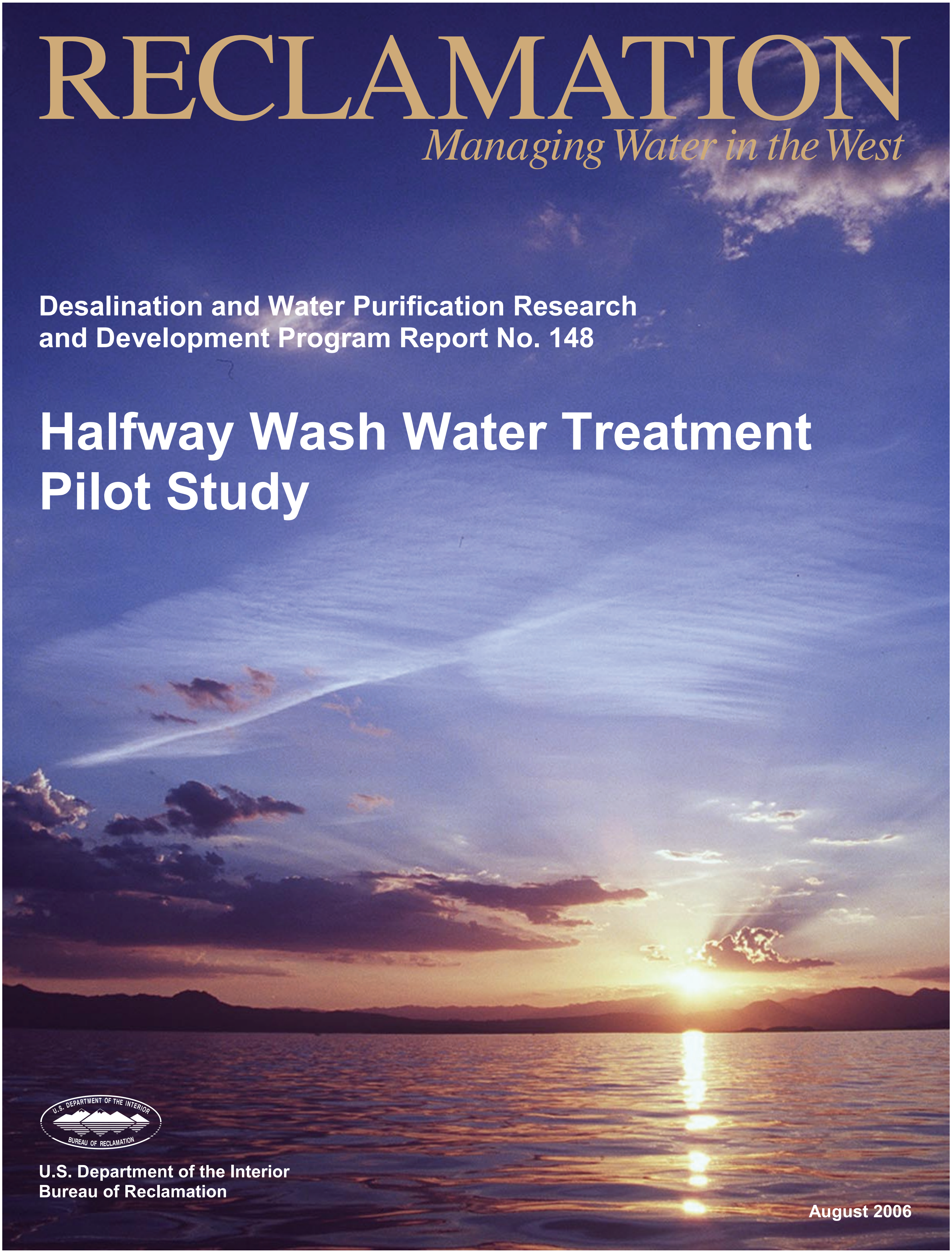

RECLAMATION

Managing Water in the West

Desalination and Water Purification Research
and Development Program Report No. 148

Halfway Wash Water Treatment Pilot Study

U.S. Department of the Interior
Bureau of Reclamation

August 2006

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14. ABSTRACT ***(Maximum 200 words)***

Halfway wash is a bend in the Virgin River near Bunkerville, Nevada, with a current water supply of ground water sufficient to support a population of 50,000 people. The Virgin Valley Water District and the Lower Colorado Regional Office of the Bureau of Reclamation are conducting a study to determine treatment requirements for the Virgin River. The treatment issues are solids, iron, manganese, sulfate reducing bacteria, and sulfate. The subsurface collector provided filtered water from the high solids river flow. Potassium permanganate ($KMnO_4$) addition and ozonation (6 milligrams per liter) were tested for oxidizing iron and manganese. Ozonation was chosen as most reliable and because it also provides disinfection prior to the desalting system. Nanofiltration (NF) and reverse osmosis (RO) were tested sequentially during the pilot test. The following two options for treatment were compared: (1) lime softening, media filtration, antiscalant, RO, with evaporation ponds for concentrate management, and (2) ozonation, dual media filters, antiscalant, RO, seeded precipitation with concentrate recycled to feed and evaporation pond for remainder.

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reverse osmosis, nanofiltration, manganese, ozonation, solids, iron, manganese, drinking water, concentrate, backwash, cost, regulations, survey

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Bureau of Reclamation
Technical Service Center
Environmental Resources Division
Water Treatment Engineering and Research Group
Denver, Colorado

Virgin Valley Water District
Mesquite, Nevada

August 2006

Disclaimer

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- Providing for appropriate commercial use and development of federally managed natural resources in an environmentally sound manner.
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- Working to transfer Federal program operations to tribal governments through Indian self-determination and self-governance agreements.
- Protecting and conserving the trust resources of American Indian and Alaska Native tribes and working with these tribes to enhance education, economic opportunities, and the quality of life for their members.
- Advancing scientific research and monitoring to improve our understanding of the interactions of natural and human systems and to reduce the impacts of hazards caused by natural processes and human actions.
- Providing useful scientific information for sound resource decisionmaking.
- Applying laws and regulations fairly and effectively, placing priority on compliance and enforcement, prevention, and problem solving.

Acknowledgements

We thank the Boulder City Office for their financial support and the Virgin Valley Water District for their dedicated assistance to the project.

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Acronyms and Abbreviations

CG-1	Collector Gallery No.1
DI	de-ionized water
EPA	U.S. Environmental Protection Agency
ft^2	square feet
g	gram
g/ft^2	grams per square feet
g/L	grams per liter
gal/week	gallons per week
HR	high range
kg	kilogram
kgal	1,000 gallons
kPa	kilo pascals—unit of pressure (see metric conversion table)
L	liter
L/min	liters per minute
LMI	brand of chemical feed pump
LR	low range
LSI	langelier saturation index
M	molar
MCL	maximum contaminant level
MDH	Minnesota Department of Health
mg	milligram
mg/L	milligram per liter
Mgal/d	million gallons per day
mL	milliliter
mL/L	milliliters per liter
mS/cm	millisiemens per centimeter—measure of conductivity
mV	millivolt
NF	nanofiltration
NTU	nephelometric turbidity unit

Acronyms and Abbreviations (continued)

ORP	oxidation reduction potential
pH	-Log 10 of hydrogen concentration
ppm	parts per million
psi	pounds per square inch
Reclamation	Bureau of Reclamation
RO	reverse osmosis
SDI	silt density index
SLC	Type of programmable logic controller (PLC) from Allen-Bradley
TCLP	toxic characteristic leaching procedure
TDS	total dissolved solids
VFD	variable frequency drive
VVWD	Virgin Valley Water District
WHO	World Health Organization
µS/cm	microsiemens per centimeter—1/1,000 of a mS/cm, used for product water conductivity; electrical signal from ions in solution
%	percent

Chemical Formulas

$BaSO_4$	barium sulfate
$B(OH)_3$	boron hydroxide
$CaCO_3$	limestone
$C_6H_8O_7$-H_2O	citric acid
CaO	calcium oxide (burned lime)
$Ca(OCl)$	calcium hypochlorite
$Ca(OH)_2$	hydrated lime
$CaSO_4$	calcium sulfate
Fe^{+2}	ferrous ion
H^+	hydrogen ion
HCl	hydrochloric acid
H_2SiO_3	silicate
H_2O	di-hydrogen oxide (water)
K^+	potassium ion
K_2CO_3	potassium carbonate
$KMnO_4$	potassium permanganate
Mn^{+2}	manganese ion
$MnO_{2(s)}$	manganese dioxide solid
$NaOH$	caustic soda, sodium hydroxide
Na_2CO_3	soda ash
Na_2SO_3	sodium sulfite—reducing agent
O_3	ozone
SiO^{-2}	silica oxide

Useful Terms

Acre-foot	Volume to cover 1 acre to 1 foot deep = 325,850 gallons or 1,233.3 cubic meters (m^3).
Alkalinity	The ability of a water to neutralize acidity due to the presence of carbonate, bicarbonate, and hydroxide ions.
Antiscalant	Synthetic polymeric solution designed to prevent crystallization of slightly soluble salts.
Argo Analyzer	GE-Betz's antiscalant prediction software.
Backwash	Flushing media filters at higher rate in the reverse direction to normal operation; often includes bursts of air to help loosen accumulates.
Bio-fouling	Accumulation of biological material on a membrane surface.
Buffering	Capacity for a solution to resist changes in composition, especially changes in pH.
Citric Acid	Chelating acid found in citrus fruits.
Clearwell	Reservoir for storing pretreated water prior to desalination.
Concentrate	Retained portion of a desalination process stream containing salts from the product stream.
Conductivity	Electrical conductance of ionized salts in solution to indicate concentration.
Desalination	Process to remove salt from water.
Element	One membrane module.
FerroVer®	Reagents for detecting iron concentration.
Flocculation	Gentle stirring or agitation to accelerate agglomeration of particles to enhance settling or floatation.
GE Water	Previously osmonics, total water treatment system provider.
Greensand	Sand media coated with manganese dioxide used to catalyze oxidation of manganese oxide and iron oxide.
Hypersperse	Antiscalant.
Jar Test	A test procedure using lab glassware for evaluating coagulation, flocculation, or sedimentation in a series of parallel comparisons.
Membrane	Semipermeable thin film, in this case, used to separate pure water from salt water.

Useful Terms (continued)

Permeate	Portion of water that has passed through a semipermeable membrane; product water from a membrane desalination process.
Rapid Mix	Tank with flash mixer for quickly mixing in chemicals.
Recovery	Ratio of product water to feed water given as a percentage.
Rejection	Degree to which desalination process excludes dissolved materials.
Rotometer	Physical device for measuring flow rate using the mass of a ball suspended in the up-flow current through a graduated clear tube to indicate flow rate.
Scale	Accumulation of precipitated salts on the membrane surface—usually occurring in the second stage.
Sparging	Blasts of air used to create turbulence in cleaning and backwashing.
Stage	A set of parallel vessels receiving feed flow from the same source.
Supersaturated	Salt solution at greater than equilibrium concentration—unstable.
Vessel	A pressure tube holding up to seven membrane elements in series.

SI Metric Conversions

From	To	Multiply by
ft	M	3.048 000 E-1
in	M	2.540 000 E-2
ft^2	m^2	9.290 304 E-2
Kgal	m^3	3.785 412
Mgal	m^3	3.785 412 E+3
acre-feet	m^3	1.233 489 E+3
lb/in^2	kPa	6.894 757
ºF	ºC	=(tf-32)/1.8

1. Executive Summary

Halfway wash is a bend in the Virgin River near Bunkerville, Nevada, a suburb of Mesquite. The area is a freeway hour northeast of Las Vegas on Interstate 15. Mesquite is one of the fastest growing communities in the State of Nevada. Their current water supply is ground water, sufficient to support a population of 50,000 people. The current population is about 16,000 and is expected to double by 2010. For long-term water supply planning, the Virgin Valley Water District (VVWD) and the Lower Colorado Regional Office of the Bureau of Reclamation are conducting a study to determine treatment requirements for the Virgin River.

The treatment issues are solids, iron, manganese, sulfate reducing bacteria, and sulfate. The pilot project was conducted at VVWD Collector Gallery No. 1 in Bunkerville. The subsurface collector provided filtered water from the high solids river flow. Potassium permanganate ($KMnO_4$) addition and ozonation (6 milligrams per liter) were tested for oxidizing iron and manganese. Ozonation was chosen as most reliable and because it also provides disinfection prior to the desalting system. Nanofiltration (NF) and reverse osmosis (RO) were tested sequentially during the pilot test.

Maximum recovery possible for this feed water was 50 percent (%). Calcium sulfate scaling occurs above 55% even with antiscalant. With the severe water shortages in the area, this level of recovery is not acceptable. Methods for removing sulfate are ion exchange, lime softening, or seeded precipitation of the RO concentrate. An exploratory estimate for ion exchange was prohibitively high ($5 per kilogallons [/kgal] for the resin). Two options for treatment are compared here:

Option 1: Lime softening, media filtration, antiscalant, RO, with evaporation ponds for concentrate management.

Option 2: Ozonation, dual media filters, antiscalant, RO, seeded precipitation with concentrate recycled to feed and evaporation pond for remainder.

The options have comparable construction costs, but the final water cost for option 2 is $1/kgal as opposed to $1.25 for option 1. Potential problems with option 1 are: carryover from the lime feed through media filters; difficult sludge settling due to the combination of iron and manganese hydroxides with the sulfates; and potential carbonate scaling due to the increase in pH from lime addition.

Further pilot testing will be necessary for option 2 to determine the retention time for the seeded precipitation process and rejection rate of boron at the higher concentration that will be attained by recycling concentrate.

2. Introduction

2.1 Purpose and Scope

The purpose of the project is to compare and evaluate treatment methods for surface water obtained from the Virgin River to bring it up to Safe Drinking Water Standards for municipal use. Surface water from the Virgin River is generally nonpotable. During low flows, the total dissolved solid (TDS) concentrations increase to well over 2,000 milligrams per liter (mg/L). The Bureau of Reclamation (Reclamation) developed a test plan, supplied equipment and expertise in setting up and monitoring pilot tests, and developed cost estimates for full-scale treatment alternatives. Virgin Valley Water District (VVWD) performed site development and conducted day-to-day operations of the pilot treatment plant.

2.2 Background

Mesquite, Nevada, is one of the fastest growing communities in the State of Nevada, and is located off Interstate 15, near the borders of Arizona and Utah, approximately 80 miles northeast of Las Vegas (see figure 1 for location). Since its incorporation in 1984, the population has grown from 1,270 to approximately 15,000. The VVWD, founded in 1993, supplies potable water to the communities of Bunkerville and Mesquite, which are located in the designated service area. Currently, the potable water source is from ground water with production wells which have a pumping capacity of 17.5 million gallons per day. The current permitted ground water allocation from the Nevada Division of Water Resources, for use by VVWD, is approximately 12,000 acre-feet per year. This is anticipated to be sufficient to support an estimated population of 50,000 people (Ball, 2002). To accommodate the increased water demand, VVWD is evaluating the potential to treat the Virgin River to potable standards as a future water resource option.

The pilot filtration project was conducted at the VVWD facility designated Collector Gallery No.1 (CG-1), located in Bunkerville, Nevada (see figure 2). CG-1 is a prototype subsurface diversion to potentially use decreed Virgin River water rights associated with Bunkerville Irrigation Company. Filtration is necessary because of the high sediment transport associated with the Virgin River.

2.3 Contaminants of Concern

Components of the water analysis used in planning the treatment tests are listed in table 1. Shaded cells are at a level above Nevada's maximum concentration limit (MCL) and U.S. Environmental Protection Agency's (EPA) secondary drinking water limits. None of the tested components exceed EPA's primary drinking water limits.

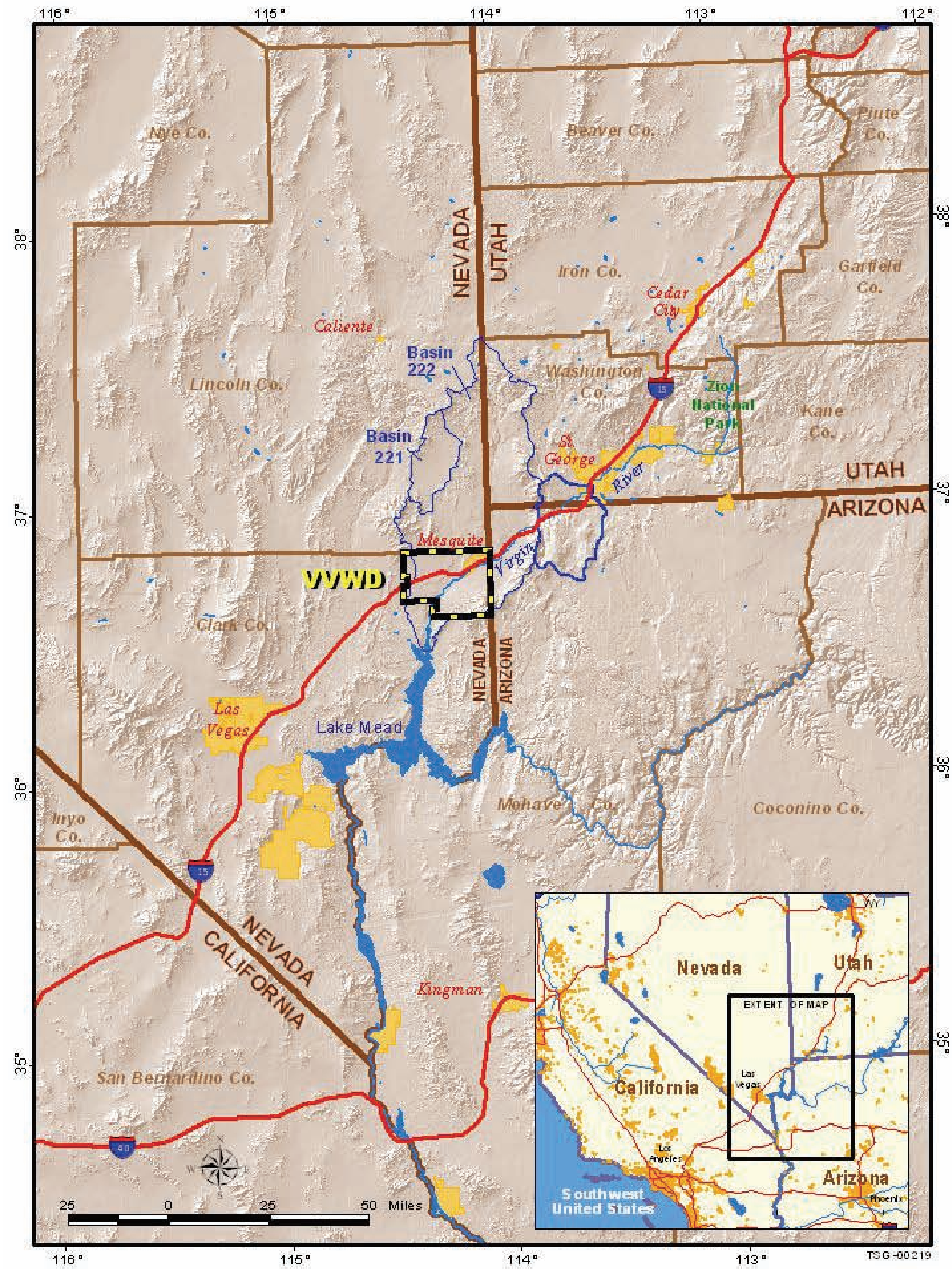

Figure 1. Location of Mesquite, Nevada, and the Virgin Valley Water District.

Figure 2. Location of Pilot Site in Bunderville, Nevada.

2.3.1 Iron and Manganese

Iron and manganese cause poor taste, brown stains on fixtures, sidewalks, and clothes. It tends to oxidize rapidly on exposure to air, leaving particulates in the water that clog pipes.

2.3.2 Magnesium and Chloride

Magnesium and chloride can lead to high blood pressure. Excessive amounts in drinking water make it difficult for people to limit their intake without using point of use reverse osmosis (RO) systems. These systems are very inefficient; for conservational purposes, it is better to serve water with lower levels of these components to the distribution system.

2.3.3 Boron

Though there is no MCL for boron, it is a concern in drinking water and in irrigation water for certain crops.

2.3.4 Sulfate

Sulfate causes problems with hardness. It precipitates in the soil when used for irrigation and causes diarrhea when used for drinking. Detergents do not work as well in water with high sulfate content leading to greater use of detergents and a greater load on the waste water treatment system.

Table 1. Analysis for CG-1 with Regulatory Limits

Analyte Name	EPA Primary Standard	EPA 2nd Standard	Nevada 2nd Standard	CG-1	Units	RL	Method	Analysis Date
pH		6.5 – 8.5	6.5-8.5	7.46	pH Units	2	EPA 150.1	6/25/2002
Aluminum		0.05 – 0.2		ND	mg/L	0.025	EPA 200.7	6/25/2002
Arsenic	0.010		0.05	0.0106	mg/L	0.025	EPA 200.7	6/25/2002
Barium	2		2	0.029	mg/L	0.003	EPA 200.7	6/25/2002
Beryllium	0.004		0.004	ND	mg/L	0.003	EPA 200.7	6/25/2002
Boron				1.6	mg/L	0.05	EPA 200.7	6/25/2002
Cadmium	0.005		0.005	ND	mg/L	0.002	EPA 200.7	6/25/2002
Calcium				490	mg/L	25	EPA 200.7	6/25/2002
Chromium	0.1		0.1	ND	mg/L	0.005	EPA 200.7	6/25/2002
Copper	1.3	1.0	1	ND	mg/L	0.002	EPA 200.7	6/25/2002
Iron		0.3	0.6	3.8	mg/L	0.05	EPA 200.7	6/25/2002
Magnesium			150	180	mg/L	0.25	EPA 200.7	6/25/2002
Manganese		0.05	0.1	0.94	mg/L	0.003	EPA 200.7	6/25/2002
Nickel			0.1	ND	mg/L	0.02	EPA 200.7	6/25/2002
Potassium				40	mg/L	1	EPA 200.7	6/25/2002
Silver		0.1		ND	mg/L	0.005	EPA 200.7	6/25/2002
Sodium				460	mg/L	25	EPA 200.7	6/25/2002
Zinc		5	5	ND	mg/L	0.05	EPA 200.7	6/25/2002
Chloride		250	400	610	mg/L	50	EPA 300.0	6/26/2002
Nitrate, as N	10		10 as (N)	ND	mg/L-N	2	EPA 300.0	6/20/2002
Sulfate		250	500	1,600	mg/L	50	EPA 300.0	6/26/2002
Bicarbonate as $CaCO_3$				200	mg/L	25	SM 2320 B	6/27/2002
Carbonate as $CaCO_3$				400	mg/L	25	SM 2320 B	6/27/2002
Hydroxide as $CaCO_3$				0	mg/L	25	SM 2320 B	6/27/2002
Total Alk as $CaCO_3$				400	mg/L	25	SM 2320 B	6/27/2002
Specific Conductance				4,600	µS/cm	1	SM 2510 B	6/28/2002
Total Dissolved Solids		500	1,000	3,910	mg/L	30	SM 2540 C	6/25/2002
Fluoride			2	0.78	mg/L	0.4	SM 4500-F C	6/24/2002
Total Phosphorus				0.035	mg/L	0.01	SM 4500Si-D	6/26/2002
Silica				22	mg/L	1	SM 4500Si-D	6/25/2002

2.3.5 Total Dissolved Solids

EPA's secondary MCL for TDS is 500 mg/L though Nevada has a higher limit of 1,000 mg/L. It is desirable to have lower TDS because of taste problems, salting out of land irrigated with high TDS waters. More water is required for drinking and irrigating when the TDS is higher.

3. Pilot Test Objectives

The pilot study objective was to determine the most economical and efficient option to produce water with a TDS concentration of 700 mg/L, which is the approximate TDS concentration of water supplied by the VVWD distribution system, or a concentration of 350 mg/L to use as a drinking water source. Either RO could be used to produce high quality water to blend with existing potable source, or nanofiltration (NF) could be used to produce the target water quality. The advantage of NF is that it can operate at a lower pressure and should then have a lower power cost than an RO system. However, since the RO product can be blended with well water, a smaller system would be required to produce the same capacity. Both processes have the same pretreatment requirements; however, depending on the blend ratio and water composition, the post treatment requirements could be less for NF than for RO.

3.1 Pretreatment

The objective of pretreatment for a desalination system is to produce water with turbidity less than 0.1 nephelometric turbidity unit (NTU), and a silt density index (SDI) less than three (3) that will produce concentrate stable enough to reach the concentrate tank before precipitating. The existing collector well operated by VVWD Ranney well does an excellent job of removing solids from the river; however the iron and manganese begin to precipitate shortly after contact with air. We also found that there were sulfate reducing bacteria present in the water that had not been included in the water analysis. Bacteria would cause fouling problems for the desalting system. For these reasons, it was necessary to add a step to disinfect and remove iron and manganese as pretreatment. Two oxidation methods were tested with coarse media filtration and greensand filtration: potassium permanganate ($KMnO_4$) oxidation, and ozonation. $KMnO_4$ reacts in water with manganese ion and iron according to the following reaction:[1]

$$3\ Mn^{+2} + 2\ KMnO_4 + 2H_2O \leftrightarrow 5\ MnO_{2(s)} + 2\ K^+ + 4\ H^+$$

Greensand is a media coated with manganese dioxide. It provides effective filtration and also controls under- and over-dosing of $KMnO_4$ which would turn the water pink. Manganese dioxide is insoluble over the entire pH range of interest in drinking water treatment. The stoichiometric ratio for manganese and iron oxidized with permanganate is:

1.9 mg/L $KMnO_4$ per mg/L of Mn^{+2} removed and

0.9 mg/L $KMnO_4$ per mg/L of Fe^{+2} removed.

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[1] Definitions of chemical formulas are listed in the front of the document under "Chemical Formulas."

The manganese ion adsorbs to manganese dioxide particles which catalyzes further oxidation. If the manganese is tied up with organic matter, then the reaction will be slower. The solution to this problem is to raise the pH to 8.5 (Degrémont, 1991).

Ozone reacts with manganese and iron in much the same way:

$$O_{3(g)} + Mn^{+2} + H_2O \leftrightarrow 2\ MnO_{2(s)} + O_2 + 2\ H^+$$

$$0.9\ \text{mg/L}\ O_{3(g)}\ \text{is required per mg/L of}\ Mn^{+2}\ \text{or}\ Fe^{+2}$$

Ozonation of manganese must be carefully controlled to prevent over oxidation to MnO_4 which will give the water a pink color.

Table 2. Oxidizing Potential of Various Reagents[1]

Oxidizing Reagent	Oxidizing Potential
Ozone	2.07
Hydrogen peroxide	1.77
Permanganate	1.67
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine gas	1.36
Hypobromous acid	1.33
Oxygen	1.23
Bromine	1.09
Hypoiodous acid	0.99
Hypochlorite	0.94
Chlorite	0.76
Iodine	0.54

[1] Source: http://www.ozoneapplications.com/info/oxidizing_potential_of_ozone.htm.

3.2 Disinfection

Disinfection will be required as part of the pretreatment and also as post treatment if the water will be used for drinking. RO and NF membranes to be tested were not compatible with oxidants. Polyamide thin film composite membrane is either completely intolerant of oxidation or can withstand 1,000 ppm hrs.[2] This means that they can handle the equivalent of 1 mg/L of free chlorine for 1,000 hours, or 2 mg/L for 500 hours. Residual manganese dioxide or ozone would have the same effect. Table 2 lists the oxidation potential of various oxidants. Ozone is

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[2] ppm hrs is mg/L * hours. If the membrane can withstand 1,000 ppm-hrs, then you can expose it to 1,000mg/L for 1 hour or 1 mg/L for 1,000 hours—supposedly with the same result.

most effective but would degrade membranes at twice the rate as free chlorine. To some extent, excess permanganate and ozone would be reduced in the greensand filter. One of the goals of the pretreatment test was to determine the oxidation potential of the pretreatment process effluent, whether this residual would degrade the membranes, and whether it would protect the membrane system from bio-fouling.

3.3 Desalination

The objectives of the desalination tests were to determine the maximum recovery rate attainable with antiscalant, the cleaning frequency, and cleaning efficacy. NF and RO membranes were tested to evaluate energy requirements and the nature of the concentrate stream with NF. RO retains most all salts while NF is more selective. The retention rates for individual ions depend on the mixture.

3.4 Stabilization

The membrane product water must be stabilized before distribution. The product water is very well defined by a water analysis; so it is possible to get a good idea of the stabilization requirements from chemistry models and the composition of the blend water. Options for stabilization additives are caustic soda, soda ash, lime, calcium hypochlorite, or hydrated lime.

3.5 Concentrate Management

The concentrate from the desalination process will have at least twice as much dissolved salt as the feed water. It will be supersaturated in slightly soluble sulfate salts. Options for management include transport to the waste water treatment plant evaporation ponds. Higher recovery, and thus smaller concentrate volume, can be attained by precipitating the sulfate and recycling the concentrate to the feed for the desalination process. Part of the pilot study will evaluate the feasibility of precipitating the concentrate with calcium sulfate and with barium sulfate. The later process may enable harvesting of barium sulfate that can be sold as drilling mud. Likewise, there is a market for calcium sulfate for producing wall board and for water treatment.

4. Pilot Test Description

4.1 Site Preparation and Pilot Plant Equipment

Reclamation's Mobile Water Treatment Pilot Plant was used at the Bunkerville well site for the field testing described in this report. This pilot plant incorporates skid-mounted equipment to test many unit treatment processes, including chemical precipitation, oxidation (ozone, permanganate), pressure clarification, greensand filtration, and membrane separation. Most of the process equipment is controlled using an Allen-Bradley SLC 500 programmable controller, and provisions are included for automatic data acquisition from the membrane separation process. Data acquisition for this test program was performed using the automatic data acquisition system with manual readings recorded once per day.

Figure 3 presents a schematic diagram of the treatment processes that were tested at the Bunkerville well site.

- $KMnO_4$ (potassium permanganate) oxidation followed by manganese–greensand filtration followed by antiscalant addition and membrane separation
- Ozone oxidation followed by manganese-greensand filtration followed by antiscalant addition and membrane separation
- Membrane separation was tested in two modes using NF membranes for the first test and RO membranes for the second
- Post-chlorination was not included in the testing, but would be incorporated as part of the prototype treatment plant.

Figure 4 shows the membrane separation schematic. Figures 5 and 6 are the actual layout of the trailer, tanks, and exterior skids at the well site. All process effluent and drain flows were directed to a drain ditch outside of the well site.

4.2 Process Selection

Potassium permanganate was selected as the oxidation chemical at the start of testing. However, it was not possible to oxidize enough of the manganese with a reasonable dose. The reaction goes more quickly at a pH of 8.5 if the manganese and iron are tied up with organic matter. Sodium hydroxide was used to raise the pH in a jar test to determine whether $KMnO_4$ could be effective at the higher pH, but the buffering capacity of the feed water is too high to allow pH adjustment with a reasonable amount of base.

