

Nanofiltration Treatment Options for Thermoelectric Power Plant Water Treatment Demands

Final Report

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Abstract

Nanofiltration (NF) can effectively treat both cooling-tower water and coal-bed methane (CBM) produced waters. NF is an attractive option over conventional reverse osmosis because it requires less power and is less likely to scale. Nanofiltration could help in minimizing water consumption and maximize water usage efficiency of thermoelectric power plants. The power plants could increase the cycles of water recirculation through cooling towers and/or used treated impaired waters. The NF system effectively removed scaling components from cooling-tower recirculating water with efficiency of > 90% and from CBM produced water with efficiency greater than 95% for most constituents including silica, monovalent and divalent species. In most cases the NF system worked better than predicted by the ROSA™, a manufacturer's desalination software used to design systems and predict how well they will work. Theoretical calculations determined that the total volume of water discharged from cooling towers can be reduced by as much as 75% using the continuous NF process compared to traditional recirculating cooling-tower operation. The total volume of water needed for blowdown could be reduced by as much as 40%. The cost for NF of cooling-tower water is estimated to be less than \$1 per 1,000 gallons. Before the successful use of a NF system in a cooling tower with similar chemistry of this pilot study, the system and pretreatment system must be designed carefully to control scaling in NF unit. In addition, NF treatment of CBM produced water will likely require a pretreatment system to control parafilms, filming agents, iron flocs, coal fines, and biological growth.

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ACKNOWLEDGEMENTS

This work was primarily funded by the National Energy Technologies Laboratory (NETL). Work related to the treatment of coal-bed methane (CBM) produced water also received funding from the State of New Mexico Funded Sandia National Laboratories and Los Alamos National Laboratory Small Business Assistance (NMSBA) program. We also want to acknowledge the support of the ConocoPhillips San Juan Business Unit, who made the CBM pilot operation possible. We thank Patrick Brady, Mark Rigali, and Paula Staniulis for their careful reviews of this report. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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1 INTRODUCTION

Large volumes of water are needed to support thermoelectric power generation. The majority of this water is used as cooling water. Thermoelectric generation was responsible for 39% of freshwater withdrawals in the United States in 2000 (USGS, 2004) and 3% of freshwater consumption (USGS, 1998), where water consumption represents the amount of water withdrawal that is *not* returned to the source. This translates to 3 billion gallons per day freshwater consumption by thermoelectric power generation (Feeley et al., 2008). As freshwater supplies become scarcer there will be increased competition and cost for freshwater usage. It is to the power generation industries' benefit to develop methods to minimize water consumption and maximize water usage efficiency. Maximizing water usage efficiency may allow power plants to expand operations while minimizing or eliminating the need for new water supplies.

This report summarizes the work conducted under Field Work Proposal (FWP) Work Package #08-014250 entitled "Nanofiltration Treatment Options for Thermoelectric Power Plant Water Treatment Demands." The purpose of this research is to evaluate the options for low-cost treatment of recirculating cooling-tower water and produced waters. The goals are to remove scaling minerals from cooling water tower such that the water can be recycled and overall water consumption reduced and to determine whether coal-bed methane (CBM) produced water can be effectively treated for water re-use (potentially by power plants). This report serves as the final report for this FWP.

This report is divided into three Sections. Section 1 is this introduction. Section 2 describes a pilot study to test the efficacy of nanofiltration (NF) at treating cooling-tower water. This section also includes theoretical calculations to determine the potential water savings by using NF to treat cooling-tower water. Section 3 describes the efficacy of NF at treating CBM produced water. The results are summarized and conclusions made for the cooling-tower and CBM pilot studies in Sections 2.6 and 3.5, respectively.

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2 NANOFILTRATION OF COOLING WATER

2.1 Introduction

As stated in Section 1, thermoelectric power plants will benefit from optimization of water usage by cooling water towers. Recirculating (closed loop) wet cooling towers are used in 41.9% of existing thermoelectric power plants (Feeley et al., 2008). The recirculating cooling tower first withdraws water from a fresh-water source and recirculates this water through the cooling tower. Salt concentrations increase as water is recirculated and the cooling water evaporates until dissolved salt concentrations reach a threshold value (the set-point). When the set-point is reached the water is discharged as blowdown and clean make-up water from the fresh-water source is added to the tower. Schematically, the fluxes of water and salt in the system are represented by Figure 1A.

For this project, we propose using nanofiltration (NF) to decrease both the amount of make-up water and blowdown needed to run a cooling water tower. In the new conceptualization, as the cooling-tower water is recirculated the water flows through a NF system to remove some of the dissolved salts. The permeate from the NF system is returned to the cooling tower and the concentrate discharged. Addition of permeate to the cooling tower assists in decreasing the volume of blowdown needed as the dissolved salt concentration should not increase as rapidly or reach an equilibrium below the set-point. The schematic of our proposed system is presented in Figure 1B.

There are two components to this work. First, a small, proof-of-concept pilot study was performed to evaluate the potential for a side stream nanofiltration (NF) water treatment process on a cooling tower at Sandia National Laboratories (SNL). The purpose of this pilot study was solely to evaluate how well NF worked at removing dissolved salts from the system. The permeate water was not returned to the cooling tower. Therefore, this pilot study did not evaluate the impact of NF on cooling-tower operations. The second component of this project was conducting some theoretical calculations to determine the potential amount of water savings in a cooling tower by a NF system.

2.2 Pilot Methods

2.2.1 Pilot Operations

The cooling tower chosen for this pilot study is on the roof of Building 823 at Sandia National Laboratories (SNL), a building containing office and laboratory space. The cooling tower, used for comfort and to process cooling loads, is part of a chilled water system, which removes the heat from the condenser water stream. This system is operational 365 days per year, 24 hours per day, and has a design flow rate of 600-1800 gallons per minute (gpm), depending on the outside temperature. Higher temperatures generally lead to higher flow rates. Evaporation rates at the cooling tower for the period January – September are shown in Figure 2. The cooling

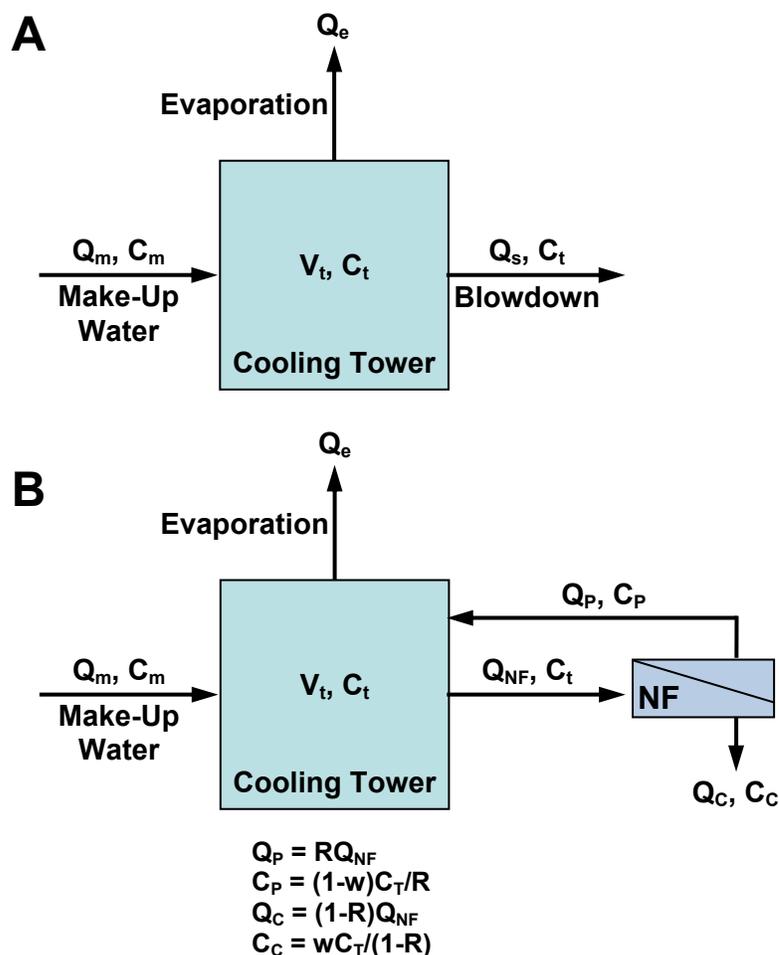


Figure 1. Flow diagrams of cooling-tower water system without (A) and with (B) nanofiltration system. Q = flow, C = concentration, m = make-up water, BD = blowdown, c = concentrate, NF = NF feed, P = permeate, e = evaporation, w = salt rejection efficiency, R = NF recovery.

tower has a groundwater source for make-up water provided by the Kirtland Air Force Base (KAFB). The chemistry is summarized in Table 1. Polyphosphate and phosphonate scale and corrosion inhibitors were added to the cooling-tower recirculating water by SNL's Facilities group. In addition, a biocide was used and a polymer was added to the recirculating water to inhibit silica scale. Additional treatment was not conducted for this pilot operation.

The cooling-tower flow diagram and the nanofiltration pilot design are summarized in Figure 3. Photographs of the system are presented in Figure 4. Using a small pump, a split stream of cooling-tower water is passed through 1 micron cartridge filters (CF) for particulate removal and then through a granular activated carbon (GAC) system to remove any chlorine and bromine from the feed water for protection of the NF membranes. After the GAC system, water is fed directly into the NF system. The NF system was designed for 30% efficiency (30% of the feed water to permeate stream and 70% of feed water to concentrate stream). Both the concentrate and permeate streams from the NF system were returned to the cooling-tower system so as not to

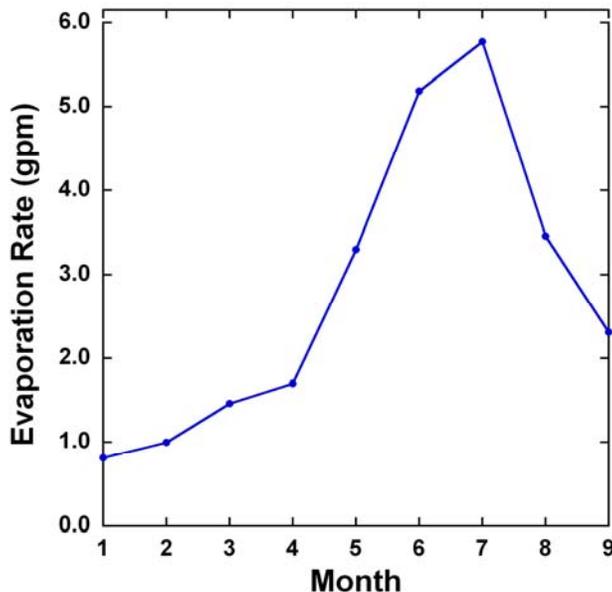


Figure 2. Evaporation Rates from Building 823 cooling water tower as a function of month.

Table 1. Raw water chemistry (mg/L)

	KAFB Water	Cooling-Tower Water
Alkalinity	130.74	427.39
Silica	31.90	121.12
Ca ²⁺	25.67	99.46
Mg ²⁺	4.86	19.29
F ⁻	6.19	20.41
Cl ⁻	25.39	90.53
Br ⁻	2.67	10.39
SO ₄ ²⁻	31.67	124.63
Free Cl ₂	0.9	0.9

impact the cooling-tower operations. Sample points are located throughout the system to verify treatment effectiveness (Table 2).

The pilot equipment was originally purchased and assembled for use on a separate project funded by the Department of Energy under SNL’s Desalination Program. The NF system is comprised of three Dow Filmtec™ NF90-4040 membranes in series (Figure 3). The concentrate stream from the first membrane is the feed to the second membrane. The concentrate stream from the second membrane is the feed to the third membrane. The permeate streams are combined into a single stream. The first membrane generates the most water with the best quality; the third and final membrane generates the lowest water volume with the highest dissolved salt concentrations.

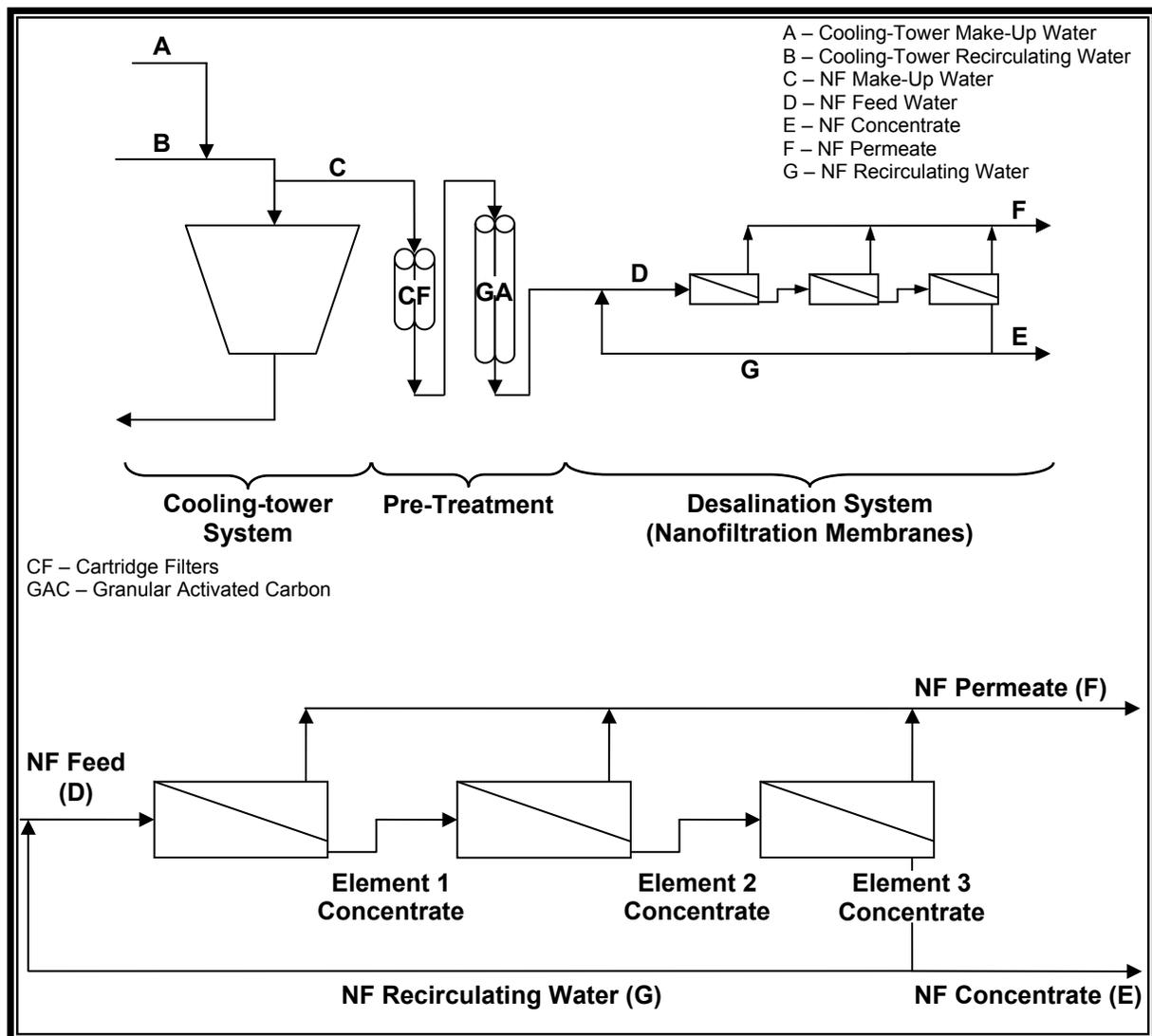


Figure 3. Nanofiltration pilot flow diagram (top) with enlargement of the nanofiltration membrane system (bottom). Note that sample point D was taken after recirculating water mixes with the NF make-up water.

Initial flow rates during the pilot operation were determined by predictive calculations conducted using Dow’s ROSA™ design program (see Section 2.2.4). Once running, the flow rates were optimized by adjusting the concentrate outlet valve, which increased or decreased the feed pressure to the NF system (depending on whether the valve was more closed or opened).

2.2.2 Water Chemistry Measurements

During the pilot operation, samples were taken for laboratory analysis on a regular basis. Sample points are shown in Figure 3 and Table 2. A Dionex IC25 Ion Chromatograph was used to measure anions (Cl^- , F^- , SO_4^{2-} , and Br^-). A Perkin Elmer Analyst 200 Atomic Absorption Spectrometer (AA) was used to measure cations (Mg^{2+} and Ca^{2+}). A Hach Sension 5 meter was



Figure 4. Photographs of nanofiltration system.

