SALINITY AND TOC REMOVAL USING NANOFILTRATION

The University of Texas at El Paso El Paso, Texas

Contract No. 1425-97-FC-81-30006E

Water Treatment Technology Program Report No. 46

August 2002

U.S. DEPARTMENT OF THE INTERIOR Bureau of Reclamation Denver Office Technical Service Center Environmental Resources Team Water Treatment Engineering and Research Group NTIS form

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Charles D. Turner John C. Walton Edward A. Bermea Mayela Quezada The University of Texas at El Paso El Paso, TX

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ABSTRACT

El Paso, Texas is located in the Chihuahuan desert and receives less than eight inches of annual precipitation. Groundwater has been the main source of water since the early 1900's. Continued drawdown and salinization of the aquifers pose a serious threat to the El Paso and Ciudad Juarez, Mexico communities. The Rio Grande is a renewable resource and water rights are being transferred from agricultural to municipal use. Currently, the Rio Grande cannot be treated without desalination during the winter season, November through January, due to high salinity. Membrane treatment can reduce both salinity and total organic carbon making winter season flows available for use.

A dual-membrane pilot system consisting of a microfiltration unit followed by a nanofiltration unit was evaluated for total organic carbon (TOC) removal and salinity reduction. This system was evaluated at the El Paso Water Utility's (EPWU) Robertson/Umbenhauer, or Canal Street, Water Treatment Plant from May through October of 1998.

The pilot performance showed effective turbidity and suspended solids removal, greater than 99.0 percent, for the microfiltration unit. The nanofiltration unit provided effective TOC removal to less than 1 mg/L in the permeate stream. The system also rejected 85 percent of total dissolved solids (TDS).

Sodium Adsorption Ratio (SAR) calculations were performed to evaluate impact on the Rio Grande from concentrate return to the river for a hypothetical 10-MGD water treatment plant. Use of selective ion rejection membranes would enable EPWU to maintain the same SAR while returning the concentrate to the Rio Grande.

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LIST OF ABBREVIATIONS

AWWARF	American Water Works Association Research Foundation
CMF	Continuous Microfilter
DBP	Disinfection by-products
DPD	Diethyl-p-phenylene-diamine
EPA	Environmental Protection Agency
EPWU	El Paso Water Utility
ESWTR	Enhanced Surface Water Treatment Rule
ICR	Information Collection Rule
IMS	Integrated Membrane Systems
MF	Microfiltration
MGD	Million Gallons per Day
NF	Nanofiltration
NTU	Nephelometric Turbidity Unit
PLC	Programmable Logic Controller
RO	Reverse Osmosis
SAR	Sodium Adsorption Ratio
SDI	Silt Density Index
SDWA	Safe Drinking Water Act
SWTR	Surface Water Treatment Rule
TDS	Total Dissolved Solids
TMP	Transmembrane Pressure
TOC	Total Organic Carbon
UF	Ultrafiltration
UTEP	University of Texas at El Paso

METRIC CONVERSION TABLE

Multiply

By

To obtain

Length		
Inches (in)	25.4 (exactly)	Millimeters (mm)
Inches (in)	2.54 (exactly)	Centimeters (cm)
Feet (ft)	30.48 (exactly)	Centimeters (cm)
Feet (ft)	0.3048 (exactly)	Meters (m)
Feet (ft)	0.0003048 (exactly)	Kilometers (Km)
Miles (mi)	1.609344 (exactly)	Kilometers (Km)
Area		
Square inches (sq.in.)	6.4516 (exactly)	Square Centimeters (cm ²)
Square feet (sq.ft.)	929.03	Square Centimeters (cm ²)
Square feet (sq.ft.)	0.092903	Square meters (m ²)
Acres (ac)	4,406.9	Square meters (m ²)
Volume		
Cubic inches (cu.in.)	16.3871	Cubic centimeters (cm ³)
Cubic feet (ft ³)	0.0283168	Cubic meters (m^3)
U.S. Gallons (gal)	3.78533	Liters (l)
U.S. Gallons (gal)	0.00378543	Cubic meters (m^3)
Acre-feet (ac-ft)	1,233.5	Cubic meters (m^3)
Acre-feet (ac-ft)	1,233,500	Liters (l)
Pressure		
Pound per sq. in. (psi)	0.689476	newtons/sq cm (N/cm ²)
Pound / square in (psi)	47.8803	pascal (Pa)
Flow		
Cubic feet per second (cfs)	0.028317	Cubic meters/second (m ³ /s)
Cubic feet per minute (cfm)	0.4719	Liters/second (l/s)
U.S. Gallons per minute (gpm)	0.06309	Liters/second (l/s)
Work and Energy		
British thermal unit (BTU)	1,055.06	joules (J)
BTU per pound (BTU/lb)	2.326 (exactly)	joules/gram (J/g)
Foot-pounds (ft-lb)	1.35582	joules (J)
Power		
BTU per hour (BTU/hr)	745.700	watts (W)
Foot-pounds/second (ft-lb/s)	1.35582	watts (W)

1.0 INTRODUCTION

El Paso's fresh groundwater supplies are dwindling as the community continues to grow. According to the 1990 census, El Paso is growing at a population rate of 2.1 percent per year and Ciudad Juarez is growing at a population rate of 5 percent per year (Boyer, 1998). El Paso is 55 percent dependent on groundwater and Ciudad Juarez is 100 percent dependent on groundwater (Perez-Santiago, nd). The aquifers are becoming saline due to rapid drawdown which leads to the intrusion of surrounding brackish water. This problem is compounded by the lack of adequate recharge from precipitation. The El Paso region receives only 8 inches of annual rainfall (Boyer, 1998). High salinity is a threat to the future use of the aquifers and in an effort to combat this problem, the El Paso Water Utilities (EPWU) has embarked on a policy to utilize more surface water from the Rio Grande River and less groundwater. When the water reaches a salt concentration of 1,000 mg/L total dissolved solids (TDS), it can no longer be used for municipal purposes due to Texas law (Rittman, 1996). As aquifer supplies are consumed, a greater percentage of the Rio Grande River will be utilized. Boyle Engineering has recommended using more surface water while decreasing groundwater dependence in a 50 year Water Resource Plan (Boyle, 1993).

Although the Rio Grande is a renewable resource, releases from Elephant Butte Reservoir are fully allocated during the irrigation season. The EPWU must obtain its Rio Grande water allocation from the El Paso County Water Improvement District. The irrigation season is defined as the months between late February and early October. The time period in which the Rio Grande cannot be used for municipal purposes without desalination is the winter season defined as the time period between November and January (Rittman, 1996). Flows during the winter season are composed primarily of groundwater return from the previous irrigation season. The water quality in the winter season is poor with TDS concentrations greater than 1,000 mg/L and sulfate concentrations greater than 300 mg/L (Turner et al, 1997). Total Organic Carbon (TOC) concentrations are also high and can lead to the formation of disinfection by-products (DBPs) during the treatment/disinfection process. If the Rio Grande water between November and January can be desalinated, more surface water can be made available to El Paso. This would reduce usage of the declining groundwater resources thereby preserving them for use during future drought periods.

1

1.1 WATER SOURCES

Currently, El Paso receives 55 percent of its water from two underground sources, the Hueco and Mesilla Bolsons. Forty percent of this water comes from the Hueco Bolson located on the east side of the Franklin Mountains. The Hueco Bolson receives little recharge and is being depleted over time. This aquifer is suffering large drawdowns and as a result is becoming saline. The Hueco Bolson is also the only water source for Ciudad Juarez (Turner et al, 1997). The remaining 15 percent comes from the Mesilla Bolson located on the west side of the mountain. groundwater in the Mesilla valley receives recharge from irrigation return flow and is becoming more saline over time. The remaining 45 percent of El Paso's total annual water supply comes from the Rio Grande only during the irrigation or summer season (Rittman, 1996). During the winter season, groundwater is the sole source of El Paso water. The groundwater is chlorinated and pumped into the distribution system. As mentioned previously, the Rio Grande is currently available for EPWU use during the February through October irrigation season. Historically, Rio Grande flows have been regulated by Caballo Reservoir releases for irrigation diversions (Hamlyn, 1997).

1.1.1 Current Treatment

Surface water is treated at two-40-million gallon per day water treatment plants. The Robertson/Umbenhauer Water Treatment Plant, also known as the Canal Street Water Treatment Plant, is located in the central part of El Paso. The Jonathan Rogers Water Treatment Plant is located in the southeastern part of the city. Both plants use conventional water treatment methods. The Robertson/Umbenhauer plant treats the surface water by screening, sand removal, two-stage sedimentation, enhanced coagulation and flocculation. This produces turbidity less than 0.1 Nephelometric Turbidity Units (NTU). Chemicals used include chlorine dioxide for disinfection and ferrous chloride for coagulation. The Jonathan Rogers Plant treats the Rio Grande using similar technology except it uses ozone for disinfection. The location of these plants as well as the Mesilla and Hueco Bolsons can be seen in Figure 1.1.



Figure 1.1.—El Paso Water and Wastewater Treatment Plant Locations

1.1.2 Water Quality Regulations

Water quality regulations are becoming more stringent over time. The Surface Water Treatment Rule (SWTR) amendments to the Safe Drinking Water Act (SDWA) require the use of a treatment process, usually filtration and disinfection, to produce potable water from a surface water source or a groundwater source which is influenced by surface water (Vickers et al, nd). The Enhanced Surface Water Treatment Rule (ESWTR) requires increased control of chlorine-resistant microorganisms such as cryptosporidium.

Secondary Federal standards of interest for drinking water include chloride, sulfate and TDS. These standards are as follows:

- DS 500 mg/L
- Chloride 250 mg/L
- Sulfate 250 mg/L

1.1.3 Alternative Treatment

Communities are looking to other means of water treatment for public consumption to meet these new regulations rather other than conventional treatment. Membrane processes are now widely being used as an alternative to conventional methods (Jacangelo and Chellam, 1998).