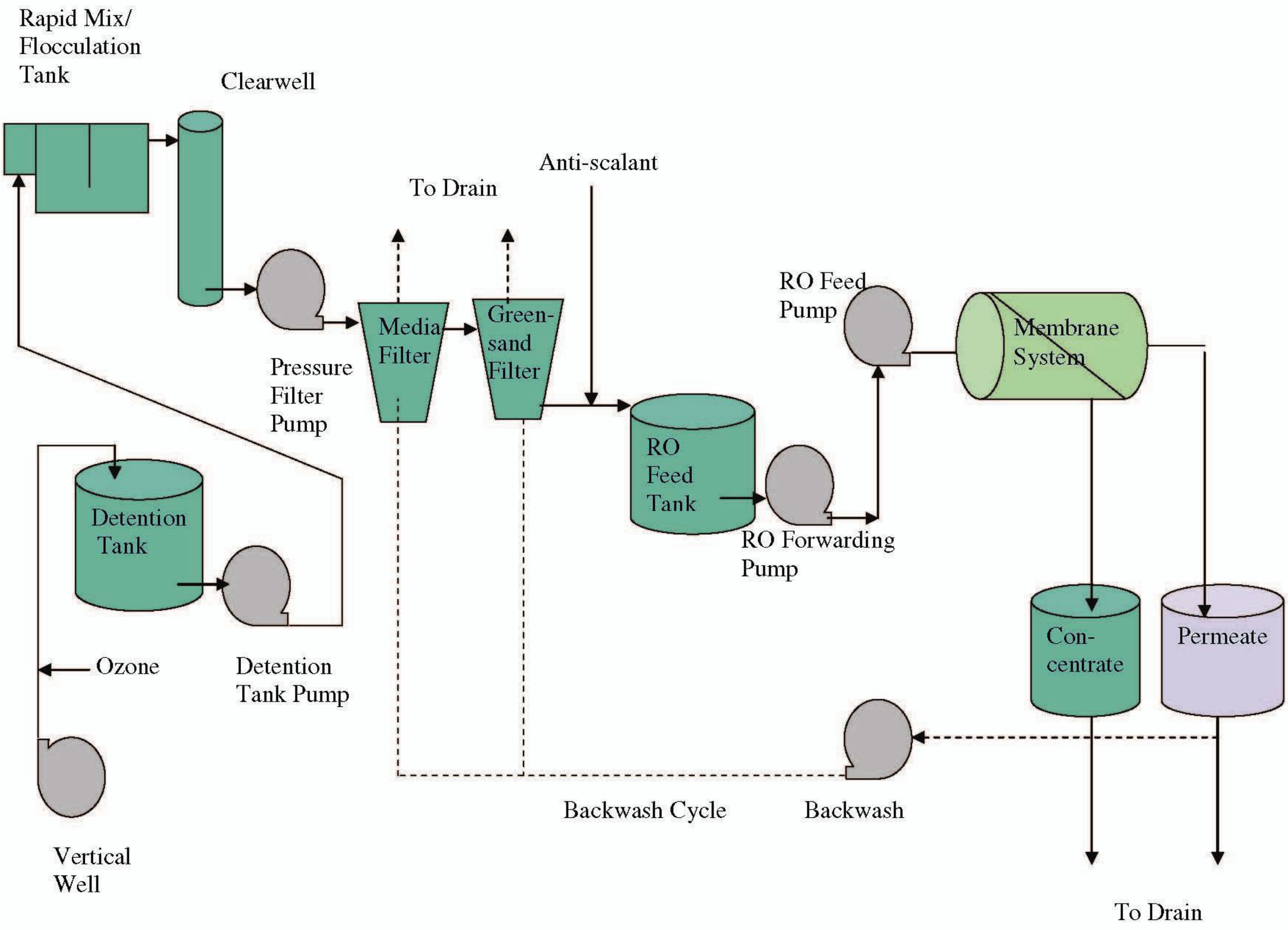

Figure 3. Mobile Treatment Plant Unit Operations, Virgin Valley Water District.

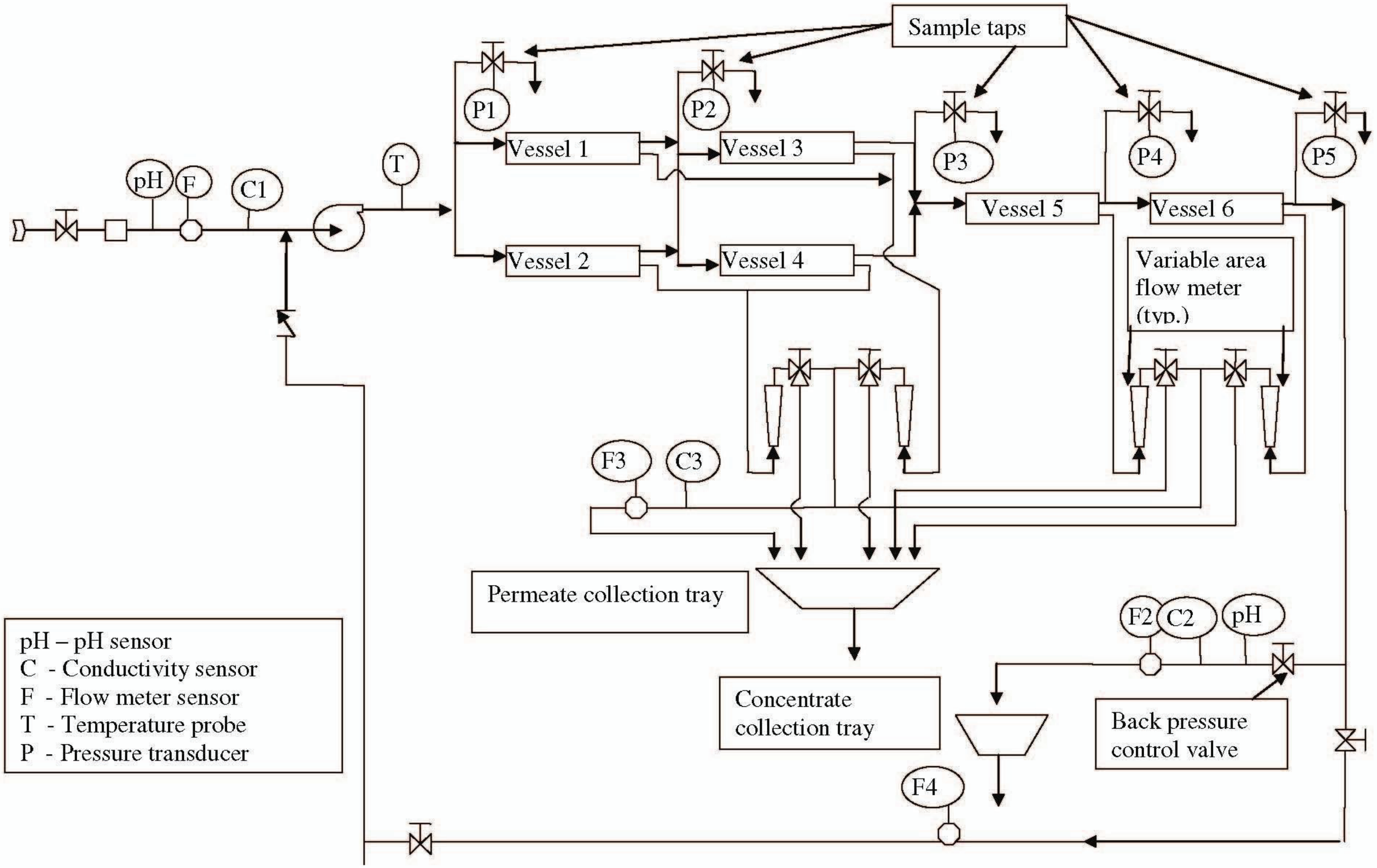

Figure 4. RO Skid Process Diagram.

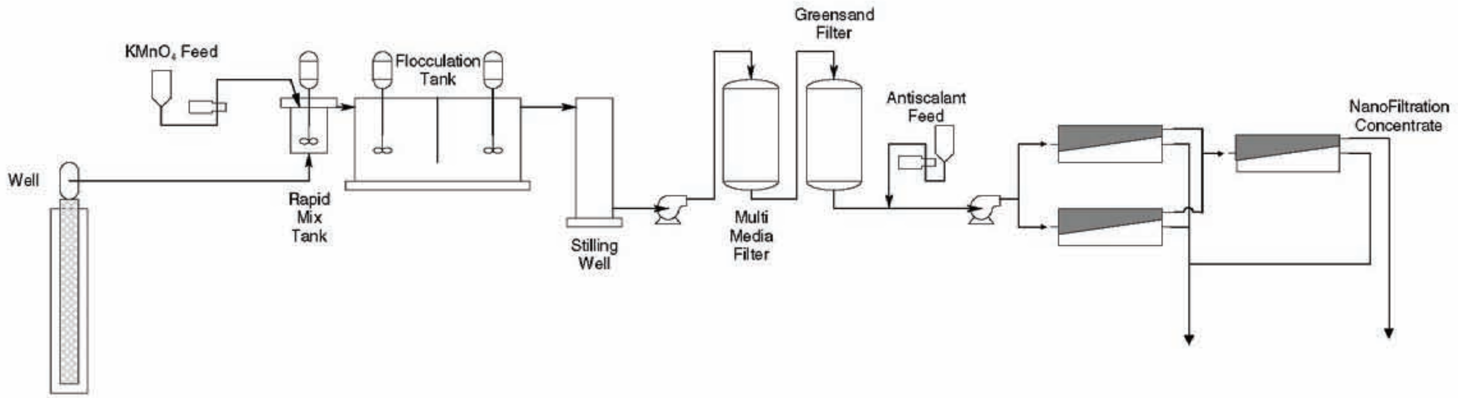

Figure 5. Potassium Permanganate Pretreatment.

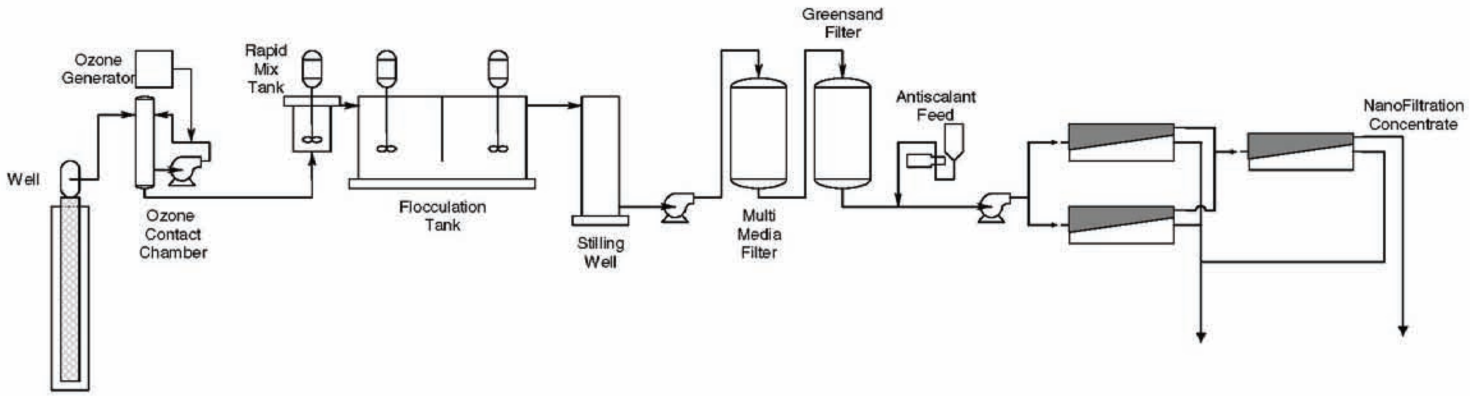

Figure 6. Ozonation/Filtration Pretreatment.

An ozone generator and contact chamber was brought to the site with the plan that ozone would also kill any bacteria in the feed water while oxidizing iron and manganese. If the ozone was not consumed adequately to protect the membranes, sodium sulfite could be added in-line ahead of the RO feed tank.

Coarse granular media and greensand media were used for filtration after the ozone contact chamber.

RO and NF membranes were chosen for the desalination system. GE Water's modeling program, Winflows, was used to predict recovery and rejection. Maximum recovery with antiscalant was estimated at 65 percent (%) however, scaling problems in the second stage indicated that this was too high. The second stage was taken out of operation, and the system was operated successfully at 50% recovery with two banks of six elements in each series.

Hypersperse 2020 MD was used as an antiscalant at a dose rate of 6 mg/L as recommended by GE Betz.

4.3 Test Procedures

4.3.1 Pretreatment

The first task was to stabilize the pretreatment system. The objective was to lower manganese concentration to less than 0.1 mg/L and iron to less than 0.05 mg/L. Jar tests were performed to determine the dose rate necessary to attain the objective with the 10-minute retention time built into the pilot system. A Hach DR2500 Laboratory Spectrophotometer was used to determine concentration of manganese and iron with Hach Method 8149 for Manganese LR (0.007–0.700 mg/L), Method 8034 for Manganese HR (0.2–20 mg/L), and Method 8008 FerroVer® Method (0.02–3.00 mg/L) for iron.

Jar tests performed to precipitate iron and manganese were:

- $KMnO_4$
- $KMnO_4$ at pH to 8.45 and 8.7 with potassium carbonate
- Aeration with $KMnO_4$
- Sodium hydroxide pH adjustment with $KMnO_4$

Pretreatment system was operated according to best jar test results with and without pH adjustment to determine additional benefit of granular media and the greensand media. SDI and turbidity were measured to determine if the system was meeting the goals of less than 3 and 0.1, respectively.

Ozonation system was installed, set up, and evaluated for achievement of pretreatment goals.

Pretreatment effluent was monitored for manganese, iron, oxidation-reduction potential (ORP), turbidity, and SDI every day.

4.3.2 Barium Sulfate Harvesting

A separate study was performed by Environmental Remedies. The complete report is included as "Appendix I, Barium Chloride Pretreatment Study." Barium chloride was added to the feed water to precipitate barium sulfate. The precipitate was washed with weak acid and product water to render pure barium sulfate. A toxic characteristic leaching procedure (TCLP) was performed on the resulting precipitate to analyze for barium. The precipitate must pass the TCLP to be classified as nonhazardous.

4.3.3 Desalting System

RO and NF were tested sequentially. First Filmtec NF90-2540 NF membranes were loaded. A record was kept of the serial numbers and locations of each element. RO membranes were tested for 3 months until January. Then Hydranautics XLFC1-2540 RO membranes were loaded. Operational data was collected automatically every 30 minutes. Manual readings were recorded once per day as a backup and instrument check as shown in table 3.

4.3.4 Cleaning

The membranes were cleaned once during the test with citric acid to determine the ability of the recommended cleaning solution to return the system to normal.

4.3.5 Concentrate Management

Jar tests were performed to determine the time necessary to precipitate the super-saturated calcium sulfate. Detailed procedures are supplied in "Appendix II, Calcium Sulfate Seeding Procedures for Precipitating Nanofiltration and Reverse Osmosis Concentrate." Known quantities of calcium sulfate were added to 2-liter samples of concentrate. Sulfate concentration was measured at intervals.

Table 3. Mobile Treatment Plant Unit Operations, Virgin Valley Water District

Virgin River Halfway Wash Treatment Study
Data Sheet

Date:	7/21/2003					
Time:	12:00 PM					
Process Data			RO System			
Pressure Clarifier Pressure:		psi[1]		PF Inlet		kPa[2]
Greensand Filter Pressure:		psi		PF Outlet		
Raw Water				P1		
Manganese Conc:		mg/L	Pressure Gauges	P2		
Iron Conc:		mg/L		P3		
Greensand Effluent				P4		
Manganese Conc:	0.27	mg/L		P5		
Iron Conc:	0.05	mg/L				
				Perm 1&2		L/min[3]
SDI	1.97		Rotometer Flow	Perm 3&4		
				Perm 5		
Turbidity	0.2	NTU		Perm 6		
Conductivity	4,850	uS/cm[4]		Feed Cond		mS/cm[5]
pH	7.36		Conductivity	Perm		uS/cm
Temp	22.2	°C[6]		Conc		mS/cm
ORP	252					
				Perm		L/min
Notes			Flow	Recycle		
				Conc		

[1] psi = pounds per square inch.
[2] kPa = kilopascal.
[3] L/min = liter per minute.
[4] uS/cm = microsiemens per centimeter.
[5] mS/cm = millisiemens per centimeter.
[6] °C = degree Celsius.

5. Pilot Test Results and Conclusions

5.1 Pretreatment

Pretreatment was optimized during the month of June 2003. Jar tests were followed by pilot system tests to validate the jar test results. Adjustments were made as necessary to optimize performance. Test backwashes were run to determine attainable flow rates for the system configuration. Some of the hoses had to be shortened and fittings enlarged to cut down the friction loss in the backwash system.

5.1.1 $KMnO_4$ Dosing

Manganese proved difficult to remove consistently with permanganate. The precipitate did not settle in the jars, and the measurement process would re-dissolve the manganese dioxide such that the unfiltered result would have more manganese than the feed water. To solve this problem and more closely simulate filtration, a sample from each jar was filtered after 10 minutes with a 45-micron filter before analyzing for manganese. Jars that had a pink tint were not tested, since the pink color means that there is un-reacted permanganate solution. Results are shown in table 4. The theoretical dose for 1.1 mg/L of manganese is 2 mg/L $KMnO_4$, as indicated by the optimum result for the jar test of between 1.5 and 2.3 mg/L.

Table 4. $KMnO_4$ Jar Test Results

Jar Number	1	2	3	4	5
$KMnO_4$ mg/L	0	1.5	2.3	2.5	3
Appearance after 10 min.	Cloudy brown	Brown	Brown	Orange	Pink
Mn^{+2} mg/L	1.1				
Mn^{+2} mg/L after filtration	0.6	0.1	0.1		

5.1.2 $KMnO_4$ with Potassium Carbonate pH Adjustment

To attempt to reduce the concentration below 0.1 mg/L, a pH adjustment titration was performed using potassium carbonate buffer from the pool maintenance department of the local hardware store. This was only to determine if a higher pH would allow a greater precipitation of manganese and iron. If so, then sodium hydroxide would be used for the pH adjustment. Table 5 gives the results for the pH adjusted jar test. The low range (0.007–0.7 mg/L) manganese method was used for the jars with more brown color that indicated positive results in previous jar tests, but these results did not correspond to those obtained from the high range (0.2–20.0 mg/L) method.

Table 5. Manganese Precipitation at pH 8.48 and 8.7 with a Range of $KMnO_4$ Doses

Jar Number	1	2	3	4	5	6
Starting pH	7.08	7.08	7.08	7.08	7.08	7.08
Volume (L)[1]	2	2	2	2	2	2
KCO_3 (mL)[2]	1.1	1.1	1.1	1.8	1.8	1.8
Adjusted pH	8.48	8.48	8.45	8.7	8.7	8.77
$KMnO_4$ (mg)[3]	2	2.4	2.6	1	1.5	2
ORP	410	424	435	342	411	431
Final pH	8.41	8.43	8.4	8.73	8.67	8.68
Filtered Mn HR[4]			0.2	0.3	0.5	0.4
Mn LR	0.318	0.361	0.582			

[1] L = liter.
[2] mL = milliliter.
[3] mg = milligram.
[4] Raw water has 1.1 mg/L Mn^{+2}; filtered water with no other treatment has 0.6 mg/L.

If we assume that the low range method (LR) is more accurate than the high range method (HR), a greater reduction in manganese can be achieved at a lower pH of 8.4 than at a slightly higher pH of 8.7. The pilot pretreatment system was operated accordingly beginning on June 20, 2003. However, the pH could not be raised higher than 7.9 in the pilot scale unit as measured at the flocculation tank. After the green sand filter, the pH had fallen to 7.4; and the effluent still contained 1.3 mg/L manganese. Since there was no more potassium carbonate in town, further attempts were postponed until some sodium hydroxide could be obtained.

5.1.3 Sodium Hydroxide pH Adjustment

A titration test was performed to determine the dose of sodium hydroxide necessary to adjust the pH to 8.5 for optimum manganese oxidation. At least 55 milliliters per liter (mL/L) of 0.05 molar (M) NaOH was required, as shown in figure 7, corresponding to a NaOH feed rate of 2.75 grams per liter (g/L) for the pilot test or about 4 kilograms (kg) per day. This chemical demand is too high to be practical. Sodium hydroxide does not mix well with water. It comes as pellets that cause an exothermic reaction in water. If too many pellets are added to the vessel at once, the mass coalesces into a rock of sodium hydroxide. We decided to try ozonation instead.

5.1.4 Ozonation

The ozone system was brought online in August 2003. Ozone level was gradually increased until iron and manganese levels were at or near the target. Samples were collected after the greensand filter. ORP levels were measured after the RO feed tank to determine if ozone quenching would be needed. The

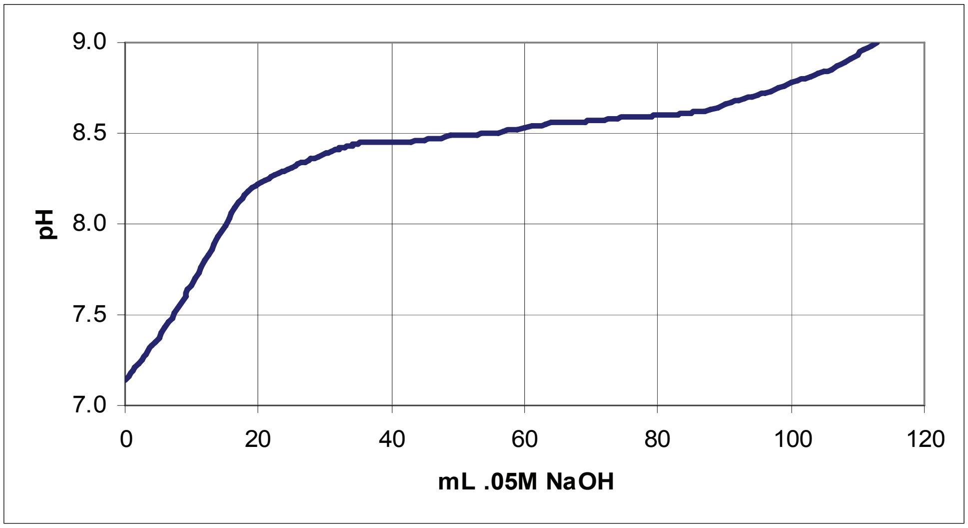

Figure 7. Adjustment of pH with Sodium Hydroxide.

manufacturer's technical representative said that it should be close to neutral ORP before the membranes, but he was not sure. The unit was run at its maximum output level which would result in a dose of 6 mg/L ozone. This is higher than the calculated dose, but ozone is used up in the process of oxidizing organic material and bacteria which is not taken into account in the theoretical calculation. The resulting ORP, as shown in figure 8, ranged between 50 and 250 millivolt (mV) with an average of about 125 mV. The ORP of distilled water was measured to be 130 mV. Assuming that de-ionized (DI) water is safe for membranes, we considered that the remaining ozone would not be harmful.

5.1.5 Antiscalant

GE-Betz's antiscalant prediction software, Argo Analyzer, was used to determine dose rate and type of antiscalant recommended for the test water. Results are included as "Appendix III, Argo Analyzer Results." The maximum recovery possible was estimated to be 68% with Hypersperse MDC 220. Calcium sulfate was determined to be the limiting salt. To be on the safe side, our initial target recovery was 60% with 6 mg/L Hypersperse MCD 220. The recommended dose was 5.66 mg/L, but it is difficult to get that precise with the LMI pump used for chemical feed.

5.2 Barium Sulfate Precipitation

Table 6 shows the results of the barium sulfate precipitation study using barium chloride. The first test was merely precipitating barium sulfate by adding barium chloride. The next test added air sparging, the next added barium sulfate crystal seeding, and the final was a repeat of the third except that the sludge was heat-treated. The test with crystal seeding had the least residual barium, while the air sparging resulted in the greatest sulfate removal.

Table 6. Sulfate Precipitation with Barium Chloride Using Four Different Methods

	Well Water		Pretreated Well Water					
	Raw	Unit	Simple Precipitation	With Air Sparging	With Crystal Seeding	With Heat Treatment of Sludge	Average	% Difference
pH	7.46		7.52	7.75	7.73	7.79	7.70	0.0
Al	0	mg/L	<0.05	<0.05	<0.05	<0.05	0.00	0.0
As	0	mg/L	<0.001	<0.005	<0.005	<0.005	0.00	0.0
Ba	0.029	mg/L	34	83.9	0.662	3.61	30.54	105,220
Be	0	mg/L	<0.005	<0.005	<0.005	<0.005	0.00	0.0
B	1.6	mg/L	1.48	1.47	1.47	1.46	1.47	-8.1
Cd	0	mg/L	<0.005	<0.005	<0.005	<0.005	0.00	0.0
Ca	490	mg/L	390	384	365	350	372.25	-24.0
Cr	0	mg/L	<0.01	<0.01	<0.01	<0.01	0.00	0.0
Cu	0	mg/L	<0.004	<0.004	<0.004	<0.004	0.00	0.0
Fe	3.8	mg/L	<0.1	0.0734	<0.1	<0.1	0.02	-99.5
Mg	180	mg/L	161	159	159	161	160.00	-11.1
Mn	0.94	mg/L	0.419	0.333	0.176	0.107	0.26	-72.5
Ni	0	mg/L	<0.04	<0.04	<0.04	<0.04	0.00	0.0
K	40	mg/L	33.7	31.9	33.8	33.3	33.18	-17.1
Ag	0	mg/L	<0.5	<0.5	<0.5	<0.5	0.00	0.0
Na	460	mg/L	433	427	432	433	431.25	-6.3
Zn	0	mg/L	<0.05	0.0503	<0.05	<0.05	0.01	0.0
Cl	610	mg/L	1,900	2,000	1,800	1,900	1,900.00	211.5
N	0	mg/L	<2	<2	<2	<2	0.00	0.0
SO_4	1,600	mg/L	22	0.41	60	9.3	22.93	-98.6
Bicarb Alk	200	mg/L	160	130	130	100	130.00	-35.0
Carb Alk	400	mg/L	<5	<5	<5	<5	0.00	-100.0
Hydroxide Alk	0	mg/L	<5	<5	<5	<5	0.00	0.0
Total Alk	400	mg/L	160	130	130	100	130.00	-67.5
Cond	4,600	µS/cm	5,840	5,870	5,600	5,650	5,740.00	24.8
TDS	3,910	mg/L	4,230	4,260	3,790	3,920	4,050.00	3.6
Fl	2	mg/L	0.49	0.59	0.56	0.53	0.54	-72.9
Total P	0.035	mg/L	0.092	0.059	0.027	0.018	0.05	40.0
Si	22	mg/L	26	26	26	25	25.75	17.0
Ba TCLP		mg/L	200	180	0.23	84	116.06	

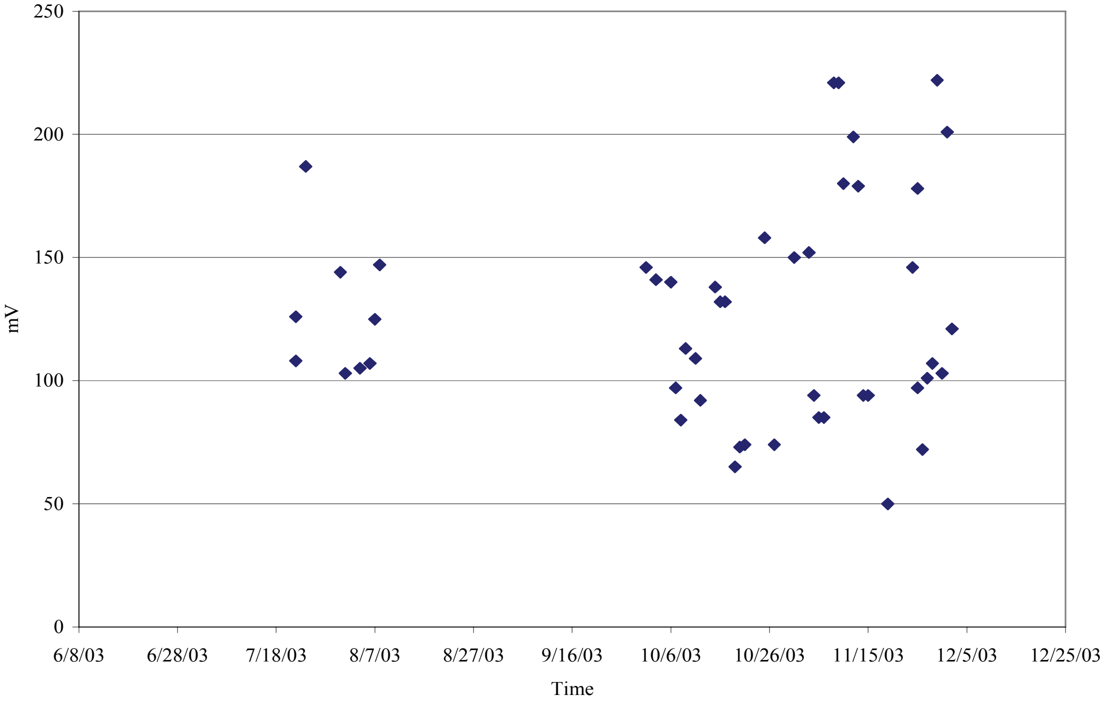

Figure 8. ORP of RO System Feed Water Over the Duration of the Pilot Study

The precipitate had to be rinsed with DI water and weak acid to dissolve carbonates and any soluble barium. It turned out that the completeness of the rinsing step was critical to passing the toxic characteristic leaching procedure (TCLP) test. The amount of DI water and acid required to do this effectively was considered excessive, however; so no further testing was done on this idea.

5.3 Nanofiltration

Nanofiltration was begun with a new membrane desalination system on July 21. The laboratory water analysis results for the feed, product, and concentrate are listed in table 7. After a couple weeks of correcting instrumentation, data collection, and automation, it was determined that the system could not run smoothly at 60% recovery. Operational data is shown in figures 9–20. Flow, pressure, recovery, rejection, and conductivity for the whole test period are shown in figures 9–12. Then the time period is broken up into smaller units to show the results of problems that arose and their solutions. Portrayal of this data is not just to illustrate our struggles to control the system but to show how these problems are represented in the operational data. If such patterns should repeat in a full-scale facility, perhaps they will be recognized for what they are and solutions put into place before the system is severely damaged.

Table 7. Nanofiltration Water Analyses

Analyte Name	EPA MCL	CG-1 Well	Concentrate	Permeate	NF Feed	Units	Detection Limit	Method
pH	6.5-8.5	7.25	4.48	4.24	7.2	pH units	1	EPA 150.1
Aluminum	0.05–0.02	<0.025	<0.025	<0.025	<0.025	mg/L	0.025	EPA 200.7-Total
Barium	2	0.0293	0.0576	ND	0.0328	mg/L	0.0025	EPA 200.7-Total
Boron		1.61	2.13	1.2	1.65	mg/L	0.05	EPA 200.7-Total
Calcium		494	1,130	2.49	514	mg/L	0.25	EPA 200.7-Total
Chromium	0.1	<0.005	0.0314	<0.005	<0.005	mg/L	0.005	EPA 200.7-Total
Iron	0.3	3.78	<0.05	<0.05	<0.05	mg/L	0.05	EPA 200.7-Total
Magnesium	125	187	358	0.682	186	mg/L	0.25	EPA 200.7-Total
Manganese	0.05	0.963	<0.0025	<0.0025	<0.0025	mg/L	0.0025	EPA 200.7-Total
Potassium		40	77.2	2.25	37.8	mg/L	1	EPA 200.7-Total
Sodium		481	598	30.4	322	mg/L	0.25	EPA 200.7-Total
Antimony	0.006	<0.005	<0.005	<0.005	<0.005	mg/L	0.005	EPA 200.8-Total
Arsenic	0.01	0.00875	0.00625	ND	0.00535	mg/L	0.005	EPA 200.8-Total
Selenium	0.05	0.0057	<0.005	<0.005	<0.005	mg/L	0.005	EPA 200.8-Total
Thallium	0.002	<0.005	<0.005	<0.005	<0.005	mg/L	0.005	EPA 200.8-Total
Chloride	250	610	1,200	44	580	mg/L	50	EPA 300.0
Nitrate, as N	10	<2	<2	<2	<2	mg/L	2	EPA 300.0
Nitrite, as N	1	<2	<2	<2	<2	mg/L	2	EPA 300.0
Sulfate	250	1,600	3,300	9.1	1,600	mg/L	50	EPA 300.0
Alkalinity, Bicarbonate (As $CaCO_3$)		400	730	<5	360	mg/L	5	SM2320 B
Alkalinity, Carbonate (As $CaCO_3$)		<5	<5	<5	<5	mg/L	5	SM2320 B
Alkalinity, Total (As $CaCO_3$)		400	730	<25	360	mg/L	25	SM2320 B
Specific Conductance		5,080	8,980	202	4,800	µS/cm	1	SM2510 B
Total Dissolved Solids	500	3,530	6,990	89	3,480	mg/L	60	SM2540 C
Fluoride	2	0.79	1.2	<0.4	0.63	mg/L	0.4	SM4500-F C
Silica Dioxide			<0.5	47.2	20.7	mg/L	0.5	SM3120B

[1] Berylium, cadmium, lead, copper, nickel, silver, zinc, tungsten, mercury were not detected in any sample and are omitted from the table.

