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Recovery optimization of membrane processes for treatment of produced water with high silica content

Arun Subramani[a*], Ron Schlicher[b], James Long[b], Jack Yu[b], Stewart Lehman[a], Joseph G. Jacangelo[a,c]

[a] *MWH, 618 Michillinda Avenue, Arcadia, California 91007, USA*
Tel.: +16265686002; Fax: +16265686015; email: Arun.Subramani@us.mwhglobal.com
[b] *MWH, 10619 South Jordan Gateway, Salt Lake City, Utah 84095, USA*
[c] *The Johns Hopkins University, Baltimore, Maryland 21205 USA*

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ABSTRACT

Disc tube (DT) and spiral wound (SW) configurations of nanofiltration (NF) and reverse osmosis (RO) processes were tested at pilot-scale using a two-pass configuration to treat produced water obtained from natural gas wells. First pass NF membranes were used to remove divalent cations from produced water. Permeate from the first pass NF membranes were used as feed to second pass RO membranes after increasing the pH to 10.0 to enhance silica solubility. To reduce the fouling potential on NF and RO membranes dissolved air floatation (DAF), ceramic ultrafiltration (UF), MYCELX cartridges, and organoclay filters were tested as pretreatment alternatives. Pretreatment processes were effective for turbidity and oil and grease removal but were not efficient in retaining organic matter, primarily protein-like and polysaccharide-like material, which eventually fouled the first pass NF membranes. The second pass RO membranes were scaled predominantly by silica. The overall feed water recovery of the two-pass NF-RO system was limited to less than 70%. Although the application of a two-pass configuration met the discharge limits for most of the contaminants in produced water, a more stringent pretreatment process for selective removal of organics and silica is essential to operate the membrane systems at recoveries greater than 85%. If treated appropriately, produced water can be employed as a true water resource to augment existing surface water streams and creeks.

Keywords: Ceramic membranes; Organic fouling; Biofouling; Silica polymerization; Two-pass configuration

1. Introduction

Produced water is a term used to describe water that is obtained along with oil and gas production. It represents the largest source of oily wastewaters [1]. The volume of produced water can be as much as 10 times the volume of oil extracted [2]. Produced water consists of a combination of organic and inorganic compounds and production chemicals [3,4]. Typical organic compounds present are aliphatic, aromatic, and polar compounds [5]. Inorganic components include sodium, potassium, calcium, magnesium, chloride, sulfate, carbonate, silicates, and borates [2]. Production chemicals can include emulsion breakers to improve

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*Corresponding author

separation of oil and water, corrosion inhibitors, oxygen scavengers, and biocides [2]. The concentration of these contaminants can vary significantly due to natural variation in the geological formation, the type of oil-based product being produced, and the mix of chemicals used in the drilling and completion of wells. Also, these waters often have elevated temperatures, reaching up to 93°C in some cases [6].

The typical methods of dealing with produced water are deep well injection and evaporation from ponds [7]. For some oil fields, a portion of the produced water is re-injected into the oil producing zones to improve oil recovery through water or steam flooding [7]. The other portion of produced water is disposed off through deep well injection or evaporation. Deep well injection is limited by the capacity of the injection wells and evaporation is subject to the local climate conditions. Thus, oil and gas companies are looking for other disposal options such as discharge to surface water bodies. Discharge limits set by local governing agencies can be very stringent. Certain discharge limits require a chloride concentration of less than 230 mg/L in the treated water [8]. Treatment of such wastewater streams to meet low chloride limit requires a technology, such as nanofiltration (NF) and reverse osmosis (RO), which can serve as an absolute barrier for various contaminants.

Conventional treatment of produced water has included gravity separation and skimming, dissolved air floatation (DAF), de-emulsification, coagulation and flocculation [9]. Low-pressure membranes, including ceramic UF, have primarily been tested in the past only for treatment of oily wastewaters and not specifically for produced water [10,11]. High-pressure membranes, such as NF and RO, have predominantly been evaluated as part of a patented treatment technology and hence limited data is available on the performance of the process [12]. Although high-pressure membrane processes such as NF and RO have been used in the past for produced water treatment [6,13–15], limited studies are available that have looked into the application of newer pretreatment technologies for controlling fouling. Also, there are limited studies available that have tested NF and RO membranes using a combination of disc tube (DT) and spiral wound (SW) configuration to control fouling and enhance feed water recovery. In this study, pilot-scale evaluation of innovative pretreatment technologies were tested and recovery optimization of NF and RO processes was conducted for produced water obtained from natural gas wells at a location in the Western United States. Practical aspects of testing NF and RO membrane systems with respect to produced water treatment are highlighted with an emphasis on lessons learned during pilot-scale testing. Specific objectives of the study were to: (1) evaluate the performance of NF and RO membranes with different operating configurations (i.e., double pass systems and multistage systems) to maximize feed water recovery and (2) evaluate the rejection property of NF and RO membranes to meet discharge limits.

2. Materials and methods

Five different pretreatment technologies evaluated at the pilot-scale were chemically-enhanced DAF, ceramic UF, organoclay filtration, and MYCELX filtration. Treatment schemes tested at the pilot-scale is illustrated in Fig. 1. A heat exchanger (HE) was installed in front of pretreatment systems to reduce the temperature of raw water (as high as 80°C). After the heat exchanger, the temperature of the water was reduced to about 25°C. Description of the pretreatment technologies is given below.

2.1. DAF

Produced water from natural gas wells was first treated in gun barrel tanks for oil and water separation. After the gun barrel tanks, the produced water was fed to a DAF system (VanAire Inc., Michigan, USA). The DAF system was used for further reduction of oil and grease and turbidity of the produced water. A hydraulic retention time of 1 h was used in the DAF. A 50% recycle of feed and an air flow of 0.28 m^3. To enhance flocculation and settling, 1–3 mg/L of polymer (and 50–100 mg/L of aluminum chlorohydrate (Baker Petrolite Chemicals, Texas, USA) were tested in the DAF system.

2.2. Ceramic UF

A ceramic UF system (Membralox Unit X15) was leased from PALL Water Processing (New York, USA). The UF system consisted of seven ceramic elements with a total membrane area of 2.5 m^2. A 50 nm alumina-zirconia type of ceramic filtration membrane was used for the study. Different transmembrane fluxes (170–255 L m^{-2} h^{-1}), feed water recoveries (75–90%), and back pulse intervals (3–5 min) were evaluated during the pilot study. A three step cleaning of the ceramic UF involved bleach and caustic soda in the first step (pH of 11.0), an alkaline cleaner in the second step, and nitric acid in the third step (pH of 2.0).