One such process is microfiltration. Micofiltration has been proven to treat water to less than the EPA recommended 0.1 NTU and satisfy the turbidity and filtration requirements of the SWTR (Vickers et al). Total organic carbon (TOC) removal can also be high. Microfiltration also removes bacteria as well as some viruses. According to Wale and Johnson, 1993, microfiltration systems now have the second largest installed base for membranes in the municipal market.

Another membrane process is nanofiltration. Nanofiltration has been proven to remove dissolved solids as well as all viruses and bacteria (Lozier et al, 1997). Interest is high in the concept of integrated membrane systems (IMS) that combine microfiltration (MF) and ultrafiltration (UF). The MF or UF process is used in series with nanofiltration (NF) or reverse osmosis (RO) to remove precursor organics, viruses, and synthetic organic compounds. The use of a MF or UF system also minimizes the fouling of NF or RO spiral wound membranes. An integrated membrane system combining microfiltration and nanofiltration was installed in Barrow, Alaska. This 40-gpm-production plant is the first of its kind operating in North America.

One of the most attractive aspects of an IMS for the Rio Grande is the controlled removal of TDS. The Rio Grande flow is available for treatment during the winter months when the TDS concentration is above 1,000 mg/L. Salinity control could be accomplished by nanofiltration. Use of a nanofiltration system to treat the Rio Grande water would require either a microfiltration system or the effluent from a conventional system.

A dual-membrane system would provide effective treatment of the Rio Grande through controlled reduction of selected multivalent ions. A benefit of treating the Rio Grande during the winter months could be the utilization of an additional water source thereby lowering the demand upon limited groundwater sources.

4

Currently, the EPWU is considering the construction of a new 80 MGD facility in Anthony, Texas on the Texas – New Mexico State line. Membrane treatment is the primary technology under consideration.

2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 CONCLUSIONS

Results from the pilot study at the Canal Street plant showed successful removal of Rio Grande contaminants. The microfiltration system showed effective removal of the following parameters:

- Turbidity 99.9 percent
- Suspended Solids 98.5 percent
- The nanofiltration system showed effective removal of the following parameters:
- Total Organic Carbon Removal to at least 1 mg/L
- Total Dissolved Solids 85 percent
- Total Hardness 92 percent
- Calcium, Magnesium and Sodium ions 92 percent, 90 percent, 76 percent
- Chloride ions 63 percent
- Sulfate ions 94 percent
- Permeate for TDS, Chloride and Sulfate concentrations were below the recommended secondary standards

Mass balance equations for ions and calculated Sodium Adsorption Ratios (SAR) indicated that the Rio Grande could be treated during the winter months, which are defined as November through January. A histogram of Rio Grande winter flow showed at least 20-MGD of flow available in the Rio Grande 85 percent of the time. Groundwater would be available during drought years.

By selecting NF membranes with a sodium rejection of 40 percent or less, the SAR of the Rio Grande would remain the same if the nanofiltration concentrate were discharged to the river. These selective membranes would keep the sodium levels in the Rio Grande at an acceptable level. Downstream irrigation users would not be affected. There were slight increases in chloride and sulfate concentrations to the Rio Grande of 7.2 percent and 11.5 percent respectively. The TDS concentration affected the Rio Grande slightly raising the TDS concentration by 6 percent.

The NF discharge calculations indicated that calcium sulfate would not reach saturation concentrations in the Rio Grande. There would be no precipitation of calcium and it can be safely assumed that the Sodium Absorption Ratio for the Rio Grande after discharge is accurate. The Rio Grande is a renewable resource and should be utilized to it's fullest potential. The EPWU is constantly working at increasing water supply to meet population driven water demands. Alternative water supplies must be considered. Treating the Rio Grande during the winter months and depending less on groundwater is one option.

2.2 **R**ECOMMENDATIONS

- Study different plant sizes, (i.e. 5 MGD (0.219 m³/s), 20 MGD (0.876 m³/s) to determine SAR effects.
- Study economic factors for 5 MGD, 10 MGD (0.438 m³/s), and 20 MGD treatment facilities.
- Evaluate the use of treated Canal Street Water Treatment Plant effluent as NF feed to maximize the utility of the capital investment in the existing facility.
- Conduct bench scale testing of selected NF membranes for various sodium rejections to demonstrate actual ion and TOC rejections for feasibility analysis.
- Analyze calcium carbonate saturation in the Rio Grande to determine if calcium precipitation could potentially impact SAR numbers.

3.0 OBJECTIVE

The objective of this research was to evaluate the effectiveness of a dual-membrane process, microfiltration and nanofiltration, for the treatment of the Rio Grande water. The capability of this technology to treat waters with high turbidity and salinity was evaluated. These types of systems have been shown to treat surface water effectively in Barrow, Alaska (Lozier et al, 1998). One problem when using this type of system in El Paso would be the disposal of the concentrate. This report also evaluates the option for safely disposing the nanofiltration concentrate into the Rio Grande. If this type of technology is feasible, previously unused winter flow from the Rio Grande can be utilized resulting in another source of water for the El Paso area.

3.1 SCOPE OF WORK

A dual-membrane pilot system was set up at the Canal Street Water Treatment Plant. The pilot system consisted of a Memcor microfiltration unit and a trailer-mounted nanofiltration unit. The microfiltration system was operational May 1998 and the nanofiltration system was operational June 1998. Source water was the Franklin Canal which diverts water directly from the Rio Grande. Microfiltration effluent was used as influent for the nanofiltration system. A backwashable strainer was used ahead of the microfiltration unit to remove larger particles and prevent fouling of the microfilter. This dual-membrane system provided continuous water filtration until October 1998. Operational and water quality data was collected to demonstrate effectiveness of both systems.

4.0 SYSTEM SETUP

The dual-membrane pilot system used in this study consisted of a Memcor Inc. microfiltration unit and a nanofiltration system constructed by Fluid Processes Inc. Hydranautics supplied the nanofiltration membranes. This particular treatment train was determined from a selection process described in *Dual-Membrane Study of the Rio Grande River Water in El Paso, Texas* (Quezada, 1998). The treatment train is shown in figure 4.2.

4.1 PILOT CONFIGURATION

The dual-membrane pilot system consisted of the following: (Quezada, 1998)

- A hose was used to transport water from the Franklin canal to the raw water tank.
- A 1-hp pump was used to pull feedwater from the Franklin Canal (shown in Figure 4.1).
- A second 1-hp pump was used to pull feedwater from the raw water tank through a 500-micron backwashable strainer.
- From the strainer, water was transported to the Memcor Continuous Microfilter (CMF) break tank.
- Microfilter (MF) permeate was pumped to a holding tank inside a trailer where the nanofiltration system was stored.
- This water was then pretreated with muratic acid and then a chloramine solution made at the site. (Overflow from the holding tank was sent back to the Canal Street Plant silt tank).
- The nanofilter (NF) feed pump transported water through a 5-micron cartridge filter and then into the nanofiltration system.



Figure 4.1.—Franklin Canal located adjacent to El Paso's Canal Street Plant



Figure 4.2.—Pilot System Treatment Train

4.1.1 Microfiltration Design

The microfiltration unit was the Memcor 3M10C Microfiltration System housing a threemicrofiltration module bank. Included with the MF unit were a separate backwash tank and an air compressor, which provided air for backwashing. Air at 90 pounds per square inch $(6.2x10^5$ Pa) was used for the air-assisted backwash and 15 pounds per square inch $(1.03x10^5$ Pa) was used for a lumen drain and a pressure integrity test (Memcor 3M10C operation and maintenance manual, 1998). Figure 4.3 shows a schematic of the unit. The Memcor system was operated by the use of "Panelview" software via an interactive terminal screen. These screens were menu driven and easy to operate.



Figure 4.3.—Memcor Pilot Unit Schematic

Figures 4.4 and 4.5 show the Memcor unit with the backwash tank and the three-module bank respectively. The specifications of the unit are listed below:

Filtration Modules	
Number	3
Pore Size	0.2 μm nominal
Flow Rates	7.5 gpm (4.7x10-4 m^3/s) each module
Membrane Area	15 m^2 each module
Membrane Material	Polypropylene
Potting Material	Polyurethane

Membranes used in this system were not chlorine tolerant. Free chlorine would damage the membranes. Any cleaning of the break tank or the raw tank had to be done with feed water or distilled water. The system used hollow fiber membranes that allowed a continuous filtration of liquid to 0.2 micron. The hollow fiber membranes were used in an "outside-in" configuration where feed water was filtered from the outside of the membranes and only clean water was left on the inside of the membrane. The system was run in direct flow, which enabled 100 percent recovery of the feed water. This type of configuration allowed for the potential of quicker fouling but there were fewer power requirements. The Memcor system utilized both ends of the first module as feed points.



Figure 4.4.—Memcor Unit with Backwash Tank



Figure 4.5.—Three Module Bank on Memcor Unit

4.1.1.2 Backwash Cycle

During the backwash cycle, pressurized air was rapidly forced through the fibers from the filtrate or lumen side to the feed side. This dislodged contaminants on the surface of the fiber as well as the porous matrix. Feedwater then washed away these dislodged particles. Pressurized air was used once again to clear out any air bubbles that could reside in the fibers. This process lasted a total of 2 minutes. The backwashing occurred every 22 minutes and helped maintain the system performance over a longer time.

