DEVELOPMENT AND PILOTING OF HIGH FLUX THIN FILM NANOCOMPOSITE RO MEMBRANES FOR OIL AND GAS APPLICATIONS

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Abstract

Effective seawater treatment solutions which can be implemented in low-weight, low-footprint configurations for enhanced oil recovery (EOR) applications are becoming increasingly important in the oil and gas industry. With the goal of achieving higher flux, Water Standard and LG NanoH_2O worked together to develop and validate a new thin-film nanocomposite (TFN) reverse osmosis (RO) membrane specifically formulated for these applications. The permeate water quality specification for the EOR water allows for higher permeate total dissolved solids (TDS) concentrations when compared with requirements for municipal seawater facilities, ideal for membranes with much higher flux (A-Value) but without the need for high salt rejection.

The pilot test was divided into several stages to assess different element configurations and lead element flux rates which, in the end, proved to be the limiting factor. High flux rates on a lead element can cause premature fouling and increase the likelihood of multiple cleanings. Test stages investigated four membrane 4M, 6M and 7M designs in regular and hybrid configurations, to determine whether EOR water quality targets could be achieved using fewer elements. One stage was repeated and run for almost one month as the preferred configuration and lead element flux for full scale designs. The pilot test showed that a regular 4M array using all 15,000 GPD elements was most feasible for balancing fouling and higher lead flux rates while achieving water quality targets, so as to enable low-weight and low-footprint system designs for EOR.

I. INTRODUCTION AND BACKGROUND

Seawater treatment equipment which can be deployed in configurations which minimize footprint and weight requirements are growing in importance in the oil and gas industry, particularly for EOR applications where space and load availabilities are constrained. Because these applications frequently require the use of desalinated and/or softened seawater with low salinity and sulfate [1] as the injection fluid, a study was commissioned to investigate various treatment options. With the goal of achieving higher flux rates than typical TFN RO membranes, development and validation began on a new TFN membrane specifically formulated for these applications. The permeate water quality specification for the EOR water allows for higher permeate total dissolved solids (TDS) concentrations when compared with requirements for municipal seawater facilities. This scenario is ideal for membranes with much higher flux (A-Value) but without the need for high salt rejection.

II. EXPERIMENTAL DESIGN

Element Preparation. To prepare for piloting, two types of 400 ft^2 TFN elements were manufactured, denoted as 'WS-R' and 'WS-ES' elements, each type exhibiting high flux and low rejection properties which are unique in the desalination industry. The WS-R element exhibited similar salt rejection properties as the WS-ES element, but operated at lower flux rates. Specifically, the WS-ES and WS-R elements operated at 8,000 GPD and 15,000 GPD (at standard seawater test conditions), respectively. Both exhibited 99.6% rejection (at seawater conditions) which, though high for some types of RO membranes such as brackish water, affords salt passage needed to conduct some types of EOR programs effectively. During preparation of these elements, neither was optimized for stringent salt rejection due to the lenient permeate quality requirements of the application.

Objectives and Key Performance Indicators. The aim of testing was to simulate the performance of high flux elements in a hybrid configuration (i.e. both WS-R and WS-ES elements within the same pressure vessel) and regular configuration (i.e. only WS-ES elements within a pressure vessel) using similar raw water quality to that of a site applicable for Water Standard's field requirements. Combining the WS-R element with WS-ES elements within single pressure vessels enabled balanced flux conditions across those pressure vessels [2]. Consequently, fouling potential in the lead elements was reduced. Success of the pilot test was determined by meeting permeate TDS, calcium, magnesium and sulfate targets without experiencing a rapid reduction in specific flux and increase in driving pressure and differential pressure.

Siting and Equipment Design. The pilot was carried out at the Port Hueneme Naval Base Desalination Testing Facility located in Southern California. Influent seawater quality data is provided in Table 1 and treated permeate requirements are set out in Table 2.