Table 2. Sample point descriptions

	Sample Description	Sampling Location
A	KAFB Water (Cooling-tower Make-up)	Basement
B	Cooling-tower Recirculating Water	Basement
C	NF Make-up	Before GAC & 1 μm CF
D	NF Feed	After GAC & recycle addition
E	NF Concentrate	Concentrate pipeline
F	NF Permeate	Permeate pipeline
G	NF Recycle Stream	(not sampled, same as E)

used to measure specific conductivity and a Hach 2100P turbidimeter was used to measure turbidity. pH was measured with a pH meter (Hach Sension 1). Total alkalinity was measured with a sulfuric acid titration; the total alkalinity was assumed to be the same as the bicarbonate (HCO_3^-) concentration. Finally, silica (SiO_2) was measured using the Hach DR2400 colorimeter silicomolybdate (Method 8185). A charge balance calculation was done and the missing positive charge was assumed to be sodium (Na^+).

2.2.3 Analysis of Scale

To determine the composition of the scale, it was analyzed in three manners. First, a 1.0N solution of hydrochloric acid (HCl) was dropped on the scale formations seen on the brine seal and fittings. It was assumed that if bubbles were observed the scale was carbonate and if bubbles were not observed, then the scale was silica. For the second method, 0.03 g of scale was also dissolved in 30 ml of hydrofluoric acid (HF). One milliliter of this solution was further diluted in 10 ml of dionized water. This 0.01% solution was analyzed by an Inductively Coupled Plasma (ICP) Mass Spectrometer (MS) (Perkin Elmer, Elan 6100). Finally, powder X-ray diffraction was used to determine the composition of the scale. Peaks were referenced to standard file JPDF-01-085-1108

2.2.4 Pilot Design and Predictive Calculations

Dow Filmtec™ desalination software, ROSA™ was used to predict permeate water chemistry and determine the optimal system flow rates and pressures. Input parameters include feed-water chemistry and Dow Filmtec™ membranes to be used in the system. Three sets of calculations were performed. The first calculation was used to determine the optimal flow rates and pressures assuming feed-water chemistry based on analysis of cooling-tower water (Table 1). The second calculation was run after completion of the pilot operation and used the data from the actual pilot operation. The purpose of this calculation was to compare membrane performance in the pilot operation to the manufacture predictions. ROSA™ chemistry input is feed-water compositions before recycle is added. As these data were not collected from the pilot operation, the make-up water chemistry (C in Figure 3 and Table 2) was used. The difference between the chemistry of the feed water and the make-up water should not be significant. This is a close approximation of the feed-water chemistry. Also, the measured feed-water flow rate (5.13 gpm) and permeate

Table 3. Summary of physical data

Observation	Units	Average (Range)	Standard Deviation
Permeate 1 Flow	gpm	0.62 (0.42-0.80)	0.09
Permeate 2 Flow	gpm	0.43 (0.28-0.58)	0.07
Permeate 3 Flow	gpm	0.3 (0.20-0.50)	0.07
Total Permeate Flow	gpm	1.34 (0.91-1.75)	0.2
Feed Flow	gpm	5.13 (4.81-5.47)	0.2
Recycle Flow	gpm	0.92 (0.30-1.0)	0.21
Concentrate Flow	gpm	3.79 (3.40-4.10)	0.15
$\Delta P (P_{\text{feed}}-P_{\text{conc}})$	psi	4 (0.0-8.0)	2.18
$\Delta P (P_{\text{feed}}-P_{\text{perm}})$	psi	48 (19-78)	20.4
Feed Pressure	psi	62 (32-91)	20.3
NF Recovery (Permeate/Feed)	%	26 (18-32)	3
System Recovery (Permeate/Makeup)	%	32 (20-39)	5
Rejection (by conductivity)	%	91 (77-95)	4

flow rates (1.34 gpm) were used in the calculations (see Table 3). These analyses were used to compare the predicted permeate chemistries with that measured during the pilot operation. It should be noted that ROSA™ adjusts the feed-water chemistry to maintain a charge balance. As sodium was not measured during the experiment, the sodium concentration was adjusted to maintain charge balance. ROSA™ is not set up to include bromide concentration. Thus, the measured concentration of bromide in meq/L was included in the concentration of chloride for these calculations. Therefore, the chemistry from the ROSA™ calculations is slightly different from what was measured. The last calculation was conducted to compare the energy requirements of a NF membrane to a brackish water reverse osmosis (BWRO) membrane. This last calculation was identical to the calculation used to compare the pilot operation data to the ROSA™ predictions except in the membrane used in the simulation. In this last calculation membrane used was the BW30-4040 instead of the NF90-4040. This BWRO membrane is now called RO-4040-FF. It was chosen for these calculations because of its similar active surface area to the NF membrane used and because it is used for water treatment of waters with similar water chemistry.

Table 4 summarizes the ROSA™-predictions for this pilot operation based on the calculation using the cooling-tower water chemistry in Table 1. Table 4 includes optimized flow rate set points (actual flow rates varied) and pressures. A 30% recovery rate was used in these ROSA™ calculations, based on the membrane design. ROSA™ also alerts the user to potential alarm conditions such as low concentrate flow, which could lead to scaling of membranes. The ROSA™ program predicted formation of scale in the absence of a scale inhibitor (and/or acid addition to minimize scale formation). However, as the cooling-tower recirculating water does have a scale inhibitor, it was still decided to run the pilot operation.

Table 4. Flow rate and pressure set points for cooling-tower pilot operation as determined by ROSA™ based on water chemistry in Table 1.

	Flow Rate (gpm)	Pressure (psig)
NF Make-up (C)	4.1	0.00
NF Feed (D)	5.1	35.25
NF Concentrate [§]	3.9	25.31
NF Concentrate (E)	2.9	25.31
NF Recycle (G)	1.0	25.31
NF Permeate (F)	1.2	---
§ - prior to split between E and G		

2.3 Pilot Operation Results

2.3.1 Pilot Operations

The pilot was operated from March 11, 2009 to May 22, 2009. The system was shut down only when the system required cleaning or GAC system replacement. Once the pilot operation was optimized, flow rates were essentially stable. The optimizing period for adjusting the concentrate outlet valve occurred from March 12 – 19. The pilot was operational for a total of 65 days after stabilization. Of those days, it was actually running for 39 days.

Operational data are summarized in Table 3 and Figures 5 and 6. The flow rates (Figure 5) and permeate pressures (Figure 6) were fairly stable throughout the pilot operation. The flow rates were also close to the set-point values recommended by the ROSA™ simulations. Increases in feed and concentrate pressures observed are an indicator of scaling on the NF system.

Cleanings were performed on March 27, April 20, 27, and May 5, 2009. All used high pH (pH near 12) wash and included a soaking period, slow rinse, and fast rinse. On May 5th, the cleaning procedure also included a low pH cleaning prior to the high pH cleaning to remove any potential carbonate scale. This combined low/high pH cleaning procedure appeared to work the best as is seen by the dramatic decrease in feed pressure after the cleaning (Figure 6).

The pressure required to make the desired permeate flow rate was higher than 35 psi predicted by the ROSA™ program. The feed pressure averaged approximately 62 psi and ranged from 32 to 91 psi (Table 3). The lower end of this range is presumable the necessary feed pressure without scaling, which matches the ROSA™ predictions of 35.25 psi (Table 4). As scale builds up in the feed channel of the membrane system, the feed pressure required to make permeate increased. One other potential cause for the increase in feed pressure is particulate content in the feed water (Section 2.3.3).

Note that for this pilot study the permeate water was not returned to the cooling tower, therefore the NF did not have any direct impact on water use in the cooling tower. However, estimates can be made of the amount of water removed from the cooling tower as well as the volumes of water that could have been returned to the cooling tower. In this case the NF system was operational for 65 days after stabilization days. The average feed flow rate was 5.1 gpm, leading to a

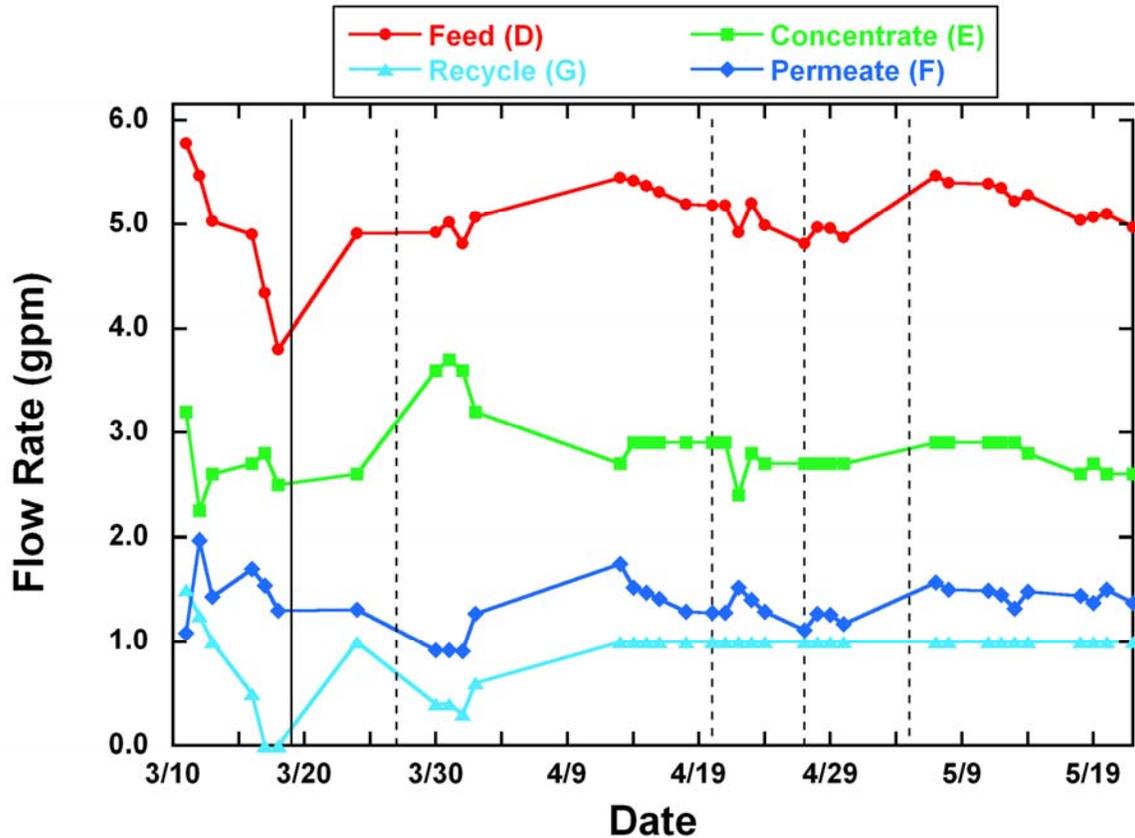


Figure 5. Measured flow rates during NF pilot. Solid vertical line denotes when system stabilized. Dashed vertical lines denote system cleanings. Refer to Figure 3 for locations in flow stream.

potential total of approximately 480,000 gallons treated. Of this, 26% or approximately 125,000 gallons could have been returned to the cooling tower as permeate. This is an overestimate of the volumes as the system was shut down for cleanings. The pilot was actually operational for 39 days. Thus, using the average feed flow rate was 5.1 gpm, approximately 290,000 gallons were treated and 75,000 gallons could have been returned to the cooling tower (note that this is just an approximation as the actual volumes were not metered).

2.3.2 Chemistry

The measured chemistry of the NF system for water samples collected at the various points in the flow stream (Figure 3) are presented in Tables 5 and 6. The NF system was very successful at removing dissolved constituents. Based on conductivity measurements of the feed and permeate streams, more than 90% of dissolved species were removed (Figure 7). The causes for spikes in conductivity (Figure 7) are unknown at this time and it is suspected that calibration procedures or other sampling problems may have inadvertently caused the apparent spikes. The spikes could also be caused by the cleaning procedures (not flushing the system fully).

Divalent ion concentrations decreased by over two orders of magnitude (Figure 8A and Table 6) (99.1 – 99.9% removal) and monovalent ions by over one order of magnitude (Figure 8B and

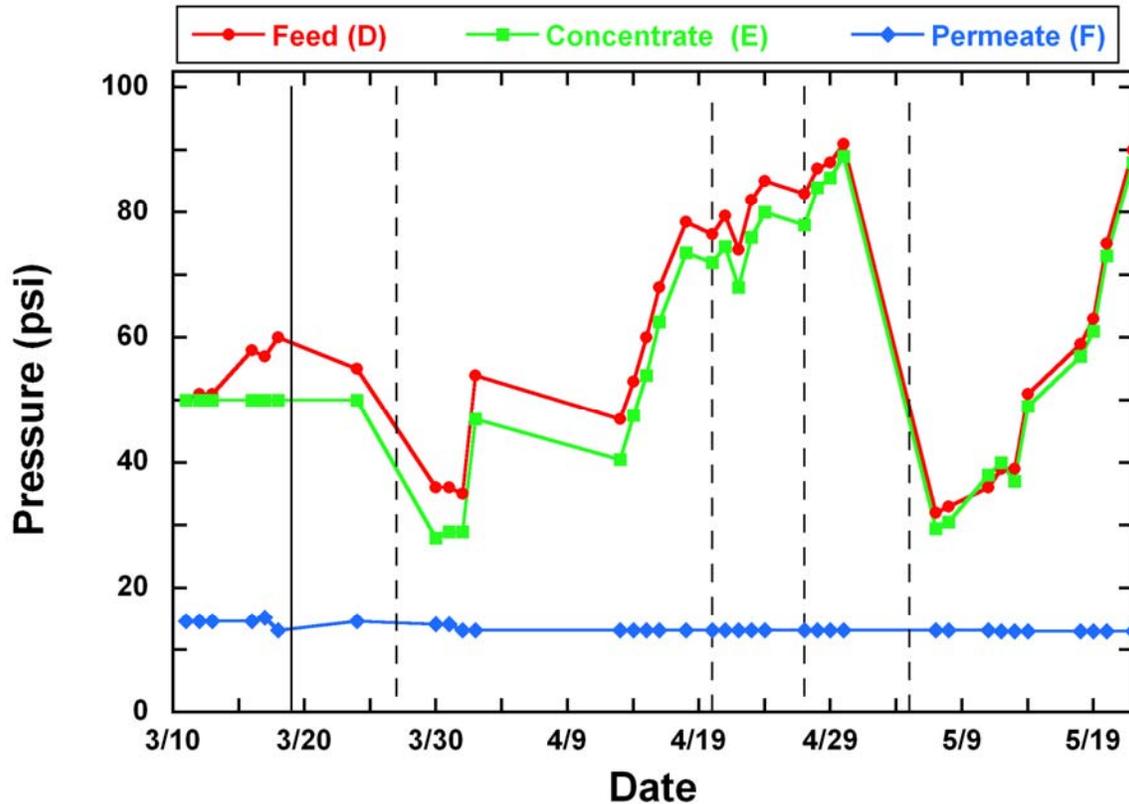


Figure 6. Measured pressures during NF pilot operation. Solid vertical line denotes when system stabilized. Dashed vertical lines denote system cleanings. Refer to Figure 3 for locations in flow stream.

Table 6) (78.0 – 95.8% removal). Almost all of the sulfate (99.9%) was removed and bromide (at 78.0% removal) had the lowest fraction removed. The next lowest percent removal was chloride at 85%. The NF was quite successful at removing monovalent anions HCO_3^- and F^- , both with 95.8% removal.

The NF system was also successful at removing almost 90% of the silica, lowering concentrations from 128 mg/L to 12.76 mg/L, an order of magnitude decrease (Figure 8C). The NF system also appeared to lower the water turbidity, though there was a lot more noise in the data (Figure 8D).

The NF membranes performed better than predicted by the ROSA™ calculations (Table 6). The salt rejection rate of the NF was 2.5% (SO_4^{2-}) to 4.8% (Mg^{2+}) better than the predictions for the divalent ions and 2.7% (Cl^-) to 14.9% (F^-) better for monovalent ions. Silica was the only dissolved constituent for which the actual removal was lower than that predicted by the ROSA™ calculations and by less than 1% (to permeate concentration of 12.8 mg/L as opposed to the predicted value of 12.0 mg/L).

Table 5. Results of chemical analysis of the NF system along the flow stream (see Figure 3 for sample locations, CT = Cooling Tower, NF = Nanofiltration).