4.1.1.3 Pressure Decay Test

A pressure decay test was performed automatically every day to check the integrity of the modules. This pressure decay test is an important testing parameter to determine the functionality of the system. The test involved the following steps:

- 1. Pressure decay test regulator was checked for 15 psi $(1.03 \times 10^5 \text{ Pa})$.
- 2. Filter lumens were drained and the filtrate side pressurized to approximately $15 \text{ psi} (1.03 \times 10^5 \text{ Pa})$ for ten seconds
- 3. Unit was stabilized for two minutes
- 4. Test period began which was two minutes long.
- 5. If initial test pressure was above 17 psi $(1.17 \times 10^5 \text{ Pa})$ and below 10 psi $(1.03 \times 10^5 \text{ Pa})$ an initial test pressure out of range alarms was triggered.
- 6. The unit was returned to normal filtration mode.
- 7. If the pressure decay was greater than $1.5 \text{ psi} (1.03 \times 10^4 \text{ Pa})$ per minute, a general pressure decay warning alarm was triggered. If a decay of 2 psi $(1.4 \times 10^4 \text{ Pa})$ per minute or more occurred, a Shutdown alarm was triggered.

4.1.1.4 Clean in Place

Although periodic backwashing will lower the transmembrane pressure (TMP), the MF system eventually required a more stringent cleaning. This clean in place (CIP) or chemical clean consisted of an acidic wash followed by a caustic wash and rinse. The acidic wash utilized citric acid and the caustic wash utilized a "Memclean" solution which was basically a sodium hydroxide solution. The CIP used filtered water from the break tank. The unit ran in recirculation mode during the CIP period. The following steps were taken to complete a CIP:

- 1. Stop the CMF by pressing "F7" on the Control Screen
- 2. Turn filtrate valve, MV5, towards break tank
- 3. Start CMF by pressing "F6" on the Control Screen
- 4. Start CIP by pressing "F5" on the Control Screen
- 5. Add 10 lb. citric acid when prompted (This will occur after 10 minutes of filtration)
- 6. Press "F5" on CIP Status Screen
- 7. If an extended soak is required, press "F8" on CIP Status Screen. Extended soak will remain in effect until "F9" is pressed on CIP Status Screen.
- 8. After a two-hour soak and filtration period, system will be paused for operator to press "F5" on CIP Status Screen.
- 9. The CMP will rinse down automatically and perform multiple backwashes. The CMF will then go into shutdown.
- 10. Turn the filtrate valve (MV-5) away from the break tank.
- 11. Start CMF by pressing "F6" on the Control Screen.
- 12. Adjust filtrate flow to setpoint with MV-4.
- 13. Record operational values and repeat steps 1 11 with "Memclean" solution.

4.1.2 Nanofiltration Design

The nanofiltration system used in this pilot was a two-stage array system. The design of the twostage array was based in part on data collection requirements set forth in the Information Collection Rule (ICR) (Quezada, 1998). The system was constructed by Fluid Processes Inc. and the spiral-wound membranes supplied by Hydranautics were 2540 ESNA. The first stage consisted of two pressure vessels, each containing three membrane elements. The second stage consisted of one pressure vessel containing three membrane elements. The system was set to run at 75 percent recovery. Figure 4.6 shows a schematic of the system.



NANOFILTRATION PILOT SCHEMATIC

Figure 4.6.—Nanofiltration Schematic

Figure 4.7 shows the nanofiltration system inside the trailer. The first stage consisted of the top two pressure vessels and the second stage contained the bottom pressure vessel.



Figure 4.7.—Nanofiltration System

4.1.2.1 Acid Pretreatment

Muratic acid was introduced into the nanofiltration feed line to keep the pH between 5.6 and 5.8. This was to ensure solubility of carbonates to minimize inorganic scaling.

4.1.2.2 Chloramine Pretreatment

Chloramines were injected at a set rate and concentration to prevent biofouling. Biofouling is the formation of a biological slime or biofilm that can be avoided by feeding chlorine into the feed water (AWWARF, 1989). Because the nanofilter membranes could not tolerate any free chlorine, chloramines were used. Chloramines are defined as chlorine that exists in a chemical combination with ammonia in water. Chloramines were made by mixing sodium hypochlorite with ammonium sulfate. Chloramines are not as effective as free chlorine but can control biofouling. Chloramines were controlled such that no more than 0.1 mg/L of free chlorine was applied to the membranes. The goal residual in the permeate stream was 1.0 mg/L of

chloramines. The mass balance calculations for determining the sodium hypochlorite ammonium sulfate mix was described by (Quezada, 1998). To determine the strength of the sodium hypochlorite, the Iodometric Method I was used which is based on Standard Method 4500-Cl B. This method was also described by Quezada, 1998.

The N,N – diethyl-p-phenylene-diamine (DPD) method was used to determine the chloramine concentration in the NF permeate stream (Quezada, 1998). This method consisted of filling two 10 ml vials with NF permeate. One vial was used as the blank and calibrates the measuring device, Hach DR100, and the other was used to measure free and total chlorine. Total chlorine was measured by adding a total chlorine reagent packet. The DR100 then measured the amount of total chlorine by color change, which is pink. The darker the color, the more concentrated the chlorine. The same procedure was used for free chlorine. The difference between total and free chlorine was combined chlorine, or chloramine. Chloramine concentrations of the NF system permeate NF system concentrate, and NF feed was checked twice a day Monday through Friday and once on Saturday and Sunday. This measuring protocol was put in place to ensure the NF membranes would not be damaged by excess free chlorine. A number of factors including temperature, reaction time, and pH affected the concentrations decrease with time as well as with temperature increases. (Speth, 1998).

5.0 PILOT OPERATION

Microfiltration commenced operation on May 11, 1998 and nanofiltration commenced operation June 11, 1998. Both systems were online until October 13, 1998.

5.1 **OPERATORS**

From May 11, 1998 to July 25, 1998 two graduate students and three undergraduate students handled operational and maintenance duties. From August 1, 1998 to the end of the study, one graduate student (Quezada) and three undergraduate students handled these duties.

5.1.1 Duties

Operational data for both systems was taken twice a day Monday through Friday and once a day on Saturday and Sunday. As well as recording this data, each shift had the following responsibilities:

- Check chloramine residual for NF feed, NF concentrate and NF permeate streams
- Perform Canal lab analysis on required samples
- Check all systems performing nominally
- Fill out MF/NF log sheets

In addition to these duties, the morning shift had these additional duties:

- Prepare chloramine solution (15 gallon $(5.7 \times 10^{-2} \text{ m}^3)$)
- Collect samples for UV-254, conductivity and anion/cation balance testing
- Collect weekly and biweekly samples

The morning shift consisted of two people due to the increased workload. Weekly duties also entailed performing UV-254 and conductivity analysis at UTEP.

The protocol for data collection was based in part on information provided by Memcor as well as the Information Collection Rule (ICR). TDS analysis was performed from April to August. Beginning in late August, TDS analysis was halted and Anion/Cation Balance analysis was started. This decision was made to determine the Sodium Absorption Ratio (SAR) for the concentrate stream, NF feed, permeate stream and eventually the Rio Grande after concentrate discharge. Because the Jonathan Rogers lab could not perform both daily TDS and the anion/cation balances, the anion/cation balance was performed twice a week instead of daily TDS analysis. It was assumed a correlation could be achieved between the conductivity and TDS samples already collected from June to August. TDS was also evaluated as part of the twice a week anion/cation balance analysis.

5.2 DATA COLLECTION

This section describes the sampling plan for the pilot study. Sampling techniques are discussed in detail in *Dual Membrane Study of the Rio Grande/Rio Bravo River in El Paso, Texas* (Quezada, 1998).

5.2.1 Canal Lab Analysis

The following table shows the protocol for analysis at the Canal Street Water Treatment Plant.

		Canal Lab			Other	
Sample	Description	Temp. pH Turbidity		SDI	Silica	
	MF					
Tank	Raw	D	D	D		
Hose-1	Filtrate	D	D	D		
	NF					
NF-4	Feed	D	D	В	D	D
NF-11	Stage 1 Conc.	В	В	В		
NF-12	Stage 1 Perm.	В	В	В		
NF-13	Stage 2 Perm.	В	В	В		
NF-14	System Conc.	D	D	В		
NF-15	System Perm.	D	D	В		

Table 5.1.—(Daily Monitoring (Canal Lab))

D - Analysis performed daily

B – Analysis performed biweekly

5.2.2 UTEP Analysis

Table 5.2 shows the protocol for data analysis at the Jonathan Rogers Water Treatment Plant.

		UTEP Lab			
Sample	Description	UV-254	Conductivity		
	MF				
Tank	Raw	D	D		
Hose-1	Filtrate	D	D		
	NF				
NF-4	Feed	D	2W		
NF-11	Stage 1 Conc.	D	2W		
NF-12	Stage 1 Perm.	D	2W		
NF-13	Stage 2 Perm.	D	2W		
NF-14	System Conc.	D	D		
NF-15	System Perm.	D	D		

Table 5.2.—Water Quality Testing (UTEP Lab)

D – Analysis performed daily

2W – Analysis performed twice a week
5.2.3 Fred Hervey Lab Analysis

Table 5.3 lists the protocol for water analysis at Jonathan Rogers and Fred Hervey Water Treatment Plants.

			Total	Са	Alkalinity	Bromide	SS
Sample	Description	TOC	Hardness	Hardness			
	MF						
Tank	Raw	W	W		2		W
Hose-1	Filtrate	W	W		2		W
	NF						
NF-4	Fæd	W	W	W	В	В	
NF-11	Stage 1 Conc.	W	W	W	В		
NF-12	Stage 1 Perm.	W	W	W	В		
NF-13	Stage 2 Perm.	W	W	W	В		
NF-14	System Conc.	W	W	W	В		
NF-15	System Perm.	W	W	W	В	В	

Table 5.3 Water Quality Testing (Conducted at Fred Hervey laboratories)

B – Analysis performed biweekly

W – Analysis performed weekly

2 – Analysis performed twice during entire study

5.2.4 Jonathan Rogers Lab Analysis

Table 5.4 shows the protocol for water quality analysis at the Jonathan Rogers Water Treatment Plant.

