeate pressure)	Permeate Hardness* ($mg/l\ CaCO_3$) (Feed = 215 mg/l)	Permeate Iron* (mg/l ion) (Feed = 1.1 mg/l)
IMS Projected Value	80.2	20.2	0.10
Project Target Design	73.6	27.8	0.11
Actual (Average of 5 Skids)	85.9	25.7	0.10

* Estimated from Conductivity

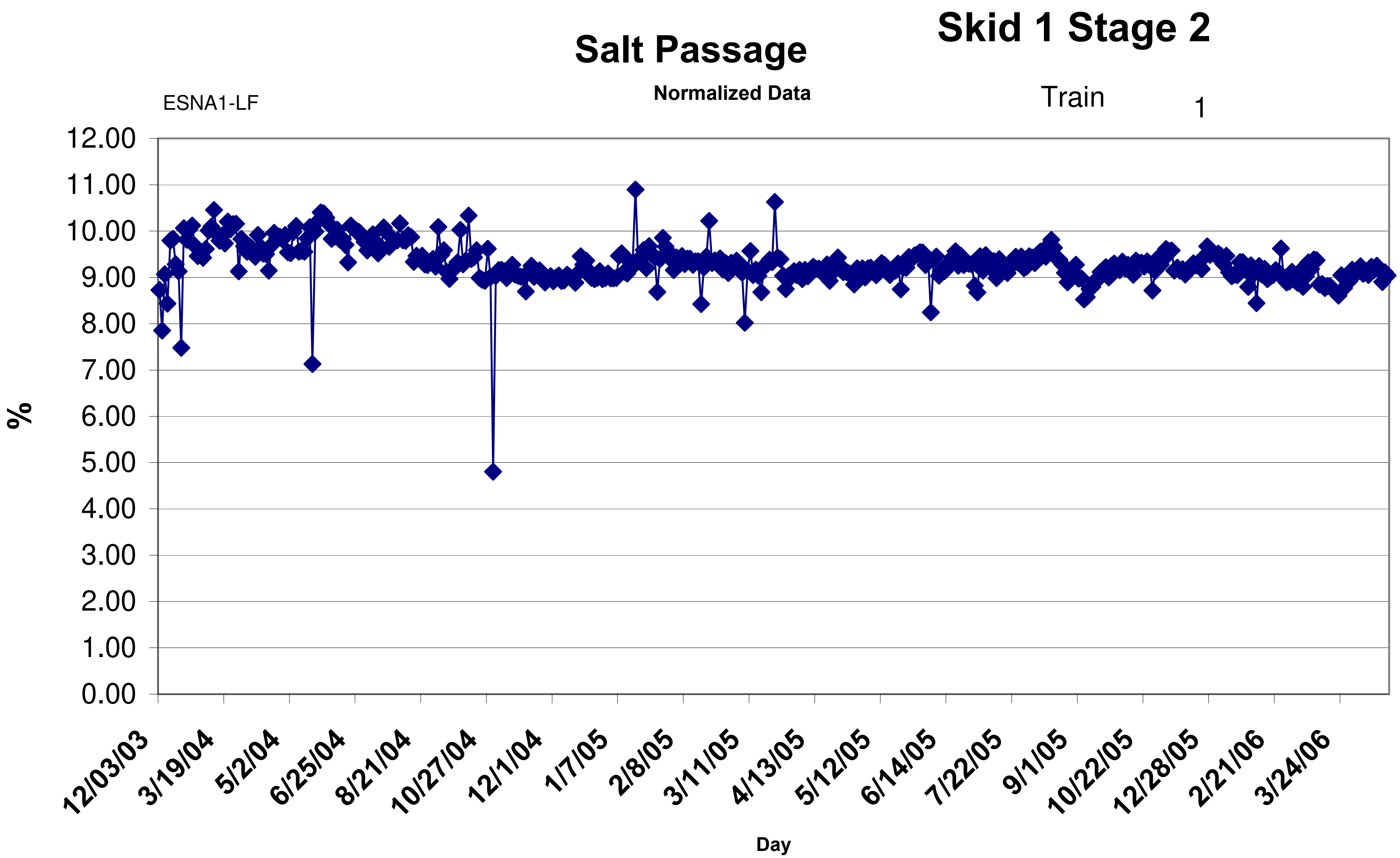
Deerfield Plant Data