2.3. Organoclay filtration

Organoclay was obtained from Aquatech Inc. (Wyoming, USA). Organoclay are chemically altered

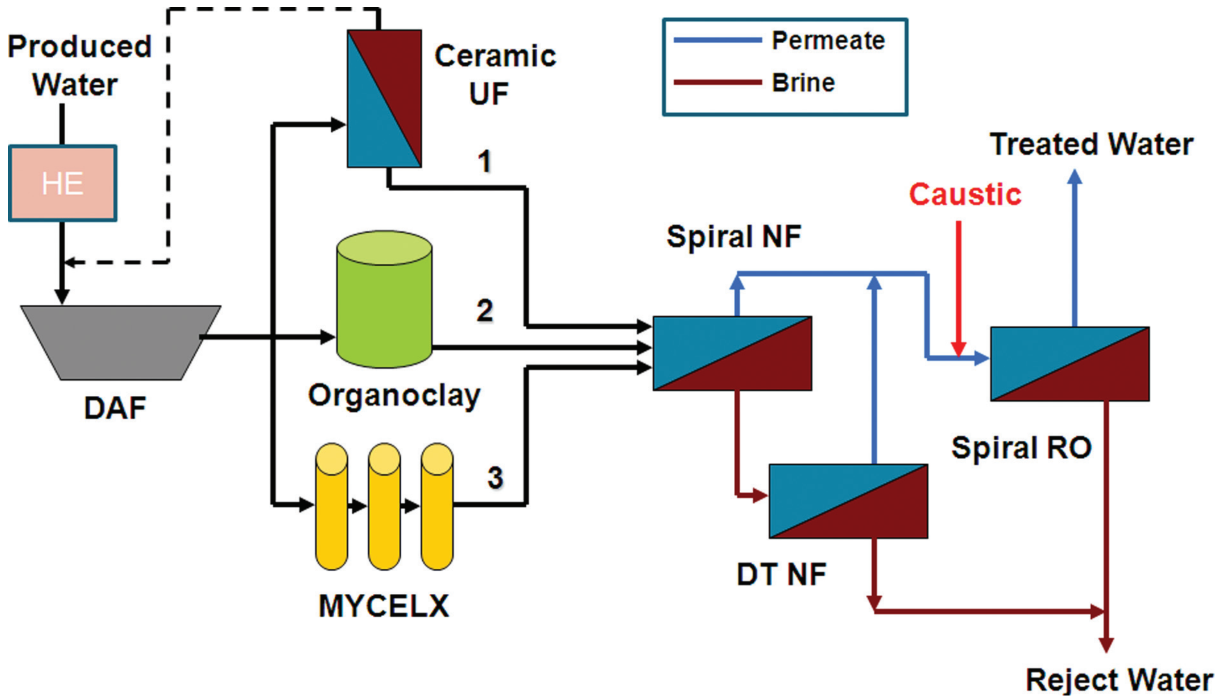

Fig. 1. Treatment schemes tested at the pilot-scale.

volcanic ash consisting of montmorillonite. They have a surface area of approximately 750 m^2/g and used for the removal of oil and grease, turbidity, metals, and olvents. An organoclay filtration bed with an empty bed contact time (EBCT) of 15 min was used. Backwashing was performed when the pressure drop across the bed exceeded 206 kPa.

2.4. MYCELX filtration

MYCELX filters were obtained from Mycelx Technologies Inc. (Georgia, USA). MYCELX technology was used as an alternative to organoclay filtration for the removal of oil and grease. The filters were coated with a patented polymeric surfactant technology to enable the removal oil droplets. MYCELX filters are considered to be effective in the removal of hydrocarbons, oil sheen, synthetic oil, and natural oil. In this study, 25 micron filters arranged in series were used. Effluent from the DAF was used as the feed to the MYCELX filters.

2.5. NF and RO membranes

Two types of NF and one type of RO membrane was used. The NF membranes used were NF270 (DowFilmtec, Minneapolis, MN) and NF90 (DowFilmtec, Minneapolis, MN). The RO membrane used was TM810L (Toray Membrane, Poway, CA). The NF270 membrane is considered to be a ''loose'' nanofiltration membrane with 40–60% rejection of $CaCl_2$ and less than 35% rejection of NaCl [16]. In contrast, the NF90 membrane is considered a ''tight'' nanofiltration membrane and has more than 85% rejection of NaCl [17]. The TM810L membrane is used for seawater desalination and is a cross linked fully aromatic polyamide composite membrane and has more than 99.75% rejection of NaCl [18]. The NF and RO membranes were tested in plate and frame and spiral wound (SW) configuration. Performance of the membrane systems was accessed by calculating rejection, flux, temperature corrected specific flux, and feed water recovery [19]. Description of the two configurations is given below.

2.5.1. DT technology

A DT system was leased from PALL Water Processing (New York, USA). The DT system consists of commercial flat sheet membranes installed in a plate and frame configuration [20]. The length of the module was 1 m and the membrane area in the module was 7.65 m^2. The module consisted of fiber glass housing capable of withstanding pressures up to 6894.75 kPa. The module consisted of unique crossflow construction with stacked membrane discs. The disc membrane stack was housed in a pressure vessel and assembled on a center tension rod using stainless steel end flanges. The extremely short feed water path across the membrane surface, followed by a 180° flow reversal greatly reduces concentration polarization on the membrane surface, reducing fouling and scaling potential. The system was operated at various recoveries (50–85%). Flux was maintained constant (30–34 L m^{-2} h^{-1}) for all the tests. To minimize the scaling potential due to sparingly soluble salts, 8 mg/L of MDC150 # 3617 (Eastern Technologies Inc., Pennsylvania, U.S.A.) antiscalant was added to the system.