Sample Location	A	B	C	D	E	F
Parameter	CT Make-up Water	CT Recirculating Water	NF Make-Up Water	NF Feed water	NF Concentrate	NF Permeate
pH	7.67 ± 0.73 (n = 16)	8.87 ± 0.08) (n = 16)	8.87 ± 0.08 (n = 17)	8.82 ± 0.11 (n = 17)	8.80 ± 0.08 (n = 17)	8.74 ± 0.63 (n = 17) [¥]
Turbidity (NTU)	0.24 ± 0.09 (n = 14)	0.50 ± 0.28 (n = 14)	0.41 ± 0.13 (n = 14)	0.36 ± 0.12 (n = 14)	0.43 ± 0.10 (n = 14)	0.20 ± 0.13 (n = 13)
Conductivity (µS/cm)	---	---	---	1275 ± 45 (n = 29)	---	83.8 ± 8.0 (n = 21)
SiO ₂ (mg/L)	31.90 ± 4.14 (n = 23)	131.1 ± 9.16 (n = 23)	117.8 ± 9.48 (n = 28)	128.2 ± 10.8 (n = 28)	167.5 ± 16.8 (n = 28)	12.76 ± 2.90 (n = 28)
HCO ₃ ⁻ (mg/L)	130.7 ± 18.1 (n = 23)	427.4 ± 22.0 (n = 23)	421.9 ± 34.2 (n = 28)	445.9 ± 23.3 (n = 28)	606.4 ± 62.7 (n = 28)	17.63 ± 3.97 (n = 28)
Cl ⁻ (mg/L)	25.39 ± 2.78 (n = 23)	90.53 ± 11.4 (n = 23)	91.33 ± 10.0 (n = 27)	98.14 ± 12.2 (n = 27)	136.6 ± 22.1 (n = 27)	13.67 ± 2.00 (n = 27)
F ⁻ (mg/L)	6.19 ± 0.55 (n = 23)	20.41 ± 1.86 (n = 23)	20.85 ± 2.10 (n = 27)	22.00 ± 1.67 (n = 27)	31.38 ± 5.80 (n = 27)	0.87 ± 0.14 (n = 27)
SO ₄ ²⁻ (mg/L)	31.67 ± 1.8 (n = 23)	124.63 ± 11.8 (n = 23)	131.0 ± 18.9 (n = 27)	141.3 ± 19.5 (n = 27)	198.1 ± 35.9 (n = 27)	0.19 ± 0.08 (n = 27)
Br ⁻ (mg/L)	2.67 ± 0.31 (n = 9)	10.39 ± 3.82 (n = 23)	11.37 ± 4.36 (n = 27)	10.55 ± 4.84 (n = 27)	13.63 ± 6.20 (n = 27)	2.50 ± 2.13 (n = 27)
Mg ²⁺ (mg/L)	4.86 ± 0.46 (n = 23)	19.29 ± 1.89 (n = 23)	20.24 ± 2.53 (n = 28)	21.05 ± 2.89 (n = 28)	29.9 ± 4.20 (n = 28)	0.14 ± 0.17 (n = 28)
Ca ²⁺ (mg/L)	25.67 ± 5.78 (n = 23)	99.46 ± 7.90 (n = 23)	102.8 ± 7.70 (n = 28)	109.2 ± 7.49 (n = 28)	153.8 ± 19.1 (n = 28)	0.90 ± 0.35 (n = 28)
Na ^{+§} (mg/L)	35	97	153	164	221	16
§ - Sodium concentration is assumed to make a perfect charge balance. Potassium concentration is assumed to be negligible.						
¥ - pH measurements in the NF permeate water are suspect as a decrease in pH in the permeate is expected due to removal of HCO ₃ ⁻ .						

2.3.3 Membrane Autopsy

At the conclusion of the pilot operation, an autopsy was performed on the final NF membrane in series for visual inspection of the membrane. The final membrane would be exposed to the highest concentrations of salts, which would lead to more precipitation than in the first two membranes. As expected, a significant amount of scale was present (Figure 9, left side). As the membranes were removed from the filter housings, the brine seal collected scale. Precipitate was observed in the concentrate water that was captured when the membranes were removed (see Figure 9, right side).

Also visible during the autopsy was black particulate matter, which is likely from the GAC beds (Figure 10). The feed end of the elements and membrane surfaces had black particles visible. The cartridge filters should have been installed downstream of the GAC beds to minimize particulate going to the NF membranes. These GAC particles could also have led to the

Table 6. Comparison of predicted and actual permeate quality for cooling-tower pilot operation.

Parameter (units)	Measured Concentrations and Percent Removed			Predicted	
	Average NF Feed	Average NF Permeate	Percent Removed	NF Permeate Conc.	Percent Removed
Na ⁺ [§] (mg/L)	153	16	89.6	31.2	82.5
Mg ²⁺ (mg/L)	20.2	0.14	99.3	1.12	94.5
Ca ²⁺ (mg/L)	103	0.90	99.1	5.61	94.5
HCO ₃ ⁻ (mg/L)	422	17.6	95.8	56.0	86.7
Cl ⁻ (mg/L)	91.3	13.7	85.0	17.0	82.3
F ⁻ (mg/L)	20.9	0.87	95.8	3.98	80.9
Br ⁻ [§] (mg/L)	11.4	2.50	78.0	---	---
SO ₄ ²⁻ (mg/L)	131	0.19	99.9	3.50	97.3
SiO ₂ (mg/L)	118	12.8	89.2	12.0	89.9
pH (---)	8.9	8.7	---	8.5	---
<p>* - Concentrations not measured but assumed based on charge balance § - Bromide concentrations included in chloride concentration for ROSA™ calculations based on charge balance because ROSA™ does not accept information for bromide. Note: Percent removed is the percentage from the ROSA™ calculated feed chemistry, which is slightly different than the measured feed chemistry. Note: K⁺, NH₄⁺, Sr²⁺, Ba²⁺, and boron concentrations assumed to be 0 for ROSA™ calculations.</p>					

observed pressure increases. Future work will have a proper design with cartridge filters installed before the NF membrane system.

2.3.4 Analyses of Scale

As mentions in Section 2.2.3, three methods were used to analyze the scale: 1) dropping HCl on the scale observed on the brine seal and fitting, 2) ICP-MS, and 3) X-ray diffraction. Bubbles were not observed when the HCl was dropped on the scale, indicating that the scale was not dominated by carbonates. Both silica and calcium were measured in the scale for the ICP-MS analysis (Table 7). However, the calcium concentration was almost 7 times higher than that of silica. Magnesium, chloride, and barium are also measured in the scale at concentrations greater than 1 ppm. Every peak on the powder X-ray diffraction characterization of the scale indexed to calcium carbonate CaCO₃ (referenced to standard file JCPDF-01-085-1108) (Figure 11). As Si was measured in the ICP-MS analysis (see Table 7) but not detected with the X-ray diffraction, silica is most likely present in an amorphous, not crystalline form.

2.4 Theoretical Calculations

The objective of these calculations is to evaluate the potential for nanofiltration (NF) to decrease make-up water needed and water discharge volume compared to tower operation without a NF system. As stated in Section 2.1, in traditional operation of a wet recirculating cooling tower,

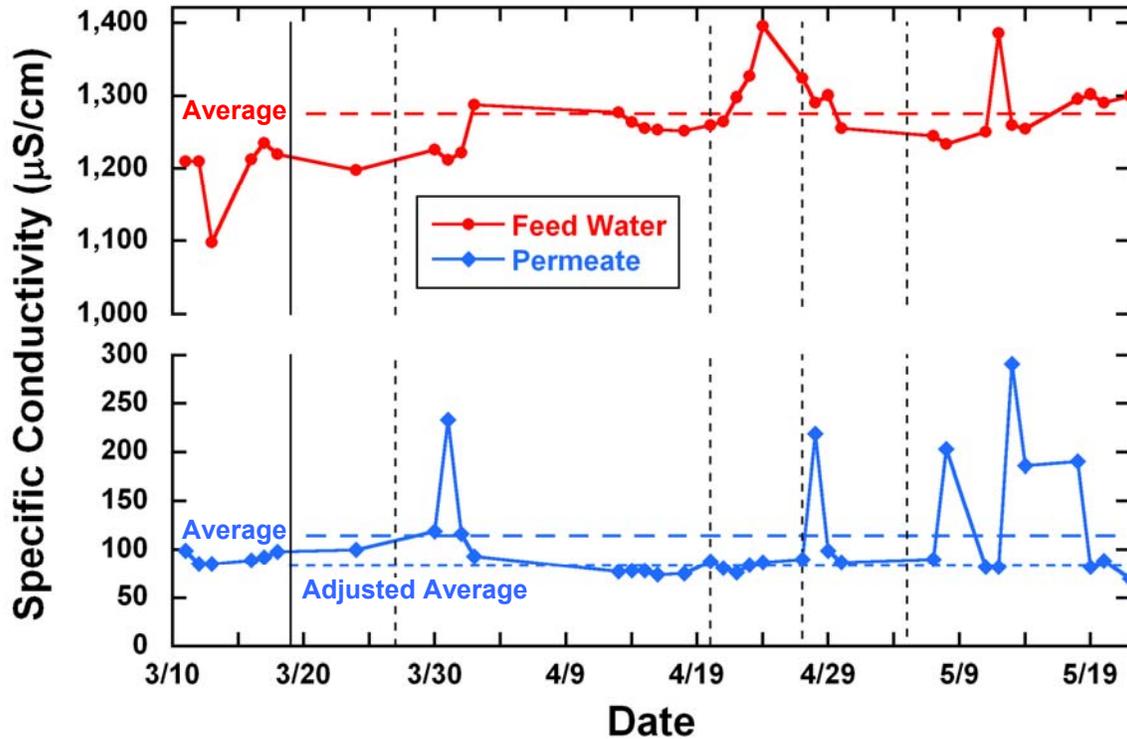


Figure 7. Measured specific conductivity during NF pilot operation. Solid vertical line denotes when system stabilized. Dashed vertical lines denote system cleanings. Refer to Figure 3 for locations in flow stream. Adjusted average for the permeate water excluded values in the conductivity spikes (values over 100 $\mu\text{S}/\text{cm}$).

Table 7. ICP-MS analyses of dissolved scale taken from NF elements.

Analyte	Concentration (ppm)
Na	0.18
Mg	2.43
Cl	3.96
Si	8.99
Ca	60.5
Fe	0.24
Zn	0.14
Br	0.20
Sr	0.59
Ba	1.25

salt concentrations increase as water evaporates until a preset value of specific conductivity (or set-point) is reached, at which time a volume of water is discharged as blowdown and replaced with make-up water (Figure 1A). This results in a lowering of the concentration of the

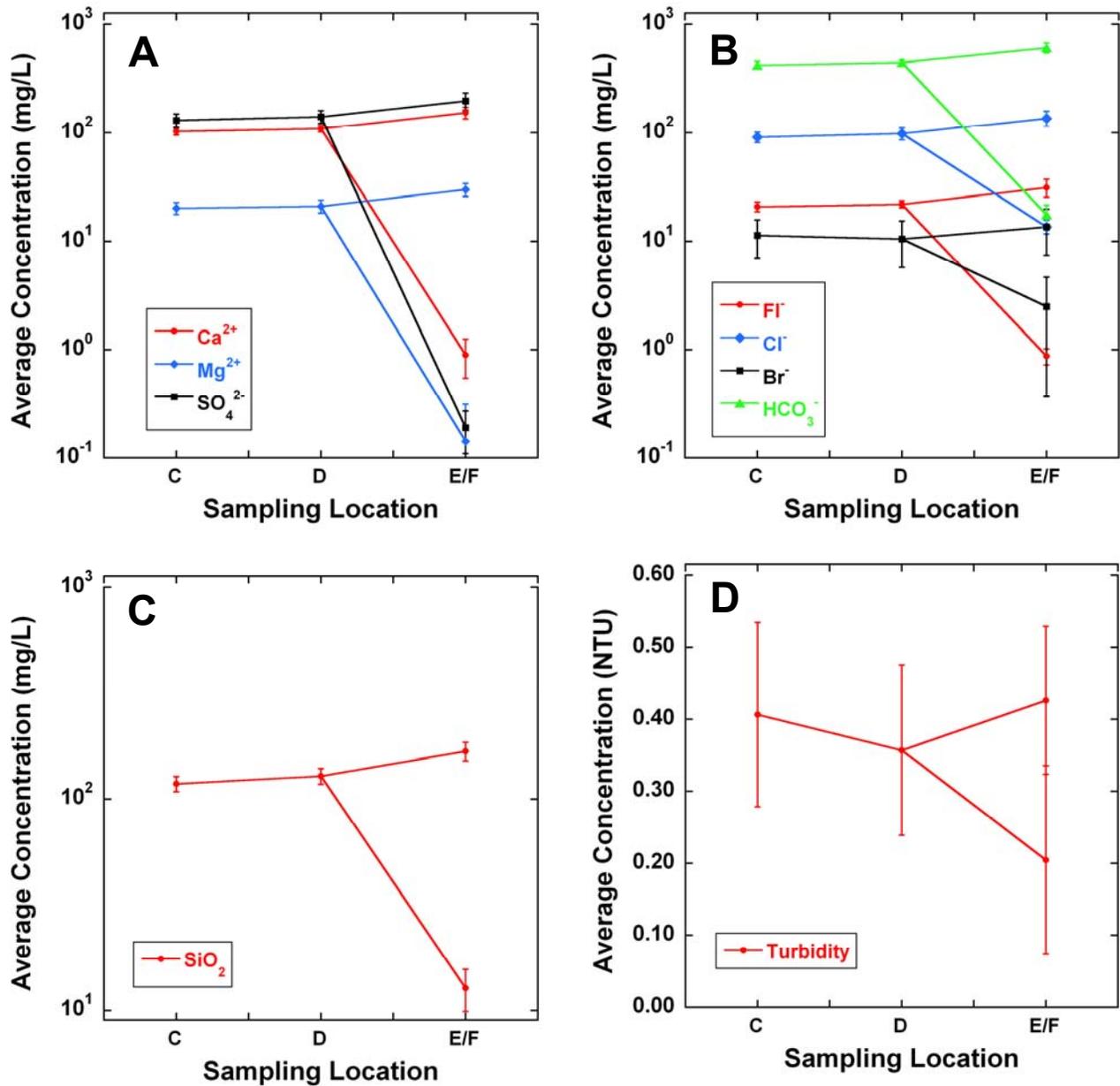


Figure 8. Average measured concentrations of divalent ions (A), monovalent ions (B), silica (C) and turbidity (D). Error bars indicate ± 1 standard deviation of the measurements. Refer to Tables 5 and 6 for actual values. Refer to Figure 3 for sample locations: C = NF make-up water, D = NF feed water, E = concentrate, and F = permeate.

recirculating water. Water usage in this system is compared to that when the cooling-tower recirculating water is run through a NF system and the permeate returned to the cooling tower (Figure 1B).

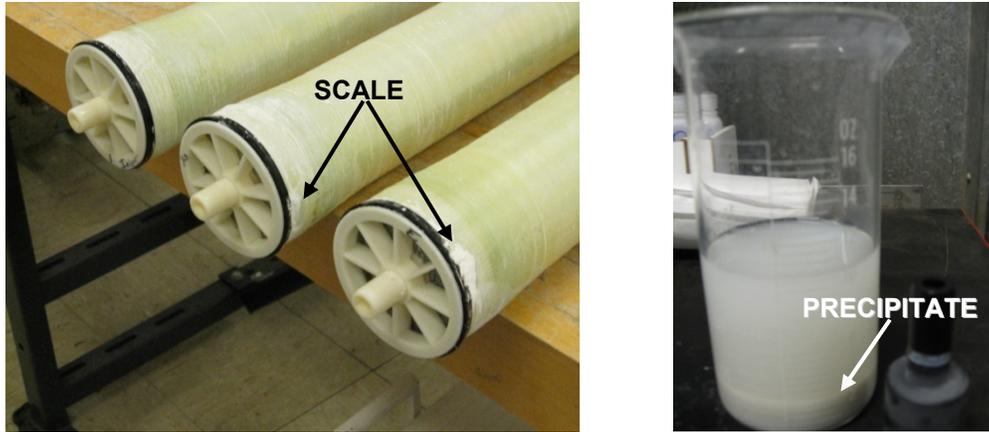


Figure 9. Photographs from membrane autopsy showing scale (left) and precipitate from concentrate water (right).



Figure 10. Photographs from membrane autopsy showing GAC particulate matter on the membrane.

