Nanofiltration

Seawater sulfate removal with nanofiltration

As global demand rises, nanofiltration technology has become essential throughout the oil and gas industry for improving the efficiency of waterflooding processes and enhancing overall oil recovery. This article discusses Synder Filtration's nanofiltration sulfate removal membrane and its significance for the treatment of water injection solutions to prevent scaling and oil well souring.

Improved Efficiency

Nanofiltration membranes have many advantages over reverse osmosis membranes and can be used for many of the same applications. A main benefit of using nanofiltration technology is the fact that elements can be run at lower operating pressures, while still providing high rejection of divalent ions and partial rejection of monovalent ions. The partial demineralization is ideal for maintaining the seawater composition and preventing the leaching of minerals from the rocks that the oil adheres to. In addition, lower fouling tendencies are typically found in nanofiltration membranes as opposed to traditional reverse osmosis membranes. For this particular membrane, standard clean-in-place (CIP) procedures can be performed and the NFS membrane provides good pH and temperature resistance for harsh conditions. It has been optimized for seawater processing conditions and serves as a viable alternative for waterflooding treatment.

Materials & Methods

Seawater Operating Conditions

The primary study for the NFS sulfate removal membrane focused on examining its flux and rejection performance against that of a leading competitor in typical seawater operating conditions. Using an incoming feed stream composed of ASTM D1141-52 grade synthetic sea salt obtained from Lakes Products Company, both membranes were assessed for performance up to 75% recovery (Table 1). Testing was conducted using a NF-2540 high-pressure cross flow filtration system capable of running elements at up to 600psi. Membrane validation consisted of an initial compaction step with RO water, followed by testing with 2,000ppm $MgSO_4$ for flux and rejection performance. Once membrane validation was complete, the elements were tested individually for their

Component	Conc. (g/L)	% of Total
NaCl	24.53	58.49
$MgCl_2$	5.20	26.46
Na_2SO_4	4.09	9.75
$CaCl_2$	1.16	2.765
KCl	0.695	1.645
$NaHCO_3$	0.201	0.477
KBr	0.101	0.238
H_3BO_3	0.027	0.071
$SrCl_2$	0.025	0.095
NaF	0.003	0.007
TOTAL	**36.032**	**100.0**

Table 1. ASTM D1141-52 Sea Salt Composition.

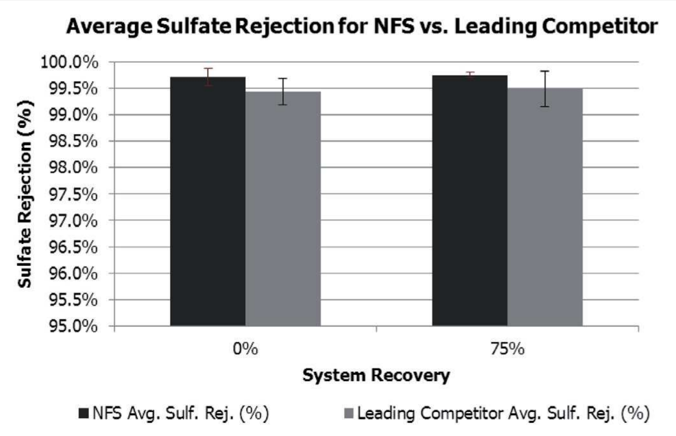

Figure 1. Average sulfate rejection performance for NFS (n=5) and leading competitor (n=2) elements with synthetic sea salt.

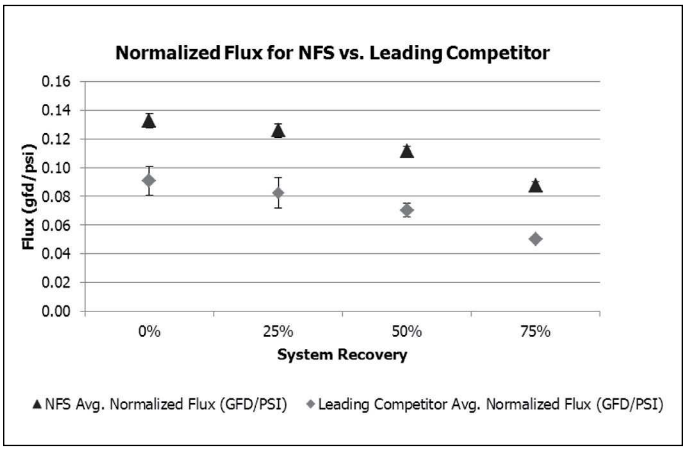

Figure 2. Normalized flux performance for NFS (n=5) and Leading competitor's (n=2) elements with synthetic sea salt.

performance in synthetic seawater.