			Anion/
Sample	Description	TDS	Cation
	MF		
Tank	Raw	2W	2W
Hose-1	Filtrate	D	
	NF		
NF-4	Feed	D	2W
NF-11	Stage 1 Conc.	2W	
NF-12	Stage 1 Perm.	2W	
NF-13	Stage 2 Perm.	2W	
NF-14	System Conc.	2W	2W
NF-15	System Perm.	D	2W

Table 5.4. —Water Quality Testing (Jonathan Rogers Laboratory)

D – Analysis performed daily

2W – Analysis performed twice a week

5.3 MICROFILTRATION OPERATION

5.3.1 Operational Data

Data collection consisted of two readings per day Monday through Friday and one reading on Saturdays and Sundays. Data collection consisted of reading data off of the "Process Status" screen of the Programmable Logic Controller (PLC).

Memcor provided a data sheet where following parameters were collected off of the "Process Status" screen:

- Time of Day
- Hour Run Meter

- Feed Pressure
- Filtrate Pressure
- TMP
- Feed Flow
- Filtrate Flow

The PLC is shown in Figure 5.1.

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Figure 5.1.—Memcor PLC Screen

5.4 NANOFILTRATION OPERATION

5.4.1 Operational Data

Operating data was taken on the system twice a day, once in the morning and once in the evening. The following data was taken:

- Pre-filter Pressure
- Post-filter Pressure
- Stage 2 influent Pressure

- Concentrate Pressure
- Stage 1 Permeate Flow
- Stage 2 Permeate Flow
- System Permeate Flow
- System Concentrate Flow
- Influent Conductivity
- System Permeate Conductivity
- System Concentrate Conductivity
- Influent pH

6.0 Results and Observations

This chapter summarizes the results from the Canal Street Plant pilot study. Results are summarized in tables and graphs and divided into operational and water quality results.

6.1 MICROFILTRATION RESULTS

6.1.1 Operational Results

Operation of the microfiltration system can be reviewed based on transmembrane pressure. A plot of transmembrane pressure and feed water temperature vs. time is seen in Figure 6.1. As expected, over time there was an increase in TMP indicating fouling. Also, TMP rose with a decrease in feed water temperature. Temporary drops in TMP were chemical clean points. Chemical cleans were generally done every three weeks after the initial break-in period. Beginning in mid-August, chemical cleans were performed more frequently. Also, the pressure decay rate increased. "Pressure Decay Rate High" warnings were seen regularly. This high decay rate was an indication of broken fibers in the module. This was confirmed when a Memcor representative came to El Paso to inspect the modules. When testing the fibers integrity, bubbles were seen giving an indication of broken fibers. Placing stainless steel pins in the fibers repaired these broken fibers. By the end of August, it was apparent that the membranes were fouled beyond repair. Treating the high turbidity surface water at a high flow rate proved to be too much for the microfiltration system. A decision was made to change out the modules September 1, 1998. This is shown by the large drop in TMP in Figure 6.1. Upon inspection of the modules, it was clear that both feed points were severely clogged. Particles had lodged in between the fibers to such a degree that many fibers broke when pressed against the casing. A decision was made to generate permeate at a rate of 15 gpm (0.95 L/s). The permeate flow rate was eventually decreased to 12 gpm (0.76 L/s) which seemed to be the best setpoint. The backwash frequency was also increased to once every 18 minutes. This helped in decreasing the fouling.



Figure 6.1.—Transmembrane Pressure, Feed Water Temperature Water Quality Results

6.1.2 Water Quality Results

These results are from system operation from June 11, 1998 to October 13, 1998. The system showed effectiveness in removing turbidity and suspended solids

6.1.2.1 Turbidity Removal

Source water turbidity averaged over 100 NTU. The Memcor microfiltration unit produced permeate water with less than 0.1 NTU. Removal efficiency was 99.883 percent. Figure 6.2 shows the performance of turbidity removal. Heavy rain in mid August was assumed to be the cause for the turbidity spikes but it is was evident that there were no effects on the removal of turbidity as the permeate turbidity maintained at approximately 0.1 NTU. Integrity problems caused high filtrate turbidity readings in August. Also, on October 9, a filtrate reading of 1.56 NTU was measured. This could be due to a number of reasons including operator error or growth in the filtrate hose. This number should not be included in the sampling. The combination of a high flux with high turbid waters led to broken fibers leading to less effective



Figure 6.2.—Turbidity Removal

treatment. Turbidity removal was more effective at a lower flux. It is likely that better pretreatment would improve turbidity removal. Overall, the microfiltration system proved very effective in removing turbidity and producing water that satisfied the maximum drinking water level for turbidity.

6.1.2.2 Suspended Solids Removal

The average source water suspended solids concentration was 149 mg/L and the average permeate water suspended solids concentration was 2.1 mg/L. The suspended solids count reached as high as 2080 mg/L on July 24, but the microfiltration unit handled this without any problems. The Memcor unit removed, on average, 98.5 percent suspended solids. Figure 6.3 shows the suspended solids removal.



Figure 6.3.—Suspended Solids Removal

6.2 NANOFILTRATION RESULTS

6.2.1 Operational Results

6.2.1.1 NF Permeate Flow Results

Figure s 6.4, 6.5, 6.6 and 6.7 describe the performance of the nanofiltration system regarding flow. The design flow for the system was 2.4 gpm (9.1 L/m). The system ran smoothly through August. By mid-September, a small drop in flow was seen. This flow dropped to approximately 2.0 gpm (7.6 L/m). By the end of the study the flow periodically measured 1.7 gpm (6.4 L/m). These were occasional drops as the flow maintained at 2.0 gpm (7.6 L/m). The average flow over the study period was 2.22 gpm (8.4 L/m) which was a 7.4 percent difference from the design flow. Stage 1 saw a 10.5 percent decrease in flow and Stage 2 saw a 7.2 percent difference. The system concentrate maintained a flow of 0.8 gpm (3.0 L/m) throughout the study. There were variations in flow during the day as flow is lower in colder water temperatures and higher in warmer water temperatures.

The drop in flow was assumed to be due to inorganic scaling because organic fouling was controlled by the injection of chloramines. Figure 6.4 details the system permeate from June 11 to October 13. The flow from June to early September stayed constant at approximately 2.4 gpm (9.1 L/m) and then gradually tapered off.



Figure 6.4.—NF System Permeate

6.2.1.2 Normalized NF Permeate

Normalization of the raw product flow data minimizes the effect caused by variations in feedwater temperature and TDS. Both of these parameters can affect water flow through the NF membrane. By normalizing the data, fouling effects can better be observed (Lozier *et al*, 1997). Normalizing yielded an average permeate flow of 2.51 gpm (9.5 L/m). This was a 4.1 percent difference to the design flux. There was still a gradual drop in flow over time but this was expected and probably due to inorganic scaling. This is shown in Figure 6.5.



Figure 6.5.—Normalized NF System Permeate

6.2.1.3 Stage 1 and 2 Permeate Flow

Figure 6.6 illustrates Stage 1 permeate flow. The stage 1 permeate began to show a decline in flow starting in late August. By the end of September, the Stage 1 flow dropped again. It is possible that these drops in flow are periods where scaling had the most effect on the system. Scaling will happen over time and its effects not seen until a later time (Turner, 1999). Figure 6.7 shows Stage 2 permeate flow. A decline in flow is shown in this chart as seen in the previous Figure s. The decline began again in late August followed by another drop in flow in late September.



Figure 6.6.—Stage 1 Permeate



Figure 6.7.—Stage 2 Permeate

6.2.1.4 Silt Density Index

Figure 6.8 shows the silt density index (SDI). The recommended maximum SDI for the NF membranes used in the study was between 4 and 5. Figure 6.8 shows the rise in SDI starting in August. This rise correlates with the decrease in system permeate flow which indicates scaling. Again, injecting anti-scalant may have minimized this effect.



Figure 6.8.—Silt Density Index

6.2.1.5 NF System Recovery

System recovery can be found by the equation $[(\mathbf{F}_p/\mathbf{F}_f) * \mathbf{100}]$, where \mathbf{F}_p is the flow of permeate and \mathbf{F}_f is the feed flow. The design recovery was set at 75 percent. The total recovery during the study can be seen on Figure 6.9. The recovery dipped as the system performed over time. It is probable that injecting anti-scalant could have kept the recovery higher but performance would still have suffered without any cleaning.



Figure 6.9.—NF System Recovery

6.2.2 Water Quality Results

These results are from system operation from June 11, 1998 to October 13, 1998. The system showed effectiveness in removing total organic carbon, TDS and hardness.

6.2.2.1 TOC Removal

During the pilot study, raw water TOC averaged 4 mg/L. Nanofiltration permeate averaged a TOC concentration of less than 2 mg/L. In all but two samples, the permeate TOC was below the 1 mg/L detection limit. In all cases, the NF system showed reliable removal of TOC. Removal of TOC is shown in Figure 6.10.



Figure 6.10.—TOC Removal

6.2.2.2 TDS Removal

The Jonathan Rogers Water Treatment Plant performed TDS analysis. The average feed water TDS concentration was 670 mg/L. The average permeate TDS was 99 mg/L. The NF system removed on average 85 percent of TDS. As the pilot study progressed into the winter season, the TDS rose as expected. The nanofiltration system handled this increase without any problems and kept the rejection rate steady. This showed effective treatment of TDS and showed promise for treatment of Rio Grande water during the winter months when TDS averages over 1000 mg/L and conventional treatment is not effective. TDS removal is shown in Figure 6.11. A gap in the data is due to a changeover in collection protocol from TDS samples to anion/cation samples.