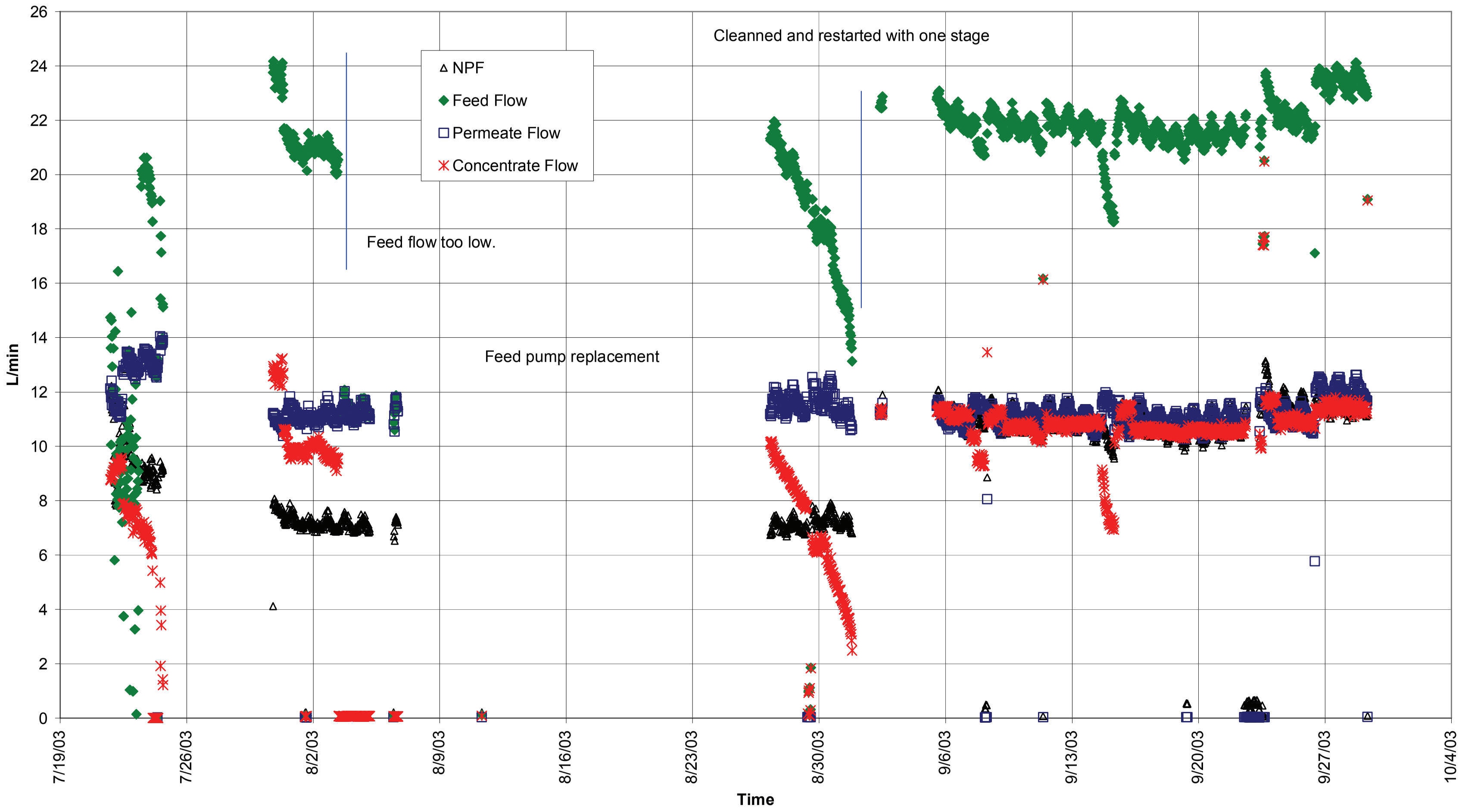

Figure 9. NF System Flows.

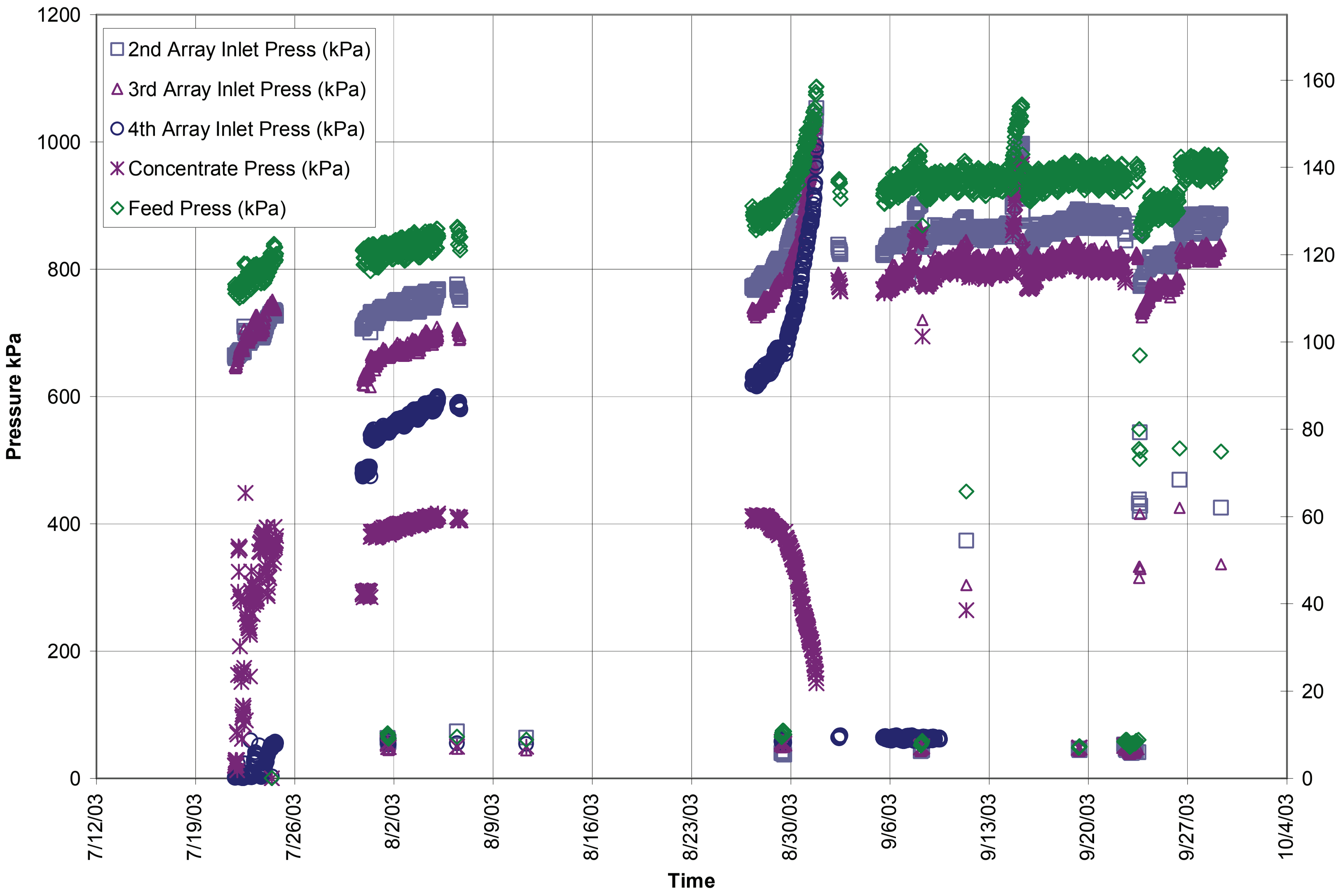

Figure 10. NF System Pressure.

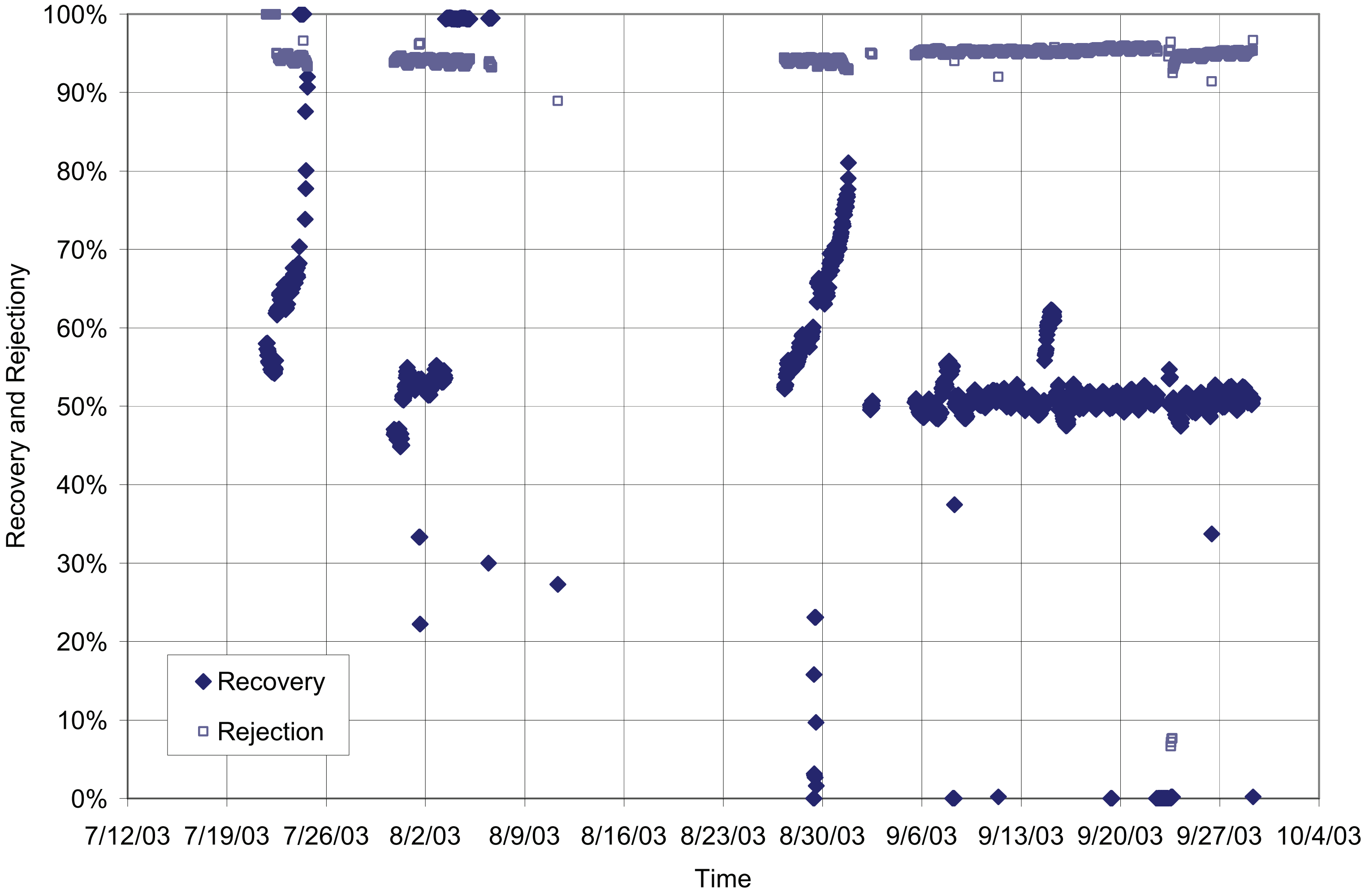

Figure 11. Recovery and Rejection.

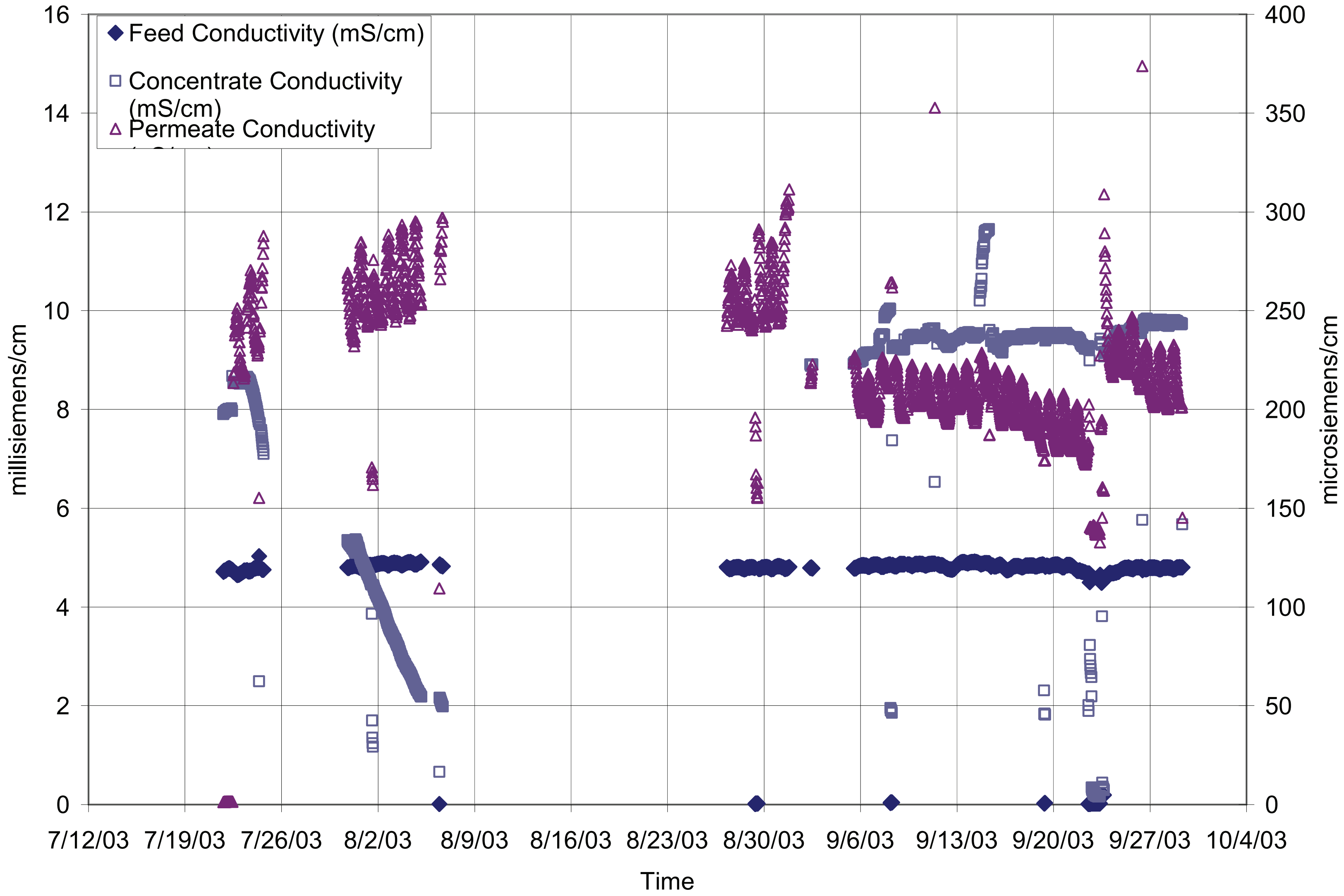

Figure 12. NF Feed, Product, and Concentrate Conductivity.

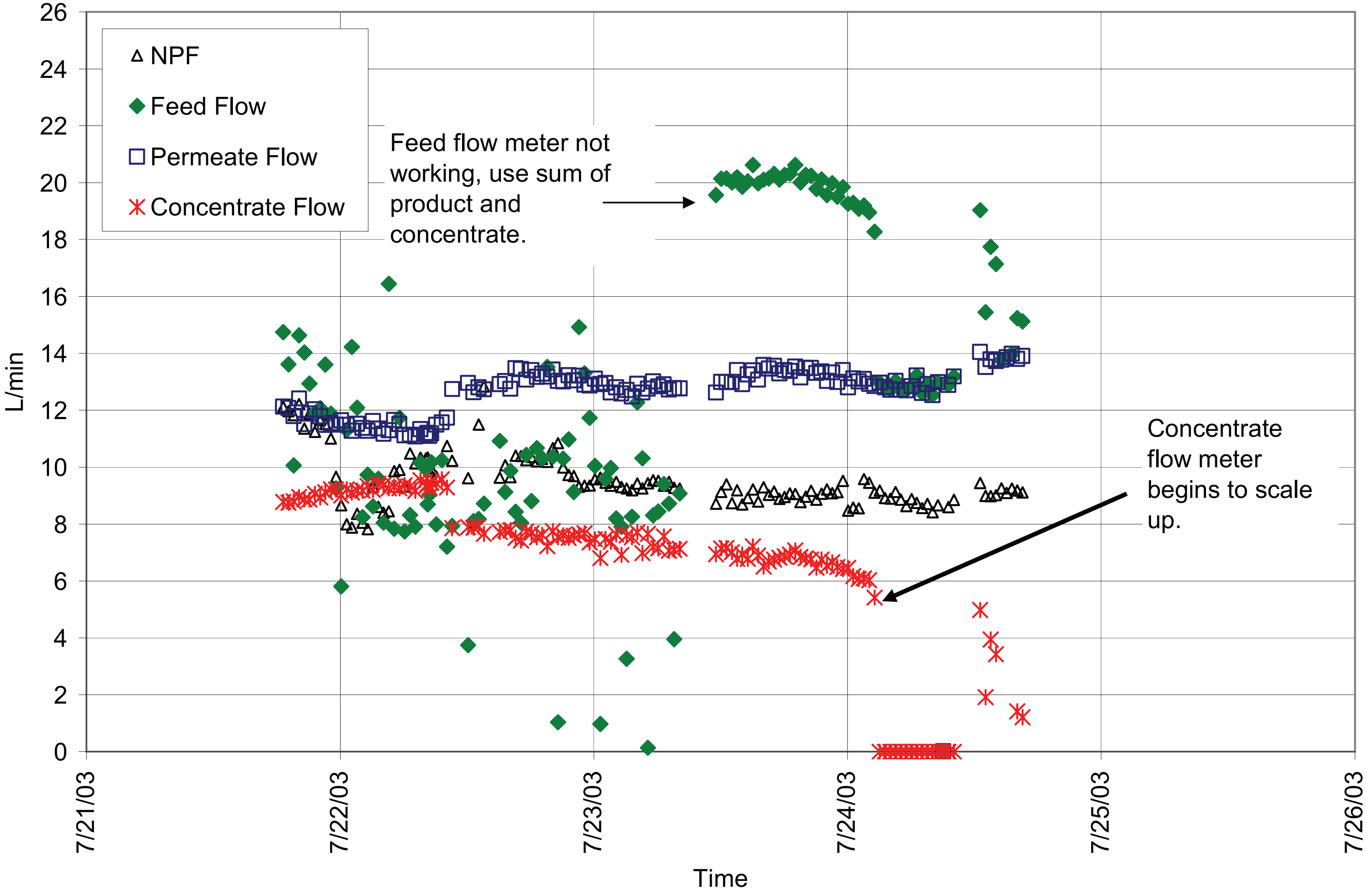

Figure 13. NF Week 1 Flows.

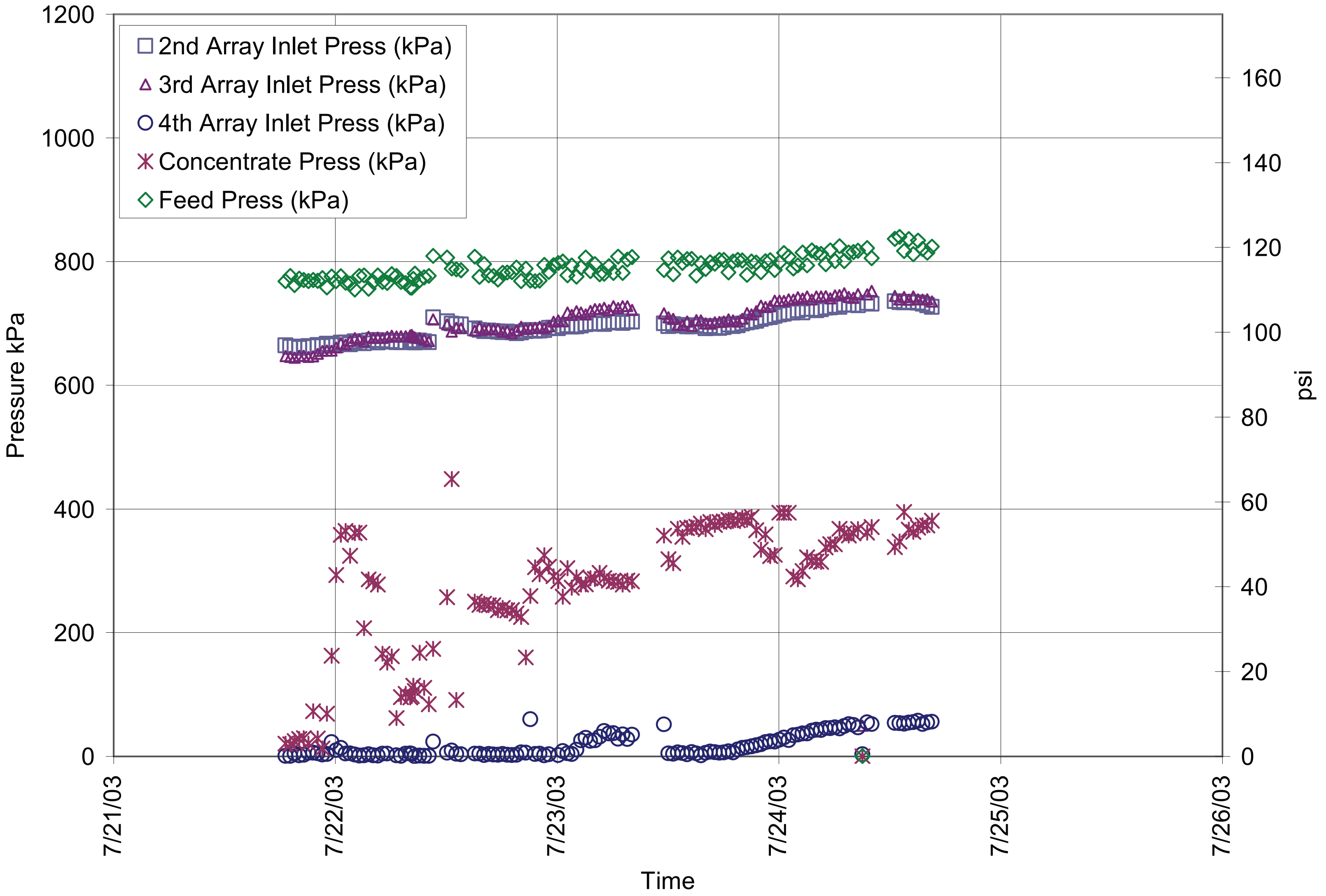

Figure 14. NF Week 1 Pressures.

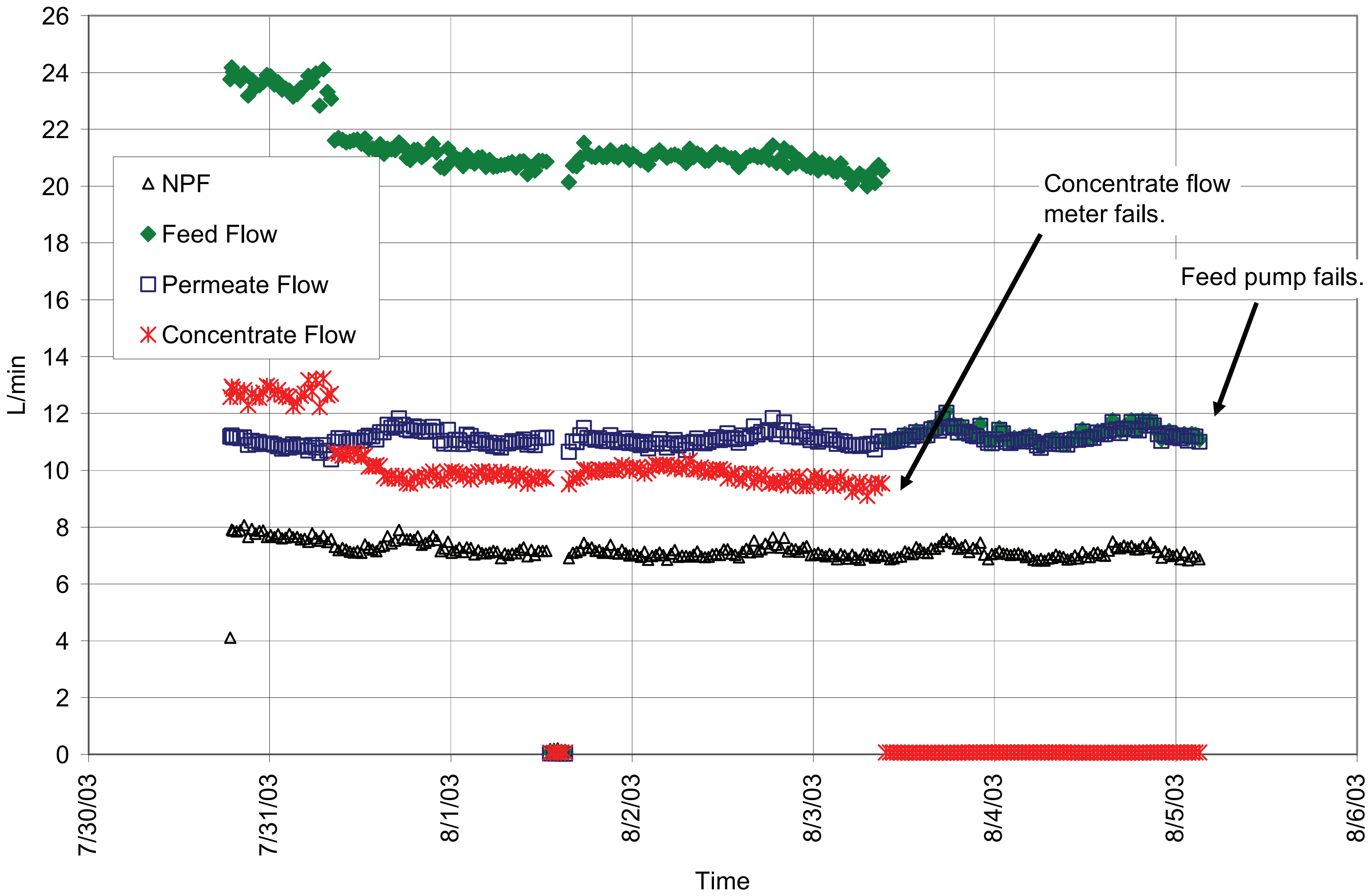

Figure 15. NF Week 2 Flows.

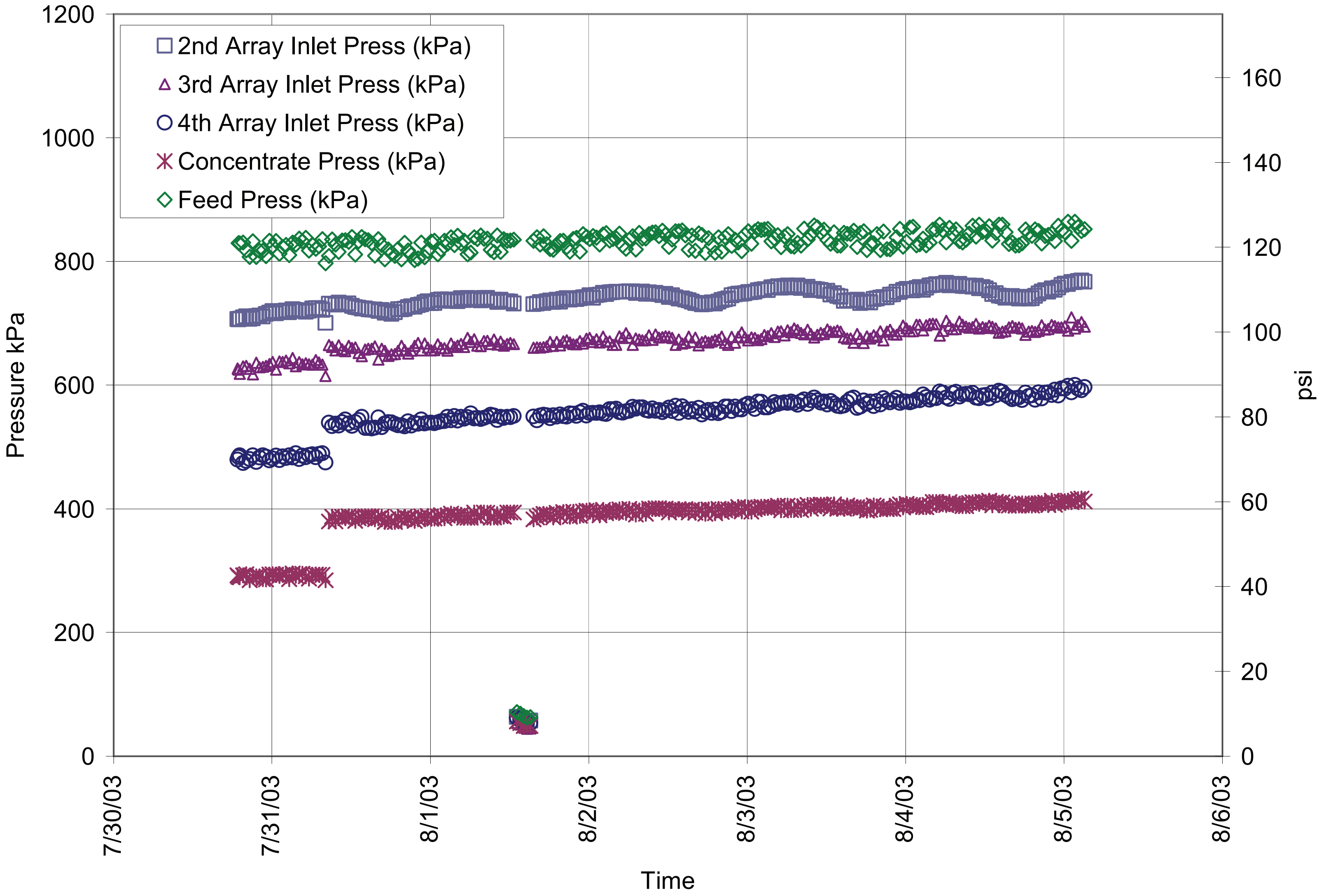

Figure 16. NF Week 2 Pressures.