Testing using the synthetic sea salt was performed at standard seawater operating conditions. Elements were tested at 330psi with a cross flow rate of 3gpm. Temperature was kept constant at 25 ± 2°C, and samples were collected and analyzed at 0% and 75% recovery. Samples were analyzed for conductivity using an Oakton PC650 meter and for sulfate concentration using a Hach DR/2400 Spectrophotometer while complete ion analysis was done by PACE Analytical Laboratory (Davis, CA).

Long Term Flux Performance

A long-term stability test was performed to monitor the flux performance of the membrane over an extended period. The element was tested under the same standard seawater conditions at 50% recovery, and received CIP regimens as needed. The CIP regimen consisted of: flushing the element with water, running continuously at pH2 for 30min, rinsing with water, running continuously at pH11 for 30min, followed by a final rinse with water.

Membrane Surface Characteristics & Fouling Potential

Further testing was completed to determine membrane surface characteristics and fouling potential. Contact angle measurements were taken using the sessile drop method for NFS using 2µl droplets of RO/DI water, diiodomethane, and glycerine by the DataPhysics OCA 15 instrument (Data Physics Inc., Germany). This data was then used to determine the surface energy. Zeta potential (mV) and isoelectric point (IEP) measurements were also taken by Anton Paar.

Organic Foulant Study

Lastly, an organic fouling study was conducted to compare the fouling tendencies of NFS against the leading competitor. 20mg/L of bovine serum albumin (BSA) was used as the foulant in the presence of 20mM NaCl and 1mM $CaCl_2$ to create an ionic composition similar to that of treated effluent. Elements were tested using an NF-202-2540 cross flow filtration system, and tested at 75psi with a crossflow rate of 5gpm. Temperature was kept constant at 25 ± 2°C, and the flux was monitored for a total of 20 hours until stabilized.

Results

Seawater Testing

A total of five NFS elements and two competitor elements were independently tested over the course of a 3-month period. Compared to the leading competitor's membrane, NFS demonstrated superior average sulfate rejection and overall flux performance. Throughout the duration of the study, NFS averaged >99.5% sulfate rejection compared to 99.2% for the leading competitor, with an increase in flux efficiency by 20-30%. A smaller flux decay of 33% was also observed for NFS, compared to 50% for the leading competitor's from 0% to 75% recovery. Figures 1 & 2 show the flux and rejection performance averages for all elements at 0% and 75% recovery.

Ion analysis performed by PACE Analytical Laboratory on two of the NFS elements and one of the leading competitors elements to confirm the sulfate rejection for the two membranes and also provided additional details on individual ion rejection with synthetic sea salt (Tables 2 & 3).

Ion	Rejection (%) at 0% Recovery	Rejection (%) at 75% Recovery
Na	33.0%	26.8%
Mg	88.9%	92.1%
Cl	34.1%	36.4%
F	ND	ND
Ca	71.0%	74.9%
K	33.3%	14.7%
Sr	81.3%	84.2%
Br	20.6%	18.2%
SO_4	99.8%	99.7%
B	15.1%	16.8%
HCO_3	73.6%	77.5%

Table 2. NFS Avg. Ion Analysis.

Ion	Rejection (%) at 0% Recovery	Rejection (%) at 75% Recovery
Na	40.8%	12.5%
Mg	88.6%	88.7%
Cl	39.1%	31.4%
F	ND	ND
Ca	71.2%	67.3%
K	33.3%	19.0%
Sr	79.5%	79.8%
Br	27.8%	14.3%
SO_4	99.6%	99.7%
B	3.2%	8.6%
HCO_3	76.6%	75.5%

Table 3. Leading Competitor Ion Analysis.

Long Term Flux Performance

NFS-2-2540TM elements were also tested for long-term flux performance over a period of 10 days.

The elements were run at 50% recovery using the sea salt composition as in the previous tests. CIP regimens were performed three times over the duration of the testing period. The element was able to withstand extended testing with the synthetic seawater and maintained above 99.5% average sulfate rejection without compromising the flux performance.

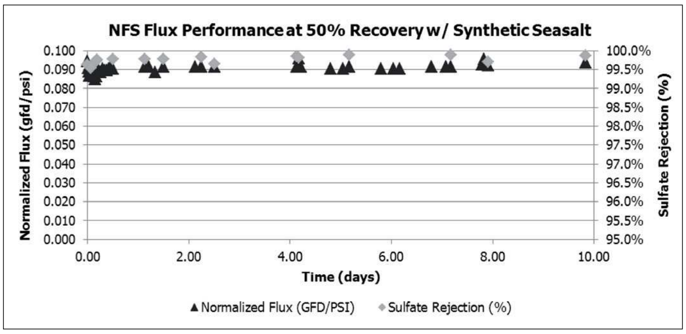

Figure 3. Flux performance of NFS at 50% recovery over 10 days.