ESNA1-LF Performance Trend



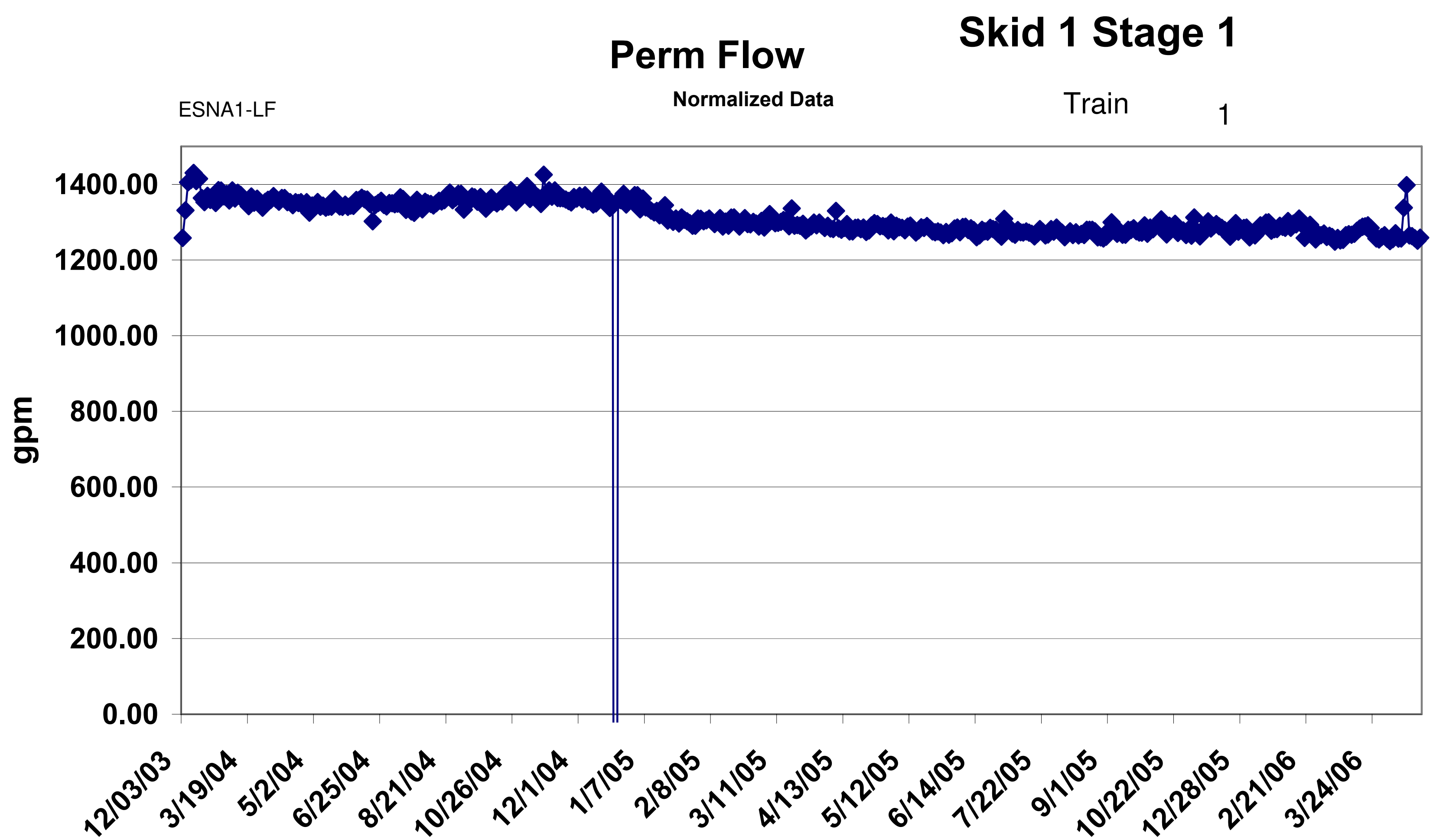
Deerfield Plant Data

ESNA1-LF Performance Trend



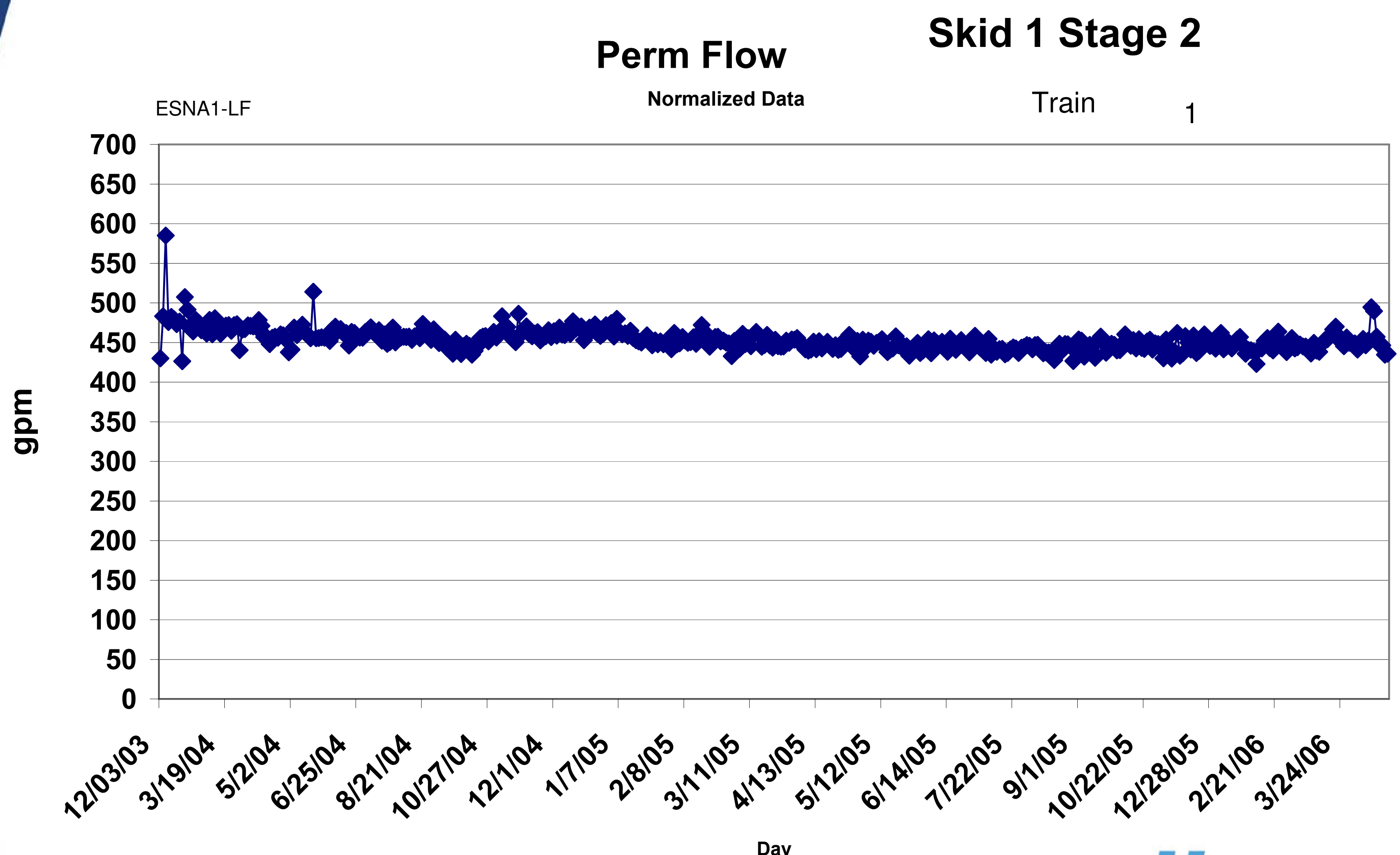
Deerfield Plant Data

ESNA1-LF Performance Trend



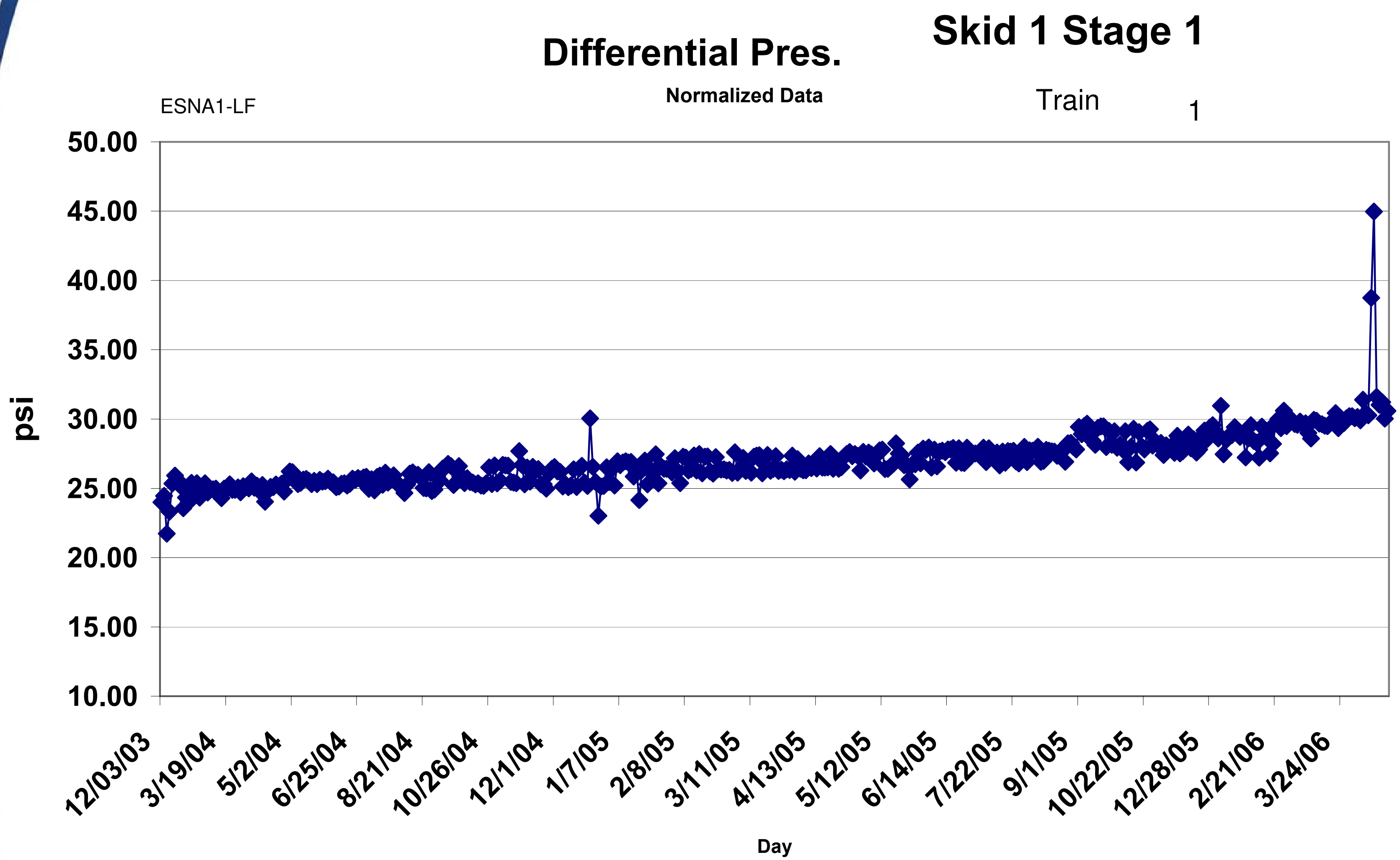
Deerfield Plant Data

ESNA1-LF Performance Trend



Deerfield Plant Data