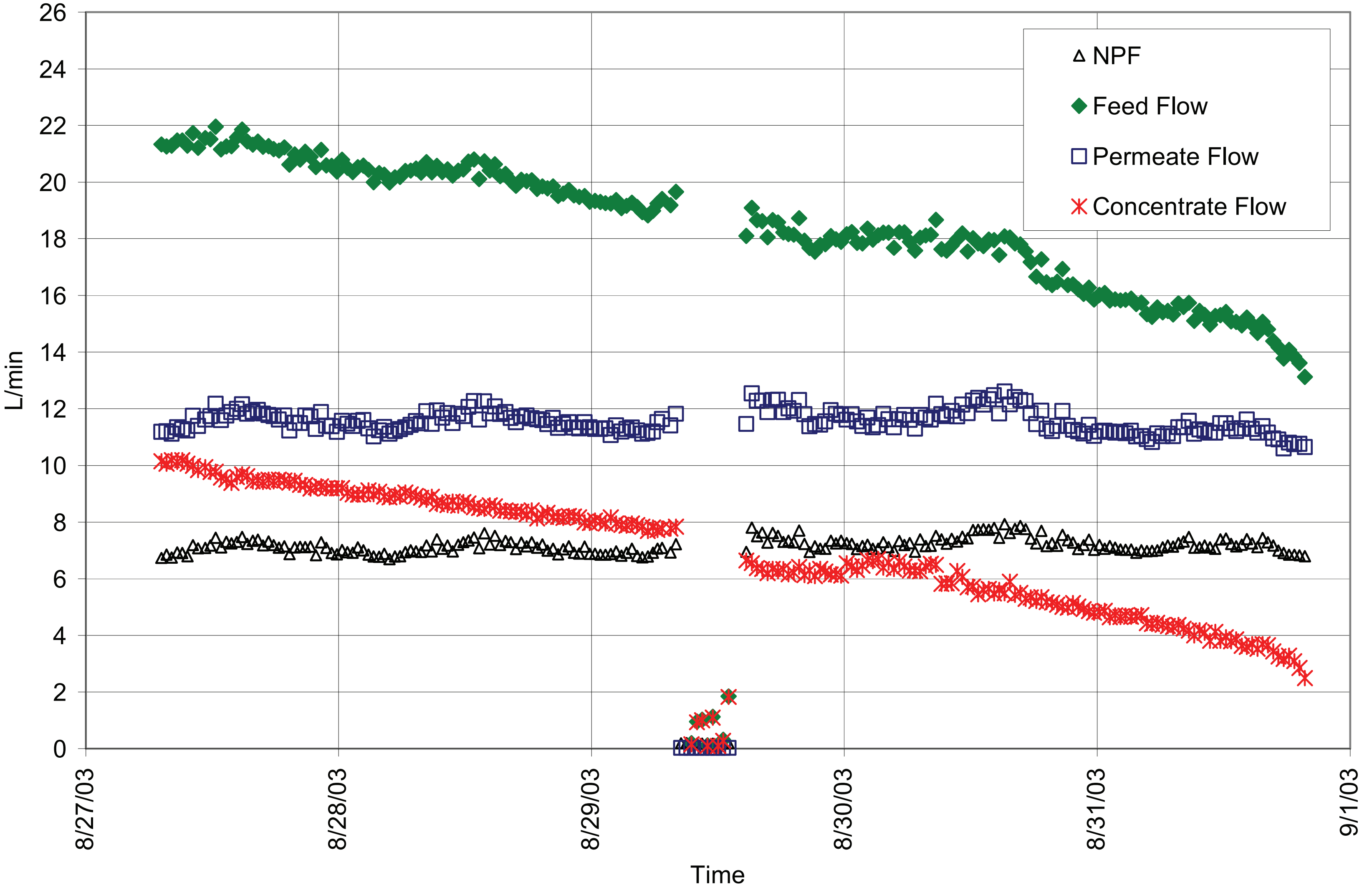

Figure 17. NF Flows During Scaling of Second Stage.

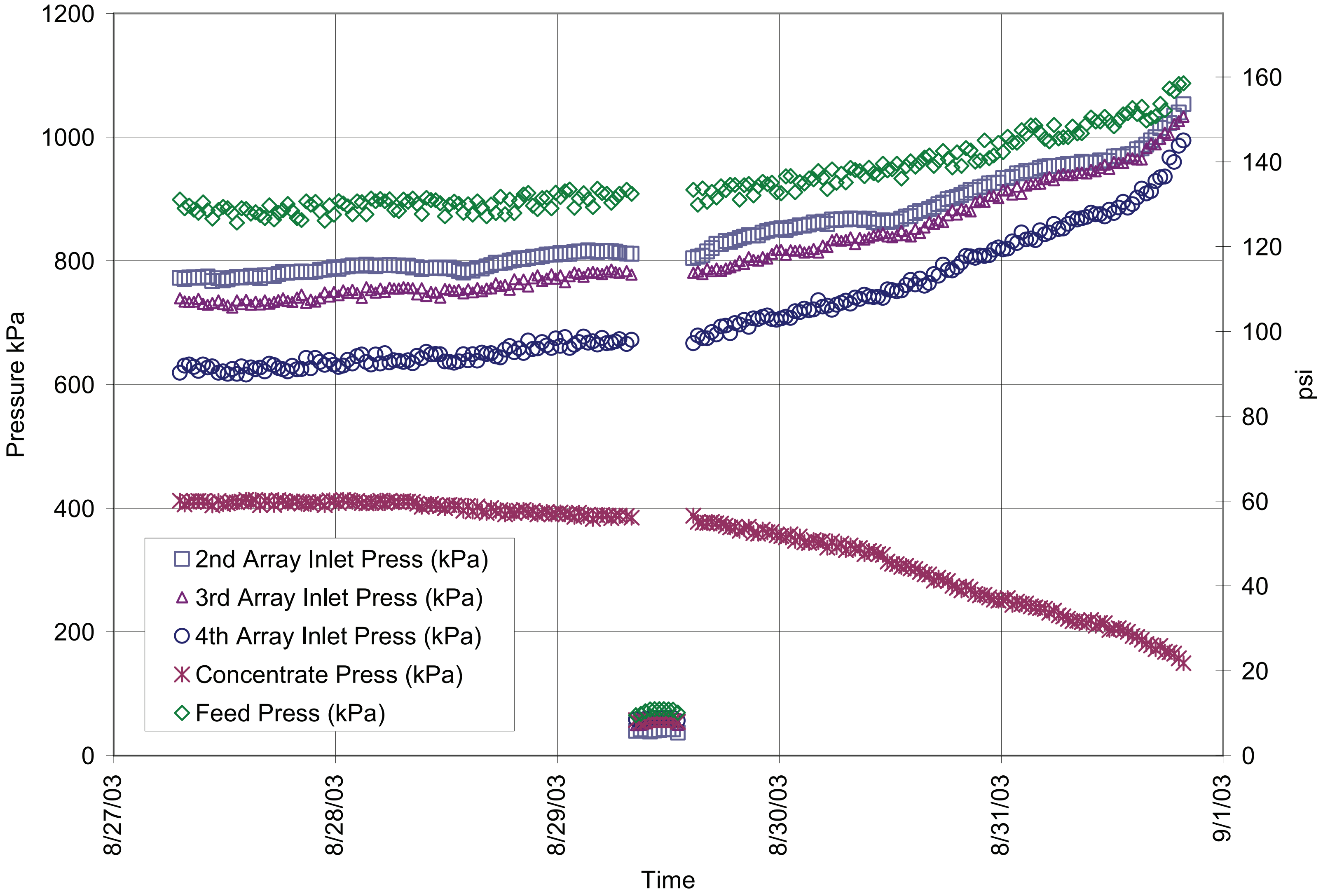

Figure 18. Pressure During NF Scaling of the Second Stage.

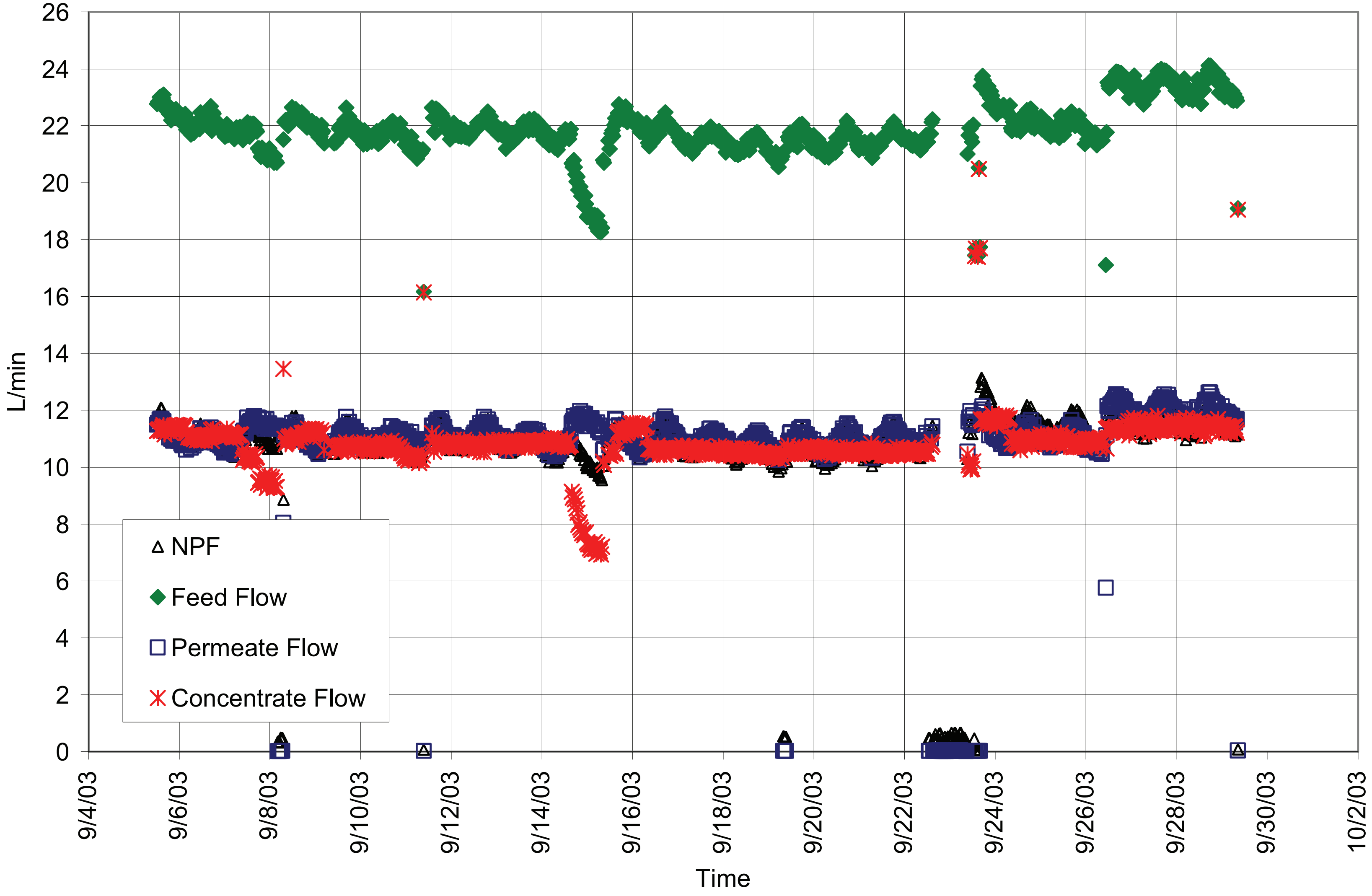

Figure 19. Flows During Stable NF Operation at 50% Recovery with One Stage.

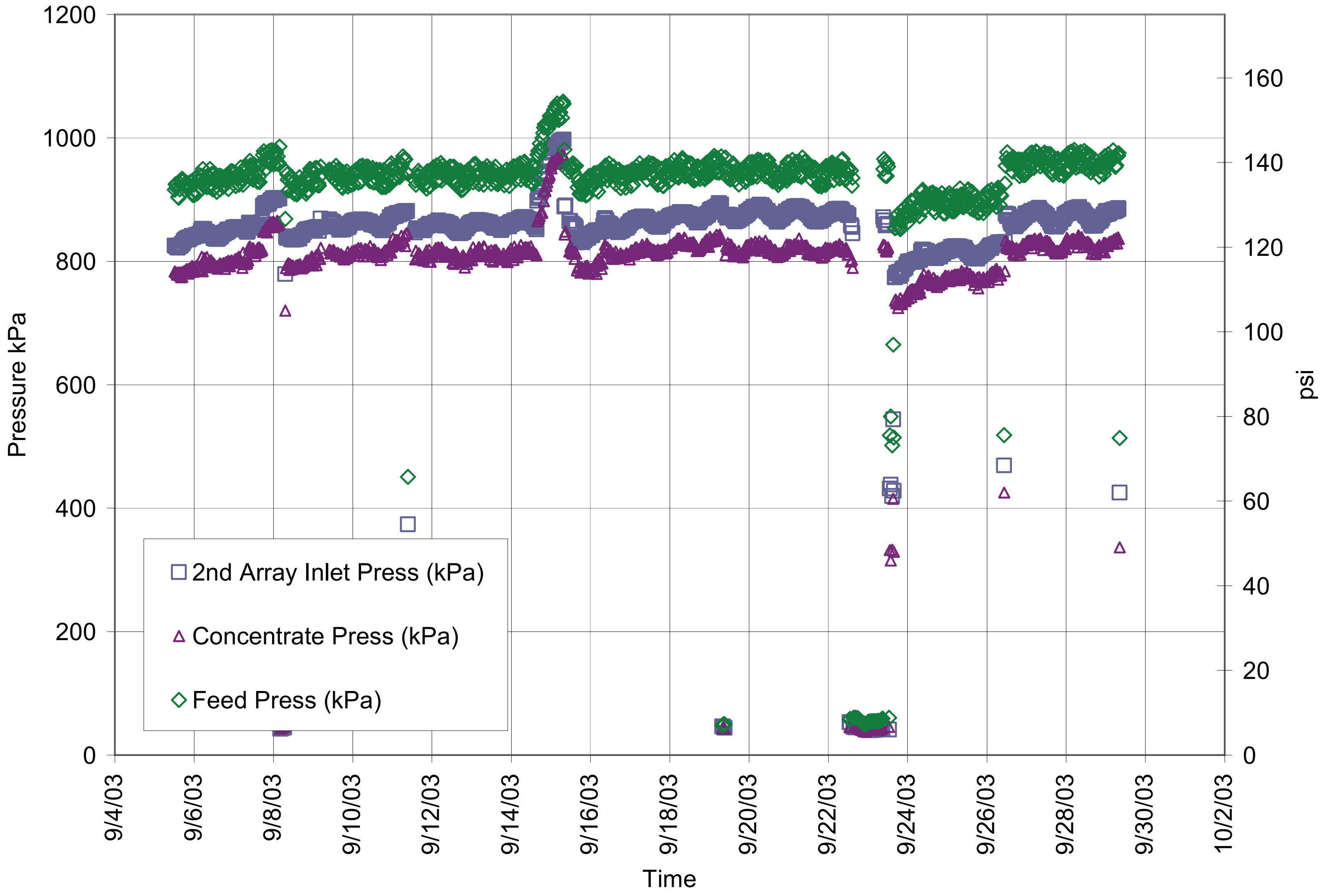

Figure 20. Pressures During Stable NF Operation at 50% Recovery with One Stage.

5.3.1 Nanofiltration - Week 1

In the process of shaking down the desalting system it was found that a few of the instruments were not functioning properly. Flows during this period are shown in figure 13 and pressures in figure 14. The feed flowmeter was defective. The problem was solved by using the sum of the concentrate and product, as both of those flowmeters were reliable. The redundant feed flowmeter was removed from data acquisition. On July 23, 2003, the concentrate flowmeter began to accumulate calcium sulfate crystals such that before the next day was over, it was completely frozen with scale deposit. The system can be managed with two flowmeters, but not with only one. The system was shut down on July 24 for repairs; the paddle wheel type flowmeters were cleaned out and replaced.

The pressure data for that week shows a gradual increase in feed pressure with a matching increase in the interstage pressures at the third and fourth vessel inlets. The concentrate pressure was erratic during the startup period. It was replaced with one that can be calibrated onsite, and then the pressure remained fairly constant between 300–400 kPa (40–60 psi). This indicates that the scaling problem was limited at this time to the flowmeter.

5.3.2 Nanofiltration – Week 2

After restarting the system and stabilizing it at 21.7 L/min feed with 55% recovery, operations were smooth until August 3 when the concentrate flowmeter once again scaled up completely. The system continued running in automatic for a couple days. Feed flow is equal to product flow which remained fairly constant because the operators were maintaining product flow by increasing or decreasing the pump speed. On August 5, 2003, the forwarding pump, which brings water to the membrane system, failed; and the system was offline for about 3 weeks while a new pump was procured.

5.3.3 Scaling the Second Stage

After the new forwarding pump was installed, the system was brought online under the former operating conditions with very short-lived success. While the system had been sitting, the calcium sulfate in the water left in the second stage vessels had begun to precipitate. Figure 15 shows the system flows with concentrate flow gradually dropping off. Figure 16 shows a mild increase in inlet pressure to the second stage vessels. Figures 17 and 18 are the flows and pressures after a brief shutdown on August 29, 2003. The concentrate pressure declined rapidly as the feed pressure rose from 900 kPa to 1,100 kPa (130 to 160 psi). While the change is not great considering that many brackish desalting plants operate at much higher pressures, the pressure difference across the stages reveals that there was a mounting barrier to water passage in the second stage. Product water exits the system after each stage, but the feed water could not pass through the last vessel. The increased pressures in the first stage caused increase in permeate flow in the first three elements of each of the first stage vessels. Recovery increased steadily causing super-saturation in the last vessel such that it became completely blocked. The second stage was taken offline and the system operated at 50% recovery with only one stage composed of a parallel set of vessels containing six elements each.

5.3.4 Cleaning of Nanofiltration Membranes

Before removing the second stage elements, we attempted to clean them with citric acid according to Hydranautics' cleaning strategy for sulfate scale. The cleaning system tank was filled with NF permeate. Citric acid was added to attain pH 4 as per instructions for mild cleaning solution 1. This solution was chosen because it is a chemical normally in stock at the VVWD and because it is indicated for calcium sulfate scale (but not for severe scaling). The cleaning was not effective. The vessel was too clogged to get good distribution of the cleaning solution throughout the membrane. Pressure differential was monitored for 1 hour. Then the elements were removed. It is recommended that in a full size plant, the elements not be allowed to get this scaled. If it does happen, the harsher recommended cleaning solution for sulfate scale (see "Appendix IV, Hydranautics' Cleaning Procedures"), consisting of 0.5% HCl (pH 2.5), should be used, especially on a second stage.

5.3.5 50% Recovery Nanofiltration

Figures 19 and 20 show normal variation in flow and pressure due to temperature change each day and night. The system ran smoothly for the rest of the test period. A temporary drop in feed flow began to cause a scaling problem on September 15, 2003, but the quick response of the operator in identifying the problem and rinsing the system with product water avoided any long lasting damage. A rinse was also performed on September 22 after a power outage caused the system to shut down. There was no significant degradation to the system in this stable test period.

5.4 Reverse Osmosis Testing

RO testing results are shown in figures 21–25. The system operated smoothly for the whole time with the exception of a few power outages. Vessels were flushed with product water after these events. After November 22, 2003, something caused degradation in the second half of the system. Figure 21 shows the concentrate conductivity dropping steadily after this date, and figure 22 shows the pressure difference across vessels three and four decrease on that date. This may have been caused by excessive ozone residual in the water used to flush after the power outage and the startup delay around November 1–18. Perhaps the ozonation came on and over dosed the RO feed water which was then used for rinsing. If so, it shows how important it is to have more ozone neutralization before the desalting system for system upsets that may introduce more ozone than intended. Water analyses for the RO feed product and concentrate are listed in table 8.

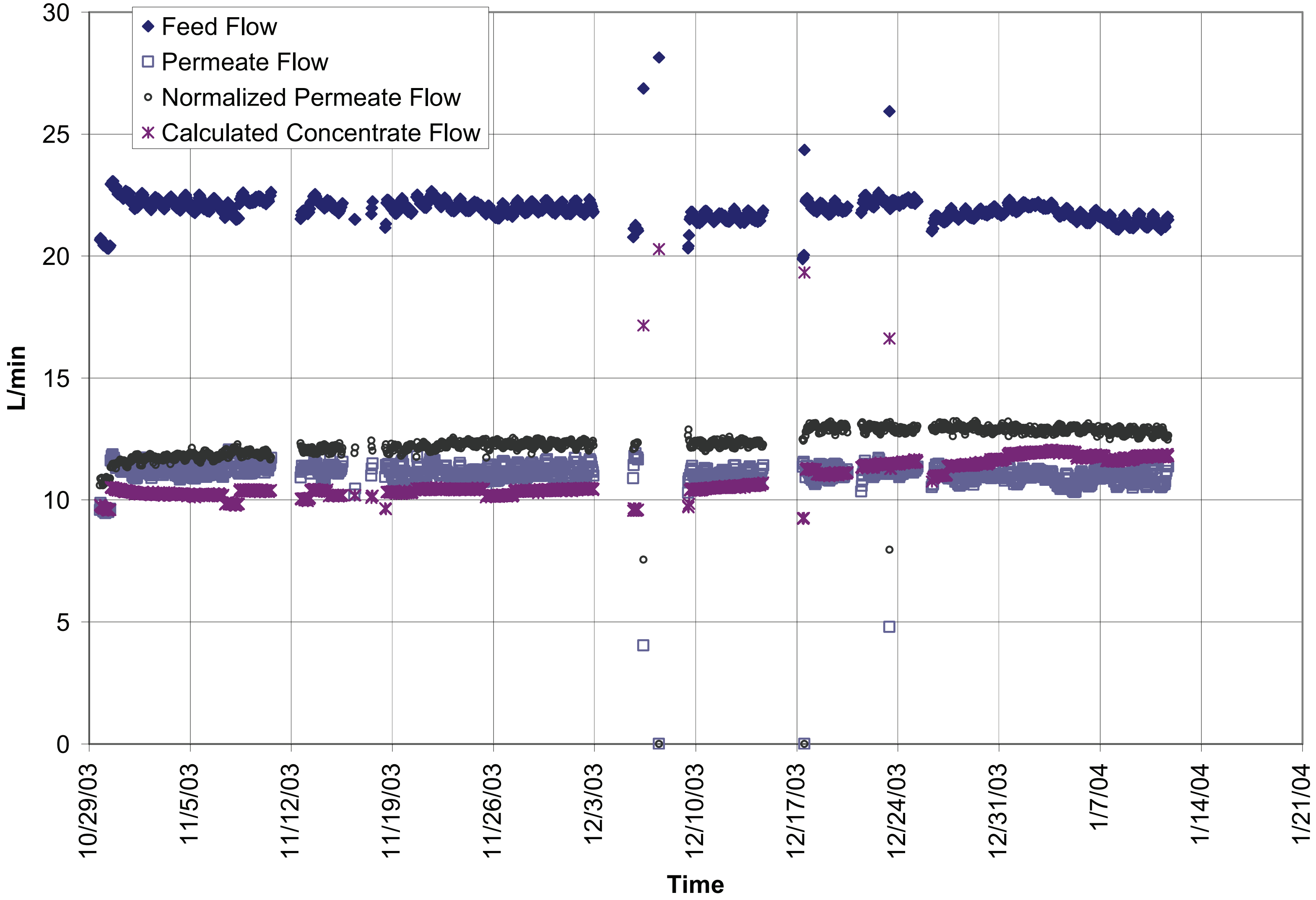

Figure 21. RO Flow Data.

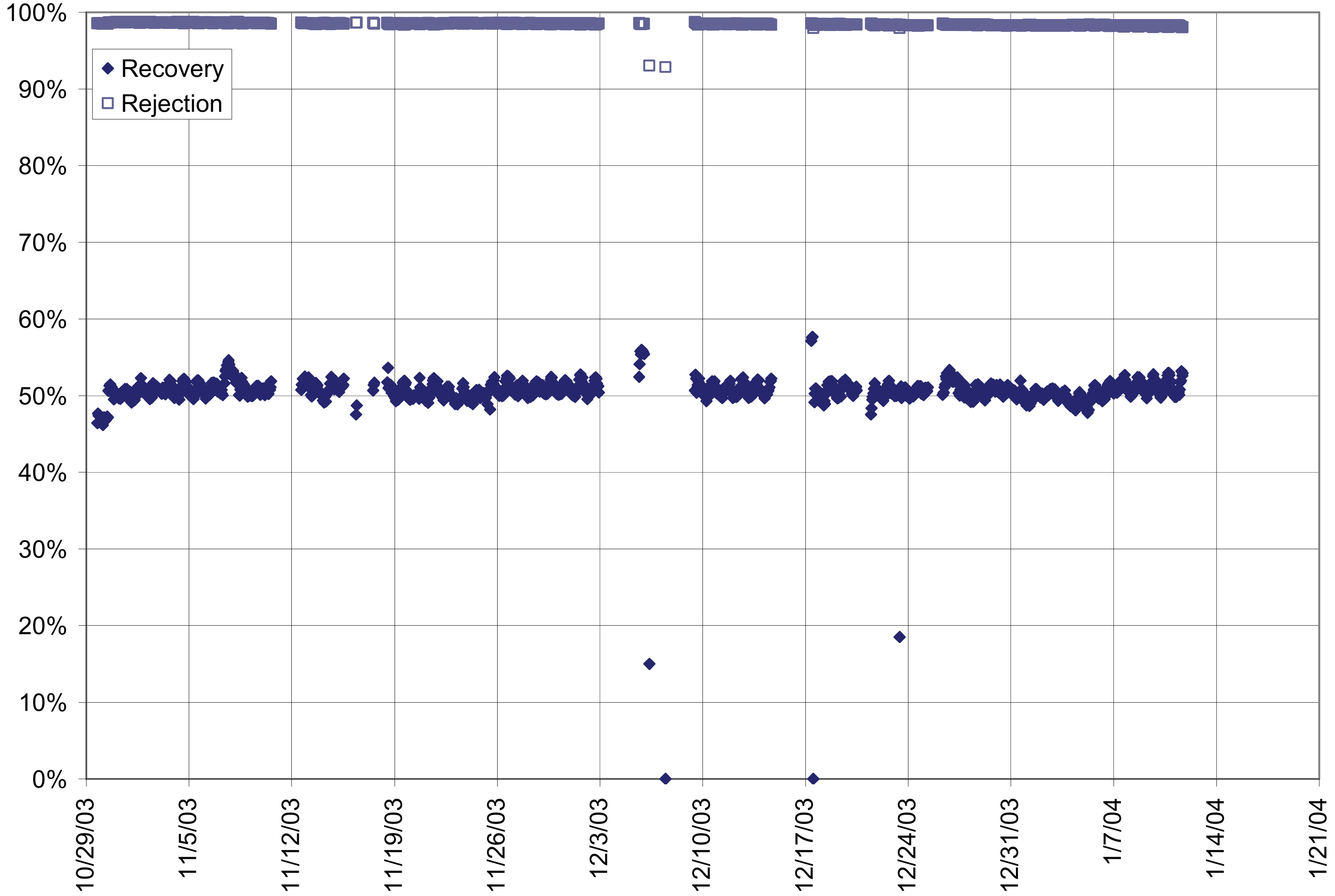

Figure 22. RO Recovery and Rejection.

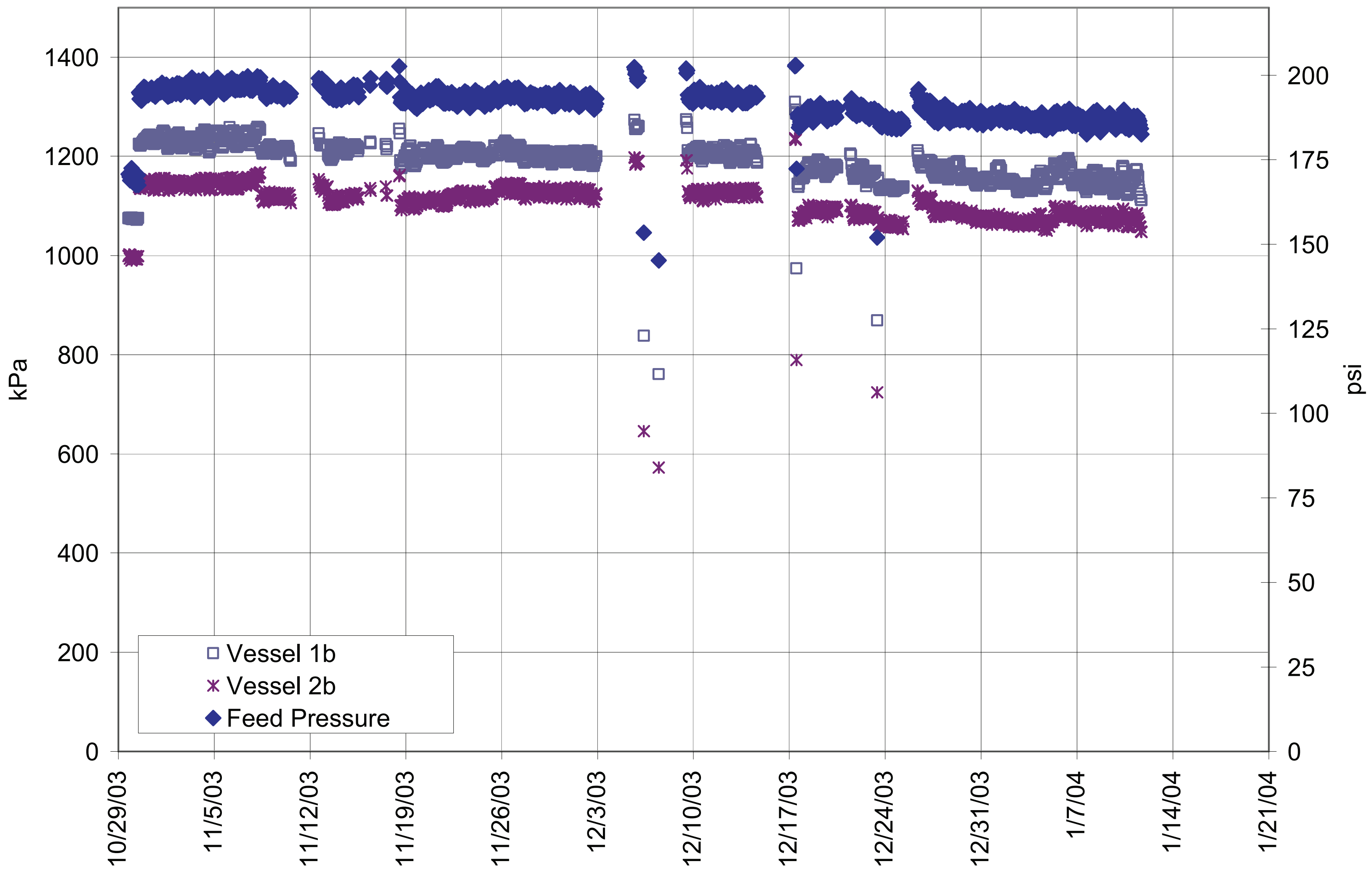

Figure 23. RO Pressure Data.