Table 1. Influent Seawater Quality

Parameter	Unit	Value
Sodium	mg/L	10,538
Potassium	mg/L	385
Magnesium	mg/L	1,280
Calcium	mg/L	384
Strontium	mg/L	7.81
Barium	mg/L	0.04
Fluoride	mg/L	1.29
Chloride	mg/L	18,899
Sulfate	mg/L	2,661
Nitrate	mg/L	0.00
Carbonate	mg/L	2.02
Bicarbonate	mg/L	154.69
Boron	mg/L	5.17
TDS	mg/L	35,498
SDI	-	1.88 - 3.23
Turbidity	NTU	< 0.073
pH	-	7.80
Average Temperature	°C	17.10

Table 2. Treated Permeate Requirements

Parameter	Unit	Value
TDS	mg/L	< 2,000
Calcium	mg/L	< 10
Magnesium	mg/L	< 10
Sulfate	mg/L	< 10

The pilot unit comprised of a seawater RO system sized to produce a design permeate flow of 20 to 40 GPM, and is depicted in Figure 1 below. The system has five 2M vessels connected in series to allow for testing of up to 10M at any one time. The system is designed to collect permeate samples and performance data for each element individually. In this study, a maximum of 7M was used. A single energy recovery device (ERI PX-90) is installed, which limits the system permeate flow mentioned above.

Figure 1. Pilot Equipment

WS-ES and WS-R elements were loaded into the pilot unit in various hybrid or regular element configuration. Each configuration was tested in a designated test stage. A summary of element configurations tested during each stage is provided in Table 3 and Figure 2.

Table 3. Element Configurations

Stage	Configuration	Array	Element Type (Position)
1	Hybrid	4M	WS-R (1); WS-ES (2-4)
2A	Regular	6M	WS-ES (1-6)
2B	Regular	4M	WS-ES (1-4)
3A	Hybrid	7M	WS-R (1); WS-ES (2-7)
3B	Regular	7M	WS-ES (1-7)

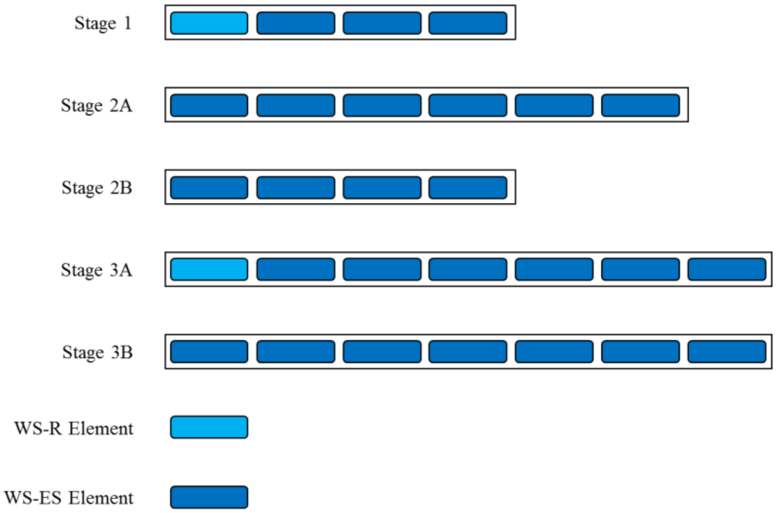


Figure 2. Element Configuration and Array Detail

Seawater from the Pacific Ocean was pumped through membrane filtration pretreatment (GE ZeeWeed 1000 ultrafiltration) external to the pilot unit for solids removal. Pretreated seawater was then transferred to the pilot unit, into pressure vessels housing the WS-ES and WS-R elements. Permeate and concentrate were disposed into the ocean. The pilot unit was equipped with antiscalant, sodium bisulfite and acid dosing systems for fouling control and cleaning.

<u>Test Plan.</u> Testing was conducted over a one-month period during March 2014. LG NanoH_2O managed onsite operations, while Water Standard reviewed pilot data remotely. Each test stage was run for one week, divided into two parts of three to four days each to assess different configurations and element flux rates. A test duration of three days was deemed adequate to allow for RO stabilization and production of reliable results, based on LG NanoH_2O experience. A summary of each test stage, the duration of testing, and target operating parameters is set out in Table 4.