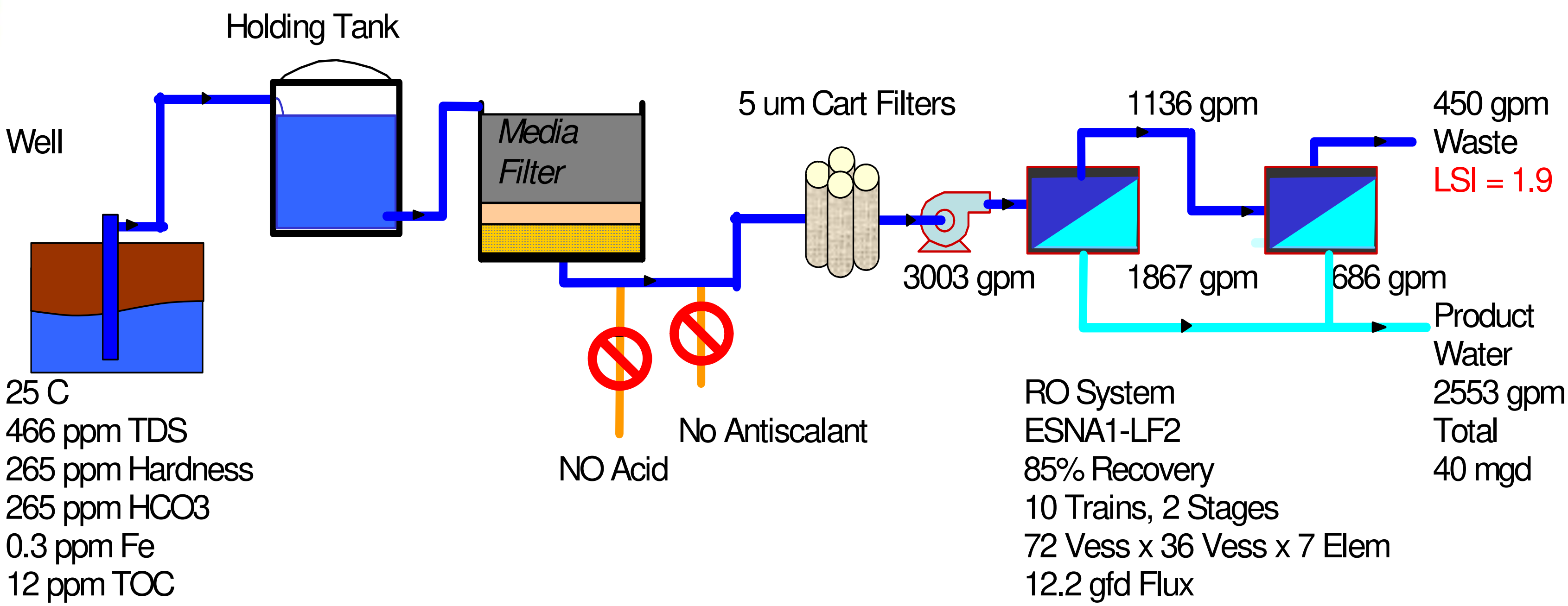
ESNA1-LF Performance Trend



NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

Boca Raton Treatment Process



City of Boca Raton, FL

RO System Design

ESNA1-LF2 (93% hrdnss rej)
- 36.8 MGD permeate
- 10 1st/2nd Stage Trains
- 72-36 array of 7M tubes
- 85% recovery
- 12.2 gfd

