Yuma Desalting Plant – Pilot Run Cooperative Research and Development Agreement
(YDP – CRADA)

Evaluation of Technological Advancements and Alternative Feed Water Supplies for Operation of Yuma Desalting Plant

Project Final Report - June 2013

REPORT DOCUMENTATION PAGE

Yuma Desalting Plant – Pilot Run Cooperative Research and Development Agreement (YDP – CRADA)

Project Final Report – June 2013

Title

Evaluation of Technological Advancements and Alternative Feed Water Supplies for Operation of Yuma Desalting Plant

Authors

Dr. Umur Yenal, Dr. Wendell P. Ela, Dr. Peter Fox, Jim Lozier, and Rich Yates

Project Parties

Metropolitan Water District of Southern California (MWD)
Southern Nevada Water Authority (SNWA)
Central Arizona Water Conservation District (CAWCD)
United States Bureau of Reclamation (USBR)

Contributors

Angela Adams, John Franklin, and Dr. Chuck Moody

ACRONYMS AND ABBREVIATIONS

A

ABS	Acrylonitrile butadiene styrene
AF	Acre-feet
AFY	Acre-feet per year of water flow (multiply by 0.620 to convert to gallons per minute or divide by 724 to convert to cubic feet per second)
Al	Aluminum
Alk	Alkalinity
Alt	Alternative
AS	Air scrub
ASU	Arizona State University
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy
Avg	Average
AZ	Arizona

B

$BaSO_4$	Barium sulfate
BDOC	Biodegradable Dissolved Organic Carbons
Br	Bromine

C

°C	Degrees Celsius
CA	Cellulose Acetate
Ca	Calcium
Ca^{2+}	Calcium ion
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CaO	Quicklime
$Ca(OH)_2$	Lime
$CaSO_4$	Calcium sulfate
CAWCD	Central Arizona Water Conservation District
C_e	Element flow coefficient
CF	Cartridge Filters
Cfs	Cubic feet per second
Cfu	Colony Forming Units
Cfu/in^2	Colony Forming Units per square inch
Cfu/ml	Colony Forming Units per milliliter
CIP	Clean-in-Place
CH_2	Methylene
Cl	Chlorine
Cl^-	Chloride ion
cm^{-1}	Per centimeter (A reciprocal wavelength (cm-1) is a simple convenient unit for comparing energies when dealing with spectra)

CO_2	Carbon dioxide
COO^-	Carboxyl functional group
CRADA	Cooperative Research and Developmental Agreement
CT	Conventional Treatment (coagulation, flocculation, and rapid sand filtration)
CT – RO	Combination of Conventional Treatment and Reverse Osmosis

D

DBPs	Disinfection Byproducts
Deg.	Degree
Diss	Dissolved
DMGF	Dual Media Gravity Filters
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
dP	Differential Pressure (difference in pressure between two locations)
DPOC	Drain Pump Outlet Channel

E

E	times ten raised to the power of
EDL	Estimated Detection Limit
Eff. or Effl.	Effluent
EFM	Enhanced Flux Maintenance
E/I	Electronics and Instrumentation
EPA	Environmental Protection Agency
ETA	Element Test Apparatus

F

°F	Degrees Fahrenheit
FA	Feed water prior to antiscalant addition
FB	Feed water after antiscalant addition
Fe/Mn	Iron/Manganese
$Fe(OH)_3$	Iron hydroxide
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
$Fe_2(SO_4)_3$	Ferric sulfate
FF	Forward flush
Ft	Foot; feet
Ft^2	Square feet
Ft^3	Cubic feet
Ft^3/sec	Cubic feet per second
FTIR	Fourier Transform Infrared Spectroscopy

G

g	Gram/grams
Gfd/psi	Gallons per square foot per day per psi
g/mL	Grams per milliliter
gal/min	Gallons per minute
gal/min/ft^2	Gallons per minute per square foot
GF	Gravity filter
Gfd	Gallons of permeate per square foot of membrane per day water flux
gal/ ft^2/day	Gallons of permeate per square foot of membrane per day water flux
Gpd	Gallons per day
Gph	Gallons per hour
Gpm	Gallons per minute
gpm/ft^2	Gallons per minute per square foot
Gpm/in^2	Gallons per minute per square inch

H

H_2SO_4	Sulfuric acid (hydrogen sulfate)
Hard.	Hardness
HCO_3^-	Bicarbonate (hydrogen carbonate ion)
HFR	High flux/recovery
Hp	Horsepower
HPC	Heterotrophic Plate Counts
hr	hours

I

IC	Inorganic carbon
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IC-ICP-MS	Ion Chromatography Inductively Coupled Plasma Mass Spectrometry
In	Inch(es)
Infl.	Influent
IT	Integrity test(ing)

K

K	Kelvin or Potassium
Kg	Kilogram(s)
kPa	Kilopascal
kPAg	Kilopascal gage pressure
kPa.L/K.mol	Kilopascal liter per Kelvin per mole
K_{SO}	Solubility constant (the equilibrium constant for a solid substance dissolving in an aqueous solution, K_{SO} is used when the solution is saturated)

L

L	Liters
Lbs	Pounds
L/h	Liters per hour
L/(h-m^2)	Liters per hour per square meter
L/(h.m^2))/bar	Liters per hour per square meter per bar
LOI	Loss on Ignition
LS	Lime Softening
L/m	Liters per minute

M

M	Meter(s)
M^2	Square meters
Max	Maximum
MBD	Mass Balance Deviation
MCL	Maximum Contaminant Level
meq	Milliequivalent
MF	Microfiltration
mg	Milligrams
Mg	Magnesium
Mg^{2+}	Magnesium ion
MGD	Million gallons per day (multiply by 1.121 to convert to acre-feet per year)
mg/L	Milligrams per liter
$Mg(OH)_2$	Magnesium hydroxide
M^3/h	Cubic meters per hour
ml	Milliliters
mL/min	Milliliters per minute
Mm	Millimeter(s)
µm	Micrometer(s)
µg/L	Micrograms per liter
µS/cm	Microsiemens per centimeter (measurement of conductivity)
Mn	Manganese
Mn^{2+}	Manganese ion
mNTU	Milli Nephelometric Turbidity Unit
MODE	Main Outlet Drain Extension
mol/L	Moles per liter
m/s	Meter per second
m/s.Pa	Meter per second per pascal
MU	Membrane evaluation research unit
mV	Millivolts
MWD	Metropolitan Water District of Southern California

N

NA	Not Available
Na	Sodium
Na^+	Sodium ion
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
NFR	Normal flux/recovery
nm	Nanometer
No	Number
NPOC	Non-purgeable organic carbon
NTU	Nephelometric Turbidity Unit

O

O	Oxygen
O&M	Operation and Maintenance
ORP	Oxidation Reduction Potential

P

P	Phosphorus
PA	Polyamide
Pa	Pascal
Perm.	Permeability
PES	Polyethersulfone
pH	A measure of the relative acidity of water. Water that has pH value less than 7 is referenced as acidic and pH value greater than 7 as basic.
PLC/PC	Programmable Logic Controller/Private Computer
Ppm	Parts per million
Psi	Pounds per square inch pressure (divide by 14.5 to convert to bars or multiply by 6.895 to convert to kilopascals)
Psi/d	Pounds per square inch per day
PS1, PS2, PS3, PS4	Pilot System 1-4
PVDF	Polyvinylidene

Q

QA	Quality Analysis
Q_{SO}	Ion Product Quotient (the equilibrium constant for a solid substance dissolving in an aqueous solution, Q_{SO} is used when the solution is not saturated)

R

Reclamation	Bureau of Reclamation
RF	Reverse filtration
RO	Reverse Osmosis

S

S	Sulfur
S^0	Elemental sulfur
SCADA/PI	Supervisory Control and Data Aquisition
Scfm	Standard cubic feet per minute
SCR	Solids Contact Reactors
SD	Standard Deviation
SDI	Silt Density Index
SEM	Scanning Electron Microscopy
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive Spectroscopy
SEM-EDX	Scanning Electron Microscopy-Energy-Dispersive X-ray Spectroscopy
SHMP	Sodium hexametaphosphate
Si	Silicon
SIB	Southerly International Boundary
SNWA	Southern Nevada Water Authority
Sr^{2+}	Strontium ion
St. Dev.	Standard Deviation
STC	Salt Transport Coefficient

T

TAT	Technical Advisory Team
TC	Total carbon
TCF	Temperature Correction Factor
TDS	Total Dissolved Solids
THM	Trihalomethane
Ti	Titanium
TIC	Total Inorganic Carbon
TMP	Trans-membrane Pressure
TOC	Total Organic Carbon
Tot	Total (the sum of dissolved and particulate iron and manganese)
TSS	Total Suspended Solids

U

USBR	United States Bureau of Reclamation

V

V1R	Vessel 1 reject water
V2R	Vessel 2 reject water

W

WMIDD	Wellton-Mohawk Irrigation and Drainage District
WQIC	Water Quality Improvement Center
WTC	Water Transport Coefficient

X

XRD	X-ray Diffraction

Y

YCWUA	Yuma County Water Users' Association
YDP	Yuma Desalting Plant
YMC	Yuma Mesa Conduit

TABLE OF CONTENTS

TABLE OF CONTENTS - *CONTINUED*

TABLE OF CONTENTS - *CONTINUED*

TABLE OF CONTENTS - *CONTINUED*

LIST OF FIGURES

LIST OF FIGURES - *CONTINUED*

LIST OF FIGURES - *CONTINUED*

LIST OF FIGURES - *CONTINUED*

LIST OF FIGURES - *CONTINUED*

LIST OF FIGURES - *CONTINUED*

LIST OF FIGURES - *CONTINUED*

LIST OF TABLES

LIST OF TABLES - *CONTINUED*

EXECUTIVE SUMMARY

The United States Bureau of Reclamation (Reclamation) and Municipal Utilities entered into Cooperative Research and Development Agreement (CRADA) in November 2009 for research at Reclamation's Water Quality Improvement Center, located adjacent to the Yuma Desalting Plant (YDP). The research was conducted to identify possible alternative YDP operating scenarios, which could improve plant performance and reduce costs. The Municipal Utilities consist of the Central Arizona Water Conservation District (CAWCD), the Metropolitan Water District of Southern California (MWD) and the Southern Nevada Water Authority (SNWA). In 2010, the Municipal Utilities funded a test under this agreement, at Reclamation's Water Quality Improvement Center (WQIC), in parallel with the YDP Pilot Run. The overall goal of that test was to provide data on polyamide (PA) membranes and the effectiveness of alternative operating processes to determine whether they might be more reliable and/or more cost effective than the YDP's current configuration.

Test Conditions

The testing occurred in two stage: Round 1 and Round 2 Screening tests, which spanned six months and comprised two subsets of tests, each three months (called Round 1 Screening and Round 2 Screening); and Round 2 Full-Array Test, which spanned nine months. Two different brackish agriculture drainage water sources served as feed supplies: drainage water from Wellton-Mohawk Irrigation and Drainage District (WMIDD) transported by the open conveyance channel known as Main Outlet Drain Extension (MODE)) and groundwater pumped from the local Yuma Mesa area, which is conveyed by a pipe system known as Yuma Mesa Conduit (YMC).

Round 1 Screening evaluated the effectiveness of four different pretreatment processes on seven types of commercially available polyamide (PA) membranes. For the MODE water, the pretreatments were partial lime softening-gravity filtration, and microfiltration. For the YMC water, the pretreatments were manganese-amended anthracite filtration with microfiltration, and greensand filtration with cartridge filters (CF). All pretreated waters were pH adjusted, chlorinated and dosed with ammonia and anti-scalant before being pumped to the Reverse Osmosis (RO) membranes.

The RO portion of Round 1 Screening was conducted at low recovery. Round 1 Screening tests generated performance data to allow the project team to select the best performing membrane on each source water/pretreatment combination. This best-performing element was then tested at full-recovery during the 9-month long Round 2 Full-Array Test. Data generated during the Full-Array Test indicates the cost-effectiveness and reliability of the treatment alternatives under circumstances similar to normal operating conditions.

Alternate Water Sources

Differences existed between the two water sources used during the project. In terms of water supply availability, MODE flow was consistent while YMC flow varied. During the research project, flow in the YMC was diverted at times to the Southerly International Boundary to reduce river salinity to meet the assurances set forth in Minute No. 242 of the International Boundary and Water Commission, United States and Mexico. This resulted in a disruption to the supply of YMC water for the project. MODE water flow was fairly consistent during the project, maintenance or system outages did not measurably disrupt water supply.

In terms of water quality, MODE water had a higher fouling potential than the YMC water due to its higher levels of particulate and organic matter. The project team also observed higher-than-expected iron and manganese concentrations and fluctuations in Total Dissolved Solids (TDS) concentration in YMC water. The YMC had lower TDS, particulate, organic matter, and Total Organic Carbon (TOC) concentrations compared to the MODE water. However, the YMC water contained elevated levels of iron and manganese that required special removal techniques.

Pretreatment Performance

The project team successfully identified pretreatment options for both feed waters which provided a water quality appropriate for satisfactory operation of downstream RO units. Pretreatment's main purpose was to efficiently remove the particulate matter and decrease iron and manganese concentrations to levels harmless for RO operation. (For a detailed discussion of pretreatment methods tested, see Section 6.2 and 7.2).

On YMC water, microfiltration more efficiently removed particulate matter, including iron and manganese, than cartridge filtration. Microfiltration operations were also more sustainable than cartridge filtration. The project team observed that pH played an important role in determining the fouling rate of the cartridge filters, with lower pH appearing to accelerate cartridge filter fouling. The project team recommends further study to identify the reasons for this behavior, as well as a cost/benefit analysis to compare microfiltration to cartridge filtration at full-scale operations.

On MODE water, partial lime softening and gravity filtration appeared to be the most sustainable pretreatment. Partial lime softening offers an advantage over microfiltration by allowing operation with less acid, which reduces acid costs. However, reduced acid costs are offset by costs to purchase, use and dispose of the lime required for the softening process.

The MODE water microfiltration unit operated with no deterioration during its first six months of operation. However during the summer of 2011, the MODE microfiltration unit began fouling extremely quickly in between scheduled backwashes and cleanings, and could not be sustainably operated. It is likely that decreasing the microfiltration feed stream pH (to improve downstream RO performance) influenced the high microfiltration fouling rate.

Membrane Performance

The lowest observed WTC[1] value among PA membranes tested during this project was almost 50% higher than that for average cellulose acetate (CA) membranes. This is significant because, taken with the overall performance data which indicates that PA membranes could be feasibly incorporated into YDP operations, the higher WTC values of PA membranes indicates that incorporating them into YDP operations could help the facility reduce its energy costs. Furthermore, microfiltration pretreatment of MODE water had a higher WTC value than MODE water pretreated by partial-lime softened water for testing of Hydranautics LFC3 (LFC3) membranes.

Round 1 and Round 2 Screening tests data showed each membrane's WTC values varied significantly depending on the source water and pretreatment. Membranes with high WTC tended to have a high STC (meaning lower-energy operation, but saltier product water). The project team chose the LFC3 membrane for long-term testing in Round 2 Full Array tests; although it had the lowest WTC values of all membranes tested in Screening tests, the LFC3 membrane also had some of the lowest STC values, and it displayed steadier operation during screening tests on all pretreatment options. Another reason to select this membrane was the fact that the supplier of another selected membrane was not willing to supply for high recovery testing.

Results from both Screening and Full-Array testing indicate that RO performance depends strongly on pH, regardless of the source water.

High-Flux and High-Recovery

The team evaluated high flux on one of the Round 2 Screening low-recovery test units and one of the Round 2 Full Array test units, to gain information on the upper performance boundary. High-flux operation may be feasible with the appropriate operating pH (perhaps

---

[1] Water Transport Coefficient (WTC) and Salt Transport Coefficient (STC) are two key indicators of membrane performance. The higher the WTC, the more energy efficient the membrane is; a lower STC indicates purer product water and a higher blending ratio for product to untreated. Higher WTCs and lower STCs help reduce operating costs.

including interstage pH adjustment), although it will yield a slightly lower WTC value. Operating at 85% rather than 80% recovery is less likely to be feasible, though the possibility warrants further examination.

Membrane Evaluation Research Unit (MU) Performance with Alternative Membranes

Two additional membrane types (Toray TML10 and Dow XFR) were evaluated as a subtest within the scope of the Round 2 Full-Array test, to provide information about whether other membranes in addition to the LFC3 would be acceptable for use at the YDP. Data from this subtest indicates that the DOW XFR is the preferred membrane (relative to LFC 3 and TML 10) for desalting the partial lime softened MODE water. Data from Screening tests suggests that the Dow XFR membrane might outperform the LFC3 and TML10 membrane on the other test treatments (including microfiltration pretreatment on MODE water); however, no Full Array test data exists to corroborate the Screening data, since the Full Array tests evaluated only the LFC3 membrane on the other treatments.

Key observations

- RO worked equally effectively on both YMC water and MODE water. However, disruption of the YMC supply to meet Minute No. 242 salinity requirements appears to make it infeasible for full-scale operation.
- Microfiltration of MODE water appears to be an operationally feasible alternative to partial lime softening as long as improved cleaning methods and scheduling (as suggested in this report) are implemented.
- PA membranes in all cases exhibited significantly higher water transport coefficients than those reported for CA membranes on MODE water. Results obtained during testing indicate that PA membranes would not be infeasible to implement at full-scale, whether treating either partial lime softened or micro-filtered MODE or YMC water. Limited data collected suggests that high-flux operations may be feasible pending further operational and economic analysis.

Recommendations

1. Conduct further RO testing on MODE water pretreated using partial lime-softening; operate with a feed pH of 6.0 – 6.2, and a reject pH of 6.3 – 6.5, at both regular flux, and on high flux (15 gallons of permeate per square foot of membrane per day water flux [gfd]) with high recovery (85%). Include a cleaning study to determine what approach will prevent rapidly declining WTC values. Conduct detailed organics analysis and lab experiments to identify membrane fouling rates at the different pH levels.
2. Conduct further RO testing on MODE water pretreated using microfiltration; operate with a feed pH of 5.6 – 5.7, and use interstage pH adjustment on the RO unit. Include a cleaning study to determine what approach will prevent rapidly increasing STC values. Conduct detailed organics analysis and lab experiments to identify membrane fouling rates at the different pHs.
3. Conduct further testing on cleaning schemes for a microfiltration unit treating MODE water, as described in Section 6.2.2.2. Conduct a cost benefit analysis.
4. Test different acid injection locations to determine whether that improves microfiltration operations, while also improving both WTC and STC values.
5. Evaluate other types of microfiltration units to determine whether the effects seen during this test apply only to the units used during the test or to others as well.
6. Conduct RO testing on MODE water pretreated by cartridge filtration. Test various CF sizes and evaluate the membrane fouling potential of water treated by the different filters. Operate the CFs at different fluxes to determine the optimal flux. As a control, operate one RO unit without upstream filtration other than gravity filters (no microfiltration or CFs).
7. Perform a detailed economic analysis for the alternatives tested, to create accurate estimates for the amount of operating chemicals needed.

1. TECHNICAL SUMMARY

Agricultural drainage water from the Wellton-Mohawk Irrigation and Drainage District (WMIDD) is currently collected in a canal system, which bypasses the Colorado River and the U.S. Bureau of Reclamation's Yuma Desalting Plant (YDP), draining into the wetlands located in Ciénega de Santa Clara (Santa Clara Slough) in Mexico. The bypassed water is not counted toward the United States' treaty deliveries to Mexico. By desalting the drainage water and conveying it to the Colorado River to satisfy part of the water allocated to Mexico under the treaty, additional water could be stored and later diverted from the Colorado River upstream for use within the U.S. The YDP is designed to recover most of the current bypass flow (a 5-year average of ~107 thousand acre-feet [AF] of water) annually in its original configuration. It is capable of treating a water source with salinities in the range of 2,850-3,450 milligrams per liter (mg/L) of TDS. Operation of the YDP could extend Colorado River water supplies to alleviate protracted drought, over allocation of supply, increased demand, as well as improve agencies' operations.

Reliable, economical and efficient functioning of the plant would be crucial for such potential long term, sustained operation. With this purpose in mind, an 11-month -long Pilot Run at one-third of the plant's capacity was performed between May 2010 and March 2011. The Pilot Run was jointly funded by Reclamation and three agencies--Central Arizona Water Conservation District, Metropolitan Water District of Southern California and Southern Nevada Water Authority, the latter referred to as the Municipal Utilities. In addition, given that the YDP process design reflects the state of the art technology available in the late 1970s, the Municipal Utilities determined that additional information regarding alternative operating scenarios for the plant was needed to generate possible cost reductions and improved performance. These scenarios integrate not only some of the technological advancements made since construction of the YDP was largely completed in 1992, but also potential alternative feed water supplies to the plant. The scenarios were evaluated via testing conducted at Reclamation's Water Quality Improvement Center (WQIC) as a parallel activity to the Pilot Run. A technical advisory team (TAT) comprised of technical representatives from Reclamation and each of the Municipal Utilities was assembled to define the specific CRADA research materials and methods, to oversee and advise on the research activity, and to assist the Research Manager with preparation of a final report on the research outcomes. A Research Manager was, in turn, hired to (1) oversee the research, (2) assist Reclamation on a day-to-day basis in the conduct of the research, (3) communicate research results periodically throughout the study and (4) prepare a report documenting the outcomes of the research.

Seven different types of polyamide RO membranes; Hydranautics ESPA2 and LFC3, Toray TML10, Koch/Fluid Systems ULP-TFC, Dow Filmtec BW30-XFR, and CSM Woongjin RE-FE and RE-CE; were tested on two different brackish water sources: (1) the Main Outlet Drain Extension (MODE) water – surface canal agricultural drainage from the Wellton-Mohawk Irrigation & Drainage District – and (2) groundwater from the Yuma Mesa Conduit (YMC), which collects agricultural drainage pumped from wells located on the Yuma Mesa and in the Yuma Valley. Partial lime softening-gravity filtration, direct filtration, manganese oxide-amended anthracite filtration and greensand filtration were evaluated as options to pretreat the two water supplies prior to desalination by reverse osmosis. In all cases, the pretreated water was pH adjusted with sulfuric acid, chlorinated and dosed with ammonia (to form chloramines) and anti-scalant before being pumped to the RO membranes. Testing was carried out in two sequential stages. Round 1 comparatively evaluated the performance of four RO membrane types (ESPA2, LFC3, TML10, and ULP-TFC) at low recovery to select the best performing element on each source water/pretreatment combination. The selected membrane, LFC3, was then operated for the long-term, high recovery testing of Round 2. Round 2 Full-Array testing lasted about nine months and used a 2 x 1 staged, 21 elements, array to achieve 80% recovery. Also in Round 2 Screening tests, three additional membrane types (BW30-XFR, RE-FE and RE-CE) were tested at conditions analogous to those of Round 1 Screening tests.

The overall goal of the Cooperative Research and Developmental Program which was carried out in part under the CRADA was to test the effectiveness of the pretreatment alternatives and of alternative RO materials and operational methods and, subsequently based on these findings, to generate conceptual level design criteria for the pretreatment and RO membranes that could be use to prepare cost opinions on cost data to determine whether these pretreatment processes might be more reliable and/or more cost effective than the YDP’s current configuration. The information will be used to help to determine which, if any, process avenue to pursue if a decision is made to consider long-term operations of the YDP. The goal for the screening tests (Round 1 and Round 2) was to evaluate the efficiency of the pretreatment alternatives in preventing fouling on various types of membranes and how specific element types respond to the water sources and pretreatment alternatives under evaluation. The results of Round 1 and Round 2 screening tests determined which RO element types are most suitable for long-term YDP operations. The goals for the full-array testing phase (Round 2 Full-Array) of the project were to generate data to evaluate the cost-effectiveness and reliability of the treatment alternatives in the long run.

The CRADA also defined the research approach to answer the specific questions listed below as identified by the TAT:

1. What are the relative advantages and disadvantages of the water sources tested (MODE and YMC)?
2. Are there factors that affect the water quality of the MODE and YMC water sources?
3. What pretreatment(s) is feasible for each water source, and what are the relative advantages and limitations of the feasible option(s)?
4. Are there any modifications to the suggested alternative(s) recommended for application or further study?
5. What are the key constituents in the water sources that cause fouling or scaling in the RO operation?
6. What are the relative advantages and the limitations of the membranes evaluated and of low pressure polyamide membranes in general relative to the cellulose acetate membranes currently used at YDP?
7. What are the relative advantages and disadvantages of the evaluated operational parameters?
8. For the two water sources and four pretreatment systems evaluated during 3-12 months operations, how well do the PA membrane elements maintain their performance as measured by operating pressure, salt passage and differential pressure?

Alternative Water Sources

Water quality fluctuations in the MODE were experienced during the testing and were expected given the surface nature of this supply. Fluctuations were caused by both environmental and artificial events, including severe storm events, seasonal temperature variations, and diversions of agricultural drainage water from the Drain Pump Outlet Channel (DPOC) into the MODE upstream of the YDP. As anticipated, the MODE water had a higher fouling potential than the YMC alternative due to higher levels of particulate and organic matter. Surprisingly (based on historical data), iron and manganese concentrations were measured as concentrations as high as 0.15 and 0.3 mg/L, respectively. Fluctuations in TDS concentration were also observed, primarily caused by diversions of well water into the MODE during the fall and winter. Nevertheless, MODE was a more reliable water source in terms of consistent availability during this study compared to the YMC alternative. No unexpected extended MODE water outage was encountered during the study period.

On the other hand, YMC water had lower TDS (1,400-1,700 mg/L), particulate (0.74 Nephelometric Turbidity Unit [NTU]), and organic matter (TOC ~1.0 mg/L) concentrations compared to the MODE water. The YMC water was expected to contain elevated levels of iron and manganese that required special removal techniques, such as greensand or conditioning on the silica sand, prior to RO treatment. Nevertheless, the main problem that became evident with using YMC water was its availability during testing. The YMC's primary function is to serve as an operational tool to help Reclamation manage the salinity of the lower Colorado River, thus enabling the United States to meet Minute No. 242 assurances to Mexico regarding the salinity of water delivered. As a result, at some times during the year, flows in the YMC are diverted to the south rather than the north, which affected the availability of YMC flows for testing at the WQIC. There was limited availability of YMC water at the WQIC at times for testing, which affected operations. Nevertheless, both the MODE and YMC pretreatment options that were identified and tested provided a water quality appropriate for satisfactory RO operation.

Pretreatment Performance

Four different alternative pretreatment trains (designated Alternative 10 and 17a for alternatives running on MODE water and Alternatives 21a and 22 for alternatives running on YMC water) were tested with the main purpose of removing the particulate matter efficiently and decreasing the concentrations of iron and manganese to levels that are suitable for sustained and cost effective RO operation. All the dual media gravity filters (DMGF), the common unit operation of all the alternatives, were initially composed of silica sand and anthracite, until greensand was installed on Alternative 22 (YMC water with DMGF and cartridge filters) in Round 2 to evaluate its relative removal efficiency for iron and manganese compared to manganese-conditioned silica sand. The installation of CF, as a precautionary particulate removal technique on this alternative, also provided enough data to compare the efficiency of CF against microfiltration. Alternatives 17a and 21a had microfiltration downstream of gravity filters to boost the removal efficiency of particulate matter, whereas Alternative 10 removed not only particulate matter, but also divalent cations and alkalinity via lime-softening.

The greensand compared to the manganese-conditioned silica-sand gravity filtration combined with anthracite did not show any significant difference in removal of turbidity, iron and manganese on YMC water. On the other hand, microfiltration (MF) performed more efficiently in removing particulate matter, including iron and manganese, compared to cartridge filtration. It also provided a sustainable and more reliable operation on treating YMC water. The pH played an important role in determining the fouling rate of CFs as the fouling rate increased at lower pH. Further study is recommended to identify the reasons of this behavior. Due to loss of water source, the effect of pH on MF unit remained undetermined while treating YMC water. However, a cost/benefit analysis should provide enough data to make a comparison between the microfiltration and cartridge filtration so as to decide which technique will be cheaper to apply while treating YMC water. Three different types of CFs were tested; (i) 20-inch [in] long 1-micrometer [μm] CFs, (ii) 10-in long 5-μm CFs, and (iii) 10-in long 1-μm CFs. Conflicting results were found in terms of which type of the cartridge filter performed with the lowest fouling rate. Therefore, on-site testing of the actual, full-size CF is recommended if CF is to be used, because extrapolation from performance data gathered during this study with other pore and vessel sizes may lead to large errors. A sustainable run was achieved for the MF unit on YMC water operating at a flux of 85–90 gfd and above. Regular biweekly citric and bleach Enhanced Flux Maintenance (EFM) controlled fouling and maintained a low and consistent trans-membrane pressure (TMP) without the need for clean in place (CIP). However, based on the MF manufacturer's (Pall Corporation) recommendations, it is recommended that CIPs be conducted semi-annually to prevent the accumulation of foulants that can be recalcitrant to chemical cleaning.

On MODE water, removal of divalent cations via lime-softening and gravity filtration (Alternative 10) ranged between 27% (for magnesium) and 95% (for manganese). This alternative also partially removed other material that might cause scaling or fouling problems in RO treatment, such as iron, manganese and silica by 75%, 95% and 46%, respectively. Sustainable operation of MODE RO units requires a feed pH of ~6.0. Partial lime-softening pretreatment creates a lower acid demand than MF pretreatment because it removes more than 80% of the total alkalinity. The acid required to drop the feed pH of RO units from 6.8 to 6.0 costs 22 times more for MF than partial lime softening pretreatment. Nevertheless, partial lime-softening incurs other chemical addition costs not incurred by MF such as lime and ferric sulfate addition.

The MODE water MF unit operated at a lower flux (66 gfd) than the YMC water MF unit (85 gfd). No deterioration in the YMC MF performance was observed in its 12 months of operation or in the MODE MF during the units initial six months of operation. However, during summer 2011, probably due to a combination of reasons, such as higher iron and manganese concentrations, diversions of different quality of water into the MODE canal, higher total organic carbon (TOC) levels during summer and the pH changes to the MF feed, sustainable operation of the MODE MF unit could not be maintained under the given operating conditions and cleaning regime. It is likely the higher MF fouling rate observed was influenced by pH being decreased (to 5.7-5.8 from 6.8) to improve downstream RO unit performance. MF cleaning and autopsy studies conducted in early 2012 showed stronger CIPs were partially successful in restoring MF performance and could likely be further improved. The study also suggested EFM efficiency could be improved by such things as adding a soaking period, using different cleaning chemicals and/or passing the cleaning solution through the fibers' pores rather than just recirculating it outside of the fibers. It was speculated that implementing these cleaning improvements on a routine basis might allow stable MF operation on MODE water (as well as YMC water).

RO Membrane Performance

Four Element Test Apparatus (ETA) units (ETAs 1-4) were used in this study to evaluate seven different types of membranes over two different rounds of testing. The ETAs operated at an average flux of 15 gfd and recovery of 13%. Toray TML 10, Koch ULP, and Hydranautics LFC3 and ESPA2 membranes were tested during Round 1, which lasted almost 3000 hours (4 months). During the 3500 hours runtime of Round 2, DOW BW30 XFR, and CSM RE-FE and RE-CE membranes were tested. Toray TML 10 was kept the same for both rounds for the purpose of direct comparison. The data gathered from ETAs over the two rounds showed that the membrane which displayed lower WTC (water transport coefficient – a measure of membrane flux per unit pressure applied) relative to the other membranes on one alternative generally exhibited relatively lower WTC for all alternatives, even though the numeric value of the WTC might vary between alternatives. This means that the rank order of the WTC values by membrane type did not depend on the source water or pretreatment type but it depended on the membrane material itself. On the other hand, the numeric values of WTC for a membrane type varied significantly depending on the pretreatment type and the source water.

Data gathered during this study showed that the membranes with high WTC tended to have high STC (salt transport coefficient – a measure of the membrane’s normalized salt passage), as well. A high WTC means lower energy use per unit of water produced. However, high salt rejection leads to lower concentration in the product water and hence a higher blending ratio potential. Both of these features help reduce the operational cost. Therefore, the decision of selecting the most appropriate membrane type for the YDP operation becomes a cost-benefit analysis. The membrane chosen for high-recovery testing, Hydranautics LFC3, had the lowest WTC, but also had some of the lowest STC values of all the elements tested in all alternatives. In addition, it displayed steadier operation in terms of WTC and STC over the duration of the study compared to the other types of membranes, regardless of the pretreatment method. Hydranautics

LFC3 was the only membrane which showed no initial WTC decline on partial lime softened MODE water during Round 1, element screening testing. Koch ULP, on the other hand, had the highest WTC and STC values among the membranes tested, regardless of the pretreatment alternative and water source.

Alternative 10 (partial lime softening) was essentially the baseline case for this study as it was the pretreatment method for YDP during the Pilot Run. In general, lower WTC and STC values were observed for partial lime softening compared to MF pretreatment of MODE water. The autopsy results showed that partial lime softening had the highest material buildup among the alternatives evaluated, while also resulting in the lowest salt passage regardless of the membrane types, with the exception of the Koch ULP. A sudden initial drop in WTC was followed by a stable run for all the membranes tested on lime-softened gravity-filtered MODE water.

Effect of pH

MU and ETA RO performance depended strongly on pH, regardless of the source water. For partial lime softened water, STC values, salt passage and B/A values increased during the first three months of Round 1 testing at feed pH of 6.8. However, when the feed pH was decreased to 5.8 and lower, both STC and WTC values declined. After detecting the same decrease in WTC values during early Round 2 (albeit for other membrane types), the feed pH was increased to 6.0, which partially recovered and stabilized the WTCs. A very minor increase in STC and B/A values was detected while operating at the feed pH of 6.0 for all membranes. Both MU and ETA membranes displayed the same behavior. It appears that the best operating pH range for partial lime softened water occurs at a feed pH from 6.0 to 6.2 and a reject pH from 6.3 to 6.5. The expected long-term WTC value for LFC 3 membranes is about 6×10^{-12} meter per second per Pascal [m/s.Pa] based on the observations of ten months of MU 4 operation. Since the material build-up in the feed spacer channel observed during the testing was high based on the autopsy results, the estimated membrane life may be lower than the manufacturer suggested 5 years. Periodic membrane cleaning could increase membrane life on partial lime softened water, but this was not evaluated in this study. Partial lime softening for future YDP operation offers a very easy transition from the existing treatment schematic, i.e. cellulose acetate (CA) membranes, to the new one with polyamide (PA) membranes. The lowest detected WTC value among PA membranes during this testing was almost 50% higher than that for CA membranes.

Even though higher WTC values were observed for the LFC3 membranes operated on MF treated compared to partially lime softened water, a stronger dependence of WTC and STC values on pH was observed. In general, the salt passage and hence STC values increased rapidly at operating pH of 6.0 and higher (for both feed and reject), while pH values less than 5.8 caused a decline in WTC values for both stages. It appears that the best feed pH range occurs between 5.8 and 6.0 in terms of maintaining high WTC values and low salt passages for RO operation on MF pretreated MODE water. For this water, interstage acid injection might be advantageous for a sustained RO operation, because RO stage 1 operation appeared stable for two months at feed pH of 5.6-5.7 (reject pH 6.1), while stage 2 salt passage increased at the rate of ~1% per month. With a feed pH of 5.5-5.6 (reject pH 5.9), as tested during the last days of operation, stage 2 STC values decreased immediately. This suggests using a feed pH of 5.6-5.7, and then an interstage acid injection to force a stage 2 reject pH of 5.9, might well allow the high WTC (relative to Alternative 10) to be maintained without incurring rapidly increasing stage 2 STC values.

High and stable or rising WTC values were observed for both YMC alternatives (MF and CF pretreatment) tested at feed pH of 6.8. MF pretreatment resulted in slightly higher values than CF pretreatment. Slight increases of STC values in the ETA membranes and the first stage elements for both MU units were monitored at the feed pH of 6.8. However, the rate of increase was higher on the second stage elements for YMC alternatives, unlike the MODE alternatives. With MF pretreatment of YMC water, decreasing the feed pH to 5.8-5.9 (reject pH of 6.3) dropped the STC values significantly, but also dropped the WTC values for both stages. A feed pH of 6.0-6.1 (reject pH of 6.5) helped to stabilize the STC values. Not enough data was collected to make a clear comment about the long-term effect of this pH on WTC values. For CF pretreated water, the same feed pH of 6.0-6.1 (reject pH of 6.5) dropped the WTC values as well as the STC values. Therefore, the best operating pH for YMC alternatives appears to lie in the range of feed pH 6.1 and 6.8, but further study would be required to fine tune this range and to determine if interstage pH adjustment would be advantageous for YMC water desalination. With

YMC water, a lower pH (5.8-6.0) consistently resulted in lower values of WTC and STC and higher CF pressure drop based on the MU, ETA and CF observed performances, indicating fouling.

High-Flux and High-Recovery

The flux increase alone (20% from 15 to 18 gfd for ETA 4 on partial lime softened water and 25% from 12 to 15 gfd for MU 1 on MF water) without any other operational changes resulted in decreased WTC values for all membrane types tested during Round 2; while no significant effect on STC values was detected. The effect on WTC was more obvious on MU 1 Vessel 3 (second stage) membranes, and no clear differences were observed in the initial STC values and the STC trends between the high-flux and regular-flux MUs. On the other hand, the increased recovery from 80% to 85% on MU 1 (MF pretreatment) after almost one and a half months of high flux operation resulted in a 20% step-change increase in WTC values during the first stage and STC values for both stages. The STC values came down soon after that but increased again later during the testing. Hence it is concluded that high-flux operation (average 15 gfd rather than 12 gfd with MU operation) may be feasible with the appropriate operating pH (perhaps including interstage pH adjustment), although a slightly lower WTC value will be experienced. Operation with 85 rather than 80% recovery is less likely to be feasible, although further examination of this possibility may be warranted.

MU Performance with Alternative Membranes

MU 2 (on partial lime softened MODE water) at feed pH 6.0-6.2 and reject pH 6.3-6.5 was operated to evaluate two alternative membrane types, Toray TML10 in the first stage and DOW XFR in the second stage. While Toray TML10 WTC values were decreasing in the first stage, DOW XFR showed an increase in the second stage. Combining this observation with ETA data for the same alternative, the authors can conclude that WTC values for DOW XFR increased initially regardless of the location of the membrane and the flux. Again regardless of the location and the flux of the membrane, the same STC values were observed in both ETA and MU units for both Toray TML10 and DOW XFR membranes. Therefore, the DOW XFR appears to be the preferred membrane (relative to Hydranautics LFC3 and Toray TML 10) for desalting the partial lime softened MODE water. Since only Hydranautics LFC3 membranes were MU tested on YMC water and MF treated MODE water there is no direct data to determine if this recommendation holds for other alternatives, however the ETA data on other alternatives showing comparable relative DOW XFR membrane performance suggests it may hold.

In summation, YMC water was equally or more readily treated for RO desalination as MODE water, however the YMC's function as a salinity management tool affects its ability to provide consistent supply of water for full-scale operations. Microfiltration of MODE water offers an operationally feasible alternative to partial lime softening with the caveat that an improved cleaning methods and scheduling (as suggested in this report) are implemented that avoid the excessively-high MF pressure drops observed during Summer 2011 operation. The limited data collected at 15 gfd average MU flux suggests this higher operational flux (than the normal 12 gfd flux) may be feasible pending further operational and economic study verification. There was no measureable improvement in RO feed water using greensand as opposed to manganese-amended silica sand in dual media gravity filters.

The results of the research indicate that low pressure polyamide RO membranes can operate sustainably and cost effectively on partial lime softened or microfiltered MODE or YMC water from which iron and manganese are removed. As anticipated, in all cases the polyamide membranes exhibited significantly higher water transport coefficients than cellulose acetate membranes, which would result in significantly lower operating pressures and energy consumption if the polyamide membranes were used at the YDP.

2. INTRODUCTION

The drainage water from the Wellton-Mohawk Irrigation and Drainage District (WMIDD) is currently conveyed to the Bypass Drain which terminates at the wetlands located in Cienega de Santa Clara (Santa Clara Slough) in Mexico, bypassing the Colorado River and the Yuma Desalting Plant (YDP). This water does not account as water deliveries to Mexico as established in the 1944 Water Treaty. The average annual salinity of most delivered water (1.36M AF/yr out of 1.5M AF/yr) to Mexico via Colorado River is regulated by Minute No. 242. This minute was implemented mainly to address the highly increased salinity values of water deliveries to Mexico due to the incorporation of WMIDD's drainage water. The main requirement of this minute is that the annual average salinity of Colorado River water delivered to Mexico (measured at the Morelos Dam) should not exceed 115 mg/L (±30 mg/L) above the annual average salinity of Colorado River water (measured at Imperial Dam). As a part of the "permanent and definitive solution" to the international salinity problem, it was authorized the construction and operation of YDP to treat WMIDD's drainage water, and deliver the treaty water as a part of treaty water deliveries to Mexico. However, mainly due to wet period in the Basin and the higher costs associated with desalting the water, YPD has mostly remained inactive since its construction. Current drought conditions, which exacerbate, the vulnerability of water shortage to Lower Basin users, have motivated the necessity of evaluating the operation of YDP. The potential operation of YDP will imply releasing less water from Lake Mead, which will increase long term storage in the reservoir, and consequently, decreasing the risk of water shortages for LB's water users.

In its current configuration, the YDP can recover most of the current bypass flow (~107 thousand AF) of water. It is capable of treating a water source with salinities in the range of 2,850-3,450 mg/L of TDS. While the actual salinity of the product water varies, the YDP was designed to have an average product water TDS of 160 mg/L. The reject stream produced during the desalting process is to be discharged in the Main Outlet Drain Extension (MODE) and conveyed through the Bypass Drain to the Ciénega de Santa Clara in Mexico.

The YDP has been operated for two periods of time in the last five years. In the first run, in 2007, Reclamation operated the plant for three months at 10-percent capacity, producing 2,632 acre-feet of product water that led to preserving 4,349 acre-feet of water in Lower Colorado River system storage. The primary purpose of this run was to demonstrate the functionality of the plant after 14 years of dormancy as well as improving plant readiness, providing data to help validate performance and cost estimates, providing water quality data, and demonstrating equipment changes. All of the demonstration run objectives were achieved.