2.5.2. SW technology

A SW RO skid was leased from PALL Water Processing (New York, USA) and used for pilot testing. In a SW system, the membrane is wound on a central tube in a spiral configuration [21,22]. Membrane leaves were separated by a feed spacer used to promote turbulence and reduce concentration polarization. A permeate spacer transports the permeate water to the center tube. The concentrate stream leaves the element to be further treated by another SW membrane element or discharged. The SW system consisted of 8 pressure vessels. Each pressure vessel accommodated a SW membrane element with nominal dimensions of 4-in. by 40-in. For the first pass testing, NF270 membranes were installed in the SW system. For the second pass testing, TM810L membranes were used. The system was operated at various recoveries (50–75% for first pass and 50–80 % for second pass). Flux was maintained constant (17 L m^{-2} h^{-1}) for all the tests. To minimize the scaling potential due to sparingly soluble salts, 8 mg/L of MDC150 (# 3617, Eastern Technologies Inc., Pennsylvania, USA) antiscalant was added to the system for the first pass. Before the second pass tests, pH of the water was raised to 10.0 by addition of sodium hydroxide to increase the solubility of silica [23]. To minimize silica scaling on the second pass membranes, an antiscalant specific to silica (Formula 3680, Eastern Technologies Inc., Pennsylvania, USA) with a dosage of 8 mg/L was used.

2.5.3. Membrane autopsy

Fouled membrane autopsy was performed using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), loss on ignition (LOI) analysis, microbiological examination, and Fourier Transform Infrared (FTIR) analysis. SEM and EDS analysis were performed to determine the morphology and inorganic constituents of the foulant layer, respectively. Before performing SEM analysis, membrane samples were dried overnight in a dessicator. After drying, membrane samples were sputter coated using Ag/Pd for 60 s prior to SEM analysis [24]. Organic content of the foulant layer was determined using LOI analysis. For LOI analysis, the foulant sample was scrapped from the membrane surface and heated at 550°C. The difference in mass of foulant before and after heating was utilized to determine the organic content of foulant layer [24]. Microbiological examination of the fouled membrane included analysis for bacteria. Gram-positive and gram-negative bacteria were analyzed using standard staining technique and light microscopy [25]. FTIR analysis was performed to estimate the nature of foulant layer. FTIR measurements were collected based on temporal coherence of a radiative source, using time-domain measurements of electromagnetic radiation. Spectra were compared against a library of more than 10,000 known constituents to determine the nature of foulant material [26].

2.5.4. Membrane cleaning

Chemical cleaning of the DT and SW membrane systems were performed with cleaning chemicals provided by PALL Water Processing (New York, USA). Low pH cleaning solution (RO Cleaner C) composed of 10–30% citric acid. High pH cleaning solution (RO Cleaner A) which was composed of 0–5% sodium hydroxide and 0–5% ethylene diamine tetra acetic acid. Cleaning was performed with a low pH solution (pH ~ 2.0) followed by use of high pH solution (pH ~ 11.0). Each cleaning cycle was performed for a period of 2 h at with clean water flush in between cleaning cycles. For high pH cleaning of NF membranes, special cleaning solution (Cleaner NFE) was used. High pH cleaning for NF membranes was performed at pH ~ 9.0. All chemical cleanings in the DT and SW system were performed at 40°C.

3. Results and discussion

3.1. Feed water quality

Average feed water quality of produced water for the year 2009 is listed in Table 1. Produced water quality fluctuated with time due to the installation of newer natural gas wells in the field. Thus, the feed water quality to the pilot testing plant was not consistent and made pilot testing more challenging. Contaminants included suspended solids, oil and grease, dissolved organics, volatile organic compounds, metals, and soluble salt. Total dissolved solids (TDS) was on average 6,507 mg/L. The pH of the produced water was approximately 7.0. The concentration of gasoline range organics (GRO) was substantially higher than diesel range organics (DRO). The 5-day biological oxygen demand (BOD_5) and chemical oxygen demand (COD) were also high in the feed water. The temperature of the produced water was as high as 80°C. The concentration of silica varied

Table 1
Average feed water quality (raw produced water) for pilot-scale testing during the year 2009

Parameter	Method	Average, mg/L	Minimum	Maximum	Standard Deviation
Oil and grease	EPA 1664A	125	52	458	98
DRO	SW8015M	4	1	9	4
GRO	SW8015M	78	18	359	84
BOD_5	EPA 405.1	765	390	1323	255
COD	EPA 410.1	1442	920	2160	495
TDS	EPA 160.1	6507	6150	7224	301
pH	SM4500 - HB	7	7.2	7.7	0.2
Alkalinity, as $CaCO_3$	EPA 310.2	2,804	2,100	4,428	460
Sodium	EPA 6010B	3,119	2,100	6,768	1,201
Chloride	EPA 9056	1,781	1,426	1,917	120
Calcium	EPA 6010B	27	7	59	17
Magnesium	EPA 6010B	3	1	5	1
Sulfate	EPA 9056	8	4	13	3
Barium	EPA 6010B	6	3	9	1
Iron	EPA 6010B	2	0.2	2.9	0.9
Selenium	EPA 6010B	0.2	0.1	0.3	0.1
Silica	EPA 6010B	67	45	100	21
Methanol	EPA 8015	225	100	460	115
Benzene	EPA 8021B	17	12	23	3
Toluene	EPA 8021B	28	24	34	2
Ethylbenzene	EPA 8021B	1	0.7	1.6	0.2
Xylene	EPA 8021B	2	1.9	2.9	0.2

between 45 and 100 mg/L in the feed water. Operating the RO process at 50% recovery with a feed water silica concentration of 100 mg/L would result in 200 mg/L of silica in the concentrate stream exceeding the solubility limit of silica. Similarly, barium sulfate, and calcium fluoride saturation was in excess of 100% and Langelier Saturation Index (LSI) was greater than 1.0 at a feed water recovery of 50%. The saturation of barium sulfate, calcium fluoride, and calcium carbonate is typically controlled by the use of an antiscalant [27,28]. But, silica saturation is difficult to control when the concentration exceeds 200 mg/L in the concentrate stream [23,29]. The presence of suspended solids, oil, and grease in the feed water can severely hinder the performance of NF and RO process due to fouling. Thus, several pretreatment techniques were evaluated for the removal of suspended solids and oil and grease. The performance of different pretreatment processes evaluated is described below.

3.2. Performance of pretreatment processes

For enhanced flocculation and settling of suspended particles, hydrocarbons, and oil and grease, chemicals were added to the feed water of the DAF. Optimum chemical dosage was determined through jar testing (3 mg/L of polymer and 50 mg/L of aluminum chlorohydrate). During pilot testing, turbidity removal between 60% and 90% was achieved consistently in the DAF system. The percentage removal of oil and grease varied between 25% and 90%. This was attributed to significant variation in the oil and grease content of the feed water. An increase in the chemical dosage to the DAF was necessary to achieve higher turbidity removal. Overall, the DAF system was efficient as the first stage of pretreatment in reducing the concentration of oil and grease and suspended solids. Thus, for all further testing, the DAF system was used as the default pretreatment step followed by either organoclay (or) MYCELX filters (or) ceramic UF.