2.4.1 Theoretical Calculation Methods

The concentration factor (X) is defined in terms of the concentration of salts in the cooling tower (C_T) and the concentration of salt in the make-up water (C_m):

$$X = \frac{C_T}{C_m} \quad (\text{eqn. 1})$$

The flow balance (eqn. 2) and salt balance (eqn. 3) for this system are, respectively:

$$Q_m = Q_e + Q_{BD} \quad (\text{eqn. 2})$$

and

$$Q_m C_m = Q_{BD} C_T \quad (\text{eqn. 3})$$

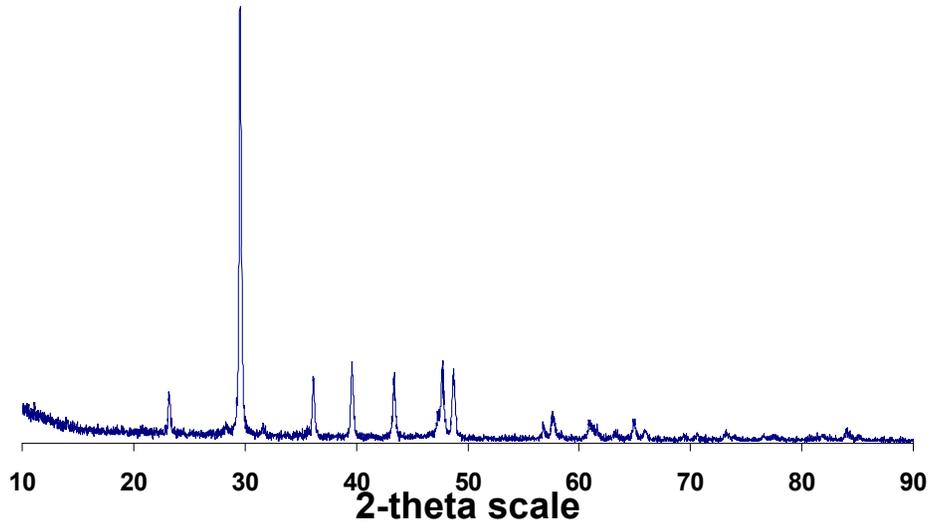


Figure 11. X-ray diffraction spectrum of scale. Every peak indexes to CaCO_3 .

where

Q_m is the flow rate of make-up water

Q_{BD} is the flow rate of blowdown, and

Q_e is the evaporation rate

Solving for Q_m in eqn. 3 and substituting into eqn. 2, we see that

$$Q_{BD} = \frac{Q_e}{(X - 1)} \quad (\text{eqn. 4})$$

Figure 1B is a schematic of the cooling tower with the NF system. In this conceptualization, all cooling-tower discharge (Q_{NF}) flows through the NF system. The flow balance (eqn. 5) and salt balance (eqn. 6) for the cooling tower with a NF system are, respectively:

$$Q_m = Q_e + Q_c \quad (\text{eqn. 5})$$

and

$$Q_m C_m = Q_c C_c \quad (\text{eqn. 6})$$

where

Q_c is the flow rate of concentrate stream and

C_c is the concentration of salts in the concentrate

By definition,

$$Q_c = (1 - R)Q_{NF} \quad (\text{eqn. 7})$$

and

$$C_c = \frac{wC_T}{(1 - R)} \quad (\text{eqn. 8})$$

where

Q_{NF} is the flow rate to the NF system,

R is the recovery of the NF system (the fraction of water entering the NF system that returns as permeate), and

w is the fraction of salts removed by NF system. Thus, substituting eqn. 7 into eqn. 5,

$$Q_m = Q_e + (1 - R)Q_{NF} \quad (\text{eqn. 9})$$

It is now possible to solve for Q_c and Q_m as a function of X , w , R , and Q_e .

For this case we assumed a $Q_e = 5.8$ gpm, as this was the maximum evaporation rate measured in the 823 cooling-tower system (see Figure 2). The fraction of salts removed by the NF system (w) was assumed to be 0.9. We calculated percent savings in make-up water and also waste water (blowdown or NF concentrate discharge) in comparison to a cooling tower that is not using a NF system.

2.4.2 Theoretical Calculation Results

It can be seen that with the use of a NF system, makeup water use can be reduced by as much as 40% with a membrane efficiency of 0.7. For concentration factors in the range typical at Sandia makeup water can be reduced by 10% - 25% (Figure 12A). There is an even larger reduction in water that is discharged as waste (Figure 12B). In this case at concentration factors typical at Sandia, there could be a 30% - 75% decrease in discharge. For these calculations, the flow rates to the NF system were in the 2 - 3 gpm for concentration factors typical at Sandia (Figure 13). Theoretically, the permeate water can make up over 25% of the make-up water volume (Figure 14).

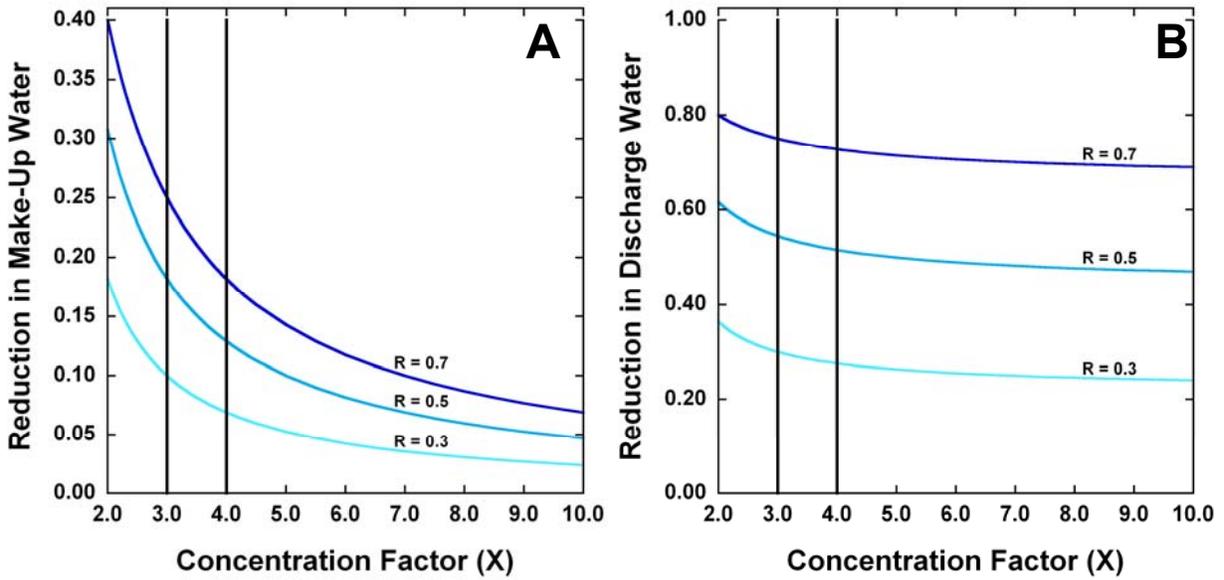


Figure 12. Reduction in make-up water needed (A) and discharge water (B) from cooling tower as a function of recovery rate (R) of the NF system and concentration factor (X). Reduction due to use of the NF system.

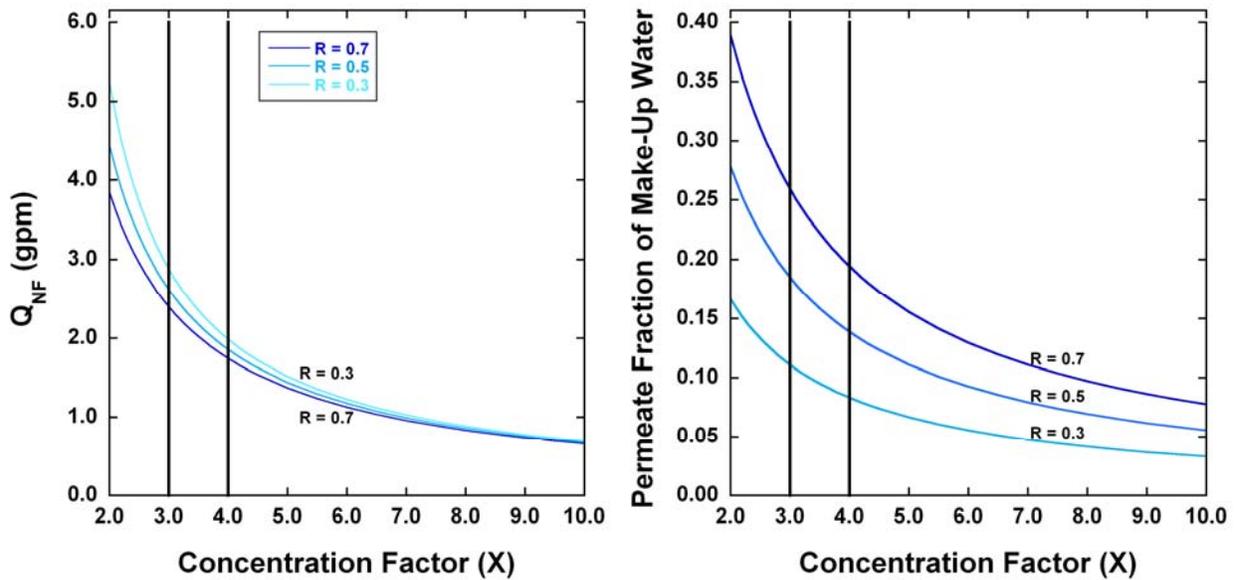


Figure 13. Flow rates into the NF system as a function of NF recovery rate (R) and concentration factor (X).

Figure 14. Fraction of make-up water from the permeate stream as a function of NF recovery rate (R) and concentration factor (X).

2.5 Discussion

2.5.1 Scaling

Scaling is clearly an issue that needs to be resolved before a NF can run successfully in this cooling-tower water system. In this case carbonate scale appears to be responsible for the pressure buildup in the NF system. This is seen by the chemical analyses of the scale (see Section 2.3.4) and also the fact that it took a low pH cleaning to decrease the feed pressure

(Figure 6). The pressure buildup started occurring less than 20 days after initiation of the pilot operation. To minimize operational costs and to maximize the life of the NF membranes, cleanings should occur no more than once per quarter. Future studies should also evaluate other options for minimizing silica scale in the nanofiltration system. In essence, we have shifted the scaling problem from the tower to the NF unit.

Solubility limits for both calcium and silica are presented in Figure 15. Note that these solubility limits assume no chemical treatment of the water. Pretreatment chemicals used to control scaling on cooling towers could increase the solubility limits for both silica and carbonate. The chemistry of the cooling-tower feed water is shown as the red points on the figure. It can be seen that silica concentration of the feed water is very close or at the solubility limits at 25 °C. The concentration of silica in the concentrate is above the solubility limit. The concentrate water is supersaturated with respect to silica. The feed water is supersaturated with respect to calcium

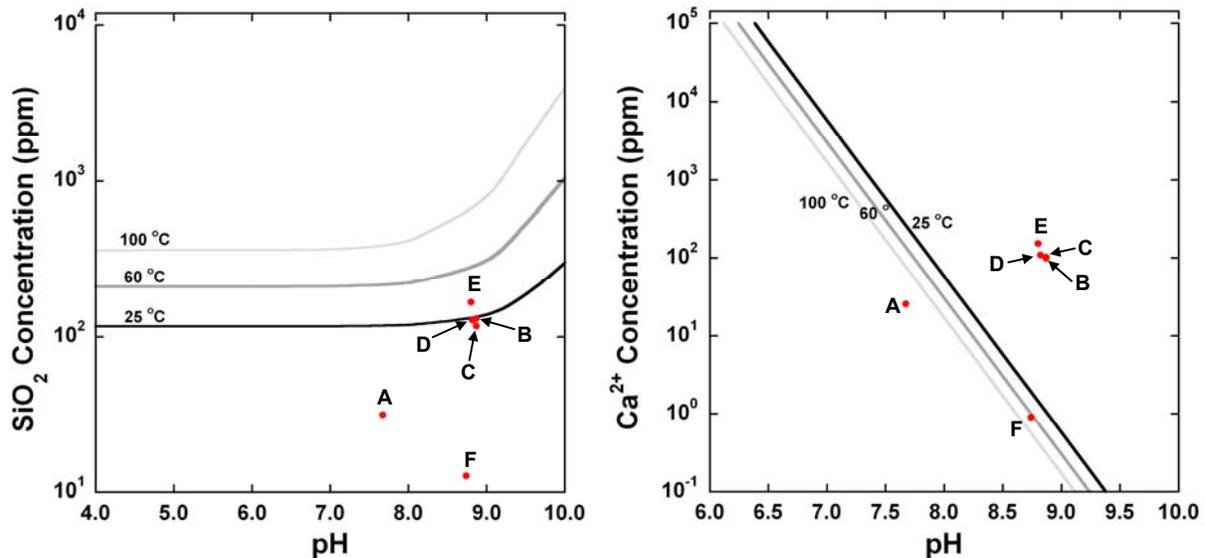


Figure 15. Solubility of silica (left) and calcium (right) as a function of pH, temperature and concentration. Red points indicate concentrations along the flow stream of the NF pilot operation. Refer to Figure 3 for sample locations: A = cooling-tower make-up water, B = cooling-tower recirculating water, C = NF make-up water, D = NF feed water, E = concentrate, and F = permeate.

(regardless of temperature). The NF system brought the calcium concentrations below the solubility limit at 25 °C. Given these observations, it is not surprising that both silica and calcium scale were detected and that calcium scale was more prevalent (given that concentrations were much greater than solubility limits).

There are a number of possible approaches to avoid the scaling problem:

- 1) Use different NF membranes with lower silica rejection ratio. A higher efficiency NF membrane will allow a higher fraction of water through as permeate and at the same time it may let more dissolve salts through. Use of a higher efficiency membrane, thus, could improve the scaling issues on the membrane surface at the same time as reducing water usage. With higher Dow NF270 and NF200 membranes, while not as well tested as the NF90-4040 used in this study, have lower predicted silica rejections and may be a better fit for this specific water chemistry. Table 8 summarizes the performance aspects of each of these membranes as predicted by ROSA™.
- 2) Use antiscalants to prevent or delay precipitation of salts of divalent cations (Ca²⁺, Mg²⁺). Antiscalants are typically less effective for SiO₂.
- 3) Control pH to keep silica and calcium or both in solution. The polymerization rate for SiO₂ is pH dependent, and a reduction of pH to ~7 or lower may be effective at minimizing SiO₂ scaling. Calcite solubility limits increase with decreasing pH, therefore, a decrease in pH may also help to control calcium scaling. This approach is being investigated in Phase 2 of the project in FY10.
- 4) Add a pre-treatment step to selectively remove SiO₂ from the input stream to the NF unit by controlled precipitation processes. This pretreatment step, while adding complexity to the system, can effectively increase the performance and recovery possible with the NF. An advanced coagulation and flocculation process for SiO₂ will be investigated in Phase 2 of the project in FY10.

Table 8. ROSA™ predicted rejection for various membranes.

	NF90-4040	NF200-4040	NF270-4040
Na ⁺	85%	42%	29%
Mg ²⁺	95%	76%	64%
Ca ²⁺	95%	69%	54%
HCO ₃ ⁻	89%	57%	40%
Cl ⁻	85%	22%	7%
F ⁻	83%	22%	7%
SO ₄ ²⁻	98%	98%	97%
SiO ₂	91%	55%	15%

- 5) Use flow reversal to avoid precipitation. The slow kinetic step in precipitation is formation of a small nucleus on which precipitation can take place. Gilron et al. (2006) have shown that periodically reversing flow direction in an RO or NF system can alternate the concentrations in various parts of the system between super-saturated and unsaturated. If the period of flow reversal is less than the induction time for nucleus formation, precipitation can be avoided, even at very large super-saturation at the end of membrane module. This approach is not feasible in the current program, but data on the degree of concentration and scaling problems observed in this project will help to evaluate the potential for the flow reversal technique to help mitigate scaling problems in the NF unit.

2.5.2 Performance of the Nanofiltration System

These pilot operation measurements have demonstrated that NF is efficient at removing scaling salts from cooling-tower recirculating water. Excessive accumulation of ions, such as Cl^- , which may be a problem for corrosion, is not expected. NF is particularly efficient at removing divalent cations and anions, which are the typical scaling components, but less efficient at removal of monovalent ions. As shown in Section 2.3.2, rejection efficiencies are greater than 99% for divalent ions, but only 78.0 – 95.8% for monovalent ions. The NF membranes performed better than expected in terms of their ability to reject the monovalent (e.g. chloride) and uncharged species (e.g. silica).

It should be noted that diurnal and seasonal variations in heat load will impact the NF system. In cooling towers used for heating and cooling operations in buildings, for example, the heat load varies considerably though the day and year. With the aim of keeping cooling-tower operation as close to steady state as possible, variations in heat load (and evaporation rate) would require variations in flow rates to the NF unit. Membrane water-treatment systems tend to work best if run continuously at constant conditions. A compromise must be found between the most efficient operating parameters for the cooling tower and the NF unit. One approach would be to install multiple NF units in parallel, which could be activated as needed. This concern is not likely to be a major problem for continuous operations such as base-load power plants, whose heat load is relatively constant, independent of daily or seasonal ambient temperature.

To improve the water savings in a cooling tower, a membrane with a higher efficiency (greater water volumes as permeate) will lead to more water savings. Such a membrane will also lead to lower concentrations of salts in the concentrate and therefore less scaling on the membrane surface. The key is to finding a balance to maximize water savings and minimize scaling both in the cooling tower and the membrane units.