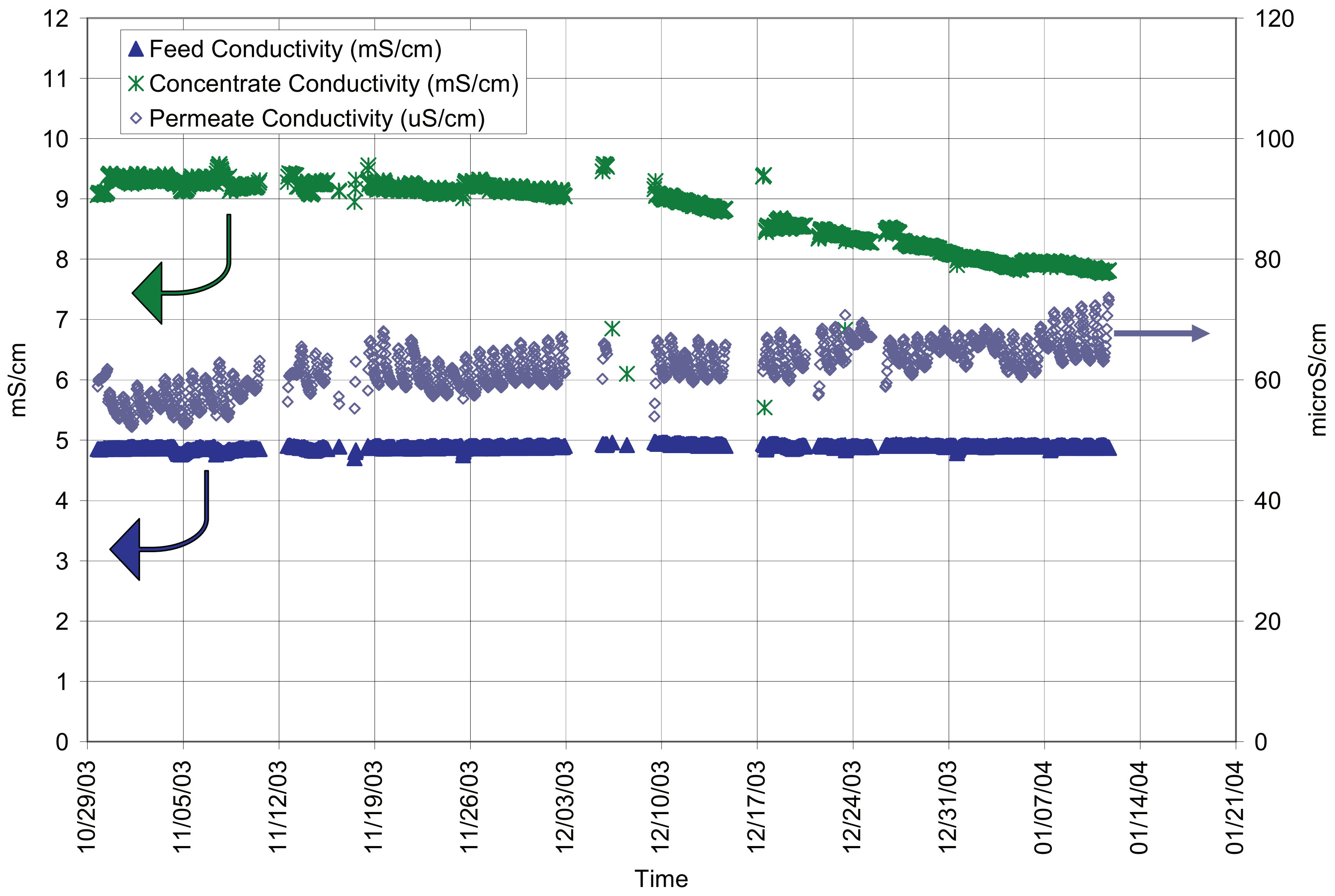

Figure 24. RO Conductivities.

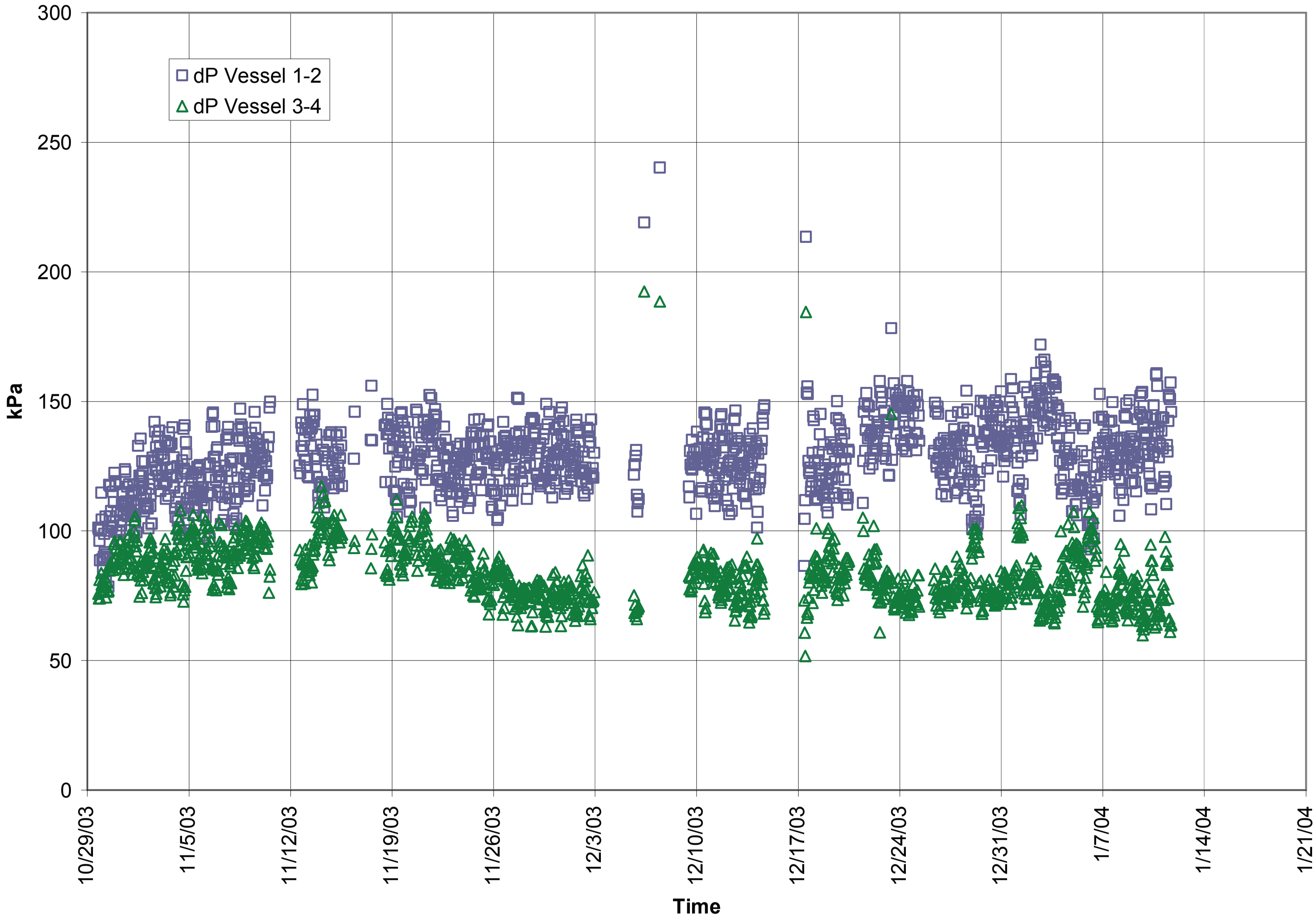

Figure 25. RO System Pressure Differences Across First and Second Half of the System.

Table 8. RO Water Analyses at End of Testing

Analyte Name	EPA MCL	CG-1 Well	Concentrate	Permeate	RO Feed	Units	Detection Limit	Method
pH	6.5-8.5	7.25	7.51	5.9	7.51	pH units	1	EPA 150.1
Aluminum	0.05-0.02	<0.025	<0.025	<0.025	0.08	mg/L	0.025	EPA 200.7-Total
Barium	2	0.0293	0.0489	<0.0025	0.028	mg/L	0.0025	EPA 200.7-Total
Boron		1.61	2.2	1.11	1.65	mg/L	0.05	EPA 200.7-Total
Calcium		494	1070	<0.25	550	mg/L	0.25	EPA 200.7-Total
Chromium	0.1	<0.005	<0.005	<0.005	<0.005	mg/L	0.005	EPA 200.7-Total
Iron	0.3	3.78	<0.05	<0.05	<0.05	mg/L	0.05	EPA 200.7-Total
Magnesium	125	187	369	<0.25	190	mg/L	0.25	EPA 200.7-Total
Manganese	0.05	0.963	<0.0025	<0.0025	<0.0025	mg/L	0.0025	EPA 200.7-Total
Potassium		40	66.6	<1	38.5	mg/L	1	EPA 200.7-Total
Sodium		481	674	11.6	424	mg/L	0.25	EPA 200.7-Total
Antimony	0.006	<0.005	<0.01	<0.01	<0.01	mg/L	0.005	EPA 200.8-Total
Arsenic	0.01	0.00875	<0.01	<0.01	<0.01	mg/L	0.005	EPA 200.8-Total
Selenium	0.05	0.0057	<0.01	<0.01	<0.01	mg/L	0.005	EPA 200.8-Total
Strontium		8.66	14.8	<0.01	8.04	mg/L	0.005	EPA 200.8-Total
Thallium	0.002	<0.005	<0.01	<0.01	<0.01	mg/L	0.005	EPA 200.8-Total
Tungsten		<0.005	<0.01	<0.01	<0.01	mg/L	0.005	EPA 200.8-Total
Chloride	250	610	1300	24	580	mg/L	50	EPA 300.0
Nitrate, as N	10	<2	<2.5	<0.1	<2	mg/L	2	EPA 300.0
Nitrite, as N	1	<2	<2.5	<0.1	<2	mg/L	2	EPA 300.0
Sulfate	250	1,600	3,500	0.65	1,800	mg/L	50	EPA 300.0
Alkalinity, Bicarbonate (As $CaCO_3$)		400	720	30	400	mg/L	5	SM2320 B
Alkalinity, Carbonate (As $CaCO_3$)		<5	<5	<5	<5	mg/L	5	SM2320 B
Alkalinity, Total (As $CaCO_3$)		400	720	30	400	mg/L	25	SM2320 B
Fluoride	2	0.79	1.3	<0.4	0.82	mg/L	0.4	SM4500-F C
Specific Conductance		5,080	8,520	61.9	5,000	µS/cm	1	SM2510 B
Total Dissolved Solids	500	3,530	6,670	34	3,530	mg/L	60	SM2540 C

[1] Berylium, cadmium, copper, nickel, silver, zinc, mercury were not detected in any sample and are omitted from the table.

5.5 Comparison of RO and NF Permeate

Figure 26 compares the water analyses for RO and NF permeate. The most striking difference is the lack of alkalinity in the NF product. The pH is lower than the RO product, and the feed pH from both analyses match that which was recorded onsite; it does not appear that the pH was adjusted during sampling or at the lab. It may be that to protect permeate electro-neutrality, more hydrogen ions pass the membrane. The absence of bicarbonate alkalinity is expected at a pH of 4.24; but whether it dissipated because of added acid in the lab, or the increased passage of hydrogen, will have to be settled next time when we record the permeate pH onsite.

Another oddity is the 22.7 mg/L of silica oxide in the NF permeate. Below pH 10, silica is mainly in the uncharged form of H_2SiO_3. This molecule may be large enough with its attendant water molecules to be excluded from the RO membrane but not the looser NF membrane. Boron is also in the uncharged form of $B(OH)_3$ below pH 9.2. It was tested for and found in both RO and NF permeates at 1.11 and 1.2 mg/L, respectively. EPA has not set an MCL for boron; they are considering a limit of 0.6 mg/L. Minnesota Department of Health (MDH) recommends a limit of 0.6 mg/L to protect the male reproductive system (MDH, 2003). The World Health Organization (WHO) has adopted 0.5 mg/L as the safe limit for drinking water (WHO, 2003). There are concerns for certain crops irrigated with boron levels in excess of 1 mg/L (Musci, 2001).

5.6 Blending and Stabilization

The target water quality for drinking is 350 mg/L using pretreated feed water. The Langelier saturation index (LSI) should be positive. Table 9 lists the blend ratios for RO and NF product with LSI before and after blending and the dose requirements to attain a LSI of 1.0 for a variety of stabilizing agents using the average rejection rate of 98.7% for NF and 99.5% for RO. Table 10 gives the chemical costs for the different options. Lime is the least expensive.

Target TDS is 700 mg/L. Table 11 gives the estimated water quality using TDS as the limiting factor based on the water analyses in tables 7 and 8. Since the overall TDS rejection is very high for NF, the blend ratios are not much different—14% for RO permeate and 15% for NF (water will not be used for irrigation).

5.7 Concentrate Management

Stabilization of the concentrate can be accomplished by seeding with calcium sulfate. The effluent from the process may be recycled to the desalination feed

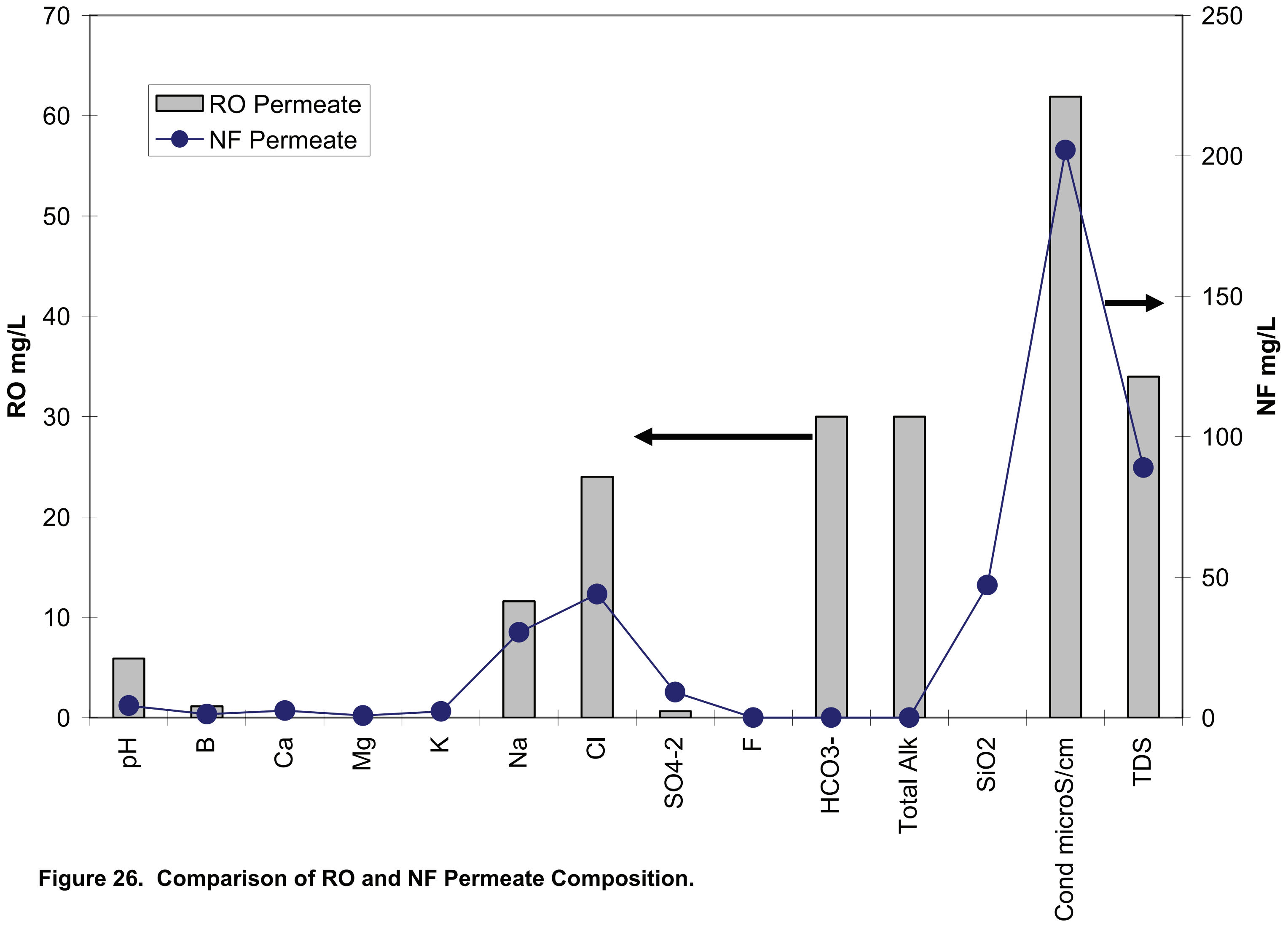

Figure 26. Comparison of RO and NF Permeate Composition.

Table 9. Unstabilized LSI and Dose Rates to Attain LSI = 1.0 for RO and NF Permeate with and Without Blending

Source	RO Permeate	RO Permeate with 9% Treated Feed Water	NF Permeate	NF Permeate with 7.7% Treated Feed Water
LSI Without Stabilization	-5.46	-2.18	-4.82	-2.44
LSI with Stabilization	+1.0	+1.0	+1.0	+1.0
Caustic Soda 98% NaOH	6.97	6.98	19.92	19.92
Soda Ash 99.16% $NaHCO_3$	18.40	18.34	52.56	52.35
Lime 90% CaO	5.35	5.34	15.28	15.24
Calcium Hypochlorite	23.57	23.54	67.33	67.20
Hydraded Lime 93% $Ca(OH)_2$	6.80	6.78	19.41	19.38

Table 10. Cost of Stabilization ($/kgal)[1]

Source	RO Permeate	RO Permeate with 9% Treated Feed Water	NF Permeate	NF Permeate with 7.7% Treated Feed Water
Caustic Soda 98% NaOH	0.003	0.003	0.01	0.01
Soda Ash 99.16% $NaHCO_3$	0023	0023	0023	0023
Lime 90% CaO	0.001	0.001	0.004	0.004
Calcium Hypochlorite	0.141	0.141	0.017	0.017
Hydraded Lime 93% $Ca(OH)_2$	0.002	0.002	0.005	0.005

[1] $k/gal = $1,000 per gallon.

Table 11. Estimated Character of Blended Irrigation Water

Analyte Name	RO 14% Blend	NF 15% Blend
Aluminum	0.011	
Barium	0.004	0.005
Boron	1.19	1.27
Calcium	77	79
Copper	0.001	
Magnesium	26.6	28.5
Potassium	5.39	7.58
Sodium	69.3	74.1
Arsenic		0.001
Strontium	1.13	
Chloride	102	124.4
Sulfate	253	247.7
Alkalinity, Bicarbonate (As $CaCO_3$)	82	54
Alkalinity, Total (As $CaCO_3$)	82	54
Fluoride	0.11	0.09
Silica Dioxide		43.23
Total Dissolved Solids	699	714
Conductivity	750	890
SAR	1.7	1.8

water. Figures 27 and 28 show the response time for sulfate precipitation attained in the jar tests. The RO concentrate precipitated best if left alone with no further chemical addition. Stirring speed had the biggest impact on precipitation of NF concentrate, though, with the slower the speeds precipitating more quickly.

5.8 Recommendations

The components that must be removed from the Virgin River for drinking or for irrigation are iron, manganese, bacteria, sulfate, and general TDS. The most efficient and economical method for removing the TDS is RO. There are several approaches for the pretreatment system to remove iron, manganese, and bacteria. The sulfate must be reduced in concentration to obtain an acceptable recovery and there are a couple of different approaches to do this. Ion exchange can selectively remove sulfate, but the cost is extremely high. For a 10-million-gallon-per-day (Mgal/d) treatment system, the cost for the ion exchange would be near

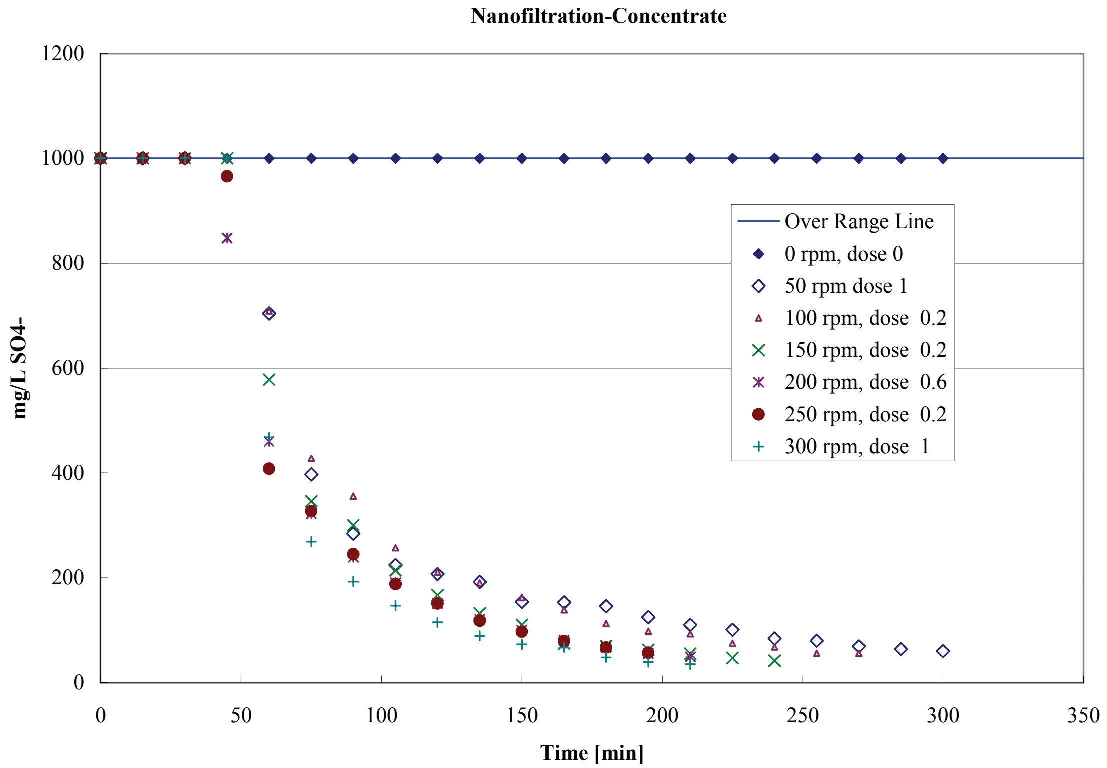

Figure 27. Calcium Sulfate Precipitation Rate from NF Concentrate.

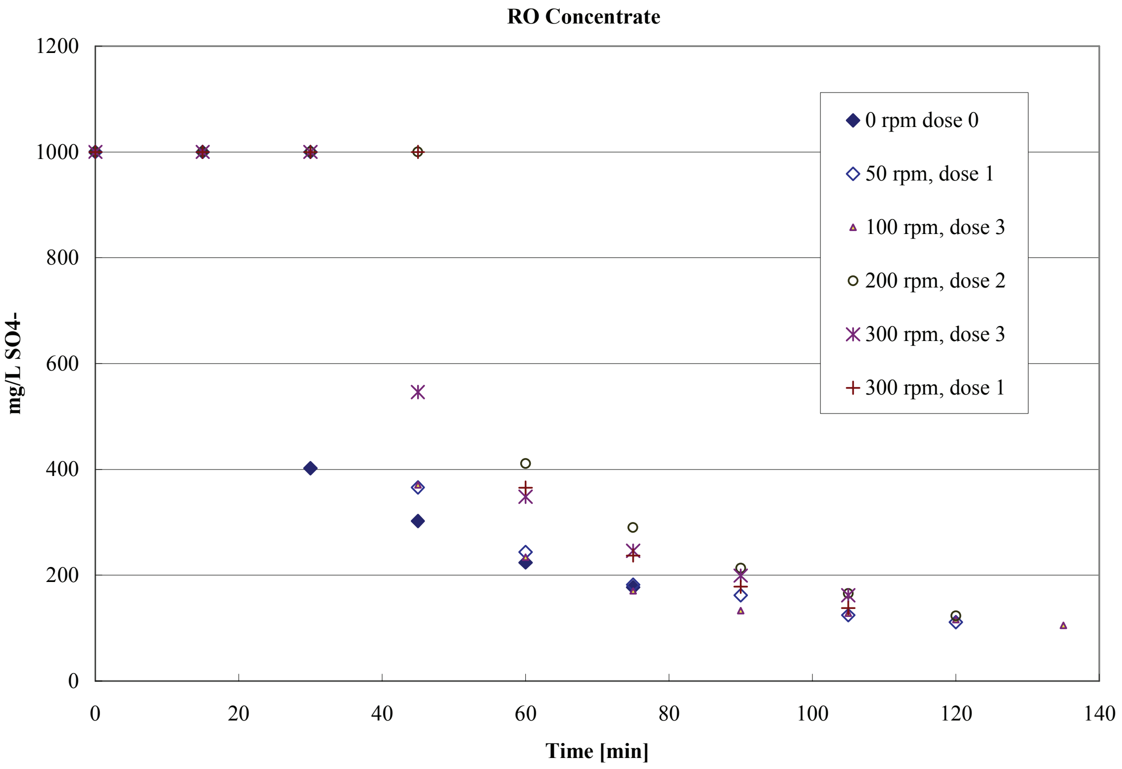

Figure 28. Calcium Sulfate Precipitation Rate from Reverse Osmosis Concentrate.

$50 million dollars. Therefore, we recommend one of two more reasonable methods for treating the Virgin River water encountered during this pilot study:

- Conventional lime softening, filtration, RO
- Ozonation, filtration, RO, concentrate precipitation, and recycle

These two processes are diagramed in figures 29 and 30. Table 12 and 13 detail cost estimates to produce 10 Mgal/d. Details of the recommended processes are documented below.

5.8.1 Conventional Lime Softening, Filtration, RO

Lime softening would require around 300 mg/L lime with chemical feed system, mixing tank, and parallel up-flow solids contactors. A multimedia filter will ensure that solids are removed. Effluent would be stored in a clear well to provide feed to the RO system. Antiscalant is dosed at 4 mg/L as insurance against scaling.

The RO system operates at 500 psi, 80% recovery, 99% rejection, feed flow of 11.26 Mgal/d. Pretreated well water can be blended with the RO product at a rate of 1.24 Mgal/d to produce 10 Mgal/d at 500 mg/L. Concentrate production rate is 2.5 Mgal/d at 17,400 mg/L. Four parallel trains with a total of 1,992 membrane elements and 332 pressure vessels are included in the estimate with all necessary instrumentation, cleaning equipment, and cartridge filters.

Concentrate piping and treatment is included at $50/kgal concentrate to carry effluent to the evaporation pond. A 10-acre evaporation pond is estimated separately to hold the concentrate for evaporation or precipitation and transport offsite. It is assumed that land cost is $5,000 per acre and clearing cost is $4,000 per acre. Dike height is 8.2 feet, and the pond has a 60-milliliter-thick liner.

This system does not include disinfection as pretreatment because the lime softening and filtration may be adequate to remove bacteria and at least 30% of the organic material. Disinfection is not included in the post treatment comparison because it would be the same for both options. Disinfection will be treated separately later in this section.

5.8.2 Ozonation, Filtration, RO, Concentrate Precipitation, and Recycle

Ozonation at 6 mg/L followed by coarse filtration and multimedia filtration proved adequate to remove iron and manganese while also killing bacteria from the well. In the proposed treatment scenario, part of the pretreated well water is blended back with the RO product to achieve 500 mg/L TDS. The system is started with 100% pretreated well water with 40% of the treated concentrate blending back in the RO feed reservoir. Over time, the blended RO feed will

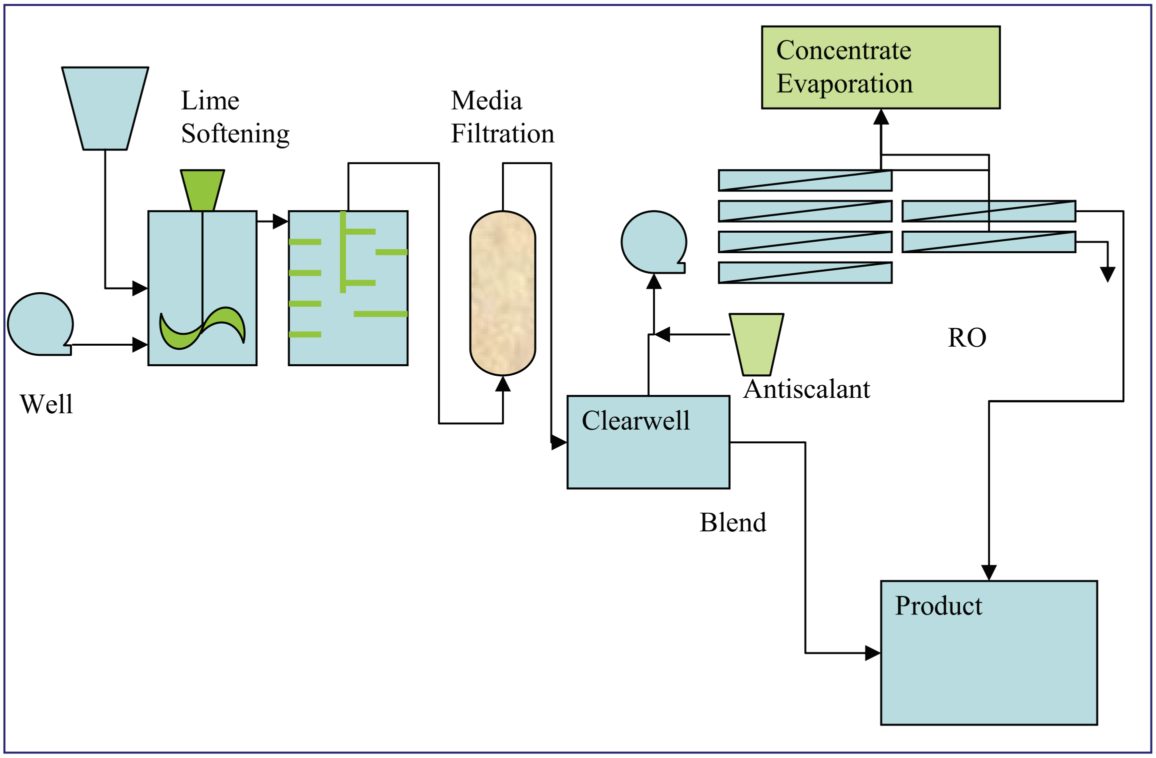

Figure 29. Conventional Pretreatment with RO.

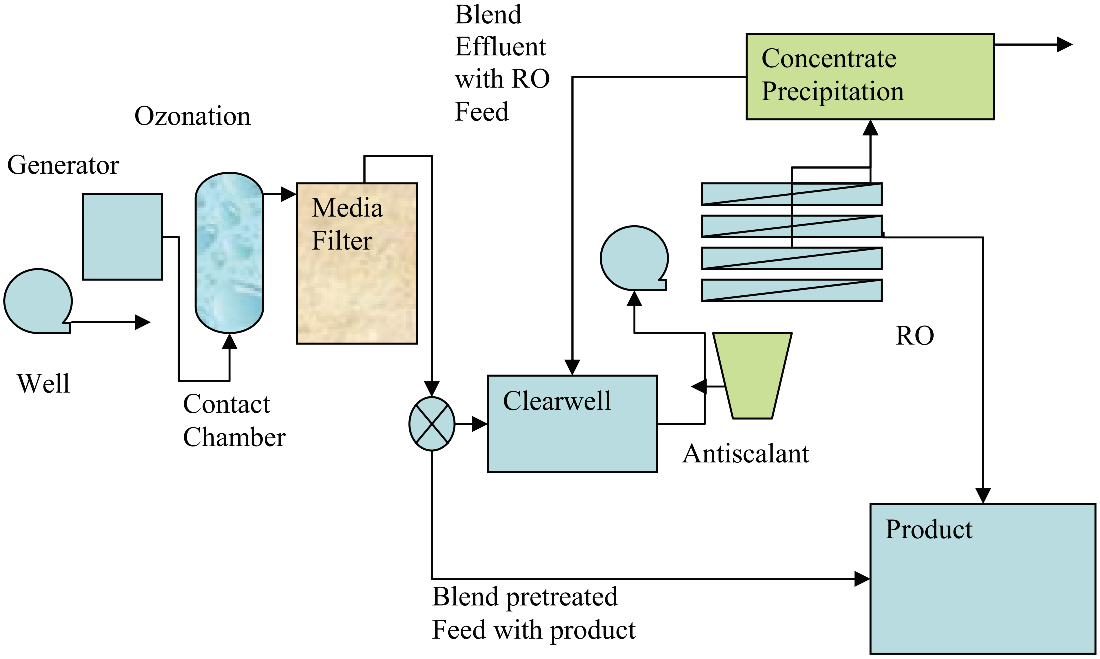

Figure 30. Ozonation/Filtration with RO Using Concentrate Precipitation and Recycle.

Table 12. Cost Estimate for 10 Mgal/d Through Conventional Pretreatment and RO

Process	Sizing Comments	Construction ($k)[1]	Operation and Maintenance per Year ($k)
Lime Addition	300 mg/L	236	1,650
Up-Flow Solids Contactor	2 contactors	986	31
Multimedia Filtration	Sand/coal/garnet Includes backwashing	597	37
Clearwell	2 million gallons	750	
Antiscalant	4 mg/L	97	225
RO	11.3 Mgal/d feed, 75% rec	10,190	9,828
Evaporation Pond	10 acres	2,646	13
Product Storage	2 million gallons	650	
Indirect Capital	32% of construction	5,169	
Capital Recovery	6%, 30 years		717
Total Costs		$21,321	$12,501
Water Cost $/kgal			$1.25

[1] $k = per 1,000 dollars.