ESNA-LF3 (98% hrdnss rej)
- 3.2 MGD permeate
- 2 each 3rd Stage Trains
- 36-18 array of 7M tubes
- 50% recovery
- 10.7 gfd

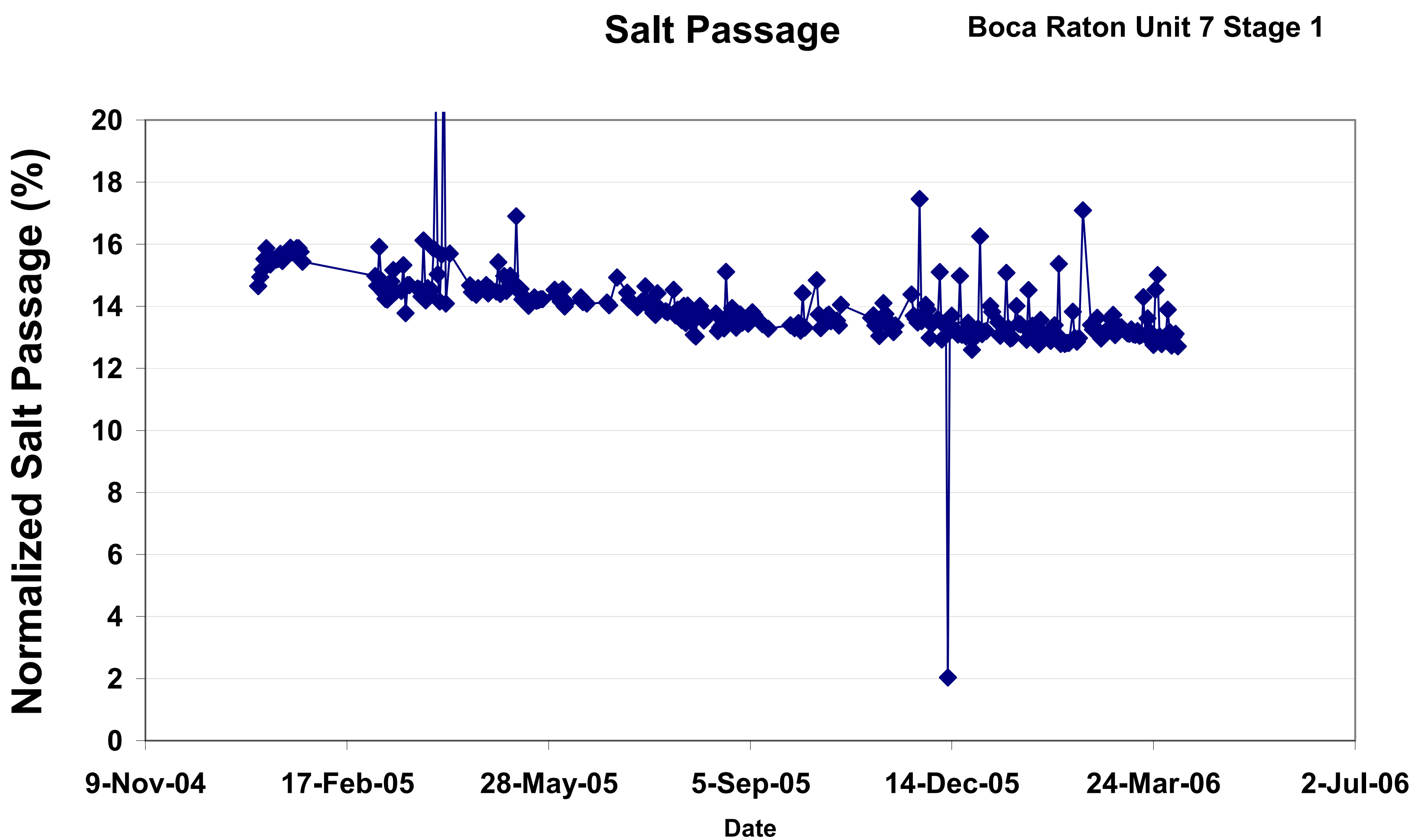
Pretreatment
- Multi-media filters
- Cartridge filters
- No antiscalant
- No acid addition

Boca Raton Separation Objective

PARAMETER	Feed	1st & 2nd Stage Perm	3rd Stage Perm
Total Hardness (mg/l $CaCO_3$)	265	50 - 80	20 - 100
HCO_3 (mg/l as ion)	265	< 175	-
TDS mg/l (sum of ions)	466	< 300	< 300
TOC (mg/l)	12	< 1.0 (THMFP < 42 ppb) THAAFP < 30 ppb)	< 1.0 (THMFP < 85 ppb) THAAFP < 70 ppb)
Color (CU)	50	< 2	< 2
Recovery		85%	50%
TMP @ 25C (Feed-Total Perm)		80 psi	100 psi
Average Flux (GFD)	-	12.2	10.7