In May 2010, a Pilot Run at up to one-third of the plant's full operating capacity was initiated. This 11–month run was conducted to evaluate the potential long term, sustained operation of the plant as a means to augment Colorado River water supplies in the midst of an unprecedented drought. Given that the plant was designed in the early years of reverse osmosis desalting technology, the Municipal Utilities determined that additional information was needed about alternative process configurations, which might generate cost reductions, for the plant. These scenarios would incorporate technological advancements achieved since the design and construction of the YDP and evaluate potential alternative feed water supplies to the plant. Hence, an evaluation of potential modifications to the plant's treatment train, membranes, and source waters was conducted at the Water Quality Improvement Center (WQIC) in parallel with the Pilot Run. The results of this research along with the findings of the Pilot Run are important in assessing long-term technology alternatives and economics for the YDP.

The Municipal Utilities, consisting of the Metropolitan Water District of Southern California (MWDSC), Southern Nevada Water Authority (SNWA) and Central Arizona Water Conservation District (CAWCD), initiated this Research Study. As part of the study, two different water sources were evaluated:

- Main Outlet Drain Extension (MODE) water, a brackish surface (canal) water originating from agricultural drainage pumped from wells in the Wellton-Mohawk Irrigation & Drainage District, and
- Yuma Mesa Conduit (YMC) water, brackish groundwater conveyed by pipeline from agricultural drainage pumped from the Yuma Mesa and Yuma Valley.

Three different pretreatments were also evaluated:

- lime softening and granular media filtration (existing YDP pretreatment) – with MODE water
- granular media filtration and microfiltration – with MODE and YDP water, and
- granular media filtration and cartridge filtration – with YMC water.

The information gathered in the Research Study will be used to help the Municipal Utilities and the United States Bureau of Reclamation (Reclamation), determine which, if any, modifications to the YDP to consider and potentially make, if a decision is made to operate the YDP for the purpose of Colorado River water supply augmentation. Test goals for the Research Study are to evaluate the effectiveness of the different pretreatments in minimizing the fouling of polyamide (PA), thin film RO membranes when operated using the two water sources. A variety of PA RO membranes were chosen for testing in represented by the following types: Hydranautics ESPA2 and LFC3, Toray TML10, Koch ULP-TFC, DOW Filmtec BW30-XFR, CSM Woongjin RE-FE and RE-CE. The desired outcome of the testing is to determine if the PA RO membranes can be operated cost effectively on each pretreated water source and further quantify differences in fouling rates between membrane types.

This report provides an overview of the specific nature of the source waters, alternative pre-treatment trains, and membranes utilized; an evaluation of the comparative performance of the various alternatives; discussion of the likely causes for the observed treatment train behaviors; and operational information necessary to allow projection of the economics for the various alternatives under a long-term YDP operation scenario.

3. BACKGROUND

The project consisted of a test-design and agreement-development phase, Rounds 1 and 2 screening test phases, a full-array testing phase and final report preparation phase. The test design and agreement development phase was completed in November 2009 and the screening test phase began in June 2010, with the initiation of project equipment and consumables procurement and planning for equipment settings and hookups. Round 1 operation began in September, 2010 and by the end of February 2011, Round 1 of the screening tests had been completed and preparations were made to begin Round 2 of the screening tests. In early March 2011, Round 2 screening tests and full-array testing phases were initiated. The testing continued until the end of December 2011. Reclamation and the Municipal Utilities shared the approximate \$1.5 million budgeted cost.

The Municipal Utilities convened a team of technical experts (the Technical Assistance Team, or TAT) to select the methods, materials, and analytics to be used for testing and for subsequently overseeing and advising on the tests as they progressed. This selection work resulted in four "alternative trains" (see Table 3.2) being chosen, although based on the results from Round 1 testing modifications to these alternative trains were made before initiation of Round 2 and full-array testing.

3.1 Project Goals

The overall goal of the YDP's research Cooperative Research and Developmental Agreement (CRADA) is to test the effectiveness of the pretreatment alternatives and alternative RO materials and operational methods and, subsequently based on these findings, to generate cost data to determine whether these pretreatment processes might be more reliable and/or more cost effective than the YDP's current configuration. The information will be used to determine which, if any, avenue to pursue if a decision is made to consider long-term operations of the YDP. The goal for Round 1 of the screening tests is to evaluate how overall effective pretreatment is in the process of preventing reverse osmosis fouling on various types of elements and how specific element types respond to the water sources and pretreatment alternatives under evaluation. The results of Round 1 help to determine which RO element types foul the least and generate information for selecting membranes for long-term YDP operations. Test goals for the full-array testing phase of the project are to generate data that can be evaluated to determine the cost-effectiveness and reliability of the treatment alternatives tested. The TAT and project funders met in early February 2011 and revised the wording of the goals to ensure it most accurately described the expected project outcome. These revised goals are listed in Table 1. Revised Project Goals.

Table 3.1. Revised Project Goals.

Phase	**Goal**
Project	Provide a technical basis for retrofit, upgrade or reconfiguration of YDP for long-term operation. *(conference call w/Chuck Cullom, CAWCD, October 19, 2009)* • Processes should be technically viable, irrespective of associated capital costs. *(Mid-project Progress Meeting, February 2, 2011)* Conduct research that will provide for process improvements *(which may or may not lead to capital improvements)* to the YDP based upon a *30*-year operational life; utilizing both MODE water and YMC groundwater; leading to preparing a final report approximately the same time as the final report for the Pilot operation. *(from November 8, 2008 meeting agenda; italics reflect modifications agreed upon during Mid-project Progress Meeting on February 2, 2011)* • *Report to be agreed to and signed off by all TAT members*
Screening	Evaluate • Which element types operate effectively on different pretreatments, in terms of maintaining initial values of the RO performance parameters. • Which RO elements are suitable for Full-Array High-Recovery testing, considering performance effectiveness and other parameters.
Full-Array Testing	Develop long-term cost and performance data at Full-Array Testing to be used in future engineering or cost studies on the YDP. Should add to the existing body of knowledge generated by YDP Upgrade. *(TAT)*

One of the objectives of the Pilot Run was to verify the suitability of the treatment processes and associated facilities currently in place at the YDP to reliably produce product water that could be used for multiple end uses. This would help determine whether any additional improvements to the YDP would be necessary to ensure reliable medium and long-term operation beyond those already identified by Reclamation, and the cost implications of such improvements. Since the initial design of the YDP, water treatment technology has advanced substantially in terms of both type and efficiency. For example, industry has developed reverse osmosis (RO) membranes that operate at lower pressure (with lower energy cost) and higher salt removal. Although lime softening followed by dual-media filtration – the original pretreatment process used at the YDP – is still considered a standard and reliable technology, many utilities are turning to the use of microfiltration or ultrafiltration as pretreatment preceding RO and the comparative efficacy of these options for the YDP case is of interest to the project funders.

Consequently, the proposed research was aimed at evaluating a new water source, contemporary pretreatment technologies such as microfiltration and ultrafiltration, and polyamide reverse osmosis membranes to gather information on pretreatment effectiveness, RO operating pressure, RO salt removal, cost-effectiveness and long-term operational reliability of the process alternatives.

It was also determined that test data would be compared to that generated from the 2007 Demonstration Run. For RO pretreatment, the 2007 Demonstration Run used conventional treatment with ferric sulfate coagulant and a polymer coagulant aid, rather than the lime softening process included in the original YDP design. The Demonstration Run used a combination of 20-year old unused and used membranes, with the used membranes showing increased salt passage. By comparison, the Pilot Run utilized the lime-softening process and unused 15-year old Fluid Systems RO membranes. Information from the Demonstration Run would be compared to information gathered during the Pilot Run and from the Research Project to evaluate according to the CRADA between Municipal Utilities and U.S. Bureau of Reclamation.

3.2 Project Approach

The research program systematically evaluated the effectiveness of preselected pretreatments and polyamide (PA) RO membranes on MODE water and YMC water supplies as identified in the CRADA agreement (*Figure 1: Selected Source Water and Pretreatment Alternatives* and *Figure 2: Reclamation and Municipal Utilities Joint Research Project Test Plan*). These figures from CRADA agreement are presented in this report as Figure 3.1 and Figure 3.2.

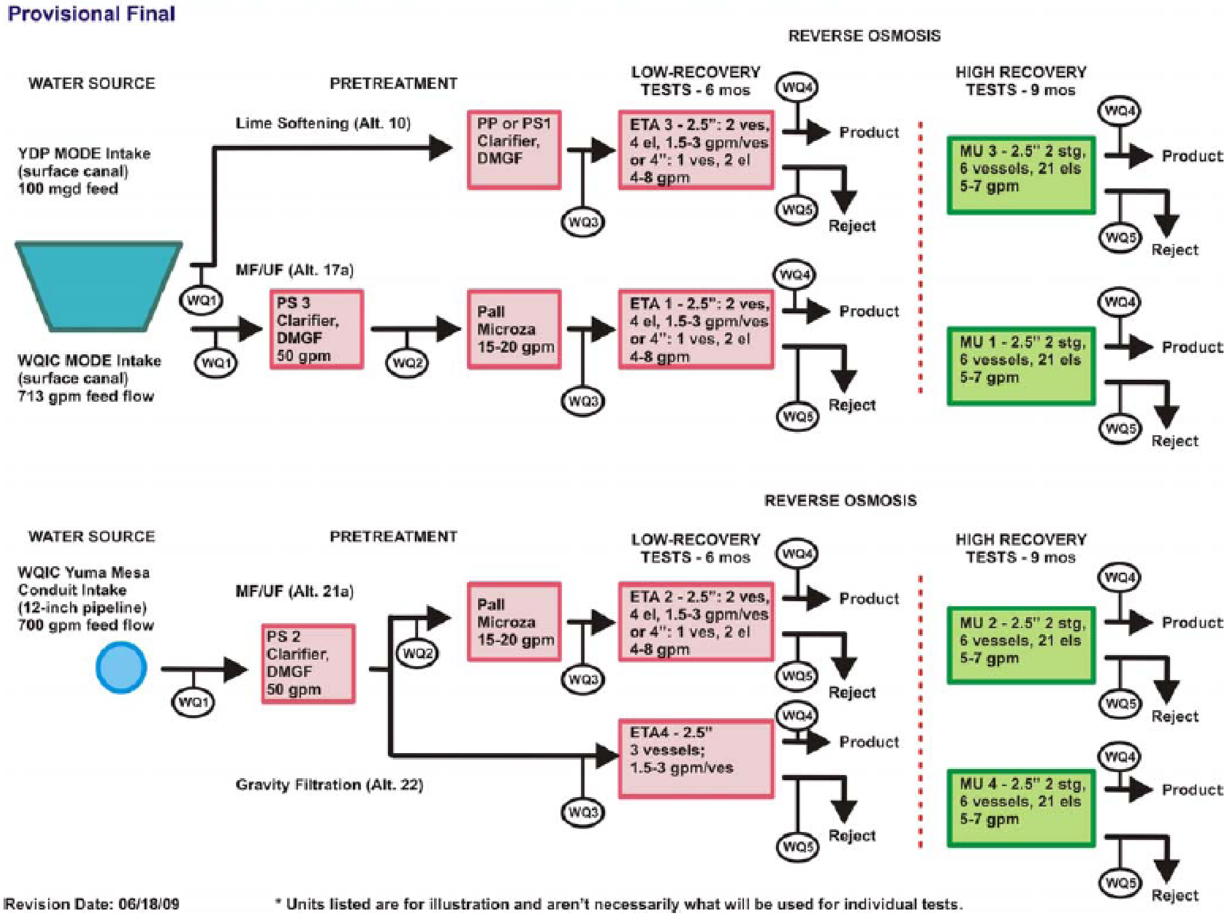
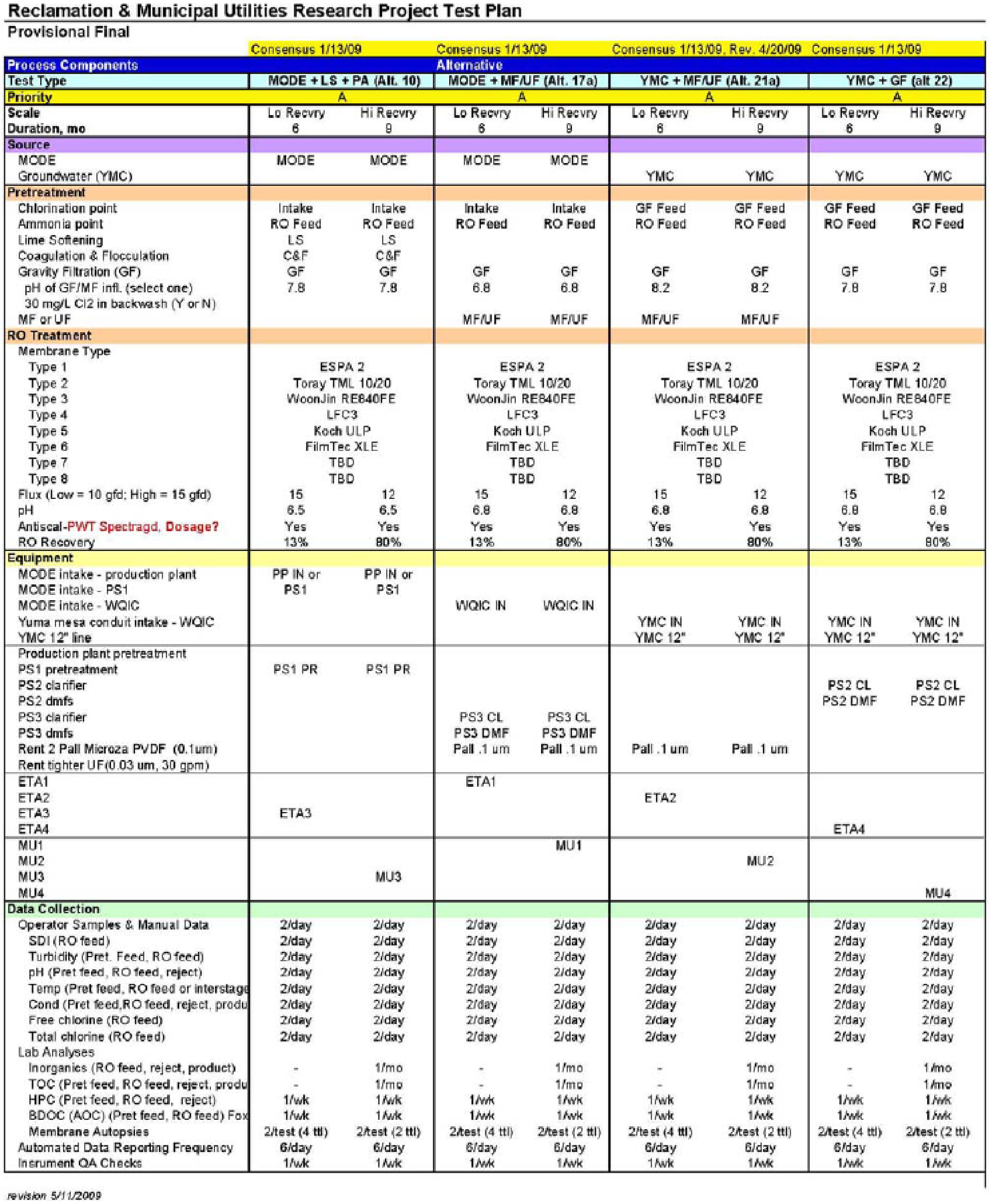


Figure 3.1. Selected source water and pretreatment alternatives.

Four parallel treatment trains were operated consisting of separate pretreatment and separate RO systems in two phases. During Rounds 1 and 2 Screening tests, seven different PA RO membranes at low recovery for three months were operated. Identical sets of RO membranes were operated in each of the four treatment trains. In Round 2 Full-Array testing, referred to as the Full-Array Testing Phase, one or more PA RO membranes from Screening tests operated at high recovery for an extended period (five to nine months). Pretreatment and RO membrane performance were quantified using continuous monitoring and periodic analysis of process operating data, and field and laboratory analysis (both routine and specialized) of water quality samples collected at key process locations at selected intervals. In addition, destructive autopsies were conducted on selected RO membranes to characterize the extent and type of fouling and scaling and to note if any membrane material changes that might suggest longer-term membrane performance changes were observable. Research for this project was conducted through the following tasks:

> *Round 1 Low-Recovery Screening Testing (Sep 2010–Feb 2011):* Process alternatives were evaluated for approximately 2500-3000 hours (approximately four months) with low-recovery Element Test Apparatuses (ETAs) to investigate four different types of membrane models (Hydranautics ESPA2 and LFC3, Toray TML10, and Koch ULP-TFC). The alternatives were assigned designations (e.g., Alternative 10, Alternative 17a, Alternative 21a and Alternative 22) based on previous and/or related tests conducted at the WQIC and are described below in Project Setup section. For additional information on alternatives, see the Materials and Methods section of the report.
>
> *Round 2 Low-Recovery Screening Testing (Mar 2011–Sep 2011):* Round 2 Low-Recovery Testing was conducted after completing Round 1 and lasted for approximately 3000-4700 hours and in this second round of low-recovery testing three more commercial PA RO membrane models (DOW Filmtec BW30-XFR, CSM Woongjin RE-FE and RE-CE) were evaluated along with one model (Toray TML10) from Round 1 to setup a base for comparison between Round 1 and Round 2 results.
>
> *Round 2 Full-Array Testing (Mar 2011–Dec 2011):* Based upon the results of testing under Round 1 and Round 2 Low-Recovery Screening Testing, Round 2 Full-Array Testing evaluated process alternatives for approximately 2500-6500 hours (approximately three to nine months) with high-recovery (~80%) membrane evaluation research units (MUs) with all MUs but one containing the same RO membrane model (Hydranautics LFC3) selected from the Round 1 screening tests. See the Materials and Methods section for more details.

Round 3 Final Report Preparation: Test Manager, Umur Yenal, prepared the final report detailing results of Round 1 and 2 researches. Reclamation and the representatives of the Municipal Utilities reviewed and commented on the report.



Reclamation & Municipal Utilities Research Project Test Plan

Provisional Final

	Consensus 1/13/09		Consensus 1/13/09		Consensus 1/13/09, Rev. 4/20/09		Consensus 1/13/09	
Process Components			Alternative					
Test Type	MODE + LS + PA (Alt. 10)		MODE + MF/UF (Alt. 17a)		YMC + MF/UF (Alt. 21a)		YMC + GF (alt 22)	
Priority	A		A		A		A	
Scale	Lo Recvry	Hi Recvry	Lo Recvry	Hi Recvry	Lo Recvry	Hi Recvry	Lo Recvry	Hi Recvry
Duration, mo	6	9	6	9	6	9	6	9
Source								
MODE	MODE	MODE	MODE	MODE				
Groundwater (YMC)					YMC	YMC	YMC	YMC
Pretreatment								
Chlorination point	Intake	Intake	Intake	Intake	GF Feed	GF Feed	GF Feed	GF Feed
Ammonia point	RO Feed	RO Feed	RO Feed	RO Feed	RO Feed	RO Feed	RO Feed	RO Feed
Lime Softening	LS	LS						
Coagulation & Flocculation	C&F	C&F						
Gravity Filtration (GF)	GF	GF	GF	GF	GF	GF	GF	GF
pH of GF/MF infl. (select one)	7.8	7.8	6.8	6.8	8.2	8.2	7.8	7.8
30 mg/L Cl2 in backwash (Y or N)								
MF or UF			MF/UF	MF/UF	MF/UF	MF/UF		
RO Treatment								
Membrane Type								
Type 1	ESPA 2		ESPA 2		ESPA 2		ESPA 2	
Type 2	Toray TML 10/20		Toray TML 10/20		Toray TML 10/20		Toray TML 10/20	
Type 3	WoonJin RE840FE		WoonJin RE840FE		WoonJin RE840FE		WoonJin RE840FE	
Type 4	LFC3		LFC3		LFC3		LFC3	
Type 5	Koch ULP		Koch ULP		Koch ULP		Koch ULP	
Type 6	FilmTec XLE		FilmTec XLE		FilmTec XLE		FilmTec XLE	
Type 7	TBD		TBD		TBD		TBD	
Type 8	TBD		TBD		TBD		TBD	
Flux (Low = 10 gfd; High = 15 gfd)	15	12	15	12	15	12	15	12
pH	6.5	6.5	6.8	6.8	6.8	6.8	6.8	6.8
Antiscal-PWT Spectragd, Dosage?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
RO Recovery	13%	80%	13%	80%	13%	80%	13%	80%
Equipment								
MODE intake - production plant	PP IN or	PP IN or						
MODE intake - PS1	PS1	PS1						
MODE intake - WQIC			WQIC IN	WQIC IN				
Yuma mesa conduit intake - WQIC					YMC IN	YMC IN	YMC IN	YMC IN
YMC 12" line					YMC 12"	YMC 12"	YMC 12"	YMC 12"
Production plant pretreatment								
PS1 pretreatment	PS1 PR	PS1 PR						
PS2 clarifier							PS2 CL	PS2 CL
PS2 dmfs							PS2 DMF	PS2 DMF
PS3 clarifier			PS3 CL	PS3 CL				
PS3 dmfs			PS3 DMF	PS3 DMF				
Rent 2 Pall Microza PVDF (0.1um)			Pall .1 um	Pall .1 um	Pall .1 um	Pall .1 um		
Rent tighter UF(0.03 um, 30 gpm)								
ETA1			ETA1					
ETA2					ETA2			
ETA3	ETA3							
ETA4							ETA4	
MU1				MU1				
MU2						MU2		
MU3		MU3						
MU4								MU4
Data Collection								
Operator Samples & Manual Data	2/day	2/day	2/day	2/day	2/day	2/day	2/day	2/day
SDI (RO feed)	2/day	2/day	2/day	2/day	2/day	2/day	2/day	2/day
Turbidity (Pret. Feed, RO feed)	2/day	2/day	2/day	2/day	2/day	2/day	2/day	2/day
pH (Pret feed, RO feed, reject)	2/day	2/day	2/day	2/day	2/day	2/day	2/day	2/day
Temp (Pret feed, RO feed or interstage	2/day	2/day	2/day	2/day	2/day	2/day	2/day	2/day
Cond (Pret feed,RO feed, reject, produ	2/day	2/day	2/day	2/day	2/day	2/day	2/day	2/day
Free chlorine (RO feed)	2/day	2/day	2/day	2/day	2/day	2/day	2/day	2/day
Total chlorine (RO feed)	2/day	2/day	2/day	2/day	2/day	2/day	2/day	2/day
Lab Analyses								
Inorganics (RO feed, reject, product)	-	1/mo	-	1/mo	-	1/mo	-	1/mo
TOC (Pret feed, RO feed, reject, produ	-	1/mo	-	1/mo	-	1/mo	-	1/mo
HPC (Pret feed, RO feed, reject)	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk
BDOC (AOC) (Pret feed, RO feed) Fox	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk
Membrane Autopsies	2/test (4 ttl)	2/test (2 ttl)	2/test (4 ttl)	2/test (2 ttl)	2/test (4 ttl)	2/test (2 ttl)	2/test (4 ttl)	2/test (2 ttl)
Automated Data Reporting Frequency	6/day	6/day	6/day	6/day	6/day	6/day	6/day	6/day
Insrument QA Checks	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk

revision 5/11/2009

Figure 3.2. Reclamation and Municipal Utilities research project test plan

3.3 Project Setup

The table below shows the various methods used in each alternative train.

Table 3.2. Alternative treatment trains and methods used in each alternative.

	Alternative 10	Alternative 17a	Alternative 21a	Alternative 22
Source Water				
MODE	X	X	--	--
YMC	--	--	X	X
Chemical Addition				
Chlorination	X	X	X	X
Sulfuric Acid	X	X	X	X
Lime Softening	X	--	--	--
Ammonium Sulfate	X	X	X	X
Anti-scalant	X	X	X	X
Pretreatment Methods				
Flocculation	X	--	--	--
Sedimentation	X	--	--	--
Dual-Media Gravity Filtration	X	X	X	X
Microfiltration	--	X	X	--
Cartridge-Filtration	--	--	--	X
PA RO Membranes	X	X	X	X

The four treatment trains consist of the following combinations of source water, pretreatment and polyamide RO membranes:

- Alternative 10: MODE water treated by chlorination, lime softening, flocculation, sedimentation, acidification to pH 7.8, gravity dual-media (anthracite and sand) filtration, chloramination, acidification to the desired operating pH (refer to Table 5.1 for the relevant operating pH), antiscalant addition , and PA RO membranes.
- Alternative 17a: MODE water treated by chlorination, gravity dual-media (anthracite and sand) filtration, acidification to the desired operating pH (refer to Table 5.1 for the relevant operating pH), microfiltration, chloramination, antiscalant addition, and PA RO membranes.
- Alternative 21a: YMC water treated by chlorination (disinfection and oxidation purposes), gravity dual-media (anthracite and sand) filtration, acidification to the

desired operating pH (refer to Table 5.1 for the relevant operating pH), microfiltration, chloramination, antiscalant addition, and PA RO membranes.

- Alternative 22: YMC water treated by chlorination (disinfection and oxidation purposes), gravity dual-media (anthracite and sand or greensand) filtration, acidification to the desired operating pH (refer to Table 5.1 for the relevant operating pH), chloramination, cartridge-filtration, antiscalant addition, and PA RO membranes.

The nature and concentration of chemical treatments used in the pre-treatment alternatives changed at various times during the study based on the chemical and physical operating processes employed and the results of the testing. Initiated by TAT discussion and recommendations, Reclamation and the Municipal Utilities discussed and agreed on the changes in chemical treatments before they were implemented.

As part of the YDP and WQIC infrastructure, Reclamation supplied the following elements of the research program:

- MODE and YMC water at the necessary flows
- Three conventional pretreatment systems (Pilot System 1 pretreatment, Pilot System 2 and 3 pretreatment)
- Four Element Test Apparatuses (ETAs) for PA RO membrane screening at low recovery (~13%)
- Four Membrane Evaluation Research Units (MUs) for pilot testing of PA RO membranes at high recovery (~80%), and
- Some of the PA RO elements for Round 2 testing

The Municipal Utilities supplied the following equipments:

- Two Pall Microza microfiltration systems, and
- PA RO elements for both Round 1 and Round 2 (low and high recovery testing)

4. ROLES AND RESPONSIBILITIES

The project organization chart is shown in Figure 4.1.

Reclamation and the Municipal Utilities provided equipment for the project as noted in Section 3.3.

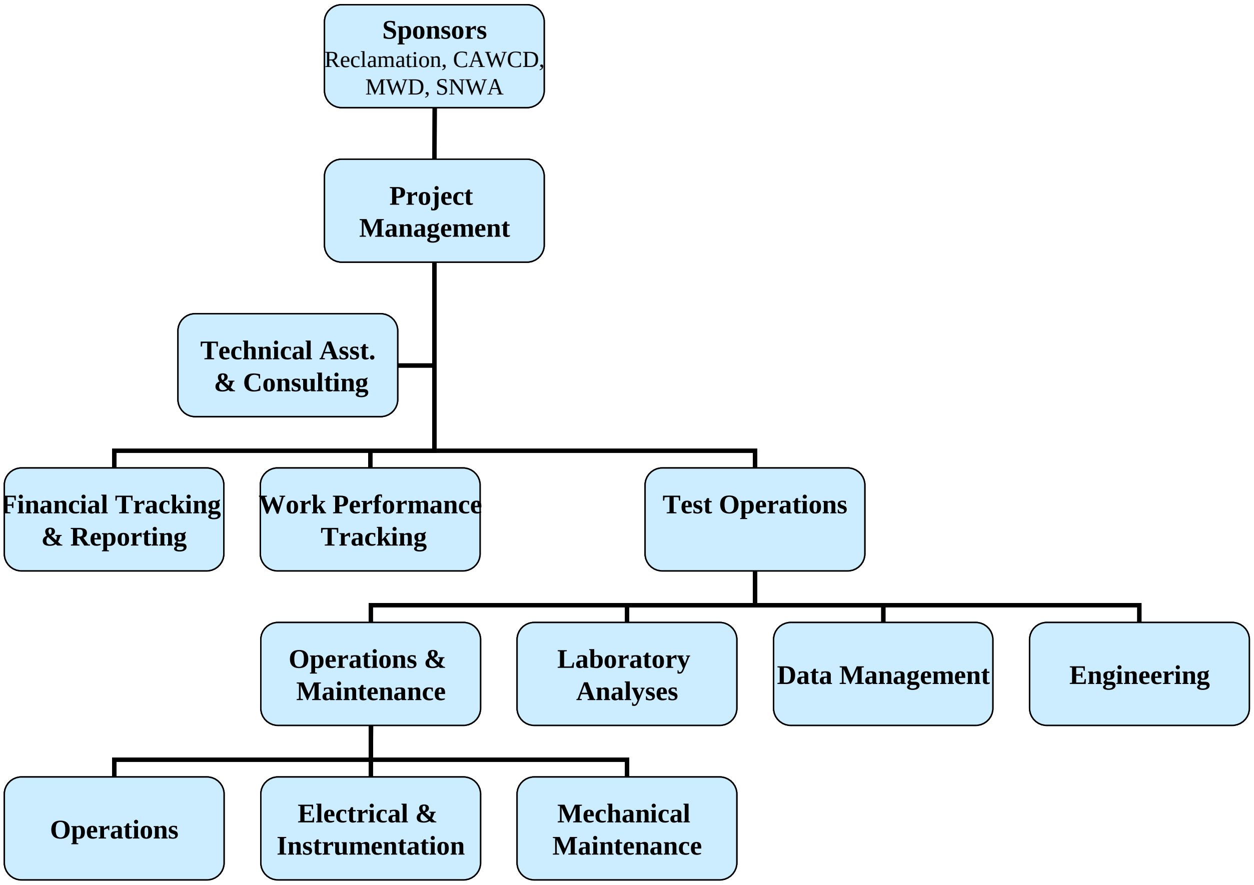


Figure 4.1. YDP research project organization chart.

The Municipal Utilities assigned an on-site Test Manager, Umur Yenal, a non-Reclamation staff member, who supervised the research, provided engineering support for data collection, analysis, and resolution of project problems, performed day-to-day duties to ensure the progress of the research project, coordinated test plan and scheduled modifications with the Reclamation staff, Reclamation–contracted support staff and Municipal Utilities' representatives, prepared monthly progress reports, evaluated the research data and became the primary contact and informational resource for the Municipal Utilities project officers and off-site project managers. The Test Manager was also primarily responsible for preparation of the draft and final versions of this project report. Refer to Appendix A-1 for the detailed explanation of his duties.

Project officers throughout the testing were Bill Hasencamp and Jan Matusak for MWDSC, Bruce Moore for SNWA and Jim Lozier as the representative of SNWA and as a member of the TAT, Chuck Cullom for CAWCD, Wendell Ela and Peter Fox as the representatives of CAWCD and as the members of the TAT, Rich Yates for MWDSC and as a member of the TAT, Mike Norris for Reclamation as the Yuma Desalting Plant Manager and Research Director, Angela Adams for Reclamation as the Program Analyst and Research Coordinator, Chuck Moody and John Franklin for Reclamation as Chemical Engineers and the members of the TAT and Umur Yenal as the Test Manager for Municipal Utilities.

Reclamation along with the Test Manager took the lead in project coordination, logistics, and technical assistance to help conduct the research. Reclamation also reviewed and commented on all reports. Communications between research project personnel located in Arizona, California and Nevada and Reclamation were maintained primarily through conference calls and e-mail messages.

5. MATERIALS AND METHODS

5.1 Experimental Matrix

The four treatment trains consist of the following combinations of source water, and pretreatment unit operations. Polyamide RO membranes were used in all treatment trains. Refer to Figure 5.1 for a schematic and Appendix A-2 for the detailed process flow diagrams of each alternative tested during the research study. The feed pH of each unit in operation during the testing is summarized in Table 5.1.

1. Alternative 10: MODE water with lime softening, flocculation, sedimentation, gravity dual-media (anthracite and sand) filtration and RO.
2. Alternative 17a: MODE water with gravity dual-media (anthracite and sand) filtration, microfiltration and RO.
3. Alternative 21a: YMC water with gravity dual-media (anthracite and sand) filtration, microfiltration, and RO.
4. Alternative 22: YMC water with gravity dual-media (anthracite and sand for Round 1 and anthracite and greensand for Round 2) filtration, cartridge-filtration, and RO.

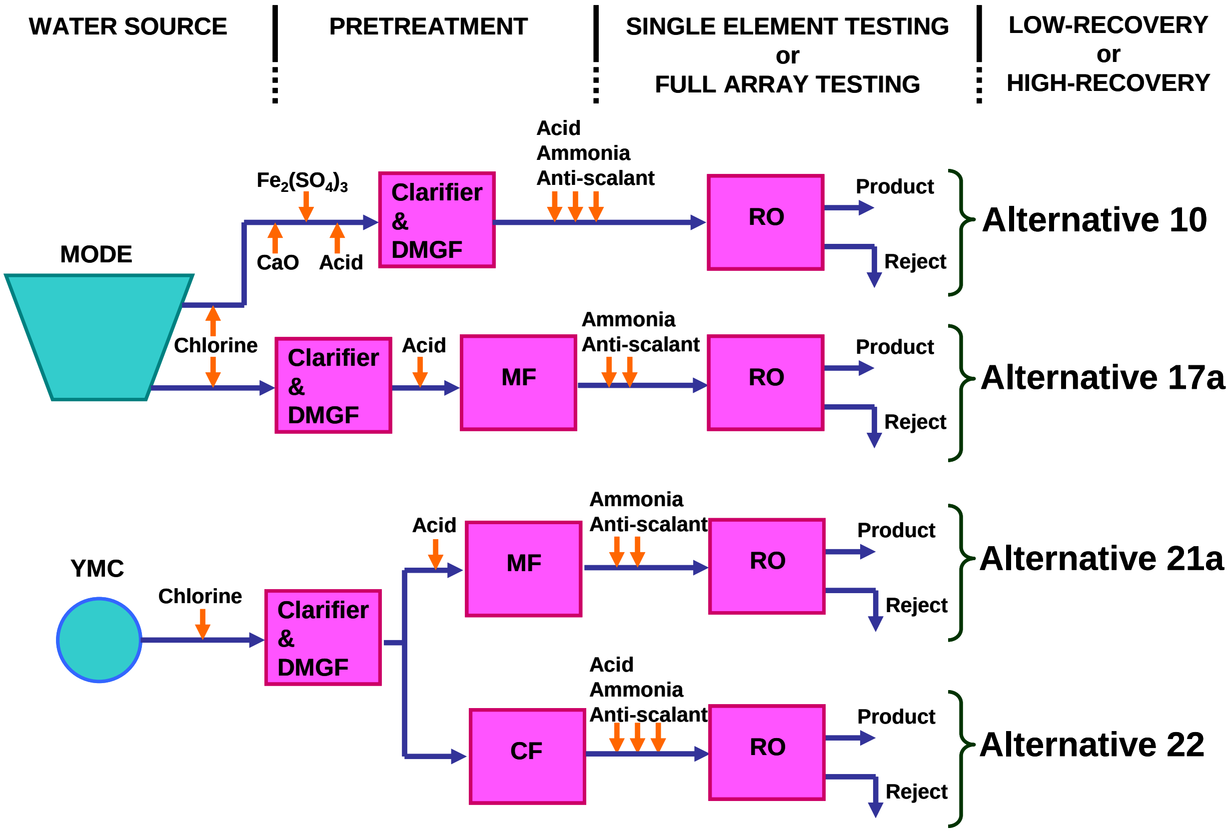


Figure 5.1. Schematic of different treatment alternatives tested during the research program.

Table 5.1. Feed pH values for each unit in operation in WQIC for MU CRADA. Blank cell indicates unit was off-line. Red cell indicates unit switched source water.

Date	***PS2***	***PS3***	***East Pall***	***West Pall***	***ETA 1***	***ETA 2***	***ETA 3***	***ETA 4***	***MU 1***	***MU 2***	***MU 3***	***MU 4***
3/11-6/17/11	7.6-7.8	7.6-8.0	6.8	6.8	6.8	6.8	6.8	5.7-5.8	6.8	6.8	6.8	5.7-5.8
6/17-7/1/11											5.4-5.5	
7/1-7/12/11			5.8-5.9				5.8-5.9	6.0-6.1	5.8-5.9			6.0-6.1
7/12-8/26/11											5.9-6.0	
8/26-9/5/11			6.0-6.1	5.7-5.8	5.7-5.8	5.9-6.0	6.0-6.1		6.0-6.1	5.9-6.0	5.7-5.8	
9/5-9/9/11						6.8				6.8		
9/9-9/29/11			-			-	-		-	-		
9/29-9/30/11												
9/30-10/3/11					-							
10/3-10/4/11									**5.7-5.8**			
10/4-10/6/11								-		**6.0-6.1**		
10/6-12/8/11				6.8								
12/8-12/26/11										**6.2-6.3**		6.2-6.3
12/26-12/30/11									**5.8-5.9**		5.8-5.9	

5.2 Analytics and Data Collection

Analysis of alkalinity, hardness, major cations and anions, TDS, TOC, HPC, trace metals, turbidity, temperature, conductivity, chlorine concentration, and pH were performed by Reclamation's on-site Lab following the *Standard Methods for the Examination of Water and Wastewater* or the instrumentation installed in the facilities of WQIC (Table 5.2).

Table 5.2. Lab and instrumental data sampling frequency and analyses.

Data Type	Personnel	Location	Frequency
		Manual Data Collection	
Flow Readings	Operator	Pretreatment and RO units	2/day
Iron & Manganese	Test Manager	Raw water, pretreatment influent, pretreatment effluent, PS2 GF effluent before cartridge filters and after cartridge filters, after MF	1/week
SDI	Operator	PS2 GF effluent, MF effluent, RO feed	2/day
Turbidity	Operator	Raw water, RO feed	2/day
pH	Operator	GF Effluent**,** RO feed and reject	2/day
Temperature	Operator	RO feed or interstage	2/day
Conductivity	Operator	RO feed, reject and product	2/day
Free chlorine	Operator	RO feed	2/day
Total chlorine	Operator	RO feed	2/day
Monochloramines	Test Manager	RO feed	2/day (weekly)
		Lab Analyses	
Iron & Manganese	Test Manager/Lab	Raw water, pretreatment influent, pretreatment effluent	1/2-weeks
Inorganics	Test Manager/Lab	Raw water, RO feed (before anti-scalant addition), reject and product	1/month
TOC	Test Manager/Lab	Pretreatment feed, RO feed (before anti-scalant addition), reject and product	1/month
HPC	Lab	Pretreatment feed, RO feed and reject	1/week
BDOC	Test Manager/ASU	Pretreatment feed, RO feed	2/month
		Automated Data Collection	
Operating parameters	SCADA/PI	All the units	24/day
Operating parameters	SCADA/PI	All the units	2/day
		Instrument QA Checks	
Operating parameters	E/I Group	All the units	1/week

The flow readings from the units, including the permeate and the reject flow rates of the RO units, were collected by the operators when the instrument data was not available for any reason. Hourly average values were recorded for all the instrument parameters read by SCADA throughout the day (24 data points per day) to analyze any anomaly that might occur in the system. This data is presented in the Appendix I. Two data points from these data, for example 8 AM and 8 PM for ETAs and 9 AM and 9 PM for PS units, were used in calculations and performance analyses. However, only flow data of MUs were used in this way. All the other measurements used in calculations in MU data analyses were recorded by the operators as an instantaneous reading from the instruments. The hourly average values were used if replacement of erroneous data was needed. For ETAs, the manual flows were measured by bucket and stopwatch techniques for all monitored streams, i.e. four individual products and two rejects per ETA. On the other hand, for MUs, only the total product (not for products of individual vessels) and reject flows can be measured manually because product backpressure valves are installed between vessels.

The Microsoft Excel workbooks including all the data for each unit were updated by the Test Manager weekly and discussed by the TAT members during the weekly conference calls. The decisions taken at the end of each conference call were executed by the Test Manager and/or personnel on duty. For sampling frequency, refer to the Table 5.2, above. More detailed tables for operating parameters and data analyses are presented in relevant sections.

BDOC Sampling

The Test Manager collected samples for biodegradable organic carbon (BDOC) analysis, to be performed by the Arizona State University (ASU) laboratory located in Phoenix, AZ. The sampling points for BDOC were pretreatment feed waters (feed of PS1, PS2 and PS3 units), RO feed waters, product of East MF unit, West MF unit, PS1 DMGF and PS3 DMGF. 500 milliliter (ml) samples were collected at each sampling point and filtered through 0.45 µm polyethersulfone filter paper in Reclamation's lab and stored and/or shipped overnight at +4 ^{o}C. Refer to Appendix A-3 for the detailed explanation of BDOC sampling, preparation and shipment. The Municipal Utilities were responsible for providing sample bottles and for sample shipping costs. Initial samples showed no change in BDOC levels. Hence, additional BDOC sampling was canceled.

Silt Density Index (SDI) Analysis

The Silt Density Index (SDI) was measured by Chemetek (Model FPA-3300) units using the method described by the American Society for Testing and Materials (ASTM) method D 4189-82. Refer to Section 5.8.2.4.1 under “Reverse Osmosis: Data Analysis” for the details of SDI measurement, calculation and analysis.

Monochloramine Analysis

The term “chloramines” is used to represent a group of organic compounds with the formulas R_2NCl and $RNCl_2$ where R represents an organic group. Chloramines are produced by substituting one, two or three hydrogen atoms in ammonia with chlorine atoms. Monochloramine occurs, as its name suggests, when one hydrogen atom is substituted with one chlorine atom in ammonia and it is an inorganic compound with the formula NH_2Cl. Dichloramine, $NHCl_2$, and trichloramine, NCl_3, might be produced as well, depending on the pH and equilibration time of the solution. Monochloramine is a stable compound in dilute solutions with pH of 7.5 to 9.0, where optimum pH is 8.3. It is used as a secondary disinfectant as an alternative to free chlorine. Although it has a weaker biocidal effect than free chlorine, it does not damage PA RO membranes. The use of monochloramine as the disinfectant also reduces the formation of trihalomethanes (THM) in water. When ammonia and hypochlorous acid react by the chemical formula below, monochloramine forms.

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$$

During this research study, combined chlorines (monochloramine, dichloramine or trichloramine), produced by adding ammonium sulfate in the feed water with free chlorine already present, were used as the disinfectant through the RO, while free chlorine was used as the disinfectant ahead of RO. For combined chlorines, mainly monochloramine was targeted to be generated. The ratio of monochloramine, dichloramine and trichloramine depends on the pH and equilibration time of the water, but at molar ratios of free chlorine to ammonia of < 1.0, monochloramine is the dominant combine chlorine constituent. Monochloramine concentrations were measured in the feed water of the RO units during their start up periods via N,N-diethyl-p-phenylenediamine (DPD) colorimetric (4500-CI G) method by Hach DR890 Portable Colorimeter. Once it was established that the total chlorine concentration was roughly the same as the monochloramine concentration, the measurement of monochloramine was discontinued to save chemical cost and operator's time on the condition that total chlorine and pH of the feed waters were measured twice a day.