Table 13. Cost Estimate for Option 2, Ozonation, Filtration, and RO with Concentrate Recycle

Process	Sizing Comments	Construction ($k)	O&M per Year ($k)
Ozonation Including Generator and Contact Chamber	6 mg/L, 2-minute retention time.	1,522	147
Coarse Media Filtration	Sand Includes backwashing	611	37
Multi Media Filtration	Sand/coal/garnet Includes backwashing	354	27
Clearwell	2 million gallons	750	
Antiscalant	15 mg/L	445	570
RO	17.5 Mgal/d feed, 50% rec	11,200	8,400
Evaporation pond	For 0.9 Mgal/d	2,388	12
Product Storage	2 million gallons	650	
Indirect Capital	32% of construction	5,556	
Capital Recovery	6%, 30 years		771
Total Costs		$23,476	$9,964
Water Cost $/kgal			$1.00

stabilize in composition. The concentrate is precipitated in an up-flow solids contactor, flowing through calcium sulfate crystals which serve as a precipitation catalyst.

The RO system is operated at 50% recovery, 400 psi, 99% rejection. The overall recovery will be 90%. Equilibrium RO feed TDS is estimated to be 8,200 mg/L. Concentrate recycle will be depleted in sulfate and have a relatively higher fraction of chlorides than the well water. Antiscalant is added at a dose of 15 mg/L of Nalco's PC-391. Ten percent of the concentrate is discharged to an evaporation pond. The cost estimate for this scenario is detailed in table 13.

6. Discussion

Removing sulfate from water is problematic. It is only slightly soluble; but precipitation of calcium sulfate, the most common form, does have a rather slow rate of formation. Therefore, it is imperative to have adequate dose and retention time in a precipitation pretreatment process ahead of a desalination system if the sulfate is to be adequately removed. It will be necessary to verify the retention time before designing a lime treatment, flocculation/clarification system. The second issue with lime precipitation pretreatment is the difficulty in predicting how the iron and manganese, which will form hydroxides rather than oxides, will affect settling of the calcium sulfate precipitate. Hydrated lime is $Ca(OH)_2$; when it is dissolved in water, the calcium ion reacts with the sulfate; and the hydroxide reacts with transition metals and also shifts the carbonate system to the HCO_3^- and H_2CO_3 forms, increasing the potential for carbonate scaling. Carbonate scaling can be handled by lowering the pH of the RO feed water, but this will add to the expense. Neutralization or other pH adjustment is not included in the above cost estimate. The third issue is that lime softening creates a large amount of sludge. It is difficult to estimate the quantity because the lime will react with carbonates in the feed water as well as the sulfate. Approximately 8 grams (g) of wet sludge are produced per 1 g lime added. With the recommended dose of 0.3 grams per liter (g/L), this facility would produce over 32 tons of sludge per day, or 42 cubic yards, from the lime softening process. The cost of sludge removal also is not included in the cost estimate. While lime softening is a well known process, and will allow for higher recoveries from the RO system, it does not produce exceptionally high quality water for the RO system. Carryover from the flocculation basin, algae growth, and variable filtrate quality from the media filters cause fouling problems with a membrane system.

Ozonation will oxidize the iron and manganese as well as destroy any bacteria and organic material in the water. Remnant particles will be removed by the graded media filters. Bacteria living in the filters will digest the remaining nutrients before the RO system. The only remaining problem is the sulfate. By concentrating the sulfate in a first pass through the RO system, the precipitation process can be accomplished without adding more chemicals other than calcium sulfate crystals in the up-flow solids contactor that will not need to be replaced, only removed from time to time to keep the volume down. The precipitate from this process will be of a higher quality as it will be predominantly calcium, barium, and strontium sulfate without any iron or manganese oxides.

Recycling a portion of the effluent of the precipitation process will actually dilute the sulfate concentration from the wells. When the process stabilizes at approximately 8,200 mg/L, the TDS will be mainly sodium and chloride. Evaporation ponds will be smaller because only 10 percent of the total water in the system will be wasted.

The issues of concern with this alternative are determining the retention time for the precipitation process and the level of boron in the product water. Boron would not be a problem with the first alternative because the concentrate is not recycled. With recycling, the concentration in the feed will increase with the TDS, depending on the boron rejection rate. Using the rejection rate for boron from the pilot test, 33%, the equilibrium total product concentration will be 1.5 mg/L—only slightly less than the feed concentration of 1.65 mg/L. A boron limit has not yet been set; but for irrigation and possible health reasons, the WHO has set the limit at 1 mg/L, as discussed earlier. Boron rejection is dependent on the pH, membrane material, and hydraulic operation of the RO system. Currently, there is no model to describe how these factors affect rejection. Therefore, boron will have to be monitored in the product water. If necessary, ion exchange can be used to remove it from a fraction of the RO product stream. The cost should not be prohibitive since the RO product water is devoid of most ions and will not deplete the resin as quickly as it would in a pretreatment system. Also, only a fraction of the total product needs to be treated to bring the final concentration down to 1 mg/L.

6.1 Residuals Management

Table 14 compares the residuals for the two options. Option 1 will require spreading land for 50 tons of sludge plus evaporation ponds for 2.5 Mgal/d of concentrate unless the concentrate can be delivered to a powerplant for cooling water. As it has been softened, it may be acceptable for this purpose. The cost estimate provides for 10 acres of evaporation ponds as a disposal solution.

Table 14. Residuals Production

	Option 1	Option 2
Sludge	32 tons sulfates and hydroxides at 25% solids (42 cubic yards) per day.	
Backwash (BW)	Loading 10 mg/L, BW 2.54 grams per square foot (g/ft^2), three per week, 1,500 square feet (ft^2)= 285,000 gallons per week (gal/week).[1]	Filter 1 loading 4 mg/L, BW: 2.54 g/ft^2, three per week, 525 ft^2 = 100,000 gal/week Filter 2 loading 1.5 mg/L, BW: 2.54 g/sq ft, three per week, 200 ft^2 = 37,000 gal/week
Precipitate		110 kilograms (240 pounds)
Concentrate	2.5 Mgal/d at 17,400 mg/L	0.5 Mgal/d at14,000 mg/L

[1] Estimate.

Option 2 produces a drier, denser precipitate from the concentrate stream at approximately 240 pounds per day. The precipitate is not soluble or hazardous, so it can be land filled. The concentrate produced will be 500,000 gallons per day of stable, predominately sodium chloride TDS. It would be more attractive as cooling water or for dust control. The cost estimate provides a 1-acre evaporation pond for concentrate disposal.

6.2 Operational Expenses

Annual costs for both options are listed in tables 12 and 13. The main expenses for option 1 are chemical costs for lime and antiscalant and power for the RO system. Option 2 main expenses are antiscalant and power for the ozone generator and the RO system. Option 2 has a lower energy cost because it is a single stage system with 50% recovery rather than a two stage system with 75% recovery.

6.3 Conclusions

Surface water from an existing Ranney well under the Virgin River can be treated to potable standards, in compliance with the Safe Drinking Water Act with an estimated cost of $1.00/kgal. The preferred methodology is by option 2 using ozonation, dual media filters, RO with 50% recovery, followed by concentration precipitation and recycle to the feed. Product water can be blended with pretreated feed water at a rate of approximately 15% pretreated water to RO product.

Further pilot testing will be required to determine precipitation retention time for sizing the up-flow solids contactor and to determine boron rejection. A decision would then be made to allow the boron concentration of about 1.5 mg/L or to add ion exchange to one-third of the RO product water to lower the concentration to meet the WHO standard.

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Appendix I

Barium Chloride Pretreatment Study

Barium Chloride Pretreatment Process

Bench-Scale Test Report

Submitted by

Scott McKeag

dba Environmental REMEDIES

on

July 30, 2003

Purchase Order Number: 03TG810644A

1. Executive Summary

Pretreatment test work on the Mesquite, Nevada, well water has been completed according to the test procedure. Analytical data suggest that all four pretreatment processes successfully reduced sulfate and carbonate levels in the Mesquite, Nevada, well water to levels that will permit higher percent recovery of high-quality water during subsequent nanofiltration (NF) or reverse osmosis (RO) processing. Additionally, the pretreatment processes significantly reduced the levels of iron, manganese, calcium, magnesium, and total alkalinity. Not all resultant test solids successfully passed the toxic characteristic leach procedure (TCLP); however, one test did pass suggesting that the pretreatment process can be performed to enhance high-quality water recovery at Mesquite, Nevada, without producing hazardous waste.

2. Introduction

Four separate, slightly different bench-scale tests were performed on identical well water samples obtained from the Mesquite, Nevada, well site on June 16, 2003 (assisted by John Wahl – Bureau of Reclamation). The well water has extremely high dissolved solids content with several analytes exceeding the Nevada maximum contaminant level (MCL). These include iron at 3.8 parts per million (ppm), magnesium at 180 ppm, manganese at 0.94 ppm, chloride at 610 ppm, and sulfate at 1,600 ppm. Removal of sulfate and carbonate from the well water using a barium chloride pretreatment will enhance the recovery of high-quality water from the nanofiltration test and/or the reverse osmosis test by removing the primary scaling anions, namely sulfate and carbonate.

3. Purpose

The barium pretreatment process was tested on the Mesquite, Nevada, well water to demonstrate that it is possible to remove sulfate and carbonate anions from the well water, thereby decreasing the scaling potential of the well water during subsequent nanofiltration and/or reverse osmosis test work, allowing increased high-quality water recovery.

4. Expectation

Each test produced approximately 10 gallons of pretreatment water that should contain approximately 1 ppm sulfate and approximately 25 ppm carbonate. This represents a 1,600-fold reduction of sulfate and a 16-fold reduction of carbonate. The current well water chloride content (650 ppm) should increase to approximately 2,000 ppm (chloride compounds do not cause scaling on membrane systems). Each test should also produce approximately 150 grams of a white precipitate of barium sulfate and barium carbonate.

5. Consideration

If the procedure is successful yet the elevated chloride level is determined to be undesirable, barium hydroxide can be used in place of barium chloride. The same effect will be achieved; but instead of an elevated chloride level, an elevated pH will result. This could be beneficial during membrane separation (increased flux) and may also remove magnesium from solution because magnesium hydroxide is nearly insoluble.

6. Reaction Vessel

All four tests were conducted in a reaction vessel consisting of a simple 5-gallon plastic open-top container. The first test procedure called for barium chloride to be added slowly while the well water was stirred gently. For the remaining three tests, a lift tube and compressed air sparger was used to achieve the desired circulation.

7. Procedure

7.1 Simple Precipitation Process

- 5 gallons (19 liters [L]) of well water were weighed and added to the reaction vessel.
- 340 grams (g) of saturated barium chloride solution (about 22.5 percent [%]) were added drop-wise while stirring gently.
- This continued until the calculated requirement of barium chloride solution is fulfilled (stociometric minus 0.5%). Stirring continued for approximately 120 minutes.
- The precipitate was allowed to settle, and the settling time was recorded.
- 1,500 milliliters (mL) of the decant solution were kept as an analytical sample.
- The remaining clear solution was decanted back into the 5-gallon sample container.
- Another 5 gallons (19 L) of well water were weighed and added to the reaction vessel, and the procedure was repeated. (This is done simply to obtain enough precipitate to run the required analytical tests.)

- The two 1,500-mL samples were combined and submitted for analysis.
- The remaining thick precipitate slurry of barium carbonate and barium sulfate was combined and rinsed with a mild sulfuric acid solution (1.5 pH) and stirred to gently dissolve the barium carbonate, forming additional barium sulfate, water, and carbon dioxide.
- The resultant precipitate was allowed to settle, and the settling time was recorded.
- The resultant clear solution shall be removed and discarded.
- The remaining thick precipitate slurry of barium sulfate was transferred to a filtering device and rinsed with four 100-mL volumes of de-ionized (DI) water to displace any remaining sulfuric acid.
- The rinsed barium sulfate solids were then dried in a microwave oven. The mass was recorded, and the sample was submitted for barium TCLP analysis.

7.2 Crystal Growth Precipitation Process

- 5 gallons (19 L) of well water were weighed and added to the reaction vessel.
- The lift tube apparatus and compressed air sparger were placed into the reaction vessel.
- The air pump was turned on and adjusted to ensure the proper amount of circulation.
- 340 g of the 22.5% barium chloride solution were added drop-wise during air sparging.
- This continued until the calculated requirement of barium chloride solution was fulfilled (stociometric minus 0.5%).
- The air pump was turned off, the precipitate was allowed to settle, and the settling time was recorded.
- 1,500 mL of the decant solution were kept as an analytical sample.
- The remaining clear solution was decanted back into the 5-gallon sample container.
- Another 5 gallons (19 L) of well water was weighed and added to the reaction vessel, and the procedure was repeated. (This is done simply to obtain enough precipitate to run the required analytical tests.)
- The two 1,500-mL samples were combined and submitted for analysis.

- The remaining thick precipitate slurry of barium carbonate and barium sulfate was rinsed with a mild sulfuric acid solution and stirred to gently dissolve the barium carbonate, forming additional barium sulfate, water, and carbon dioxide.
- The resultant precipitate was allowed to settle, and the settling time was recorded.
- The resultant clear solution was removed and discarded.
- The remaining thick precipitate slurry of barium sulfate was transferred to a filtering device and rinsed with four 100-mL volumes of DI water to displace any remaining sulfuric acid.
- The rinsed barium sulfate solids were then dried in a microwave oven. The mass was recorded, and the sample was submitted for barium TCLP analysis.

7.3 Seeded Crystal Growth Precipitation Process

- 5 gallons (19 L) of well water were weighed and added to the reaction vessel.
- The lift tube apparatus and compressed air sparger were placed into the reaction vessel.
- The air pump was turned on and adjusted to ensure the proper amount of circulation.
- Approximately 2 g of fine crystalline barium sulfate were added to the reaction vessel.
- 300 g of the 25% barium chloride solution were added drop-wise during air sparging.
- This continued until the calculated requirement of barium chloride solution was fulfilled (stociometric minus 0.5%).
- The air pump was turned off, the precipitate was allowed to settle, and the settling time was recorded.
- 1,500 mL of the decant solution were kept as an analytical sample.
- The remaining clear solution was decanted back into the 5-gallon sample container.
- Another 5 gallons (19 L) of well water was weighed and added to the reaction vessel, and the procedure was repeated. (This is done simply to obtain enough precipitate to run the required analytical tests.)
- The two 1,500-mL samples were combined and submitted for analysis.

- The remaining thick precipitate slurry of barium carbonate and barium sulfate was rinsed with a mild sulfuric acid solution and stirred to gently dissolve the barium carbonate, forming additional barium sulfate, water, and carbon dioxide.
- The resultant precipitate was allowed to settle, and the settling time was recorded.
- The resultant clear solution was removed and discarded.
- The remaining thick precipitate slurry of barium sulfate was transferred to a filtering device and rinsed with four 100-mL volumes of DI water to displace any remaining sulfuric acid.
- The rinsed barium sulfate solids were then dried in a microwave oven. The mass was recorded, and the sample was submitted for barium TCLP analysis.

7.4 Seeded Crystal Growth Precipitation Process with Thermal Treatment of Resultant Solids

- 5 gallons (19 L) of well water were weighed and added to the reaction vessel.
- The lift tube apparatus and compressed air sparger were placed into the reaction vessel.
- The air pump was turned on and adjusted to ensure the proper amount of circulation.
- Approximately 2 g of fine crystalline barium sulfate were added to the reaction vessel.
- 300 g of the 25% barium chloride solution were added drop-wise during air sparging.
- This continued until the calculated requirement of barium chloride solution was fulfilled (stociometric minus 0.5%).
- The air pump was turned off, the precipitate was allowed to settle, and the settling time was recorded.
- 1,500 mL of the decant solution were kept as an analytical sample.
- The remaining clear solution was decanted back into the 5-gallon sample container.
- Another 5 gallons (19 L) of well water were weighed and added to the reaction vessel, and the procedure was repeated. (This is done simply to obtain enough precipitate to run the required analytical tests.)

- The two 1,500-mL samples were combined and submitted for analysis.
- The remaining thick precipitate slurry of barium carbonate and barium sulfate was rinsed with a mild sulfuric acid solution and stirred to gently dissolve the barium carbonate, forming additional barium sulfate, water, and carbon dioxide.
- The resultant precipitate was allowed to settle, and the settling time was recorded.
- The resultant clear solution was removed and discarded.
- The remaining thick precipitate slurry of barium sulfate was transferred to a filtering device and rinsed with four 100-mL volumes of DI water to displace any remaining sulfuric acid.
- The rinsed barium sulfate solids were then dried in a microwave oven. The mass was recorded.
- The dried solids were heated to 500 degrees Celsius for 48 hours to strengthen and grow the barite crystals, and then the sample was submitted for barium TCLP analysis.

8. Calculations

Chemical/mass calculations to determine the appropriate amounts of barium chloride to use to form a maximum of barium sulfate and barium carbonate and a minimum of excess barium in solution was recorded.

9. Observations

When collected, the well water was a clear, uncolored liquid. However, when test work began 10 to 14 days later, the water was a rusty red color. This coloration is assumed to be related to the oxidation of reduced iron species. During all four bench-scale tests, this rusty red coloration was removed with the resultant pretreated water being a clear colorless liquid and the barium sulfate precipitate being a pinkish-beige color. Upon rinsing with mild sulfuric acid the precipitate became a brilliant white suggesting that the iron was removed from the precipitate.

10. Analytical Data

Analytical procedures were performed by NEL Laboratories in Las Vegas, Nevada. The results are also presented in table A.1. The simple precipitation process samples were labeled BoR-100, the crystal-growth precipitation process

Table A:1. Results of Barium Chloride Precipitation Study

	Well Water		Pretreated Well Water[1]				Calculations			
	Raw	Unit	BoR-100	BoR-200	BoR-300	BoR-400	Sumation	Average	Difference	% Diff.
pH	7.46		7.52	7.75	7.73	7.79	30.79	7.70	-0.24	0.0
Al	0	ppm	<0.05	<0.05	<0.05	<0.05	0	0.00	0.00	0.0
As	0	ppm	<0.001	<0.005	<0.005	<0.005	0	0.00	0.00	0.0
Ba	0.029	ppm	34	83.9	0.662	3.61	122.172	30.54	-30.51	105,220.7
Be	0	ppm	<0.005	<0.005	<0.005	<0.005	0	0.00	0.00	0.0
B	1.6	ppm	1.48	1.47	1.47	1.46	5.88	1.47	0.13	-8.1
Cd	0	ppm	<0.005	<0.005	<0.005	<0.005	0	0.00	0.00	0.0
Ca	490	ppm	390	384	365	350	1489	372.25	117.75	-24.0
Cr	0	ppm	<0.01	<0.01	<0.01	<0.01	0	0.00	0.00	0.0
Cu	0	ppm	<0.004	<0.004	<0.004	<0.004	0	0.00	0.00	0.0
Fe	3.8	ppm	<0.1	0.0734	<0.1	<0.1	0.0734	0.02	3.78	-99.5
Mg	180	ppm	161	159	159	161	640	160.00	20.00	-11.1
Mn	0.94	ppm	0.419	0.333	0.176	0.107	1.035	0.26	0.68	-72.5
Ni	0	ppm	<0.04	<0.04	<0.04	<0.04	0	0.00	0.00	0.0
K	40	ppm	33.7	31.9	33.8	33.3	132.7	33.18	6.83	-17.1
Ag	0	ppm	<0.5	<0.5	<0.5	<0.5	0	0.00	0.00	0.0
Na	460	ppm	433	427	432	433	1725	431.25	28.75	-6.3
Zn	0	ppm	<0.05	0.0503	<0.05	<0.05	0.0503	0.01	-0.01	0.0
Cl	610	ppm	1,900	2,000	1,800	1,900	7,600	1,900.00	-1,290.00	211.5
N	0	ppm	<2	<2	<2	<2	0	0.00	0.00	0.0
SO_4	1,600	ppm	22	0.41	60	9.3	91.71	22.93	1,577.07	-98.6
Bicarb Alk	200	ppm	160	130	130	100	520	130.00	70.00	-35.0
Carb Alk	400	ppm	<5	<5	<5	<5	0	0.00	400.00	-100.0
Hydroxide Alk	0	ppm	<5	<5	<5	<5	0	0.00	0.00	0.0
Total Alk	400	ppm	160	130	130	100	520	130.00	270.00	-67.5
Cond	4,600	uS/cm	5,840	5,870	5,600	5,650	22,960	5,740.00	-1,140.00	24.8
TDS	3,910	ppm	4,230	4,260	3,790	3,920	16,200	4,050.00	-140.00	3.6
Fl	2	ppm	0.49	0.59	0.56	0.53	2.17	0.54	1.46	-72.9
Total P	0.035	ppm	0.092	0.059	0.027	0.018	0.196	0.05	-0.01	40.0
Si	22	ppm	26	26	26	25	103	25.75	-3.75	17.0
Ba TCLP		ppm	200	180	0.23	84	464.23	116.06		

[1] BoR-100: Simple precipitation process
BoR-200: Crystal-growth precipitation process
BoR-300: Seeded crystal-growth precipitation process
BoR-400: Thermally treated, seeded crystal-growth process

samples were labeled BoR-200, the seeded crystal-growth precipitation process samples were labeled BoR-300, and the thermally treated, seeded crystal-growth process samples were labeled BoR-400.

11. Data Presentation

All four pretreatment procedures resulted in near identical aqueous results and, therefore, shall be discussed as if one using averaged data. The barium TCLP results were extremely variable as expected and shall be discussed individually.

12. Aqueous Analytical Data

The reduction of soluble sulfate and carbonate as well as the concomitant increase in chloride and total dissolved solids (TDS) were a forgone conclusion, but significant reductions of other potentially harmful dissolved solids were also achieved. Individual analytes will be discussed below.

12.1 pH

The pH of the well water was largely unaffected by the barium chloride pretreatment. The well water had an initial pH of 7.46, well within Nevada's MCL range of 6.5 to 8.5. The well water treated by the simple precipitation process had the lowest final pH of 7.52. The other pretreatment procedures used air sparging to agitate the solution, and these had slightly higher pH levels of 7.75, 7.73, and 7.79. Undoubtedly, the higher pH is due to carbon dioxide introduced during air sparging.

12.2. Aluminum

Aluminum is below detection limits (0.05 ppm) in both the treated and untreated well water.

12.3 Arsenic

Arsenic values are not available for the untreated well water, but the treated well water is below the detection level of 0.005 ppm and well below Nevada's MCL of 0.05 ppm.

12.4 Barium

Barium values are higher than expected and suggest that either the reaction did not go to completion or that the calculated dosages of barium chloride ($BaCl_2$) were too high. Barium levels for the untreated well water were extremely low at 0.029 ppm; whereas, barium values for the treated well water ranged from 0.662 to 83.9 ppm with an average value of 30.5 ppm. The first two experiments (simple precipitation and crystal growth precipitation) were dosed at 340 g of saturated $BaCl_2$ solution per 19 liters of well water and resulted in barium values of 34 and 83.9 ppm, respectively. For the last two experiments (seeded crystal growth precipitation and thermally treated, seeded crystal growth precipitation), the barium chloride saturation level was calculated to be slightly different requiring only 320 g of saturated $BaCl_2$ solution per 19 liters of well water. The barium values for these two experiments were much closer to the expected 1-ppm level at 0.662 and 3.61 ppm, respectively. This would tend to support the argument that experimental error was the reason for the higher barium levels in the first two experiments and not incomplete reaction.

12.5 Beryllium

Beryllium was below detection limits (0.005 ppm) in both the treated and untreated well water.

12.6 Boron

Boron values were slightly decreased in the treated well water, averaging 1.47 ppm as compared to the untreated well water that had a value of 1.6 ppm.

12.7 Cadmium

Cadmium was below detection limits (0.005 ppm) in both the treated and untreated well water.

12.8 Calcium

Treated well water calcium results were reduced on average by 24%. This was unexpected as soluble calcium should not participate in the precipitation reaction but, instead, should become more soluble as a calcium chloride, charge/solution-balancing cation. Calcium values were slightly higher in the first two experiments (simple precipitation and crystal growth precipitation) at 390 and 384 ppm, respectively, and slightly lower in the last two experiments (seeded crystal growth precipitation and thermally treated, seeded crystal growth precipitation) at 365 and 350 ppm, respectively. Whether this observation is significant or not is impossible to tell at this time. It may be possible that, at 490 ppm, the untreated well water might have been supersaturated with respect to a calcium-bearing species and that any precipitation would have caused a minor co-precipitation and subsequent lower calcium levels.

12.9 Chromium

Chromium was below detection limits (0.01 ppm) in both the treated and untreated well water. This value is far less than Nevada's MCL of 0.1 ppm for chromium.

12.10 Copper

Copper was below detection limits (0.004 ppm) in both the treated and untreated well water. This value is far less than Nevada's MCL of 1 ppm for copper.

12.11 Iron

Iron was reduced by 99% on average in the treated well water at an average value of 0.093 ppm as compared to the untreated well water at 3.8 ppm. Nevada's MCL for iron is 0.6 ppm, and the barium chloride pretreatment process clearly reduced the iron levels below the MCL.

12.12 Magnesium

Magnesium levels were also reduced in the treated well water. This is a completely unexpected result. Magnesium levels were dropped an average of 11% from 180 ppm in the untreated well water to 160 ppm in the treated well water. Nevada's MCL for magnesium is 160 ppm.

12.13 Manganese

Manganese in the untreated well water was at 0.94 ppm, well above Nevada's MCL of 0.1 ppm. The barium chloride pretreatment process reduced the manganese levels by 72% on average. The manganese levels varied somewhat in the treated samples ranging from 0.107 to 0.419 ppm. Again, the last two experiments' (seeded crystal growth precipitation and thermally treated, seeded crystal growth precipitation) results were significantly different than the first two experiments' (simple precipitation and crystal growth precipitation) results at 0.107 and 0.178 ppm compared to 0.333 and 0.419 ppm, respectively.

12.14 Nickel

Nickel was below detection limits (0.004 ppm) in both the treated and untreated well water. This value is far less than Nevada's MCL of 0.1 ppm for nickel.

12.15 Potassium

Potassium values for the treated well water were slightly reduced compared to the untreated well water. The average treated potassium value of 33.2 ppm is 27% lower than the untreated well water value of 40 ppm.

12.16 Silver

Silver was below detection limits (0.05 ppm) in both the treated and untreated well water.

12.17 Sodium

The average sodium value for the treated well water was 431 ppm. This is slightly lower than the untreated well water value of 460 ppm but is not considered significant.

12.18 Zinc

Zinc was below detection limits (0.05 ppm) in three of the four treated well water samples and at 0.0503 ppm for the fourth sample. Zinc was not detected in the untreated well water sample. Regardless, these values are far less than Nevada's MCL of 5 ppm for zinc.

12.19 Chloride

As expected, chloride levels in the treated well water samples were at about 2,000 ppm, ranging from 1,800 to 2,000 ppm. This is due to the addition of barium chloride as a source of barium for the procedures. Chloride level in the untreated well water was 610 ppm while the Nevada MCL is 400 ppm.

12.20 Nitrate

Nitrate was below detection limits (2 ppm) in both the treated and untreated well water. This value is far less than Nevada's MCL of 10 ppm for nitrate as Nitrogen.

12.21 Sulfate

Sulfate is the main anion complex of concern. The untreated well water contained 1,600 ppm sulfate, more than three times Nevada's MCL of 500 ppm for sulfate. On average, the sulfate level was dropped by 98% in the treated well water when compared to the untreated sample. The treated well water sulfate levels ranged from 0.41 ppm to 60 ppm with an average of 22.9 ppm. This was slightly higher than anticipated but still represented an enormous reduction in sulfate levels.

12.22 Bicarbonate Alkalinity

A reduction in bicarbonate alkalinity was not anticipated; yet, a 35% reduction was achieved. Bicarbonate alkalinity values for the treated well water samples ranged from 100 to 160 ppm with an average of 130 ppm.

12.23 Carbonate Alkalinity

Carbonate alkalinity was reduced by 100%. A significant reduction was anticipated but not absolute removal. All treated well water samples were below the detection level of 5 ppm. The formation of calcium carbonate during nanofiltration or reverse osmosis treatment leads to reduced flux and increased operating cost. The complete removal of carbonate alkalinity is extremely significant to the Mesquite project.

12.24 Hydroxide Alkalinity

Hydroxide alkalinity was below detection level (5 ppm) for the untreated and treated well water samples.

12.25 Total Alkalinity

Total alkalinity represents the simple addition of carbonate alkalinity, bicarbonate alkalinity, and hydroxide alkalinity; wherefore, in the absence of hydroxide alkalinity and the complete removal of carbonate alkalinity, total alkalinity simply represents the amount of bicarbonate alkalinity. Total alkalinity values for the treated well water samples averaged 130 ppm representing a 67% reduction in total alkalinity as compared to the untreated well water value of 400 ppm.

12.26 Specific Conductance

As expected, the addition of barium chloride to cause barium carbonate and barium sulfate precipitation increased the specific conductance of the treated well water samples by 24% from 4,600 microsiemens per centimeter (uS/cm) in the untreated sample to 5,740 uS/cm. Again, there is a significant difference in the first two experiments (5,855 uS/cm, on average) with the second two experiments (5,625 uS/cm) suggesting experimental error (overdosing of $BaCl_2$) in the simple precipitation process and the crystal growth process. Adjusting for this error suggests a specific conductance increase of only 18.3%. This increase in specific conductance will require slightly higher operating pressures during nanofiltration or reverse osmosis treatment.

12.27 Total Dissolved Solids

As anticipated, the removal of carbonate and sulfate combined with the addition of chloride maintained the overall TDS at present levels. If the TDS values for the first two experiments are ignored ($BaCl_2$ overdosing), the TDS of the treated well water samples decreased slightly from 3,910 ppm in the untreated well water sample to an average of 3,855 ppm.

12.28 Fluoride

Fluoride levels were reduced 31% during barium chloride treatment. Untreated well water contained 0.78 ppm fluoride while the average treated value was 0.54 ppm. The reason for this reduction is not understood, but both treated and untreated values are far below Nevada's MCL of 2 ppm for fluoride.

12.29 Total Phosphorus

Once again, if the first two experimental results are ignored ($BaCl_2$ overdosing), phosphorus levels were slightly reduced during the barium chloride pretreatment process. The untreated well water phosphorus level was 0.035 ppm, and the treated well water sample value was 0.023 ppm.

12.30 Silica

Silica values increased slightly during the barium chloride pretreatment process from 22 ppm in the untreated well water sample to an average of 26 ppm for the treated well water sample. This 15% increase is not thought to be significant but must be considered during design because without sulfate and carbonate in the system, silica may be the membrane foulant of most concern.

13. TCLP Analytical Data

It is extremely exciting that one of the sulfate residues passed the TCLP. It is also exciting that the seeded crystal growth process resulted in a passing value because this is a simple cost-effective way to form the barium sulfate/carbonate crystals.

The simple precipitation process resulted in a TCLP value for barium of 200 ppm. The crystal growth process resulted in a TCLP value for barium of 180 ppm. The seeded crystal growth process resulted in a TCLP value for barium of 0.23 ppm. Also, the thermally treated, seeded crystal growth process resulted in a TCLP value for barium of 84 ppm.

Although it is encouraging to think that the pretreatment process can be accomplished without creating a hazardous waste, it is still unknown whether it is the precipitate formation process or the washing/rinsing process that is most important to passing the TCLP. It is my gut-feel as the person that performed the procedures that the washing and rinsing of the filter cake is the most important.