For the testing with organoclay filter, DAF effluent was used as feed and operated as a down flow pressure filter. As solids built up in the organoclay media, the differential pressure increased and the unit was backwashed. When the system was operated at a high hydraulic loading rate, backwashing was necessary almost every day. But, the system achieved only 30–45% removal of oil and grease. Overall, the relatively poor performance of the organoclay filter was due to the fact that the constituents being measured as oil and grease were dissolved or liquefied. Thus, the oil and grease passed through the organoclay filter without being adsorbed.

MYCELX filters were evaluated as an alternative to the organoclay filter for oil and grease removal. Even with the DAF achieving good turbidity removal, the first MYCELX cartridge filter plugged within one day

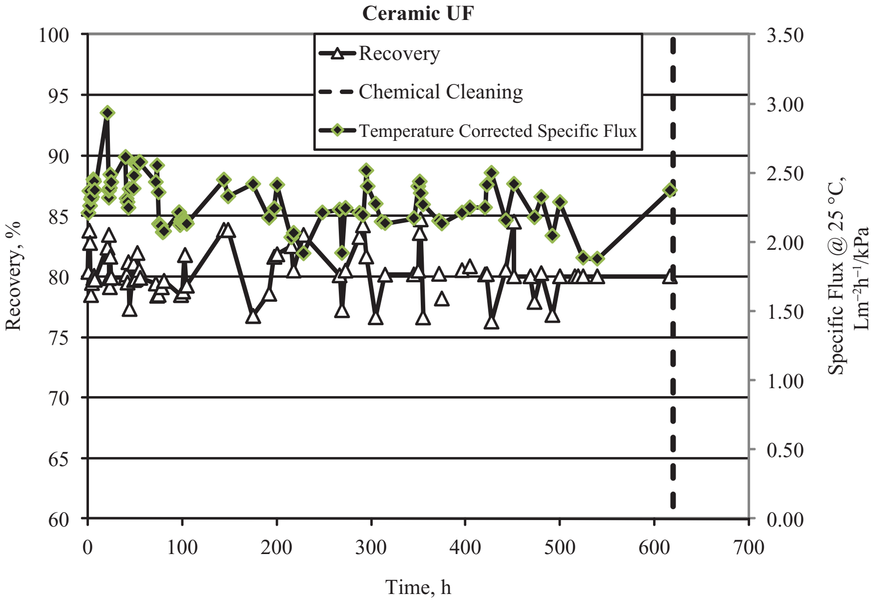

Fig. 2. Performance of ceramic UF system used for pretreatment of RO.

of operation. In terms of performance for oil and grease removal, the MYCELX filter did not perform as well as expected. Only 18% removal of oil and grease was achieved.

Oil and grease removal through the ceramic UF was much lower than expected, averaging only 25% removal. The low oil and grease reduction by the ceramic UF was also associated with the dissolved or liquefied organics in the water because solids and oil particles should not pass through the 50 nm pores of the ceramic UF. Performance of the ceramic UF is shown in Fig. 2. During startup, a feed water recovery of 80% was achieved without any decline in the specific flux. For the first 100 hours of operation, no substantial decrease in the specific flux was observed. After the initial operation period, the specific flux decreased steeply requiring chemical cleaning of the membrane to restore the specific flux to initial values. Recoveries greater than 80% led to steep decline in the specific flux. A flux decline of about 14% was observed during 550 hours of operation. Utilization of periodic high frequency back pulsing did not improve the performance (with respect to fouling) of the ceramic membrane. Cleaning at elevated temperature (60°C) was found to be more effective than cleaning at ambient temperature.

3.3. *Limiting recovery of RO process*

To determine the maximum recovery achievable in a single pass, tests were conducted using a ‘‘tight’’ NF membrane (NF90). The NF90 membrane was installed in the DT system and tested to determine if the discharge limits can be met in a single pass and estimate the maximum achievable feed water recovery and fouling potential. The feed water recovery and temperature corrected specific flux for DT system with NF90 membranes are shown in Fig. 3. Pretreatment consisted of DAF and ceramic UF membranes. At a recovery of less than 50%, no substantial decrease in specific flux was observed. But, as the recovery was increased further (more than 55%) a gradual decrease in the specific flux was observed. Within 120 hours of operation, a decrease of more than 25% in the specific flux was observed suggesting that fouling/scaling of the membrane occurred. But, during the entire duration of operation, no substantial increase in the differential pressure across the module was observed. Even after cleaning with both low pH and high pH solutions at the end of operation, the specific flux was not recovered to initial values suggesting irreversible fouling/scaling has occurred on the membrane surface.

During the testing of NF90, silica concentrations in the feed were between 90 and 100 mg/L. Silica rejection was more than 90% by the NF90 membrane. Hence, with more than 90% rejection of silica by the membrane, the concentration of silica in the concentrate stream of the NF90 membrane was more than 245 mg/L exceeding the silica solubility limits. Although a silica specific antiscalant at a dosage of 8 mg/L was used as pretreatment for the NF90 membrane, the irrecoverable specific flux after chemical cleaning suggested that a hard silica scale had formed

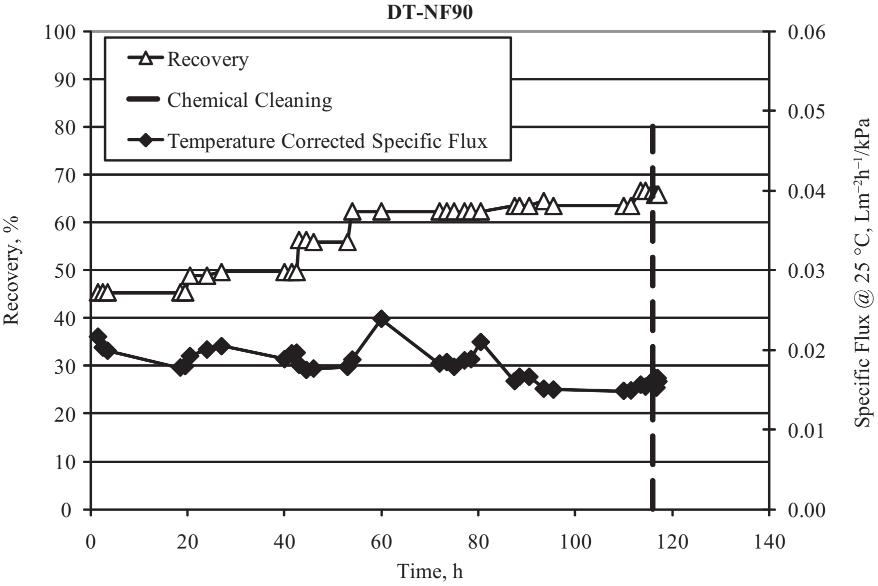

Fig. 3. Performance of DT-NF90 system used for determining limiting recovery of RO process.