2.5.3 Costs Estimates

We estimate that the operational costs for running a NF system will be \$0.50 – \$0.90 per 1,000 gallons. This cost estimate is based on the procedures presented in Chapter 9 of the Desalting Handbook for Planners (Watson et al., 2003). Year 2000 is the cost basis year for these estimates and the level of accuracy for the data is ± 30 percent. This cost estimate accounts for the costs of routine maintenance and operations, chemical costs for pre-treatment, post-treatment

and membrane cleaning, electricity costs, and membrane replacement costs. It is assumed that the annual labor rate for maintenance and operation is either \$25,000 (value given in Watson et al., 2003) or \$50,000, electricity costs are either \$0.06/kWh (value given in Watson et al., 2003) or \$0.09/kWh (Michael Hightower personal communication), and membrane replacement costs are \$0.02/m³.

The range in cost is based on the differences between surface water and groundwater source waters and the low and high labor and electrical costs listed in the above paragraph. Chemical costs and electricity charges are both higher for surface water. Electrical costs for treating surface water includes power for intake pumps, power for pre-treatment pumps, process power, distribution pump power and building services. Electrical costs for treating groundwater include power for well pumps, process power, distribution pump power and building services.

Our estimate of \$0.50 – \$0.90 per 1,000 gallons should only be taken as an approximation. First, as stated in Watson et al. (2003), there is a level of accuracy of ± 30 percent in the estimates. The main reason to believe that our estimates are too high is the increase in costs and labor rates since year 2000. This was partially accounted for by increasing the labor rate to \$50,000 for a higher estimate. A reason to believe that the estimates are low is that some of the costs are already part of running a power plant. These include the costs of pumping the water to the plant and discharge costs, some of the treatment costs and perhaps of the of labor costs for maintenance.

Capital costs are also not included in these estimates. Watson et al. (2003) give estimates for capital costs; however, it is difficult to differentiate what is already available in the power plant and what would have to be built. We assume that the facility, concentrate discharge piping, water intake structure, pretreatment and post-treatment equipment are already available. One structure that may have to be built is the process building for the membranes systems. For an 8,000 m³/day system, the cost for this is estimated to be \$550,000, assuming a cost of \$150/ft².

It should be noted that our cost estimate was based on treating 8,000 m³/day or 1,500 gpm. This value was determined by a discussion with Michael Hightower, an expert at Sandia on the Energy-Water Nexus, who stated that for a typical coal-fire power plant cooling tower, the flow rate is 5,000 gpm with 3,500 gpm going to evaporation and 1,500 gpm going to blowdown. Our estimates thus assume that all of the blowdown is treated by NF. This assumption was made in order to be conservative on the costs of the NF as the costs generally decrease logarithmically as the plant capacity decreases (also on a logarithmic scale).

2.5.4 Comparison of NF to RO Membranes

ROSA™ generates power (kW) and specific energy (kWh/lgal) for each calculation. As mentioned in Section 2.2.4, calculations were run to compare the energy requirements of a NF membrane to a reverse osmosis (RO) membrane. This last calculation was identical to the calculation used to compare the pilot operation data to the ROSA™ predictions except in the membrane used in the simulation (BW30-4040 instead of NF90-4040). Comparison of specifications of the membranes are shown in Table 9. It can be seen that the operating pressure

Table 9. Comparison Specifications for of NF to RO membranes

Product Specification	FILMTEC NF-4040	FILMTEC RO-4040-FF
Active Area (m ²)	7.6	7.9
Permeate Flow Rates (gpd)	3,050	2,400
Typical Recovery Rate (%)	15	15
Typical Stabilized Salt Rejection (%)	> 99% [¥]	99.5 [§]
Minimum Salt Rejection (%)	98.0%	98.0
Typical Pressure (psi)	130	225
Maximum Operating Pressure (psi)	600	600
Maximum Differential Pressure (psi)	15	15
[¥] - for 2.000 ppm MgSO ₄ at 130 psi, 25 °C, pH 8 and 15% recovery [§] - for 2.000 ppm NaCl at 225 psi, 25 °C, pH 8 and 15% recovery		

needed to run the RO membrane is significantly higher (225 psi as compared to 130 psi) than the NF membrane. It is also worth noting that while the salt rejection rates appear comparable, the NF was tested with divalent ions (MgSO₄) and the RO membrane was tested with monovalent ions (NaCl), due to differences in design of NF and RO membranes. ROSA™ calculated that the specific energy of the RO membrane would be 2.65 kWh/kgal in comparison to 1.41 kWh/kgal. This translates to a savings of 1.24 kWh/kgal or a 47% savings in energy.

Not included in the ROSA™ calculations are the impact of scaling on power consumption. As membranes scale, power needs increase to maintain a constant permeate flow. RO membranes are more likely to scale than NF membranes. Thus, as scaling occurs on the membranes the power consumption for RO membranes will increase at a faster rate than that of an NF membrane. In addition, RO membranes may need more cleaning and increased replacement frequency, which may increase the operational costs.

Another method used to compare RO to NF membranes was to conduct the same calculations described in Section 2.5.2, except for a brackish water RO membrane. These calculations resulted in a 35% - 40% savings in using an NF membrane, slightly lower than that calculated above.

2.6 Summary and Conclusions

Through pilot operation measurements and model calculations we have verified that nanofiltration is an attractive option for controlling scaling and substantially reducing the water discharged in cooling-tower operations. We have characterized the performance of an NF unit on recirculating water in a cooling tower located in Building 823 at Sandia National Laboratories, and estimated the capacity of an NF unit required to operate this cooling tower in continuous operation.

The conclusions from this study of nanofiltration treatment options for thermoelectric power plant water treatment demands are as follows:

- 1) Nanofiltration can effectively remove scaling components from cooling-tower recirculating water with efficiency of > 99% for divalent ions, 78% - 95.8% for monovalent ions and almost 90% for silica, with less power consumption than conventional reverse osmosis treatment.
- 2) Concentration of scaling compounds can be controlled to a desired level in the cooling tower to prevent scaling.
- 3) Scaling of problem components in the NF unit must be addressed when designing a system.
- 4) Total volume of water discharged can be reduced by as much as 75% using the continuous NF process compared to 'normal' recirculating cooling-tower operation.
- 5) Total volume of water needed for blowdown could be reduced by as much as 40% using the continuous NF process compared to 'normal' recirculating cooling-tower operation.
- 6) Operational costs for operating a NF system are estimated to be \$0.50 – \$0.90 per 1,000 gallons. It is also estimated that a NF system would use 35% to 47% less energy than an RO system.

3 NANOFILTRATION OF PRODUCED WATER

3.1 Introduction

The primary goal of this pilot study was to evaluate treatment of coal-bed methane (CBM) with nanofiltration (NF) membrane systems. This information can be used to determine whether CBM produced water can be effectively treated for water re-use (potentially by power plants). This treatment program is divided into two segments: pre-treatment (including granulated activated carbon (GAC) and ultrafiltration (UF)) and NF treatment.

It should be noted that the work presented in this report was not only funded by NETL, but also leveraged funds from the State of New Mexico Funded Sandia National Laboratories and Los Alamos National Laboratory Small Business Assistance (NMSBA) program as well as generous in-kind contributions by ConocoPhillips. ConocoPhillips provided produced water, site security, storage tanks, berms to contain potential spills, and safety training for personnel working at the site. Much of the equipment used in the pilot operation was purchased prior to this project and had been used in demonstration pilot studies conducted between 2006 and 2008. Partners will continue to be ConocoPhillips, Biosphere Environmental Science & Technology (BEST), New Mexico State University (NMSU), and the United States Department of Agriculture (USDA).

A Salt Water Disposal (SWD) Facility owned and operated by ConocoPhillips is located close to the CBM site, also in the San Juan Basin just south of the Colorado state line. It is a deep well produced water injection facility used primarily for disposal of brackish produced waters from CBM wells. It is the desire of ConocoPhillips to eventually desalinate produced water from this facility for their operational uses. For this reason, water samples from the facility were collected, analyzed and results compared to those of the raw produced water at the CBM site. This was done to evaluate how applicable the results from the CBM pilot operation would be to the waters at the SWD facility.

3.2 Site Description

The pilot operation used produced water from ConocoPhillips SAN JUAN 32-8 #237A well pad. The site is approximately 500 feet from NM Highway 511 (Figure 16). The closest town is Bloomfield, NM. The pilot equipment is located in a 20-foot long transportainer at the well site (Figures 17 and 18). The pilot equipment was powered by a leased diesel generator.

Natural gas (methane) is produced from the well of interest. In 11 months of 2007, the gas production was 410 billion cubic feet (bcf) with a cumulative production of 8.37 trillion cubic feet (tcf). Water production from this well is approximately 15 to 37 barrels per day (bpd). Natural gas and produced water are pumped from the Fruitland coal formation between 70 feet and 100 feet below the ground surface using a reciprocating piston pump. This mixture is sent to a gas-water separator, with the produced water going to a temporary storage tank. The water is



Figure 16. Map of Four Corners area showing site location.

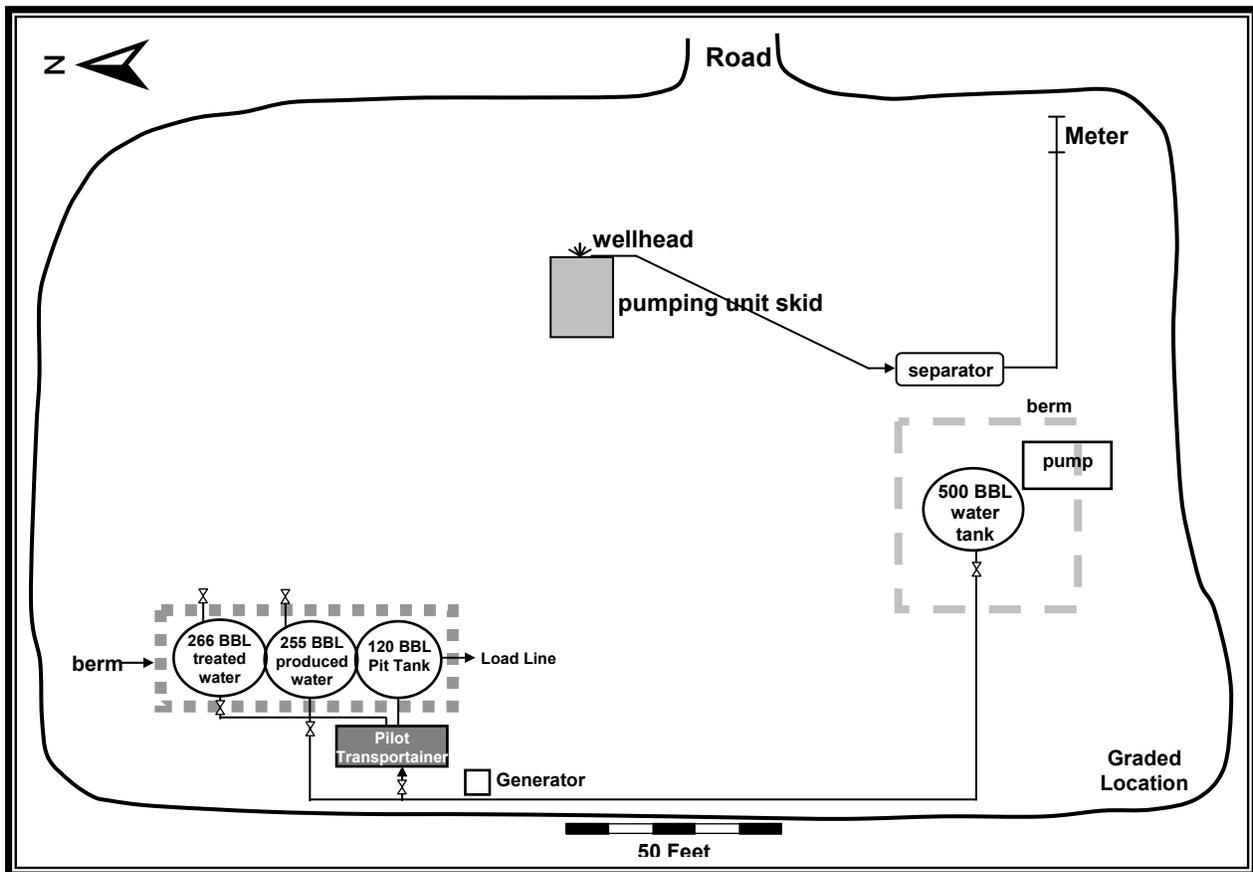


Figure 17. Coal-bed Methane site layout (scale only approximate).



Figure 18: Photograph of transportiner used for pilot study looking to the northwest.

normally transported off-site and reinjected into the formation at the SWD facility described above.

3.3 Methods

3.3.1 Equipment Description

The pilot operation flow diagram is summarized in Figure 19. Two NanoCeram-PACB™ (Part No. PAC2.5-20) granulated activated carbon (GAC) filters were the first step of the pre-treatment line. The cartridges used were 2.5” diameter × 20” long. The literature for these filters claim they are designed for the removal of small particles, bacteria and viruses and are “highly efficient for removing chlorine, bromine, and iodine; and should also prove to be efficient with other contaminants known to be removed by carbon such as TOC’s,”

After passing through the GAC cartridges, the water passed through the UF system, a Homespring™ Water Purifier System (UF211). The maximum ratings for peak flow and continuous flow for this system are 11 and 4.5 gpm, respectively. Typical system efficiency is 95% with > 99.99999%, 99.999%, and 99.95% removal of bacteria, viruses, and cysts, respectively. This system is a “dead end”, as opposed to a cross-flow, system where all the water must flow through the membrane instead of across the membrane where the product is both a permeate and a concentrate (like our NF system). When the UF system was tested without using the GAC filters, pressure began to build up within hours of commencing flow. The system was

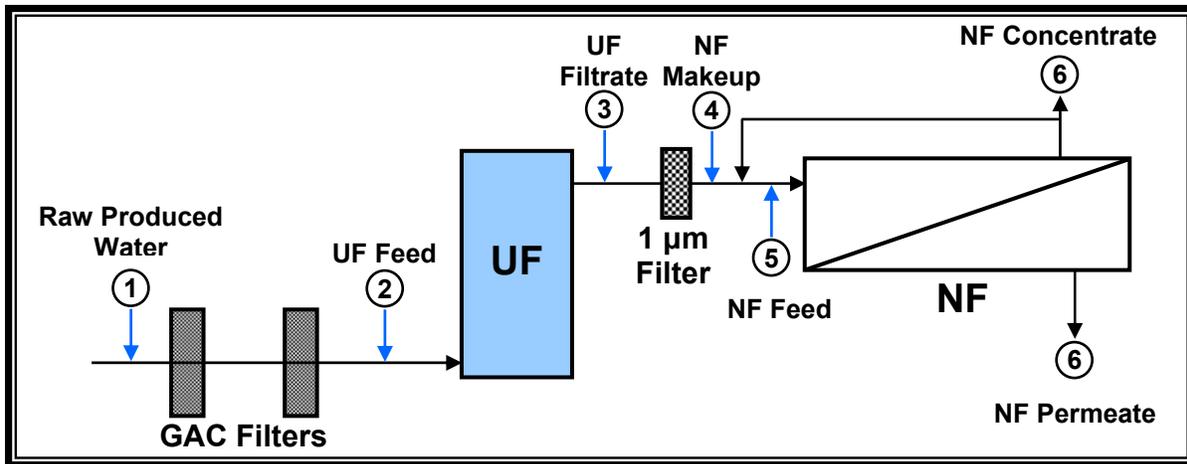


Figure 19. Schematic of the produced water treatment system including numbered sampling points referred to in Figures 21 - 24 that the NF system was actually three NF modules in series as shown in Figure 3. Note that UF filtrate is pumped into a tank. Water from that tank then passes through the 1 μ m cartridge filter and the NF system.

successfully cleaned with a solution adjusted with caustic soda beads to a pH between 10 and 12 non-ionic containing a surfactant/dispersant (Alconox) and sodium hypochlorite (1.5 mg/L Free Chlorine, minimum). However, it would foul quickly again when flow started.

Effluent from the UF system was stored in a tank. Water from the tank was pumped through a 1 μ m cartridge filter and then through the NF cartridges. As with the cooling water tower pilot operation, the NF system was comprised of three Dow Filmtec™ NF90-4040 membranes in series (Figure 3, bottom).

3.3.2 Pilot Design and Predictive Calculations

Dow Filmtec™ desalination software, ROSA™ was used to 1) determine the optimal system flow rates and pressures and 2) predict permeate water chemistry to compare measured membrane performance with that predicted by the manufacturer. The design optimization calculations determined that the NF membranes require approximately 340 psi of pressure and flow rates should be approximately 4.5 gallons per minute. A 30% recovery rate was used in these ROSA™ calculations, based on the membrane design. For the predictive calculations, feed chemistry (Appendix A) and flow parameters (Table 10) from the test run on October 7, 2009 was used in a ROSA™ calculation.