14. Mass Balance

It is my experience that mass balance attempts at the bench-scale stage are extremely inaccurate but can alert designers to potential issues. Since there was no apparatus available to measure the mass of the 19 plus liters of resultant water from each experiment, this part of the mass balance shall be ignored. However, a known mass of saturated $BaCl_2$ solution was added to each experiment, a known mass of well water was used in each experiment, a known mass of sulfate and carbonate were present in the well water from each experiment, and a known mass of precipitate was removed from each experiment; therefore, the calculation of a solids mass balance should be possible.

The following facts and constants were used to calculate the mass balance:

- Each experiment used approximately 38 kilograms of well water.
- The well water is assumed to contain 1,600 milligrams per liter (mg/L) sulfate and 400 mg/L carbonate.
- 98% of the sulfate was removed.
- 100% of the carbonate was removed.

- The saturated $BaCl_2$ was calculated to be 22.5% for the first two experiments.
- The saturated $BaCl_2$ was calculated to be 25% for the last two experiments.
- 340 g of saturated $BaCl_2$ solution were added to the first two experiments.
- 300 g of saturated $BaCl_2$ solution were added to the last two experiments.
- $BaCl_2$ has a molecular weight of 207.
- Barium has a molecular weight of 137.
- Chlorine has a molecular weight of 35.
- Air-dried sulfate/carbonate cake contains 20% moisture.

Calculations suggest that the first two experiments—namely, the simple precipitation process and the crystal growth precipitation process—should have resulted in 211 g of damp barium sulfate/carbonate cake ignoring other cation and anions removed from solution. Similar calculations for the second two experiments—namely, the seeded crystal growth precipitation process and the thermally treated, seeded crystal growth precipitation process—should have resulted in 208 g of damp barium sulfate/carbonate cake ignoring other cation and anions removed from solution.

The simple precipitation experiment resulted in 189 g of damp barium sulfate/carbonate cake. The crystal growth precipitation experiment resulted in 203 g of damp barium sulfate/carbonate cake. The seeded crystal growth precipitation experiment resulted in 194 g of damp barium sulfate/carbonate cake. The thermally treated, seeded crystal growth precipitation experiment resulted in 179 g of damp barium sulfate/carbonate cake.

These mass balance calculations suggest that reasonable balances were achieved for all four experiments and were 89.6% for the simple precipitation experiment, 96.2% for the crystal growth precipitation experiment, 93.3% for the seeded crystal growth precipitation experiment, and 86.1% for the thermally treated, seeded crystal growth precipitation experiment.

15. Crystal Settling

One disappointing aspect of the experiments was the extremely slow settling times. All four experiments, regardless of the process, required an excess of 2 hours to produce a relatively clear supernate. Within the first 30 minutes, all experiments showed complete settling of the larger particles or crystals; but a “cloud” of colloidal particles persisted for an additional 90 minutes. These extremely fine barium-bearing colloids may cause filtering difficulties during pilot-scale operation, if optioned. The settling time of the sulfuric acid washed solids was much more reasonable at 15 to 20 minutes, and the colloidal "cloud" was not observed.

16. Discussion

The aqueous analytical results are very promising. The results suggest that the pretreatment process can be used to reduce the most troublesome scaling anions from the well water prior to nanofiltration or reverse osmosis and, thereby, increasing the amount of high-quality water recovered. Conventional wisdom suggests that nanofiltration or reverse osmosis could recover approximately 20% to 25% of the untreated well water at Mesquite, Nevada, and using antiscalant chemicals may be able to push that number to 40 to 45%; but beyond this, major membrane scaling will occur. It is clear that at the reduced sulfate and carbonate levels combined with mild specific conductance increases provided by the pretreatment process will allow greater recovery using nanofiltration or reverse osmosis. How much greater is hard to tell. With 98% of the sulfate removed and 100% of the carbonate alkalinity removed it is possible that 80% to 90% recovery is possible without the use of antiscalant chemicals.

The untreated well water exceeds six of Nevada's MCLs including iron, magnesium, manganese, chloride, sulfate, and TDS. The treated well water only exceeds four of Nevada's MCLs including barium (manageable), manganese (slightly), chloride, and TDS. With this in mind, there may be some creative sorption, ion exchange, and blending technologies that could be used in conjunction with the barium chloride or barium hydroxide pretreatment process to avoid nanofiltration and/or reverse osmosis altogether.

The TCLP analyses are also promising, but more knowledge needs to be gathered to ensure that every batch of barium sulfate/carbonate filter cake can be processed so as to pass TCLP. Also, the nature of the spent sulfuric acid wash solution must be determined, and decisions must be made on how best to deal with it. Can it be used multiple times? Want are the consequences of this?

17. Conclusion

The bench-scale test results of the barium chloride pretreatment process was promising enough to move forward with the pilot-scale test.

It would also be wise to perform another identical bench-scale test using barium hydroxide instead of barium chloride. This would provide similar analytical results without the huge increase in chloride, TDS, and specific conductance. The pH of the well water will be driven upwards which may result in significant magnesium hydroxide formation (insoluble), will increase flux through membrane systems providing the pH is not too high, and can be brought back into pH compliance using carbon dioxide which will keep the specific conductance and TDS low. This barium hydroxide approach may not be as economically feasible as the barium chloride approach due to chemical cost but may result in a treated well water that needs no further treatment (i.e., no nanofiltration or reverse osmosis). Regardless, it would be wise to know if this modification of the pretreatment process would provide a benefit.

18. Recommendations for Pilot-Scale Testing

If it is decided to move forward with the pilot-scale test work, it may be wise to perform the pretreatment test work in batch fashion rather than continuously as currently proposed. This would give more control over the chemistry and allow for extended settling time. Using two large Rain-for-Rent containers (10,000 gallons) on an alternating basis will reduce the need for large colloidal filters and will minimize delivery time and setup time required on site.

Cost Considerations

The following cost consideration should be included in any forward planning. Barium chloride is not cheap. Neither is barium hydroxide. The cheapest hard quote received on barium chloride was in 50-pound bags at \$0.72 per pound. Since 300 g of 25% barium chloride solution was needed to treat 5 gallons, it will cost \$4.32 per 1,000 gallons using the \$0.72-per-pound bagged price. Suggestions were made (but no firm quote to support) that, in bulk containers, the price could be as low as \$0.25 per pound which would reduce the cost to \$1.50 per 1,000 gallons. This price seems reasonable but may not be when added to the capital and operating cost of a large nanofiltration or reverse osmosis plant.

Appendix II

Calcium Sulfate Seeding Procedures for Precipitating Nanofiltration and Reverse Osmosis Concentrate

Calcium Sulfate Seeding Procedures for Precipitating Nanofiltration and Reverse Osmosis Concentrate

1. Purpose

The purpose of this procedure is to develop a jar test protocol for the precipitation of calcium sulfate ($CaSO_4$) from the Virgin River water prior to being treated by the reverse osmosis (RO) technique in Mesquite, Nevada. This test protocol outlines a detailed procedure that can be used in jar tests to test and evaluate the removal technique. It can be used to perform preliminary evaluations of treating oversaturated water with $CaSO_4$.

2. Background

In an attempt to address the water needs of the exponentially growing town of Mesquite, Nevada, the Bureau of Reclamation and the Virgin Water Valley District (VVWD) have come together to explore the options of diverting and treating the poor water quality of the Virgin River. One potential treatment method for the $CaSO_4$ in the water is to precipitate the $CaSO_4$ out of the water prior to the water being run through the reverse osmosis system. This treatment method must first be evaluated using jar tests before further assessment of this method can be determined. This protocol was designed to carry out jar tests and determine if the addition of $CaSO_4$ is a plausible solution for the removal of $CaSO_4$.

3. Training

Individuals involved in performing this test should have read the protocol in its entirety as well as have a complete understanding of the procedure and desired reaction of $CaSO_4$ prior to completing the procedure.

4. Interferences

According to the Material Safety Data Sheet on calcium sulfate, none of the other existing constituents in the Virgin River water should cause a threat to this procedure. However, according to the *Hach Water Analysis Handbook*, there could be potential interferences with the sulfate analyses with a few constituents. The concentrations of each of these constituents are lower than the amount which would alter the sulfate analyses results.

5. Equipment and Materials

- Nanofiltration concentrate/RO concentrate water to be treated.
- Water must be sampled no more than 24 hours prior to being treated.
- Calcium sulfate ($CaSO_4$).
- Concentrate meter.
- Analytical scale.
- Jar test apparatus.
- Multiple stirrers with continuous speed variation from about 20 to 150 revolutions per minute.
- An illuminated base for observation of the precipitation process.
- Jars or beakers are all of the same size and shape.
- Sulfate kit to analyze sulfate concentration.
- UniCell vials.
- Syringe.
- Barium chloride ($BaCl_2$).
- Weigh paper.
- Spatula.
- Gloves.
- Goggles.
- Timer.
- Damp cloth.
- Dry cloth.
- pH meter.

6. Safety Precautions

- Safety goggles should be worn while handling the $CaSO_4$.
- Clean up all spills promptly.

- Follow protocol procedures and record observations to ensure knowledge of the outcome and to ensure improved future preparation.

7. Prerequisites

- Verify all equipment used for this jar test is working correctly and calibrated according to manufacturer's specifications.
- All components stated in section 5 of this protocol must be clean and available prior to testing.
- Create an Excel spreadsheet to collect and record all data.

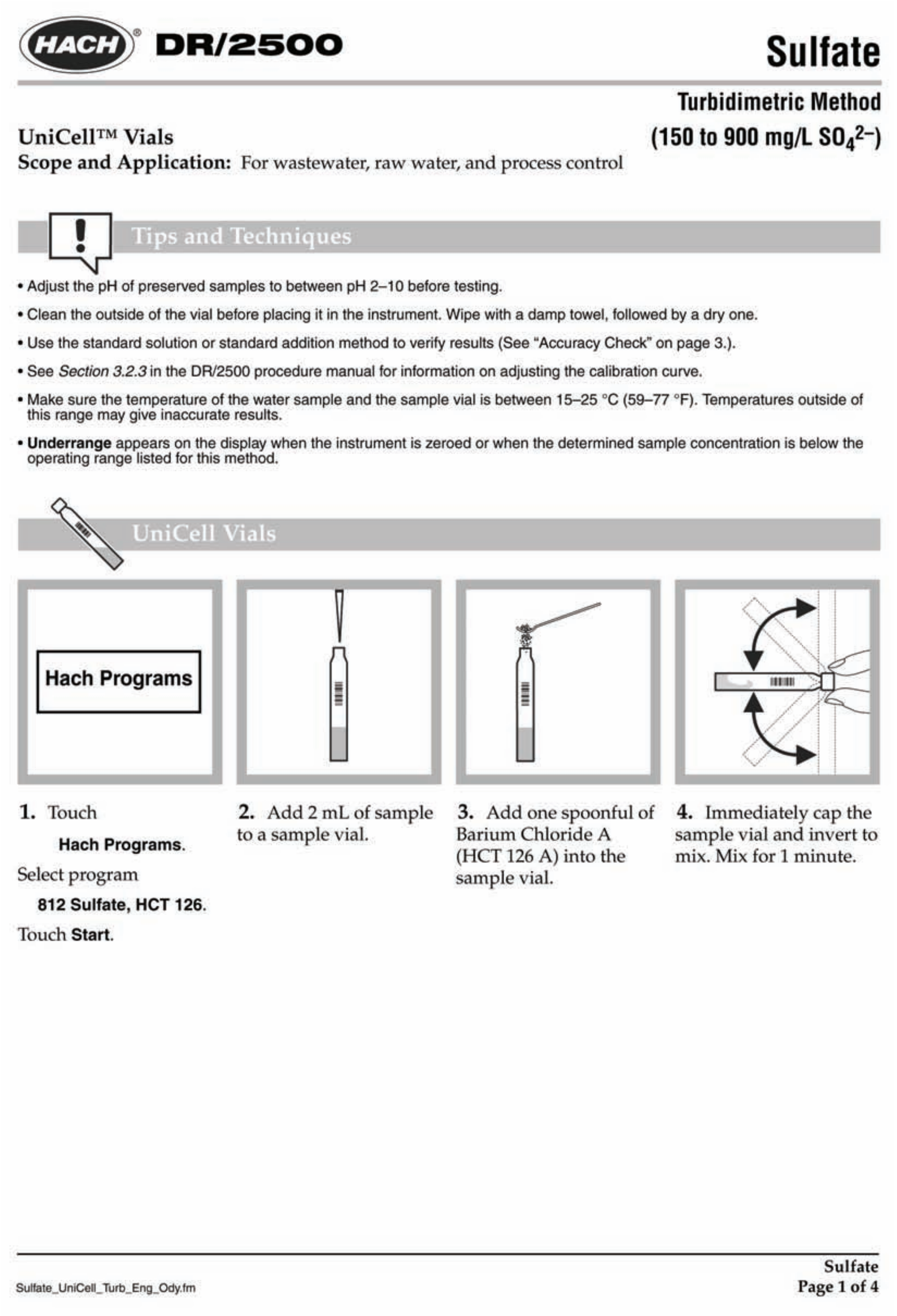
8. Sampling

Water samples should be taken directly from the appropriate locations and placed in clean jars. The jar should be filled with an appropriate amount of water (according to the Excel spreadsheet) and is now ready for jar test performing.

9. Procedure for Jar Tests

- Set up apparatus.
- Collect seven water samples. Use 1 liter of water for each jar.
- Place six of the jars on the jar test apparatus.
- Set the stirring speed.
- Add the appropriate dosages to the jars. This will be time T = 0. (Test the correct amount of dosage by first adding a small amount of calcium sulfate and observing the reaction.)
- Note any immediate observations.
- After 15 minutes, note the physical appearance, test and record the conductivity, and test each solution for SO_4^{-2}.
- Repeat every 15 minutes for 4 hours.

10. Procedure for Sulfate Turbidimetric Method



HACH DR/2500

Sulfate

Turbidimetric Method

(150 to 900 mg/L SO_4^{2-})

UniCell™ Vials

Scope and Application: For wastewater, raw water, and process control

Tips and Techniques

- Adjust the pH of preserved samples to between pH 2–10 before testing.
- Clean the outside of the vial before placing it in the instrument. Wipe with a damp towel, followed by a dry one.
- Use the standard solution or standard addition method to verify results (See "Accuracy Check" on page 3.).
- See *Section 3.2.3* in the DR/2500 procedure manual for information on adjusting the calibration curve.
- Make sure the temperature of the water sample and the sample vial is between 15–25 °C (59–77 °F). Temperatures outside of this range may give inaccurate results.
- **Underrange** appears on the display when the instrument is zeroed or when the determined sample concentration is below the operating range listed for this method.

UniCell Vials

1. Touch **Hach Programs**. Select program **812 Sulfate, HCT 126.** Touch **Start**.

2. Add 2 mL of sample to a sample vial.

3. Add one spoonful of Barium Chloride A (HCT 126 A) into the sample vial.

4. Immediately cap the sample vial and invert to mix. Mix for 1 minute.

Sulfate_UniCell_Turb_Eng_Ody.fm

Sulfate
Page 1 of 4

5. Touch the timer icon.

Touch **OK**.

A 30 second reaction period will begin.

6. Wipe the outside of the zero (**white** cap) and sample vials with a damp towel, followed by a dry one, to remove fingerprints or other marks.

7. When the timer beeps, place the zero vial into the cell holder.

8. Touch **Zero**.

The display will show:

0 mg/L SO_4^{2-}
Underrange

9. Place the sample into the cell holder.

Results will appear in mg/L SO_4^{2-}.

Interferences

The ions listed in the following table have been individually tested up to the given concentrations. Cumulative effects and the influence of other ions have not been evaluated.

Interfering Substance	No interference up to:
K^+, Na^+	2000 mg/L
Ca^{2+}, NO_3^-, Cl^-	1000 mg/L
Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, NH_4^+, Ni^{2+}, Si^{2+}, Sn^{2+}, Zn^{2+}	500 mg/L
Al^{3+}, Pb^{2+}, Hg^{2+}, PO_4^{3-}, CO_3^{2-}, I^-, CN^-, NO_2^-	50 mg/L
Cr^{6+}	20 mg/L
Ag^+	2.5 mg/L

Sample Collection, Storage, and Preservation

Analyze samples within 3 hours after collection for best results. Samples may be stored up to 28 days at 4 °C (39 °F). Warm samples to room temperature before analysis.

Accuracy Check

Standard Additions Method (Sample Spike)

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Touch **Options**. Touch **Standard Additions**. A summary of the standard additions procedure will appear.
3. Touch **OK** to accept the default values for standard concentration, sample volume, and spike volumes. Touch **Edit** to change these values. After values are accepted, the unspiked sample reading will appear in the top row.
4. Prepare three sample spikes. Fill three mixing cylinders with 25 mL of sample. Use a pipet to add 0.2 mL, 0.4 mL, and 0.6 mL of 2500-mg/L SO_4^{2-} standard, respectively, to each sample and mix thoroughly.
5. Transfer 5 mL of each sample spike to a sample vial and analyze each sample spike as described in the procedure above, starting with the 0.2 mL sample spike. Accept each standard additions reading by touching **Read**. Each addition should reflect approximately 100% recovery.
6. After completing the sequence, touch **Graph** to view the best-fit line through the standard additions data points, accounting for matrix interferences. Touch **View: Fit**, then select **Ideal Line** and touch **OK** to view the relationship between the sample spikes and the "Ideal Line" of 100% recovery.

See *Section 3.2.2 Standard Additions* on page *36* for more information.

Standard Solutions

Prepare a 500-mg/L sulfate standard solution as follows:

1. Using Class A glassware, pipet 20 mL of Sulfate Standard Solution, 2500-mg/L, into a 100-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily. Perform the SulfaVer procedure as described above.
2. To adjust the calibration curve using the reading obtained with the 500-mg/L standard solution, touch **Options** on the current program menu. Touch **Standard Adjust**.
3. Touch **On**. Press **OK** to accept the displayed concentration. If an alternate concentration is used, touch the number in the **Adjust to** field and enter the actual concentration. Touch **OK**.

See *Section 3.2.3 Adjusting the Standard Curve* on page *38* for more information.

Method Performance

Precision

Standard: 750 mg/L SO_4^{2-}

Program	95% Confidence Limits of Distribution
812	672–828 mg/L SO_4^{2-}

See *Section 3.4.3 Precision* on page *42* for more information, or if the standard concentration did not fall within the specified range.

Sensitivity

Program	Portion of Curve	∆Abs	∆Concentration
812	Entire range	0.010	5 mg/L SO_4^{2-}

See *Section 3.4.5 Sensitivity* on page *43* for more information.

Summary of Method

Sulfate ions in the sample react with barium chloride in aqueous solution and form a precipitate of barium sulfate. The resulting turbidity is measured photometrically.

Required Reagents

Description	Unit	Cat. No.
Sulfate - SO_4^{2-}, HR, UniCell™ HCT 126	23/pkg	HCT 126

Optional Reagents

Description	Unit	Cat. No.
Sulfate Standard, 2500-mg/L as SO_4	500 mL	14252-49
Sulfate Standard, 2500-mg/L as SO_4, 10-mL Ampules	16/pkg	14252-10

Optional Apparatus

Description	Unit	Cat. No.
Cylinder, mixing, graduated 25-mL	each	20886-40
Pipettor, Jencons, 1–5 mL	each	27951-00
Replacement tips for 27951-00	100/pkg	27952-00
Pipettor, Jencons, 100–1000 µL	each	27949-00
Replacement tips for 27949-00	400/pkg	27950-00

11. Complete Data Tests

Sections 9 and 10 should be completed for both the nanofiltration concentrate and the RO concentrate.

Appendix III

Argo Analyzer Results

Argo Analyzer

Report for
3.6 USGPM
Membrane Separation Plant
at
Mesquite

Prepared by : Saied Delagah
Thursday, April 15, 2004

If you have questions or concerns about the use or distribution of Argo Analyzer please contact your regional BetzDearborn representative.

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BetzDearborn

Argo Analyzer

Report 7/3/2018 for 3.6 USGPM Membrane Separation plant at Mesquite

INTRODUCTION.

The following report is prepared from the details completed for the Raw Water prepared to be supplied to a Membrane Separation Plant operating as specified. The information is given for guidance only.

RAW WATER.

The Raw Water details show :
Surface Water has been selected as the source of the raw water.
The water has been analysed recently

FEEDWATER.

The following is reported for the Feedwater using the Raw Water as basis :

Total Hardness is derived from Calcium ion and Magnesium ion values
Calcium Hardness is derived from the Calcium ion Value
Magnesium Hardness is derived from the Magnesium ion Value
Alkalinity value is derived from the Bicarbonate ion Value
CO2 value is calculated from the raw water pH and Bicarbonate/Alkalinity value
The raw water TDS value has been calculated by summing the individual ions
Conductivity reported is based on TDS x 0.65
The Sodium Absorption Ratio (SAR) indicates that this water is suitable for irrigation

PRETREATED WATER.

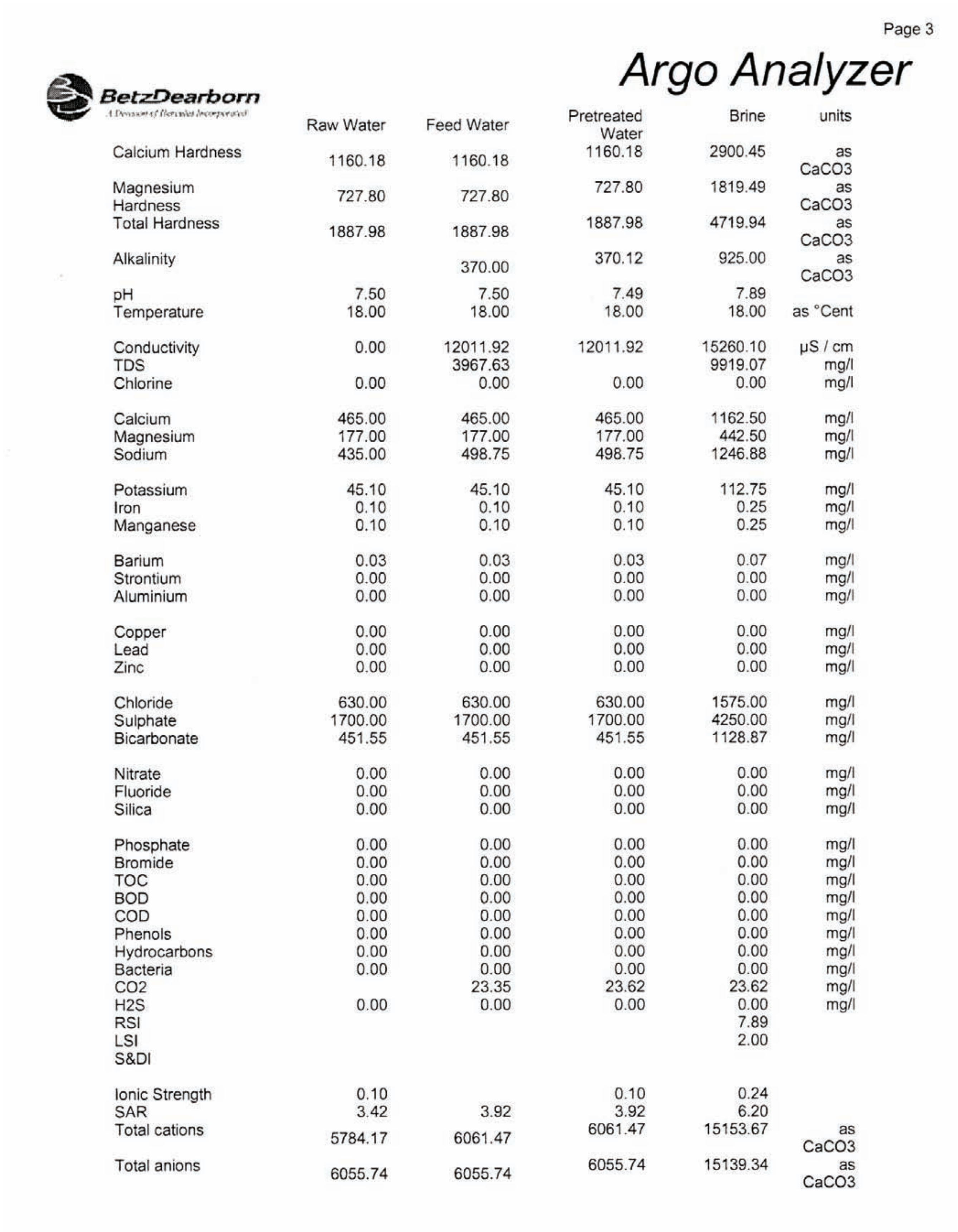
The Pretreated Water is as follows :
The feedwater has been prepared for introduction into a membrane separation plant operating at 60.0% recovery.
The pH does not need adjustment. Scale control will be by the addition of Chemical Inhibitor only.
In order to control the precipitation of limited solubility salts it will be necessary to dose 5.66ppm of Hypersperse MDC220
An arrangement to flush out pretreated water from the membranes at each plant shutdown is highly recommended.
The following ions are presented at the maximum permitted concentration (mg/l) as the presence was not indicated in the Raw Water:
Strontium - 135.23mg/l Fluoride - 67.37mg/l Aluminium - 0.08mg/l Silica - 46.94mg/l
The maximum values are given for guidance only and are not considered in the program calculations.It may be necessary to increase the dose of antiscalant to control the above salts at these levels.

BRINE.

The following is reported for the Brine :
The Brine projection is from the pretreated feedwater passing over polyamide spiral wound membranes when operating at a recovery of 60.0%
The LSI of the brine is 2.00
The saturation indicies of the limited solubility salts being controlled by inhibition are :
CaSO4 :0.7%, BaSO4 :0.1,
The above are based on the maximum inhibition possible for the selected product
The maximum possible recovery using this pretreated water, with the selected antiscalant, based on the scale potential, is 68.0%
The limiting salt is Calcium Sulphate

CHEMICAL DOSING.

Feed water chemical consumption :
The plant output is 3.6 USGPM operating at 60.0% recovery
The raw water requirement will be 6.0 USGPM
Based on the plant operating 24 hours per day, 7 days per week, 52 weeks per year, this plant will produce 1886976.0US Gallons per year from a feed flow of 3144960.0US Gallons per year . The plant will consume a total of 148.5 pounds per year of Hypersperse MDC220



Argo Analyzer

BetzDearborn
A Division of Hercules Incorporated

	Raw Water	Feed Water	Pretreated Water	Brine	units
Calcium Hardness	1160.18	1160.18	1160.18	2900.45	as CaCO3
Magnesium Hardness	727.80	727.80	727.80	1819.49	as CaCO3
Total Hardness	1887.98	1887.98	1887.98	4719.94	as CaCO3
Alkalinity		370.00	370.12	925.00	as CaCO3
pH	7.50	7.50	7.49	7.89	
Temperature	18.00	18.00	18.00	18.00	as °Cent
Conductivity	0.00	12011.92	12011.92	15260.10	µS / cm
TDS		3967.63		9919.07	mg/l
Chlorine	0.00	0.00	0.00	0.00	mg/l
Calcium	465.00	465.00	465.00	1162.50	mg/l
Magnesium	177.00	177.00	177.00	442.50	mg/l
Sodium	435.00	498.75	498.75	1246.88	mg/l
Potassium	45.10	45.10	45.10	112.75	mg/l
Iron	0.10	0.10	0.10	0.25	mg/l
Manganese	0.10	0.10	0.10	0.25	mg/l
Barium	0.03	0.03	0.03	0.07	mg/l
Strontium	0.00	0.00	0.00	0.00	mg/l
Aluminium	0.00	0.00	0.00	0.00	mg/l
Copper	0.00	0.00	0.00	0.00	mg/l
Lead	0.00	0.00	0.00	0.00	mg/l
Zinc	0.00	0.00	0.00	0.00	mg/l
Chloride	630.00	630.00	630.00	1575.00	mg/l
Sulphate	1700.00	1700.00	1700.00	4250.00	mg/l
Bicarbonate	451.55	451.55	451.55	1128.87	mg/l
Nitrate	0.00	0.00	0.00	0.00	mg/l
Fluoride	0.00	0.00	0.00	0.00	mg/l
Silica	0.00	0.00	0.00	0.00	mg/l
Phosphate	0.00	0.00	0.00	0.00	mg/l
Bromide	0.00	0.00	0.00	0.00	mg/l
TOC	0.00	0.00	0.00	0.00	mg/l
BOD	0.00	0.00	0.00	0.00	mg/l
COD	0.00	0.00	0.00	0.00	mg/l
Phenols	0.00	0.00	0.00	0.00	mg/l
Hydrocarbons	0.00	0.00	0.00	0.00	mg/l
Bacteria	0.00	0.00	0.00	0.00	mg/l
CO2		23.35	23.62	23.62	mg/l
H2S	0.00	0.00	0.00	0.00	mg/l
RSI				7.89	
LSI				2.00	
S&DI					
Ionic Strength	0.10		0.10	0.24	
SAR	3.42	3.92	3.92	6.20	
Total cations	5784.17	6061.47	6061.47	15153.67	as CaCO3
Total anions	6055.74	6055.74	6055.74	15139.34	as CaCO3

This projection has been prepared
for the 3.6 USGPM membrane plant at Mesquite

Dose Projection and Product Selection Summary

Selected Product : Hypersperse MDC220
Required Dosage : 5.66 mg/l
Usage Rate : 0.41 lb/day

Degrees of Saturation in Concentrate as %

Saturation	$CaSO_4$	$BaSO_4$	$SrSO_4$	CaF_2	SiO_2
Without Inhibitor	219.58	1074.84	0.00	0.00	0.00
With Inhibitor	73.19	10.24	0.00	0.00	0.00

The projected calcium carbonate saturation level is 2.00 expressed as LSI
The limit for LSI is 3 with inhibitor and 0.0 without.

The projection is for a 3.6 USGPM membrane separation plant, operating at 60% recovery.

The foregoing recommendations are given in good faith and are based on the analytical and operation data you have entered, and on application data which we believe to be correct. No warranty as to specific application is expressed or implied since conditions of use and other contributory factors are beyond our control Please seek advice from your BetzDearborn membrane specialist with regard to any particular query.

Appendix IV

Hydranautics' Cleaning Procedures

HYDRANAUTICS
A Nitto Denko Corporation
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Technical Service Bulletin

July 2003 TSB107.10

Foulants and Cleaning Procedures for composite polyamide RO Membrane Elements (ESPA, ESNA, CPA, LFC, and SWC)

This bulletin provides general information about the usual foulants affecting the performance of Hydranautics' Composite Polyamide Reverse Osmosis (RO) membrane elements and the removal of these foulants. The information in this bulletin applies to 4-inch, 6-inch, 8-inch, and 8.5-inch diameter RO membrane elements.

Note: The Composite Polyamide type of RO membrane elements may not be exposed to chlorinated water under any circumstances. Any such exposure will cause irreparable damage to the membrane. Absolute care must be taken following any disinfection of piping or equipment or the preparation of cleaning or storage solutions to ensure that no trace of chlorine is present in the feedwater to the RO membrane elements. If there is any doubt about the presence of chlorine, perform chemical testing to make sure. Neutralize any chlorine residual with a sodium bisulfite solution, and ensure adequate mixing and contact time to accomplish complete dechlorination. Dosing rate is 1.8 to 3.0 ppm sodium bisulfite per 1.0 ppm of free chlorine.

Note: It is recommended that all RO membrane cleaning operations should be closely coordinated with Hydranautics during the RO membrane element warranty period. Hydranautics field service personnel are available to be on site for cleaning assistance, should the need arise. Please contact Hydranautics for current charges for this service.

Note: The use of cationic surfactant should be avoided in cleaning solutions, since irreversible fouling of the membrane elements may occur.