on the membrane surface. NF90 membrane is also a rough and hydrophobic membrane [30] making it difficult to clean silica scale formed on the membrane surface. Since silica scaling of the membrane was restricting the overall feed water recovery of the high-pressure membrane process, further membrane tests were conducted to increase the silica solubility limit in the feed water by increasing the pH of the solution. In order to increase the pH of the solution, hardness related to calcium was reduced to prevent the precipitation of calcium carbonate ($CaCO_3$). Hence, a two pass membrane system was implemented. In the two pass system, the permeate from the first pass was used as feed to the second pass membrane. In the first pass, a loose NF membrane (NF270) was employed to remove hardness and alkalinity so that the pH could be raised to 10.0 in the second pass utilizing a RO membrane.

3.4. Performance of first pass NF membranes

In order to determine the limiting recovery of a ''loose'' NF membrane, NF270 was installed in a DT configuration. Performance of the DT-NF270 membrane is shown in Fig. 4. The specific flux varied during the initial 10 hours of operation primarily due to membrane compaction and system stabilization. After the initial 10 hours of operation, the specific flux began to stabilize. After the initial stabilization period, the specific flux was stable until a feed water recovery of 70% was reached. Beyond a feed water recovery of 70% the specific flux decreased gradually with time.

After determining the limiting recovery of the NF270 membrane, a SW configuration was evaluated for the first pass. The feed water recovery and temperature corrected specific flux for SW system with NF270 membranes used for the first pass are shown in Fig. 5(a). The system was operated with different pretreatment schemes. Although the specific flux seemed to fluctuate within the first 140 hours of operation, there was no substantial difference in the rate of decrease in the specific flux for the membrane when operated with different pretreated waters. Hence, it was not possible to conclusively determine the best pretreatment process for the spiral NF270 membrane with respect to fouling. After the initial tests, feed water from the DAF followed by organoclay filter was used to obtain performance data at higher recoveries. Hence, the recovery of the system was increased to 70% and then to 75% from 140 to 200 hours of operation. When the recovery was increased, a gradual decrease in the specific flux was observed. Within 60 hours of operation at recovery greater than 70% the specific flux decreased by 13%. During the entire duration of operation, the differential pressure across the module increased from 137 to 186 kPa. No chemical cleaning cycles were performed for the SW-NF270 membrane system.

In order to increase the feed water recovery of the first pass, a DT-NF270 system was used to treat the concentrate obtained from the SW-NF270. The system was operated for a total duration of approximately 100 hours. The recovery of the system was maintained at about 71%. The flux was maintained constant at

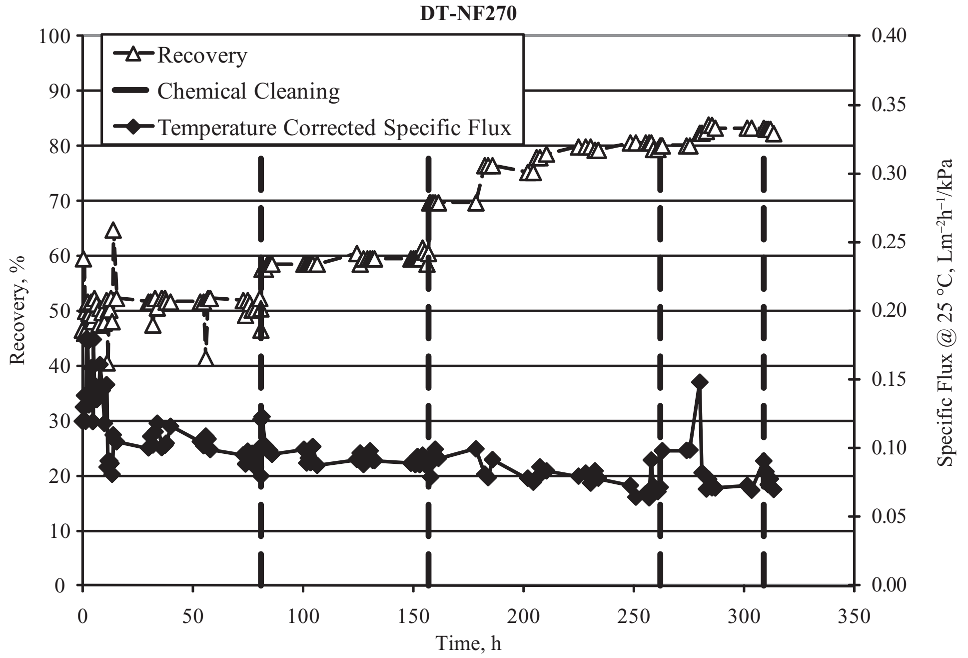

Fig. 4. Performance of DT-NF270 used for determining limiting recovery of NF process.

about 17 L m^{-2} h^{-1}. The specific flux decreased by 50% in 24 h. Although the specific flux decreased substantially within the first 24 hours of operation, it was recovered to initial value by flushing only with RO permeate. The recovery of specific flux suggested that the foulant layer deposited on the membrane surface was not irreversibly adhered and was loosely deposited on the membrane surface. Previous studies have shown that NF270 is a relatively smooth and hydrophilic membrane with lesser organic fouling potential [30,31]. Thus, organic adsorption on the membrane was reversible and specific flux was recoverable with RO permeate flushing. During the entire duration of operation, the differential pressure across the module was constant and did not increase. No chemical cleaning cycles were performed for the DT-NF270 membrane system while treating the SW-NF270 concentrate stream. Only flushing with RO permeate was performed periodically.