3.3.3 Test Description

The pilot operation with the NF filters was operated on 4 separate dates: October 7, 14, 15, and 21 2009. On October 6, 2009 the system UF system was run without the NF system. On October 21st a different pre-treatment system was tested for a different project. Only data collected on the NF system on October 21st are included. The duration of the tests ranged between 2 and 7 hours. During the tests operation data were collected and recorded 3 – 6 times. Only one sample per day was collected for chemical analysis.

Table 10. Operational data for CBM pilot operation

Parameter/Date Collected	10/06/2009	10/07/2009	10/14/2009	10/15/2009
Approximate hours of Operation	6	3	7	2
Pressure Before GAC Filters (psi)	64 – 98 (85)	86 – 93 (90)	47 – 62 (52)	52 – 69 (61)
Pressure After GAC Filters (psi)	64 – 84 (80)	77 – 92 (85)	40 – 56 (48)	45 – 60 (54)
Δ Pressure - GAC Filters (psi)	0 – 6.5 (2.4)	1 – 11 (5)	2 – 7 (4)	4 – 9 (7)
Pressure Before UF System (psi)		62 – 76 (70)	29 – 40 (37)	39 – 43 (41)
Δ Pressure - UF System (psi)	62 – 82 (76)	3.5 – 3.5 (3.5)	25.5 – 38.3 (33.7)	31.5 – 40.5 (36.2)
Feed Pressure NF #1 (psi)	N/A	340 – 345 (341)	340 – 340 (340)	340 – 340 (340)
Feed Pressure NF #2 (psi)	N/A	340 – 345 (341)	Not Recorded	Not Recorded
Feed Pressure NF #3 (psi)	N/A	335 – 340 (336)	Not Recorded	Not Recorded
Influent Flow Rate (gpm)	2.39 – 3.51 (2.71)	2.92 – 2.38 (3.15)	2.66 – 3.51 (2.93)	2.66 – 3.73 (3.16)
Inflow to UF System (gpm)	Not Recorded	2.56 – 2.81 (2.69)	2.29 – 2.60 (2.55)	2.29 – 2.77 (2.58)
UF-Filtrate Flow Rate (gpm)	2.13 – 2.44 (2.31)	2.72 – 3.00 (2.86)	2.40 – 2.76 (2.55)	2.42 – 2.95 (2.74)
NF Make up Flow Rate (gpm)	N/A	2.9 – 2.9 (2.9)	Not Recorded	Not Recorded
NF Permeate Flow Rate #1 (gpm)	1.99 – 2.27 (2.15)	0.64 – 0.68 (0.66)	0.51 – 0.52 (0.52)	0.60, 0.60
NF Permeate Flow Rate #2 (gpm)	N/A	0.42 – 0.45 (0.44)	0.38 – 0.43 (0.41)	0.42, 0.42
NF Permeate Flow Rate #3 (gpm)	N/A	0.30 – 0.30 (0.30)	0.28 – 0.38 (0.35)	0.28, 0.28
Total NF Permeate Flow Rate (gpm)	N/A	1.36 – 1.43 (1.40)	1.20 – 1.33 (1.28)	1.30, 1.30
NF Concentrate Flow (gpm)	N/A	1.4 – 1.4 (1.4)	Not Recorded (Estimated to be constant at 1.4)	Not Recorded (Estimated to be constant at 1.4)
NF Recycle Flow (gpm)	N/A	1.60 – 1.75 (1.71)	Not Recorded, (Estimated to be constant at 1.7)	Not Recorded (Estimated to be constant at 1.7)
NF System Recovery (Permeate/Inflow)	N/A	0.29 – 0.32 (0.30)	Not Recorded	Not Recorded

In addition to evaluating NF system, source water samples were collected and analyzed to evaluate the variability in water chemistry. Six samples of produced water were collected and analyzed on August 10, October 6, 14, 15, 16, and 21st. Three separate samples were collected and analyzed from the SWD facility on October 7, 15, and 22, 2009. The purpose of collecting these samples is to determine if the water chemistry is significantly different from the produced water collected at the CBM site and to evaluate the variation in chemistry over time. As a range of waters are disposed of at the SWD facility, it is expected that the chemistry will be more variable than at the CBM site.

3.3.4 Water Analyses

Water analyses were conducted in the field as well as water samples collected for laboratory analyses. Laboratory analyses were conducted by Envirotech Analytical Laboratory located in Farmington, NM. These analyses include major cations and anions, pH, specific conductivity, total dissolved solids (TDS), silica, boron, and barium. Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) were also analyzed. For samples of raw produced water, UF filtrate and NF permeate collected on October 21, 2009 a more complete analyses was conducted including volatiles, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), additional metals and cyanide, mercury, radium-226, radium-228, and uranium-238.

Field measurements include specific conductivity, turbidity, pH and iron. A Hach Sension 5 meter was used to measure specific conductivity and a Hach 2100P turbidimeter was used to measure turbidity. pH was measured with a pH meter (Hach Sension 1). Total iron was measured using the Hach DR 2400 (Method 8008) (FerroVer).

3.4 Results

3.4.1 Pressure and Flow Rates

Operational data for the tests are presented in Table 10. Prior to use of the GAC filters that produced the best results, the pressure differential for the UF system increased from 62 to 82 psi in a matter of 2 hours. This large pressure build up indicated that an improved pre-treatment system before the UF system was needed in order to run the UF successfully. With the NanoCeram-PACB™ GAC filters, there an initial pressure differential increase in the UF system from 25.5 to 38 psi was observed over approximately 2.5 hours. After this initial pressure build-up the pressure differential stabilized and even decreased to 32 psi, indicating that these GAC filters were a sufficient pre-treatment method for our pilot operation. In order the run the pilot operation successfully, the GAC filters had to be replaced every 2 to 6 hours. Therefore, these filters are not a viable pre-treatment option for long-term or larger-scale pilot operations.

Inflow pressure into the NF system remained very constant at 340 psi, indicating that the NF system was not fouling over the time scale of the tests. Much longer-term tests would need to be conducted in order to determine how long it would take the NF modules to foul.

3.4.2 Source Water Chemistry

Results of the analyses on the raw produced water samples are summarized in Appendix A and Figure 20. It can be seen that the produced water is dominated by bicarbonate, chloride and sodium. Magnesium, potassium, barium are present at concentrations above 10 mg/L. Nitrate, phosphate, sulfate, calcium, boron and silica are also present at the mg/L level. Less than 1 mg/L levels of fluoride, iron, chromium, nickel, selenium, silver, and cyanide were also detected in the water. Fluoride, iron, chromium, nickel, selenium, silver, and cyanide are not discussed further in this report, as their initial concentrations are so low. Considerable variability in produced water chemistry was observed. Bicarbonate concentrations ranged from 6,480 to 8,520 mg/L, potassium ranged from 33.10 to 274 mg/L, phosphate ranged from 0.42 to 21.5 mg/L, and

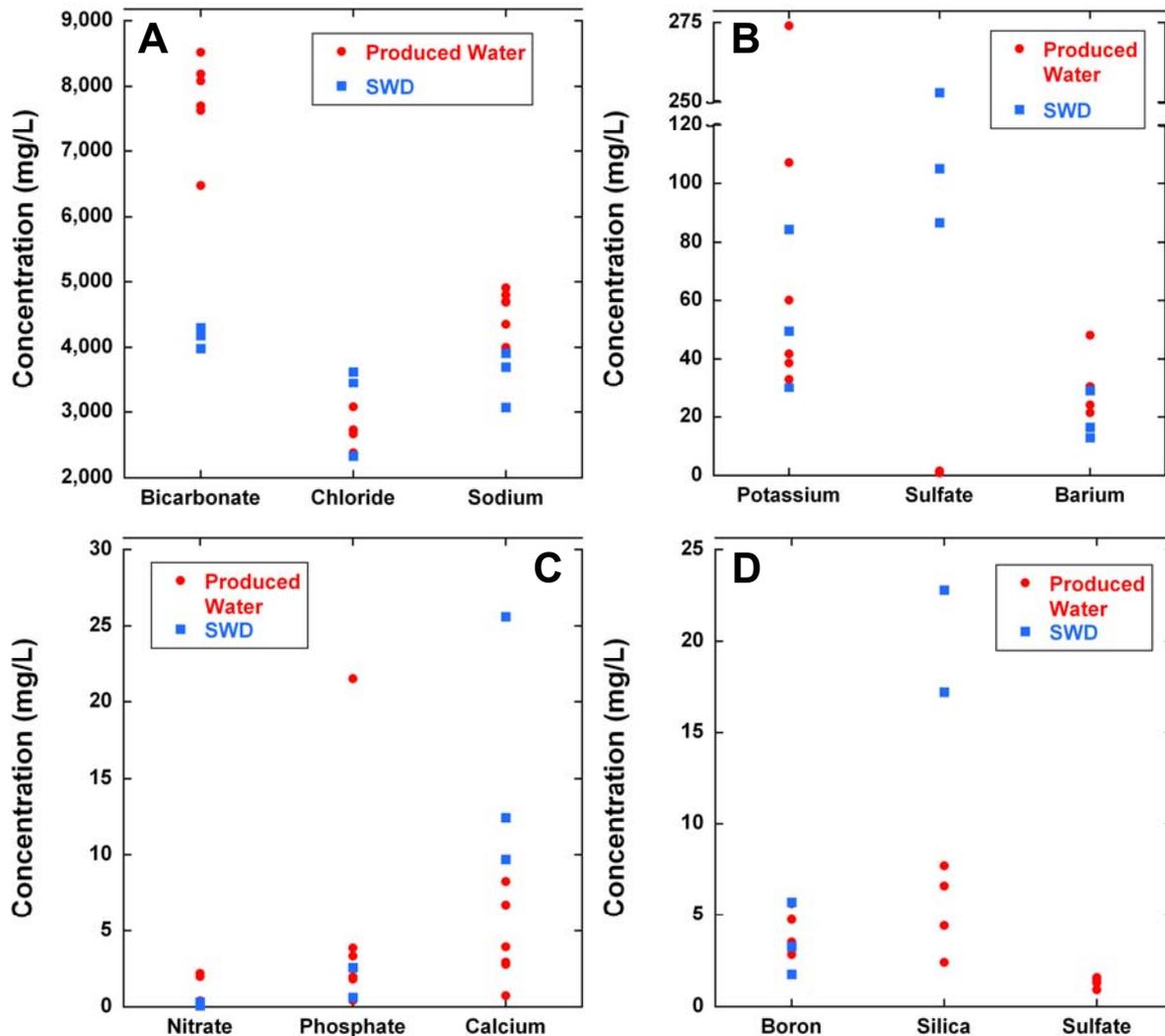


Figure 20. Results of water analyses of produced water from ConocoPhillips CBM well and water samples from the SWD facility. Note that sulfate is plotted twice (B and D) and not shown for the SWD in D.

calcium ranged from 0.74 to 8.26 mg/L. The other constituents showed less variability. The more complete analyses for the sample on collected October 21, 2009 detected the following volatiles: benzene, toluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, acetone, isopropylbenze, 4-isopropylbenze, n-propylbenzene, sec-butylbenzen and xylenes (Appendix A). Radium-226, Radium-228, and phenolics were detected. Chromium, nickel, selenium, silver and cyanide were detected at very low levels.

Parameters concentrations for samples collected from the SWD were in the same range as those measured for the produced water, with some exceptions (Figure 20). Bicarbonate concentrations were higher in the produced water than the SWD water. Sodium concentrations were also slightly higher. Sulfate concentrations were higher in the SWD water, ranging from 86.7 to 253 mg/L as opposed to 0.921 to 1.58 mg/L in the produced water. Calcium and silica

concentrations were also higher in the SWD. As only three samples over a short period of time were collected from the SWD, it is more difficult to evaluate variability. The variability in the analyzed chemistry for these SWD samples does not seem as large as that for the produced water.

3.4.3 Filtrate Water Chemistry

Results of the chemical analyses on water samples collected during the pilot operation are summarized in Appendix A. The GAC filters were most effective at removing the particulate matter responsible for turbidity in the water. This is seen by an almost two order of magnitude drop in turbidity measurements pre- and post- GAC filters (Figure 21A). The NF system also decreased the turbidity, but by less than 1 order of magnitude. The pre-treatment (UF and GAC) did not appear to have a significant impact total dissolved solids (TDS) or specific conductivity (Figure 21B and C) or dissolved constituents (Figures 22 and 23).

Examination of bulk parameters demonstrate that the NF system could decrease specific conductivity from approximately 20,000 – 29,000 $\mu\text{mhos/cm}$ to less than 400 – 600 $\mu\text{mhos/cm}$, on average a 98% decrease (Figure 21B). Likewise, TDS decreased from greater than 12,000 – 16,000 mg/L to less than 230 - 440 mg/L, also on average a 98% decrease (Figure 21C).

In most cases dissolved constituent concentrations decreased by 1 – 2 orders of magnitude (Figures 22 and 23). On average, this translates to a 93.7% removal of trivalent ion phosphate, 87.9%, 95.3%, and 97.6%, and almost 100% removal of divalent ions calcium, magnesium, sulfate, and barium respectively, and 96.0%, 96.2%, 97.7%, and 98.4% removal of monovalent ions potassium, chloride, sodium, and bicarbonate, respectively. A consistent pattern between valence of the ions and the decrease in concentration by the NF system is not observed; nor does the initial concentration of the ion appear to impact the fraction removed.

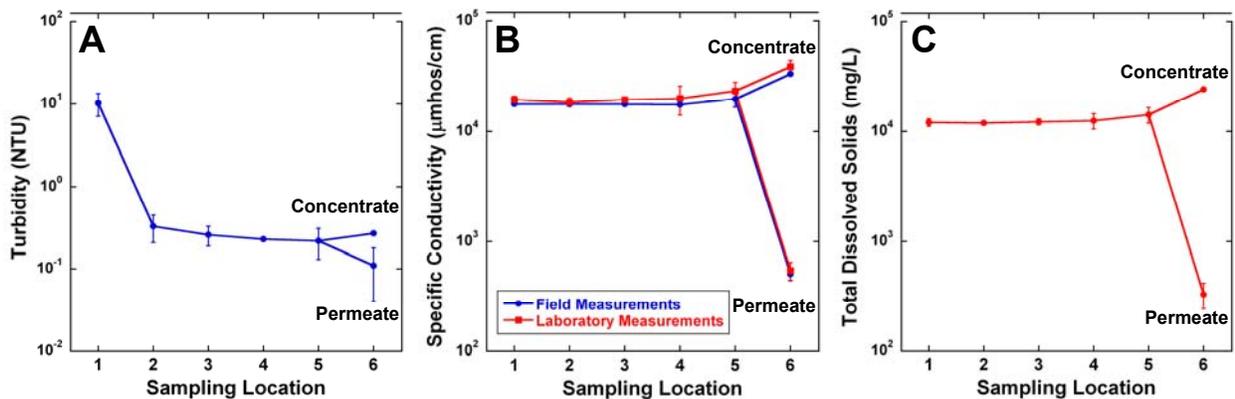


Figure 21. Average measured turbidity (A), specific conductivity (B), and total dissolved solids (TDS) (C). Error bars indicate ± 1 standard deviation of the measurements. Refer to Appendix A for actual values. Refer to Figure 19 for sampling locations: 1 = Raw Produced Water, 2 = GAC effluent, 3 = UF effluent, 4 = NF make-up water, 5 = NF feed water, 6 = NF concentrate and permeate.

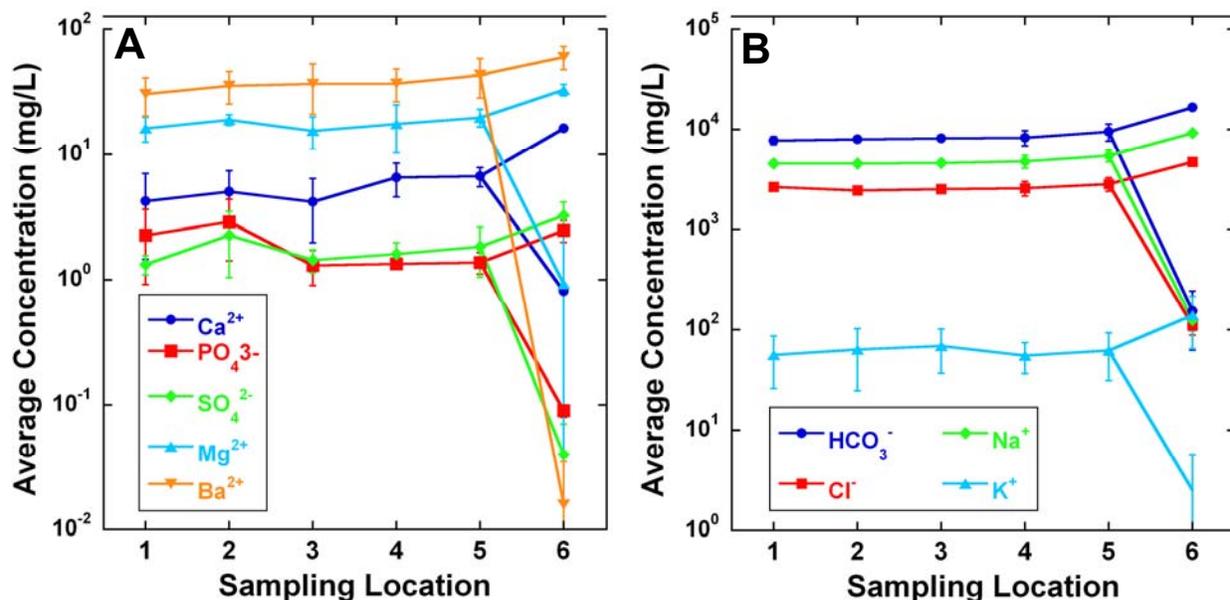


Figure 22. Average measured concentrations of divalent ions (A) and monovalent ions (B). Error bars indicate ± 1 standard deviation of the measurements. Refer to Appendix A for actual values. Refer to Figure 19 for sampling locations: 1 = Raw Produced Water, 2 = GAC effluent, 3 = UF effluent, 4 = NF make-up water, 5 = NF feed water, 6 = NF concentrate and permeate.