Figure 6.11.—TDS Removal

6.2.2.3 Hardness Removal

Average feedwater hardness measured 239 mg/L, which is classified as "hard" water. "Hard" water is classified as concentrations between 150 to 300 mg/L, expressed as CaCO₃ (Masters, 1991). NF permeate water averaged 19 mg/L which can be classified as "soft" water. "Soft"

water is classified as concentrations less than 50 mg/L, expressed as $CaCO_3$ (Masters, 1991). Average hardness removal by the NF system was 92 percent. Figure 6.12 shows hardness removal.



Figure 6.12.—Hardness Removal

6.2.2.4.—Ion Removal

The anion/cation balance provided results on calcium, magnesium, sodium, chloride and sulfate removal. The NF system proved very effective in removal of these ions. The concentrate stream contained high concentrations of these ions due to the reduced NF flow through each membrane element. The feedwater salt concentrations rose as the pilot study entered the winter season, which was expected, and the NF was very effective in handling this rise in concentration.

Calcium.—The nanofiltration system was effective in removing calcium ions from the feed water. The raw water averaged 72 mg/L calcium and the permeate water averaged 5.4 mg/L calcium. This was a removal of 92 percent calcium from the feed water. The concentrate water had an average of 229 mg/L of calcium. Figure 6.13 shows the calcium removal.



Figure 6.13.—Calcium Removal

Magnesium.—The feed water averaged 14 mg/L magnesium and the permeate water averaged 1.23 mg/L magnesium. The nanofiltration system effectively removed 90 percent of the magnesium ions from the source water. The concentrate water had an average of 46 mg/L magnesium. Figure 6.14 shows magnesium removal.



Figure 6.14.—Magnesium Removal

Sodium.—The feed water averaged 131.5 mg/L sodium and the permeate averaged 30.7 mg/L. This was a removal of 76.4 percent. The concentrate water had an average of 397 mg/L sodium. Figure 6.15 shows sodium removal.



Figure 6.15.—Sodium Removal

Chloride.—Average raw chloride concentration in the canal was 108 mg/L and the average nanofiltration permeate chloride concentration was 39 mg/L. This gives an average chloride removal of 63 percent. Concentrate water averaged 623 mg/L. Figure 6.16 shows chloride removal.



Figure 6.16.—Chloride Removal

As the winter season approached, chloride concentrations increased but the nanofiltration system was able to handle this increase without any problems.

Sulfate.—Sulfate feedwater concentration averaged 230 mg/L and the NF permeate averaged 13 mg/L. Average sulfate removal was 94 percent. Concentrate water averaged 686 mg/L. Figure 6.17 shows sulfate removal.



Figure 6.17.—Sulfate Removal

7.0 IMPACT OF NANOFILTRATION DISCHARGE ON THE RIO GRANDE

A concern with using membrane treatment for Rio Grande water is the disposal of the concentrate stream. For every 10 gallons (38L) of water treated, 1.0 to 1.5 gallons (3.8L-5.76L) of concentrate are generated. Most nanofiltration membranes have high rejections of monovalent cations such as sodium and even higher rejections of multivalent cations such as calcium and magnesium. High concentrations of sodium in the Rio Grande River can cause damage to crops and croplands. If irrigation water is high in sodium, soil mineral particles tend to disperse and the hydraulic conductivity decreases leading to a lack of water supply to crops (Jensen, 1980). The most significant irrigation parameter is the Sodium Adsorption Ratio (SAR) which is the proportion of sodium to calcium and magnesium in water. SAR values are used to evaluate the suitability of a water source such as the Rio Grande for application to specific crops on various types of soils. The SAR equation is as follows (Jensen, 1980):

 $SAR = Na/(Ca + Mg)^{1/2}$

Units are expressed in milliequivalents/L. The concentration of sodium is an important parameter in the SAR. The lower the concentration of sodium, the smaller the impact will be to the discharge site. A low SAR (2 to 10) indicates little danger from sodium; medium hazards are between 7 and 8; high hazards between 11 and 26, and very high hazards above 26 (Fetter, 1994).

During this study, the nanofiltration membranes used had a high rate of rejection for all ions, including sodium. The ESNA1-2540 membranes, which were used in this study, had an average salt rejection of 80 percent. Both mono and multivalent ions were easily rejected. Multivalent ions are rejected at a much higher rate than monovalent ions; roughly proportional to the square of the ionic charge (Turner *et al*, 1999). High sodium in concentrate discharged to the river or canal has a negative impact in irrigation, primarily by raising the SAR leading to dispersion of the soil. Nanofiltration membranes need to be selective to control rejection of salts, particularly

sodium. Nanofiltration membranes can average 98 percent rejection for multivalent cations such as calcium and magnesium and low rejection for monovalent cations such as sodium. For applications at Canal Street, sodium rejection should be low in order to maintain a low SAR in the source water.

This section will evaluate high and low sodium rejection membranes on a hypothetical 10-MGD water treatment plant. If 10 MGD of flow can be generated in the winter, the dependence on the aquifers will be reduced. The impact of concentrate discharged and Rio Grande flow available can be analyzed to determine if a larger capacity plant is feasible.

The impact of discharging nanofiltration waste into the river is evaluated for membranes with assumed sodium rejections of 60 percent, 40 percent and 20 percent. The specifications of these membranes were obtained from Osmonics Inc. This impact is compared with the membranes used in the study (76 percent sodium rejection). A mass balance of flow and salts is used to check the impact on the Rio Grande. This impact also includes calcium, magnesium, chloride, sulfate and Total Dissolve Solids.

7.1 **RIO GRANDE RIVER HISTORICAL FLOW**

Before membrane performance was compared, the Rio Grande was evaluated to determine if winter flow was consistently available for use. Figure 7.1 shows the annual flow of the Rio Grande River from 1985 – 1995. The flow was cyclic due to irrigation release from Elephant Butte Reservoir. The Rio Grande flow was high in the summer and low in the winter. Winter season flow was mostly made up of irrigation return from the previous growing season.



Figure 7.1.—10-Year Rio Grande Flow

Averaging the monthly flow results in the flow patterns shown in Figure 7.2.



Figure 7.2.—Rio Grande Average Monthly Flow, 1985 – 1995

The rise in flow during the months of March and April was due to an unusually wet season in 1986 shown in Figure 7.2. Currently, the two conventional water treatment plants in El Paso cannot treat the Rio Grande River during the winter season due to high TDS values. Winter season is defined as the period of November through January. If sufficient winter surface flow were available, membrane treatment could be used to control salinity. Using data collected by the El Paso Water Utilities, the winter flows were analyzed. Data was evaluated from 1936 to 1995.

Figure 7.3 shows the average monthly winter flow for the Rio Grande River. The peak in 1986 was from an unusually wet winter season.



Figure 7.3.—Average Monthly Winter Flows – Nov., Dec., Jan.

The Rio Grande flow during the winter season averaged less than 200-MGD ($8.76 \text{ m}^3/\text{s}$) with the exception of 1986. This winter data can be further evaluated on the frequency of flow during the winter season. Figure 7.4 shows a histogram for the Rio Grande flow during the winter season.



Figure 7.4.—Rio Grande Flow Histogram

7.2 DETERMINATION OF ADEQUATE FLOW

The histogram shows the majority of winter flow was between 50 MGD ($2.19 \text{ m}^3/\text{s}$) and 200 MGD ($8.76 \text{ m}^3/\text{s}$). Almost 100 percent of the flow was accounted for at a flow of 300 MGD ($13.14 \text{ m}^3/\text{s}$). At least 20 MGD ($0.876 \text{ m}^3/\text{s}$) of flow was available 85 percent of the time. Out of the 180 winter months, there were 16 where the flow was equal to or less than 10 MGD. There was sufficient flow in the river to provide feed for a 10-MGD ($0.438 \text{ m}^3/\text{s}$) plant approximately 90 percent of the time. The descriptive statistics of the Rio Grande winter flow are listed in Table 7.1 below.

Parameter	MGD
Mean	110
Standard Error	13
Median	80
Mode	130
Standard Deviation	180
Sample Variance	32000
Skewness	6.9
Range	1700
Minimum	2.2
Maximum	1700
Sum	19000
Count	180
Confidence Level (95.0%)	27

Table 7.1.— Rio Grande Flow Statistics

The high standard deviation was due to the extremely wet season in 1986. The mean was also skewed due to this high flow. Figure 7.5 shows the average monthly winter flow with the year 1986 omitted.



Figure 7.5.—Average Monthly Winter Flow – 1986 point omitted

A more representable description of the winter flow can be seen without 1986. With the exception of a few low points from 1954 - 1958 and in 1964, the flows were above 25 MGD (1.09 m³/s). With 1986 omitted, the descriptive statistics in Table 7.2 provide a better representation of water available from the Rio Grande.

Parameter	MGD
Mean	85
Standard Error	4.2
Median	79
Mode	130
Standard Deviation	56
Sample Variance	3200
Kurtosis	0.3
Skewness	0.7
Range	280
Minimum	2.2
Maximum	280
Sum	15000
Count	177
Confidence Level (95.0%)	8.4

Table 7.2.—Rio Grande Flow Statistics (1986 deleted)

The mean was 85 MGD ($3.72 \text{ m}^3/\text{s}$). The standard deviation was 56. The most frequent discharge, the mode, was 130 MGD ($5.69 \text{ m}^3/\text{s}$). This is further indication that the Rio Grande River would have sufficient flow during the winter season to support the construction of membrane treatment facilities. For this calculation, a 10-MGD ($0.438 \text{ m}^3/\text{s}$) treatment facility was used. Since the drought years can be handled by withdrawal from the aquifers, the size of the membrane treatment system becomes a function of the value of maintaining long term reserves in the aquifers. This is complicated by the utilization of the same aquifers during the summer months.

A comparison was made between the original river flow and the river flow after intake into the 10-MGD (0.438 m^3/s) water treatment plant. Figure 7.6 shows a comparison between the flow before and after the withdrawal of 16.7 MGD (0.73 m^3/s) for treatment. A withdrawal of

16.7 MGD (0.73 m^3/s) from the Rio Grande was used assuming 60 percent permeate recovery to produce 10 MGD (0.438 m^3/s). Figure 7.6 shows the few years during the period where no flow would be available for water treatment. During these no-flow years, groundwater would have to be used.