5.3 Source Waters

The two water sources selected for the research program are discrete and unique for the Yuma region. One is the Main Outlet Drain Extension (MODE) water – agricultural drainage water from the Wellton-Mohawk Irrigation & Drainage District (WMIDD) – and the second is the brackish groundwater from the nearby Yuma Mesa Conduit (YMC), which collects agricultural drainage pumped from the Yuma Mesa and Yuma Valley.

5.3.1 Main Outlet Drain Extension (MODE)

The MODE is an open canal that is exposed to environmental events that might change the water quality in the canal. The severity of the event determines the intensity of the water quality change. The operation of the canal, such as the flow rate in the canal, the source of water flowing in the canal, the season, etc. also affects the water quality significantly. Please, refer to results section of the report for the details of the water quality data.

MODE water, which represents the current source water for the YDP, served as the feed to Alternative 10 and Alternative 17a treatment trains throughout the research testing. Total dissolved solids (TDS) concentration of MODE water ranges from 2,400-2,800 mg/L. MODE water, being a surface supply, has a higher fouling potential due to higher levels of particulate and organic matter. It is susceptible to the annual fluctuation in the temperature. The biological activity in the MODE canal affects both organic and inorganic contaminant levels.

5.3.2 Yuma Mesa Conduit (YMC)

The YMC is a closed pipe conveyance. YMC water served as the feed to Alternative 21a and Alternative 22 treatment trains. The TDS concentration of YMC water ranged from 1,400-1,700 mg/L, as well as the level of particulate and organic matter are lower in the YMC water compared to MODE water. On the other hand, the YMC water contains elevated levels of iron and manganese that requires removal prior to RO treatment.

5.4 Chemicals

The chemicals added to the feed streams of all alternatives included sodium hypochlorite (bleach), ammonium sulfate, anti-scalant, and sulfuric acid.

5.4.1 Sulfuric Acid

The sulfuric acid addition is for adjusting the feed water pH prior to RO treatment. Acid was dosed ahead of the MF units on Alternatives 17a and 21a to help minimize mineral precipitation in the MF modules. The pH of source waters is around 7.5 to 8. The precipitation of calcium needs to be avoided by lowering the pH. The solubility of calcium increases significantly by a factor of 100 while decreasing the pH from 8.0 to 7.0. The cost for lowering the pH in all alternatives tested during this study, with the exception of Alternative 10 (lime softened MODE water), was estimated as having a significant effect on the overall cost.

Concentration of sulfuric acid used in pH adjustment was 93.0% with a density of 1.828 grams per milliliter (g/ml) and it was used without any dilution. The target dosage and drawdown values were calculated for each alternative at different possible flow rates and they are presented in Table 5.3, below. However, the acid dosing in each injection point was controlled by automated closed loop systems. The pump speed was adjusted by a controller that compares the real time pH value to the set point of that particular alternative.

Table 5.3. Target dosage and drawdown values for each alternative.

Treatment Alternative	Chemical	Concentration (neat) %	Target dosage mg/L	Process flow L/min	Target drawdown mL/min
ETA and MU at their designed flow rates + 1 gpm of overflow + slipstream (~16 gpm):					
Alt. 10 - MODE - LS	Sulfuric acid H_2SO_4	93.0%	6.1	61	**0.2**
Alt. 22 - YMC - GF	Sulfuric acid H_2SO_4	93.0%	59	61	**2.1**
ETAs at their designed flow rates + 1 gpm of overflow + slipstream (~10.5 gpm):					
Alt. 10 - MODE - LS	Sulfuric acid H_2SO_4	93.0%	6.1	40	**0.1**
Alt. 22 - YMC - GF	Sulfuric acid H_2SO_4	93.0%	59	40	**1.4**
MUs at their designed flow rates + 1 gpm of overflow + slipstream (~8 gpm):					
Alt. 10 - MODE - LS	Sulfuric acid H_2SO_4	93.0%	6.1	30	**0.1**
Alt. 22 - YMC - GF	Sulfuric acid H_2SO_4	93.0%	59	30	**1.1**
While running MF units at 15 gpm (single module; 40 gfd):					
Alt. 17a - MODE - MF	Sulfuric acid H_2SO_4	93.0%	92	57	**3.1**
Alt. 21a - YMC - MF	Sulfuric acid H_2SO_4	93.0%	59	57	**2.0**
While running MF units at 30 gpm (single module; 80 gfd):					
Alt. 17a - MODE - MF	Sulfuric acid H_2SO_4	93.0%	92	114	**6.1**
Alt. 21a - YMC - MF	Sulfuric acid H_2SO_4	93.0%	59	114	**3.9**
While running MF units at 60 gpm (double module; 80 gfd):					
Alt. 17a - MODE - MF	Sulfuric acid H_2SO_4	93.0%	92	227	**12.3**
Alt. 21a - YMC - MF	Sulfuric acid H_2SO_4	93.0%	59	227	**7.9**

5.4.2 Antiscalant

Addition of antiscalant is specifically for preventing the precipitation of sparingly soluble salts in source waters, such as barium sulfate, calcium sulfate and calcium carbonate. Different types of antiscalants were considered for this research study (Table 5.4).

Table 5.4. Antiscalants considered for the research study.

Company	Product	Cost	Alt 10 MODE-LS	Alt 17 MODE	Alt 21&22 YMC	Alt 23 YMC-LS	Alt 10 MODE-LS	Alt 17 MODE	Alt 21&22 YMC	Alt 23 YMC-LS	Alt 10 MODE-LS	Alt 17 MODE	Alt 21&22 YMC	Alt 23 YMC-LS
-	-	$/kg	Dosage (mg/L)				Quantity (x1000kg/period)				Cost (x1000$/period)			
Avista	Vitec 3000	8.14	2.0	2.0	2.0	2.0	93	93	93	93	760	760	760	760
AWC	A-102 Plus	1.54	0.5	0.8	2.0	1.0	23	35	93	47	36	54	144	72
BWA	Flocon 260	3.39	1.0	1.3	1.3	1.0	47	61	61	47	158	205	205	158
Ecolab	Flocon 260	4.94	1.0	1.5	1.4	1.0	47	70	65	47	231	346	323	231
Ecolab	FP 8106	5.71	2.7	3.8	3.5	2.7	126	177	163	126	719	1012	932	719
GE	Hypersperse MDC 150	5.36	2.0	-	-	2.0	94	-	-	95	505	-	-	510
GE	Hypersperse MSI 310	8.23	-	3.0	2.5	-	-	138	114	-	-	1132	940	-
KingLee	Pretreat Plus-Y2K	NA	0.5	3.5	2.5	0.5	23	163	117	23	NA	NA	NA	NA
Nalco	PermaTreat PC-191T	2.16	1.6	2.2	2.0	-	75	103	91	-	162	222	197	-
PWT	SpectraGuard	1.56	2.7	2.7	2.7	2.7	126	126	126	126	196	196	196	196
thermPhos	SPE 0001	2.02	1.4	2.6	2.3	1.7	65	121	107	79	132	246	217	161
thermPhos	SPE 0109	2.75	1.5	2.9	2.4	1.8	70	135	112	84	192	372	308	231
Thatcher	SHMP	3.63	1.0	1.0	1.0	1.0	47	47	47	47	169	169	169	169

AWC A-102 Plus produced by American Water Chemicals, Inc. was selected by TAT members for use throughout the study. AWC A-102 Plus is a multifunctional antiscalant and antifoulant for reverse osmosis systems. It is designed to inhibit inorganic scale formation, such as calcium carbonate, calcium sulfate, metal oxides, silica, barium sulfate and strontium sulfate, in membrane separation processes. It is also listed by the manufacturer as an effective way to control iron precipitation. It is an approved product by the National Sanitation Foundation (NSF) for potable drinking water production via membrane separation processes. Another reason for selecting A-102 Plus was its environmentally compatible feature, where the discharge of reject water into the environment might be a concern, like the YDP reject discharge into MODE canal.

The manufacturer’s suggested dosing for A-102 Plus was 0.5 mg/L and 0.8 mg/L for Alternative 10 and Alternative 17a, respectively, running on MODE water; and was 2.0 mg/L for YMC alternatives. Nevertheless, the dosing for the MODE water alternatives was increased to 1.0 mg/L due to the pump and the dilution factor restrictions. The dilution factor was 1:20 for each alternative. However, the maximum dilution factor suggested by the manufacturer was 10 because the antiscalant loses its fungal growth inhibition due to the high dilution of the preservative. Hence, the operators refreshed the antiscalant in the dosing tanks every week throughout the testing to prevent any biological activity. Prominent g/4b 1001 chemical dosing pumps with 0.08-6.64 ml/min flow range were used for each RO unit in operation. Static mixers were installed in each RO unit after the antiscalant injection points, even though the high-pressure feed pumps of the units were likely sufficient to supply adequate mixing of the chemical.

5.4.3 Sodium Hypochlorite (Bleach)

The addition of bleach to the feed waters was for two main reasons. The first one was for disinfection of the influent water. The membranes are vulnerable to microbial growth and therefore biofouling. In order to protect the membranes the addition of a disinfectant is necessary. The second reason was to satisfy the chlorine demand and to oxidize the iron and manganese in the source waters, mainly YMC water. Oxidized iron and manganese were aimed to be removed by gravity filtration or microfiltration. However, a strong oxidizing agent like free chlorine can easily damage the PA membranes. Therefore, addition of ammonium sulfate is essential to convert the free chlorine to combined chlorine, mainly monochloramine. Combined chlorine is not a disinfectant as efficient as free chlorine but it is more practical to use since its oxidation effect on the membranes is minimal. A combined chlorine concentration of 1-2 mg/L and free chlorine level < 0.1 mg/L in the RO feed waters was targeted throughout the whole study period.

Gamma/4b 1602NS chemical injection pumps with flow ranges of 0.18-16.20 mL/min were used for the neat bleach injection. The concentration of bleach was 12.5% with a density of 1.2 g/ml. The rate of bleach injection was adjusted to keep the target chlorine levels in the RO feed, which depended on the water composition, i.e. chlorine demand of the source water, and the flow rate of the units in operation. Since PS1 supplied the feed water for PS3 throughout the study, bisulfite dosing was necessary for Alternative 17a at the times when the chlorine injection for PS1 was high. A 40% sodium bisulfite solution with density of 1.34 g/ml was used for this purpose.

5.4.4 Ammonium Sulfate

The addition of ammonium sulfate, $(NH_4)_2SO_4$, is essential to convert the free chlorine to combined chlorine, mainly monochloramine, because a strong oxidizing agent like free chlorine can easily damage the PA membranes. The concentration of the ammonium sulfate used was 13×10^{-3} g/ml and prepared by adding 1 kilogram (kg) of ammonium sulfate in 20 liters (L) of RO product water. The target dosage of ammonium sulfate was six times the free chlorine concentration to have a large safety factor to ensure that no free chlorine was present in the RO feed. Please, refer to Appendix A-4 for the target dosage and drawdown values of ammonium sulfate addition.

5.5 Water Disinfection Monitoring

Disinfection of the feed water is a very important step for the RO operations to control biofouling. However, if the technique involves an oxidizing agent that can damage the RO membrane material (e.g., free chlorine with PA membranes) by staying in the feed water, then reducing that agent and monitoring the level becomes as important as achieving good disinfection of the feed water. The chances of the reducing process failing can not be discarded. Therefore, different monitoring techniques, creating redundancies in the warning system, were incorporated into each RO treatment train. Each monitoring technique has its disadvantages as well as its advantages. Hence, the TAT decided to use more than one technique, listed below, to minimize or eliminate the possibility of membrane damage due to oxidation. In case of an increase in the free chlorine level to a pre-set alarm concentration for a pre-set duration, regardless of the monitoring method reporting it, the downstream RO units were automatically shut down.

5.5.1 Free Chlorine Analysis

Two types of techniques were used to measure free chlorine. The first one was the DPD (N, N-diethyl-p-phenylenediamine) method and it was measured twice a day. The (lack of) frequency of this measurement did not allow it to be the main monitoring mechanism for the operation of the RO units. Therefore, in-line free chlorine analyzers, which were already installed on most of the RO units, were decided to be used as the primary method for monitoring. The disadvantages of the free chlorine analyzers were their slow response time and their dubious accuracy at low free chlorine levels. A free chlorine analyzer was used in each RO unit to monitor and confirm the absence of free chlorine residual in the feed water and to trigger RO shutdown if the free chlorine exceeded a pre-set maximum concentration.

5.5.2 Oxidation Reduction Potential (ORP) Analysis

In the case of RO processes, ORP can be defined as a measure of the tendency of a solution to oxidize or reduce a chemical substance, e.g. RO membrane. ORP was used as an indirect measure for the presence or absence of free chlorine, depending upon its value. It is an electric current measured in millivolts (mV). It depends on multiple components of the solution, i.e. temperature, pH, etc. Hence, ORP is considered water specific. Rosemont ORP sensors (Model 3500) and analyzers (Model 1056) were purchased and used in this study. Since ORP is water specific, a test was employed after installation of the probes and analyzers to correlate the free chlorine concentration (oxidizing potential) with the ORP sensor response and subsequently to set points for RO shutdown.

The test run on Alternative 21a is presented here as an example (Figure 5.2). The ammonia injection was shut down gradually while the system was running stable. While keeping the pH constant, free chlorine, total chlorine and ORP levels were measured and recorded (Figure 5.2). Based on the results a set point as measured by the ORP sensor as mV was determined, above which the RO unit would be shut down. The set points were decided for the other alternatives following the same procedure. However as the water composition changed seasonally, there were minor changes applied to the set points throughout the testing. Please, see Appendix A-5 for the remainder of the ORP set point determination test results.

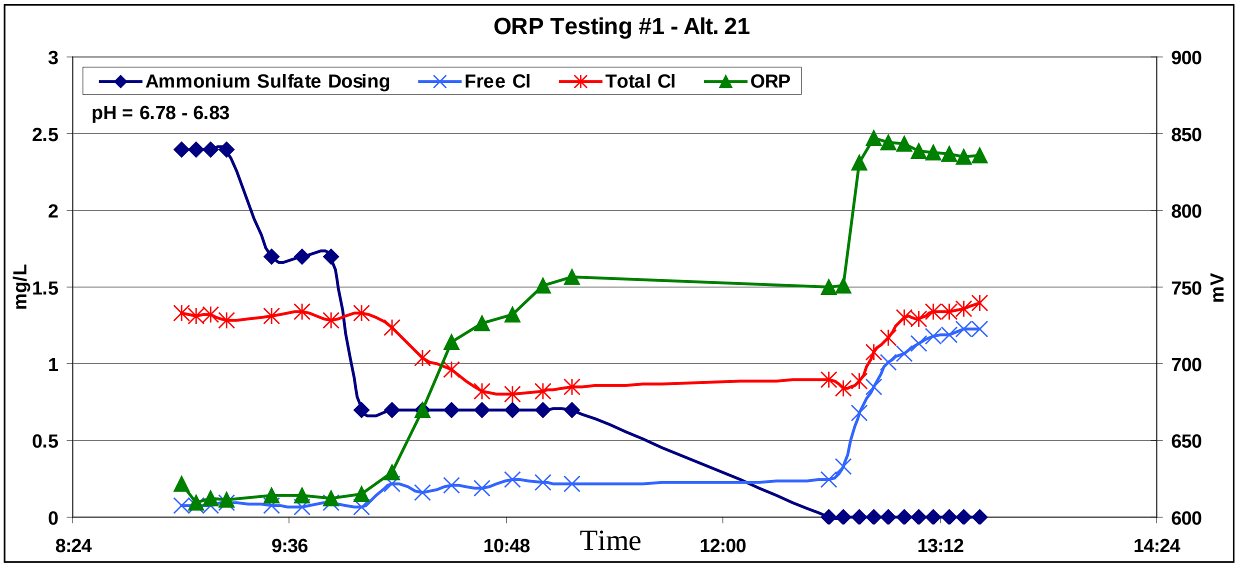


Figure 5.2. ORP testing for Alternative 21a performed on September 16, 2010.

5.6 Sedimentation – Solids Contact Reactor (SCR)

Solids contact reactors (SCRs) are used for carrying out chemical precipitation reactions (e.g, lime softening) and for removing suspended particles from water. By addition of chemicals, specific ions can be targeted for removal. In PS1 operation (Alternative 10) and in the original design of YDP, the addition of lime, $Ca(OH)_2$, and ferric sulfate, $Fe_2(SO_4)_3$, are added to remove not only the suspended solids (turbidity) from the MODE water but also almost all the hardness ions. Ferric sulfate helps in coagulating the suspended solids in the MODE water so that they can contact with and settle together with solids formed from lime addition. The sludge that is formed includes calcium carbonate, $CaCO_3$, magnesium hydroxide, $Mg(OH)_2$, and iron hydroxide, $Fe(OH)_3$.

A 10 foot (ft) diameter and 11 ft height SCR was utilized on each pilot system. PS1 served Alternative 10, PS3 served Alternative 17a and PS2 served both Alternatives 21a and 22. The Test Manager and the operators monitored the SCRs for any iron formation, accumulation and/or staining during the test. The SCR operated without any chemical addition (contrary to regular SCR operation), and were used as simple gravity settlers and equalization basins. The feed water for each alternative passed through the reactors. The residence times for the SCRs were 86 and 108 minutes for PS2 and PS3, respectively. Having such residence times in the reactors and the chlorine injection point prior to the reactors helped in partial removal of suspended materials as well as oxidized iron and manganese via unintentional sedimentation in the SCRs. Therefore, the rake of SCRs was used with 35% speed and a blowdown valve was opened for 10 seconds with a frequency of once per shift to prevent solids accumulation in the SCR.

5.7 Filtration

Filtration separates solid particles from the liquid in which they are suspended. The particles are taken apart from the liquid phase via a filter media while the liquid is passing through it. The media has to be chemically inert to the mixture and it has to hold paths large enough for the liquid to flow and small enough to intercept the particles. The media used in filtration can be sand, coal, anthracite or other granular materials. The process is both physical and chemical and sometimes even biological. While straining plays an essential role in the process, it is not the predominant one that makes filtration a successful unit operation. Adsorption, absorption and sedimentation on the media are other mechanisms that take place during a filtration procedure.

5.7.1 Dual Media Gravity Filtration

Filtration via Dual Media Gravity Filters was selected as a pretreatment technique for RO operation for Alternatives 17a, 21a and 22. The DMGFs installed on PS2 and PS3 consisted of 6 individual filter beds, each being 30 inches (in) in diameter (4.91 square foot [ft^2] approach area). They provided depth filtration for the feed water. The product could be discharged into two separate filter effluent tanks, each of which had the ability to pump the filtrate into either the backwash tank or the RO unit feed tanks. During the testing period, different filter operational variations were used. The dual media filters ran at an approach velocity of 3.05 gallons per minute per square foot (gpm/ft^2), 15 gallons per minute (gpm) (56.8 liters per minute [L/min]) per filter, throughout the testing. Backwash flow rates of 300 L/min for fourteen minutes and 270 L/min for one minute were used for cleaning and to maintain stratification. The flow rates were set by adjusting the backwash pump discharge valve. The backwash waste sump system disposed of the waste streams from the gravity filters for both PS units. The gravity filters were backwashed once in four days for PS3 DMGF cells (MODE water) and once in five days for PS2 DMGF cells (YMC water), initially. After Alternative 22 switched to using greensand filtration, the backwash frequency for PS2 DMGF cells was increased to once in three days. The two effluent tanks installed were used for holding two different types of filtrates after this point. Turbidity and pH of each separate cell on PS2 and PS3 were measured automatically via a sample system.

Conditioning of the Gravity Filters for Removal of Manganese

DMGFs on PS2 were “conditioned” to increase the removal efficiency of manganese prior to the initiation of the research study due to the high concentrations of manganese and iron in YMC water (Figure 5.3). Even though, the filters ran for almost two months on the source water with a free chlorine level of 1.0 mg/L or more in the effluent prior to the official start of Phase 1 testing, the TAT decided that the conditioning was necessary due to lack of water quality analysis at the time.

A two stage process was used for the conditioning of the Alternatives 21a and 22 gravity filter cells. The first stage rapidly deposited additional manganese dioxide (MnO_2) on the surface of the filter media. The second stage fully oxidized the manganese oxide on the surface and augmented it with additional manganese oxide mass. For a media treating water with filter effluent free chlorine residual of 0.5-1.5 mg/L a manganese oxide loading of at least 3 mg Mn/g media would be considered sufficient. Stage 1 was adapted primarily from Merkle et al., 1997 and Knocke et al., 1990, while stage 2 was adapted from Bailey in Appendix A of Knocke et al., 1990. Please, refer to Appendix A-6 for the details of each step.

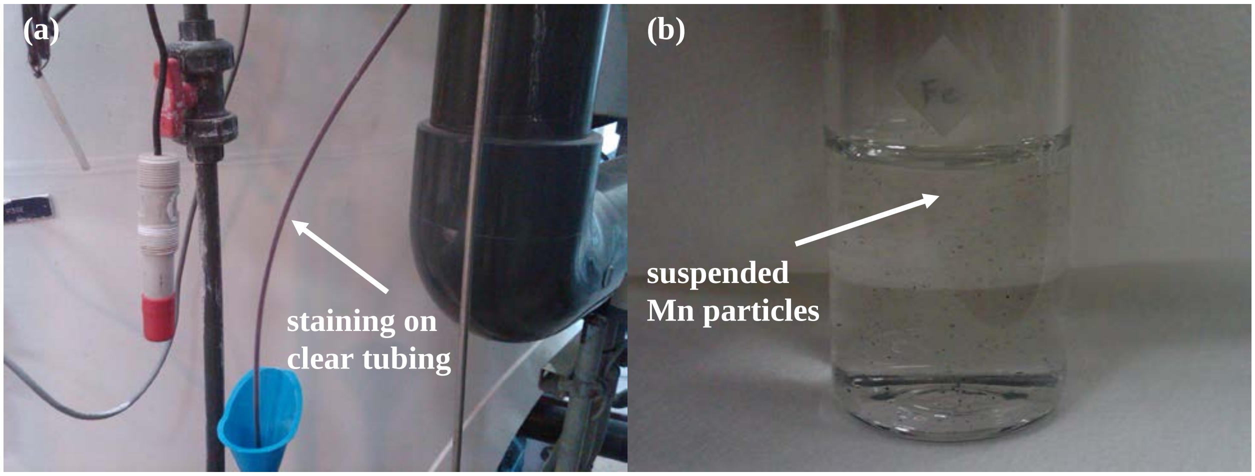


Figure 5.3. Pictures showing (a) staining on the clear tubing and (b) suspended manganese particles in the YMC water.

5.7.2 Greensand Gravity Filtration

Greensand is a manganese dioxide (MnO_2) coated media that is available commercially. The material of the media is a zeolite mineral and the coating is generally carried out by a two step process with manganese sulfide and potassium permanganate. At the end of those steps, a black precipitate of manganese dioxide on the granules is achieved. This surface is then used to enhance the oxidation and removal of manganese by adsorbing dissolved Mn^{+2} ions. The kinetics of this uptake and oxidation is a function of the adsorption sites on the media, the oxidizing agent (free chlorine in this case) concentration and the pH of the feed water. The reaction rate increases with increasing free chlorine concentration and increasing pH.

The use of greensand filter media during this research appeared at the end of Round 1. After analyzing the water quality results from Round 1 and visual observations during that period, it was determined that the removal of iron and manganese in PS2 treating YMC water was not sufficient. Due to iron presence in the feed water and fouling due to manganese precipitation on the membrane material, the degradation of membrane material represented some concerns. Hence, the operation of PS2 was divided into two separate paths with Alternative 21a left running on anthracite/silica sand media, while Alternative 22 began running on anthracite/greensand media.

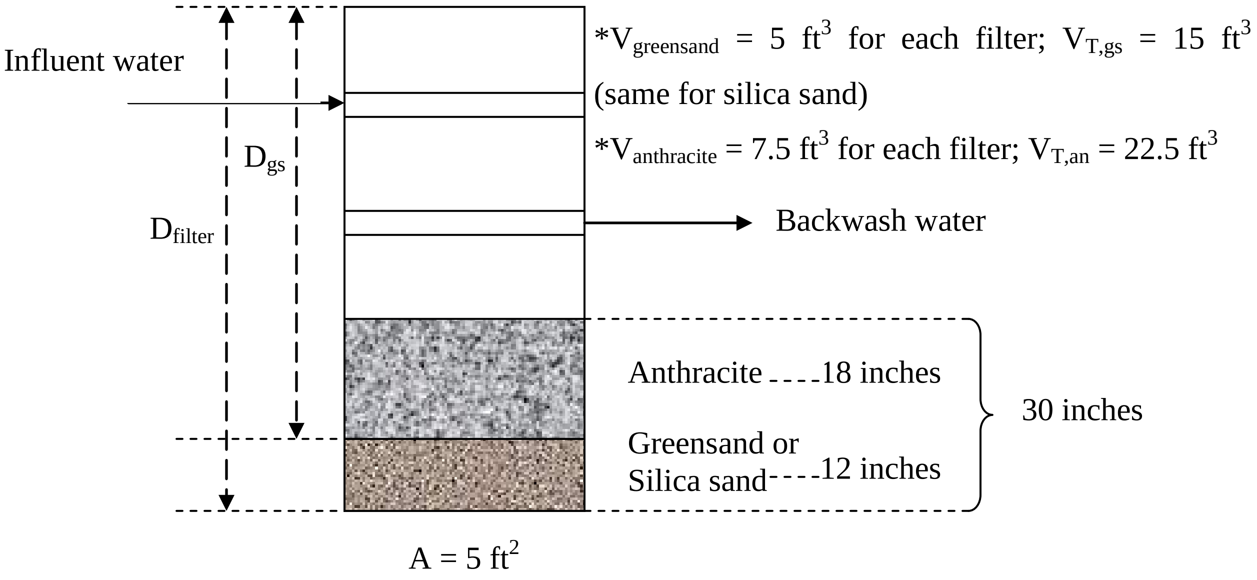


Figure 5.4. Schematic for PS2 and PS3 gravity filters

Greensand media was installed and conditioned in three gravity filters of PS2. Ten bags of greensand, each containing 0.5 cubic feet (ft^3) of media (5 ft^3 of greensand in each filter), were installed in each gravity filter to give a media height of 12 inches. Three filters (numbers 4, 5 and 6) were in operation with greensand and anthracite. While two cells were in service as the feed supply for Alternative 22, the third filter was on standby and placed on-line when a filter was removed from service for backwash. The stand-by filter received a ten-minute rinse prior to being placed on-line. The filter that was backwashed was then placed in stand-by mode. The backwash frequency was one filter a day (48-hour rotation). Unlike the silica sand/anthracite gravity filters, backwash flow rates for filters 4-6 were maintained at 365 L/min for the first fourteen minutes and lowered to 300 L/min for the last minute of backwash because the greensand is denser than the silica sand. This method and flow rates supplied good stratification in the greensand and anthracite media mixture.

5.7.3 Cartridge Filtration

Cartridge filtration is widely used in the reverse osmosis treatment area, mostly as a ‘safety’ or secondary filter to catch solids that have not been removed by the primary filtration process or where a failure in the primary process occurs so that these solids do not enter the RO elements. Cartridge filters are generally installed upstream of the RO process to provide a physical barrier for blocking particles in the feed. Two types of cartridge filters are available; (i) depth filters and (ii) pleated filters. During this study, Hytrex depth cartridge polypropylene microfibers filters, manufactured by General Electric Company, were used.

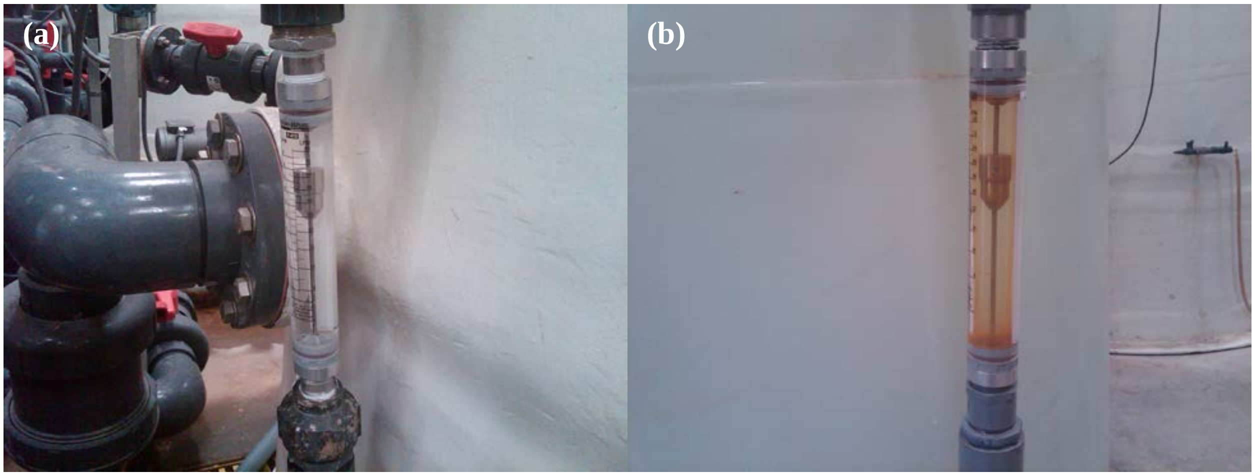


Figure 5.5. Picture showing the staining of the rotameter installed on (b) Alternative 22 compared to the one installed on (a) Alternative 21a.

During the early part of Phase 1 testing, a difference in the physical appearance of two rotameters was observed (Figure 5.5). The rotameter that was installed on Alternative 21a after microfiltration stayed clear for several months after the initiation of the runs. However, the rotameter that was installed on Alternative 22, which had the same water source with the same pretreatment technique, except without MF, had a rusty color on its inside surface after the same amount of operating time. That difference in the rotameters physical appearance suggested that particulate iron that was captured by microfiltration was escaping through the pretreatment running on Alternative 22 and ending up possibly in the reverse osmosis membranes. Therefore, the TAT decided to install cartridge filter housing on Alternative 22 prior to RO treatment.

Later during the testing, two more cartridge filter housings were installed on the same alternative to try the effects of different pore (1-μ and 5- μ) and cartridge filter (10-in and 20-in long) sizes on the removal efficiency of SDI and the length of the cartridge filter lifetime. The flux used in cartridge filters was kept the same, 4.32 gpm/ft^2, during the whole study.

Figure 5.6. Cartridge filter housing installed on Alternative 22.

5.8 Pressure Driven Membranes

Pressure driven membrane processes are used worldwide to treat surface, oceanic, and brackish water, as well as a variety of industrial solutions for recovery of desired product. The operation of pressure driven membranes depends on an applied pressure to the feed stream to pass the water through a membrane to produce a low-concentration permeate stream. This general term is being used for many types of membrane processes that work on the same concept. All pressure membrane systems consist of a feed stream, a membrane and a product stream. A concentrate stream is formed if the system is based on a cross-flow process.

A membrane is a physical barrier that separates the constituents of the feed stream from the product stream by allowing only certain species to pass through, while others are rejected. All membranes are specifically designed to reject certain target species and allow product species to pass. Membranes can be categorized into two main classes based on the mass transfer principles through them: porous and non-porous. The porous membranes operate on the basic principle of filtering/sieving in which some particles cannot pass through the membrane because they have a larger diameter than the pore size of the membrane. Non-porous membranes operate on the principle of solution-diffusion and their ability to separate species depends on the differing rates of diffusion of the species through the membrane. During this project both types of membranes were used. Microfiltration membranes are an example of porous membranes, while reverse osmosis membranes are non-porous.

There are four general types of pressure membrane systems. They are mainly distinguished by the size of the solute that they separate. Shown in Table 5.5 below, they are arranged by the size of the particles that are separated from the fluid, which also correlated to the pressure typically required to drive the flow through the membrane. This correlation is intuitively correct because as the pore size decreases (MF >> RO), the tendency for membranes to resist mass transfer increases, and therefore the driving force (applied pressure) increases to create the same flux.

Table 5.5. Type of pressure membrane processes.

	Pressure Membrane Processes		
Category	**Process**	**Pore Size (μm)**	**Pressure (kPag)**
Porous	Microfiltration	0.1 - 10	<70
	Ultrafiltration	0.005 - 0.1	100 - 500
Non-Porous	Nanofiltration	0.001 - 0.005	500 - 1400
	Reverse Osmosis	0.0001 - 0.001	1400 - 8300

5.8.1 Microfiltration

As illustrated in Table 5.5 above, microfiltration (MF) has the largest pore size (0.1 – 10 μm) among the pressure membrane processes. It successfully removes large colloids, suspended particles, bacteria, and in filters using pore size of 0.2 μm and smaller, it has been proven to remove Giardia lamblia cysts and Cryptosporidium oocysts. No requirement of chemical treatment for the feed water makes the MF processes popular in water treatment industry.

There are various filter and media types used in MF today, including polyvinylidene fluoride (PVDF), polyethersulfone (PES), polypropylene, ceramic and cellulose acetate. Each media type is unique in performance specifications. In addition to various media types for MF, there are also various filter designs such as pleated cartridge, hollow fiber, capillary, and surface module. An MF unit can be designed to operate in cross-flow or dead-end characteristics. The former creates two continuous flows from the process, product and concentrate, while the latter has a single product stream and an occasional backwash flow in which the continuous filtration is ceased. In cross-flow filtration the influent flow is parallel to the membrane surface, product flows through, and concentrate is a separate waste stream. In dead-end filtration, the feed stream is directed into the membrane and there is no concentrate, or reject stream, except during the backwash cycle. A typical backwash consists of an air-scour on the cake buildup side of the membrane followed by a high flow rate flush, during which there is no product recovery. MF with a dead-end filtration is a more efficient process than cross-flow filtration and is preferred in treating large volume, low solid concentrated waters.

Microfiltration was selected to serve as the primary pretreatment process for, Alternatives 17a and 21a, two of the four alternative treatment trains in the testing. The purpose of microfiltration in this testing was to replace lime-softening, settling and dual-media gravity filtration processes. In each alternative, a Pall MF unit containing one Pall Microza PVDF, hollow-fiber membrane modules (0.1 μm nominal pore size; 538 ft^2 outside surface area per module) operated in dead-end mode to produce filtrate for subsequent RO treatment and for MF unit reverse filtration.

5.8.1.1 Manufacturer Description

Pall Corporation has annual sales of more than $2 billion and is the largest supplier of filter products and separation systems in the world. Pall membrane filters are currently installed and operating at over 250 drinking water and wastewater sites around the world.

5.8.1.2 Equipment Description

Two pilot units with the model number USV-1/2G were supplied for the testing. The self-contained system requires a process inlet at pressure and delivers filtered product to a holding tank with the ability of delivering the product water directly to a discharge header. The unit comes with a feed tank and a reverse filtration tank made out of polyethylene. Each tank had a holding capacity of 150 gallons with automatic level controls.

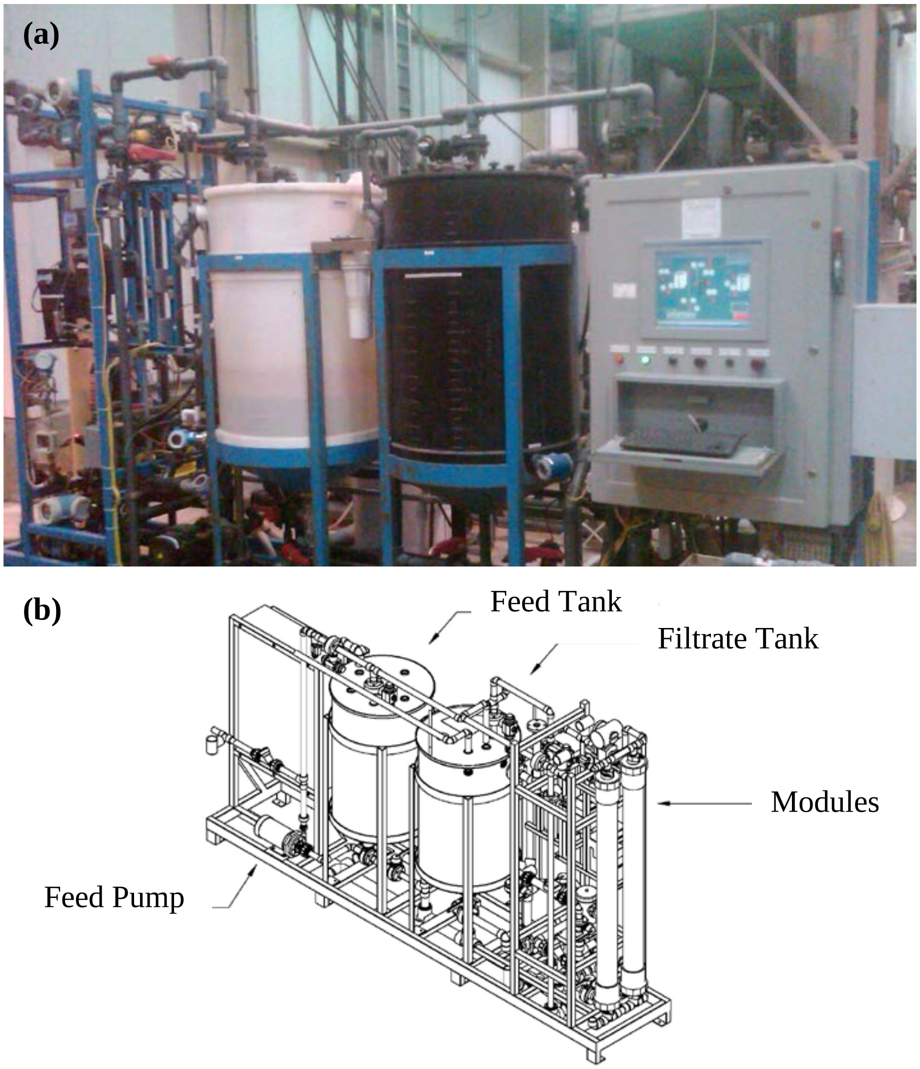


Figure 5.7. (a) Picture of East Pall MF unit and (b) Left rear isometric view of Pall MF pilot system (figure is adapted from Pall Corporation).

The skid included a Programmable Logic Controller/Private Computer (PLC/PC) based control, data logging and remote monitoring system. It is programmed to automatically control the process, with the exception of Clean In-Place (CIP). However, the Enhanced Flux Maintenance (EFM) cleanings were preferred to be performed manually throughout the testing. Pall provided two of the same units, each designed to handle filtrate flows of at least 30 gpm based on historical water quality data. The computer, which can be accessed remotely, monitored and recorded trans-membrane pressure (TMP), flow rate and turbidity for performance assessments. In addition, operating temperature, pressure and other parameters useful for optimizing operation were monitored during the testing.

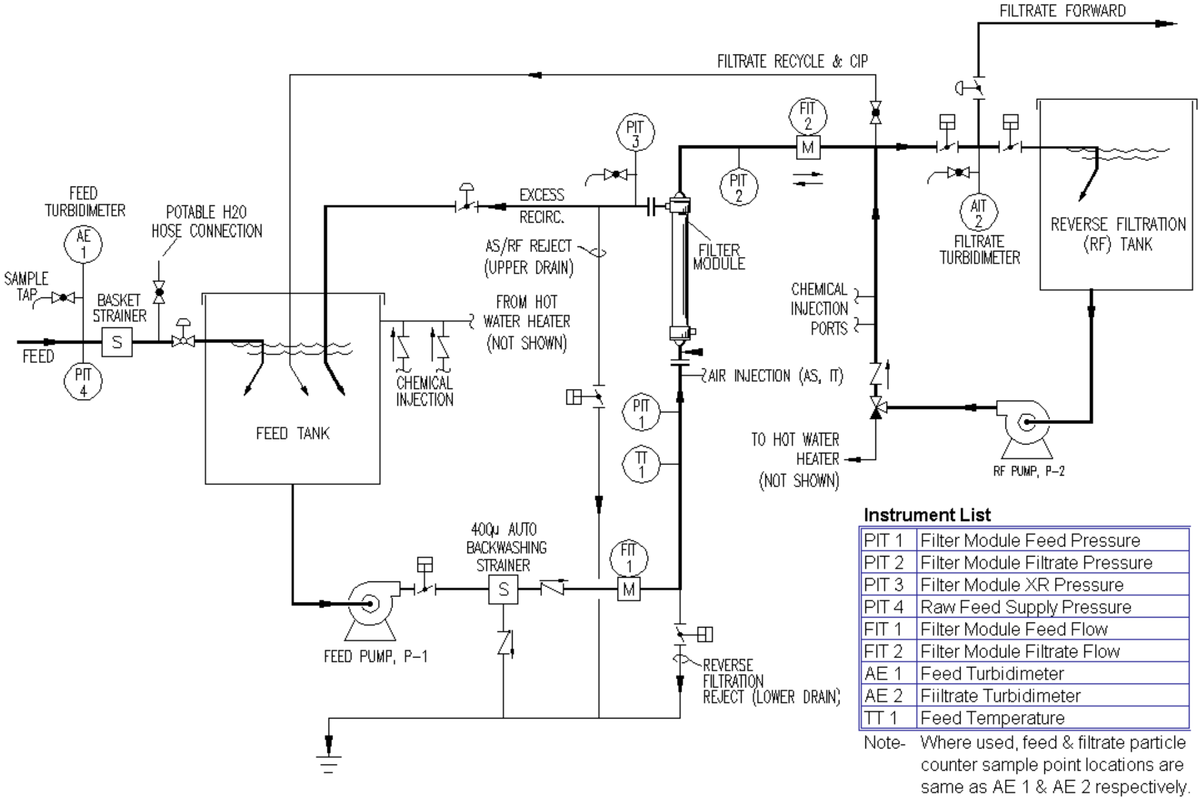
Table 5.6. Operating parameters, materials and dimensions of Pall MF units.