The NF system has mixed results at removing non-charged species silica and boron (Figure 23). Silica decreased from 1.9 – 4.8 mg/L to less than the detection limit of 0.1 mg/L. A dramatic drop was not observed for boron, where the concentrations decreased, but less than 1 order of magnitude (29.9 – 56.4% removal).

Interestingly the NF also caused the pH to drop from an average 8.1 to 7.6 (Figure 24). The most dramatic drop was observed in a field measurement taken on October 7, 2009 where the pH decreased from 8.2 to 6.3. This pH drop is most likely due to the removal of HCO_3^- without the removal of CO_2 , which will drive the following equation to the right, thus decreasing the pH:



The more complete analysis on water samples collected on October 21, 2009 also showed that the NF was effective at decreasing concentrations of other compounds. Benzene, 1,3,5-trimethylbenzene, isopropylbenzene, 4-isopropylbenzene, n-propylbenzene, sec-butylbenzene and xylenes, arsenic and copper (which were detected in the UF filtrate), nickel and selenium concentrations were all reduced to levels below their practical quantitation limits (PQL). Toluene, 1,2,4-trimethylbenzene, acetone, total recoverable phenolics, radium, and cyanide concentrations were lower in the NF permeate than the raw produced water. In general, the concentrations of the volatiles decreased after UF treatment and again after NF treatment. The other compounds saw most of the decrease from the NF system.

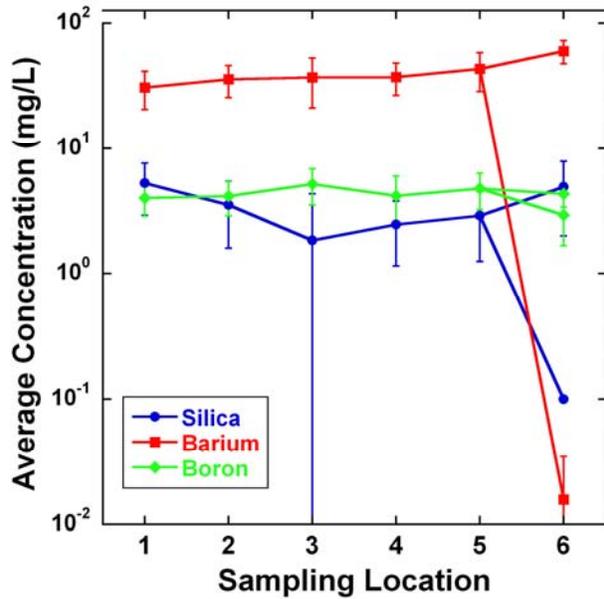


Figure 23. Average measured concentrations of uncharged species. Error bars indicate ± 1 standard deviation of the measurements. Refer to Appendix A for actual values. Refer to Figure 19 for sampling locations: 1 = Raw Produced Water, 2 = GAC effluent, 3 = UF effluent, 4 = NF make-up water, 5 = NF feed water, 6 = NF concentrate and permeate.

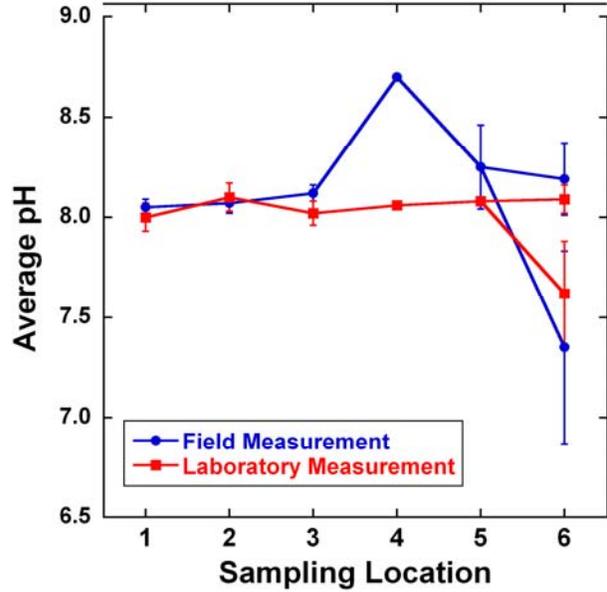


Figure 24. Average pH. Error bars indicate ± 1 standard deviation of the measurements. Refer to Appendix A for actual values. Refer to Figure 19 for sampling locations: 1 = Raw Produced Water, 2 = GAC effluent, 3 = UF effluent, 4 = NF make-up water, 5 = NF feed water, 6 = NF concentrate and permeate.

3.4.4 Comparison to ROSA™ Predictions

Comparison of ROSA™ predictions with collected data are presented in Table 11. The measured percent removal for each constituent was higher than predicted. There was a greater than 10% or greater difference in percent removed for potassium, sodium, bicarbonate, and chloride concentrations where the measured permeate concentration was 1.69, 128, 102, and 140 mg/L as opposed to the predicted 15.6, 894, 1,638, and 429 mg/L, respectively.

3.5 Summary and Conclusions

A small-scale pilot study was run to test how effective NF will be at treating CBM produced water. The goal of this pilot study is to provide information to assist in the determination of whether CBM produced water can be effectively treated for water re-use (potentially by power plants). Scaling was not observed in the NF system. The pilot operation would need to be run for a much longer time to evaluate scaling. However, both carbonate and silica scaling are not expected as both calcium and silica concentrations are well below their respective solubility limits (Figure 15). Other CBM source water could have different chemistry and scaling potential would have to be evaluated.

Table 11. Comparison of predicted and actual permeate quality for CBM pilot operation run on October 7, 2009

Parameter (units)	Measured Concentrations and Percent Removed			Predicted	
	NF Feed	Average NF Permeate	Percent Removed	NF Permeate Conc.	Percent Removed
K ⁺ (mg/L)	96.8	1.69	98.3%	15.57	83.9%
Na ⁺ (mg/L)	5,650	128	97.7%	894.04	84.2%
Mg ²⁺ (mg/L)	17.2	0.152	99.1%	0.94	94.5%
Ca ²⁺ (mg/L)	6.57	<0.01	>99.8%	0.35	94.7%
HCO ₃ ⁻ (mg/L)	10,300	102	99.0%	1637.67	84.1%
NO ₃ ⁻ (mg/L)	0.055	---	---	0.03	45.5%
Cl ⁻ (mg/L)	2,880	140	95.1%	429.36	85.1%
F ⁻ (mg/L)	0.28	0.01	96.4%	0.05	82.1%
SO ₄ ²⁻ (mg/L)	2.74	0.03	98.9%	0.06	97.8%
SiO ₂ (mg/L)	4.8	<0.1	>97.9%	0.41	91.5%
Ba	59.3	<0.001	100%	3.18	94.6%
pH (---)	8.1	6.48	N/A	7.83	N/A

Note: NH₄⁺ and Si²⁺ concentrations assumed to be 0 for ROSA™ calculations.
Measurement error in permeate NO₃⁻ concentration, thus results not reported.

The NF system was quite effective at decreasing charged dissolved constituents concentrations 1 – 2 orders of magnitude and in the case for barium over 3 orders of magnitude. The NF system worked well for both mono- and multivalent ions. Removal efficiencies ranged from 87.9% (phosphate) to almost 100% removal. Phosphate was the only ion that had less than 95% removal. Concentrations that started in the 1,000's mg/L range (bicarbonate, sodium, and chloride) generally dropped to the 100's mg/L range, and sometimes below 100 mg/L.

The NF system has mixed results in removing uncharged species. While source water silica concentrations were not high (less than 10 mg/L), the measurements of silica concentrations in the permeate were less than the analytical detection limit of 0.01 mg/L. Boron concentrations decreased, but only by 29.9 – 56.4%.

Pre-treatment is a key component for the effective use of a NF system in the treatment of produced waters. The pre-treatment system for the water used in this pilot operation had to effectively remove parafilms, filming agents, iron flocs, coal fines and successfully control biological growth. Because of these components to the water, the UF system used in this pilot operation would build up in a manner of hours. Use of the GAC filters allowed the pilot operation system to run for a day, but was only a short term solution. For future pilot studies, an investment in a pre-treatment system will be needed.

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APPENDIX A: WATER ANALYSIS RESULTS

Appendix A Water Analysis Results

Raw Produced Water

Parameter↓/Date Collected→	08/10/2009	10/06/2009	10/14/2009	10/15/2009	10/16/2009	10/21/2009
pH	8.03	8.12	7.99	8.00	7.94	7.93
pH [§]	---	---	8.02	8.04	---	7.96
Specific Conductivity (µmhos/cm)	19,600	18,300	17,000	20,700	20,200	20,800
Specific Conductivity [§] (µmhos/cm)	---	---	17,763	17,680	---	17,600
Turbidity [§] (NTU)	---	---	12.83	9.45	---	6.07
TDS (mg/L)	12,730	11,520	10,370	12,340	12,870	12,580
SAR	211.5	235	214	204	227	287
Bicarbonate as CaCO ₃ (mg/L)	7,630	7,700	6,480	8,080	8,520	8,190
Carbonate as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hydroxide as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nitrate (mg/L)	2.20	0.192	0.400	0.273	0.248	2.00
Nitrite (mg/L)	0.018	<0.01	0.013	0.024	0.042	---
Chloride (mg/L)	3,080	2,370	2,380	2,670	2,720	2,730
Fluoride (mg/L)	2.06	0.400	0.770	0.655	0.589	0.417
Phosphate (mg/L)	21.5	3.86	3.34	1.98	1.82	---
Sulfate (mg/L)	1.50	1.58	0.921	1.30	1.35	1.34
Iron (mg/L)	1.25	<0.01	0.187	0.328	0.063	0.009
Calcium (mg/L)	8.26	2.79	0.739	6.72	2.93	3.95
Magnesium (mg/L)	17.6	14.1	15.7	20.3	19.7	10.5
Potassium (mg/L)	274	107	33.10	38.6	41.8	60.1
Sodium (mg/L)	4,690	4,350	4,000	4,700	4,910	4,800
Boron (mg/L)	---	5.64	3.38	3.51	2.82	4.74
Barium (mg/L)	---	48.1	30.1	30.6	24.1	21.4
Silica (mg/L)	---	7.7	4.4	2.4	6.6	---
TOC (mg/L)	35	20	12	11	9.1	---
DOC (mg/L)	---	26	16	10	8.9	---
COD (mg/L)	224	---	---	---	---	---
BOD (mg/L)	10.1	---	---	---	---	---
[§] - Field Measurement TOC – Total Organic Carbon DOC – Dissolved Organic Carbon COD – Chemical Oxygen Demand BOD = Biological Oxygen Demand						
SAR – Sodium Adsorption Ratio = $\frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$						

Salt Water Disposal Facility

Parameter/Date Collected	10/07/2009	10/15/2009	10/22/2009
pH	8.03	8.04	7.83
Specific Conductivity (µmhos/cm)	15,200	15,800	14,000
TDS (mg/L)	10,380	9,870	8,130
SAR	150	134	137
Bicarbonate as CaCO ₃ (mg/L)	4,300	4,180	3,980
Carbonate as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Hydroxide as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Nitrate (mg/L)	0.243	0.081	0.334
Nitrite (mg/L)	0.014	1.80	---
Chloride (mg/L)	3,620	3,450	2,330
Fluoride (mg/L)	2.19	0.309	<0.01
Phosphate (mg/L)	2.57	0.633	---
Sulfate (mg/L)	105	86.7	253.00
Iron (mg/L)	0.068	0.425	0.405
Calcium (mg/L)	25.6	12.4	9.7
Magnesium (mg/L)	15.7	27.4	17.3
Potassium (mg/L)	84.4	49.5	30.1
Sodium (mg/L)	3,910	3,700	3,070
Boron (mg/L)	5.72	1.75	3.28
Barium (mg/L)	29.0	16.5	12.9
Silica (mg/L)	22.8	17.2	---
TOC (mg/L)	110	45	---
DOC (mg/L)	76	52	---
^s - Field Measurement SAR – Sodium Adsorption Ratio = $\frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$ TOC – Total Organic Carbon DOC – Dissolved Organic Carbon			

GAC Effluent

Parameter/Date Collected	10/06/2009	10/14/2009	10/15/2009
pH	8.18	8.04	8.07
pH [§]	---	8.02	8.08
Specific Conductivity (µmhos/cm)	18,600	20,000	16,700
Specific Conductivity [§] (µmhos/cm)	---	17,750	17,730
Turbidity [§] (NTU)	---	0.21	0.26
TDS (mg/L)	11,890	11,810	12,130
SAR	224	205	196
Bicarbonate as CaCO ₃ (mg/L)	7,820	7,960	8,160
Carbonate as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Hydroxide as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Nitrate (mg/L)	3.50	0.074	0.453
Nitrite (mg/L)	<0.01	1.29	0.031
Chloride (mg/L)	2,480	2,400	2,500
Fluoride (mg/L)	2.06	1.15	0.395
Phosphate (mg/L)	3.22	4.20	1.29
Sulfate (mg/L)	2.0	1.21	3.64
Iron (mg/L)	<0.01	0.045	0.234
Calcium (mg/L)	2.62	5.25	7.29
Magnesium (mg/L)	17.2	19.1	20.9
Potassium (mg/L)	108	40.0	42.1
Sodium (mg/L)	4,520	4,510	4,600
Boron (mg/L)	5.60	3.27	3.57
Barium (mg/L)	47.3	28.5	31.3
Silica (mg/L)	4.8	4.5	1.3
TOC (mg/L)	18	16	11
DOC (mg/L)	22	12	11
[§] - Field Measurement TOC – Total Organic Carbon DOC – Dissolved Organic Carbon			
SAR – Sodium Adsorption Ratio = $\frac{[Na^+]}{\sqrt{([Ca^{2+}] + [Mg^{2+}]) / 2}}$			

Ultrafiltration Effluent

Parameter/Date Collected	10/06/2009	10/16/2009	10/21/2009
pH	8.09	7.98	7.98
pH [§]	---	8.14	7.90
Specific Conductivity (µmhos/cm)	18,500	19,200	20,300
Specific Conductivity [§] (µmhos/cm)	---	17,720	17,650
Turbidity [§] (NTU)	---	0.25	0.25
TDS (mg/L)	11,400	12,890	12,380
SAR	216	218	282
Bicarbonate as CaCO ₃ (mg/L)	7,730	8,600	8,200
Carbonate as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Hydroxide as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Nitrate (mg/L)	0.064	0.145	1.90
Nitrite (mg/L)	<0.01	0.047	---
Chloride (mg/L)	2,280	2,700	2,600
Fluoride (mg/L)	0.344	0.563	0.336
Phosphate (mg/L)	1.60	1.02	---
Sulfate (mg/L)	1.68	1.10	1.53
Iron (mg/L)	<0.01	0.035	0.011
Calcium (mg/L)	2.09	6.49	4.00
Magnesium (mg/L)	17.0	19.3	10.5
Potassium (mg/L)	104	41.6	61.0
Sodium (mg/L)	4,300	4,900	4,720
Boron (mg/L)	6.50	3.33	5.75
Barium (mg/L)	54.5	23.5	32.9
Silica (mg/L)	3.6	<0.1	---
TOC (mg/L)	17	9.2	---
DOC (mg/L)	16	12	---
[§] - Field Measurement TOC – Total Organic Carbon DOC – Dissolved Organic Carbon			
SAR – Sodium Adsorption Ratio = $\frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$			