Figure 7.6.—Impact on Flow in the Rio Grande for 10 MGD (0.438 m³/s) Withdrawal

7.3 HISTORICAL WINTER SALT CONCENTRATIONS OF THE RIO GRANDE

Average winter Rio Grande flow and concentrations for calcium, magnesium, sodium, chloride, sulfate and TDS were taken from the EPWU database. The flow and concentrations used are as follows:

Rio Grande flows	- 107 MGD (4.7 m ³ /s)
Average calcium concentration	– 122 mg/L
Average magnesium concentration	– 29 mg/L
Average sodium concentration	- 343 mg/L

Average chloride concentration	– 298 mg/L
Average sulfate concentration	- 503 mg/L
Total Dissolved Solids	– 1512 mg/L

Figure 7.7 shows the calcium, magnesium, and sodium concentrations through the time period of 1936 – 1995. Figure 7.8 shows the chloride and sulfate concentrations through the same time period.



Figure 7.7.—Ca, Mg, Na Concentrations of Rio Grande

Figure 7.7 shows a higher amount of sodium in the river than calcium and magnesium. The large spike in sodium concentration between 1954 - 1960 was mostly attributed to drought years. During this time, the river averaged 2 (0.088 m³/s) to 5 MGD (0.22 m³/s) of flow. Smaller spikes in calcium and magnesium were also seen. Because the average sodium concentration was already high, SARs would be minimized if the sodium concentration in the NF concentrate stream was as low as possible.



Figure 7.8.—CI and SO4 Concentrations of Rio Grande

Figure 7.8 shows a higher amount of sulfate in the Rio Grande than chloride. The large spikes in both concentrations were due to the drought period as previously mentioned. Figure 7.9 shows the TDS concentration of the Rio Grande over the time period 1936 – 1995.



Figure 7.9.—Rio Grande TDS

During the winter season, the TDS concentrations in the Rio Grande were very high. Again, this was due to the high salinity from the irrigation return flow. The average TDS during this time period was 1510 mg/L. Conventional plants in El Paso cannot treat water of this poor quality.

7.4 RIO GRANDE SALT IMPACT

The following assumptions were used to determine the NF concentrate impact to the Rio Grande. The test membrane data was compared with membrane specifications obtained from Osmonics, Inc. These membranes will be referenced as "comparative" membranes in this chapter. Assumptions:

- 10-MGD $(0.438 \text{ m}^3/\text{s})$ water treatment plant
- 60 percent permeate recovery of feed water
- 16.7 MGD $(0.73 \text{ m}^3/\text{s})$ feed to system.
- 6.7 MGD $(0.29 \text{ m}^3/\text{s})$ waste flow
- One-stage nanofiltration system used for treatment
- Six membrane elements per pressure vessel

- Average permeate recovery per element 10 percent
- Feed to each pressure vessel $-60,000 \text{ gpd} (0.0026 \text{ m}^3/\text{s})$
- Comparative Membranes
 - 98 percent rejection of calcium and magnesium
 - 60 percent, 40 percent, 20 percent rejection of sodium
 - 98 percent rejection of sulfate
 - 60 percent, 40 percent, 20 percent rejection of chloride
- Test Membranes at Canal Street Plant (measured values)
 - 92 percent rejection of calcium
 - 90 percent rejection of magnesium
 - 76 percent rejection of sodium
 - 94 percent rejection of sulfate
 - 63 percent rejection of chloride
- Various Rio Grande flows (107, 100, 85 and 50 MGD) 4.69, 4.38, 3.72, 2.19 m³/s)
- Salt concentrations were taken from EPWU database (1936-1995)

The NF test membrane discharge was compared to comparative NF membranes. Mass conservation equations were used to determine flow and concentration to demonstrate the feasibility of a 10-MGD (0.438 m³/s) membrane treatment plant. Assuming an initial flow of 60,000 gpd (0.0026 m³/s) of feed water to each pressure vessel, the impact of NF concentrate to the river can be evaluated under different conditions of the Rio Grande and NF membrane types. Varying sodium rejection rates will help determine the best type of membrane to use and varying the river flows will help determine the impacts on the Rio Grande. NF membranes with 98 percent calcium and magnesium rejection were evaluated with varying sodium rejections of 60 percent, 40 percent and 20 percent. The test NF membrane with 92 percent calcium rejection, 90 percent magnesium rejection and 76 percent sodium rejection was then evaluated for Rio Grande impact. Chloride and sulfate concentrations in the concentrate stream were also evaluated as well as the TDS concentrations.

7.4.1 Membrane Element Flow

A single stage 10-MGD ($0.438 \text{ m}^3/\text{s}$) nanofiltration system with 60 percent recovery was used to illustrate impact on SAR in the river. Since the concentrate would be returned to the river, there was no need to achieve a higher recovery thereby eliminating the need for a second stage. If the permeate flow was 10-MGD ($0.438 \text{ m}^3/\text{s}$), approximately 16.7 MGD ($0.73 \text{ m}^3/\text{s}$) of feedwater was required. Each pressure vessel was assumed to contain six membrane elements. A flow of 60,000 gpd ($0.0026 \text{ m}^3/\text{s}$) to each pressure vessel was assumed. This was based on a reasonable membrane element flux (Osmonics membrane specifications, 1999) and number of pressure vessels. Each element was assumed to have a 10 percent permeate recovery of the feed water.

The following equations were used to determine concentrate flow through the individual membrane elements. Again, 10 percent permeate recovery is assumed for each membrane element. Concentrate flow out of one element is used as feed to the next element.

- Flow to first element: $Q_{1f} = 60,000 \text{ gpd}$
- Flow to second element: $Q_{2f} = Q_{1f} * 0.9$
- Flow to third element: $Q_{3f} = Q_{2f} * 0.9$
- Flow to fourth element: $Q_{4f} = Q_{3f} * 0.9$
- Flow to fifth element: $Q_{5f} = Q_{4f} * 0.9$
- Flow to sixth element: $Q_{6f} = Q_{5f} * 0.9$
- Flow out of vessel: $Q_{endc} = Q_{6f} * 0.9$

This final flow, Q_{endc} , was classified as the system concentrate flow from the pressure vessel. The permeate flow from each membrane element could also be calculated by similar equations.

- Flow from first element: $Q_{1p} = Q_{1f} * 0.1$
- Flow from second element: $Q_{2p} = Q_{2f}*0.1$
- Flow from third element: $Q_{3p} = Q_{3f} * 0.1$
- Flow from fourth element: $Q_{4p} = Q_{4f} * 0.1$
- Flow from fifth element: $Q_{5p} = Q_{5f} * 0.1$

- Flow from sixth element: $Q_{6p} = Q_{6f} * 0.1$
- Flow out of vessel: $Q_{endp} = \Sigma Q_{np}$

The final permeate flow out of the pressure vessel was simply the sum of the entire individual permeate flows from each element. Table 7.3 shows the concentrate and permeates flows as they passed through each element.

	Membrane Elements						
	#1	#2	#3	#4	#5	#6	Product
Flow (gpd)							
Feed Flow	60000	54000	48600	43700	39400	35400	
Permeate Flow	6000	5400	4860	4374	3940	3540	28100
Concentrate Flow	54000	48600	43700	39400	35400	31900	31900

Table 7.3.—Element flow calculations

Table 7.3 shows more concentrate flow than permeate flow out of the pressure vessel. This was without any recirculation of the system concentrate. It can be assumed that at least 25 percent of the flow would need to be recirculated back to the feed of membrane element #1.

7.4.2 Membrane Element Concentrations

Given the initial concentration of salts in the river and membrane rejection rates, permeate and waste concentrations were calculated. The concentration of the individual salts that were rejected from each pressure vessel were calculated using the permeate recovery of each membrane element and salt rejection rates. As feed water traveled through each element, the flow decreased while the salt concentration rose. These concentrations were calculated for each membrane element.

The concentration of salts as the flow passed through each element were defined as follows:

- Concentration to first element:	$C_{1f} = C_f$
- Concentration to second element:	$C_{2f} = ((Q_{1f} * C_{1f}) - (Q_{1p} * C_{1p}))/Q_{2f}$
- Concentration to third element:	$C_{3f} = ((Q_{2f}^*C_{2f}) - (Q_{2p}^*C_{2p}))/Q_{3f}$
- Concentration to fourth element:	$C_{4f} = ((Q_{3f}^*C_{3f}) - (Q_{3p}^*C_{3p}))/Q_{4f}$

- Concentration to fifth element:	$C_{5f} = ((Q_{4f}^*C_{4f}) - (Q_{4p}^*C_{4p}))/Q_{5f}$
- Concentration to sixth element:	$C_{6f} = ((Q_{5f} * C_{5f}) - (Q_{5p} * C_{5p}))/Q_{5f}$
- Concentration out of vessel:	$C_{out} = ((Q_{6f} * C_{6f}) - (Q_{6p} * C_{6p}))/Q_{out}$

As the flow reduced through the pressure vessel, the concentration of salts increased to preserve mass. The final concentration from each pressure vessel was much higher than the original feed concentration but the flow of the concentrate stream was much lower than incoming flow.

7.4.3 Determination of Concentrate Stream Salts

The first step in this evaluation was to determine the final salt concentrations in the concentrate stream. This was done using the mass balance equations described in the previous section. Tables 7.4, 7.5 and 7.6 list final results using average salt concentrations in the Rio Grande as the initial feed concentration. Final salt concentrations out of the last element were listed in the concentrate row because they were accounted for as concentrate and not feed. The test membranes using actual rejection rates were evaluated for Rio Grande impact. Also, different membranes using Osmonics specifications were evaluated for comparison.