Boca Raton Plant Data

ESNA1-LF2/3 Performance Trend

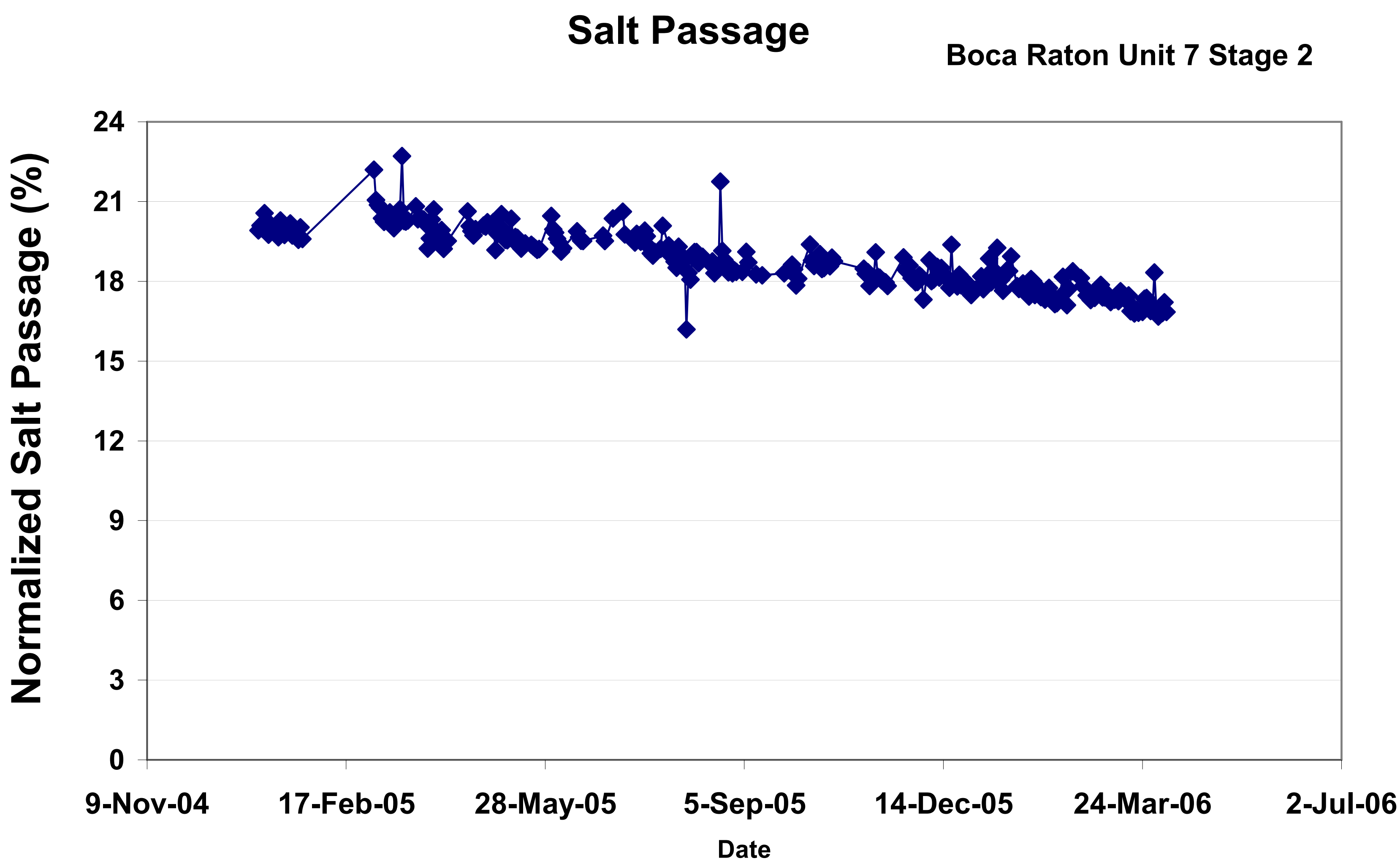


NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

Boca Raton Plant Data

ESNA1-LF2/3 Performance Trend

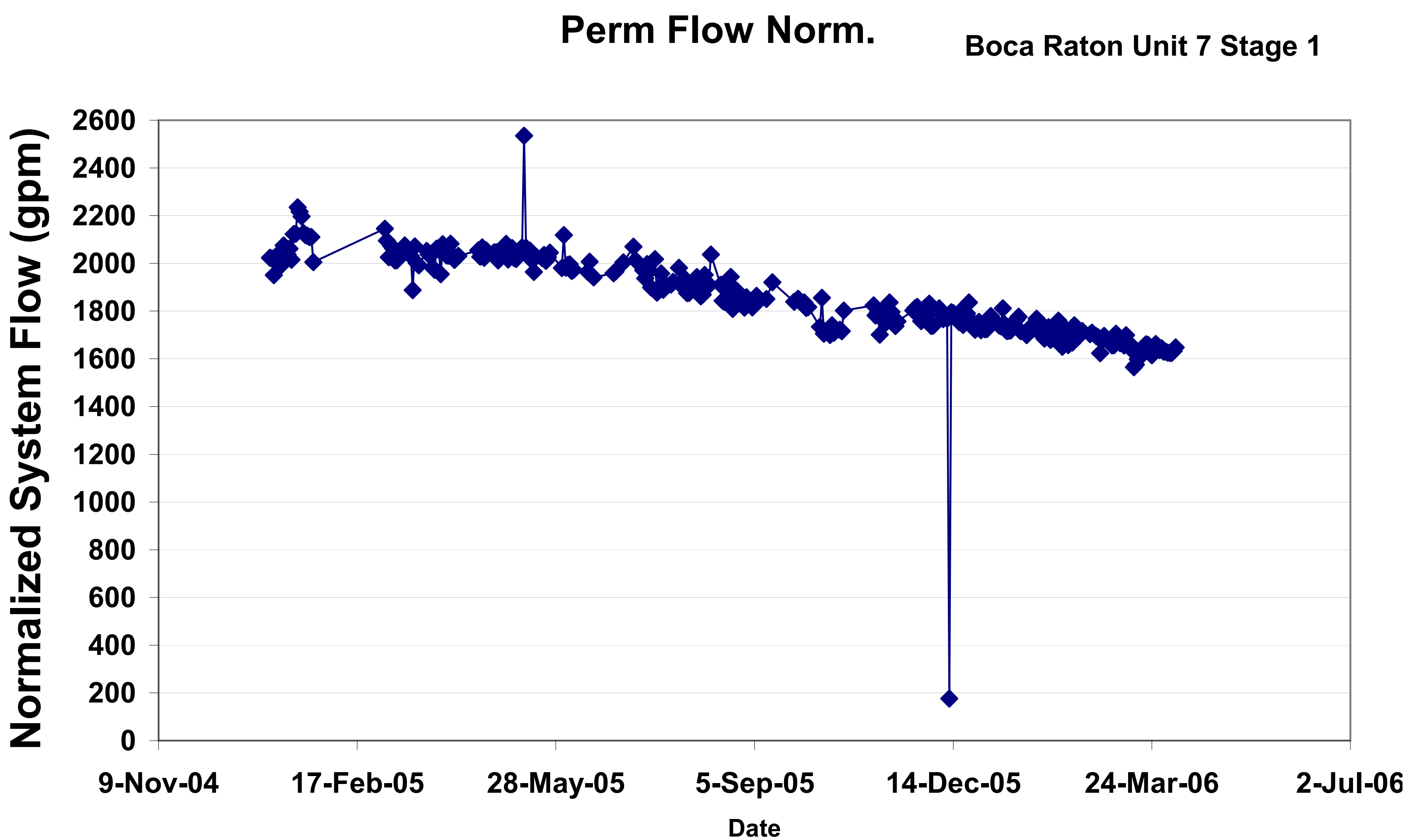


NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

Boca Raton Plant Data

ESNA1-LF2/3 Performance Trend

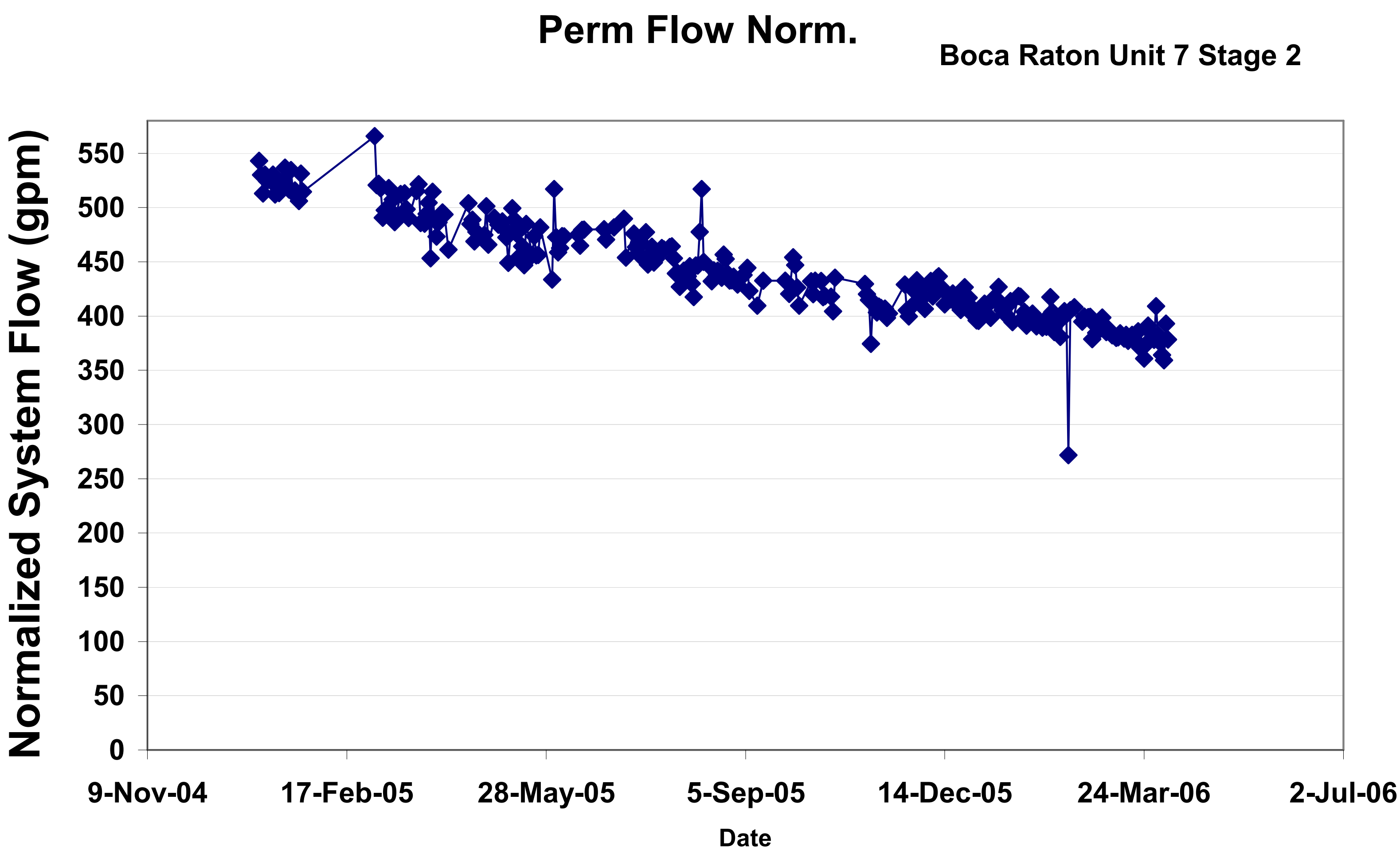


NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

Boca Raton Plant Data