Nanofiltration Make-Up Water

Parameter/Date Collected	10/07/2009	10/14/2009	10/15/2009
pH	8.07	8.03	8.07
pH [§]	8.70	---	---
Specific Conductivity (µmhos/cm)	16,500	26,800	16,600
Specific Conductivity [§] (µmhos/cm)	17,575	---	---
Turbidity [§] (NTU)	0.23	---	---
TDS (mg/L)	10,860	14,730	11,910
SAR	260	223	202
Bicarbonate as CaCO ₃ (mg/L)	7,060	9,880	7,880
Carbonate as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Hydroxide as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Nitrate (mg/L)	0.033	0.091	2.30
Nitrite (mg/L)	0.011	0.013	0.033
Chloride (mg/L)	2,200	3,040	2,520
Fluoride (mg/L)	0.20	0.236	0.347
Phosphate (mg/L)	1.51	1.27	1.28
Sulfate (mg/L)	1.93	1.68	1.21
Iron (mg/L)	0.146	0.068	0.236
Calcium (mg/L)	4.88	8.73	6.04
Magnesium (mg/L)	9.53	23.9	19.6
Potassium (mg/L)	75.6	50.7	39.1
Sodium (mg/L)	4,280	5,610	4,540
Boron (mg/L)	6.27	2.81	3.46
Barium (mg/L)	49.7	31.7	30.5
Silica (mg/L)	2.2	3.9	1.3
TOC (mg/L)	14	22	11
DOC (mg/L)	12	25	11
[§] - Field Measurement TOC – Total Organic Carbon DOC – Dissolved Organic Carbon			
SAR – Sodium Adsorption Ratio = $\frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$			

Nanofiltration Feed water

Parameter/Date Collected	10/07/2009	10/14/2009	10/15/2009
pH	8.10	8.07	8.06
pH [§]	8.40	8.10	---
Specific Conductivity (µmhos/cm)	21,600	20,000	28,700
Specific Conductivity [§] (µmhos/cm)	22,000	17,600	---
Turbidity [§] (NTU)	0.15	0.28	---
TDS (mg/L)	14,910	11,550	16,000
SAR	263	210	246
Bicarbonate as CaCO ₃ (mg/L)	10,300	7,360	10,800
Carbonate as CaCO ₃ (mg/L)	< 0.1	< 0.1	< 0.1
Hydroxide as CaCO ₃ (mg/L)	< 0.1	< 0.1	< 0.1
Nitrate (mg/L)	0.055	0.059	0.177
Nitrite (mg/L)	0.014	0.012	0.039
Chloride (mg/L)	2,880	2,380	3,260
Fluoride (mg/L)	0.284	0.353	0.459
Phosphate (mg/L)	1.56	1.07	1.51
Sulfate (mg/L)	2.74	1.27	1.52
Iron (mg/L)	<0.01	0.041	0.016
Calcium (mg/L)	6.57	5.58	7.90
Magnesium (mg/L)	17.2	19.0	23.4
Potassium (mg/L)	96.8	37.8	51.6
Sodium (mg/L)	5,650	4,640	6,100
Boron (mg/L)	6.52	3.60	4.22
Barium (mg/L)	59.3	29.9	40.9
Silica (mg/L)	4.8	2.0	1.9
TOC (mg/L)	15	15	15
DOC (mg/L)	19	13	13
[§] - Field Measurement TOC – Total Organic Carbon DOC – Dissolved Organic Carbon			
SAR – Sodium Adsorption Ratio = $\frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$			

Nanofiltration Concentrate

Parameter/Date Collected	10/07/2009	10/14/2009	10/15/2009
pH	8.15	8.10	8.02
pH [§]	8.37	7.77	7.45
Specific Conductivity (µmhos/cm)	32,700	42,800	41,500
Specific Conductivity [§] (µmhos/cm)	33,450	33,767	33,000
Turbidity [§] (NTU)	0.26	0.28	0.27
TDS (mg/L)	24,140	23,630	24,800
SAR	308	286	954
Bicarbonate as CaCO ₃ (mg/L)	17,000	16,300	16,600
Carbonate as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Hydroxide as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1
Nitrate (mg/L)	0.100	0.478	1.61
Nitrite (mg/L)	0.024	0.020	0.065
Chloride (mg/L)	4,460	4,590	5,130
Fluoride (mg/L)	0.335	0.757	0.092
Phosphate (mg/L)	3.03	2.09	2.33
Sulfate (mg/L)	4.27	2.57	2.95
Iron (mg/L)	<0.01	0.112	0.050
Calcium (mg/L)	15.9	16.8	1.61
Magnesium (mg/L)	30.7	35.5	3.65
Potassium (mg/L)	192	86.3	8.49
Sodium (mg/L)	9,110	9,000	9,570
Boron (mg/L)	5.27	3.38	4.38
Barium (mg/L)	72.8	47.7	60.0
Silica (mg/L)	3.0	8.3	3.5
TOC (mg/L)	710	21	*
DOC (mg/L)	700	23	23
[§] - Field Measurement TOC – Total Organic Carbon DOC – Dissolved Organic Carbon * - Reported results: 11, 1100 1300			
SAR – Sodium Adsorption Ratio = $\frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$			

Nanofiltration Permeate

Parameter/Date Collected	10/07/2009	10/14/2009	10/15/2009	10/21/2009
pH	6.48	6.24	6.09	5.86
pH [§]	6.83	7.77	7.45	7.75
Specific Conductivity (µmhos/cm)	590	622	398	574
Specific Conductivity [§] (µmhos/cm)	573	497	400	451
Turbidity [§] (NTU)	0.17	0.03	0.06	0.18
TDS (mg/L)	330	440	230	320
SAR	70.4	14.5	NA	121
Bicarbonate as CaCO ₃ (mg/L)	102	280	78.4	150
Carbonate as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1	<0.1
Hydroxide as CaCO ₃ (mg/L)	<0.1	<0.1	<0.1	<0.1
Nitrate (mg/L)	0.400	0.004	0.400	0.100
Nitrite (mg/L)	<0.01	0.002	0.100	---
Chloride (mg/L)	140	100	91.8	106
Fluoride (mg/L)	0.009	0.021	0.018	0.022
Phosphate (mg/L)	0.100	0.073	0.088	---
Sulfate (mg/L)	0.030	0.038	0.023	0.083
Iron (mg/L)	<0.01	<0.01	0.001	<0.01
Calcium (mg/L)	<0.01	3.20	<0.01	<0.01
Magnesium (mg/L)	0.152	3.40	<0.01	0.049
Potassium (mg/L)	1.69	7.25	0.583	0.516
Sodium (mg/L)	128	156	89.0	125
Boron (mg/L)	4.57	2.04	1.84	3.27
Barium (mg/L)	<0.001	0.020	<0.001	0.041
Silica (mg/L)	<0.1	<0.1	<0.1	---
TOC (mg/L)	6.3	2.7	1.8	---
DOC (mg/L)	5.5	5.0	3.5	---
[§] - Field Measurement TOC – Total Organic Carbon DOC – Dissolved Organic Carbon SAR – Sodium Adsorption Ratio = $\frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$				

Volatiles, Sample Collected October 21, 2009

Analysis	Units	Raw Produced Water		UF Effluent		NF Permeate	
		Result	PQL	Result	PQL	Result	PQL
Benzene	µg/L	1.6	1.0	1.6	1.0	ND	1.0
Toluene	µg/L	6.6	1.0	5.2	1.0	1.8	1.0
Ethylbenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
Methyl tert-butyl ether (MTBE)	µg/L	ND	1.0	ND	1.0	ND	1.0
1,2,4-Trimethylbenzene	µg/L	290	5.0	55	1.0	3.2	1.0
1,3,5-Trimethylbenzene	µg/L	230	5.0	98	1.0	ND	1.0
1,2-Dichloroethane (EDC)	µg/L	ND	1.0	ND	1.0	ND	1.0
1,2-Dibromoethane (EDB)	µg/L	ND	1.0	ND	1.0	ND	1.0
Naphthalene	µg/L	ND	2.0	ND	2.0	ND	2.0
1-Methylnaphthalene	µg/L	ND	4.0	ND	4.0	ND	4.0
2-Methylnaphthalene	µg/L	ND	4.0	ND	4.0	ND	4.0
Acetone	µg/L	28	10	22	10	14	10
Bromobenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
Bromochloromethane	µg/L	ND	1.0	ND	1.0	ND	1.0
Bromodichloromethane	µg/L	ND	1.0	ND	1.0	ND	1.0
Bromoform	µg/L	ND	1.0	ND	1.0	ND	1.0
Bromomethane	µg/L	ND	1.0	ND	1.0	ND	1.0
2-Butanone	µg/L	ND	10	ND	10	ND	10
Carbon disulfide	µg/L	ND	10	ND	10	ND	10
Carbon Tetrachloride	µg/L	ND	1.0	ND	1.0	ND	1.0
Chlorobenzene	µg/L	ND	1.0	ND	1.0	3.0	1.0
Chloroethane	µg/L	ND	2.0	ND	2.0	ND	2.0
Chloroform	µg/L	ND	1.0	ND	1.0	ND	1.0
Chloromethane	µg/L	ND	1.0	ND	1.0	ND	1.0
2-Chlorotoluene	µg/L	ND	1.0	ND	1.0	ND	1.0
4-Chlorotoluene	µg/L	ND	1.0	ND	1.0	ND	1.0
cis-1,2-DCE	µg/L	ND	1.0	ND	1.0	ND	1.0
cis-1,3-Dichloropropene	µg/L	ND	1.0	ND	1.0	ND	1.0
1,2-Dibromo-3-chloropropane	µg/L	ND	2.0	ND	2.0	ND	2.0
Dibromochloromethane	µg/L	ND	1.0	ND	1.0	ND	1.0
Dibromomethane	µg/L	ND	1.0	ND	1.0	ND	1.0
1,2-Dichlorobenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
1,3-Dichlorobenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
1,4-Dichlorobenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
Dichlorodifluoromethane	µg/L	ND	1.0	ND	1.0	ND	1.0
1,1-Dichloroethane	µg/L	ND	1.0	ND	1.0	ND	1.0
1,1-Dichloroethene	µg/L	ND	1.0	ND	1.0	ND	1.0
1,2-Dichloropropane	µg/L	ND	1.0	ND	1.0	ND	1.0
1,3-Dichloropropane	µg/L	ND	1.0	ND	1.0	ND	1.0

PQL = Practical Quantitation Limits

Volatiles, Sample Collected October 21, 2009 (continued)

Analysis	Units	Raw Produced Water		UF Effluent		NF Permeate	
		Result	PQL	Result	PQL	Result	PQL
2,2-Dichloropropane	µg/L	ND	2.0	ND	2.0	ND	2.0
1,1-Dichloropropene	µg/L	ND	1.0	ND	1.0	ND	1.0
Hexachlorobutadiene	µg/L	ND	1.0	ND	1.0	ND	1.0
2-Hexanone	µg/L	ND	10	ND	10	ND	10
Isopropylbenzene	µg/L	16	1.0	8.8	1.0	ND	1.0
4-Isopropyltoluene	µg/L	3.9	1.0	1.6	1.0	ND	1.0
4-Methyl-2-pentanone	µg/L	ND	10	ND	10	ND	10
Methylene Chloride	µg/L	ND	3.0	ND	3.0	ND	3.0
n-Butylbenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
n-Propylbenzene	µg/L	15	1.0	11	1.0	ND	1.0
sec-Butylbenzene	µg/L	4.1	1.0	1.9	1.0	ND	1.0
Styrene	µg/L	ND	1.0	ND	1.0	ND	1.0
tert-Butylbenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
1,1,1,2-Tetrachloroethane	µg/L	ND	1.0	ND	1.0	ND	1.0
1,1,2,2- Tetrachloroethane	µg/L	ND	2.0	ND	2.0	ND	2.0
Tetraohloroethene (PCE)	µg/L	ND	1.0	ND	1.0	ND	1.0
trans-12-DCE	µg/L	ND	1.0	ND	1.0	ND	1.0
trans-1,3-Dichloropropene	µg/L	ND	1.0	ND	1.0	ND	1.0
1,2,3-Trichlorobenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
1,2,4-Trichlorobenzene	µg/L	ND	1.0	ND	1.0	ND	1.0
1,1,1-Trichloroethane	µg/L	ND	1.0	ND	1.0	ND	1.0
1,1,2-Trichloroethane	µg/L	ND	1.0	ND	1.0	ND	1.0
Trichloroethene (TCE)	µg/L	ND	1.0	ND	1.0	ND	1.0
Trichlorofluoromethane	µg/L	ND	1.0	ND	1.0	ND	1.0
1,2,3-Trichloropropane	µg/L	ND	2.0	ND	2.0	ND	2.0
Vinyl chloride	µg/L	ND	1.0	ND	1.0	ND	1.0
Xylenes, Total	µg/L	28	1.5	12	1.5	ND	1.5

PQL = Practical Quantitation Limits

Sample Collected October 21, 2009

Analysis	Units	Raw Produced Water		UF Effluent		NF Permeate	
		Result	PQL	Result	PQL	Result	PQL
Polychlorinated biphenyls (PCBs)							
Aroclor 1016	µg/L	ND	1.0	ND	1.0	ND	1.0
Aroclor 1221	µg/L	ND	1.0	ND	1.0	ND	1.0
Aroclor 1232	µg/L	ND	1.0	ND	1.0	ND	1.0
Aroclor 1242	µg/L	ND	1.0	ND	1.0	ND	1.0
Aroclor 1248	µg/L	ND	1.0	ND	1.0	ND	1.0
Aroclor 1254	µg/L	ND	1.0	ND	1.0	ND	1.0
Aroclor 1260	µg/L	ND	1.0	ND	1.0	ND	1.0
Polycyclic aromatic hydrocarbons (PAHs)							
Naphthalene	µg/L	ND	2.0	ND	2.0	ND	2.0
1-Methylnaphthalene	µg/L	ND	2.0	ND	2.0	ND	2.0
2-Methylnaphthalene	µg/L	ND	2.0	ND	2.0	ND	2.0
Acenaphthylene	µg/L	ND	2.5	ND	2.5	ND	2.5
Acenaphthene	µg/L	ND	6.0	ND	5.0	ND	5.0
Fluorene	µg/L	ND	0.80	ND	0.80	ND	0.80
Phenanthrene	µg/L	ND	0.60	ND	0.60	ND	0.60
Anthracene	µg/L	ND	0.60	ND	0.60	ND	0.60
Fluoranthene	µg/L	ND	0.30	ND	0.30	ND	0.30
Pyrene	µg/L	ND	0.30	ND	0.30	ND	0.30
Benz(a)anthracene	µg/L	ND	0.070	ND	0.070	ND	0.070
Chrysene	µg/L	ND	0.20	ND	0.20	ND	0.20
Benzo(b)fluoranthene	µg/L	ND	0.10	ND	0.10	ND	0.10
Benzo(k)fluoranthene	µg/L	ND	0.070	ND	0.070	ND	0.070
Benzo(a)pyrene	µg/L	ND	0.070	ND	0.070	ND	0.070
Dibenz(a,h)anthracene	µg/L	ND	0.070	ND	0.070	ND	0.070
Benzo(g,h,i)perylene	µg/L	ND	0.080	ND	0.080	ND	0.080
Indeno(1,2,3-cd)pyrene	µg/L	ND	0.080	ND	0.080	ND	0.080
OTHER							
Mercury	mg/L	ND	0.00020	ND	0.00020	ND	0.00020
Phenolics, Total Recoverable	µg/L	17	2.5	18	2.5	3.6	2.5
Total Organic Carbon (TOC)	mg/L	8.6	2.0	9.1	2.0	5.0	2.0
Radium-226	pCi/L	9.13 ±2.20	---	9.12 ±2.23	---	0.297 ±0.313	---
Radium-228	pCi/L	6.25 ±1.32	---	4.39 ±0.941	---	0.282 ±0.295	---
Uranium-238	Mg/L	ND	0.0010	ND	0.0010	ND	0.0010
Arsenic	mg/L	ND	0.001	0.010	0.001	ND	0.001
Aluminum	mg/L	ND	0.001	ND	0.001	ND	0.001
Cadmium	mg/L	ND	0.001	ND	0.001	0.063	0.001
Chromium	mg/L	0.006	0.001	ND	0.001	0.003	0.001
Cobalt	mg/L	ND	0.001	ND	0.001	ND	0.001
Copper	mg/L	ND	0.001	0.005	0.001	ND	0.001
Lead	mg/L	ND	0.001	ND	0.001	ND	0.001
Manganese	mg/L	ND	0.001	ND	0.001	ND	0.001
Molybdenum	mg/L	ND	0.001	0.181	0.001	0.018	0.001
Nickel	mg/L	0.097	0.001	0.131	0.001	ND	0.001
Selenium	mg/L	0.001	0.001	ND	0.001	ND	0.001
Silver	mg/L	0.001	0.001	ND	0.001	0.002	0.001
Zinc	mg/L	ND	0.001	ND	0.001	0.006	0.001
Total Cyanide	mg/L	0.008	---	0.004	---	0.002	---