To determine the rejection capability of the first pass SW-NF270 membrane and its applicability as first pass membrane system, water quality parameters were monitored during operation. Feed and permeate water quality from the SW-NF270 membrane is listed in Table 2. The rejection of BOD_5, COD, TDS, and alkalinity was low. Among the individual ion rejections, the rejection of calcium was approximately 90% and rejection of magnesium was more than 40%. The rejection of chloride was negligible. The rejection of sodium was also low (less than 15%). The rejection of sulfate was greater than 85% and the Ammonia-N was rejected less than 5%. The rejection of barium was about 30% where as selenium rejection was approximately 5%. Rejection of boron and selenium were low (less than 10%).

3.5. Performance of second pass RO membranes

The second pass membrane system consisted of a seawater RO membrane, TM810L. The pH of the feed water was increased to 10.0 before the second pass membrane operation to increase the solubility of silica. Feed water recovery and temperature corrected specific flux for SW system with TM810L membranes used for the second pass is shown in Fig. 5(b). The system was operated in four different batches after the permeate water from the first pass (SW-NF270 and DT-NF270) membrane was stored and pH adjusted. The four batches of operation presented in Fig. 5(b) are from 0 to 29 hours, 29 to 40 hours, 40 to 80 hours, and 80 to 114 hours. For all the tests, on average the specific flux decreased by more than 65%. The net operating pressure increased significantly for tests 1 and 4. The differential pressure also increased by 40% during operation. The significant increase in feed pressure requirement, increase in net operating pressure, decrease in specific flux, and, increase in differential pressure suggested significant fouling and scaling of the membranes. The membranes were cleaned after 80 hours of operation using only high pH (12.0) cleaning solution. The specific flux recovered to initial value

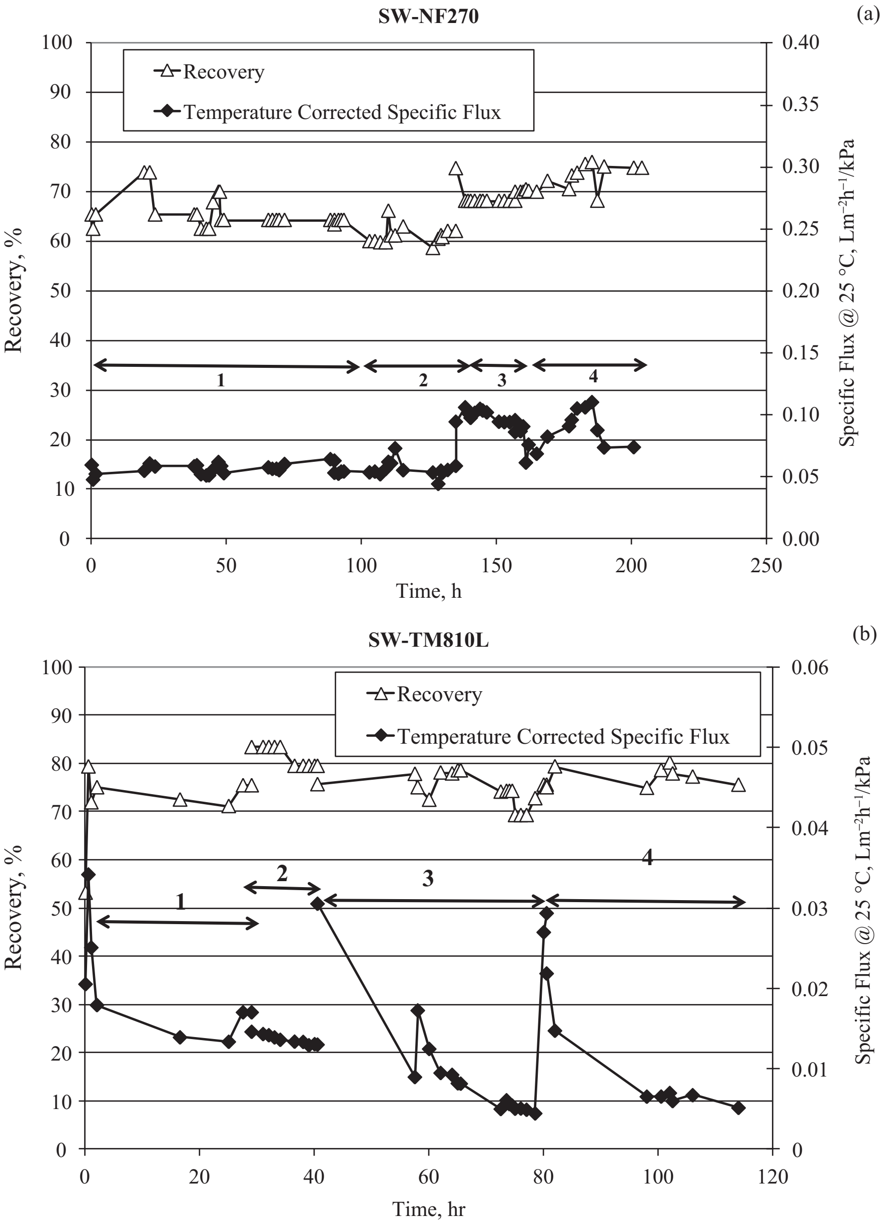

Fig. 5. Performance of first pass (a) and second pass (b) membrane. The numbered regions represent different pretreatment schemes for the first pass and varying recoveries for the second pass. Note: First pass 1: Pretreatment was DAF→Ceramic UF; 2: Pretreatment was DAF→OrganoClay; 3: Pretreatment was DAF→MYCELX; 4: Pretreatment was DAF→OrganoClay. Second pass Regions 1,2,3, and 4 represent different tests performed with varying recovery.

after chemical cleaning suggesting that chemical cleaning was effective.

Water quality obtained for the second pass RO membrane is listed in Table 3. The rejection of TDS and alkalinity was more than 95%. The rejection of BOD_5 was 72% and the rejection of COD was 63%. Since the TM810L membranes are RO membranes with high rejection capability, TDS and alkalinity rejection was high and easily met discharge limits. The rejection of BOD_5 was low as it was associated with the passage of methanol through the RO membrane. The rejection of methanol is low through a RO membrane due to its low molecular weight (32.04 g/mol). All ions were rejected greater than 95% except for ammonia-N and boron. The rejection of ammonia-N was less than 25% and boron rejection was approximately 75%. Ammonia rejection by RO membranes is a function of pH. The feed pH was 10.0 ($\pm$0.1) for the tests with SW-TM810L membranes. Lower pH leads to the formation of ammonium (NH_4^+) ions (higher rejection). Beyond a