Table 4. Testing Matrix

Week	Stage	Day 1 - 3				Day 4 - 7			
		Permeate Flow	FWR	Max Flux	Feed Pressure	Permeate Flow	FWR	Max Flux	Feed Pressure
		GPM	%	GPD	PSI	GPM	%	GPD	PSI
1	1	17.5	36.9	20.8	773	18.5	42	22.4	825
2	2[1]	17.5	40	20.3	732	17.5	36.9	22.1	740
3	3A	23	50	21.5	795	23	53	22.4	828
4	3B	23	49	23.7	772	23	53	25.5	815
[1]Day 1 – 3 only: 6M loaded, but collected data from 4M									

Flow, pressure, pH, temperature, and ionic water quality data was collected from each array and between elements using online and manual methods. During Stage 2B testing, data was collected for a 4M array although the pressure vessel was loaded with six elements in order to attain required flow conditions in each element. Testing, as defined in Table 4, was used as a screening process for each configuration. A preferred configuration which met treated water quality targets without rapid reduction in specific flux, increase in driving pressure, and escalation in differential pressure, in accordance with key performance indicators, was designated for validation testing. Validation testing occurred for one month during May 2014, to obtain additional operating data and assess the repeatability of the prior experiment.

III. RESULTS AND DISCUSSION

Screening. A summary of key data collected during each stage of the pilot study is set out in Table 5. Treated permeate quality specifications were achieved during each of these stages.

Table 5: Screening Test Results

Stage	Array (Position)	Lead Flux	Flux	Feed Pressure	DP
		GFD	GFD	PSI	PSI
Stage 1.1	WS-R (1); WS-ES (2-4)	15	15.3	805	11.5
Stage 1.2	WS-R (1); WS-ES (2-4)	17.8	16.5	920	9.1
Stage 2A.1	WS-ES (6)	15.3	9.2 - 10.3	728 - 741	12.7 - 16.1
Stage 2A.1	WS-ES (4)	19.9	14.4	728 - 744	7
Stage 2A.2	WS-ES (6)	15.9	9.7 - 10.1	744 - 747	14.1 - 15.7
Stage 2B.1	WS-ES (4)	22.9	15.5	756 - 769	12.3
Stage 2B.2	WS-ES (4)	22.4	14.8	770 - 796	10.2 - 15.4
Stage 3A.1	WS-R (1); WS-ES (2-7)	16.8	11.7	880	14.3 - 14.6
Stage 3A.2	WS-R (1); WS-ES (2-7)	17.6	11.7	960	13.1 - 16.2

Stage 2B, with a 4M regular configuration, emerged as the preferred scenario to undergo validation testing due to its high flux operation and ability to achieve treated water quality targets. Data was logged into LG NanoH2O's QSee software for analysis. Normalized permeate flow (NPF), normalized salt passage (NSP) and differential pressure (DP) trends obtained during the screening phase of Stage 2B testing are provided in Figure 3 below.