If additional information is needed, please contact the Technical Services Department at:

HYDRANAUTICS
401 Jones Rd.
Oceanside, CA 92054

Tel# (760) 901-2500
Fax# (760) 901-2578
e-mail: info@hydranautics.com
Internet: www.membranes.com

RO Membrane Fouling and Cleaning

During normal operation over a period of time, RO membrane elements are subject to fouling by suspended or sparingly soluble materials that may be present in the feedwater. Common examples of foulants are:

- Calcium carbonate scale
- Sulfate scale of calcium, barium or strontium
- Metal oxides (iron, manganese, copper, nickel, aluminum, etc.)
- Polymerized silica scale
- Inorganic colloidal deposits
- Mixed inorganic/organic colloidal deposits
- NOM organic material (Natural Organic Matter)
- Man-made organic material (e.g. antiscalant/dispersants, cationic polyelectrolytes)
- Biological (bacterial bioslime, algae, mold, or fungi)

The nature and rapidity of fouling depends on a number of factors, such as the quality of the feedwater and the system recovery rate. Typically, fouling is progressive, and if not controlled early, will impair the RO membrane element performance in a relatively short time. Cleaning is recommended when the RO shows evidence of fouling, just prior to a long-term shutdown, or as a matter of scheduled routine maintenance. Fouling characteristics that signal the need to clean are:

- A 10-15% decrease in normalized permeate flow.
- A 10-15% decrease in normalized permeate quality.
- A 10-15% increase in normalized pressure drop, as measured between the feed and concentrate headers.
- In the event you do not normalize your operating data, the above values still apply if you do not have major changes in critical operating parameters. The operating parameters that have to stay constant are permeate flow, permeate back-pressure, recovery, temperature, and feed TDS. If these operating parameters fluctuate, then it is highly recommended that you normalize the data to determine if fouling is occurring or if the RO is actually operating normally based on the change in a critical operating parameter. Hydranautics offers a free normalization software program called ROData, which can be downloaded from our web site at www.membranes.com.

Monitoring overall plant performance on a regular basis is an essential step in recognizing when membrane elements are becoming fouled. Performance is affected progressively and in varying degrees, depending on the nature of the foulants. Table 1 "RO Troubleshooting Matrix" provides a summary of the expected effects that common foulants have on performance.

RO cleaning frequency due to fouling will vary by site. A rough rule of thumb as to an acceptable cleaning frequency is once every 3 to 12 months. If you have to clean more than once a month, you should be able to justify further capital expenditures for improved RO pretreatment or a re-design of the RO operation. If the cleaning frequency is every one to three months, you may want to focus on improving the operation of your existing equipment but further capital expenditure may be harder to justify.

It is important to clean the membranes when they are only lightly fouled, not heavily fouled. Heavy fouling can impair the effectiveness of the cleaning chemical by impeding the penetration of the chemical deep into the foulant and in the flushing of the foulant out of the elements. If normalized membrane performance drops 30 to 50%, it may be impossible to fully restore the performance back to baseline conditions.

One RO design feature that is commonly over-looked in reducing RO cleaning frequency is the use of RO permeate water for flushing foulants from the system. Soaking the RO elements during standby with permeate can help dissolve scale and loosen precipitates, reducing the frequency of chemical cleaning.

What you clean for can vary site by site depending on the foulant. Complicating the situation frequently is that more than one foulant can be present, which explains why cleanings frequently require a low pH and high pH cleaning regiment.

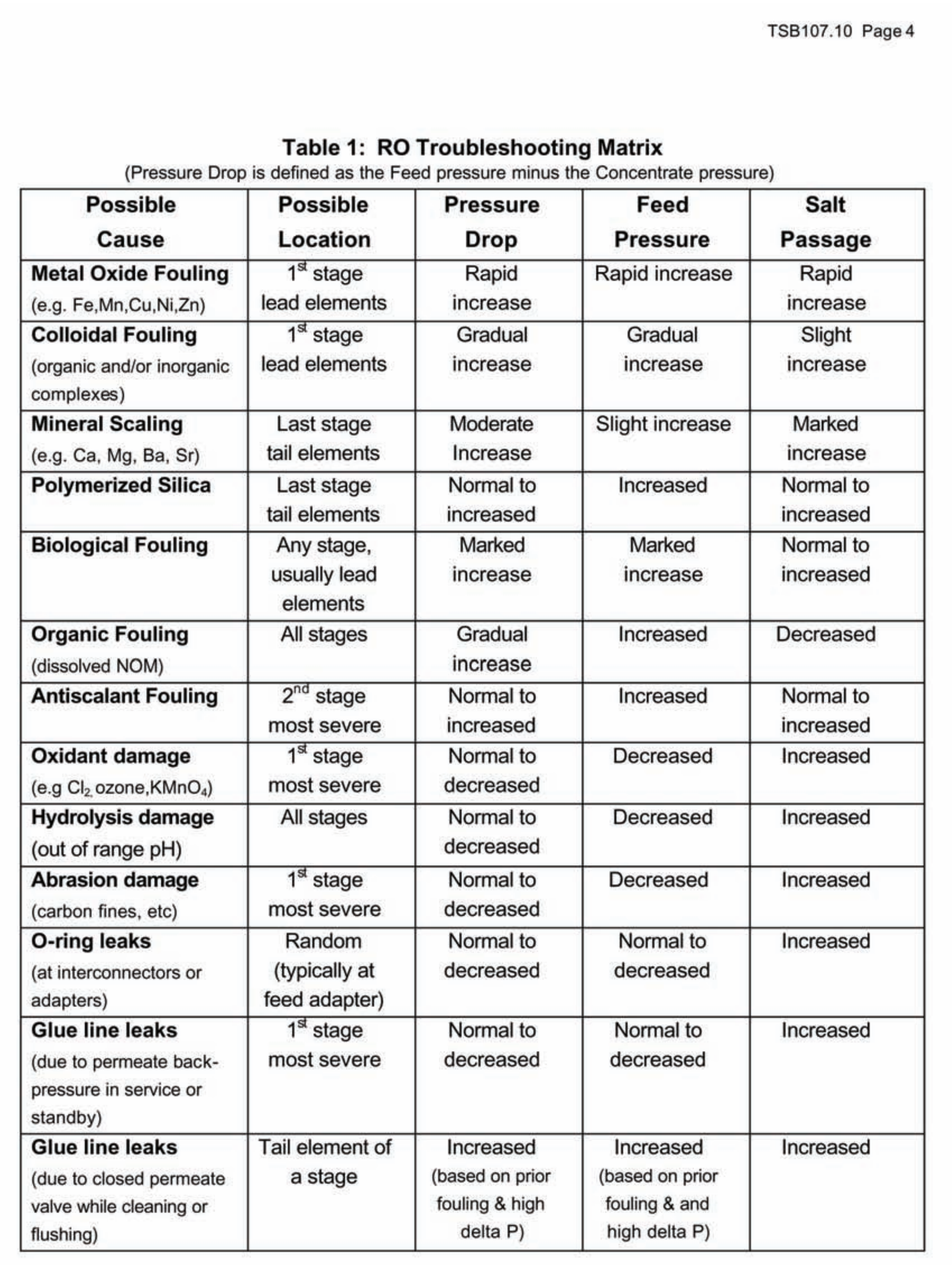


Table 1: RO Troubleshooting Matrix

(Pressure Drop is defined as the Feed pressure minus the Concentrate pressure)

Possible Cause	Possible Location	Pressure Drop	Feed Pressure	Salt Passage
Metal Oxide Fouling (e.g. Fe,Mn,Cu,Ni,Zn)	1st stage lead elements	Rapid increase	Rapid increase	Rapid increase
Colloidal Fouling (organic and/or inorganic complexes)	1st stage lead elements	Gradual increase	Gradual increase	Slight increase
Mineral Scaling (e.g. Ca, Mg, Ba, Sr)	Last stage tail elements	Moderate Increase	Slight increase	Marked increase
Polymerized Silica	Last stage tail elements	Normal to increased	Increased	Normal to increased
Biological Fouling	Any stage, usually lead elements	Marked increase	Marked increase	Normal to increased
Organic Fouling (dissolved NOM)	All stages	Gradual increase	Increased	Decreased
Antiscalant Fouling	2nd stage most severe	Normal to increased	Increased	Normal to increased
Oxidant damage (e.g Cl_2, ozone, $KMnO_4$)	1st stage most severe	Normal to decreased	Decreased	Increased
Hydrolysis damage (out of range pH)	All stages	Normal to decreased	Decreased	Increased
Abrasion damage (carbon fines, etc)	1st stage most severe	Normal to decreased	Decreased	Increased
O-ring leaks (at interconnectors or adapters)	Random (typically at feed adapter)	Normal to decreased	Normal to decreased	Increased
Glue line leaks (due to permeate back-pressure in service or standby)	1st stage most severe	Normal to decreased	Normal to decreased	Increased
Glue line leaks (due to closed permeate valve while cleaning or flushing)	Tail element of a stage	Increased (based on prior fouling & high delta P)	Increased (based on prior fouling & and high delta P)	Increased

Discussion on Foulants

Calcium Carbonate Scale: Calcium carbonate is a mineral scale and may be deposited from almost any feedwater if there is a failure in the antiscalant/dispersant addition system or in the acid injection pH control system that results in a high feedwater pH. An early detection of the resulting calcium carbonate scaling is absolutely essential to prevent the damage that crystals can cause on the active membrane layers. Calcium carbonate scale that has been detected early can be removed by lowering the feedwater pH to between 3.0 and 5.0 for one or two hours. Longer resident accumulations of calcium carbonate scale can be removed by a low pH cleaning with a citric acid solution.

Calcium, Barium & Strontium Sulfate Scale: Sulfate scale is a much “harder” mineral scale than calcium carbonate and is harder to remove. Sulfate scale may be deposited if there is a failure in the antiscalant/dispersant feed system or if there is an over feed of sulfuric acid in pH adjustment. Early detection of the resulting sulfate scaling is absolutely essential to prevent the damage that crystals can cause on the active membrane layers. Barium and strontium sulfate scales are particularly difficult to remove as they are insoluble in almost all cleaning solutions, so special care should be taken to prevent their formation.

Calcium Phosphate Scale: This scale is particularly common in municipal waste waters and polluted water supplies which may contain high levels of phosphate. This scale can generally be removed with acidic pH cleaners. At this time, phosphate scaling calculations are not performed by the Hydranautics RO Design software. As a rule of thumb, contact Hydranautics technical department if phosphate levels in the feed are 5 ppm or higher.

Metal Oxide/Hydroxide Foulants: Typical metal oxide and metal hydroxide foulants are iron, zinc, manganese, copper, aluminum, etc. They can be the result of corrosion products from unlined pipes and tanks, or result from the oxidation of the soluble metal ion with air, chlorine, ozone, potassium permanganate, or they can be the result of a pretreatment filter system upset that utilizes iron or aluminum-based coagulant aids.

Polymerized Silica Coating: A silica gel coating resulting from the super-saturation and polymerization of soluble silica can be very difficult to remove. It should be noted that this type of silica fouling is different from silica-based colloidal foulants, which may be associated with either metal hydroxides or organic matter. Silica scale can be very difficult to remove by traditional chemical cleaning methods. Contact Hydranautics technical department if the traditional methods are unsuccessful. There does exist harsher cleaning chemicals, like ammonium biflouride, that have been used successfully at some sites but are considered rather hazardous to handle and can damage equipment.

Colloidal Foulants: Colloids are inorganic or mixed inorganic/organic based particles that are suspended in water and will not settle out due to gravity. Colloidal matter typically contains one or more of the following major components: iron, aluminum, silica, sulfur, or organic matter.

Dissolved NOM Organic Foulants: The sources of dissolved NOM (Natural Organic Matter) foulants are typically derived from the decomposition of vegetative material into surface waters or shallow wells. The chemistry of organic foulants is very complex, with the major organic components being either humic acid or fulvic acid. Dissolved NOMs can quickly foul RO membranes by being absorbed onto the membrane surface. Once absorption has occurred, then a slower fouling process of gel or cake formation starts. It should be noted that the mechanism of fouling with dissolved NOM should not be confused with the mechanism of fouling created by NOM organic material that is bound up with colloidal particles.

Microbiological Deposits: Organic-based deposits resulting from bacterial slimes, fungi, molds, etc. can be difficult to remove, particularly if the feed path is plugged. Plugging of the feed path makes it difficult to introduce and distribute the cleaning solutions. To inhibit additional growth, it is important to clean and sanitize not only the RO system, but also the pretreatment, piping, dead-legs, etc. The membranes, once chemically cleaned, will require the use of a Hydranautics approved biocide and an extended exposure requirement to be effective. For further information on biocides, refer to Hydranautics Technical Service Bulletin TSB-110 "Biocides for Disinfection and Storage of Hydranautics Membrane Elements".

Selection and Use of Cleaning Chemicals

There are a number of factors involved in the selection of a suitable cleaning chemical (or chemicals) and proper cleaning protocol. The first time you have to perform a cleaning, it is recommended to contact the manufacturer of the equipment, the RO element manufacturer, or a RO specialty chemical and service supplier. Once the suspected foulant(s) are identified, one or more cleaning chemicals will be recommended. These cleaning chemical(s) can be generic or can be private-labeled proprietary chemicals. Typically, the generic chemicals can be of technical grades and are available from local chemical supply companies. The proprietary RO cleaning chemicals can be more expensive, but may be easier to use and you cannot rule out the advantage of the intellectual knowledge supplied by these companies. Some independent RO service companies can determine the proper chemicals and cleaning protocol for your situation by testing at their facility a fouled element pulled from your system.

It is not unusual to use a number of different cleaning chemicals in a specific sequence to achieve the optimum cleaning. Typically, a low pH cleaning is used first to remove foulants like mineral scale, followed by a high pH cleaning to remove organic material. There are times that a high pH cleaning is used first to remove foulants like oil or biological matter, followed by a low pH cleaning. Some cleaning solutions have detergents added to aid in the removal of heavy biological and organic debris, while others have a chelating agent like EDTA added to aid in the removal of colloidal material, organic and biological material, and sulfate scale. An important thing to remember is that the improper selection of a cleaning chemical, or the sequence of chemical introduction, can make the foulant worse.

General Precautions in Cleaning Chemical Selection and Usage

- If you are using a proprietary chemical, make sure the chemical has been qualified for use with your Hydranautics membrane by the chemical supplier. The chemical supplier's instructions should not be in conflict with Hydranautics recommended cleaning parameters and limits listed in this Technical Service Bulletin.
- If you are using generic chemicals, make sure the chemical has been qualified for use with your Hydranautics membrane in this Technical Service Bulletin.
- Use the least harshest cleaning regiment to get the job done. This includes the cleaning parameters of pH, temperature, and contact time. This will optimize the useful life of the membrane.
- Clean at the recommended target temperatures to optimize cleaning efficiency and membrane life.
- Use the minimal amount of chemical contact time to optimize membrane life.
- Be prudent in the adjustment of pH at the low and high pH range to extend the useful life of the membrane. A "gentle" pH range is 4 to 10, while the harshest is 2 to 12.

- Typically, the most effective clean-up sequence is low pH followed by high pH solutions. One known exception is that oil-fouled membranes should not use a low pH clean-up first as the oil will congeal.
- Cleaning and flushing flows should be in the same direction as the normal feed flow to avoid potential telescoping and element damage.
- When cleaning a multi-stage RO, the most effective cleaning is one stage at a time so cleaning flow velocities can be optimized and foulants from upstream stages don't have to pass through down-stream stages.
- Flushing out detergents with higher pH permeate can reduce foaming problems.
- Verify that proper disposal requirements for the cleaning solution are followed.
- If your system has been fouled biologically, you may want to consider the extra step of introducing a sanitizing biocide chemical after a successful cleaning. Biocides can be introduced immediately after cleaning, periodically (e.g. once a week), or continuously during service. You must be sure that the biocide is compatible with the membrane, does not create any health risks, is effective in controlling biological activity, and is not cost prohibitive.
- For safety reasons, make sure all hoses and piping can handle the temperatures, pressures and pH's encountered during a cleaning.
- For safety reasons, always add chemicals slowly to an agitated batch of make-up water.
- For safety reason, always wear safety glasses and protective gear when working with chemicals.
- For safety reasons, don't mix acids with caustics. Thoroughly rinse the 1st cleaning solution from the RO system before introducing the next solution.

Selecting a Cleaning Solution

Table 2 lists the recommended generic chemical solutions for cleaning an RO membrane element based on the foulant to be removed.

Important: It is recommended that the MSDS of the cleaning chemicals be procured from the chemical supplier and that all safety precautions be utilized in the handling and storage of all chemicals.

Table 2: Hydranautics Recommended Chemical Cleaning Solutions

Foulant	**Gentle Cleaning Solution**	**Harsher Cleaning Solution**
Calcium carbonate scale	1	4
Calcium, barium or strontium sulfate scale	2	4
Metal oxides/hydroxides (Fe, Mn, Zn, Cu, Al)	1	5
Inorganic colloidal foulants	1	4
Mixed Inorganic/organic colloidal foulants	2	6
Polymerized silica coating	None	7
Biological matter	2	3 or 6
NOM organic matter (naturally occurring)	2	3 or 6

Table 3 "Hydranautics Recipes for Cleaning Solutions" offers instructions on the volumes of bulk chemical to be added to 100 U.S. gallons (379 liters) of make-up water. Prepare the solutions by proportioning the amount of chemicals to the amount of make-up water to be used. Make-up water quality should be of RO permeate or deionized (DI) quality, and be free of chlorine and hardness. Before forwarding the cleaning solution to the membranes, it is important to thoroughly mix it, adjust the pH according to the target pH, and stabilize the temperature at the target temperature. Unless otherwise instructed, the cleaning design parameters are based on a chemical recirculation flow period of one hour and an optional chemical soak period of one hour.

Table 4 "Hydranautics Maximum pH and Temperature Limits for Cleaning" highlights the maximum pH and temperature limits for specific membranes, after which irreparable membrane damage can occur. A suggested minimum temperature limit is 70 F (21 C), but cleaning effectiveness and the solubility of the cleaning chemical is significantly improved at higher temperatures.

Description of Cleaning Solutions

Note: The notation (w) denotes that the diluted chemical solution strength is based on the actual weight of the 100% pure chemical or active ingredient.

Solution 1: This is a low pH cleaning solution (target pH of 4.0) of 2.0% (w) citric acid ($C_6H_8O_7$). It is useful in removing inorganic scale (e.g. calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate) and metal oxides/hydroxides (e.g. iron, manganese, nickel, copper, zinc), and inorganic-based colloidal material. Note: Citric acid has chelating properties that function better when an upward pH adjustment is performed using ammonium hydroxide. Sodium hydroxide should not be used for pH adjustment. Citric acid is available as a powder.

Solution 2: This is a high pH cleaning solution (target pH of 10.0) of 2.0% (w) of STPP (sodium tripolyphosphate) ($Na_5P_3O_{10}$) and 0.8% (w) of Na-EDTA (sodium salt of ethylaminediaminetetraacetic acid). It is specifically recommended for removing calcium sulfate scale and light to moderate levels of organic foulants of natural origin. STPP functions as an inorganic-based chelating agent and detergent. Na-EDTA is an organic-based chelating cleaning agent that aids in the sequestering and removal of divalent and trivalent cations and metal ions. STPP and Na-EDTA are available as powders.

Solution 3: This is a high pH cleaning solution (target pH of 10.0) of 2.0% % (w) of STPP (sodium tripolyphosphate) ($Na_5P_3O_{10}$) and 0.25% (w) Na-DDBS ($C_6H_5(CH_2)_{12}$-SO_3Na) (sodium salt of dodecylbenzene sulfonate). It is specifically recommended for removing heavier levels of organic foulants of natural origin. STPP functions as an inorganic-based chelating agent and detergent. Na-DDBS functions as an anionic detergent.

Solution 4: This is a low pH cleaning solution (target pH of 2.5) of 0.5% (w) of HCL (hydrochloric) acid. It is useful in removing inorganic scale (e.g. calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate and metal oxides/hydroxides (e.g. iron, manganese, nickel, copper, zinc) and inorganic-based colloidal material. This cleaning solution is considered to be harsher than Solution 1. HCL acid, a strong mineral acid, is also known as muriatic acid. HCL acid is available in a number of concentrations: (18 ^{0} Baume = 27.9%), (20 ^{0} Baume = 31.4%), (22 ^{0} Baume = 36.0%).

Solution 5: This is a high pH cleaning solution (target pH of 11.5) of 1.0% (w) of $Na_2S_2O_4$ (sodium hydrosulfite). It is useful in the removal of metal oxides and hydroxides, and to a lesser extent calcium sulfate, barium sulfate and strontium sulfate. Sodium hydrosulfite is strong reducing agent and is also known as sodium dithionite. Sodium hydrosulfite is available as a powder.

Solution 6: This is a high pH cleaning solution (target pH of 11.5) of 0.1% (w) of NaOH (sodium hydroxide) and 0.03% (w) of SDS (sodium dodecylsulfate). It is useful in the removal of organic foulants of natural origin, colloidal foulants of mixed organic/inorganic origin, and biological material (fungi, mold, slimes and biofilm). SDS is a detergent that is an anionic surfactant that will cause some foaming. This is considered to be a harsh cleaning regiment.

Solution 7: This is a high pH cleaning solution (target pH of 11.5) of 0.1% (w) of NaOH (sodium hydroxide). It is useful in the removal of polymerized silica. This is considered to be a harsh cleaning regiment.

> **Important: It is recommended that the MSDS of the cleaning chemicals be procured from the chemical supplier and that all safety precautions be utilized in the handling and storage of all chemicals.**

Table 3: Hydranautics Recipes for Cleaning Solutions

The quantities listed below are to be added to 100 U.S.gallons (379 liters) of dilution water.

Cleaning Solution	Bulk Ingredients	Quantity	Target pH Adjustment	Target Temp.
1	**Citric acid** (as 100% powder)	17.0 pounds (7.7 kg)	Adjust to pH 4.0 with ammonium hydroxide.	104 F (40 C)
2	**STPP** (sodium tripolyphosphate) (as 100% powder) **Na-EDTA** (Versene 220 or equal) (as 100% powder)	17.0 pounds (7.7 kg) 7.0 pounds (3.18 kg)	Adjust to pH 10.0 with sulfuric or hydrochloric acid.	104 F (40 C)
3	**STPP** (sodium tripolyphosphate) (as 100% powder) **Na-DDBS** Na-dodecylbenzene sulfonate	17 pounds (7.7 kg) 2.13 pounds (0.97 kg)	Adjust down to pH 10.0 with sulfuric or hydrochloric acid.	104 F (40 C)
4	**HCl acid** (hydrochloric acid (as 22^0 Baume or 36% HCL)	0.47 gallons (1.78 liters)	Slowly adjust pH down to 2.5 with HCL acid. Adjust pH up with sodium hydroxide.	95 F (35 C)
5	**Sodium hydrosulfite** (as 100% powder)	8.5 pounds (3.86 kg)	No pH adjustment is required.	95 F (35 C)
6	**NaOH** (sodium hydroxide**)** (as 100% powder) (or as 50% liquid) **SDS** (sodium dodecylsulfate)	0.83 pounds (0.38 kg) 0.13 gallons (0.49 liters) 0.25 pounds (0.11 kg)	Slowly adjust pH up to 11.5 with sodium hydroxide. Adjust pH down to 11.5 by adding HCL acid.	86 F (30 C)
7	**NaOH** (sodium hydroxide) (as 100% powder) (or as 50% liquid)	0.83 pounds (0.38 kg) 0.13 gallons (0.49 liters)	Slowly adjust pH up to 11.5 with sodium hydroxide. Adjust pH down to 11.5 by adding HCL acid.	86 F (30 C)

Table 4: Hydranautics pH and Temperature Limits for Cleaning

(See Table 3 for target pH and temperatures)

Membrane	45 C (113 F)	35 C (95 F)	30 C (86 F)
CPA	2-10	2-11.5	2-12
ESPA	2-10	2-11.5	2-12
LFC	2-10	2-11.5	2-12
SWC	2-10	2-11	2-12
ESNA	3-10	2-11.5	2-12

Note: The above cleaning parameters denote the maximum temperature limits for a corresponding range of pH. Cleaning operations performed at the extremes may result in a more effective cleaning, but can shorten the useful life of the membrane due to hydrolysis. To optimize the useful life of a membrane, it is recommended to use the least harshest cleaning solutions and minimize the contact time whenever possible.

Table 5: Cleaning and Flushing Flow Rates per RO Pressure Tube

(Pressures are not to exceed 60 psi (4 bar) at inlet to tubes.)

Element Diameter	GPM	LPM
4-inches	6 to 10	23 to 38
6-inches	12 to 20	46 to 76
8-inches	24 to 40	91 to 151
8.5-inches	27 to 45	102 to 170

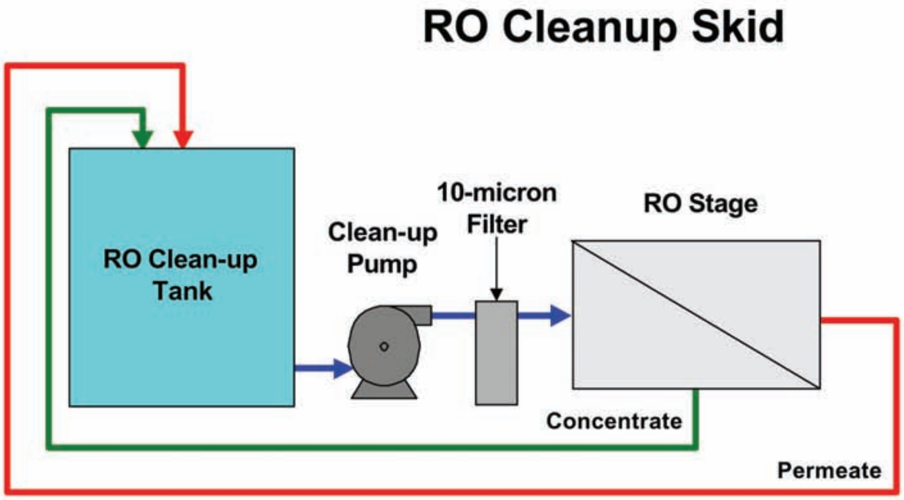
Table 6: Cleaning Solution Volume Requirement per RO Element

(these volumes do not include volumes required for piping, filters, etc)
(these volumes do not include initial 20% of volume dumped to drain)

Element Size	Normal Fouling (Gallons)	Heavy Fouling (Gallons)	Normal Fouling (Liters)	Heavy Fouling (Liters)
4 x 40 inches	2.5	5	9.5	19
6 x 40 inches	5	10	19	38
8 x 40 inches	9	18	34	68
8.5 x 40 inches	10	20	38	76

RO Cleaning Skid

The successful cleaning of an RO on-site requires a well designed RO cleaning skid. Normally this skid is not hard piped to the RO skid and uses temporary hosing for connections. It is recommended to clean a multi-stage RO one stage at a time to optimize cross-flow cleaning velocity. The source water for chemical solution make-up and rinsing should be clean RO permeate or DI water and be free of hardness, transition metals (e.g. iron), and chlorine. Components must be corrosion proof. Major cleaning system components are:



- RO Cleaning Tank: This tank needs to be sized properly to accommodate the displacement of water in the hose, piping, and RO elements. The table below denotes the amount of chemical solution that needs to be made for a single RO element. The tank should be designed to allow 100 % drainage, easy access for chemical introduction and mixing, a recirculation line from the RO Cleaning Pump, proper venting, overflow, and a return line located near the bottom to minimize foam formation when using a surfactant.
- RO Cleaning Pump: This pump needs to be sized to develop the proper cross-flow velocity to scrub the membrane clean. The maximum recommended pressure is 60 psi (4 bar) at the inlet to the pressure vessels to minimize the production of permeate during cleaning and reduce the convective redeposition of foulant back on to the membrane surface. The table below denotes the flow rate ranges for each pressure tube.
- RO Cleaning Cartridge Filter: Normally 5 to 10-micron and is designed to remove foulants that have been displaced from the cleaning process.
- RO Tank Heater or Cooler: The maximum design temperature for cleaning is 113^0 F (45^0 C). It should be noted that heat is generated and imparted by the RO Cleaning Pump during recirculation.
- RO Tank Mixer: This is recommended to get optimal mixing of chemical, though some designers rely solely on the slow introduction of chemical while maintaining a recirculation through the RO Cleaning Pump back to the tank.
- Instrumentation: Cleaning system instrumentation should be included to monitor flow, temperature, pressure, and tank level.
- Sample Points: Sample valves should be located to allow pH and TDS measurements off the RO Cleaning Pump discharge and the concentrate side recirculation return line.

- Permeate Return Line: A small amount of the cleaning solution can permeate through the membranes and so a permeate-side return line back to the RO Cleaning Tank is required.

  Important: The permeate line and any permeate valves must always be open to atmospheric pressure during the cleaning and flushing steps or damage to RO elements can occur. If the permeate line is closed, the permeate pressure can build up and become higher than the feed-side pressure of the tail elements. This can result in excessive permeate back-pressure which can damage the membrane glue lines in the tail elements.

RO Membrane Element Cleaning and Flushing Procedures

The RO membrane elements can be cleaned in place in the pressure tubes by recirculating the cleaning solution across the high-pressure side of the membrane at low pressure and relatively high flow. A cleaning unit is needed to do this. RO cleaning procedures may vary dependent on the situation. The time required to clean a stage can take from 4 to 8 hours.

A general procedure for cleaning the RO membrane elements is as follows:

1. Perform a low pressure flush at 60 psi (4 bar) or less of the pressure tubes by pumping clean water from the cleaning tank (or equivalent source) through the pressure tubes to drain for several minutes. Flush water should be clean water of RO permeate or DI quality and be free of hardness, transition metals, and chlorine.

2. Mix a fresh batch of the selected cleaning solution in the cleaning tank. The dilution water should be clean water of RO permeate or DI quality and be free of hardness, transition metals, and chlorine. The temperature and pH should be adjusted to their target levels.

3. Circulate the cleaning solution through the pressure tubes for approximately one hour or the desired period of time. At the start, send the displaced water to drain so you don't dilute the cleaning chemical and then divert up to 20% of the most highly fouled cleaning solution to drain before returning the cleaning solution back to the RO Cleaning Tank. For the first 5 minutes, slowly throttle the flow rate to 1/3 of the maximum design flow rate. This is to minimize the potential plugging of the feed path with a large amount of dislodged foulant.. For the second 5 minutes, increase the flow rate to 2/3 of the maximum design flow rate, and then increase the flow rate to the maximum design flow rate. If required, readjust the pH back to the target when it changes more than 0.5 pH units.

4. An optional soak and recirculation sequence can be used, if required. The soak time can be from 1 to 8 hours depending on the manufacturer's recommendations. Caution should be used to maintain the proper temperature and pH. Also note that this does increase the chemical exposure time of the membrane.

5. Upon completion of the chemical cleaning steps, a low pressure Cleaning Rinse with clean water (RO permeate or DI quality and free of hardness, transition metals, and chlorine) is

required to remove all traces of chemical from the Cleaning Skid and the RO Skid. Drain and flush the cleaning tank; then completely refill the Cleaning Tank with clean water for the Cleaning Rinse. Rinse the pressure tubes by pumping all of the rinse water from the Cleaning Tank through the pressure tubes to drain. A second cleaning can be started at this point, if required.

6. Once the RO system is fully rinsed of cleaning chemical with clean water from the Cleaning Tank, a Final Low Pressure Clean-up Flush can be performed using pretreated feed water. The permeate line should remain open to drain. Feed pressure should be less than 60 psi (4 bar). This final flush continues until the flush water flows clean and is free of any foam or residues of cleaning agents. This usually takes 15 to 60 minutes. The operator can sample the flush water going to the drain for detergent removal and lack of foaming by using a clear flask and shaking it. A conductivity meter can be used to test for removal of cleaning chemicals, such that the flush water to drain is within 10-20% of the feed water conductivity. A pH meter can also be used to compare the flush water to drain to the feed pH.

7. Once all the stages of a train are cleaned, and the chemicals flushed out, the RO can be restarted and placed into a Service Rinse. The RO permeate should be diverted to drain until it meets the quality requirements of the process (e.g. conductivity, pH, etc.). It is not unusual for it to take from a few hours to a few days for the RO permeate quality to stabilize, especially after high pH cleanings.

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