Table 2
Water quality from first pass SW-NF270 system

Analyte	Units	Feed	Permeate	% Rejection
DRO	mg/L	<0.75	<0.75	–
BOD_5	mg/L	836	641	23.3
COD	mg/L	1235	778	37.0
TDS	mg/L	6428	5171	19.6
Alkalinity	mg/L as $CaCO_3$	2213	1660	25.0
Chloride	mg/L	1831	1742	4.8
Sulfate	mg/L	6.2	1.5	75.8
Silica	mg/L	60.0	48.0	20.0
Ammonia-N	mg/L	5.3	4.6	12.9
Phosphorous	mg/L	<0.1	<0.1	–
Barium	mg/L	5.2	3.1	40.1
Boron	mg/L	10	9	12.5
Iron	mg/L	<0.1	<0.1	–
Calcium	mg/L	54	5	90.7
Magnesium	mg/L	2.4	1.3	46.0
Potassium	mg/L	18.8	16.6	11.9
Sodium	mg/L	2,261	1,886	16.6
Selenium	mg/L	0.10	0.08	21.5
Methanol	mg/L	267	280	–
Toluene	mg/L	18.4	17.8	3.3
Ethylbenzene	mg/L	0.5	0.6	–
m+*p* Xylene	mg/L	6.0	5.6	6.7
o Xylene	mg/L	1.5	1.4	6.8

Table 3
Water quality from second pass TM810L RO system

Analyte	Units	Feed	Permeate	% Rejection
DRO	mg/L	<0.75	<0.75	–
BOD	mg/L	371	104	72.0
COD	mg/L	660	240	63.6
TDS	mg/L	6,495	297	95.4
Alkalinity	mg/L as $CaCO_3$	2,676	55	97.9
Chloride	mg/L	1,829	15	99.2
Sulfate	mg/L	2	ND	100.0
Calcium	mg/L	5	0.01	99.8
Silica	mg/L	61	1	98.1
Ammonia-N	mg/L	3	2	23.1
Barium	mg/L	3	0.03	99.2
Boron	mg/L	8	2	75.0
Magnesium	mg/L	1	ND	100.0
Sodium	mg/L	3141	22	99.3
Selenium	mg/L	0.18	0.05	73.1
Methanol	mg/L	120	114	4.8
Toluene	mg/L	10.3	1.9	82.0
Ethylbenzene	mg/L	0.1	0.02	78.8
m+*p* Xylene	mg/L	3.0	0.2	93.1
o Xylene	mg/L	0.9	0.04	95.9

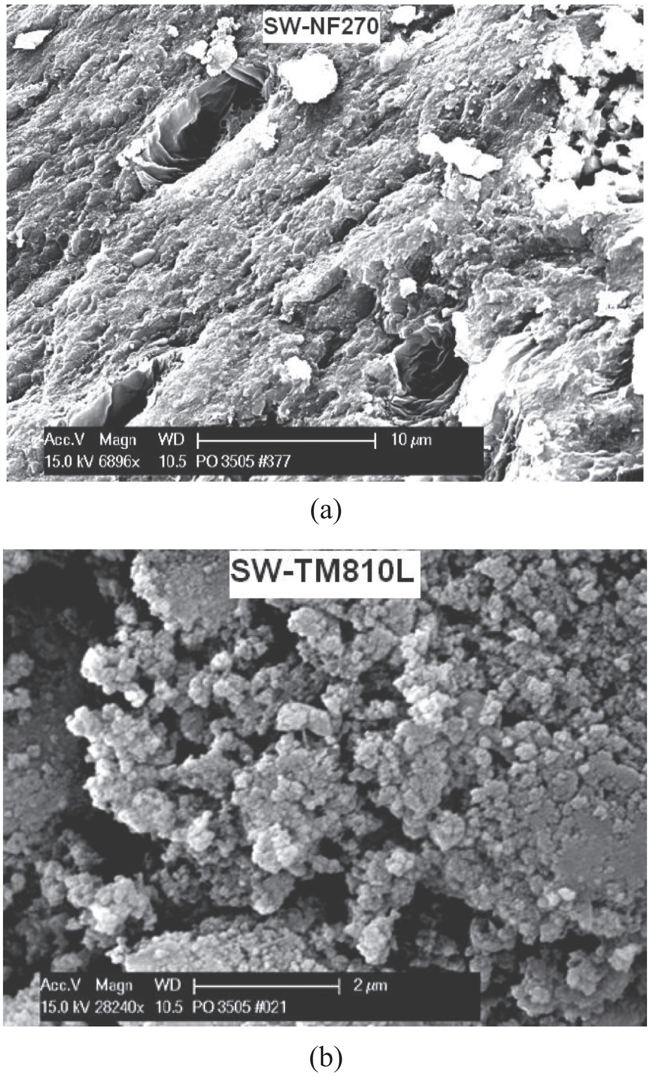

Fig. 6. SEM image of foulant layer on first pass NF membrane (a) and second pass RO membrane (b).

pH of 9.5, the dominant form of nitrogen compounds is ammonia, which is an uncharged molecule and difficult to reject by RO membranes, hence the rejection of ammonia-N is low [32]. Among the metals, selenium rejection was approximately 73%. The rejection of boron (75%) was better when compared to the SW-NF270 membrane since boron speciates into the borate anion form at high pH and results in better rejection by the SW-TM810L membranes.

3.6. Nature of foulant layer

Autopsy of membrane elements removed from the first pass SW-NF270 and second pass SW-TM810L were performed to determine the nature of foulant and scalant deposited on the membrane surface. A loss on