Performance	Process Capacity	: 2.2-6.8 m^3/h (10-40 gpm)
Dimensions	Membrane Area	: 50 m^2 (538 ft^2)
	Module Length	: 2.16 m (85 in)
	Module Diameter	: 0.165 m (6.5 in)
	Nominal Pore Size	: 0.1 μm
Operating Conditions	Max Operating Temperature	: 40°C (104°F)
	Max Transmembrane Pressure	: 3 bar (43.5 psi)
	Max Inlet Pressure	: 3 bar (43.5 psi)
	pH Range	: 1-10 long-term operational
	pH Range	: 1-13 short-term cleaning
Materials	Membrane	: PVDF
	Housing	: ABS resin
	Potting Material	: Polyurethane resin
	Gaskets	: Silicone
	Antifreeze/Bacteriostat	: 40% $CaCl_2$ solution

Each unit was supplied with two Microza hollow fiber membrane filtration modules, model number UNA-620A, with dimensions of 7-ft long and 6-in diameter. However, only one module was used during the testing per each unit due to the chosen operating flux. The other two modules were kept in the cold storage at 4 ^oC as spare ones. The modules have 0.1 μm nominal pore size, which enables the removal of particles, bacteria, colloidal silica and turbidity. The values from testing are presented in the relevant results section. The material of the hollow fiber membrane is PVDF, which is resistant to oxidizing agents. Hence, free chlorine was used for the disinfection purposes throughout the testing. The foulants accumulated on the membrane during the production mode were removed by periodic air-scouring combined with permeate back flushing that lasted for 80 seconds in total. Both units are equipped with 400 μm self-cleaning strainers for removal of tramp solids. The units operate at high water recovery rates, typically 95%-98% to minimize cost per volume of water filtered.

Two turbidity meters for feed and filtrate streams with model numbers HACH Model 1720E and HACH Model 660, respectively were provided by the manufacturer on the skid of the unit. One air compressor, having dimensions of 68-in long, 48-in wide and 77-in tall that weighs 800 pounds (lbs), was supplied by the manufacturer for both units. The test rig has the dimensions of 172-in long, 33-in wide and 106-in tall and weighs about 2500 lbs. The freight, start-up assistance and initial training to operate the units properly were provided by Pall Corporation.

5.8.1.3 Pilot Start-up



Instrument List

PIT 1	Filter Module Feed Pressure
PIT 2	Filter Module Filtrate Pressure
PIT 3	Filter Module XR Pressure
PIT 4	Raw Feed Supply Pressure
FIT 1	Filter Module Feed Flow
FIT 2	Filter Module Filtrate Flow
AE 1	Feed Turbidimeter
AE 2	Fiiltrate Turbidimeter
TT 1	Feed Temperature

Note- Where used, feed & filtrate particle counter sample point locations are same as AE 1 & AE 2 respectively.

Figure 5.8. Schematic of Pall MF pilot system (figure adapted from Pall Corporation).

Pall Corporation provided the technical support to ensure the operation of the MF units. After the delivery of the units, a Pall field engineer was on site to optimize system parameters and to provide operator training. The initial Clean-In-Place (CIP) procedure was also performed by the same field engineer. At the time, the procedure was demonstrated to the operators and the subsequent cleanings were performed the same way, but without a Pall field engineer's supervision. Throughout the study, Pall, Reclamation and the Testing Manager coordinated and planed such procedures in advance.

5.8.1.4 Maintenance of Equipment

Pall supplied, at Pall's expense, the necessary replacement parts required due to the normal wear and tear of everyday operation. The remainder of the maintenance operations was provided by Reclamation and/or its contractor, KTS Engineered Systems.

Reclamation provided the following MF operation and maintenance supplies during the testing duration: cleaning chemicals for the CIPs and EFMs; the utility supply and plumbing and electrical connections as required by Pall; one dedicated analog phone line for remote monitoring to be used for both units; assistance with maintenance and cleaning procedures as necessary; unloading and reloading of delivered equipment and forklift rental for this purpose; unpacking and repacking of the pilot units; climate controlled shelter for the pilot units; and the required water sample analyses.

5.8.1.5 Operation of Equipment

5.8.1.5.1 Filtrate Production

The feed water begins to fill the feed tank when the unit is initiated. After the water level reaches an operator pre-set volume, the feed pump starts to fill the module from the bottom and also the system piping with the feed water. About 10% of the feed water flow is returned as excess recirculation back to the feed tank. The filtered water, called filtrate, exits the module from the top. It fills the reverse filtration tank initially, prior to filling the filtrate tank. The larger particles in the feed water are trapped via the strainer. The strainer is controlled to automatically back flush to drain when it reaches a specific differential pressure.

The operation of the unit is controlled by specific setup parameters, set points, and instruments. Transmembrane pressure (TMP) is a calculated parameter used as a measure of the module's performance. It is one of the most important parameters for the unit since it is used to protect the module from high operating pressures. The unit is set to give a warning alarm when the TMP reaches 40 psi and to shut itself down at 45 psi. Timer settings or total filtrate produced are used to trigger air scrub (AS) and reverse filtration (RF) cycles. All the sequences are controlled by the PLC installed on the unit's skid.

The water production rates of the MF units were adjusted by setting the flux. A typical average flux, 60 gfd, was chosen as the initial set point for each MF unit. The fluxes of the units were then adjusted by monitoring their performances. Flux set points are summarized in Table 5.7, below. The water recovery of the unit directly depends on the backwash frequency and the operating flux. Both MF units were operated at 97% recovery during the whole testing.

Table 5.7. Pall MF units operating flux regime.

Date	East MF - YMC	West MF - MODE
	Flux (gfd)	Flux (gfd)
09.01.2010 - 10.26.2010	60	60
10.26.2010 – 01.12.2011	70	60
01.12.2011 – 04.25.2011	80	66
04.25.2011 – 09.22.2011	85	66
09.22.2011 – 09.30.2011	85	50
09.30.2011 – 10.07.2011	93.5	50
10.07.2011 – 10.25.2011	East Pall MF unit operation discontinued on 10.03.2011	50
10.25.2011 – 11.02.2011		60
11.02.2011 – 12.30.2011		50

The following equations define the primary calculated measures of MF operation and performance.

$$V_P = Q_{MF} \times T_{Op}$$

$$V_{NP} = V_P - V_{BW}$$

$$R_{MF} = \frac{V_{NP}}{V_P} \times 100$$

where, V_P is the volume of water produced between each backwash cycle [gal]

V_{BW} is the volume of water used for each backwash cycle [gal]

V_{NP} is the volume of net water production [gal]

Q_{MF} is the volumetric flow rate of the MF unit [gpm]

T_{Op} is the operation time between each backwash cycle [minutes]

R_{MF} is the water recovery of the MF unit [%]

In order to keep the downstream RO units running without disruption the East and West Pall MF modules were interchanged several times in November and December, 2011. Details and discussion are provided in the Results and Discussion Section subsequently.

5.8.1.5.2 Cleaning Cycles

A number of variations of cleaning cycles and procedures were used for maintaining the performance of the MF modules. Pall MF units are designed to automatically clean the modules by air scrub (AS), reverse filtration (RF), forward flush (FF), and enhanced flux maintenance (EFM). However, all the EFMs were performed manually throughout the testing. For more aggressive cleaning, filtering was periodically stopped and manual CIP (Clean-in-Place) procedures were used.

Backwash (AS/RF/FF Cycles)

During an AS, low-pressure air is injected on the feed side (the bottom) of the module via the compressor. The air bubbles scrub the fibers of the module to loosen the particles accumulated on the surface. Then, the module drain valve opens and the RF pump starts pumping clean filtrate to back flush the membrane fibers once the RF cycle starts. Typically, AS and RF are very short (80 seconds in total) and performed simultaneously. The FF following the cycle of AS/RF carries the particles to drain. This regeneration cycle produces approximately 14-

17 gallons of backwash waste every 15-25 minutes. The operation resumes automatically after the cycles complete. As different fluxes, hence different flow rates, were tried throughout the testing, the backwash timing was adjusted to keep the water recovery constant at 97%.

Enhanced Flux Maintenance (EFM)

During an EFM filtrate production is stopped and the feed tank is drained. 30 gallons of filtrate is then transferred from the filtrate tank to the feed tank passing through the water heater. The temperature of the filtrate is increased to 100 ^{o}F. Half an hour (30 minutes) circulation of the heated water through the module and through the fully open excess recirculation valve back to the feed tank starts after the addition of the appropriate chemicals, i.e. sodium hypochlorite or citric acid depending on the type of the EFM. This is followed by an RF and a 90-second filter-to-drain flush phase. A fully executed EFM cycle takes about 39 minutes. The regular operation of the unit starts after the free chlorine level in the filtrate decreases down to 1.0 mg/L. The purpose of the final step is to protect the RO membranes downstream of the MF units.

Table 5.8. Pall MF Units EFM regime.

Date	East MF - YMC		West MF - MODE	
	Bleach EFM	Acid EFM	Bleach EFM	Acid EFM
09.01.2010 – 11.09.2010	weekly	None	weekly	None
11.09.2010 – 01.12.2011	biweekly	biweekly	weekly	biweekly
01.12.2011 – 06.08.2011	monthly	biweekly	weekly	biweekly
06.08.2011 – 07.12.2011	monthly	biweekly	biweekly	weekly
07.12.2011 – 10.07.2011	monthly	biweekly	biweekly	as necessary
10.07.2011 – 11.18.2011	East Pall MF unit operation		biweekly	as necessary
11.18.2011 – 12.30.2011	discontinued on 10.03.2011		biweekly	weekly

EFM frequency and chemical concentrations can be set based upon feed water quality and project goals. Two types of EFMs were used in the testing. The first was a low-pH citric acid EFM (1% citric acid solution) and the second was a high-pH sodium hypochlorite (bleach) EFM. At least 50 mg/L of free chlorine concentration in the spent solution at the end of the EFM cycle is needed for an efficient bleach EFM. Therefore the starting concentration of the bleach EFM was set to 250 mg/L of free chlorine. The automated EFM cycles and the chemical injection systems installed on the unit were not used. Chemicals were added by the operators manually for each EFM. Please, refer to Appendix B-1 for the details of the calculations and the data collected during the EFM cycles for both units.

Typically the free chlorine concentration prior to starting the bleach EFM cycle was between 150-300 mg/L. This concentration normally dropped down to 40-150 mg/L for the West Pall MF unit and 100-200 mg/L for the East Pall MF unit. This not only showed that the water composition of each water source was in fact different but also showed that the water composition of the water sources changes during the year. 1% citric acid solution supplied a cleaning at pH of ~2.5. Lower pH (<2.0) was achieved by adding sufficient sulfuric acid (H_2SO_4) on two occasions for the West Pall MF unit on November 9 and 11, 2011, while trying to improve the cleaning efficiency of citric acid EFM. The EFM type and frequency for each unit – East and West Pall MF units– are presented in Table 5.8, above. Further discussions of these cleaning routine variations are provided in the Results and Discussion section.

Clean-in-Place (CIP)

CIP procedures are performed at longer intervals than the other cleaning regimes with the frequency and nature of cleaning depending on the contaminants in the water and the operation history of the unit. This is a manual, operator-initiated, computer-aided procedure that requires mixing chemicals and letting the mixture circulate through the module. When completed, the chemicals are neutralized and the system is drained. CIP procedures are designed to restore the performance of the module to its original condition. The regular CIPs performed throughout the testing took 4.5 to 5 hours.

A regular CIP procedure used by Pall Corporation to clean membranes starts with a fresh water rinse and continues with a circulated sodium hydroxide and bleach solution through the system for two hours. A second rinse follows the high-pH cleaning. Subsequently, the citric acid solution is used to further clean the membranes with low pH water, followed by another final rinse. Operators were always available during the CIPs and observed both cleaning steps and recorded the TMPs before and after each cleaning step. The total time required for a CIP (4.5-5 hours) includes the time to drain the feed water tank, make the chemicals used for cleaning, perform the entire procedure, and reset the unit for operation. The high-pH cleaning solution is prepared by adding sodium hydroxide and 12.5% sodium hypochlorite into 40 gallons of heated water (90-104 ^{o}F). The desired concentrations of sodium hydroxide and sodium hypochlorite are 1.0% NaOH and 1,000 mg/L total residual chlorine. The low-pH cleaning solution is prepared by adding citric acid into 40 gallons of heated water (90-104 ^{o}F) to produce a concentration of 2.0%. At the end of each CIP, it was targeted to have TMP and membrane permeability values close to the values at the beginning of the testing period. Achieving this target is a necessary but not solely sufficient indication that the unit was cleaned and restored to its original operating conditions (more discussion on this point is provided in the Results and Discussion Section).

5.8.1.5.3 Integrity Testing

Integrity testing (IT) is performed periodically on the MF units. A rough indication of membrane integrity can be performed by evaluating the size of the particles that pass through the membrane in question. Hence, the filtrate turbidity can be an approximate way to analyze it. However, another valuable way to investigate the integrity of a membrane is through a pressure decay test. The procedure for this test is fairly simple. A known amount of pressure, less than the pressure that causes the air to flow through the membrane, is applied and the decay of that pressure is measured in a certain time period, i.e. 5 minutes for this project. A decay rate of more than 1 psi in 5 minutes indicates that one or more of the fibers within the membranes are broken, thus sacrificing integrity of the membrane, and indicating a need for repair.

IT is normally performed with the air pressure applied on the filtrate side of the module to avoid the possibility of driving particles on the membrane deeper into the membrane surface. This approach is also a good method of checking for possible leaks on the unit. An IT shall be performed on the feed side only when the cleanness of the module is certain, such as after a CIP is performed. However, all the ITs performed throughout the testing were on the feed side. It is believed this may have affected the performance of the MF units, especially the performance of the West Pall MF unit. When this was realized, the IT was discontinued on November 18, 2011. Another anomaly that might have affected the performance of the West Pall MF unit happened by mid-August 2011, when the starting pressure for the IT increased to almost 40 psi due to an accidental adjustment on the air inlet valve. The error was corrected by mid-October. The integrity of the membranes for both East and West Pall MF units were checked regularly throughout the testing until IT was discontinued in mid-November 2011. No indications of faulty fibers were observed at any time on any MF unit.

5.8.1.6 Operating Parameters

During the filtrate production, the parameters listed in Table 5.9 below were recorded either automatically by the PLC installed on the unit or manually by the operators on duty. The PLC records all of the flow data, pressure information, backwash cycles, AS data, EFM data, etc. that are not shown in the table and are not used in the performance analyses.

Table 5.9. Parameters measured during the regular filtrate production of MF units.

Parameter	Units	Range	Tag
Automated Data			
Feed Pressure	psi	Variable	PIT-4
Feed Turbidimeter Flow	GPH	4-6	FM-1
TMP	psi	Variable	TMP
Module Feed Flow	gpm	Variable	FIT1
Module Feed Temperature	^{0}F	70-100	TT1
Feed Turbidity	NTU	0.1-10	AIT-1
Volume of Filtrate Today	Gal.	Variable	Screen
Filtrate Pressure	psi	5-10	PIT2
Filtrate Flow	gpm	10-30	FIT2
Filtrate Turbidity	mNTU	0.1-5.0	AIT2
Filtrate Turbidimeter Flow	GPH	4-6	FM-2
Air Scour Flow	scfm	3-5	FIT5
Air Scour Supply Pressure	psi	30-40	Gauge
Volume of Filtrate until AS	gpm	Variable	Screen
Time to EFM	min	Variable	Screen
Supply Air Pressure	psi	90-100	Gauge
Manual Data			
Feed Turbidity	NTU	0.1-5.0	Manual
Feed pH	pH	6.80	Manual
Filtrate Turbidity	NTU	0.1-5.0	Manual
Filtrate Free Chlorine	mg/L	1-1.5	Manual
Filtrate SDI	%	0-3	Manual

During an EFM cycle, some other parameters are recorded manually by the operator on duty, such as free chlorine concentration prior to EFM, TMP prior to EFM, free chlorine concentration 5 minutes after the initiation of the EFM, free chlorine concentration 5 minutes before the completion of the EFM, TMP after EFM, filtrate free chlorine concentration after the completion of the EFM, pH of the cleaning solution prior to initiation of the EFM, pH of the cleaning solution after the completion of the EFM, etc. All of the performance data is presented in Appendix B-1 and all the manual data is presented in Appendix B-2.

The parameters recorded are then used in analyzing the performance and the efficiencies of the Pall MF units. Important calculations used for that purpose are summarized below.

- Temperature corrected flux

$$J_t \text{(at 25 } ^{o}\text{C)} = [Q_p / S] \times e^{-0.0239 \times (T-25)}$$

where,
J_t is the filtrate flux at time t [gfd or L/(h-m^2)]
Q_p is the filtrate flow [gpd or L/h]
S is the membrane surface area [ft^2 or m^2]
T is the temperature of the feed water [°C]

- Transmembrane pressure

$$TMP = [(P_f + P_c) / 2] - P_p$$

where,
TMP is the transmembrane pressure across the membrane [psi or bar]
P_f is the inlet pressure to the feed side of the membrane [psi or bar]
P_c is the outlet pressure on the concentrate side of the membrane [psi or bar]
P_p is the filtrate pressure on the treated water side of the membrane [psi or bar]

- Specific flux

$$J_{tm} = J_t \text{(at 25 } ^{o}\text{C)} / \text{TMP}$$

where,
J_{tm} is the specific flux at time t [gfd/psi or (L/(h.m^2))/bar]

5.8.2 Reverse Osmosis

When two volumes of water at different concentrations are separated by a semi-permeable membrane that allows water pass while retarding the transport of solutes, water will flow into the volume of higher concentration to dilute the solution in order to reach equilibrium through diffusion. Because the semi-permeable membrane will allow the passage of water and reject the passage of ions, such as sodium (Na^+), calcium (Ca^{2+}), chloride (Cl^-) ions, etc., and other molecules, the flow of water through it creates pressure on the high concentration side of the system called osmotic pressure. However for water purification, it is desirable to reverse this process and collect pure water or drive water out of a concentrated solute solution. This is achieved by applying pressure, in excess of the osmotic pressure, on the high concentration side of the system and physically forcing the water in the opposite direction through the membrane and in the opposite direction of chemical equilibrium. In a solution, the pressure will be characterized as an ideal gas of equal molecular concentration and the osmotic pressure, π [kPa], is calculated by the van't Hoff formula:

$$\pi = cRT$$

where, c is the molar concentration of the solute [mol/L]
R is the ideal gas constant [8.314 kPa.L/K.mol]
T is the absolute temperature [K]

This means that the osmotic pressure is not dependent on the size or type of the molecule, but rather only on the molar concentration. Therefore, the applied pressure required to overcome the osmotic pressure in high solute concentrations directly depends only on the molar concentrations of the dissolved ions.

Scientific study of the osmotic mechanisms coupled with the necessity to treat water, have led to the development of advanced and efficient RO processes. There are four main types of membrane configurations available in RO technology, including plate and frame, tubular, hollow fiber, and spiral wound. As compared with the other membrane, the spiral wound design greatly increases the membrane surface area of contact with raw water relative to the module's volume, but is prone to fouling.

One of the objectives of this study was to evaluate the fouling and scaling potential of spiral wound membranes manufactured by various companies when applied to potential source waters for YDP operation. The RO test units included four element test apparatus (ETAs) and four membrane testing units (MUs).

5.8.2.1 Membrane Selection

The Yuma Desalting Plant was designed to operate using cellulose acetate (CA) membranes as this was the only commercially available RO membrane type available at the time of design development. Currently, CA membranes are not readily available in the market and there are not many manufacturers that still produce CA membranes. With the exception of limited resistance to oxidizing agents, such as free chlorine, CA membranes do not have many operational advantages over polyamide membranes (PA). PA membranes are built with an ultra thin polymer salt rejecting layer on top of a microporous support layer that enables them to have a significantly higher specific flux (higher flux per unit area of membrane per unit of net driving pressure) and higher salt rejection than CA membranes. Furthermore, PA membranes have a wider range of operating pH, from 3 to 11, compared to CA membranes which must be operated within a narrow pH range (5.3 to 5.7) to minimize the rate of hydrolysis. Finally, PA RO membranes are chemically stable and typically achieve a 5-year or longer life compared to only 3 years for CA. The disadvantage of RO units running with PA membranes is the need of dechlorination or ammonium ion injection (to convert free chlorine to chloramines). However, CA membranes also oxidize when operated on pretreated MODE water that contains free chlorine and the feed water must also be chloraminated at the YDP. Therefore, the use of chloramination will be a common operation for both PA and CA membranes at the YDP. Considering the many advantages of PA membranes over CA membranes and having a sizeable amount of data with CA membranes during the demonstration run and pilot run of the YDP, TAT members decided to test PA membranes only during this research study.

Table 5.10. Membrane types and manufacturers selected and estimated unit costs.

Manufacturer	Membrane Type	Unit Cost	Round Used	RO Unit
Hydranautics	ESPA2-LD	$154.65	Round 1	ETA
Hydranautics	LFC3-LD	$200.65	Round 1 & 2	ETA & MU
CSM-Woongjin	RE2540-FE	$119.50	Round 2	ETA
CSM-Woongjin	RE2540-BLN	$108.50	Round 2	ETA
Koch - Fluid Systems	2540-TFC-ULP	$144.08	Round 1	ETA
Toray	TML10	$179.09	Round 1 & 2	ETA & MU
DOW - Filmtec	BW30-XFR	$70.00	Round 2	ETA & MU

The membranes used in Round 1 (Element Screening Test) were chosen based on the TAT members' judgement as to the membranes with the best chance for success (i.e. moderate pressure, low fouling membranes) in a full-scale long-term YDP operation. Additional membrane types were tested in Round 2. The purpose for the ETA testing was not to evaluate the membrane elements so much as to evaluate the pretreatment options and waters in conjunction with various membrane types. Evaluation of the long-term high recovery performance of the selected membrane from Round 1 was carried out in MU testing. The membranes selected for testing are presented in Table 5.10, above.

Table 5.11. RO elements used in ETAs for Round 1 and Round 2 testing.

Element a			Element b		
Manufacturer	**Model**	**Pfa[1], psi**	**Manufacturer**	**Model**	**Pfb[2], psi**
ETA Round 1 RO Elements					
Toray	TML10	150	Hydranautics	LFC3-LD	149
Hydranautics	ESPA2-LD	110	Koch	ULP	105
ETA Round 2 RO Elements					
CSM	RE-FE	141	DOW	BW30-XFR	141
CSM	RE-CE	174	Toray	TML10	155

[1] Pfa is estimated ETA feed pressures for 15 gfd flux in lead element, emphasized as "a".

[2] Pfb is estimated ETA feed pressures for 15 gfd flux in tail element, emphasized as "b".

Even though there were eight membrane types selected for testing in Round 1 and Round 2 during the ETA runs, Toray TMG10 was taken out of the experiment matrix to include Toray TML10 in the second round. The purpose was to have a common element in both of the runs to be able to make a direct comparison. Thus, it was aimed to minimize the effect of environmental factors and water quality difference between Round 1 and Round 2 testing. The types of the membranes tested in each round and their locations in the ETAs are presented in Table 5.11, above.

5.8.2.2 Element Test Apparatus (ETA)

ETA pilot-scale screening units are fully instrumented and electronically controlled. They are used for testing individual membrane elements, either 2.5-in or 4-in in diameter, before they are taken to pilot-scale, full-recovery systems. Two 2.5-in and two 4-in pressure vessels (80-in long and each holding two elements) are mounted on a metal frame skid.

Four ETA units (ETAs 1-4) were used for this research study to evaluate seven different types of membranes in two different rounds. Round 1, which lasted almost 3000 hours (4 months), tested four different types of membranes (Table 5.11). ETA 2, running on Alternative 22, had a lower runtime than the other three ETAs due to a combination of YMC flow disruptions and gravity filter conditioning. Round 2 that lasted more than 3500 hours tested three more membrane types (Table 5.11), plus the Toray TML10 was used for both rounds for the purpose of direct comparison.

ETAs operated at an average 15 gfd and approximately 13% water recovery during the testing. Assuming the average membrane area per element as 25 ft^2, ETAs ran at a feed flow rate of 8.0 gpm. The element types were paired in the ETA pressure vessels to be compatible in terms of operational requirements to allow for valid performance data production. The purpose for ETA runs (Round 1 and Round 2) were to test the fouling potential and single element production characteristics of different types of membranes manufactured by various companies.

Operating pressures for feed, permeate and reject streams; feed water pH, conductivity, temperature, chlorine residual, turbidity, SDI and chemical additions; permeate and reject flow rates, conductivities, temperatures; and reject pH were measured and recorded twice a day (8 AM and 8 PM) during the testing. Calibration checks and corrections were performed weekly on each instrument used for performance analyses. Calculations presented below in summary and in Appendix A-7 with details were carried out by the Test Manager and shared with the TAT members for their comments and suggestions about the operation of the ETAs. Necessary adjustments were executed by the operators.

Some but not all the calculated parameters that were scrutinized during the ETA testing are presented in Data Analysis section, below. Please, refer to Appendix A-7 for the details of the calculations and Appendices D, E, I and J for the actual data recorded throughout the testing.

5.8.2.3 Membrane Evaluation Research Unit (MU)

MUs are pilot scale, full recovery, mobile testing units that use 2.5-in or 4-in diameter membrane elements. They are fully instrumented and electronically controlled units and they can be used for high-recovery testing (up to 85%). The MUs are designed to be used after demonstrating a membrane and pretreatment process at the screening level, and before testing it on a demonstration scale system. MUs incorporate a 2-1 array and consist of 21 spiral wound, 2.5-in by 40-in elements.

Selection of MU Water Recovery

RO projections conducted by Dr. Chuck Moody, a TAT member from USBR, and by the antiscalant manufacturers, e.g. AWC, using the feed water chemistry associated with each alternative showed absence of scaling at 80-percent recovery with the use of antiscalant. For Alternatives 21 and 22, an average silica concentration of 24 mg/L in Yuma Mesa Conduit (YMC) water would limit recovery to less than 85 percent based on an estimated reject silica concentration of 157 mg/L and the application of a conservative silica solubility limitation ($\leq$100% saturation). Current antiscalant products have been demonstrated to retard silica scaling at reject concentrations as high as 200 mg/L, in which case, RO recoveries of 85% are most likely achievable. With the lime-softened water in Alternative 10 and the use of antiscalant, operation of an MU at 85% recovery is achievable without scaling. With un-softened MODE water as in Alternative 17a where calcium sulfate controls recovery (~1.34 times oversaturated in reject), a maximum recovery of 85% may or may not be achievable without antiscalant addition.

The current design recovery for YDP is 73% in section 1 (Hydranautics, where each vessel contains seven 8.5-in-diameter by 40-in-long elements) and 70% recovery in sections 2 and 3 (Fluid Systems, where each vessel contains four 12-in-diameter by 60-in-long elements). Generally, RO systems that are designed with two stages and low flux operate at a maximum of 80% recovery. Higher recoveries are possible with optimized flux balancing between the stages, however minimum brine flow and maximum lead element flux limitations defined by the manufacturer must be met in order to meet the warranty conditions. If higher recoveries will be considered for the YDP after the economic analyses, then modifications to the plant's design may be necessary.

In the case of YDP operation higher than 80% recovery, some disadvantages may emerge as well as advantages. Reducing the RO feed flow, for example, may lower pretreatment costs in proportion to the flow rate reduction. It also reduces the reject flow, which is generally desirable for an RO plant, especially where the reject disposal costs are high (e.g., evaporation ponds). However, YDP reject is intended to be discharged to the Cienega de Santa Clara rather than to an evaporation pond, so for this particular case, reject disposal costs are largely non-existent. On the other hand, increasing the recovery will not only decrease the already low reject flow but also increase the salt concentration in it. Both of them may adversely affect the ecosystem of the Cienega de Santa Clara.

The disadvantages, on the other hand, include a higher RO product salinity and the requirement of a modest increase in feed pressure. With the increasing recovery, stage 2 flux decreases relative to stage 1 flux without incorporation of an interstage boost pump. Increasing reject concentrations may also increase the cost for antiscalant and decrease the safety factor for control of scaling due to the water composition fluctuations throughout the year. The minimum reject flow requirement for the tail element may become a problem to match, as well.

Considering all the advantages and disadvantages listed above, at the January 2009 TAT meeting, the TAT selected a water recovery of 80 percent for full-recovery reverse osmosis (RO) tests. Another rationale was to evaluate the four selected alternatives under uniform RO operating conditions and initially to operate all four MUs at the same recovery.

Table 5.12. The calculation of RO unit flow rates at specified flux and water recovery.

RO Units Operating Flow Rates

ETA			**MU**		
Estimated membrane area	25	ft^2	Estimated membrane area	25	ft^2
No of elements/vessel	2	-	No of elements/vessel	7	-
No of vessels/unit	2	-	No of vessels/unit	3	-
Total membrane area	100	ft^2	Total membrane area	525	ft^2
Max membrane flux	15	gfd	Max membrane flux	12	gfd
Max permeate flow	1500	gpd	Max permeate flow	6300	gpd
Recovery	13	%	Recovery	80	%
Feed flow	11538	gpd	Feed flow	7875	gpd
Feed flow =	***8.01***	***gpm***	***Feed flow =***	***5.47***	***gpm***
Feed flow =	***30.33***	***L/min***	***Feed flow =***	***20.70***	***L/min***

The two-stage MUs, each containing twenty one 2.5-in diameter by 40-in long RO elements in a 2:1 array of three 7-element vessels, ran at a water flux of 12 gfd. Each RO unit operated with a feed flow of 20.7 L/min, a product flow of 16.6 L/min, and a reject flow of 4.1 L/min. For the reject flows, Hydranautics recommends 1.2 gpm (4.5 L/min). RO reject flow varies inversely with recovery. At 80-percent recovery, the reject flow of 4.1 L/min remained below the Hydranautics recommended minimum value. Although MU 1, like all other MUs, initially was operated with 80% recovery, from early November, 2011 until the test termination, MU 1 (Alternative 17a) ran with a recovery of 85% and water flux of 15 gfd average, which produced a reject flow of 3.8 L/min from the Hydranautics LFC elements.

5.8.2.4 Data Analysis

The daily measurements were analyzed by a set of calculations in Microsoft Excel. They are reported and discussed in the results section. The calculations were carried out by the equations presented below.

5.8.2.4.1 Silt Density Index (SDI)

The SDI provides a useful indicator of particle content (and conceptually therefore, fouling potential) in the RO feed water, overcoming the relative insensitivity of standard turbidity measurements. Samples for SDI measurements are passed at a constant pressure of 30 psi through a 0.45-µm membrane filter at constant temperature (± 1^{o}C). Particle accumulation reduces the filtration rate over the 15-minute standard test period. Flow data yields a plugging factor, defined as the percentage decrease in the flow passing through the filter compared to the original rate. SDI values are then calculated as follows:

$$\mathrm{SDI} = \frac{PF}{t} = \frac{\left[1-\frac{t_i}{t_f}\right]\times 100}{t}$$

where, SDI is the silt density index [-]

PF is the plugging factor [%]; the time-dependent percentage decrease in flow rate

t is the total elapsed flow time [minutes]

t_i is the initial time required to collect 500 ml sample [minutes]

t_f is the time required to collect 500 ml sample after the test time t [minutes]

The SDI instruments were from Chemetek (Model FPA-3300). RO membrane warranty generally depends on maintenance of SDI < 3.0 in RO influent, although values below 5.0 are often considered adequate to protect RO membranes from fouling due to influent particle accumulation.

5.8.2.4.2 Water Transport Coefficient (WTC or A)

Reverse osmosis hydraulic performance is described in terms of a temperature-adjusted water transport coefficient (A) defined by:

$$A = \frac{F}{P_{avg} - P_P - [\pi_{avg} - \pi_P]} \quad \text{[m/s.Pa]}$$

where, F is the permeate flux (Q_P/S)

Q_P is the volume rate of flow of permeate [m^3/s]

S is the nominal membrane surface area [m^2]

P_{avg}, P_P are the pressures in the unit feed and permeate streams, respectively, and

π_{avg} and π_p are the osmotic pressures in the unit feed and permeate streams [Pa]

The water transport coefficient values are usually displayed as 10^{-12} m/s.Pa. Calculated values were adjusted to 25°C using the temperature correction factor:

$$A_{25} = A \times 1.028^{(25-T)}$$

where, T is temperature in °C

5.8.2.4.3 *Salt Transport Coefficient (STC or B)*

The salt transport coefficient (B) is defined as:

$$B = \frac{F \times TDS_p}{TDS_{avg} - TDS_p} \text{ [m/s]}$$

where, F is the permeate flux (Q_P/S)

Q_P is the volume rate of flow of permeate [m^3/s]

S is the nominal membrane surface area [m^2]

TDS_P is the permeate salt concentration [mg/L]

TDS_{avg} is the effective salt concentration on the feed (reject) side of the membrane [mg/L]

The salt transport coefficient values are usually displayed as 10^{-6} m/s. And they were adjusted to 25°C using again the same correction as for the A coefficient temperature adjustment:

$$B_{25} = B \times 1.028^{(25-T)}$$

where, T is temperature in °C

All other related calculations used in the analysis of the data are presented in the results section and the details of the calculations presented above are listed in Appendices A-7 and A-8, including TDS concentrations, average pressure, net pressure, differential pressure, flow rate, recovery rate, element flow coefficient, water flux, B/A ratio, salt passage ratio and chemical dosage calculations.

5.9 Post-mortem Analyses

To provide information on the test membranes' conditions prior to testing and their physical and chemical properties, one of each type test membrane was autopsied at the University of Arizona. All the elements retired in Round 1 and Round 2 ETA testing and some selected elements from Round 2 MU testing were autopsied, as well.

5.9.1 Membrane Autopsy and Sampling Procedure

The membrane autopsy procedure can be summarized briefly as follows:

1. Photograph element before opening
2. Log date, time, membrane type and any initial observations of condition
3. Remove fiberglass casing
4. Photograph membrane sheets immediately after unrolling
5. Log visual observations about unrolled membrane appearance, condition, etc.
6. Measure area inside glue lines of active membrane surface

7. Cut sample (~1ft^2) of concentrate spacer and permeate spacer and save in labeled zip lock bag

8. Cut representative samples (~ 1ft^2) of membrane for HPC analysis. Place in sterile container and hold at 4˚C until analyzed

9. Cut representative samples (~1in^2) of membrane for Scanning Electron Microscopy (SEM) and Scanning Electron Microscopy–Energy-Dispersive X-ray Spectroscopy (SEM-EDX) analysis. Place in loosely covered container and air dry before analysis

10. Cut representative samples (~1in^2) of membrane for Fourier Transform Infrared Spectroscopy (FTIR) analysis, store in tightly sealed container at 4˚C until analyzed

11. Depending on the amount of material on membrane surface designate an area between 4 - 10 ft^2 for scraping.
    a. Pre-weigh and label (pinholes) four aluminum weigh boats (3 are process blanks)

    b. Scrape designated area and place residue in weigh boat

    c. Dry all boats at ~80˚C overnight (>8 hours [hr])
    d. Dry all boats at ~105˚C to constant weight (< 4% change) and record weights

    e. Split desiccated sample
        i. One split for X-ray Diffraction (XRD) and TOC/TIC analyses.
        ii. One split (reweighed after splitting) for loss on ignition analysis. Ignite at 550˚C for minimum of 1 hour and constant weight (< 4% change).

12. Scrape additional sample of ~ 2.0 g for Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) sample. Place in tightly sealed container and store at 4˚C until analyzed

5.9.2 Membrane Autopsy Analyses

The analyses performed during the autopsies, along with a brief description of the process, are listed below:

SEM: A scanning electron microscope is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

SEM-EDX: Scanning electron microscopes equipped with an energy-dispersive X-ray spectroscopy, which is an analytical technique used for the elemental analysis or chemical characterization of a sample, can provide rapid qualitative, or with adequate standards, quantitative analysis of elemental composition with a sampling depth of 1-2 microns. X-rays may also be used to form maps or line profiles, showing the elemental distribution in a sample surface. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another.

FTIR and ATF-FTIR: Fourier Transform Infrared Spectroscopy and Attenuated Total Reflectance-FTIR are closely related analytical techniques used to identify mainly organic materials. FTIR analysis results in absorption spectra which provide information about the chemical bonds and molecular structure of a material. The FTIR spectrum can be used to identify the material with a comparison method to a known sample.

XRD: X-ray Diffraction is a technique used for analyzing the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. This technique is commonly used to identify unknown substances by comparing the unknown data against a known database. It is simple to prepare the samples and a relatively quick analysis technique.

TOC: Total Organic Carbon (TOC) is the amount of carbon incorporated in organic compounds. It is used as a water quality indicator. TOC analysis involves removing the inorganic carbon (IC) portion (dissolved carbon dioxide and carbonic acid salts) prior to measuring the total carbon (TC). After purging an acidified sample with carbon-free air or nitrogen that takes away the IC, non-purgeable organic carbon (NPOC) is measured, which is TOC. The difference between TC and NPOC can be quantified as IC.

HPC: The heterotrophic plate count (HPC) is a procedure to estimate the number of live, culturable heterotrophic bacteria in water. Heterotrophic bacteria use organic compounds for most or all of their carbon requirements to survive. Most bacteria in water are heterotrophs.

Hence, this is a broadly used procedure to determine the efficiency of the disinfection technique being used. Together with TOC, HPC can give a significant hint if the fouling that occurs on the membranes is of biological origin.

Loss on Ignition (LOI): Loss on Ignition (LOI) measures the organic content of the material under investigation. It consists of igniting a sample of the material at a specified temperature (550 ^{o}C), allowing volatile substances to escape, until its mass stops to change. The test requires placing a known amount of the material in a tared, pre-ignited crucible. It is then placed in a temperature-controlled furnace for a set time (2 hours). Removing from the furnace and cooling it in a water-free atmosphere, and re-measuring the mass are the last steps. The process must be repeated until the weight of the cooled down sample is stable.

6. MODE RESULTS

6.1 Raw Water Quality

Raw water quality for the MODE canal is presented in Table 6.1. The sampling point is the MODE entrance of YDP. Average, minimum and maximum values over a year long timeframe are shown with the standard deviation (St. Dev.) for the more than 70 samples that were collected. Calcium, magnesium, sodium, chloride and sulfate ions make up more than 80% of the total dissolved solids in MODE water. However, the significance of iron and manganese concentrations in MODE water can not be discounted, especially after summer 2011 (refer to the iron and manganese results in Section 6.2.2.3). Please, refer to Appendix C-1 for the details of Table 6.1 and Section 6.2.2.3 for iron and manganese results.

Table 6.1. MODE raw water quality between January 2011 and January 2012.

Parameter	**Units**	**Average**	**Minimum**	**Maximum**	**St. Dev.**
pH	-	8.0	7.3	8.3	0.2
Conductivity	*µS/cm*	3,923.1	2450.0	4,520.0	326.9
Barium	*µg/L*	31.6	23.8	41.8	3.8
Calcium	*mg/L*	170.1	120.0	200.0	15.2
Iron	*µg/L*	63.0	16.3	240.0	29.9
Magnesium	*mg/L*	76.7	39.7	91.3	7.8
Manganese	*µg/L*	74.4	1.7	295.0	63.3
Potassium	*mg/L*	7.2	4.9	8.2	0.5
Sodium	*mg/L*	606.6	343.0	708.0	54.7
Strontium	*mg/L*	2.4	1.5	2.8	0.3
Sum of Cation	*meq*	41.3	24.3	48.1	3.6
Bicarbonate	*mg/L*	364.5	291.0	412.0	22.8
Chloride	*mg/L*	621.9	353.0	735.0	61.8
Nitrate as N	*mg/L*	4.5	1.8	6.4	0.9
Silicon Dioxide	*mg/L*	18.9	9.9	26.1	3.0
Sulfate	*mg/L*	857.7	500.0	1,000.0	82.4
Sum of Anion	*meq*	42.0	25.4	48.5	3.6
Tot. Alk. as $CaCO_3$	*mg/L*	299.0	238.0	338.0	18.6
Tot. Hard. as $CaCO_3$	*mg/L*	739.0	463.0	854.0	67.3
Total Organic Carbon	*mg/L*	2.4	2.1	3.4	0.4
Total Salt[1]	*mg/L*	2,727.9	1,660.0	3,110.0	228.1

[1] Total salt is measured gravimetrically by CEM AVC80 Microwave Moisture/Solid Analyzer.

6.1.1 Turbidity

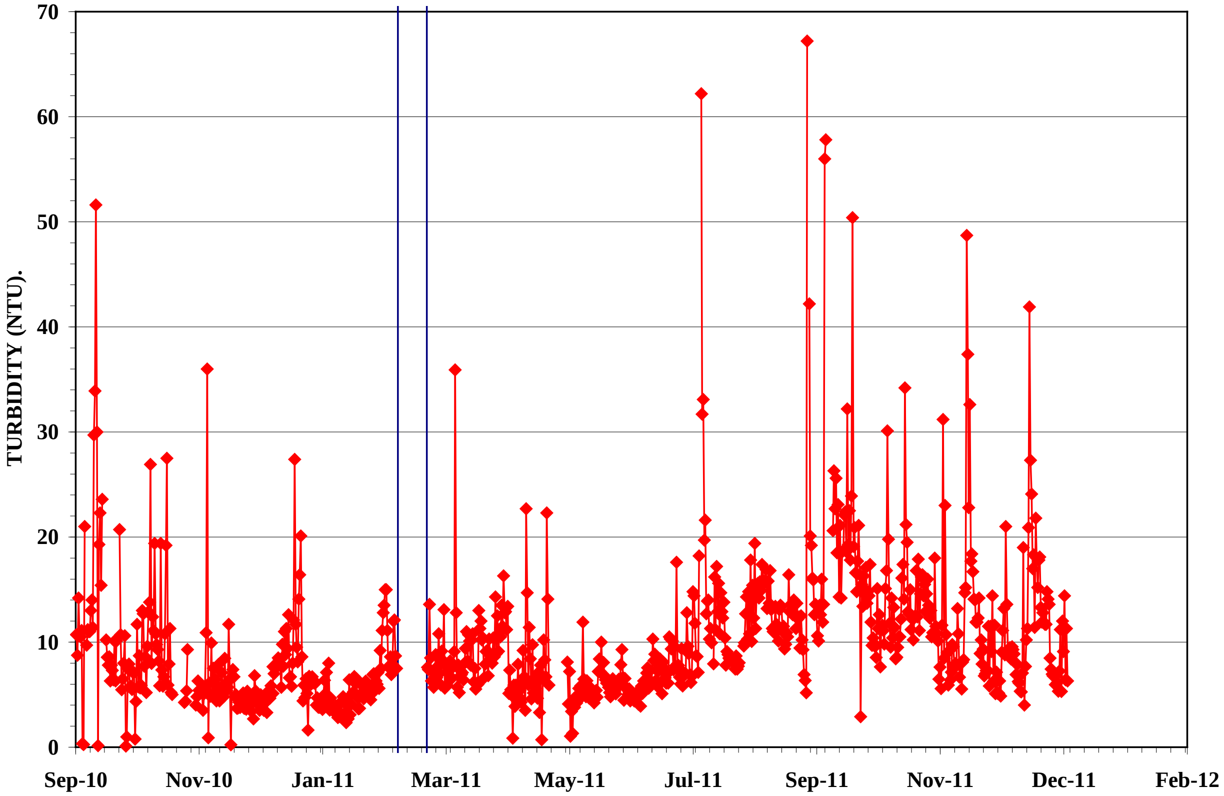


Figure 6.1. Manual turbidity measurements on PS3 SCR effluent (Alternative 17a). The blue vertical lines bracket the one week period in which MODE water was unavailable due to canal maintenance.