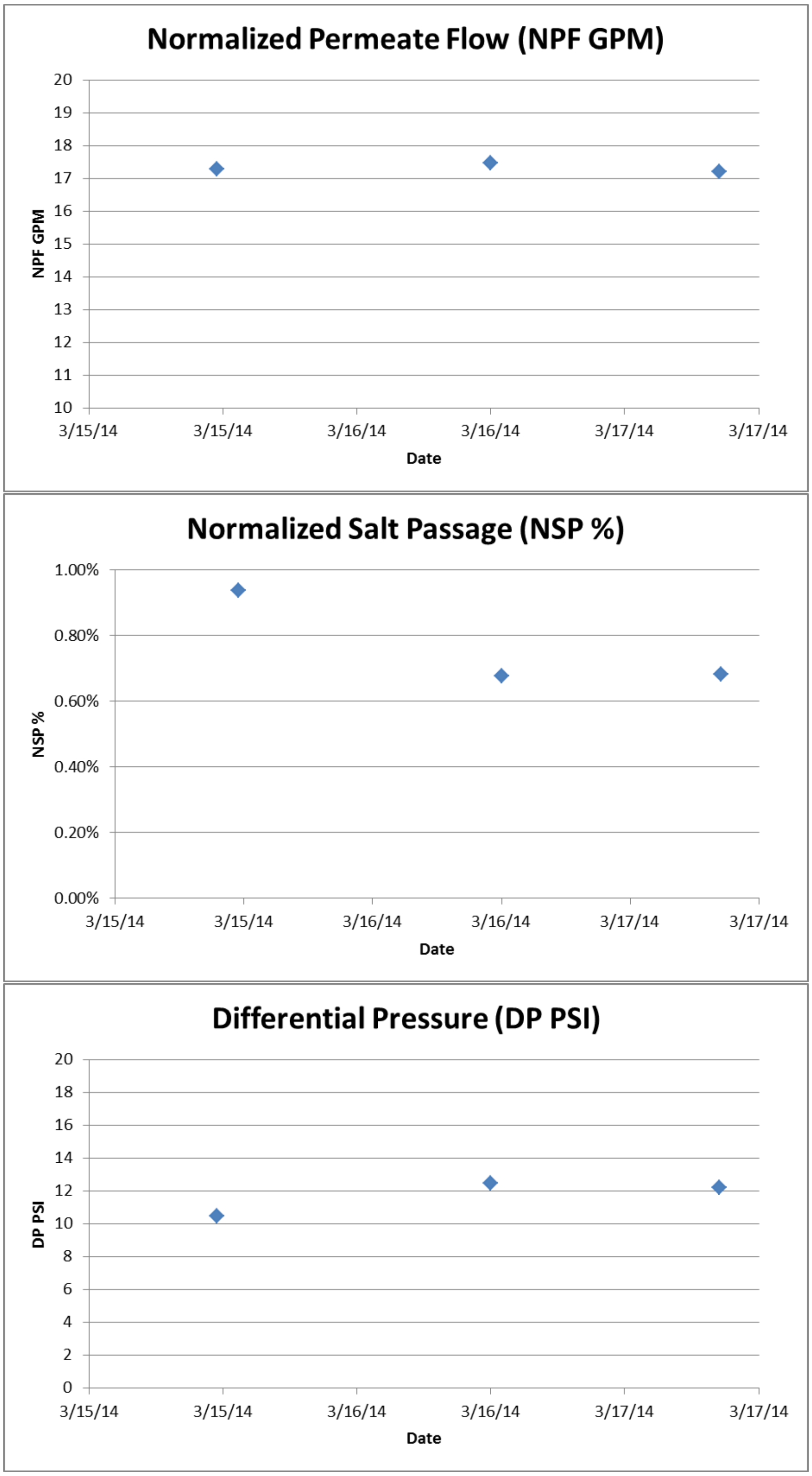
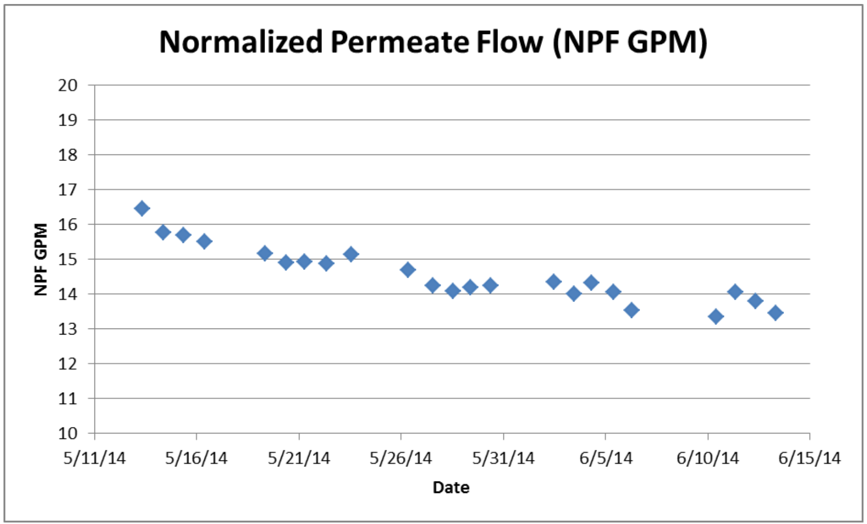