Membrane Surface Characteristics & Fouling Potential

Contact angle measurements, surface free energy, and zeta potential measurements were taken to analyze the membrane surface characteristics and the fouling potential of the membrane. The contact angle measurements using RO water averaged just under 30°, and the contact angle measurements were used to determine the surface energy which was just under 60 mN/m (Table 4).

Zeta potential and isoelectric point measurements were also determined from samples sent to Anton Paar. Fig. 4 shows the test results for NFS, which displayed a negative surface charge in both the neutral and basic pH regime. The isoelectric point was approximately 3.6, indicating a slightly acidic surface.

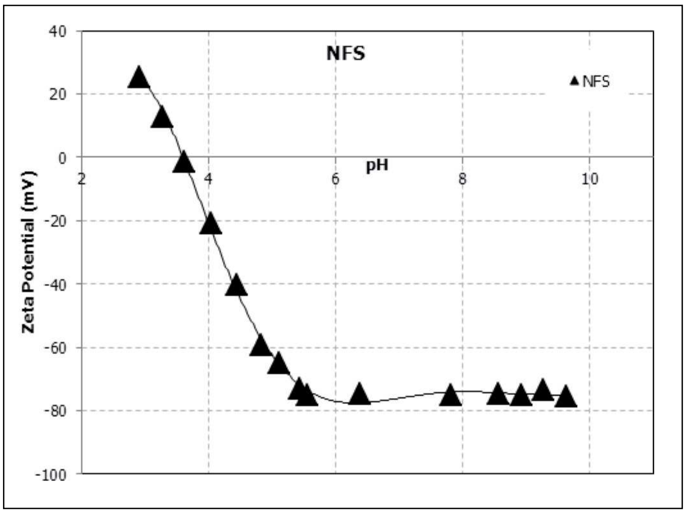

Figure 4. Zeta potential measurement for NFS.

Organic Fouling Study

A short organic foulant study was also conducted to observe the fouling tendencies of NFS compared to the leading competitor's element. NFS demonstrated superior flux performance in the presence of BSA. The flux decay observed was also less, with NFS at 8% and the leading competitor at 18%. Both elements were validated before and after the fouling test, and both met the minimum flux and $MgSO_4$ requirements.

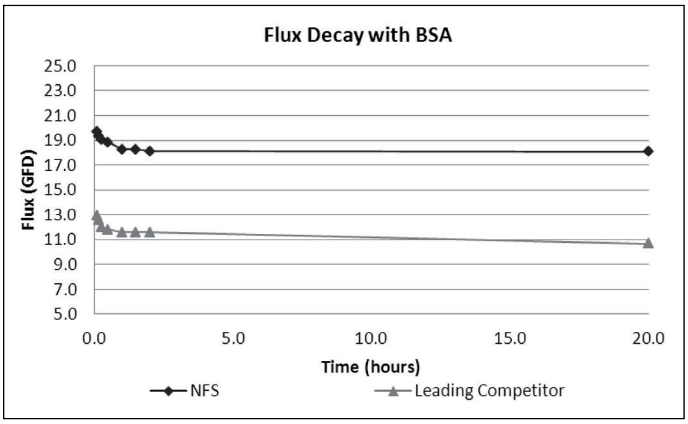

Figure 5. Flux decay for NFS and leading competitor with BSA as the organic foulant.

Membrane	Dosing Liquid			Surface Energy (mN/m)
	RO Water	Diiodomethane	Glycerine	
NFS	28.3°	38.2°	45.7°	59.3

Table 4. Average Contact Angle & Surface Energy Values for NFS.

Discussion

The results of the synthetic seawater study show that NFS demonstrates superior sulfate rejection and flux performance compared to that of the leading competitor in a feed stream comprised of ASTM D1141-52 grade synthetic sea salt. The average sulfate rejection from 0% to 75% recovery was >99.5% for NFS and a 20-30% increase in flux was observed across all five trials.

"..significantly reduces the presence of sulfate while providing a 20-30% increase in flux efficiency.."

Full ion analysis by PACE Analytical confirmed the sulfate results and provided more information about the full ion rejection performance of the membrane. The higher sulfate, strontium, and boron rejection compared to the leading competitor makes this membrane ideal for seawater waterflooding usage to prevent scaling and pipe constriction in oil recovery applications. Low contact angle measurements and significantly lower flux decay during the BSA fouling test further highlight the anti-fouling properties of the membrane, while the slightly lower iso-electric point suggest a greater negative surface charge at both neutral and basic pH conditions. These characteristics make the NFS membrane a viable alternative for sulfate removal in enhanced oil recovery applications. ●

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