7.4.3.1 Comparative Membranes

Specifications from Osmonics Desal-5 Nanofiltration membranes were used for the following calculations. Calcium and magnesium rejections were listed at 98 percent. The sodium rejections used were variable; 60 percent, 40 percent and 20 percent. Sulfate rejections were assumed at 98 percent. Chloride rejections were assumed to be variable with the sodium rejections.

7.4.3.1.1.—Calcium and Magnesium Concentrations

Table 7.4 lists the concentrations for calcium and magnesium as passage was made through the individual membrane elements. Calcium and magnesium rejection rates were assumed to be 98 percent (Osmonics Desal-5 specification, 1999).
	Men	Membrane Elements 98% rejection Ca & Mg							
	#1	#2	#3	#4	#5	#6	Product		
Ca Concentration (mg/L)									
Feed Ca	122	135	150	166	185	205			
Permeate Ca	2.4	2.7	3	3.3	3.7	4.1			
Concentrate Ca	120	133	147	163	181	201	227		
Mg Concentration (mg/L)									
Feed Mg	29	32.2	35.7	39.5	43.8	48.6			
Permeate Mg	0.6	0.6	0.7	0.8	0.9	1			
Concentrate Mg	28.4	31.5	34.9	38.8	43	47.7	53.9		

Table 7.4.—Comparative NF Membrane Concentrations (Ca, Mg)

7.4.3.1.2.—Sodium Concentrations

Table 7.5 lists the sodium concentrations as passage was made through the membrane elements. The table lists the comparison between different sodium rejections. Sodium rejections of 60 percent, 40 percent and 20 percent were evaluated.

	#1	#2	#3	#4	#5	#6	Product
Na Concentration (mg/L)							
60% Rejection							
Feed Na	343	366	390	416	444	474	
Permeate Na	137	146	156	167	178	190	
Concentrate Na	206	220	234	250	266	284	505
Na Concentration (mg/L)				-			
40% Rejection							
Feed Na	343	358	374	391	408	426	
Permeate Na	206	215	225	235	245	256	
Concentrate Na	137	143	150	156	163	171	445
Na Concentration (mg/L)							
20% Rejection							
Feed Na	343	351	358	366	375	383	

Table 7.5.— Comparative NF Membrane Concentrations (Na)

7.4.3.2 Test Membrane Rejections

Table 7.6 lists the calcium, magnesium and sodium concentrations through each membrane element. The rejections are from the test membranes used in the study.

	Membrane Elements							
	#1	#2	#3	#4	#5	#6		
Ca Concentration (mg/L)								
(92% rejection)								
Feed Ca	122	135	148	163	180	199		
Permeate Ca	9.8	10.8	11.9	13.1	14.4	15.9		
Concentrate Ca	112	124	136	150	166	183		
Mg Concentration (mg/L)								
(90% rejection)								
Feed Mg	29	31.9	35.4	39.2	43.5	48.2		
Permeate Mg	2.9	0.6	0.7	0.8	0.9	1		
Concentrate Mg	26.1	31.3	34.7	38.4	42.6	47.3		
Na Concentration (mg/L)								
(76% rejection)								

Table 7.6.—Test NF Membrane Concentrations

7.4.4 Determination of Salt Impact to Rio Grande

The impact of discharging NF concentrate to the river was evaluated using the mass balance equations shown below.

$$\begin{split} Q_{blend} &= Q_{river \ after \ intake} + Q_{concentrate} \\ Q_{river \ after \ intake} &= Q_{river} - Q_{f} \\ C_{blend} &= (Q_{river \ after \ intake} \ * \ C_{river} + Q_{concentrate} \ * \ C_{concentrate})/Q_{blend} \end{split}$$

The blend was considered the addition of the concentrate stream to the river, which was depleted by the intake flow to the water plant. The flow and the concentrations of salts in the river after intake to the plant plus the flow and concentrations of the nanofiltration concentrate were balanced to conserve salt mass and flow. Instantaneous mixing was assumed when the concentrate stream was discharged to the river. The individual salt impact was calculated for the test membranes and the hypothetical membranes. Gaps in data in the following figures indicate drought periods in the Rio Grande where flow was insufficient to sustain a 10-MGD (0.438 m³/s) plant. The gaps in data are from November 1954 to January 1958 and November 1964 to January 1966.

7.4.4.1 Calcium Impact to Rio Grande

Figures 7.10 and 7.11 show the comparison between the test membranes and the comparative membranes for calcium impact to the Rio Grande.

7.4.4.1.1.—Comparative Membranes

Figure 7.10 shows more calcium and magnesium in the river after NF discharge. The calcium concentration in the river rose 10.9 percent

7.4.4.1.2.—Test Membranes

Figure 7.11 shows a calcium increase in the Rio Grande after NF discharge of 10.4 percent.

7.4.4.2 Magnesium Impact to Rio Grande

Figures 7.12 and 7.13 show the comparison between the test membranes and the comparative membranes for magnesium impact.

7.4.4.2.1.—Comparative Membranes

Figure 7.12 shows the magnesium impact to the Rio Grande using the comparative membranes. An 11.3 percent increase in magnesium was calculated after NF discharge.

7.4.4.2.2.—Test Membranes

Figure 7.13 shows the magnesium impact to the Rio Grande using the test membranes. A 10.1 percent increase was calculated in the river after NF discharge.



Figure 7.10.—Calcium Impact to Rio Grande, Comparative Membrane



Figure 7.11.—Calcium Impact to Rio Grande, Test Membrane



Figure 7.12 Magnesium Impact to Rio Grande, Comparative Membrane



Figure 7.13 Magnesium Impact to Rio Grande, Test Membrane

7.4.4.3 Sodium Impact to Rio Grande

Figures 7.14 and 7.15 show the comparison between the test and comparative membranes for sodium impact to the Rio Grande. Each figure shows impact with sodium rejections of 60 percent, 40 percent and 20 percent.

7.4.4.3.1.—Comparative Membranes

Increases in sodium to the Rio Grande of 2.1 percent, 4.1 percent and 4.2 percent were calculated for sodium rejection membranes of 20 percent, 40 percent and 60 percent, respectively. If these sodium increases were compared with the calcium and magnesium impacts, the ratio of sodium to calcium and magnesium was very small. The sodium impact with 20 percent sodium rejection membranes can be seen in figure 7.14

7.4.4.3.2.—Test Membranes

An increase in sodium in the Rio Grande of 8.4 percent was calculated for the test membranes. The ratio of sodium to calcium and magnesium, in this case, was larger due to the higher amount of sodium in the river. This is seen in Figure 7.15.

7.4.4.4 Chloride Impact to Rio Grande

Figures 7.16 and 7.17 show the chloride impact to the Rio Grande for the test membranes, 63 percent rejection, and the comparative membranes, 20 percent rejection.

7.4.4.4.1.—Comparative Membranes

The chloride impact to the Rio Grande was calculated as only 0.2 percent using the 20 percent rejection membranes. This is obvious since 80 percent of chlorides pass into the permeate stream. The impact is seen in Figure 7.16.

7.4.4.4.2.—Test Membranes

The chloride impact with the test membranes increased the concentration 7.2 percent. This can be seen in Figure 7.17.

7.4.4.5 Sulfate Impact to Rio Grande

Figures 7.18 and 7.19 show sulfate impact to the Rio Grande for the test membranes, 94 percent sulfate rejection and the comparative membranes, 98 percent rejection.

7.4.4.5.1.—Comparative Membranes

Sulfate concentrations rose 2.1 percent in the Rio Grande after NF discharge. This is seen in Figure 7.18.

7.4.4.5.2.—Test Membranes

The sulfate concentration in the Rio Grande rose 11.5 percent after NF discharge. This is seen in Figure 7.19.



Figure 7.14 Sodium Impact to Rio Grande, Comparative Membrane



Figure 7.15 Sodium Impact to Rio Grande, Test Membrane



Figure 7.16 Chloride Impact to Rio Grande, Comparative Membrane



Figure 7.17 Chloride Impact to Rio Grande, Test Membrane



Figure 7.18 Sulfate Impact to Rio Grande, Comparative Membrane



Figure 7.19 Sulfate Impact to Rio Grande, Test Membrane

7.4.4.6 TDS Impact to Rio Grande

The TDS impact to the Rio Grande was also evaluated in the same manner as the other salt concentrations.

7.4.4.6.1.—Comparative Membranes

TDS impact was analyzed for membranes with 20 percent sodium rejection. The TDS concentration in the Rio Grande was determined from the other ions already calculated. To maintain electronuetrality, the chloride rejection was assumed to be the same as the sodium rejection, 20 percent. Total dissolved solids was determined from the following equation (Masters, 1991):

$TDS = \Sigma Cations + \Sigma Anions$

The major cations in the Rio Grande are calcium, magnesium and sodium. The major anions are chloride, sulfate and carbonate. Chloride was assumed to have a 20 percent rejection and sulfate a 98 percent rejection. Again, this was to maintain electronuetrality between the ions. Since the sum of the cations must equal the sum of the anions, the individual ions were balanced to determine the carbonate concentration. Once the carbonate concentration was known, the TDS concentration was found. Figure 7.20 shows the TDS impact from the 20 percent sodium rejection comparative membrane. TDS concentrations rose an average 7.8 percent from the original Rio Grande TDS. Although less sodium and chloride was rejected to the river, the calcium and magnesium rejections are very high, 98 percent.



Figure 7.20.—TDS Impact to Rio Grande, Comparative Membrane

7.4.4.6.2.—Test Membranes

Using an average of 85 percent rejection determined from the study, the TDS value in the concentrate stream and the final TDS concentration in the Rio Grande after discharge were calculated. The TDS concentrations were calculated in the same manner as the individual ion concentrations. Table 7.7 lists the TDS concentration through each membrane element. A slight increase in the final concentration from the initial concentration is shown.