ESNA1-LF2/3 Performance Trend

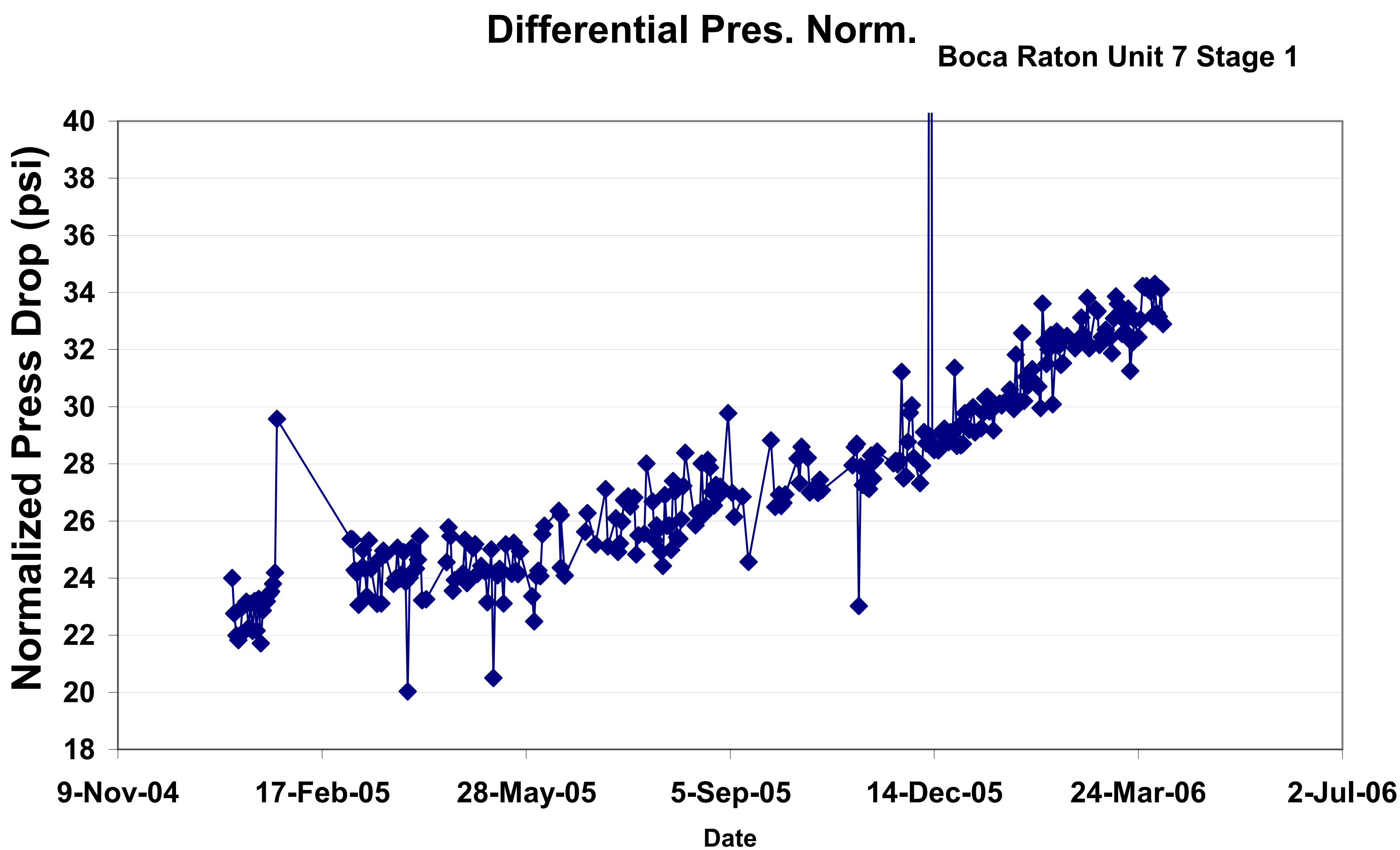


NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

Boca Raton Plant Data

ESNA1-LF2/3 Performance Trend

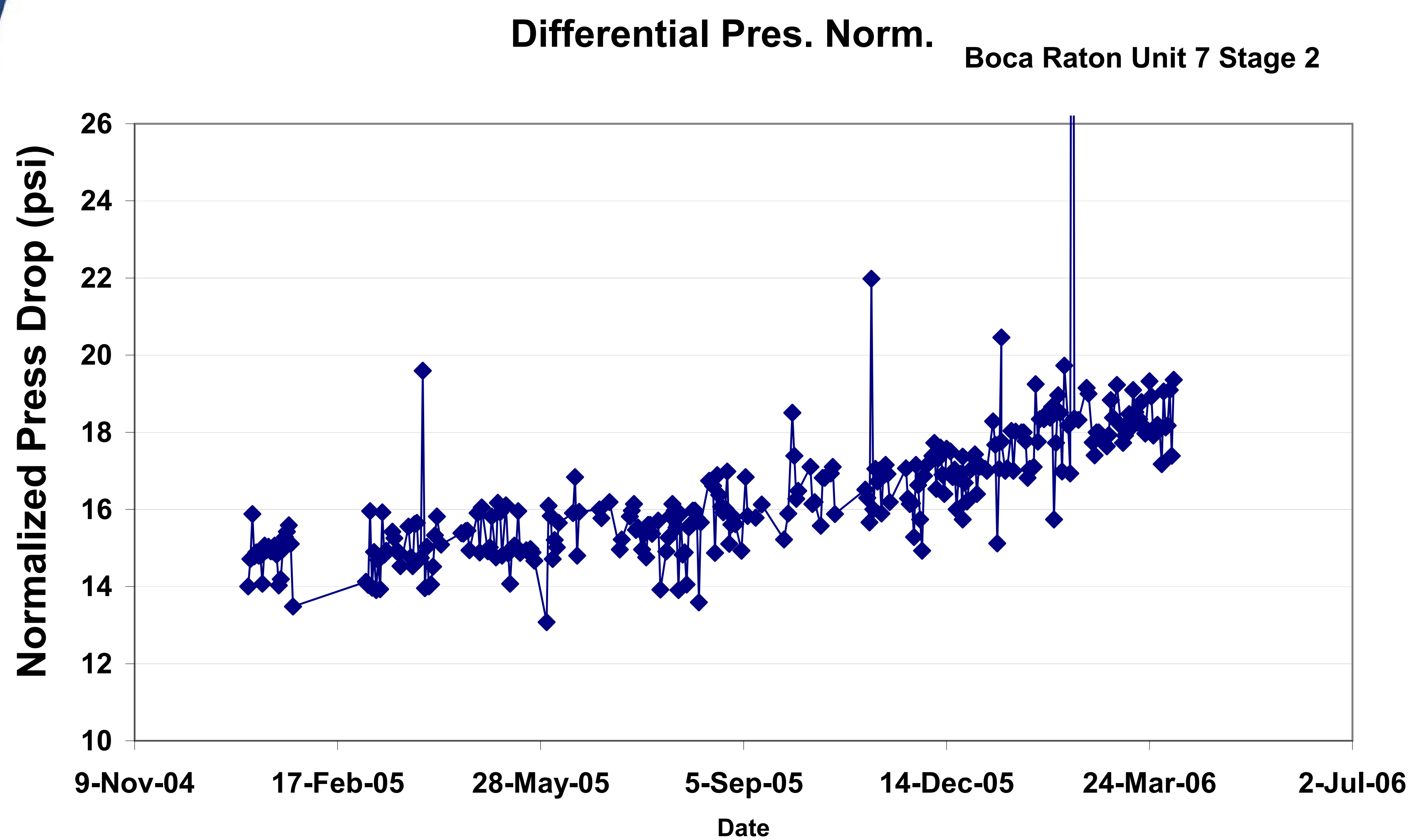


NITTO DENKO

HYDRANAUTICS www.membranes.com A Nitto Denko Company

Boca Raton Plant Data

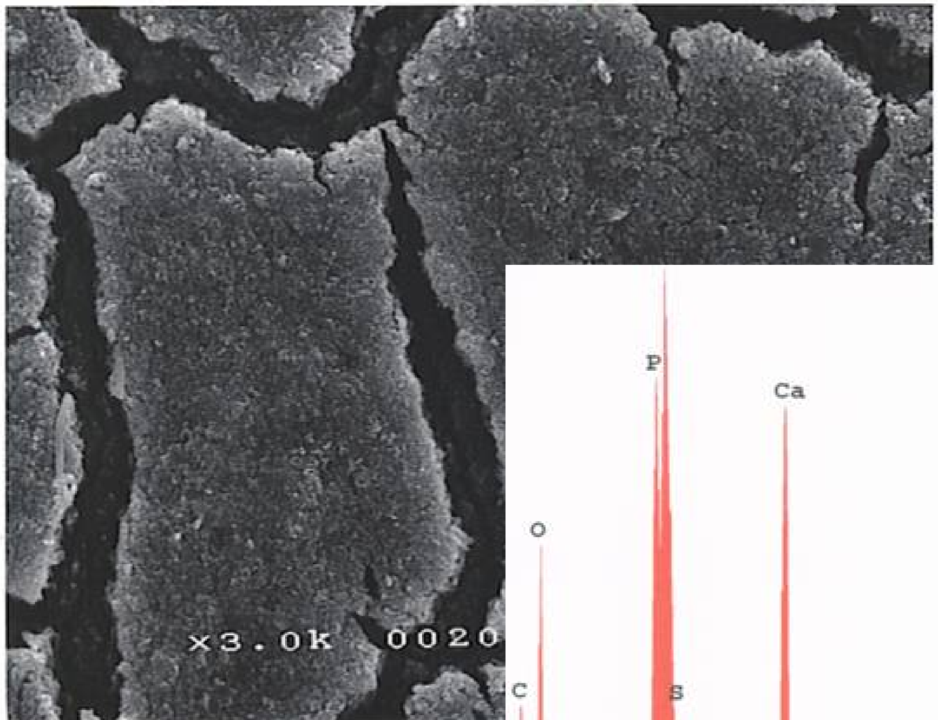
ESNA1-LF2/3 Performance Trend



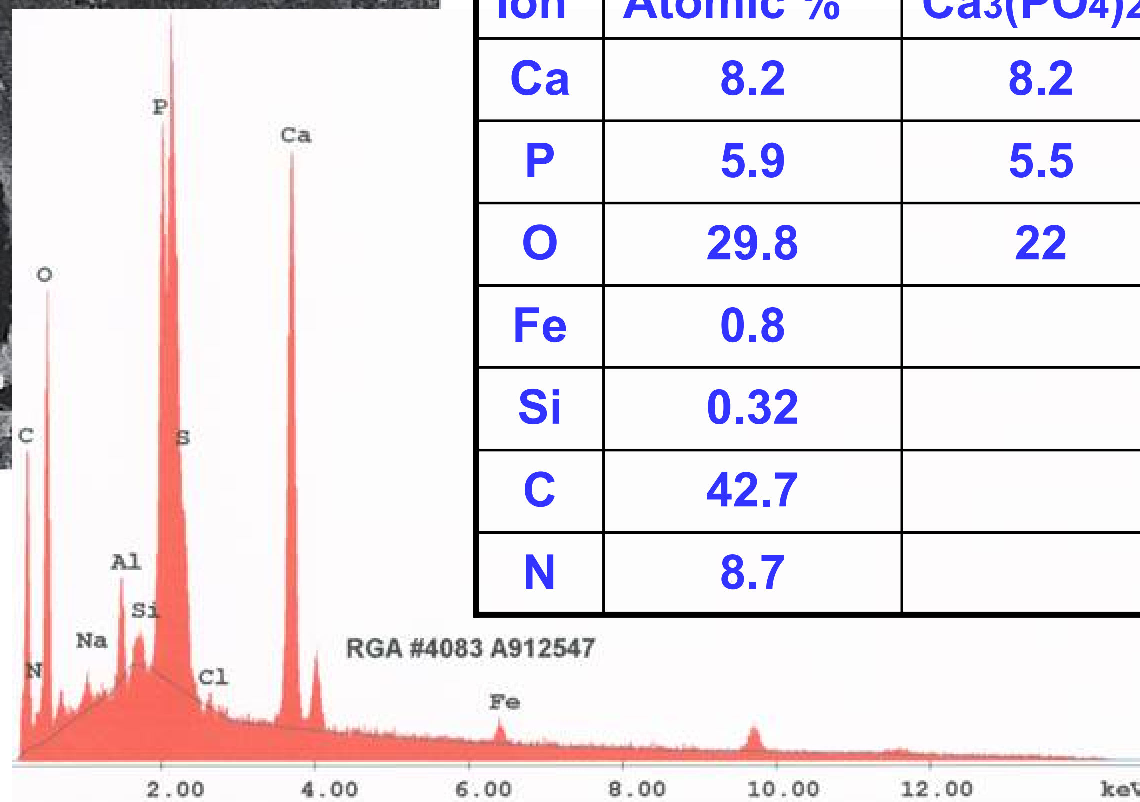
NITTO DENKO

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