Turbidity data of the effluent of PS3 SCR (Alternative 17a) was collected for almost sixteen months during the testing. It was expected that turbidity would be seasonably variable due to changes in the algal and other biotic activity as well as due to storm events that would affect the open channel water quality. Turbidity in MODE water also varied as the flow in the canal fluctuated with the addition of water from the Drain Pump Outlet Channel (DPOC) drainage system, consisting of 24 drainage wells. DPOC's flows into the MODE canal varies through time as Reclamation makes adjustments to meet the assurances contained in IBWC Minute No. 242 as explained in the Introduction section. This generally is most pronounced between summer and the end of the year. Increases in the flow in the canal stir up material deposited on the bottom which may cause high turbidity in the YDP influent water. Such an increase in the SCR effluent was observed during summer 2011 (Figure 6.1).

6.1.2 Seasonal Variations

Seasonal variations in other water quality parameters of MODE water, such as TOC and iron and manganese concentrations, were observed as well during the testing period. TOC and temperature varied throughout the year of 2011. The correlation between the two parameters, as expected, was noteworthy. Water temperature increased by summer and decreased by fall of 2011 in the MODE canal. Measured TOC concentration followed the same pattern (Figure 6.2). However, the lack of complete correlation between TOC and temperature as seen in the January, June and July data points (Figure 6.2), suggest temperature is not the only independent driver for TOC variation. At this time other influences have not been identified.

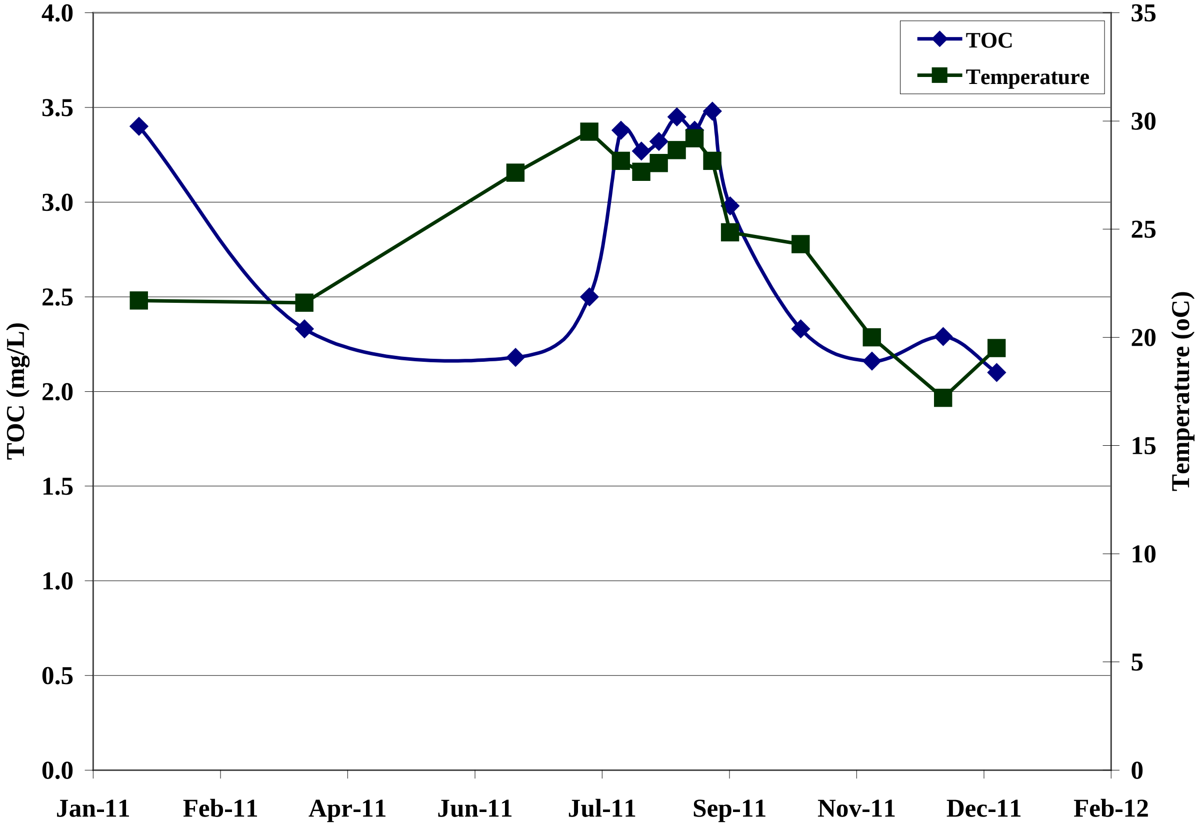


Figure 6.2. TOC fluctuation with the seasonal temperature variation in raw MODE water.

Other than the hump during the summer, there is no significant variation of any major ions observed in the raw MODE water throughout the sampling period, January through December 2011 (Figure 6.3). The time of this increase matched with the time of the turbidity increase. Hence, they may be influenced by the same factor, DPOC diversion and the flow increase in the canal. The total salt concentration in raw MODE water fluctuated between 2500 and 3000 mg/L, averaging ~2700 mg/L.

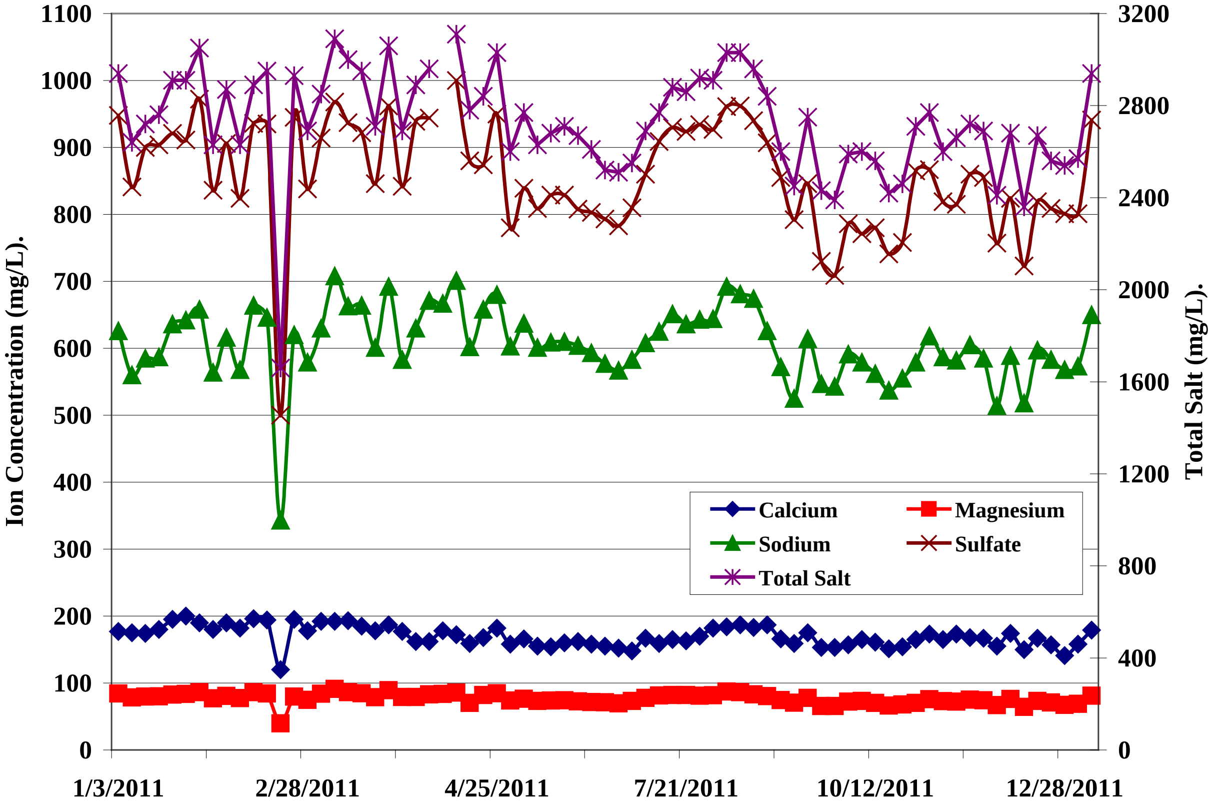


Figure 6.3. Major ions and total salt concentration in raw MODE water.

The concentrations of total iron in raw MODE water was relatively constant until summer 2011 when an increase occurred (approximately at the same time as the turbidity increase discussed above) before subsiding back to earlier levels in late fall. It is hypothesized that with the increased flow in the canal, deposited iron on the bottom of the canal was re-suspended and this elevated the observed concentration in the sampling point at the YDP (Figure 6.4). The other, probably correlated, hypothesis is that iron might be chelated with organics and as the concentration of organics increases during summer, iron concentration also increases.

Manganese concentration at the YDP intake moved approximately in the opposite manner to iron concentrations. The concentrations dropped to their lowest levels in summer 2011 and then began to rebound back to earlier levels in fall 2011. The manganese concentration changes by more than a factor of two during this oscillation. A more detailed analyses and discussion about iron and manganese levels in both MODE and YMC waters is in later sections of this report.

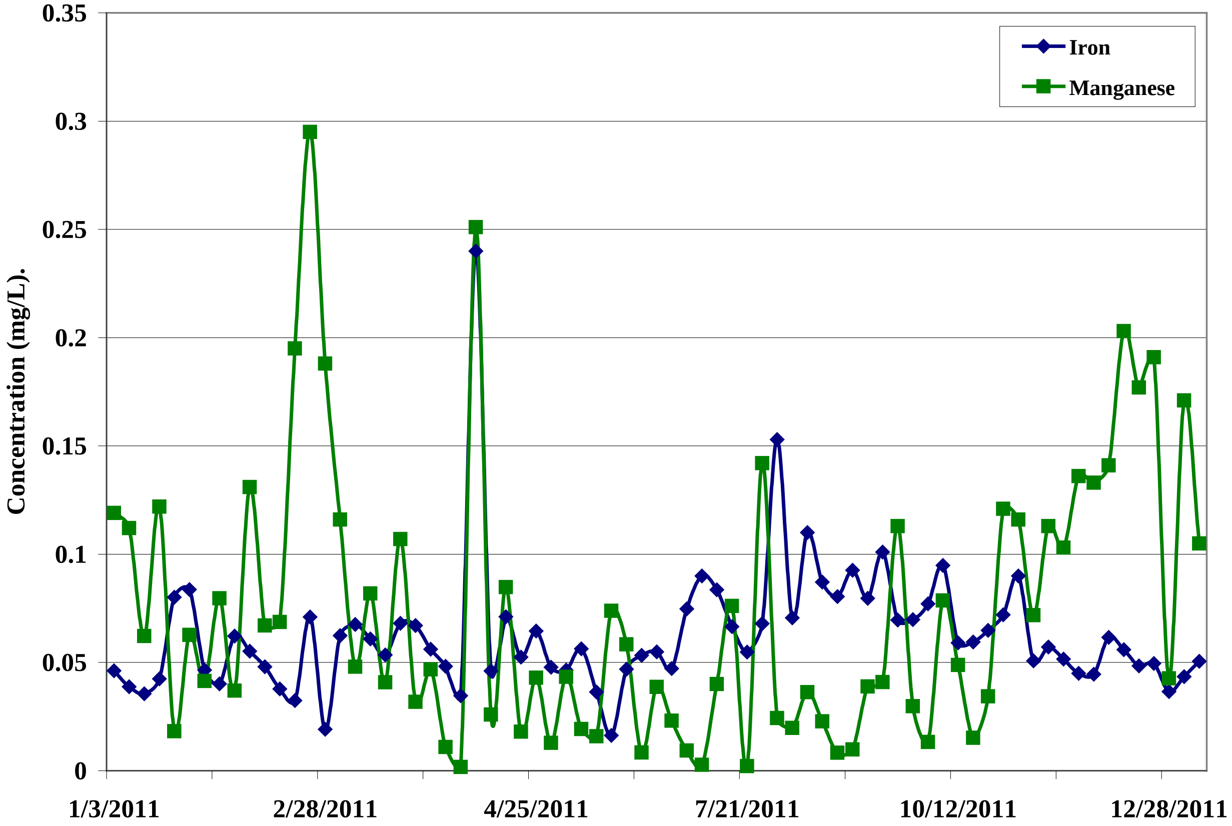


Figure 6.4. Iron and manganese concentrations in raw MODE water.

6.2 Pretreatment Performance

The two alternatives running on MODE water were Alternative 10, lime softening with flocculation and sedimentation followed by dual media gravity filtration, and Alternative 17a, dual media gravity filtration followed by microfiltration. In both alternatives, anthracite was the top layer and silica sand was the second layer in the gravity filters.

6.2.1 Alternative 10

Alternative 10 RO units were running on lime-softened gravity-filtered MODE water. Each operation in the Alternative 10 pre-treatment train is analyzed in separate sections below.

6.2.1.1 Lime Softening with Ferric Sulfate

Quicklime (CaO) is mixed with water to make a lime slurry, a thick solution with lime ($Ca(OH)_2$), before pumping it into PS1 SCR together with ferric sulfate. As the name softening suggests, this process is designed to remove the hardness ions as well as suspended particles from the water. The formation of sludge and the settling process are improved by the addition of ferric sulfate.

Table 6.2. PS1 SCR effluent water quality between January 2010 and December 2010.

Parameter	Units	Average	Min	Max	St.Dev.	% Rem
pH	-	9.8	7.9	10.2	0.4	-
Conductivity	*µS/cm*	3517.4	3010.0	4160.0	294.9	-
Barium	*µg/L*	11.3	5.0	29.3	4.1	64.4
Calcium	*mg/L*	90.3	61.7	175.0	21.1	46.9
Iron	*µg/L*	16.0	1.4	63.1	14.0	74.7
Magnesium	*mg/L*	56.4	37.6	81.1	8.0	26.5
Manganese	*µg/L*	3.8	0.4	51.5	11.1	95.0
Potassium	*mg/L*	7.1	6.2	8.1	0.5	1.5
Sodium	*mg/L*	569.3	473.0	684.0	50.9	6.2
Strontium	*mg/L*	1.3	1.0	2.6	0.3	43.8
Sum of Cation	*meq*	34.1	28.1	43.0	3.4	-
Bicarbonate	*mg/L*	13.7	0.0	385.0	65.0	96.3
Chloride	*mg/L*	591.2	483.0	722.0	53.1	4.9
Nitrate as N	*mg/L*	4.1	3.0	5.1	0.4	9.8
Silicon Dioxide	*mg/L*	10.2	2.7	17.5	3.7	46.2
Sulfate	*mg/L*	820.4	689.0	955.0	79.3	4.4
Sum of Anion	*meq*	35.4	30.0	43.4	3.3	-
Tot. Alk. as CaCO3	*mg/L*	52.9	33.3	316.0	45.7	82.3
Tot. Hard. as CaCO3	*mg/L*	456.9	368.0	770.0	74.3	38.2
Total Organic Carbon	*mg/L*	2.0	1.9	2.2	0.1	18.0
Total Salt[1]	*mg/L*	2193.6	1860.0	2820.0	220.8	19.6

[1] Total salt is measured gravimetrically by CEM AVC80 Microwave Moisture/Solid Analyzer.

The effects of this overall process can be seen in the SCR effluent water quality parameters. Removal of divalent cations was achieved up to 95%. Total hardness was removed by 40%, whereas more than 80% of the total alkalinity and almost all bicarbonate were removed, as well. PS1 was successful in decreasing the concentrations of some substances that might possibly cause scaling or fouling problems during RO treatment, such as iron, manganese, barium, strontium and silicon dioxide (by 75%, 95%, 64%, 44% and 46%, respectively). 18% of the total organic carbon (TOC), a key membrane foulant, was also removed by softening and ferric coagulation. On the other hand, it had practically no effect on the monovalent cations, chloride and sulfate concentrations.

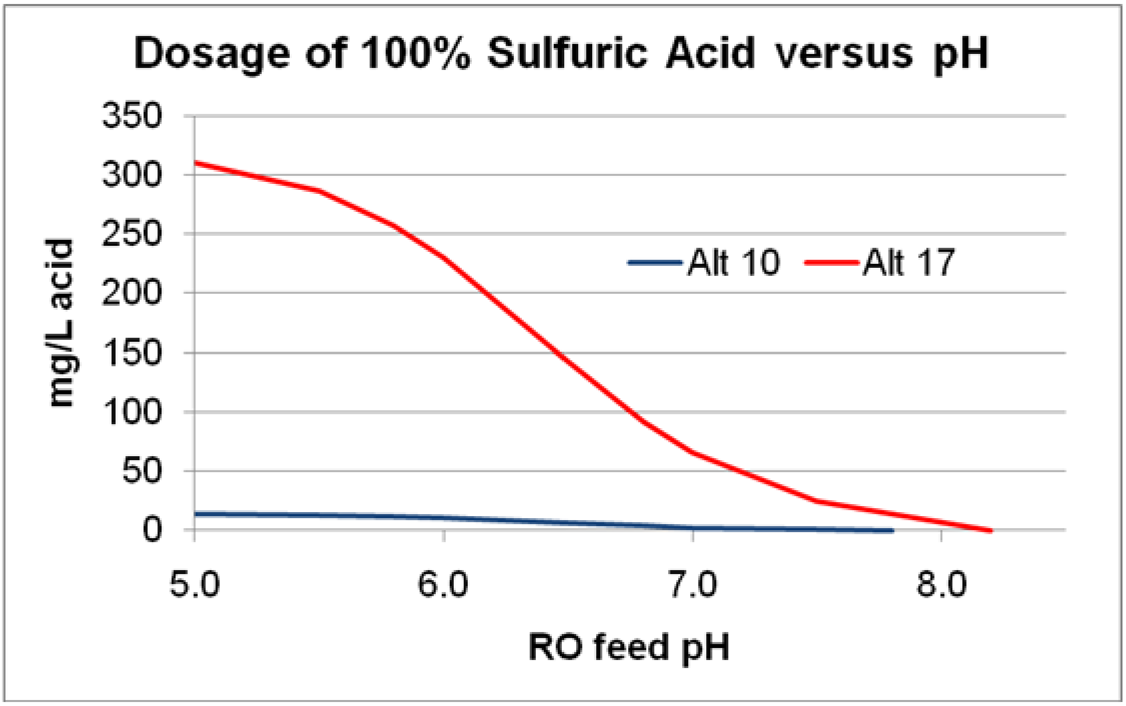


Figure 6.5. Comparison of sulfuric acid dosing for Alternative 10 and Alternative 17a.

Another advantage of the lime softening process is the amount of acid required to drop the operating pH lower than 6.8 to control and minimize the possibility of scaling. It is lower than for the other alternatives because almost all the buffering capacity (alkalinity) of the water has been removed. Per calculations provided by Dr. Chuck Moody, operation of Alternative 10 at a feed pH of 6.0 compared to pH of 6.8 requires an additional 6.5 mg/L of 100% sulfuric acid. This, at $220/ton (in February 2011 dollars) and 80% recovery, adds $2.40/af to the cost of RO product. When the operating pH of the feed water drops to 5.5, the additional acid requirement becomes 9.2 mg/L of 100% sulfuric acid compared to the operating feed pH of 6.8. Assuming the same price for the sulfuric acid and again at 80% recovery, the additional cost to cost of RO product becomes $3.40/af. However, these numbers are higher for Alternative 17a, in which the buffer capacity of the raw water is unchanged during pre-treatment.

Operating Alternative 17a at feed pH of 6.0, compared to pH of 6.8, requires an additional 138 mg/L of 100% sulfuric acid and adds $52/af to the cost of RO product with the same assumptions as above. This value becomes $73/af when the operating feed pH drops to 5.5 with the same assumptions. The cost of acid is significantly lower in Alternative 10 compared to Alternative 17a. However, the cost of lime and ferric sulfate will be additional and needs to be estimated in a separate economics analyses to compare and find the most suitable option financially.

The need for RO feed acidification is a function of $CaCO_3$ scale control, which is provided mainly by antiscalant, and balance between increase in salt transport coefficient (B) and decrease in water transport coefficient (WTC). The latter is unique to YDP. The pH of the softened and non-softened water to control $CaCO_3$ precipitation probably will not be too different when a modern antiscalant is used (not Sodium hexametaphosphate [SHMP]). Therefore, the cost of acid addition may not be significantly different between softened and non-softened water for $CaCO_3$ precipitation control purpose only. However, costs will be higher if a lower pH is needed to control increasing salt passage. The economics and cost/benefit analyses are not part of this research study.

6.2.1.2 Gravity Filtration

Combined effluent of the gravity filters operating on PS1 was used as the feed water for the RO units running on Alternative 10. Presented below is the turbidity reading of the ETA 4 and MU 4 feed waters (and MU 2, Round 2, phase II), the RO units running downstream of the PS1 gravity filters. Even though most of the removal was achieved by lime softening and SCR processes, gravity filters were successful in decreasing the remaining turbidity by more than 90%

in general. The scattering in the data is probably due to the very low levels of turbidity, which were getting close to the detection limit of the turbidimeters used.

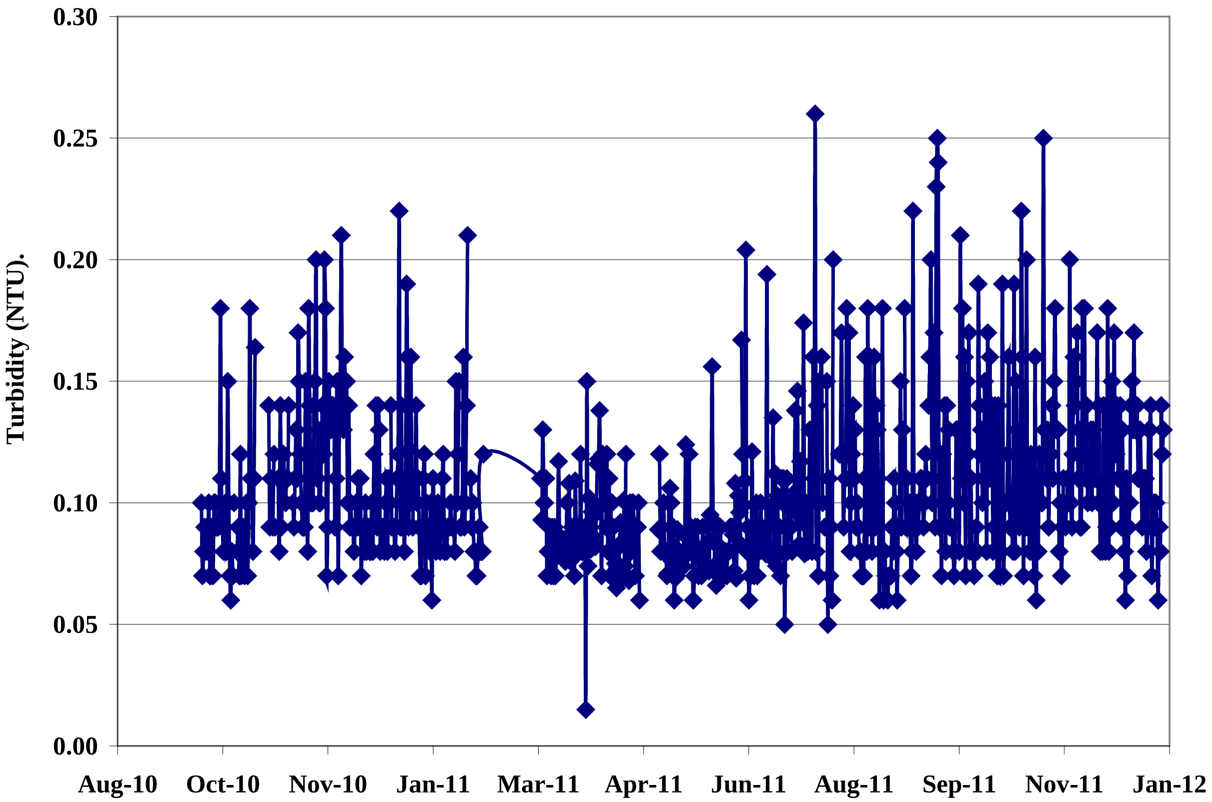


Figure 6.6. Turbidity profile for PS1 gravity filter combined effluent.

6.2.2 Alternative 17a

Alternative 17a was running on MODE water with direct gravity filtration and microfiltration used as pretreatment for RO operation. Each operation is analyzed in separate sections and some of the significant results are presented below.

6.2.2.1 Gravity Filtration

The turbidity level in MODE water, especially in Alternative 17a, is significantly higher than in the other alternatives. The gravity filters of PS3 (Alternative 17a) efficiently removed incoming turbidity. The results are presented in Pretreatment Performance Section 6.2. The dual media gravity filters removed on average 85% of the influent turbidity and dropped it down to 0.5-2.0 NTU. The feed turbidity for the DMGF on PS3, which is the SCR effluent, were presented in the previous section, 6.1.1 Turbidity

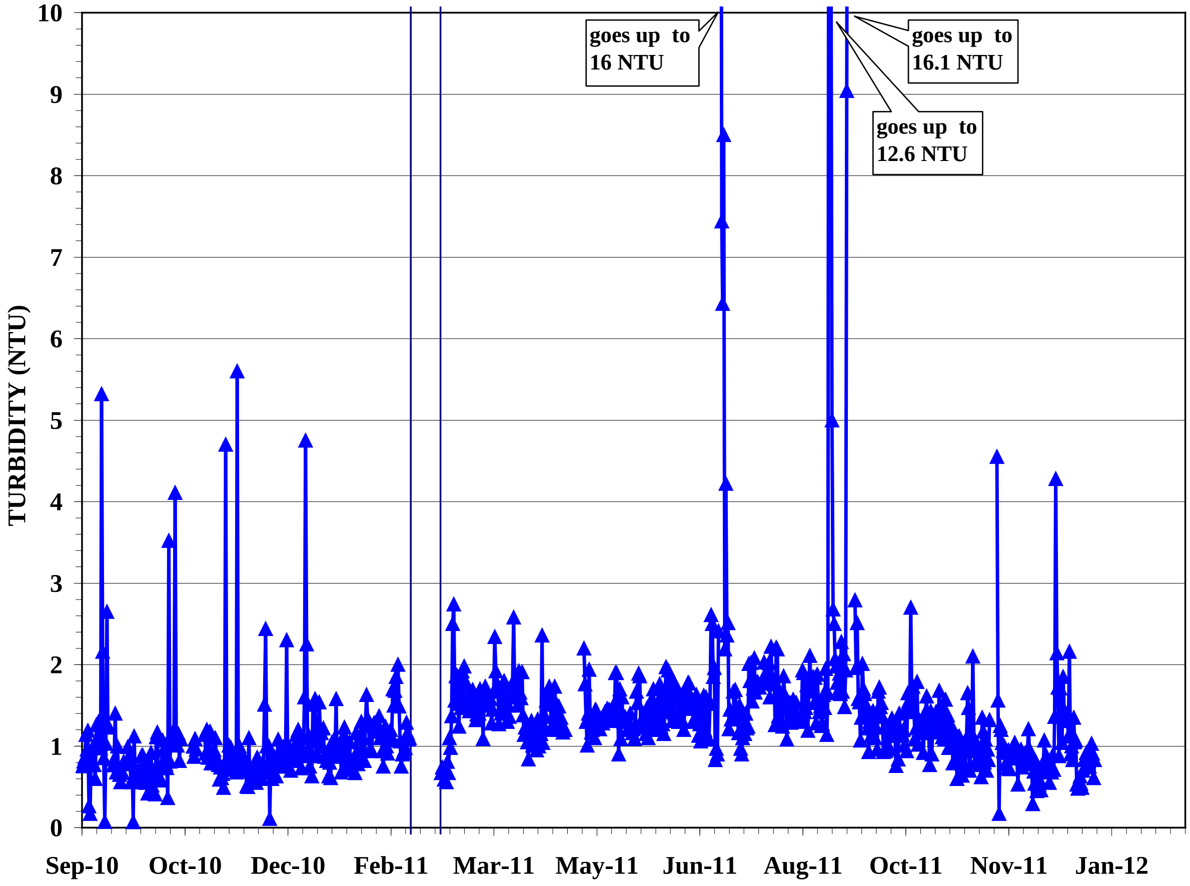


Figure 6.7. Combined effluent turbidity profile for PS 3 gravity filters. MODE was diverted for maintenance purposes for one week represented by the blue lines.

This early success of the DMGF in maintaining the filtrate turbidity at less than 1.0 ended possibly because of the diversions into the MODE canal started by the end of 2010. It is possible that the composition of the materials that contribute to turbidity changed since the authors saw a decrease in the feed turbidity to the DMGFs (Figure 6.1) in April 2011 during the period when the effluent turbidity was constant and relatively high. The gradual increase in the chlorine demand of the MODE water (Figure 6.8, below) that started around the same time might be another indication of such water quality changes. The increase in chlorine demand indicates an increase in biological activity, with a concomitant increase in biologic-based colloidal matter that is small in size and more difficult to remove by the DMGF. And this may also cause more fouling to downstream membranes. The amount of chlorine that was injected at the intake structure needed to be increased during this period in order to keep the free chlorine level at the DMGF combined effluent at the desired value of 1.5 mg/L. Later in the study on July 22, 2011, due to a biological growth problem that occurred in ETA 1 (see Section 6.3.1.2), the free chlorine level of the DMGF effluent was increased to 2.0 mg/L to supply better disinfection for the RO operation. This elevated level was kept until the end of the testing.

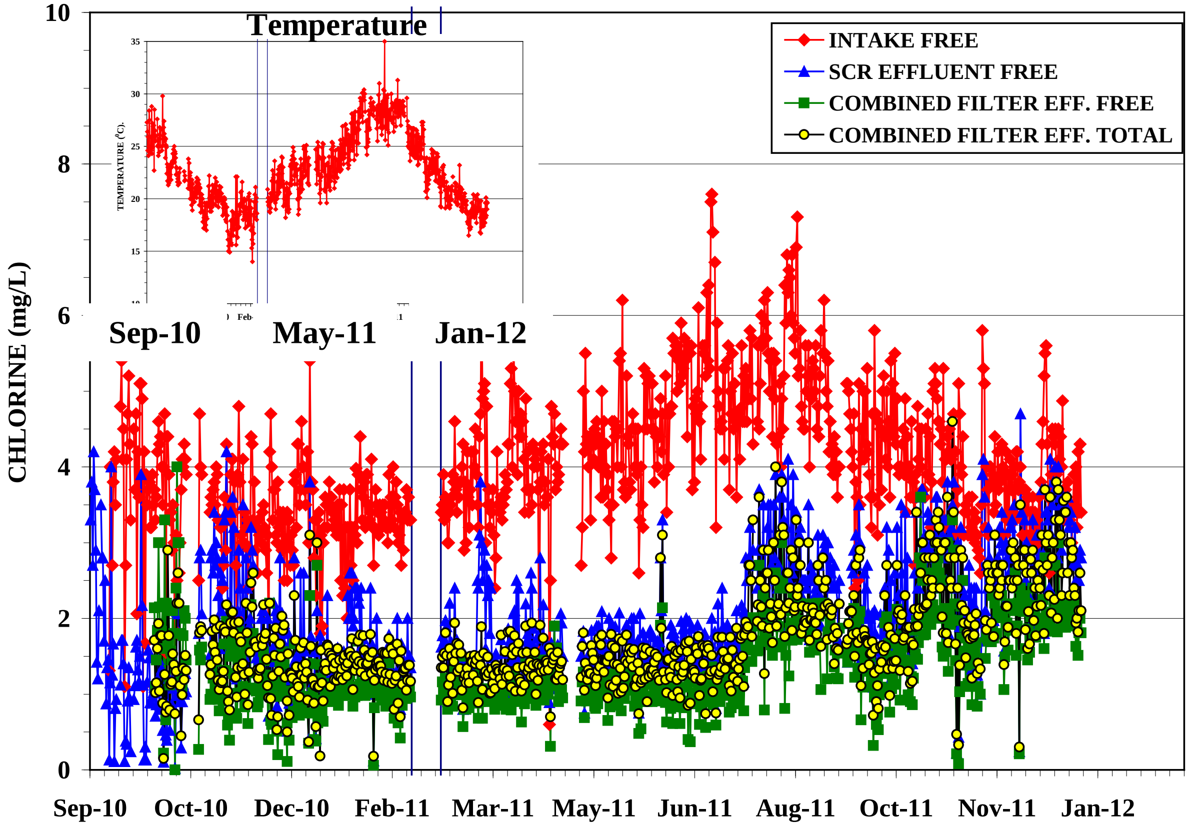


Figure 6.8. PS3 total and free chlorine level profiles.

A significant drop in the chlorine demand of the MODE water was observed after summer 2011, possibly because the water temperature –hence the TOC– started to decrease at the same time (see Section 6.1.2, Figure 6.2). The measured temperature at the DMGF effluent is presented in PS3 total and free chlorine level profiles, Figure 6.8. The close relation between the chlorine demand and the temperature of MODE water can be seen clearly. The chlorine demand of the raw MODE water almost returned to historical low levels by the end of 2011.

6.2.2.2 Microfiltration

West Pall MF Unit was running on Alternative 17a with a single MF module on the downstream of PS3 DMGFs. Initially, it ran at 60 gfd (22.4 gpm) with 97% water recovery. Transmembrane pressure (TMP) as an operating parameter is a clear indication of how a dead-end filtration unit is performing. West Pall MF TMP and specific flux were around 5-6 psi and 10-11 gfd/psi, respectively, when it was first placed in operation. The TMP profile for September 2010 is presented below as an example for its initial performance.

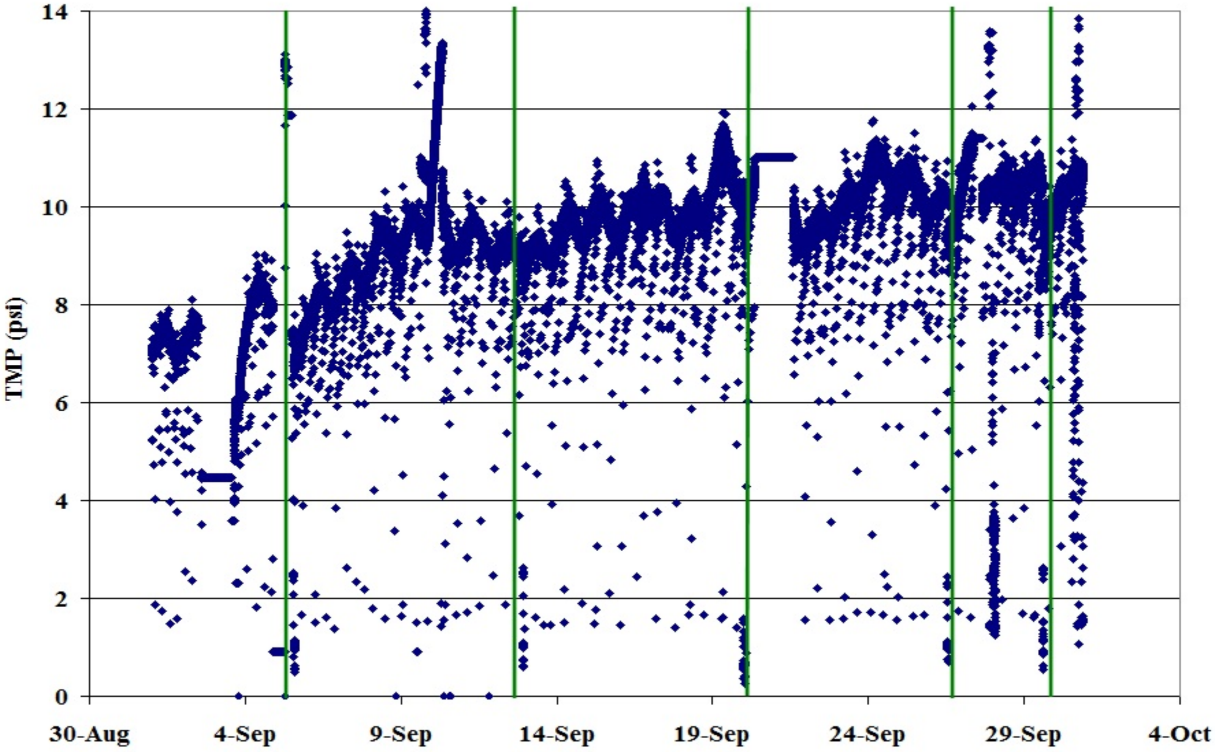


Figure 6.9. West Pall MF Unit TMP Profile for September 2010. Green vertical lines indicate timing of bleach EFMs.

Once a week bleach EFM was performed to inhibit possible biological activity on the membrane surface. The bleach EFMs are indicated by the green lines on the plots.

The TMP quickly increased to 10 psi following the start up and stayed constant for a couple of weeks until it started increasing again coincident with the cooling of water temperature in early October. It gradually rose for the next couple weeks. On October 18, the TMP increased very rapidly from 18 psi to 36 psi in three hours due to an increase in the turbidity of the MODE water. The PS3 SCR effluent, turbidity level was measured as 19.4 NTU and that affected all the units downstream, including DMGF and West Pall MF. The feed turbidity for the MF unit was recorded as 4.5 NTU whereas the filtrate quality stayed unaltered around 5 mNTU. The chlorine demand of MODE water also increased at the same time as the turbidity increase, further indicating the change.

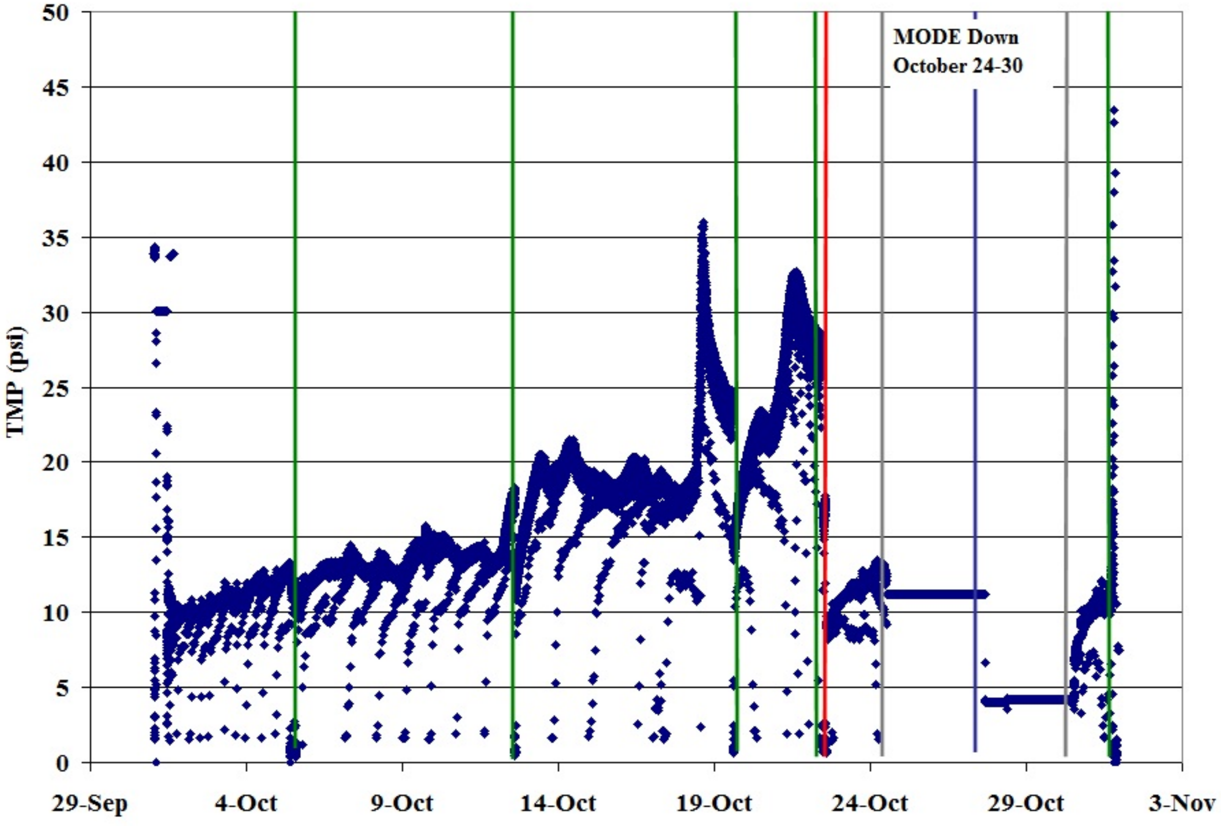


Figure 6.10. West Pall MF Unit TMP Profile for October 2010. Green and red vertical lines indicate timing of bleach and acid EFMs, respectively.

Another high turbidity event occurred on October 20 and 21, and the TMP increased once again to more than 30 psi. An unscheduled bleach EFM on October 22nd (Figure 6.10, above) was performed in response to the TMP increase. However, this unscheduled cleaning did not help very much and the TMP only dropped to 15 psi after the EFM. Considering the possibility of inorganic fouling and the lack of success in the previous bleach EFM, a citric acid EFM was performed for the first time on October 22nd two hours after a bleach EFM. TMP decreased down to 15.5 psi after the bleach EFM whereas acid EFM brought the TMP down to around 8 psi. The acid EFMs are indicated with red lines on the plots.

The rate of increase in the TMP after the bleach and acid EFMs on October 22, 2010, was significantly lower compared to the values before them. However, the first CIP for the West Pall MF unit, indicated by the blue line on the plot, was performed on October 27-28 as a precaution while the MODE was shutdown between October 24 and 30. After the MODE began operating again, a TMP of ~6.5 psi and a specific flux of ~10 gfd/psi were observed initially. The tests performed after this CIP showed that the module installed on the unit had 93.8% of new membrane permeability and this number was used as the baseline permeability for comparison purposes in the future CIPs. The results of the CIP cleanings are presented in the *"Autopsy Results and Cleaning Study"* section.