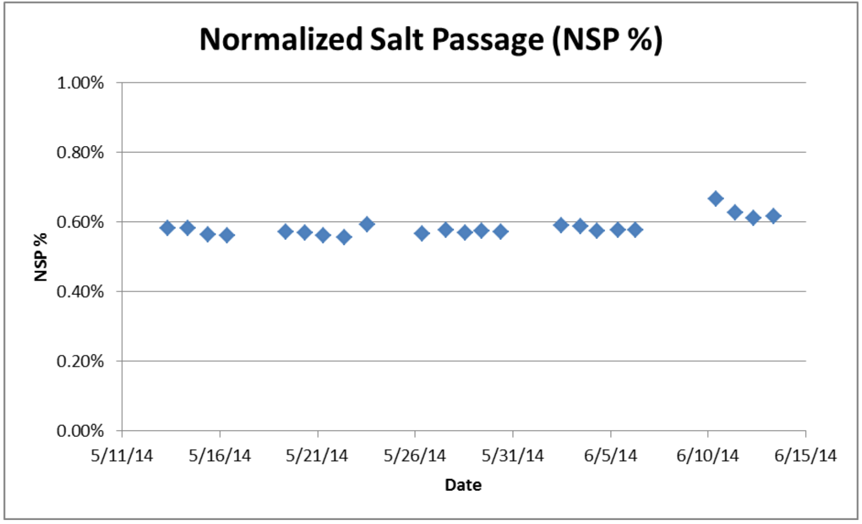
Figure 3. Stage 2B Screening - NPF, NSP and DP

Validation Testing. Stage 2B was repeated and run for almost one month as the preferred configuration and lead element flux rate for full scale designs, to validate data obtained during the screening phase. The Stage 2B repeat was conducted using the same elements used during the screening phase, over the course of a one-month period. A summary of key operational data collected during this phase is set out in Table 6. NPF, NSP and DP trends are depicted in Figure 4.

Table 6. Validation Test Results

Stage	Configuration (Position)	Lead Flux	Flux	Feed Pressure	DP
		GFD	GFD	PSI	PSI
Stage 2B Validaton	WS-ES (4)	19.4 - 20.0	15.6	770 - 863	13 - 18





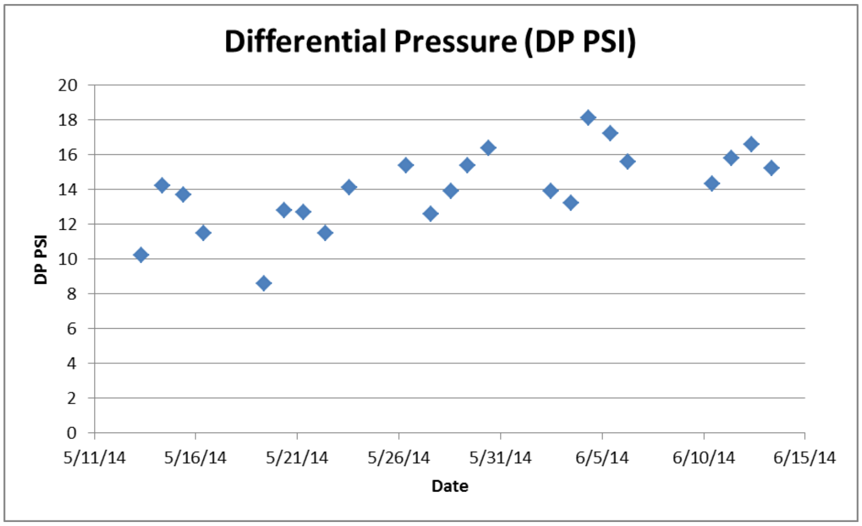


Figure 4. Stage 2B Validation – NPF, NSP and DP

Data indicated that validation testing of Stage 2B began at much higher pressures relative to the screening test. The lead element flux obtained in the original 2B Stage was also unable to be reproduced, suggesting that organic surface fouling had occurred on the membrane, with a minor amount of feed spacer fouling. The increased pressure and fouling was attributed to an integrity breach of the pretreatment. Figure 3 reflects a decreasing trend in NPF, with relatively stable NSP and DP which increased but fluctuated significantly. NSP increased on June 11 due to system shutdown. These trends were expected, based on experience with RO systems that are shut down without preservation over a period of 48 hours or more. Data also indicated depressed lead element flux, and therefore fouling, though overall performance appeared to stabilize after several days.