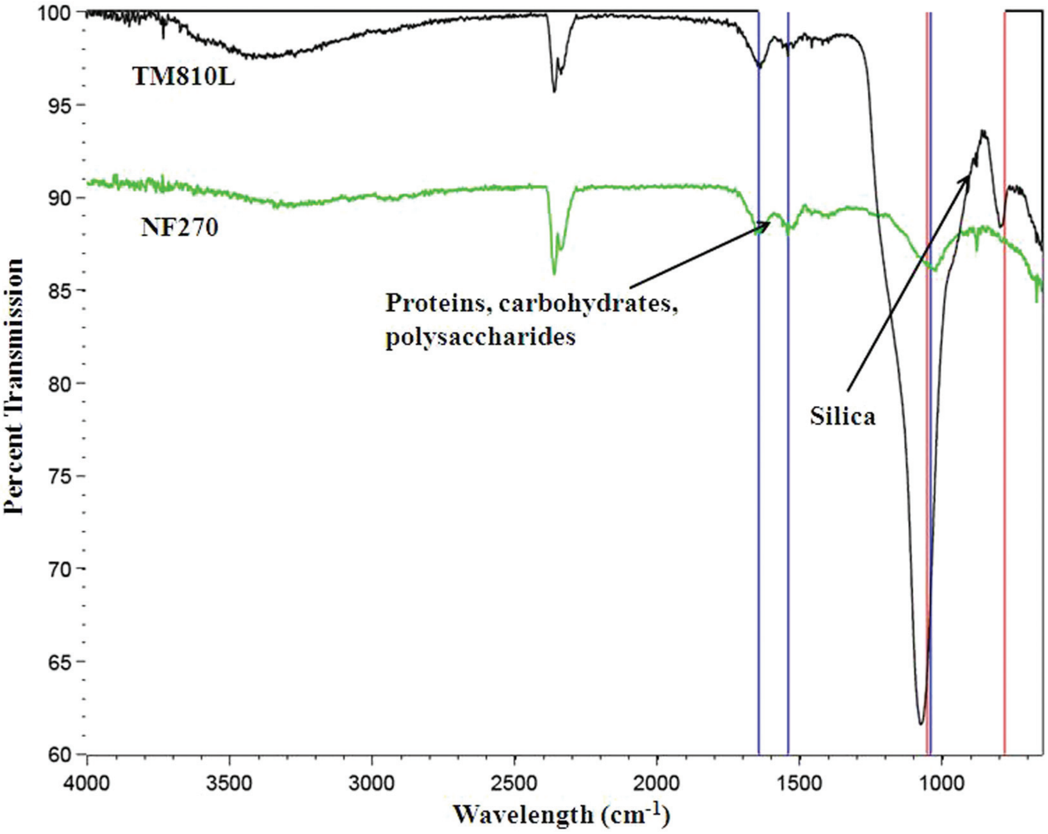

Fig. 7. FTIR spectra for first pass (NF270) and second pass (TM810L) membrane.

Table 4
Elemental composition of membrane foulant layer obtained from EDS analysis

Element, wt%	First pass – NF	Second pass – RO
Carbon	48.9	19.2
Oxygen	38.2	46.8
Sodium	< 0.2	< 0.2
Magnesium	0.5	0.3
Aluminum	2.8	3.5
Silicon	4	24.1
Phosphorous	1.4	0.6
Sulfur	1.1	0.4
Potassium	< 0.2	0.8
Calcium	1.2	2.1
Iron	2	2.3

ignition (LOI) test was performed to determine the organic content of the foulant material deposited on the membrane surface. A LOI value of 85% was found for the SW-NF270 membrane suggesting the presence of significant organic content deposited on the membrane surface. The LOI value for the SW-TM810L membrane was 22%, suggesting low concentrations of organic matter deposited on the membrane. SEM images of the fouled membranes are shown in Fig. 6. Since the SW-NF270 membrane was used for the first pass, organic matter not removed from the pretreatment processes reached the membrane surface and eventually deposited. Since the organics were removed by the SW-NF270 membrane and the permeate was used as feed to the second pass SW-TM810L membrane, deposition of organic matter was not significant on the second pass membrane.

FTIR spectra for the fouled first pass NF and fouled second RO membrane is shown in Fig. 7. The wavelength region between 1,500 and 1,700 cm^{-1} represents protein-like, carbohydrate-like, and polysaccharide-like material deposited. The wavelength region between 800 and 1,000 cm^{-1} represents Si–O bonds. Presence of carbohydrates, polysaccharide-like, and protein-like material was evident on both the membrane surfaces [33]. But, Si–O bonds were found only on the second pass RO membrane. Also, gram-positive and gram-negative bacteria were identified on both SW-NF270 and SW-TM810L membranes. The presence of bacteria on the membrane surface can lead to biofouling issues eventually and cause a decrease in the performance of the membrane and auxiliary equipments.

To determine the inorganic constituents of the deposit layer, EDS was performed in combination with the SEM. The elemental composition of the foulant layer is shown in Table 4. Since the SW-NF270 membrane was fouled by predominantly organic matter (from LOI results), the weight percent of inorganic elements such as silicon was low (less than 4%) suggesting the presence of only a small amount of clay on the membrane. For the second pass membrane (SW-TM810L), a high silicon content (24%) was found which suggested the presence of significant amounts of silica scale and some inorganic clay matter in the form of and aluminum silicates. The presence of silica as aluminum silicates suggested the co-polymerization of silica with aluminum.

Since the first pass membrane system was fouled significantly with organic matter, optimization of pretreatment by addition of higher dosage of coagulant to aggregate the organic matter (by charge screening) for more efficient removal in the pretreatment system (DAF, organoclay) needs to be tested. While utilizing ceramic UF membranes for organic removal, the addition of powdered activated carbon (PAC) before the ceramic UF could possibly assist in further removal of organic material. The second pass membrane system consisting of the TM810L was fouled significantly with silica. Although the pH of the feed water was increased to 10.0, silica precipitation was not prevented on the membrane surface. To increase the recovery of the second pass system, silica levels in the feed water need to be reduced by utilizing other pretreatment processes such as chemical softening, electrocoagulation, and ion exchange [34–36].

4. Conclusions

High-pressure membrane processes such as NF and RO effectively reduced chloride concentration to less than 230 mg/L in the treated water to meet surface discharge limits. Discharge limits for metals were also met using high-pressure membranes. The performance of the NF and RO membranes was plagued by fouling and scaling issues. Fouling of the membranes was predominantly due to the presence of organic matter and scaling was due to high concentrations of silica in the raw produced water. The use of pretreatment process reduced the concentration of suspended solids and oil and grease content but a major fraction of the organics passed through the pretreatment process and reached the NF and RO membranes. The fouling potential of NF and RO membrane was not substantially different for the various pretreatment processes utilized but the performance of pretreatment processes differed substantially. The first pass NF membranes were used to remove a large fraction of scaling precursors such as calcium, from the feed water so that scaling issues due to calcium carbonate was restricted in the second pass. By using a second pass RO membrane, more than 95% reduction of TDS in the feed water was achieved. Although a variety of discharge limits were met by using the two-pass membrane system, the overall feed water recovery was restricted to less than 70% due to organic fouling on the first pass membranes and silica scaling on the second pass membranes. Restriction of fouling and scaling on the NF and RO membrane system by using pretreatment processes specific for the removal of organics and silica is essential to achieve higher feed water recoveries.

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