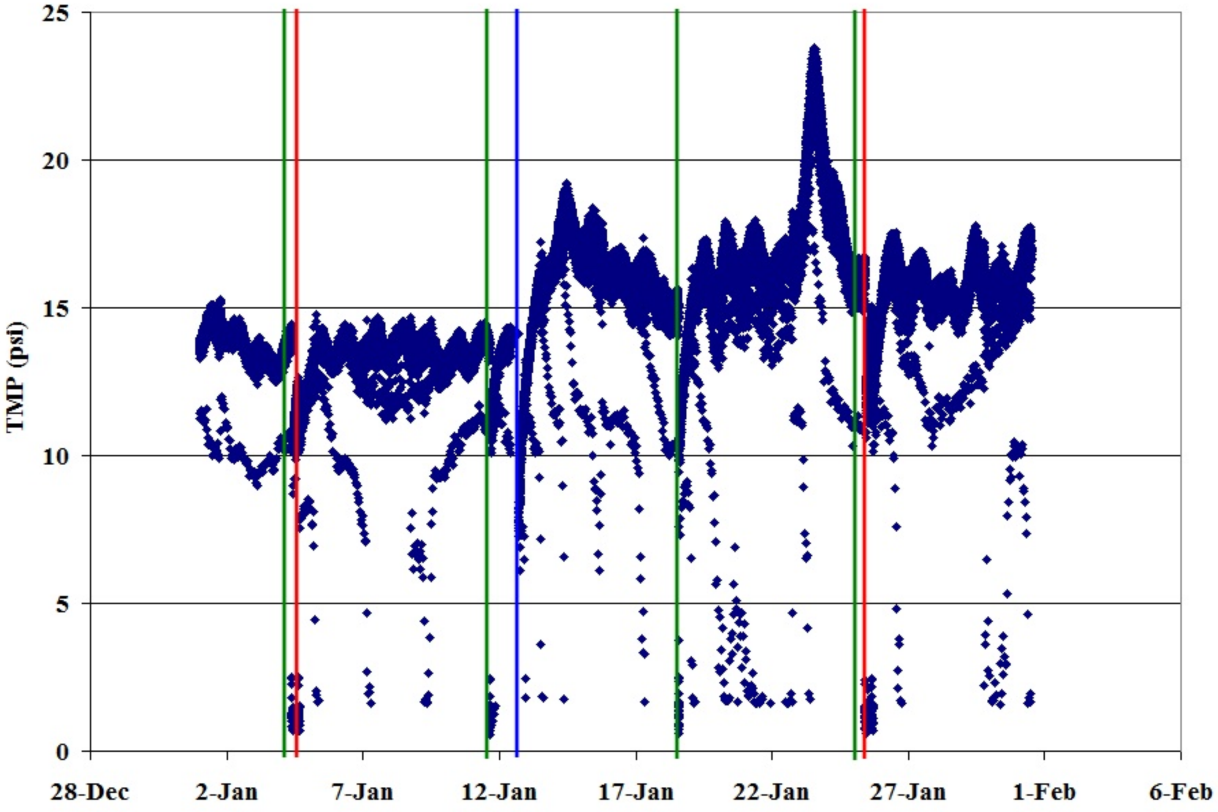


Figure 6.11. West Pall MF Unit TMP Profile for January 2011. Green, red, and blue vertical lines indicate timing of bleach and acid EFMs and CIPs, respectively.

Citric acid EFMs were executed from November 9, 2010, on a regular biweekly basis after noticing the positive effect of the one in late October. The West Pall MF unit performed very consistently with TMP fluctuating around 12-15 psi and specific flux around 4-5 gfd/psi for almost four and a half months. The unit ran with 60 gfd until January 12, 2011. After being convinced that a sustainable run with the given conditions is achievable, it was decided to increase the flux by 10% to 66 gfd (24.7 gpm).

Another CIP was performed on January 12, 2011 before the flux was increased to make sure that the unit was clean enough to allow a direct comparison between the 60 gfd and 66 gfd flux performances. The membrane permeability testing showed that the module regained 88.1% of new membrane and 93.9% of the baseline permeability.

The CIP performed on January 12, 2011 is indicated with the blue line in the plot presented above (Figure 6.11). The effect of the flux increase on January 12, after the CIP was immediately observed (Figure 6.11). The rate of increase in the TMP was substantial and the level where it stabilized (15-18 psi) was slightly higher than the level where the TMP initially stabilized (12-15 psi) with 60 gfd. From this point forward, the West Pall MF unit operated consistently with a TMP of 15-20 psi and a specific flux of 3.5-5 gfd/psi for another four and a half months until early June. It should be noted that when the MODE was shutdown for cleaning between April 25 and May 3, 2011, another CIP was performed right before placing the unit on-line. The CIP again brought the specific flux of the unit back up to 10 gfd/psi. However, the rate of decrease was extensive.

The TMP increased slightly reaching levels up to 25-28 psi in June, even though the water temperature was increasing at the time. The reason for this rise in TMP values might be due to increased biological activity and/or the changing water quality in the MODE canal. As mentioned earlier in the report, Section 6.1.2 Seasonal Variations, the TOC level together with the iron and manganese concentrations in the MODE water started to increase in June 2011. Since higher recovery of TMP after citric acid EFMs was observed compared to the ones after bleach EFMs in May, it was decided to do weekly citric acid EFMs and biweekly bleach EFMs starting from June 8.

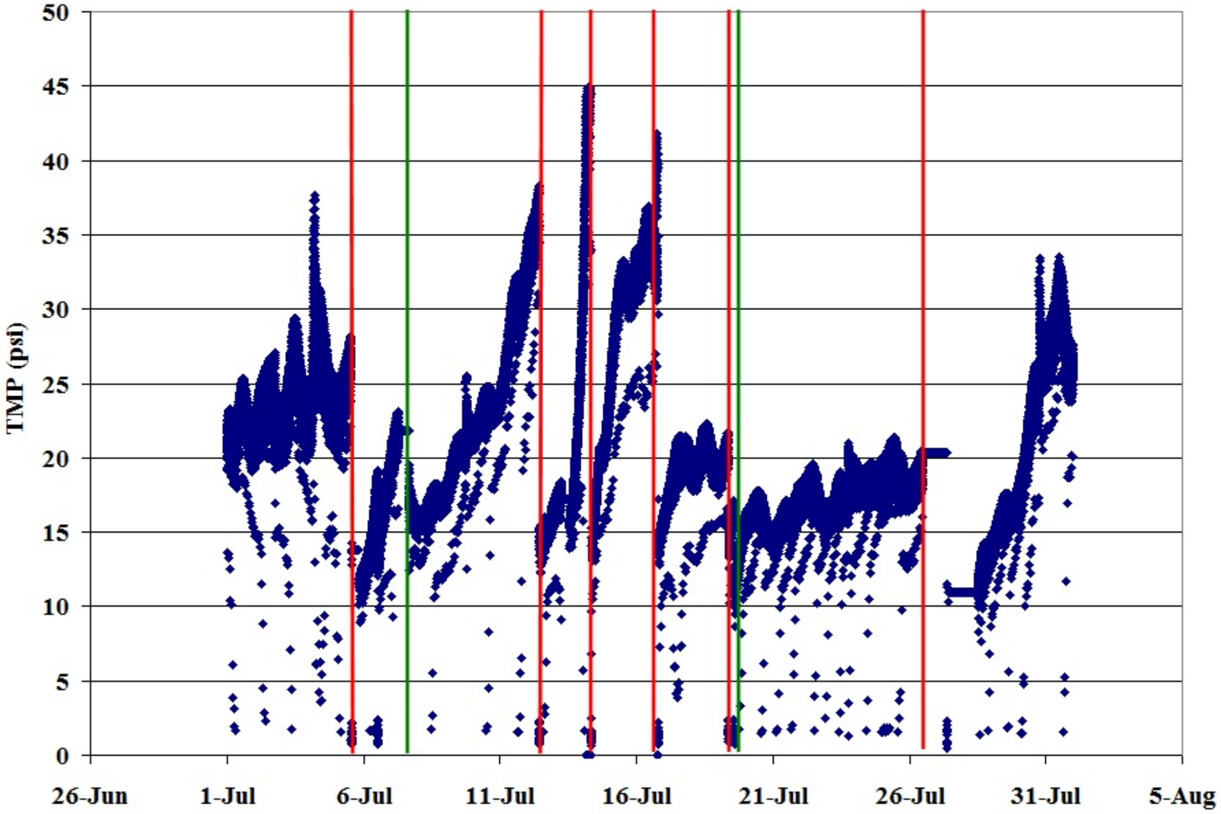


Figure 6.12. West Pall MF Unit TMP Profile for July 2011. Green and red vertical lines indicate timing of bleach and acid EFMs, respectively.

During the second week of July, three unscheduled citric acid EFMs, two days apart from each other, needed to be carried out due to TMP levels reaching above the warning level of 40 psi. Even though it looked like the trend settled down during the third week, it picked up again more aggressively by the end of July and early August (Figures 6.12 and 6.13). As a result, it was decided to cancel the scheduled citric acid EFM on July 12, 2011 and do one as needed while keeping the same schedule for the bleach EFM. Some possible reasons for this sudden change of operational behavior were discussed and possible causes noted as increasing iron and manganese concentrations, diversion of DPOC water to the MODE canal, and higher TOC concentrations in summer temperatures. Discussions of these possible explanations are summarized below in bullets.

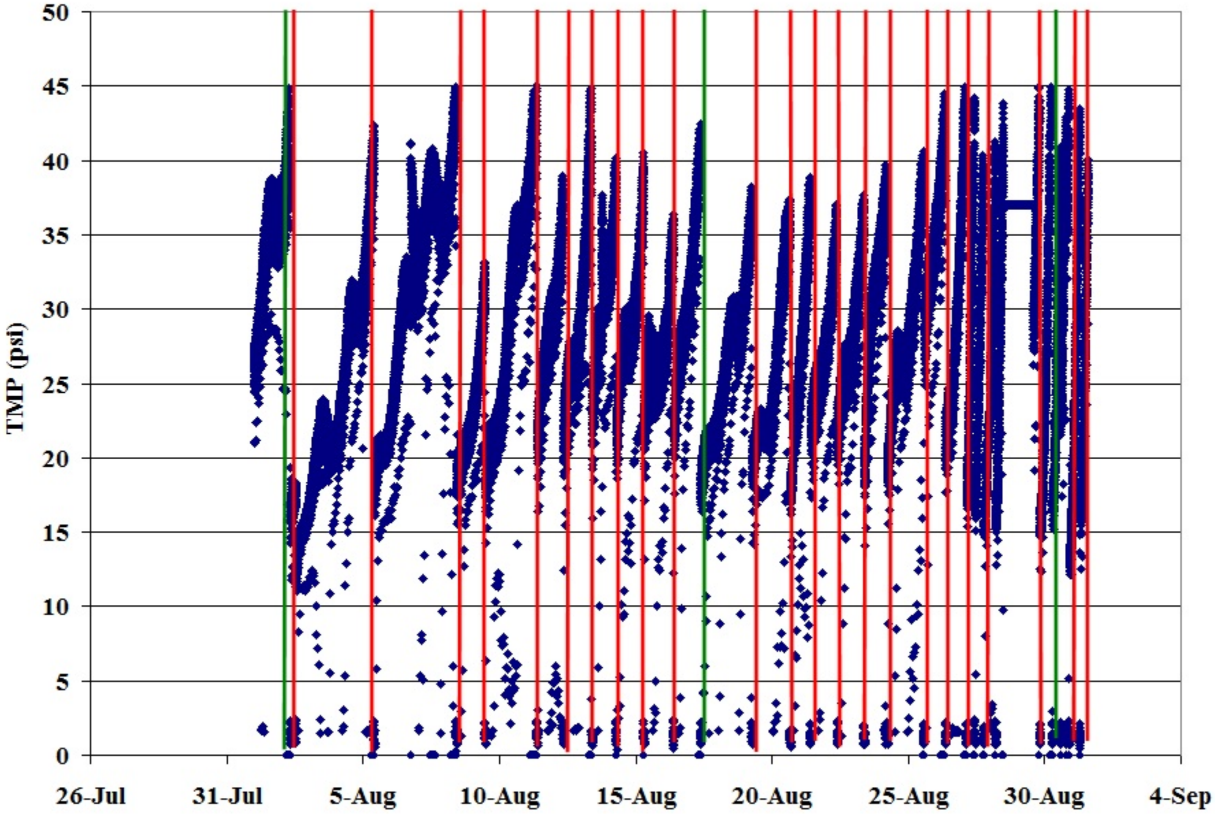


Figure 6.13. West Pall MF Unit TMP Profile for August 2011. Green and red vertical lines indicate timing of bleach and acid EFMs, respectively.

- *Iron and manganese concentrations:* As previously presented in Section 6.1.2, the iron and manganese concentrations started to increase by the end of June and early July. It is possible that the size of the particulate iron and manganese was small enough to pass through the gravity filters but be, at least, partially collected by microfiltration. Dissolved iron and manganese detected in the effluent of the West Pall MF unit and the feed of the RO units downstream suggested partial removal. However, the data record, particularly for MF effluent was not sufficiently detailed in either frequency or analytical resolution to definitively suggest the degree to which iron and/or manganese increased accumulation on the MF fibers could have contributed to the frequent cleaning required in August, 2011. More detailed iron and manganese profiles and discussion for PS3 are presented below and in Section 6.2.2.3, as well.

- *Diversion of DPOC Water to MODE:* Diversion of DPOC water to the MODE might be an explanation for the rise in iron and manganese levels since it is known that the ground water in the Yuma area has considerable amounts of iron and manganese. Verification of this hypothesis would require sampling of the DPOC water versus other MODE water sources.
- *Higher TOC concentration:* The TOC concentration in the MODE canal increased as the ambient temperature increased which is expected in an open channel subject to algal and other biotic growth (Figure 6.2). The elevated biological activity increased the amount of the biomass and some fraction of this biomass would likely be deposited in the microfiltration unit's fibers. Since the source water was chlorinated at the intake structure prior to reaching any of the unit operations, all the biomass was inactive, hence undetectable via HPC analyses. But the effect of this biomass was observed in Figure 6.8 presented in Section 6.2.2.1 as an increase in the chlorine demand.
- The pH of the water may also have played a significant role in the fouling rate of the MF unit. When the pH was decreased from 6.8 to 5.8 on August 26, 2011 with the objective of improving the MU 3 operation, the cleaning frequency of the West Pall MF unit noticeably increased. The immediate increase in the frequency of EFMs after August 26 can be seen in Figure 6.13 above. The same effect was observed in the cartridge filter study running on Alternative 22 with YMC water. This is discussed in more detail in Section 7.2.2.

Further testing and more detailed water quality analysis are required to reach a definite conclusion for the reason for this fouling and the type of compound or compounds that cause it. However, having all these possibilities examined, one might hypothesize that the reason for the fouling could be a type of organic or inorganic complex with iron and/or manganese. Ferric iron, for example, is normally insoluble in water. However, it might form complexes with organic ligands that are quite soluble in water. Thus, the increased soluble iron and manganese and the increased TOC could likely be correlated and simply explained by chelation. The chelation can also be a strong function of pH. Decreasing the pH can decrease the formation constant and release iron which will form hydroxide complexes and foul.

One example for this type of organic ligand is the iron-catechol complex. Catechol, which is also known as 1,2-dihydroxybenzene, is an organic compound that is mainly used as a precursor to pesticides. Therefore, biodegradation of the aromatic hydrocarbons, such as pesticides, can be the source of catechol, especially in regions like Yuma, where agricultural land is abundant. A study by Anastasia J. Sugeng from the College of Public Health at the University of Arizona showed that the total amount of pesticides used in Yuma in June-2011 reached an astonishing amount of 6.3 million pounds. The usage of total pesticides had never reached one million pounds per month in the 6 years prior to that.

Chelation can also occur via commonly used fertilizers in the agriculture industry as well as natural biotic products including cell tissue degradation products and microbial exopolymers. Formation of organic compounds that iron or manganese can form complexes with was substantially increased, especially during the summer 2011, which corresponded with the period when higher concentrations of iron and manganese in MODE water were experienced. The factors necessary for such organic compounds to form substantial concentrations of complexes with iron and manganese, the chemical paths during this process, and the effects of temperature and pH on the process need to be investigated further to reach a more precise explanation. Another potential contributor to MF fouling is organic-calcium complexes. It is reported in earlier studies that when calcium concentration is high, it increases TOC fouling. However, the higher concentration of oxidizing agent, which was chlorine during this project, and addition of a flocculating agent, such as aluminum sulfate, might help to improve the removal efficiencies of iron and manganese via coagulation, flocculation and filtration.

The presence or absence of accumulation of iron and manganese on the microfiltration unit stayed undetected throughout the research testing because there was no clear indication of concentration difference for the unit’s influent and effluent at any point of time during the testing, even though iron and manganese were always detected in the filtrate of microfiltration unit. Another CIP was performed on the West Pall MF unit on February 16, 2012 to recover the membrane permeability. A two-step CIP, with 3% by weight oxalic acid as the first step and 1% NaOH with 0.5% NaOCl as the second step, was performed. The membrane permeation rate was recovered by almost 90% and the unit operated successfully for the following two months after that. Please, refer to the "*Autopsy Results and Cleaning Study*" section for the details of this cleaning and testing. The amount of iron and manganese in the spent cleaning solution was measured as 4.25 g and 1.13 g, respectively, dousing the following assumptions:

- earlier CIPs did not remove any iron or manganese from the unit since no significant recovery of the performance was observed;
- the average flux for the unit was 55 gfd (20.55 gpm) and;
- the time for accumulation was 6 months, from July until the end of December;

then, the concentration needed to cause the measured accumulation on the unit can be calculated as;

$$V_{treated} = 55 gfd \times 538\, ft^2 \times 30 days / month \times 6 months = 5.33 Mgal$$

$$C_{Fe} = \frac{4.25 g}{5.33 Mgal} \times \frac{10^6\, \mu g / g}{3.785 \times 10^6 L / Mgal} = 0.21 \mu g / L$$

$$C_{Mn} = \frac{1.13 g}{5.33 Mgal} \times \frac{10^6\, \mu g / g}{3.785 \times 10^6\, L / Mgal} = 0.06 \mu g / L$$

Therefore, the change in the concentrations of iron and manganese would be undetected via Inductively Coupled Plasma Mass Spectrometry (ICP-MS) since the detection level for the unit is 0.2 μg/L. On the other hand, the total amount of the material accumulated would be enough to cause fouling issues on the MF unit because the amount of water treated is ample.

There were four CIPs performed in September. The TMPs after each CIP are marked with red circles in Figure 6.14. The first one was on September 6 after the MODE was not operating for about five days. Initially, a lower TMP and a higher specific flux were observed with this regular CIP when the unit came back online on September 10. However, the rate of fouling was still very high so that daily EFMs were needed. Therefore, on September 16, another regular CIP was performed, which brought the initial TMP and specific flux to the same values achieved after the previous CIP. Unfortunately, no change was observed in the fouling rate.

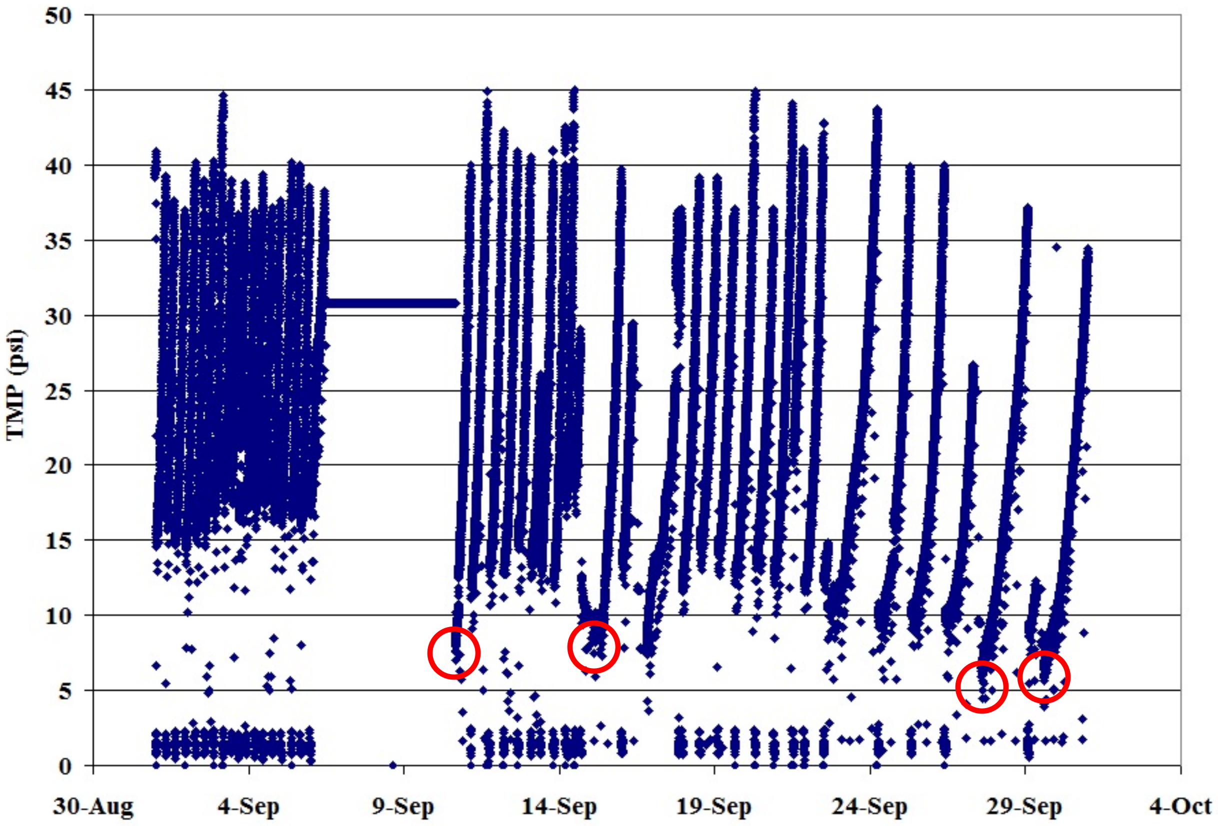


Figure 6.14. West Pall MF Unit TMP Profile for September 2011.

The flux of the unit was decreased from 66 gfd to 50 gfd on September 22 due to the persistence of the high fouling rate. Following the flux change, an enhanced CIP, with double-dosed double-citric acid cycles (applied twice), was performed on September 27 aiming to improve the efficiency of the cleaning. However, again no significant change was recorded. Consequently, another enhanced CIP was performed on September 29. The pH of the cleaning solution was brought down to 1.5-1.8 by adding sulfuric acid (H_2SO_4) as well as the citric acid since iron, at that time, was the main suspect for the fouling and the rate and extent of iron dissolution is inversely proportional to pH. Iron is known to be more soluble at lower pH. The idea was to dissolve and remove the iron by lowering the pH. However, no change in the fouling rate after this CIP was observed. All the CIPs executed in September lowered the initial start-up TMPs to the original clean membrane value but did not significantly change the fouling rate.

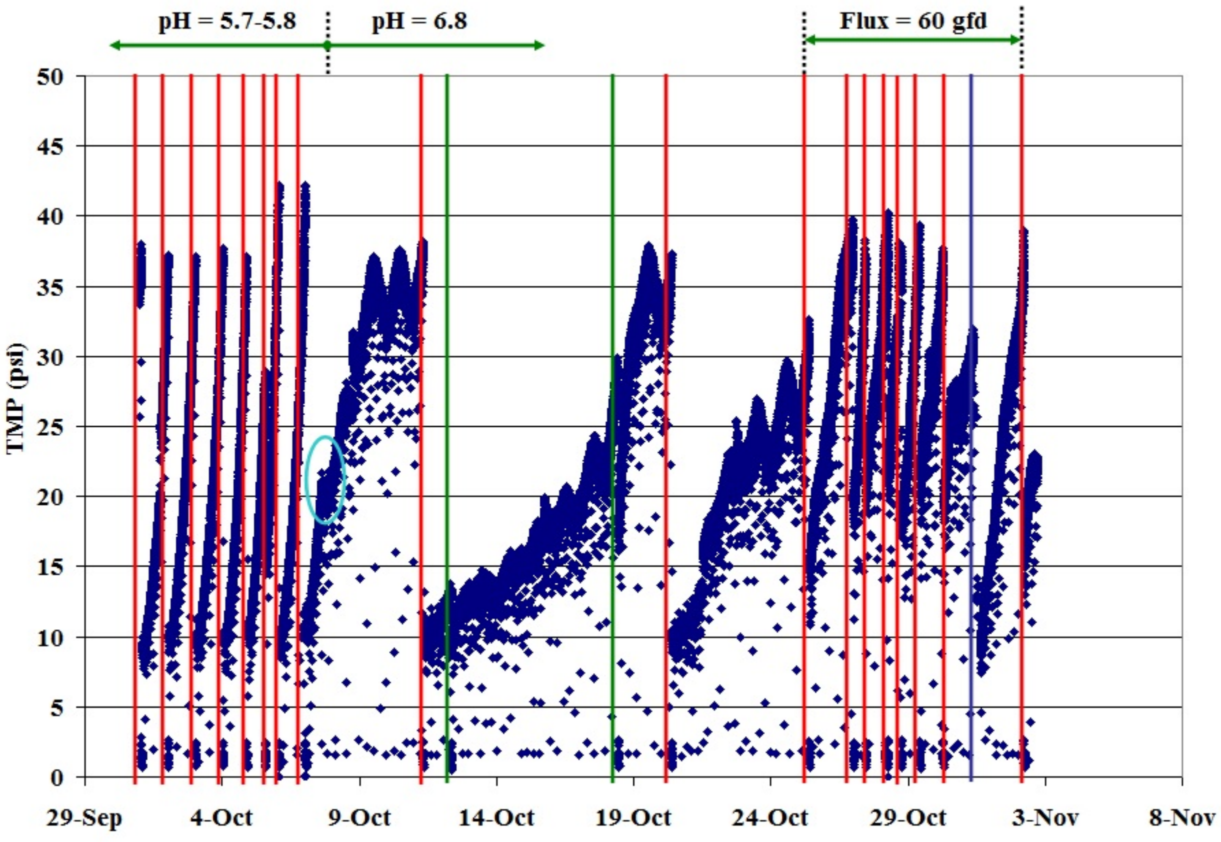


Figure 6.15. West Pall MF Unit TMP Profile for October 2011. Green and red vertical lines indicate timing of bleach and acid EFMs, respectively. The blue circle highlights the immediate response to the pH change on the slope of the TMP profile.

After no noteworthy improvement was detected with the different types of CIPs and flux changes performed, the attention of the group diverted to other possible operating parameter changes. During summer 2011, the pH effect was tested on the fouling rate of the cartridge filters running on Alternative 22 with YMC water. It was observed that the fouling rate was higher with a lower feed pH of around 5.8, compared to the fouling rate at feed pH of around 6.8. Thus, a new acid injection line was installed for the West Pall MF unit so that it could run with a different feed pH than MU 3 running downstream of it. The feed pH for the MF was then adjusted to 6.8 on October 7. The immediate response to the pH change was witnessed on the slope of the TMP profile, marked with a blue circle in Figure 6.15. Slightly slower rate of increase and stabilization of TMP around 35 psi were observed for the first time since early July.

The citric acid EFM on October 11 dropped the TMP down to ~10 psi and no remarkable effect of the bleach EFM performed the next day was observed. The sequence of the two EFMs was reversed the following week. Bleach EFM on October 18 dropped the TMP only down to ~16 psi, which quickly increased to 38 psi in one day. Citric acid EFM on October 20 dropped the TMP down to 9.4 psi, showing that the low pH cleaning was more effective than bleach cleaning. Hence, the problem was believed to be related to inorganic fouling.

On October 25, the flux was increased to 60 gfd after a citric acid EFM. The TAT decided that the performance of the unit was sustainable with the operating pH of 6.8 and the flux of 50 gfd. The adverse affect of this flux increase to 60 gfd was in plain sight and resumption of daily citric acid EFMs was immediately needed (Figure 6.15). The idea of foulant buildup being the reason for this behavior was refuted by performing a regular CIP carried out on October 31(indicated by the blue line in Figure 6.15), and continuing to run with the same conditions. The initial startup TMP dropped to 7.5 psi as it always did after each previous CIP but the rate of increase did not show a significant change. Therefore, the flux was dropped back to 50 gfd on November 2 after a citric acid EFM.

The TMP increased rapidly following the EFM of November 2 and the flux adjustment, probably due to the temperature drop of about 8 ^{o}F in one day. Then, it fluctuated until November 6 with the diurnal temperature change. When the TMP eventually reached 40 psi on November 7, a citric acid EFM was performed dropping the TMP down to about 14 psi. The next day a regular scheduled weekly bleach EFM was executed. TMP was recorded as 12 psi following this EFM. The rate of increase was quite significant, even though it was slower than the one recorded the previous week. A smaller slope was expected after dropping the flux by 17%. Therefore, two more citric acid EFMs were performed on November 9, a regular one, and November 11, a low-pH one. The pH for the second EFM was adjusted to 1.5 by adding sulfuric acid. The encouraging results from earlier citric acid EFMs showed that the fouling might be related with inorganic materials. Hence, the foulant was aimed to be removed via lowering the pH further. However, neither of the acid EFMs achieved TMPs less than 14.5 psi.

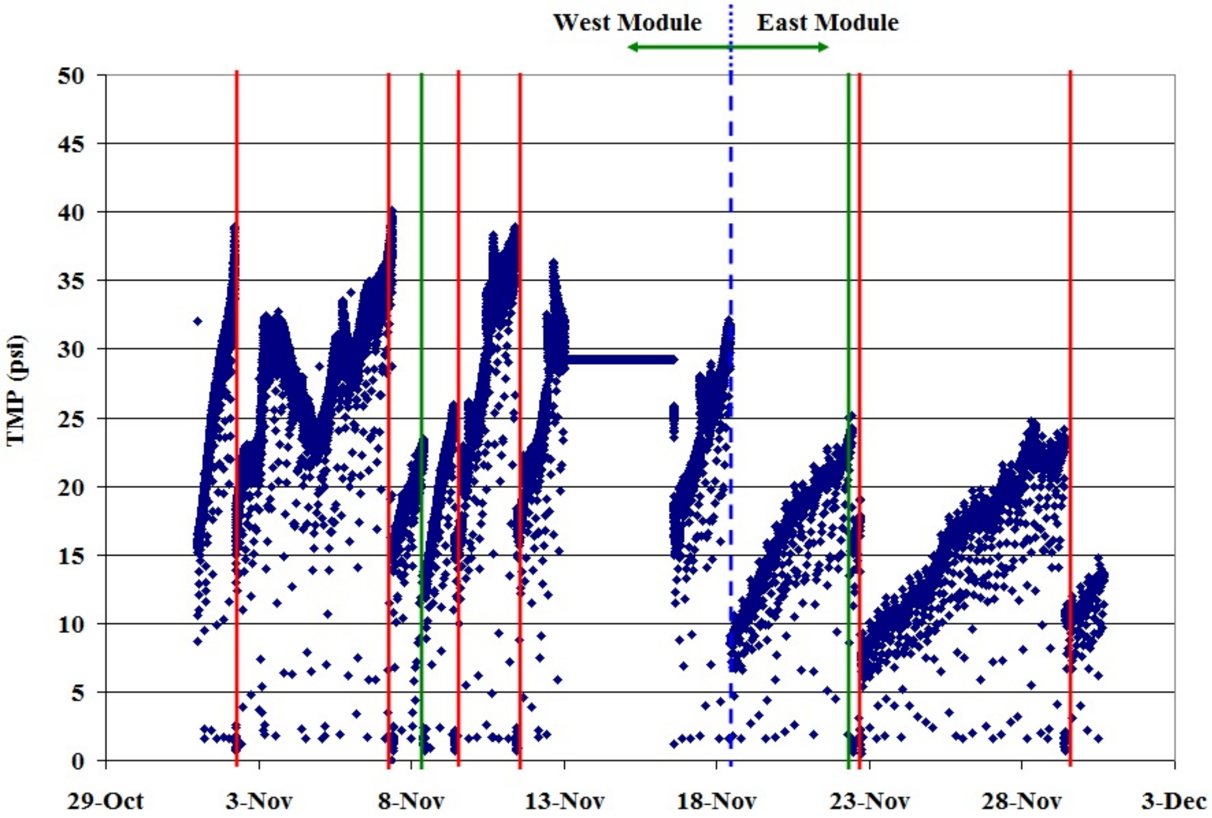


Figure 6.16. West Pall MF Unit TMP Profile for November 2011. Green and red vertical lines indicate timing of bleach and acid EFMs, respectively.

The fluctuation of the TMP matched with the temperature fluctuation of the source water. This fluctuation reflects operation at constant filtrate flow (flux), where higher TMP is needed at lower temperature and vice versa in proportion to the change in water viscosity with changing water temperature, in other words, trying to compensate for the increase in the viscosity of water. Hence, when the temperature was lower, the TMP was higher to maintain a given flux, resulting in more fouling. On the other hand, recording a 10 psi lower TMP on November 4 compared to the day before cannot be explained by only the change in viscosity. A possible explanation for this behavior could be that the unit was getting rid of the material that was the reason for fouling, probably via the backwash cycles. The unit might be operating around a critical flux, meaning when the actual flux got higher (as the temperature goes down), it clogged up the membrane but when it got lower (as the temperature goes up), the backwash cycles cleaned the membrane.

The intake turbidity of PS1 was high during the same period. Hence, after considering the idea of the PS1 intake structure being the possible cause for the high fouling rate, on November 13, the West Pall MF was shutdown together with the other units running on MODE water and the intake structure of PS1 was cleaned. No change was noted in the fouling rate afterwards when the unit was returned to service on November 16. Therefore, on November 18, the module was removed from the West Pall unit and replaced with the module from the East Pall MF unit to determine whether the high fouling rate experienced by the West Pall unit was caused by a change in the fouling potential of the MODE water or by a change in the performance of the West Pall module. Citric acid EFM frequency was reduced to weekly. The East module was operated for approximately 5 days and, on November 22, a bleach EFM was performed, which dropped the TMP to 15.4 psi, followed by a citric acid EFM, that dropped it to 7.7 psi, confirming that inorganics were still the main cause of fouling.

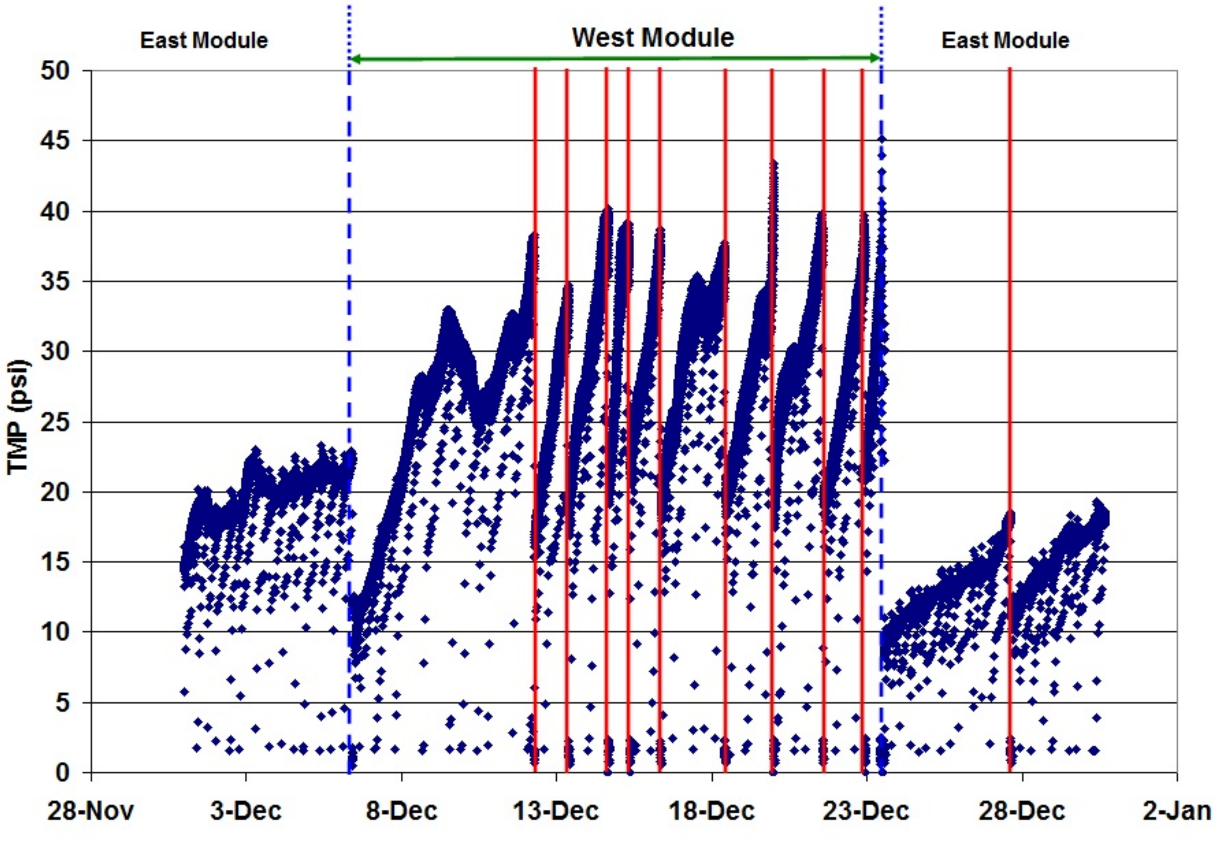


Figure 6.17. West Pall MF Unit TMP Profile for December 2011. Green and red vertical lines indicate timing of bleach and acid EFMs, respectively. The dashed blue vertical lines indicate when modules were switched between East and West units.

A much lower rate of TMP increase was observed with the East Pall unit's module operating in the West Pall unit. The East Pall MF unit's module was kept in the West Pall unit until December 6. During this time, the West Pall MF unit's module was kept in bleach solution to prevent any biological activity. When it was installed back into the unit (December 6) and started running, a low TMP as well as a low fouling rate was observed initially. The run looked promising and sustainable for the first six days. However, nine citric acid EFMs were carried out in the following eleven days. All of them resulted in post-EFM TMPs of 17 psi or higher, in an increasing fashion. On December 23, the TMP after the citric acid EFM was 25.1 psi. It was decided that this type of operation was not sustainable and the modules of the units were switched once again to supply water in a reliable and consistent way for the downstream MU operation until the end of testing, December 30, 2011. A regularly scheduled weekly citric acid EFM was performed on the unit on December 27 dropping the TMP down to 11.6 psi.

MF Autopsy Results and Cleaning Study

The high fouling rate on the West Pall, running on MODE water, became an important issue after summer 2011. Neither more frequent EFMs nor CIPs were able to maintain a reasonable rate of TMP increase. To evaluate if the problem was the module itself and not the source water, the East Pall MF unit's module was installed on the West Pall MF unit and ran for a couple of weeks (see discussion and Figures 6.16 and 6.17, above). The same high fouling rate did not occur with the East Pall MF unit's module running on MODE water. Therefore, the TAT decided that the problem was the module so the question became could the unit be cleaned and its performance restored. What fouled the fibers and what the mechanism of the fouling was is beyond the scope of this study since the main objective of this research was to learn about the feasibility and the sustainability of the alternatives tested. Hence, the Test Manager and the operators followed a simple procedure summarized in steps below for analyzing and understanding the fouling issue. Employees from Pall Corporation were on-site to assist with the procedure.

1. First it was established that the MF unit as a whole was working properly and that the problem could be isolated down to rapid fouling of the modules fibers.

2. Sections of seven fibers from the West Pall module were removed on February 7, 2012 and the bore of the cut fibers (effluent side) was plugged using the steps described below.
    - The module was placed on a table and secured with straps.
    - A small window was cut at both ends of the module.

Figure 6.18. Pictures showing West Pall MF unit module's autopsy and fiber removal process.

- Seven individual fibers were cut and removed from the module.
- A small vacuum cleaner cleared out the resulting shavings.
- Clamps were placed over each window to reseal the module.

Figure 6.19. Pictures showing (a) the clamps for closing the windows in place after the fiber removal procedure and (b) the pins plugging the cut fibers.

3. The removed fibers were taken to the Pall Corporation laboratory and a cleaning study was run.

Charles Liu from Pall Corporation performed a cleaning study on the fibers removed and found that the fiber samples, prior to cleaning, had membrane permeability of about 56-57% of the new fiber's permeability. After soaking three separate fibers (A, B and C) in bleach (A), citric acid (B) and iron-out (C) solutions for about 68 hours as Step 1, the permeability recovery reached 77-89% of the new fibers. After Step 2, soaking for about 22 hours in citric acid (A) or bleach (B and C) solutions, the permeability reached 94-101% of new fiber performance. The cleaning regimes are summarized in Table 6.3. Effect of each regime on fiber permeability is shown in Figure 6.20.

Table 6.3. Cleaning regimes Pall Corporation used for MF fibers removed from West Pall module.

Cleaning Regime ID	Step 1 (68 hours)	Step 2 (22 hours)
A	5000 mg/L NaOCl and 1% NaOH	2% citric acid
B	3% citric acid	5000 mg/L NaOCl and 1% NaOH
C	2% Super Iron Out (oxalic acid)	5000 mg/L NaOCl and 1% NaOH

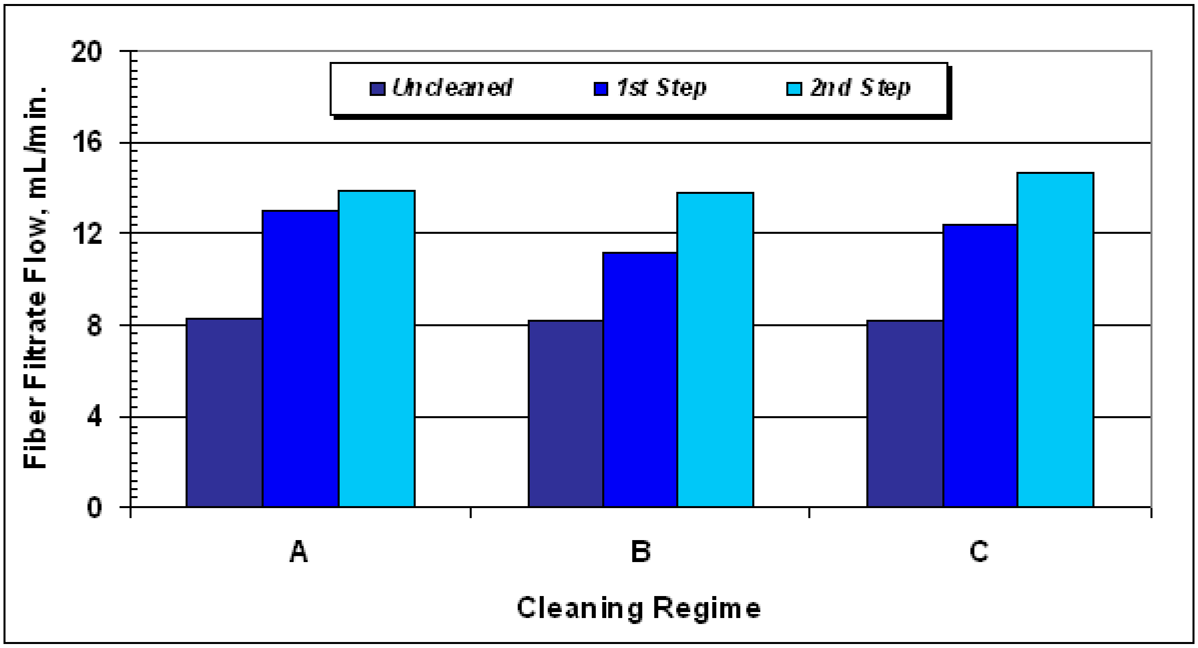


Figure 6.20. Membrane permeability of the fibers before and after each cleaning step.