Treated permeate salinity, calcium, sulfate and magnesium targets were met during the pilot study, as reported in Table 7. Therefore, a regular configuration of all WS-ES elements in a short vessel array is an effective treatment solution for EOR applications whose water quality targets align with those specified in Table 2. Laboratory conductivity measurements matched field measurements, demonstrating the accuracy of field results.

Table 7. Specific Ion Analysis

Treatment Location	**Date**	**Cond.**	**B**	**Ca**	**K**	**Mg**	**Na**	**Sr**	**SO_4**
		µS/cm	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Feed (Post ERI)	3/16	51,400	5.17	384	385	1,280	10,538	7.81	2,661
Permeate	3/16	408	1.11	0.72	3.14	0.86	74.13	0.00	2.82
Feed (Post ERI)	3/17	51,700	5.08	383	381	1,291	10,601	7.85	2,652
Permeate	3/17	384	1.06	0.71	2.86	0.83	69.58	0.01	2.63

To assess the accuracy of LG NanoH_2O's projection program, Q+, for each of the target ions for this study, a projection using data collected from the field on a selected date was compared to autopsy data for each element (i.e. flux and rejection). This comparison is presented in Table 8.

Table 8. Comparison of Actual and Projected Specific Ion Data - Stage 2B, March 16

Parameter	Units	Actual	Projected
Pressure	PSI	756	758.4
Ca	mg/L	0.78	0.72
Mg	mg/L	2.63	0.86
SO4	mg/L	2.1	2.8

The limiting factor for this study was the lead element flux rate. High lead element flux rates can cause premature fouling and increase the likelihood of multiple cleanings. A fouled lead element will raise the DP across the element and increase overall feed pressure in order to maintain permeate production requirements. To avoid fouling in TFN lead elements used in seawater applications, it was ascertained that a lead element flux rate of lower than 19.1 GFD [3] was therefore preferred for designs when the silt density index (SDI) feed water is less than three.

Autopsy. The lead element used during the Stage 2B screening and validation tests was autopsied to analyze fouling on the membrane. An image from the fouling analysis is presented in Figure 5. The analysis indicated that the lead face of the membrane contained a small amount of silt and some organic fouling, but less than expected based on operational data trends. The feed spacer contained only a small amount of organic fouling. The element did not appear to be biologically fouled due to a lack of slime, gel or odor.

Figure 5. Lead Element Autopsy

IV. CONCLUSION

High flux TFN elements were evaluated for EOR applications at the Port Hueneme Naval Base Desalination Facility. Several hybrid and regular configurations were tested in 4M, 6M and 7M arrays to evaluate the most stable treatment option. Configurations using all WS-ES (15,000 GPD) elements emerged as feasible options to balance elevated lead flux rates with fouling. Elements with rejection as low as 99.5% are suitable for reaching the water quality targets required. The 4M configuration using all WS-ES elements offered compelling potential for EOR applications with limited space and weight availability, based on its ability to meet treated water requirements at high lead element flux rates using fewer elements than alternate configurations tested. However, further consideration of lead element flux is required in order to reduce estimated cleaning frequencies.

V. REFERENCES

1. Stover, R. High Recovery Using Closed Circuit Desalination Processes for Inland Brackish Oil and Gas Applications, IDA World Congress, Tianjin, China, 2013.
2. Penate, B. and Garcia-Rodriguez, L., Reverse osmosis hybrid membrane inter-stage design: A comparative performance assessment, Desalination, 281 p354, 2011.
3. Q+, LG NanoH_2O Reverse Osmosis System Design Software, Version 2.2, www.lg-nanoh2o.com, 2014.