Table 7.7 TDS Concentrations by Membrane Element

		Membrane Elements							
	#1	#2	#3	#4	#5	#6	Product		
TDS Concentration (mg/L)									
Feed TDS	1510	1540	1560	1590	1620	1640			
Permeate TDS	1290	1310	1330	1350	1370	1400			
Concentrate TDS	227	231	234	238	242	246	1670		

The TDS impact to the Rio Grande was evaluated using the same mass balance calculations as in the previous section. This impact can be seen in Table 7.8.

	Flow	TDS
	(MGD)	(mg/L)
River	100	1510
	85	1510
	70	1510
	50	1510
River after intake	83.3	-
	68.3	-
	53.3	-
	33.3	-
Concentrate Stream	6.7	1670
River after NF discharge	90	1520
	75	1860
	60	2330
	40	2170

Table 7.8.—TDS Impact to Rio Grande – Test Membrane

Using the EPWU database with these calculations yielded Figure 7.21. The figure shows only a 6 percent increase in TDS concentration to the river. Using these types of membranes, NF concentrate could safely be disposed in the Rio Grande without a negative impact to the river. Again, the gaps in data indicate a drought period.



Figure 7.21.—TDS Impact to Rio Grande, Test Membrane

7.4.5 SAR Impact to Rio Grande

Once the impact from the individual salts has been calculated, the Sodium Adsorption Ratio was calculated to determine the full irrigation impact to the Rio Grande. Table 7.9 lists the final concentrations and SAR in the river after discharge for the hypothetical NF membranes. Various Rio Grande flows were listed. Note that the salt concentrations in the river before and after were the same. The test membranes and comparative membranes can be SAR impacts to the Rio Grande.

7.4.5.1 Comparative Membranes

Table 7.9 shows a decrease of 2.1 percent to 4.3 percent in SAR with flows varying from 40 MGD ($1.75 \text{ m}^3/\text{s}$) to 90 MGD 3.94 m³/s) for membranes with sodium rejections of 20 percent. Membranes with sodium rejections of 60 percent showed an increase in SAR from 0.4 percent to 1.0 percent with flows varying from 40 MGD ($1.75 \text{ m}^3/\text{s}$) to 90 MGD ($3.94 \text{ m}^3/\text{s}$). This table

shows the effects of river flow and membrane sodium rejection have on the SAR. Although the sodium concentrations rose with decreased flow, the calcium and magnesium concentrations increased at a greater rate. If the sodium impact was less than the calcium and magnesium impact, the SAR will decrease. To lower the SAR value, the sodium rejection in the river needed to be low. By applying the equations used for Table 7.9 to the entire database, a graphical comparison of the Rio Grande

				Na		Na		Na	
	Flow	Са	Mg	(60% Rej.)		(40% Rej.)		(20% Rej.)	
	(MGD)	(mg/L)	(mg/L)	(mg/L)	SAR	(mg/L)	SAR	(mg/L)	SAR
River	100	122	29	343	7.24	343	7.24	343	7.24
	85	122	29	343	7.24	343	7.24	343	7.24
	70	122	29	343	7.24	343	7.24	343	7.24
	50	122	29	343	7.24	343	7.24	343	7.24
River	83.3	-	-	-	-	-	-	-	-
after intake	68.3	-	-	-	-	-	-	-	-
	53.3	-	-	-	-	-	-	-	-
	33.3	-	-	-	-	-	-	-	-
Concentrate	6.7	227	53.9	505	7.83	445	6.9	391	6.06
Stream									
River after	90	130	30.9	355	7.27	351	7.18	347	7.09
NF discharge	75	131	31.2	358	7.28	352	7.17	347	7.07
	60	134	31.8	361	7.28	354	7.15	348	7.03
	40	140	33.2	370	7.31	360	7.11	351	6.93

Table 7.9 SAR Calculations – Comparative Membranes

Sodium Adsorption Ratio before discharge was made to the Rio Grande Sodium Adsorption Ratio after discharge. Figure 7.22 shows a SAR comparison between the before and after NF discharges using 20 percent sodium rejection NF membranes. Figure 7.23 shows that an overall decrease in the SAR value occurs when the concentrate stream was discharged to the river.

A 60 percent rejection of sodium yielded an increase of just 0.4 percent of the original river SAR. The 40 percent and 20 percent sodium rejection membranes, however, yielded decreases of 1.0 percent and 2.2 percent in the river's original SAR.



Figure 7.22.—SAR impact to Rio Grande, Comparative Membrane - 20 percent Na rejection



Figure 7.23.—SAR impact to Rio Grande, Comparative Membrane - 40 percent Na rejection

7.4.5.2 Test Membranes

This same calculation can be performed for the test membranes. The rejection rates determined from the study were 92 percent calcium, 90 percent magnesium and 76 percent sodium. Determination of the results from the previous section revealed that the impact to the Rio Grande would be greater than the hypothetical NF membranes. Table 7.10 shows SAR values for different flows. Figure 7.24 shows the SAR impact the test membranes would have on the Rio Grande. The test membranes with 76 percent sodium rejection increased the SAR by 1.9 percent.



Figure 7.24.—SAR impact to Rio Grande, Comparative Membrane - 60 percent Na rejection

		Ca	Mg	Na	
	Flow	(92% Rej.)	(90% Rej.)	(76% Rej.)	
	(MGD)	(mg/L)	(mg/L)	(mg/L)	SAR
River	100	122	29	343	7.24
	85	122	29	343	7.24
	70	122	29	343	7.24
	50	122	29	343	7.24
River after intake	83.3	-	-	-	-
	68.3	-	-	-	-
	53.3	-	-	-	-
	33.3	-	-	-	-
Concentrate Stream	6.7	219	51.4	558	8.81
River after NF discharge	90	129	30.7	359	7.37
	75	131	31.0	362	7.39
	60	133	31.5	367	7.43
	40	138	32.7	379	7.52

Table 7.10.—SAR Results – Test Membranes

7.5 CALCULATIONS OF CALCIUM SULFATE SATURATION

It was assumed in the previous section that the salts, mainly calcium, stayed in solution. It is possible that some calcium could precipitate out of the solution due to oversaturation. Two factors could cause this. The first is that the concentrate stream has a high concentration of salts, calcium concentrations averaged 197 mg/L to 205 mg/L compared to the calcium concentration in the Rio Grande which averages 122 mg/L. The second is that the winter months already have high concentrations of dissolved solids. If calcium sulfate was oversaturated and calcium precipitated out of solution, the actual concentration of calcium in the SAR calculation would be lower and the SAR would be higher which leads to false reports on the NF concentrate impact to the Rio Grande.

A generalized equation describing the equilibrium condition in which a solid dissociates into its ionic components (dissolution) at the same rate that ionic components are recombining into the solid form (precipitation) is given as follows: (Masters, 1991)

Solid $\leftarrow aA + bB$

Where A and B are the ionic components that make up the solid. Applying this to the basic equilibrium equation gives the following:

$$[A]^{a}[B]^{b}/[solid] = K$$

As long as there is still solid present in equilibrium, its affect can be incorporated into the equilibrium constant yielding the final equation:

$$[\mathbf{A}]^{\mathbf{a}}[\mathbf{B}]^{\mathbf{b}} = \mathbf{K}_{\mathbf{sp}}$$

If the product of the ionic molar concentrations is less than the solubility product constant, the solution is undersaturated. If the ionic molar concentration product is greater than the solubility product constant, the solution is supersaturated and precipitation will progress until the ionic concentrations are reduced to equal those of a saturated solution (Viessman and Hammer, 1993).

For calcium sulfate, (Gypsum), K_{sp} is 2 x 10⁻⁵ (Sawyer *et al*, 1994). An example of this calculation can be determined from the January 1995 data point of the EPWU database. In this case, the following data was calculated for the test membranes. The salt concentrations listed are for the river after the concentrate stream discharge.

Ca = 114.7 mg/L $SO_4 = 396.7$ mg/L Molecular weight of calcium = 40 g/mol Molecular weight of sulfate = 96 g/mol Molar concentration = concentration/molecular weight [Ca] = .003M [SO₄] = .001M [Ca] * [SO₄] = 1.79 x 10⁻⁶M

In this case, the product of the ionic molar concentrations (1.79×10^{-6}) is less than K_{sp} , 2 x 10^{-5} which indicates the solution is undersaturated and all ionic components stay in solution. These calculations can be performed for all the data points in the database. The log_{10}

can be taken of the ratio of the molar concentration product to the solubility constant to display the results more effectively. This ratio will either be a positive or negative number. If the solution is undersaturated, the log of the ratio will be negative. If the solution is oversaturated, the log of the ratio will be positive. Continuing the above example, the log_{10} of the ratio is as follows:

> [Ca] * [SO₄]/ K_{sp} 1.79 x 10^{-6} M/2 x 10^{-5} = 8.96 x 10^{-2} log (8.96 x 10^{-2}) = -1.048 which indicates undersaturation.

A graph of the log_{10} of the ratio is shown in Figure 7.25. Figure 7.26 shows that the ionic components of calcium sulfate stay in solution through the entire database and would not precipitate out leading to false SAR calculations.



Figure 7.25.—SAR impact to Rio Grande, Test Membrane - 76 percent Na rejection



Figure 7.26.—Saturation of Calcium Sulfate

There are two possible reasons for calcium sulfate remaining soluble. One is the small amount of flow being released to the Rio Grande as concentrate. The second is Muratic acid was injected into the nanofiltration feed line to minimize scaling. Because of this, the pH levels in the concentrate stream were always below 6.0, which helps to keep ions in solution.

7.6 CALCIUM CARBONATE SATURATION

It could be assumed that there would be no precipitation from oversaturation of calcium carbonate due to acid addition which lowers carbonate concentrations.

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