There are two main outcomes of Pall Corporation's cleaning study. The first is that there is no statistically significant difference among the three cleaning regimes in terms of permeability recovery at a confidence level of 95%. The second is that the fouling is believed to be caused by the combination of metals (likely iron) and organic matter after examining the permeability recovery following each cleaning step.

4. Based on the results of the Pall Corporation laboratory cleaning study on the membrane fibers removed from the West Pall module, a short validation study was conducted at the WQIC on the full unit operating on MODE water and with the West Pall module in operation. The West Pall module was cleaned (in-place in the West Pall unit) using a special chemical cleaning scheme and solutions that Pall Corporation and the TAT agreed on. Please, see below for the detailed explanation of the solutions and cleaning scheme.

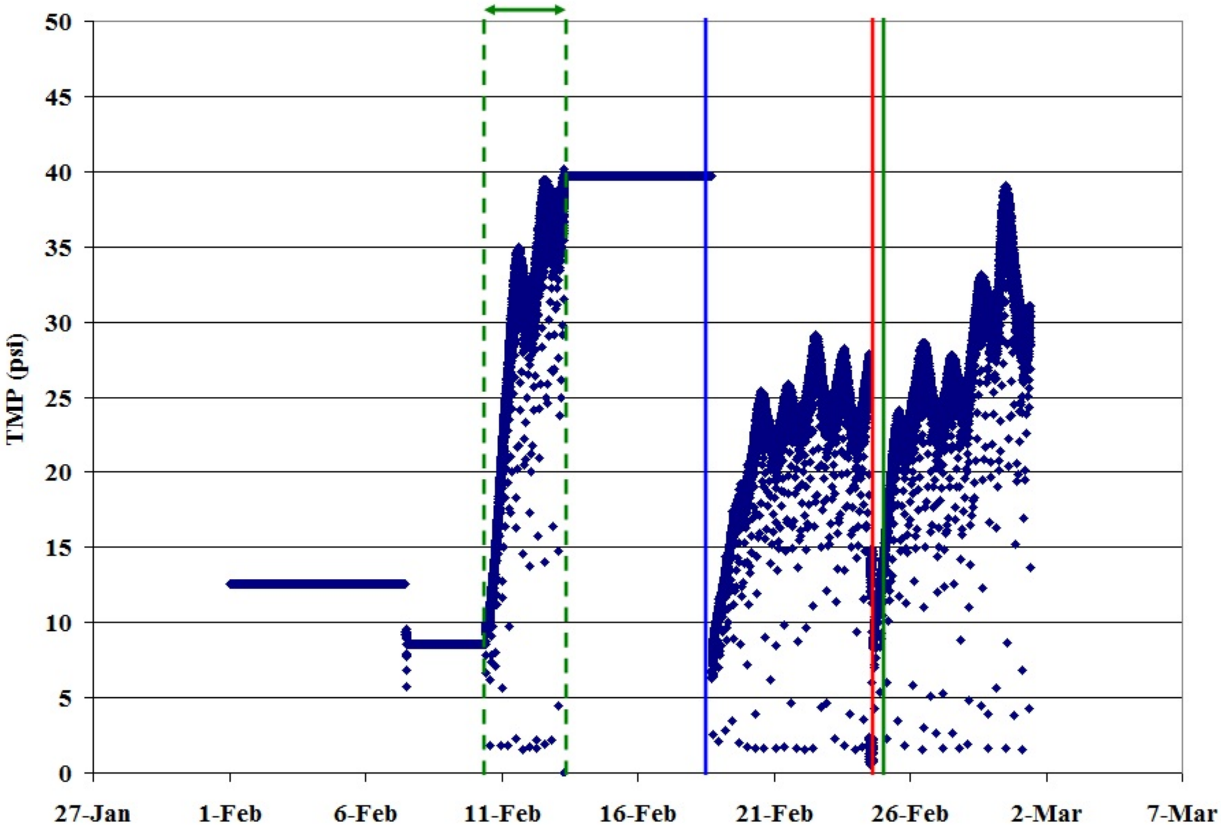


Figure 6.21. West Pall MF Unit TMP Profile for February 2012. Green, red and blue vertical lines indicate timing of bleach and acid EFMs and CIPs, respectively. The green dashed lines

bracket the modules performance prior to undertaking the special cleaning procedure resulting from the individual fiber cleaning study conducted by Pall Corporation.

The fibers looked very clean during the initial visual observation when the fibers were removed for test cleaning by Pall Corporation. In addition, the test run after plugging the fibers (but before any cleaning was done) showed a TMP of about 9 psi. This value was lower than what the average TMP had been in the previous couple of months (about 15-20 psi after EFMs). Therefore, the West Pall MF unit was run for couple of days until the TMP reached 39 psi, the runtime shown between the two dashed green lines in Figure 6.21. The purpose for this run was to build up material on the fibers of the module so that the real efficiency of the proposed CIP by Pall would be tested.

On the basis of Pall's suggestions, the length of the first step, which was thought to be unnecessarily long in the laboratory test on single fibers, was shortened for the CIP cleaning (represented as the blue line in Figure 6.21) to an overnight soaking while making sure that the cleaning solution was flowing through the fibers of the membrane, not just cycling outside of them and cleaning only the surface. Super Iron Out (first step) and bleach-sodium hydroxide (second step) were used as summarized below:

- Step 1: 23 hour permeate recirculation with 3.0% "Super Iron Out" (oxalic acid). Make-up water was RO product water. pH of the cleaning solution was 2.17 at the end of the run.
- Step 2: 24 hour permeate recirculation with 1.0% sodium hydroxide with 0.5% sodium hypochlorite. Make-up water was RO product water. pH of the cleaning solution was 12.57 at the end of the run.

After the CIP was completed, a membrane permeability test was performed on the unit and showed that about 90% of the original permeability of the module was recovered. Hence, the CIP with Super Iron Out was considered somewhat successful but not enough to fully recover the performance of the unit back.

5. The West Pall MF unit was run on MODE water for two weeks to test the effectiveness of the cleaning afterwards.

The run started on Saturday, February 18, 2012. The initial TMP was as low as 7 psi and followed a diurnal fluctuation, (Figure 6.21). This was the same behavior that the unit had prior to December, 2011. However, this time the TMP shifted about 10-11 psi downwards, probably due to the CIP cleaning effect. Previously the same diurnal fluctuation was seen around 36-37 psi. The specific flux was initially above 9 gfd/psi and stabilized around 2.5 gfd/psi.

Table 6.4. Membrane permeability comparison for West Pall MF unit throughout the testing.

Date and ID	*% Perm. of New Membrane*	*% Perm. of Baseline CIP*
New Membrane	100	N/A
10/26/10 (Baseline)	93.8	100.0
1/12/11 CIP	88.1	93.9
2/16/12 Pre-CIP	29.4	31.3
2/16/12 Iron Out	57.5	61.3
2/16/12 Caustic/Chlorine	84.2	89.8
3/15/12 Iron Out	71.0	75.6
3/16/12 Caustic/Chlorine	85.6	91.3

After the CIP, the TMP of the unit fluctuated around 25 psi for almost one week. In light of the results observed until then and after consulting with Pall Corporation, a couple of ideas emerged, including i) running the unit as it was and watching the performance; ii) decreasing the flux down to 40 gfd; iii) increasing the backwash frequency; and iv) performing another CIP with some minor changes in the procedure. It was decided to run a citric acid EFM as the first step and run a bleach EFM two hours after that to see the relative TMP changes, because decreasing the flux or increasing the backwash frequency would have added another variable in the equation and would have been more related to optimizing the performance of the unit, rather than trying to determine if the cleaning was successful or not. Therefore, the EFMs were performed and the unit placed back online. It ran another week to observe the efficiency of the EFMs and compare them with the CIP. TMP dropped again to 7 psi. However, this time the rate of increase was higher compared to that observed right after the CIP. Even though the TMP increased to almost 39 psi (due at least in part to the decrease of temperature on February 28), it dropped back down to below 30 psi later (Figure 6.21).

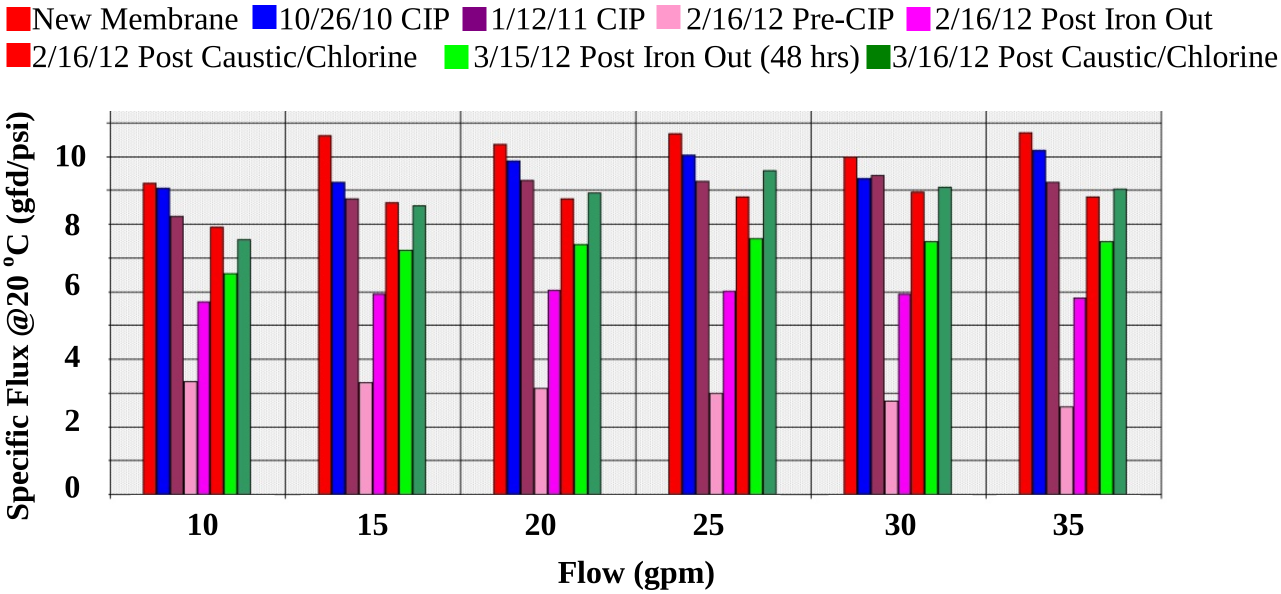


Figure 6.22. Specific flux comparisons at different flow rates and permeability recoveries for West Pall MF unit after different CIPs performed throughout the testing.

The unit was shutdown for almost eleven days until it was decided to test another CIP with some slight changes in the procedure. The new procedure involved a Super Iron Out solution (3% by weight) recirculation for 24 hours at pH of 2.00-2.50 at ambient temperature and a soaking period of 24 hours with the same cleaning solution as the first step. After measuring the membrane permeability, the second step was a caustic/chlorine solution with 1.0% sodium hydroxide and 0.5% sodium hypochlorite recirculation for another 24 hours at pH >13.0 at ambient temperature. And finally, the membrane permeability was measured. Results are presented in Table 6.4 and Figure 6.22, above.

At the end of the CIP (March 16, 2012), the membrane permeability recovered by 91.3%, with an increase of 1.5% compared to the previous CIP. The initial TMP and specific flux were almost 5.5 psi and 10 gfd/psi, respectively. The drop in the ambient temperature from 73 ^{o}F down to 61 ^{o}F on the same day the unit started running again showed its effect as a steep rise in the TMP. It increased almost 23 psi in the first 70 hours. However, it stabilized and trended downward as the temperature started increasing and fluctuated around 20 psi until a turbidity spike in the MODE water on March 25 (presented in Figure 6.23 with the TMP profile). The weekly scheduled regular citric acid EFM dropped the TMP only down to 15 psi, as well as all the other EFMs performed after this point. However, the rate of fouling was significantly lower and the TMP fluctuated between 20 and 30 psi. The original condition of the unit was never re-achieved completely (compare to early 2011 performance). Despite this, a sustainable run with weekly EFMs was indicated as achievable after the CIPs performed during the cleaning study of West Pall MF unit.

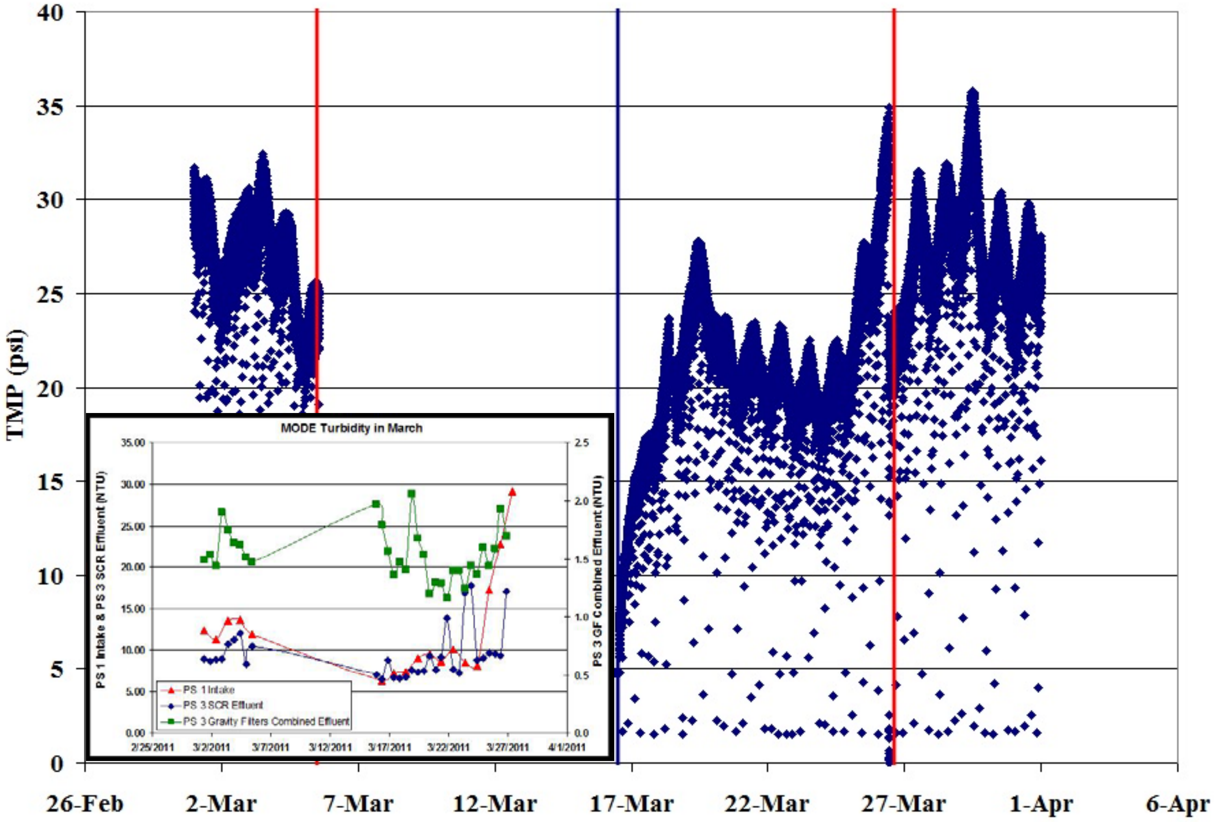


Figure 6.23. West Pall MF Unit TMP Profile for March 2012. Red and blue vertical lines indicate timing of acid EFMs and CIP, respectively.

A simple comparison graph of the TMP profiles for the West Pall MF unit observed at different times of the research testing (prior to Summer 2011, during Summer 2011, after Summer 2011 for both the West and East Pall modules), prior to the cleaning study CIPs, and after the cleaning study CIPs) is presented, below. When the TMP curves in that graph are examined, it can be seen that the initial starting TMP is not the only or necessarily most important parameter. The rate of increase in the first 1,000 to 1,500 minutes is a key parameter that defines the length of the run before the TMP reaches the cleaning-level (40 psi). During April and June 2011, the initial TMPs after a regular weekly EFM were higher than the ones after summer and in February 2012, but the rate of increase in April and June was lower than the later ones. This shows that there was a significant loss of permeability in the West Pall module, which was partially, but not totally, recovered by the CIP performed in February 2012 (looking at the TMP and specific flux curves of "before CIP" and "after CIP"). It is also important to notice where the specific flux stabilizes for each of these periods. The stabilized-level in the specific flux curves is lowest in April 2011 and highest "Before CIP 2012" (Appendix B-3). The October 2011 specific flux curve did not even have the time to stabilize before the high TMP shutdown limit was reached. The CIP in February 2012 brought that level back up partially but an immediate loss was observed right after the EFM on February 24. The second CIP performed during the cleaning study did a better job in recovering the performance of the unit.

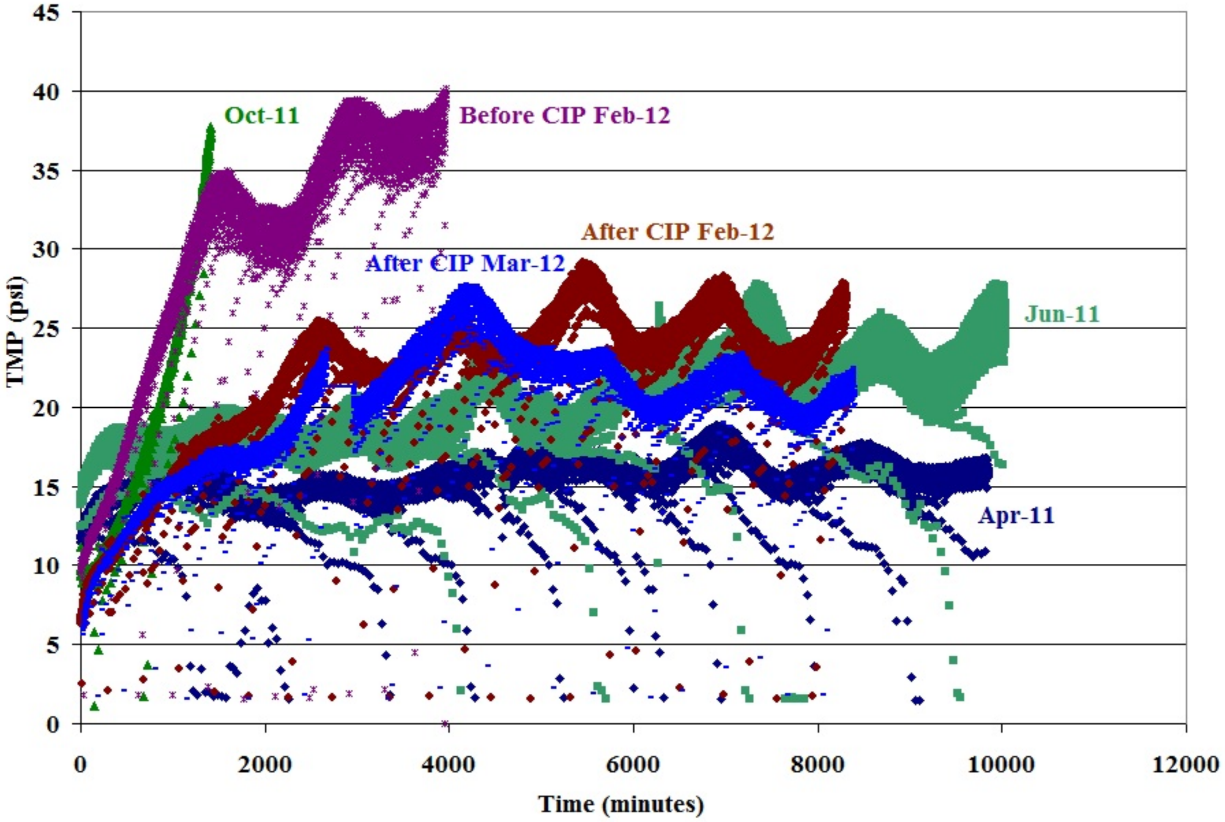


Figure 6.24. West Pall MF Unit TMP comparison plots.

Analyzing these results and observations, it could be concluded that the CIPs during the cleaning study were partially successful and could likely be improved to obtain a better cleaning efficiency. It is also very likely the EFM efficiency could be improved, for instance by adding a soaking period; using different chemicals or different concentrations of the same chemicals; or passing the cleaning solution through the fibers' pores rather than just recirculating on the outside of the fibers as was done during this cleaning study. Reliance on EFMs that do not utilize permeate recirculation most likely result in buildup of an iron-organics foulant that became increasingly harder to remove by CIP over time (aging, recalcitrant fouling).The earlier CIPs and all the EFMs that were performed during the testing may have only cleaned the surface of the fibers but not inside the pores. The feed-side ITs, even though they were cancelled by November 2011, may have also contributed to the decreased performance of the unit, since they would push the material built up on the membrane, deeper into the pores, making it harder to remove. The parameters, such as the type of cleaning, the strength of the cleaning solutions, the frequency of the cleanings, the duration of the cleanings, etc., are extremely important, not only from the operational point of view, but also in determining the economic cost of the unit's operation.

Integrity Test (IT) Results

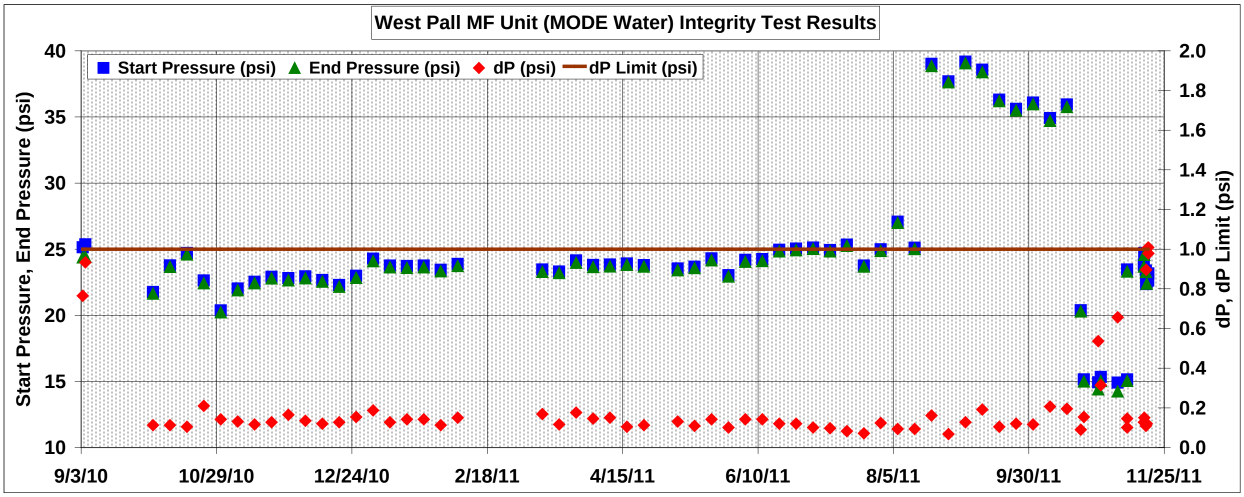


Figure 6.25. Integrity test (IT) results for the West Pall MF units through Research study.

One anomaly that might have affected the performance of the West Pall MF unit happened by mid-August 2011, when the starting pressure for the IT increased to almost 40 psi due to an accidental adjustment on the air inlet valve. The error was corrected by mid-October.

The integrity of the membranes for the West Pall MF unit was checked regularly throughout the testing until IT was discontinued in mid-November 2011. No indications of faulty fibers were observed at any time on any MF unit.

6.2.2.3 Iron and Manganese Removal

In previous sections of the report (particularly section 6.1.2), iron and manganese concentrations in MODE water and removal efficiencies via the pretreatment techniques used were discussed briefly. During this research study, it was observed that the concentrations of iron and manganese fluctuated depending on both operational and environmental factors, such as the flow rate in the MODE, diversion of DPOC water, storm events and agricultural operations. This study was unable (nor was it tasked with mechanistically explaining) the pattern of each of these factors and their individual impact on the water quality in the MODE. That said, it seems likely the iron and manganese concentrations, solubility and size distribution in the particle/colloidal fractions may have a significant impact on overall process performance and therefore need to be investigated in a separate study that focuses on the water quality.

Iron Removal

Total iron concentration in Alternative 17a pretreatment was measured at certain locations to study the efficiency of each unit operation. SCR influent concentrations were measured after the chlorine injection point. Generally, iron is very easy to oxidize from its soluble state, Fe^{+2}, to its insoluble state, Fe^{+3}. Therefore, all the iron from this point forward in the treatment train was expected to be fully oxidized and removable via the SCR and DMGF combination. Two important points stand out in Figure 6.26. The first one is the change in the water composition after summer 2011 and the second one is the removal of the particulate iron. In the earlier sections of the report, the change in the water composition in the MODE was mentioned. The increase in the iron concentration by September 2011 is indicative of this change. The total iron concentration did not return to pre-summer levels until the end of this research study. This graph also shows that DMGF were removing iron throughout the study, but the amount removed increased significantly beginning in early September.

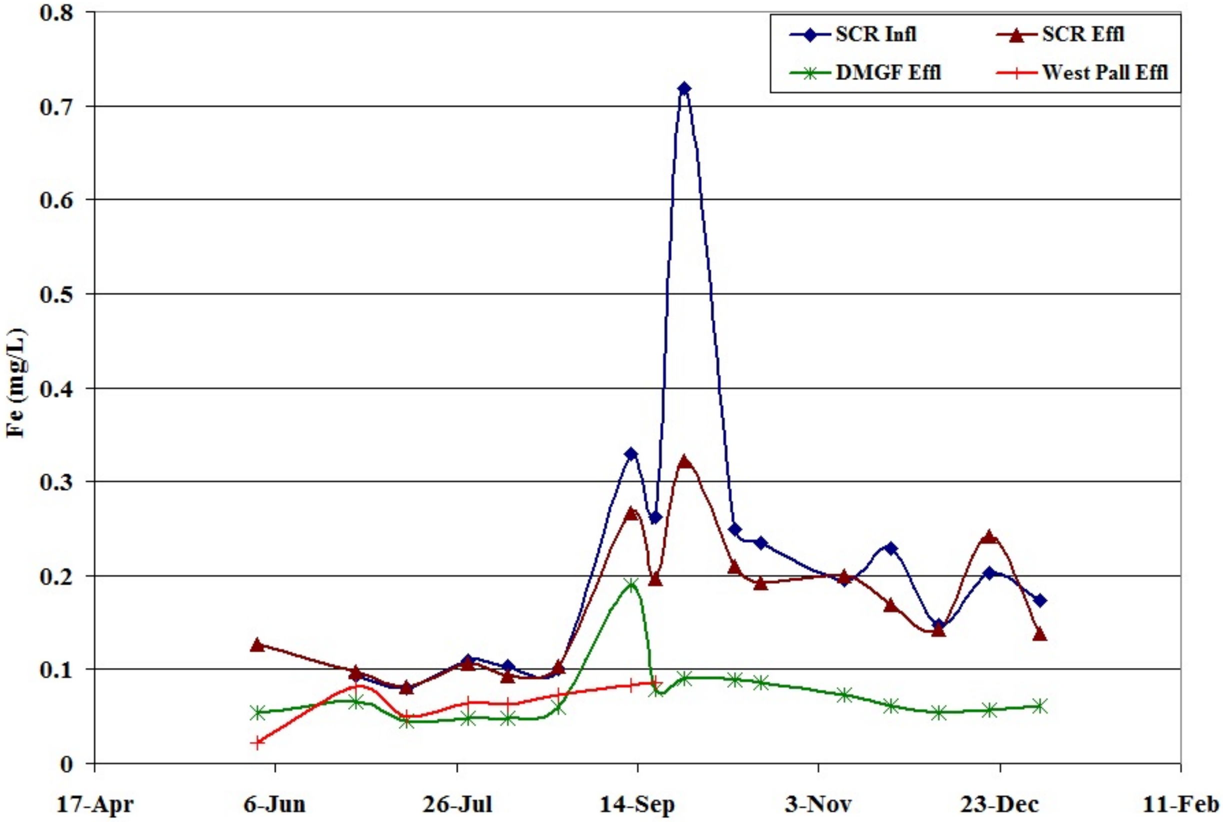


Figure 6.26. Total iron concentration profiles through Alternative 17a pretreatment operations between June and December 2011.

When the removal efficiencies of each unit running on PS3 were examined, an indication of the iron composition can be observed. The removal efficiency of the SCR was inconsequential throughout the study except in September and October. This shows that the particulate iron coming into the YDP via the MODE increased considerably during these two months. However, most of the removal was achieved via DMGF treatment throughout the rest of the testing period. The fact that there was no significant change in the iron concentration measured at the effluent of the DMGFs shows the increase measured after summer was probably due to particulate iron. The iron that was left in the water after the gravity filters was either in dissolved form (might be also iron-organic complex) or in particulate (colloidal) form with sizes smaller than 0.1 μ, since the dissolved iron concentration that was measured at the effluent of the MF unit was practically the same as the concentration at the DMGF effluent. Figure 6.27 shows that there was no noteworthy removal of dissolved iron in PS3 pretreatment prior to summer 2011. However, 20% or less dissolved iron removal efficiency was recorded in the second half of the study.

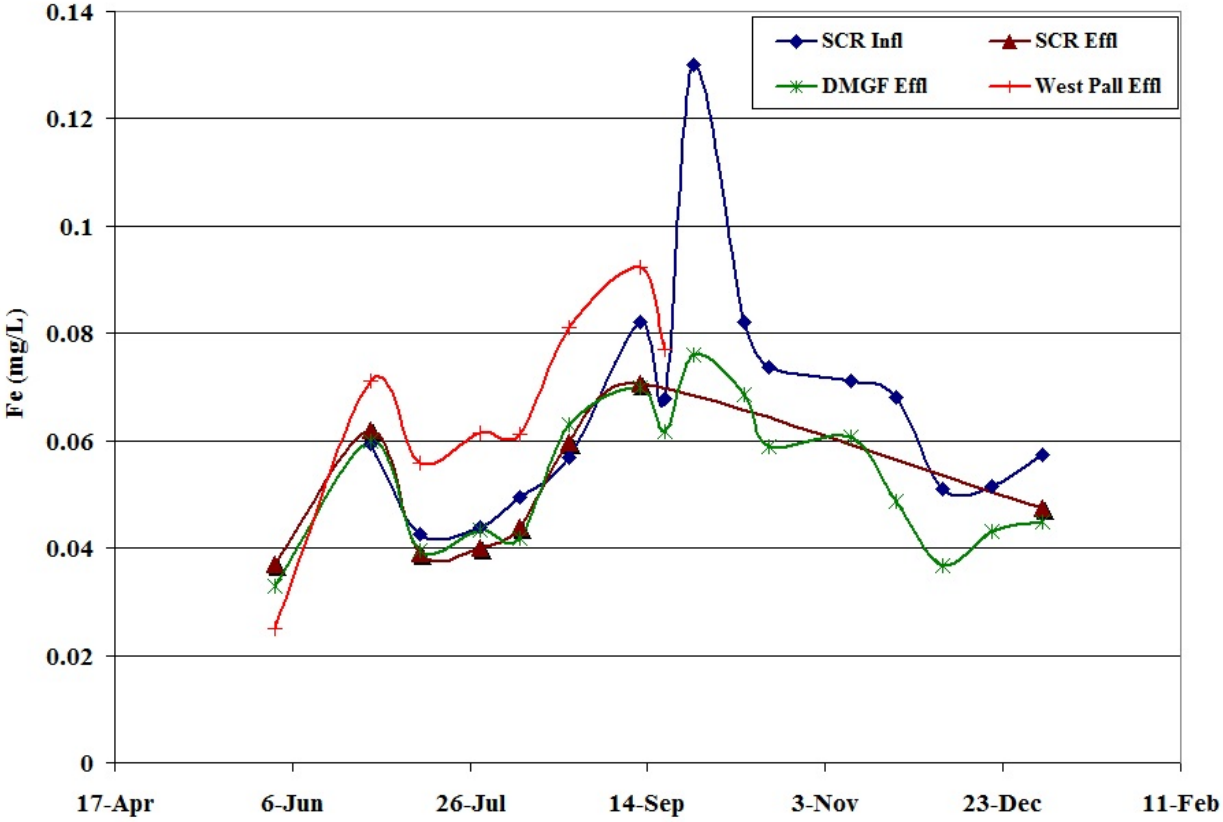


Figure 6.27. Dissolved iron concentration profiles through Alternative 17a pretreatment operations.

On the other hand, the amount of water treated via microfiltration was sufficiently large that the accumulation on the fibers caused by even a relatively small fractional removed iron could be significant in reducing the performance of the unit. The iron that was removed would possibly remain undetected via ICP-MS analysis because the concentration change could be very little. However, even though the ICP-MS measured change in iron in grab samples before and after MF indicates negligible removal, when the West Pall MF unit was cleaned, 4.25 mg of iron was collected in the cleaning solution.

Manganese Removal

The total manganese concentration in PS3 followed the same pattern as the total iron concentration. It rose rapidly in late summer 2011 and stayed around 0.3 mg/L afterwards until the end of the study. However, the manganese level prior to September 2011 was always below 0.05 mg/L, except for the first sampling occasion in June at the SCR effluent of 0.19 mg/L. This shows that the change in the water composition during summer affected the manganese levels in the MODE, as well. The composition of the manganese entering the YDP changed. Both the particulate manganese and the dissolved manganese increased around the same time. Almost half of the total manganese, 0.3 mg/L, in the MODE was coming from the dissolved portion, 0.15 mg/L, measured at the SCR influent. Dissolved manganese was partially removed in the SCR (Figure 6.29), however, the removal efficiency for total manganese in the DMGF was very high, averaging around 93% after September 2011 (Figure 6.28).

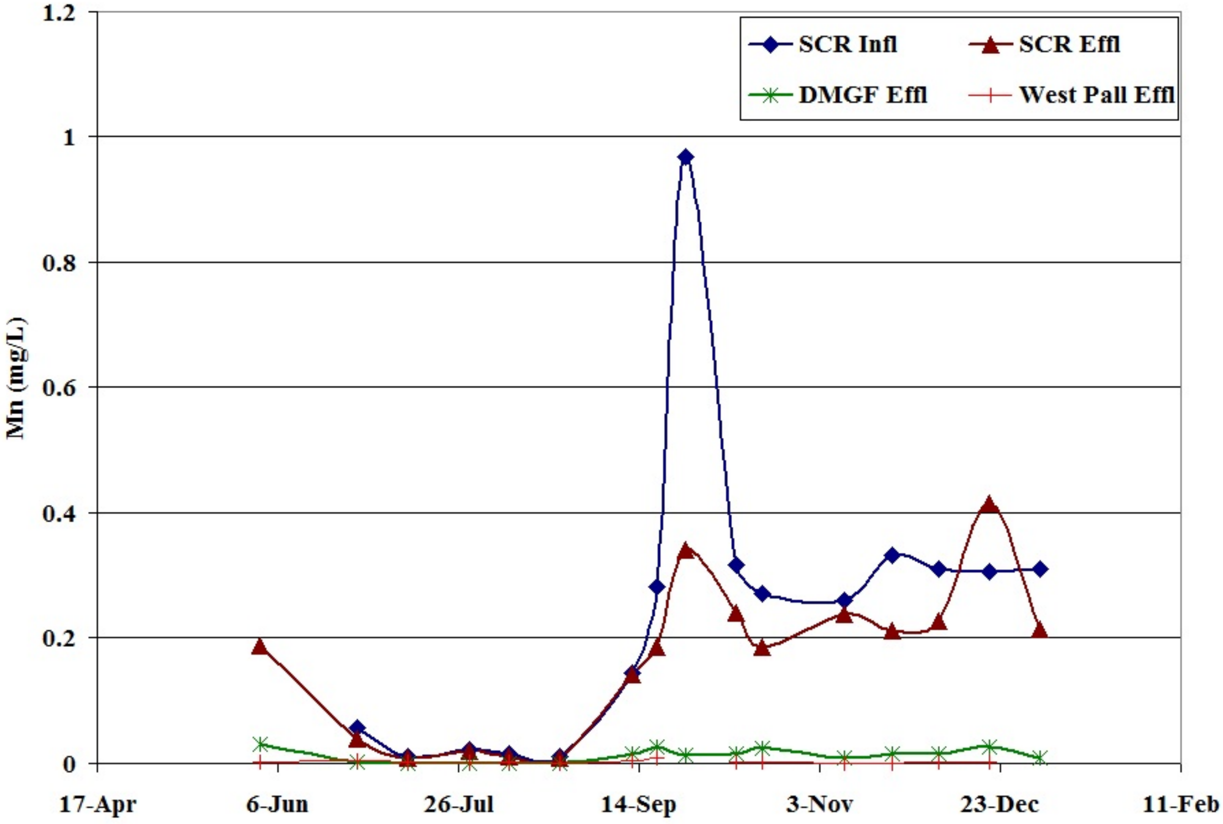


Figure 6.28. Total manganese concentration profiles through Alternative 17a pretreatment operations between June and December 2011.

It was interesting to see the removal of dissolved manganese in the SCR because dissolved manganese removal typically requires an active manganese surface for adsorption and oxidization. There are two possible explanations for this behavior. The first one is the sedimentation of the particles smaller than 0.45 μm in the SCR. The dissolved portion of the manganese was operationally defined as that passing through a 0.45 μm filter. However, this type of definition is water specific and it does not necessarily mean that any particle that can pass through a 0.45 μm filter is truly dissolved in the water. In fact, particles that were so-called dissolved did get removed via sedimentation in the SCR. The second and less likely explanation for this behavior is that the manganese surface that formed and was visible on the SCR surface helped remove the dissolved portion of the ion. The former one is a more likely explanation because the removal of total manganese via the West Pall Mf unit is obvious, proving that particular manganese sizes between 0.1 μm (microfiltration size) and 0.45 μm (filter paper size) exists. Please, see the zoomed in plots for DMGF and West Pall MF effluents in the upper left corner of Figure 6.29.

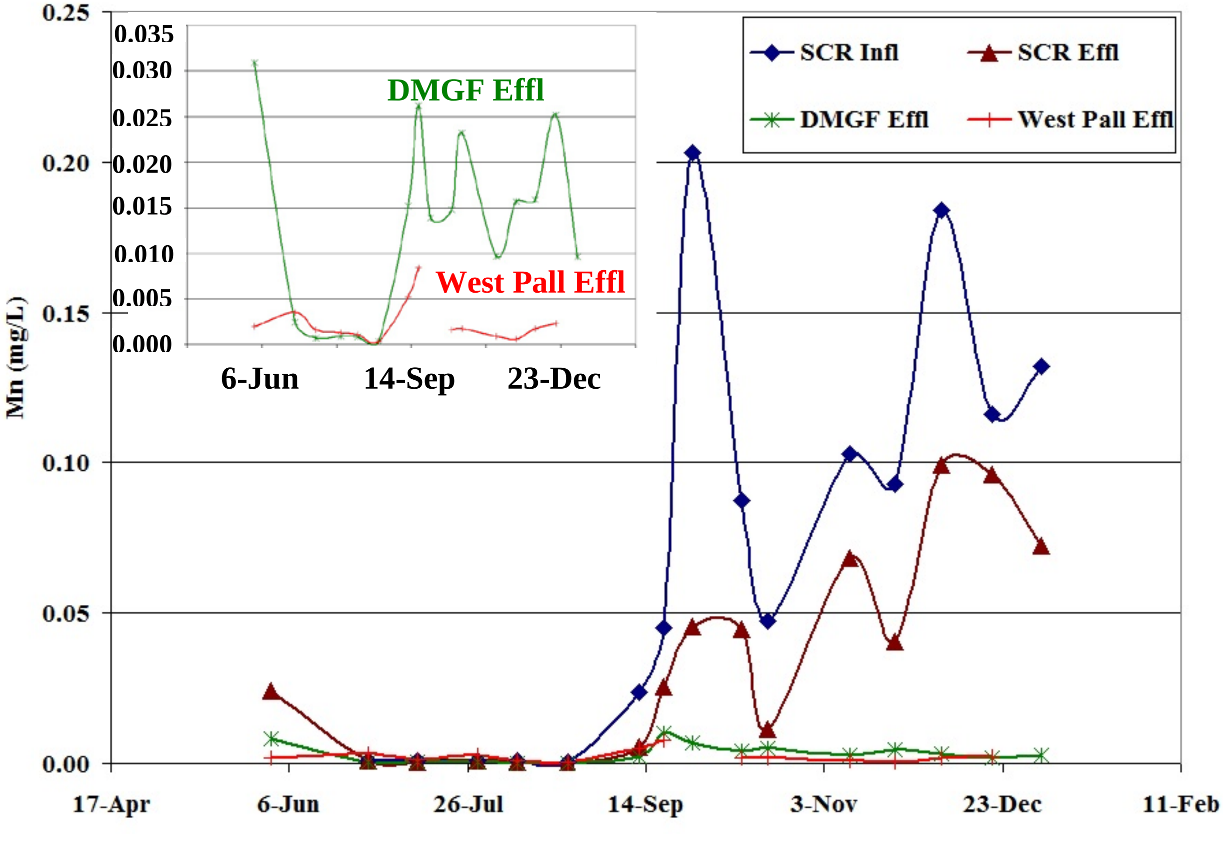


Figure 6.29. Dissolved manganese concentration profiles through Alternative 17a pretreatment.