Analysis of Fouled Membrane from Lead Element



SEM of Membrane Surface covered with foulant. 3000X



EDAX of Membrane Surface covered with foulant.

Ion	Atomic %	$Ca_3(PO_4)_2$
Ca	8.2	8.2
P	5.9	5.5
O	29.8	22
Fe	0.8	
Si	0.32	
C	42.7	
N	8.7	

Boca Raton Plant Data

Performance Results

PARAMETER	Feed	1st & 2nd Stage Perm	Target
Total Hardness (mg/l $CaCO_3$)	387	75	50 - 80
HCO_3 (mg/l as CaCO3)	209	74	< 175
TDS mg/l (sum of ions)	387	137	< 300
TOC (mg/l)	12	< 0.8 (THMFP 16 ppb) THAAFP 15 ppb)	< 1.0 (THMFP < 42 ppb) THAAFP < 30 ppb)
Color (CU)	35	1.2	< 2
Recovery		85%	85%
TMP @ 25C (Feed–Total Perm)		69 psi	<80 psi
Average Flux (GFD)	-	12.2	12.2

Conclusions

- Novel NF membrane chemistry allows controlled variation of the hardness rejection
- Modification of the surface results in a smoother, less charged surface which reduces fouling
- High rejection of NOM materials results in low disinfection by-products and meets Federal standards