6.2.3 BDOC Analyses

During Round 1, BDOC samples were collected at four different locations on Alternatives 10 and 17a running with MODE water, including PS1 SCR effluent, PS3 gravity filter effluent, and ETA 1 and ETA 4 influents. ETA 1 followed PS3 and the West Pall MF unit, and ETA 4 had the PS1 as pretreatment. There were no prominent BDOC concentrations detected at any of the sampling locations. It is significant that higher DOC and BDOC concentrations were measured in the effluent of West Pall MF unit compared to its feed concentrations. All the samples collected at this location had the same elevated level in concentration. All the samples analyzed had consistently low levels of DOC and BDOC so no further sampling was undertaken. Table 6.5 below shows the average DOC and BDOC concentrations for the referred locations.

Table 6.5. DOC and BDOC concentrations in pretreatment units of MODE water.

Sampling Location	*DOC (mg/L)*	*BDOC (mg/L)*
PS1 SCR Effluent	2.1	0.13
PS3 GF Effluent	2.3	0.17
ETA 1 Influent (West Pall MF unit effluent)	2.9	0.37
ETA 4 Influent (PS1 GF Effluent)	2.0	0.20

6.3 RO Performance

RO units running on MODE water operated between September 2010 and December 2011. RO performance results are reported in three separate sections depending on their operating parameters and purposes. The element screening (low recovery or ETA) results presented in Section 6.3.1 are investigated in two segments: Round 1 and Round 2. The results from the two-stage MU units running with standard fluxes (12 gfd average) in Round 2 full-array testing are presented and discussed in Section 6.3.2 following the element screening results. The results from the two units running at high-recovery (85%) and high-flux (15 gfd on average for MU and 18 gfd for associated ETA) and one MU testing with two other membrane types (Toray

TML and DOW XFR) are presented in Section 6.3.3. HPC results for all the RO units are presented in a separate section, Section 7.4.

6.3.1 Element Screening (low-recovery)

Four ETA units (ETAs 1-4) were used during the testing to evaluate seven different types of membranes in two different rounds of operation. Round 1 that lasted almost 3,000 hours (4 months) tested four different types of membranes (Toray TML 10, Koch ULP, and Hydranautics LFC3 and ESPA2). Due to a combination of YMC flow disruptions and gravity filter conditioning, ETA 2 on Alternative 22 had a lower runtime (~2,400 hours) than the other three ETAs. Round 2, which lasted more than 3,500 hours, tested three more membrane types (DOW BW30 XFR, CSM FE and CE). Toray TML 10 was kept the same for both rounds for the purpose of direct comparison. During Round 1 and Round 2, ETAs operated at an average 15 gfd and approximately 13% water recovery. The average membrane area per element was assumed as 25 ft^2, initially, until the actual membrane areas were measured. Hence, the ETAs ran at a feed flow rate of 8.0 gpm. However, the performance results shown subsequently were updated with the actual membrane areas based on the average areas measured in autopsies of retired elements. The purpose for ETA runs (Round 1 and Round 2) was to test the fouling potential and performance relative to different waters and pretreatments of different types of membranes manufactured by various companies.

The water transport coefficient (A), salt transport coefficient (B), B/A ratio, water flux, percent salt passage, percent water recovery, product flow rate, product total dissolved solids concentration and product pressure for each element were calculated and monitored daily by the Test Manager and operators and evaluated weekly by the TAT members. Other parameters measured, calculated and monitored in the same manner include temperature, feed and reject pH, feed free and total chlorine concentrations, feed SDI, feed and reject flow rates, feed and reject total dissolved solids concentrations, feed and reject pressures and percent salt mass balance deviation for each unit and differential pressure and element flow coefficients for each vessel. However, only feed temperature and pH of the units, water transport coefficient, salt transport coefficient, B/A ratio for each element and the element flow coefficient for each vessel are presented in the following discussion. All ETAs were operated on RO permeate for two hours at the start of each round to flush the new membranes. Please refer to the appendix for the other results.

6.3.1.1 Round 1 Testing

ETAs 1 and 4 started running on September 28, 2010 for Round 1 testing. Operating on pretreated MODE water, ETA 4 (Alternative 10) ran with a feed pH of 6.8 until January 6. The pH was reduced to 5.8 until the end of Round 1 testing to stop the increase in STC values and to stabilize the decreasing WTC values. On the other hand, ETA 1 (Alternative 17a) ran with a feed pH of 6.8 throughout all Round 1. The temperature and feed pH profiles for both of the units are presented in Figure 6.32, below. The early WTC values following the initiation of the testing ranged between 7 and 14.5 × 10^{-12} m/s.Pa. The Koch ULP element had the highest and Hydranautics LFC3 had the lowest WTC values for both of the MODE alternatives (Figure 6.30). Even though the starting WTC values for both alternatives were very close to each other, the decline in WTC for ETA 4 running on lime-softened MODE water was quite significant compared to ETA 1 running on microfiltered MODE water.

The WTC values to which Alternative 10 (ETA 4) approximately settled were lower, especially for Koch ULP and Toray TML10 than those for ETA 1. A slight difference was also observed for Hydranautics ESPA2. However, Hydranautics LFC3 performed with very stable WTC values, around 7 × 10^{-12} m/s.Pa, throughout Round 1 regardless the pretreatment type.

The absolute values of initial salt transfer coefficient (STC) for all tested membranes except Koch ULP were lower on Alternative 10 (ETA 4) than Alternative 17a (ETA 1). Only Koch ULP had a higher starting STC on ETA 4 than ETA 1. A direct correlation between the WTC and STC of a membrane was observed during Round 1. This means that the membranes having higher WTC tended to have higher STC, as well. Hence, Koch ULP had the highest WTC and the highest STC among the four membranes tested. The increase in the STC values throughout Round 1 is presented in Table 6.6.

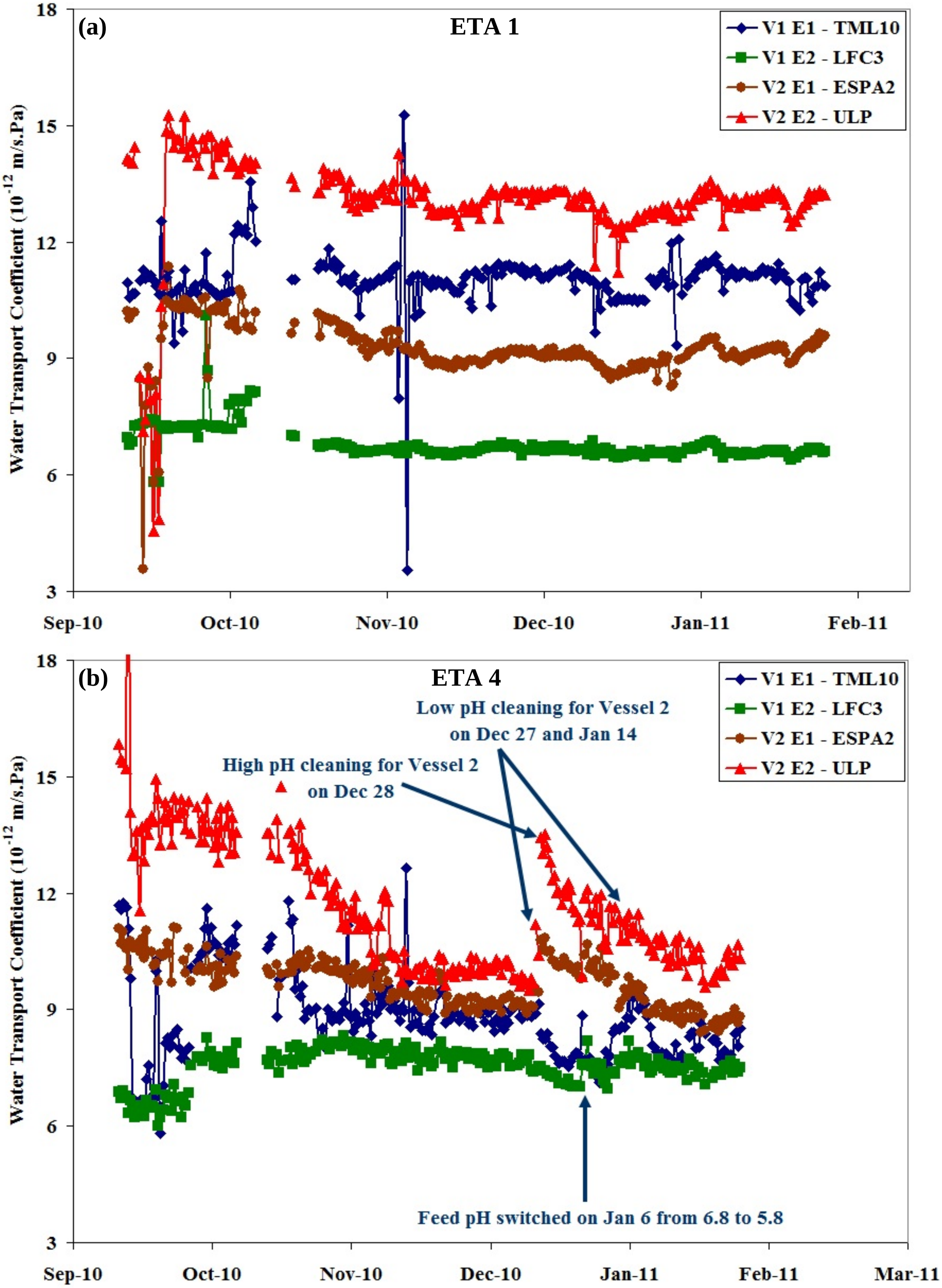


Figure 6.30. Water transport coefficient profiles for (a) ETA 1, Alternative 10, and (b) ETA 4, Alternative 17a, during Round 1.

Table 6.6. Percent change in STC for membranes tested in ETA 1 and ETA 4 over entire trial duration. The values in parenthesis represent the percent change in STC for the trial duration prior to any cleaning on the unit.

	ETA 1 (Alt. 17a)		**ETA 4 (Alt. 10)**	
	% change	**% per 1000hr**	**% change**	**% per 1000hr**
Toray TML10	12.24	4.31	-3.93	-1.60
Hydranautics LFC3	22.07	7.77	29.08	11.82
Hydranautics ESPA2	27.34	9.62	11.06 (30.53)	4.12 (18.49)
Koch ULP	22.30	7.85	-5.55 (26.89)	-2.06 (16.29)

The percent changes per 1000 hours were significantly higher in ETA 4 for all membranes but Toray TML10 (Table 6.6). In fact, they were high enough for ESPA2 and ULP (the values presented in parenthesis in Table 6.6) to motivate cleaning ETA 4 Vessel 2 on December 27, December 28, and January 14 with low pH, high pH, and low pH solutions, respectively. Please, refer to Appendix A-9 and A-10 for the high and low-pH cleaning procedures. While the WTC for both membranes in vessel 2 was restored temporarily, the trend in STC increase continued following both low and high pH cleanings. After a very rapid decrease in WTC for both membranes in the week following the December 28, high pH cleaning, the feed pH of ETA 4 was dropped to 5.8 (from 6.8) on January 6, 2011. This change in the feed pH helped to stabilize the STC immediately and, arguably, the WTC in the long term. The effect of the pH change on WTC in the ETA 4 elements was not clear cut as vessel 2 element WTCs declined further after the change and the vessel 1 element response was negligible.

A second low pH cleaning was performed for ETA 4 Vessel 2 on January 14 aiming to drop the STC values back to their original starting levels. This low pH cleaning partly achieved its aim (Table 6.6 and Figure 6.31) in that the ESPA2 and ULP STC values immediately decreased. The STC of Hydranautics LFC3 and Toray TML10 followed almost the same pattern in both ETA 1 and ETA 4 during Round 1. LFC3 had a slightly lower STC value than TML10 in ETA 1. They both showed a slight decrease during the last month of the ETA 4 run after the feed pH change in January. This decrease was enough to bring the STC for TML10 below its starting value, causing a negative percent change. There was no significant change of WTC observed for neither TML nor LFC3 in ETA 4 due to the pH change.

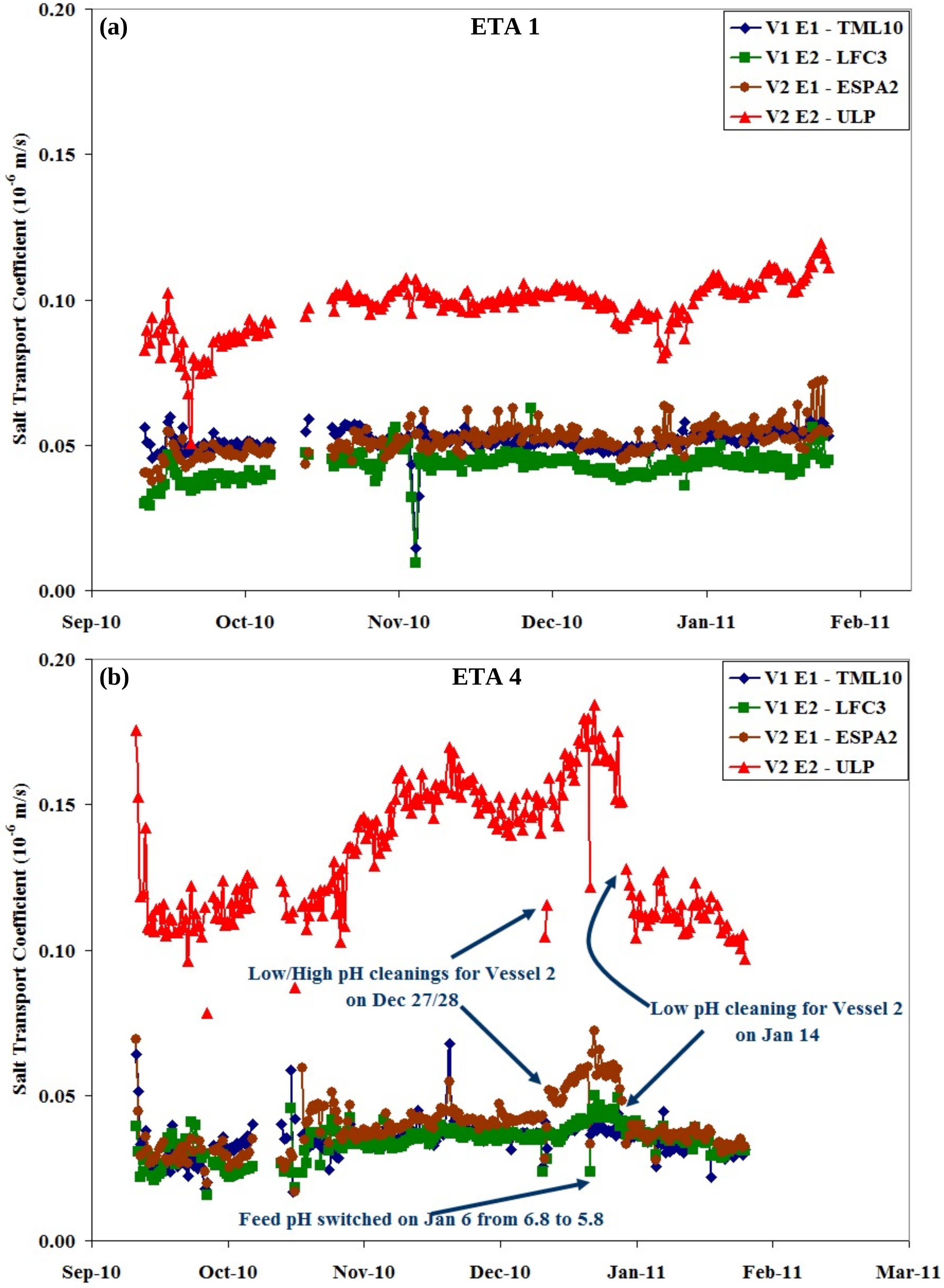


Figure 6.31. Salt transport coefficient profiles for (a) ETA 1 and (b) ETA 4 during Round 1.

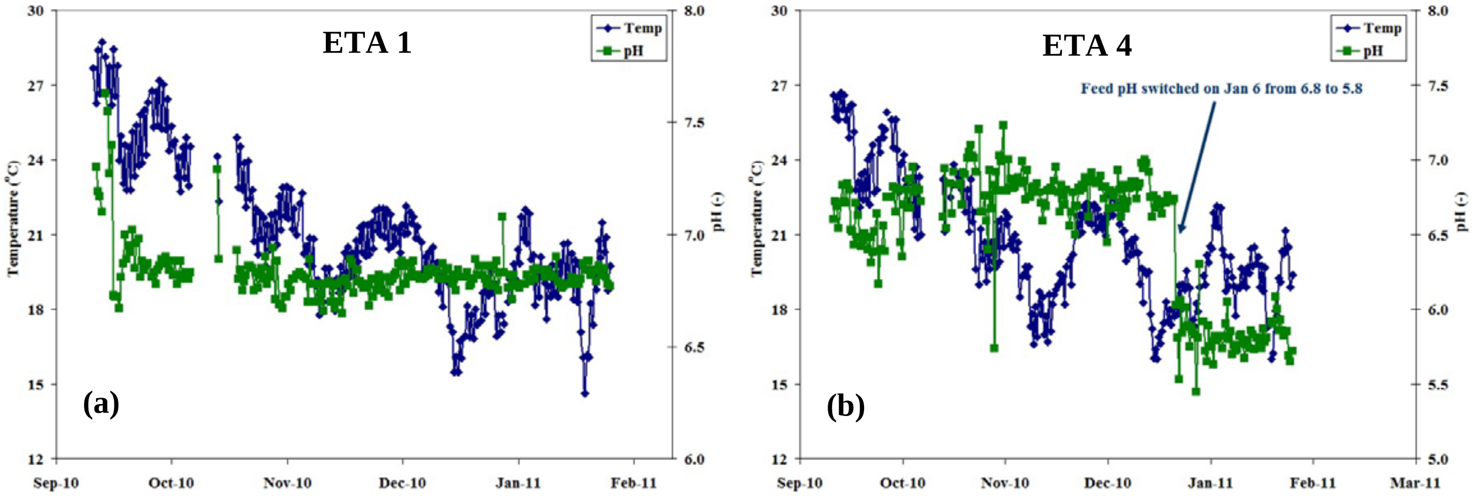


Figure 6.32. Temperature and pH profiles for (a) ETA 1 and (b) ETA 4 during Round 1.

A large drop in water temperature from high twenties to mid teens in degrees Celsius took place through Round 1 between September and January. However, no clear pattern on neither WTC nor STC coefficients was observed in either of the units due to that temperature drop. All the parameters presented are temperature corrected as defined in the Methods and Materials section of the report.

As with the STC, B/A ratios for ETA 4 were relatively lower than the ones for ETA 1. The only exception was the Koch ULP element, which had a higher B/A ratio in ETA 4 compared to ETA 1. The minor increase in this parameter for all the membranes through Round 1 is due to a combination of the WTC loss and STC increase, which could be explained by fouling on the membrane surface. Membrane degradation is often a major suspect for a B/A ratio increase in time. However, the reason is unlikely to be membrane degradation in this situation since all WTC values stayed constant or decreased slightly. The sharp increase in B/A ratio for the Koch ULP and the small increase in Hydranautics ESPA2 in ETA 4 Vessel 2 were restored after the cleanings and the pH adjustment. This restoration also suggests membrane degradation is not a dominant factor. More stable WTC, STC and B/A ratio parameters were achieved by the end of the run for Round 1 membranes.

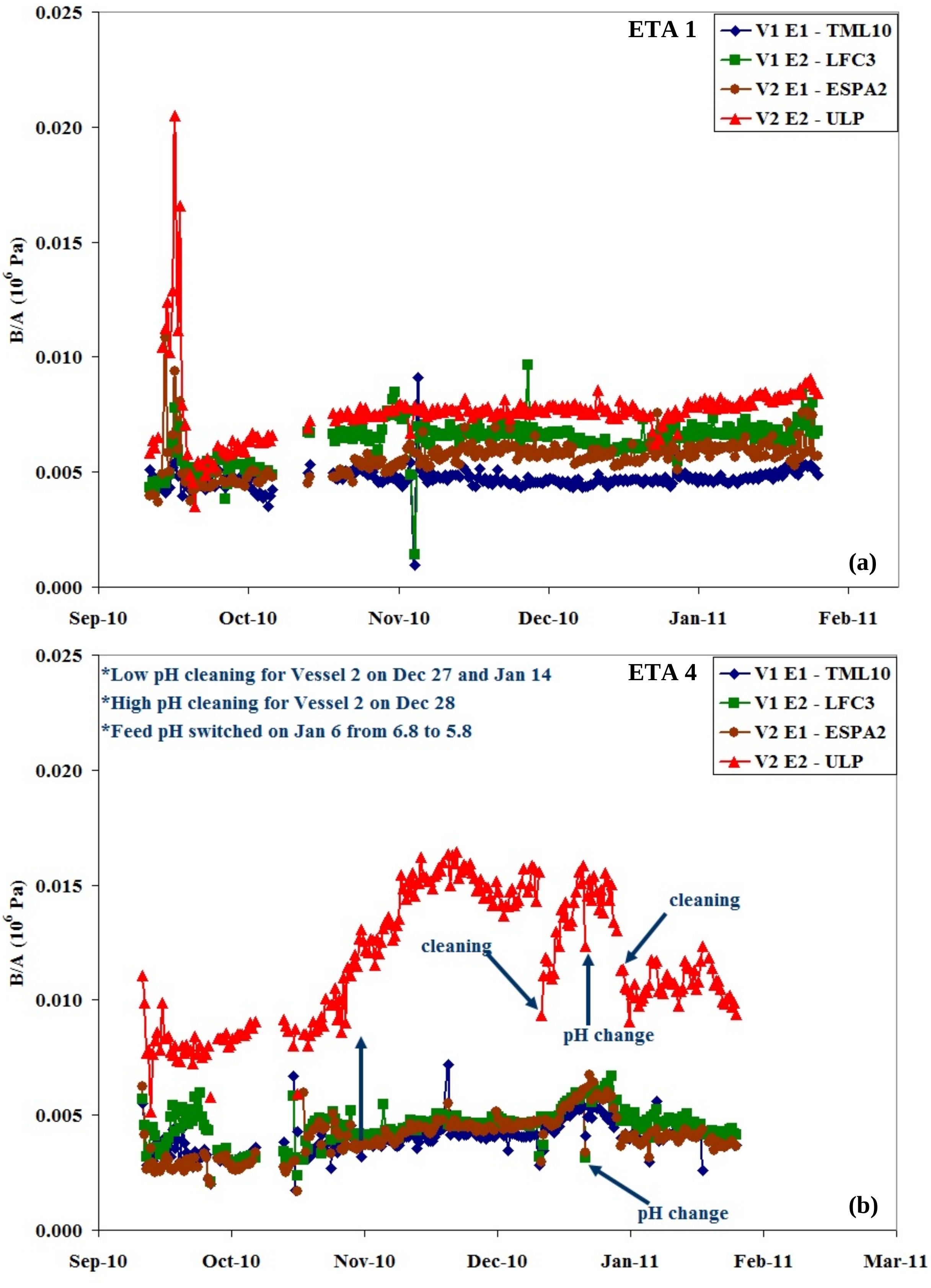


Figure 6.33. B/A ratio profiles for (a) ETA 1 and (b) ETA 4 during Round 1.

The pressure drop across each RO stage is an indicator of possible fouling. The temperature corrected element flow coefficient (C_e) is calculated for each vessel and normalizes the pressure drop by flow rate and temperature (Figure 6.34). After the fluctuation during the first month of operation, a very stable C_e was observed for both vessels in ETA 1. Hence, C_e values show no evidence of fouling in ETA 1. On the other hand, a slow but continuous decrease in both vessels of ETA 4 was observed until the pH switch. The lower feed pH helped to stabilize the C_e values and the low and high pH cleaning events in December for Vessel 2 restored the C_e back to its initial value. In fact, a minor increase in the C_e was witnessed for Vessel 1 in ETA 4 after the pH adjustment, meaning the foulant material may possibly be removed successfully by low pH operation and/or cleaning (although this conjecture is not supported by a return of the WTC to their initial values (see Figure 6.30)).

In summary, based on the operating and the calculated parameters of the ETA units, fouling and material buildup was indicated on ETA 4 running on lime-softened MODE water (current pretreatment method of YDP). The decrease in the WTC and C_e values and the increase in STC and B/A ratios were indications of this fouling. Lowering the feed pH helped to rectify this and helped to stabilize the parameters during the last month of operation, although whether or not the WTC stabilized cannot be positively concluded because of the short operational time after the pH change. Hydranautics LFC3 performed stably regardless of the pretreatment type with MODE water, even though it had the lowest WTC. The low STC value may make it a favorable membrane for this type of water for extended operation (depending on the economic trade-off between WTC and STC effects).

The Round 1, ETA 1 and 4 rejection rates for the important constituents, including major cations and anions, are calculated using the feed and product concentrations of the relevant ions that were measured in the lab by ICPMS (Table 6.7). Please, see Appendix C-2 for the detailed water quality analyses of the feed, product and reject streams of each ETA unit.

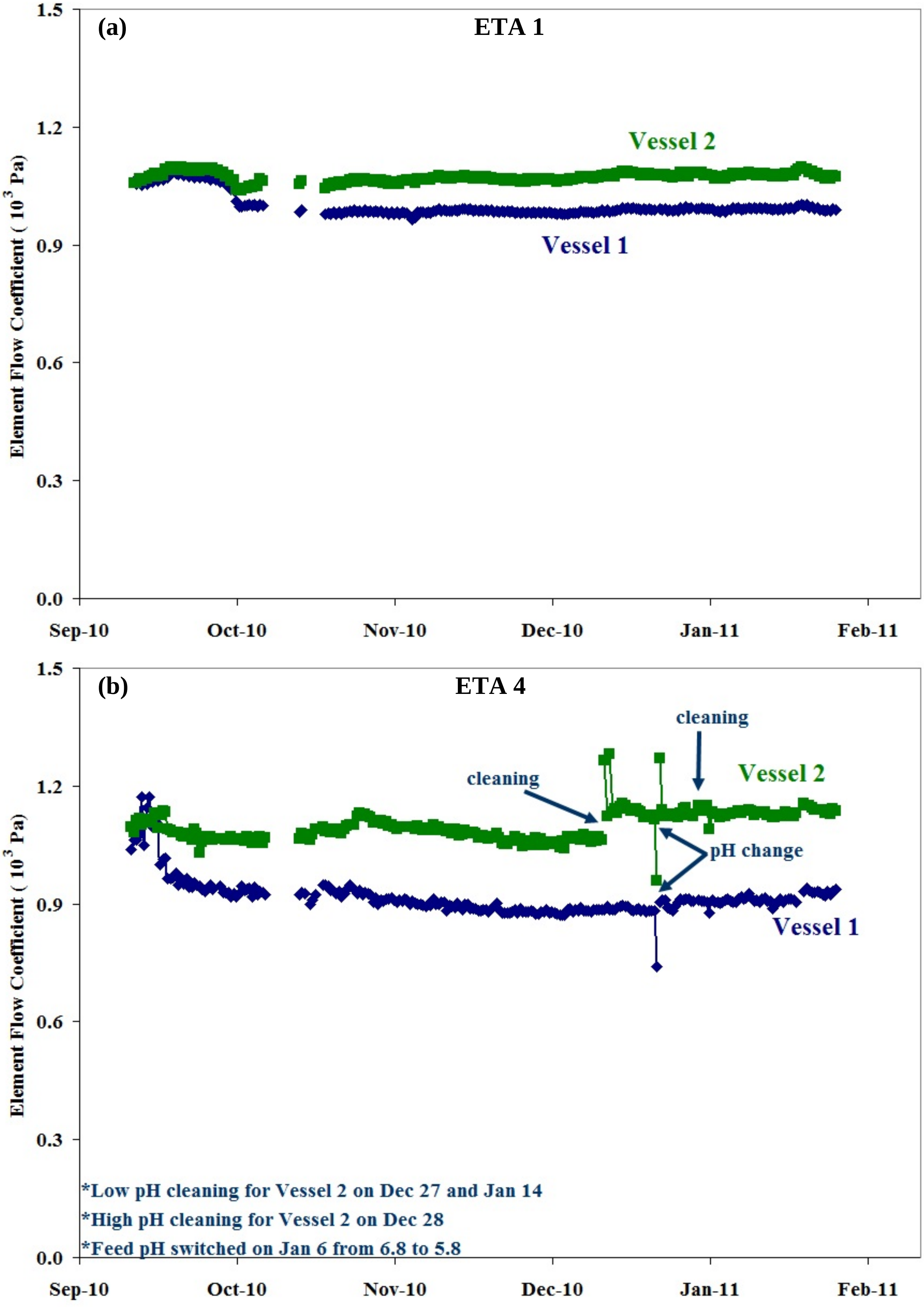


Figure 6.34 Element flow coefficient (C_e) profiles for (a) ETA 1 and (b) ETA 4 during Round 1.

The Koch ULP showed much lower rejection rates while treating the MODE water compared to the other tested membranes (Table 6.7). Those numbers are highlighted in the table. This matches with the relatively elevated salt passage and STC values of ULP during Round 1. The ULP's overall total salt rejection is below 99% for ETA 1 and below 98% for ETA 4 (lime-softened MODE water), while all the other membranes had higher than 99% rejection for the total salt concentration. The bicarbonate, hence the total alkalinity, rejection rate is much lower in lime-softened MODE water since the pre-treatment removes the buffering capacity significantly, so the pH difference between product and concentrate streams is accentuated for this pretreatment approach.

Table 6.7. Rejection rates (in %) of important parameters for each membrane tested in ETA 1 and ETA 4 during Round 1. Lower rejection rates compared to its accompanied membranes are highlighted in the table.

	ETA 1				**ETA 4**			
	TML10	**LFC3**	**ESPA2**	**ULP**	**TML10**	**LFC3**	**ESPA2**	**ULP**
Bicarbonate	96.19	96.38	96.22	95.45	75.81	82.79	78.31	76.71
Calcium	99.94	99.97	99.98	99.94	99.94	99.99	99.95	99.76
Chloride	99.22	99.24	99.16	98.21	99.19	99.11	98.97	97.03
Conductivity	99.23	99.32	99.27	98.52	99.41	99.42	99.29	97.61
Iron	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Magnesium	99.95	99.99	99.99	99.95	99.95	100.00	99.96	99.75
Manganese	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Nitrate as N	96.93	96.20	96.04	91.72	96.60	95.15	94.75	91.17
Potassium	99.13	99.33	99.24	98.33	99.37	99.68	99.45	97.78
Silicon Dioxide	99.44	99.36	99.17	97.44	99.40	99.18	98.90	97.33
Sodium	99.07	99.17	99.11	98.19	99.36	99.39	99.25	97.45
Strontium	99.95	99.98	99.98	99.95	99.96	100.00	99.96	99.78
Sulfate	99.83	100.00	100.00	100.00	99.84	100.00	100.00	99.18
Sum of Anion	98.98	99.00	98.94	98.30	98.97	99.00	98.83	97.44
Sum of Cation	99.40	99.47	99.44	98.86	99.53	99.56	99.46	98.11
Tot. Alk. as CaCO3	96.26	96.45	96.29	95.53	75.88	82.84	78.35	76.78
Tot. Hard. as CaCO3	99.95	99.98	99.98	99.95	99.95	99.99	99.96	99.75

Total Organic Carbon	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total Salt	99.12	99.19	99.14	98.57	99.19	99.29	99.12	97.80

6.3.1.2 Round 2 Testing

ETAs 1 and 4 started running on March 11, 2011 for Round 2 testing. The main purpose of Round 2 testing was to evaluate three additional membrane types from two different manufacturers. Operating on pretreated MODE water, ETA 4 (Alternative 10) ran with a feed pH of 5.8 until July 1. The pH then increased to 6.0 for the next three months until the end of Round 2 testing. On the other hand, ETA 1 (Alternative 17a) ran with a feed pH of 6.8 until August 26. The pH was then dropped to 5.8 for the next five weeks until the end of Round 2 testing. None of these pH adjustments were done for improving the ETA performances. They were carried out to improve the MU performances running on the same alternatives. However, the changes, as expected, affected the ETAs. The effects of these modifications are discussed in details, below. Temperature and feed pH profiles for both of the units are presented in Figure 6.37, below. ETA 1 and ETA 4 operated about 4,400 hours and 4,700 hours, respectively, during Round 2.

The early WTC values ranged between 8 and 11.5 × 10^{-12} m/s.Pa, with Toray TML10 and CSM CE having the highest and CSM FE having the lowest WTC values for both of the alternatives (Figure 6.35). Even though the starting WTC values of each membrane pair running on the two different alternatives were very close to each other, a very different trend in each alternative was observed right away. The decline on ETA 4 (the same tendency as in Round 1) running on lime-softened MODE water was significant in the first month of Round 2 testing. On the other hand, membranes running on ETA 1 with microfiltered MODE water showed an increase in their WTC values during that time. This trend on both alternatives continued until a shutdown event on April 25, 2011. The purpose of this shut-down event was to clean the PS 1 intake structure and sluice the MODE entrance to the YDP to reduce the sediment near and inside the intake structure. The expected benefit of this cleaning was lower turbidity and better chlorine control after getting rid of the sediments that include not only inorganic but also organic materials. The units were back online on May 4 after almost 9 days of downtime. While the units were down, they were flushed with RO product water on a daily basis. The other somewhat long-term shutdown events are highlighted by small arrows without written explanations (Figure 6.35).

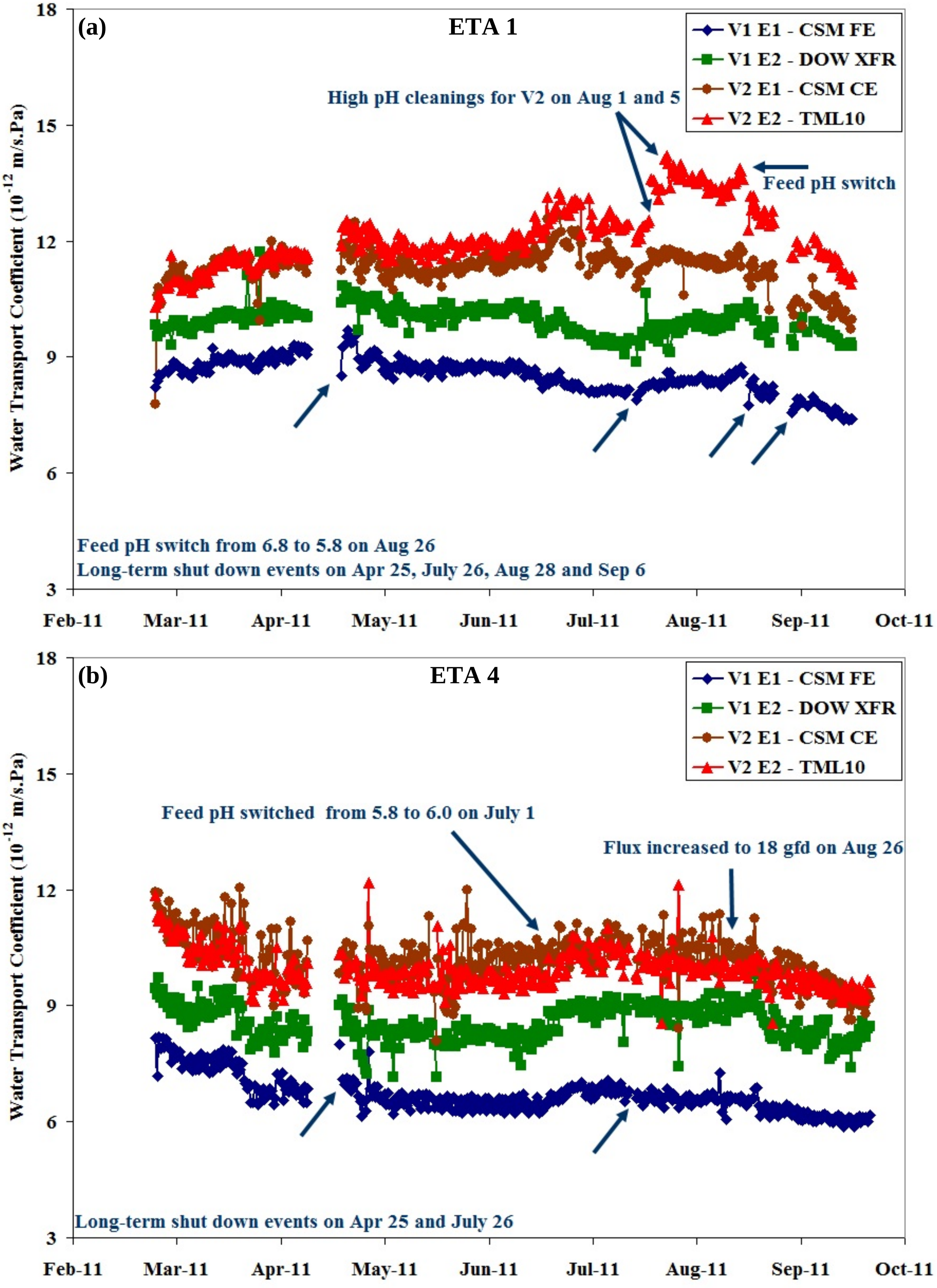


Figure 6.35. Water transport coefficient profiles for (a) ETA 1 and (b) ETA 4 during Round 2.

WTC for all the membranes on both alternatives stabilized after this shut-down event until roughly the end of June (~ 6 weeks). This might be due to the daily flushing of the elements with RO product water, which has a pH of about 5.5, during the shutdown. It might as well be due to the effect of cleaning the PS 1 intake structure. However, the stabilized values were drastically different on each alternative. The membranes on ETA 4 had much lower WTC values than their pairs on ETA 1.

By the end of June, there were a couple of changes in the MODE water. The first one, as it was mentioned earlier in the report, was that the water composition changed. Higher dissolved iron and manganese concentrations started to be recorded. The increase in the TDS was clear, as well. About 400 mg/L of increase was monitored even in the lime-softened water, Alternative 10. Please, refer to Appendix C-2 for the detailed feed TDS concentrations of ETA 1 and ETA 4. At the same time, higher HPC results, an indication of biofouling was recorded on ETA 1 by the end of June. This might be due to the change in the water quality and water composition. However, a more likely (and possibly related) reason for that might be the lower chlorine concentrations during that time (Appendices E-1 and E-2). Therefore, a decrease in the WTC for all the membranes in ETA 1 was monitored during the month of July. The total chlorine level in ETA 1 feed was increased to 2.0 mg/L as a precaution and a cleaning applied, which slowed down the decrease of WTC. Two high-pH cleanings for Vessel 2 were carried out in the first week of August. The cleanings seemed to reverse the decline in the WTC values.

However on August 26, in response to deteriorating MU 3 performance (see later discussion) the pH of the RO feed for Alternative 17a was decreased from 6.8 to 5.8, which affected ETA 1 operation. WTC values for all the membranes in ETA 1 started to decrease again following this pH switch and continued until the end of Round 2.

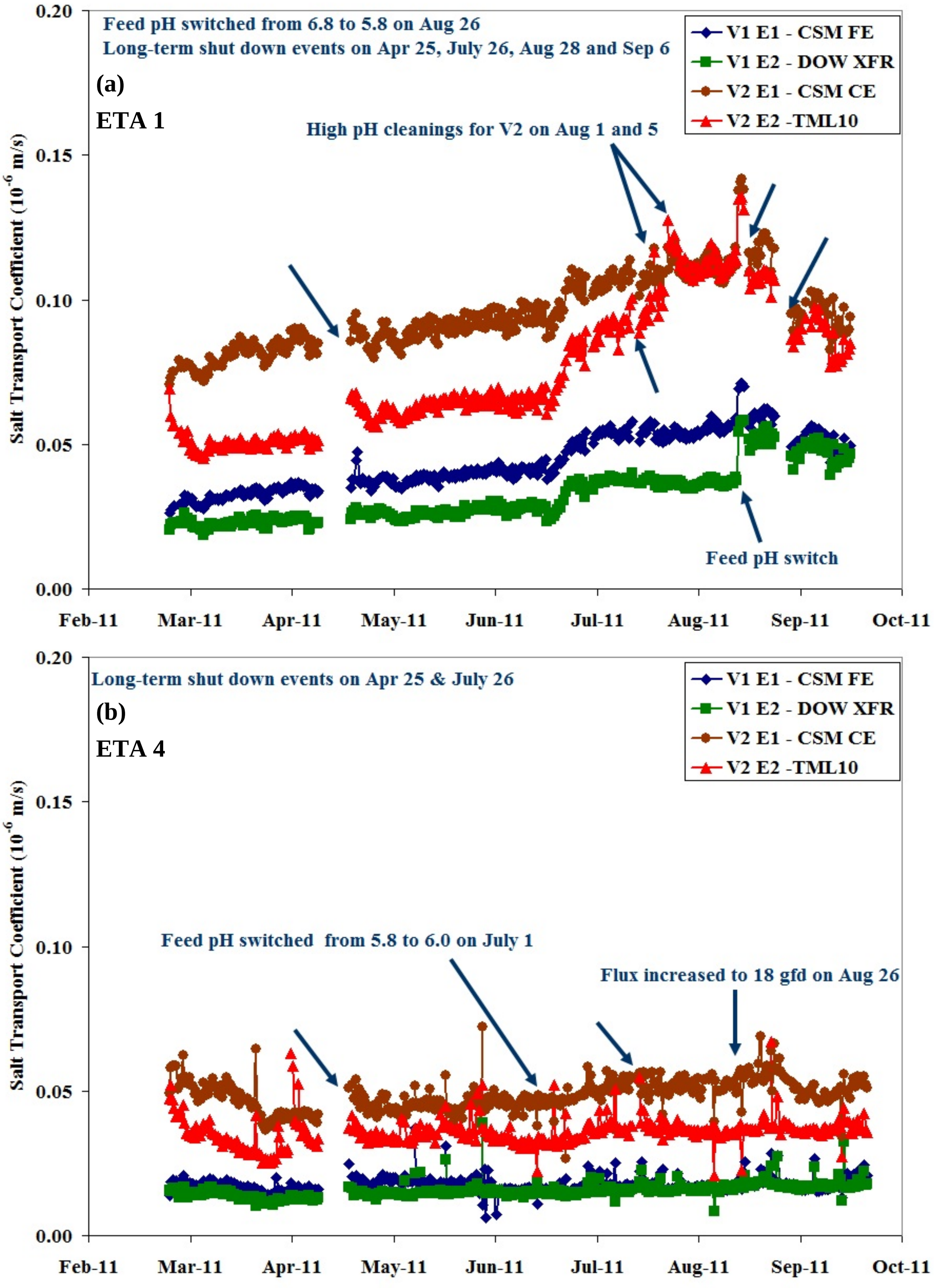

Feed pH switched from 6.8 to 5.8 on Aug 26
Long-term shut down events on Apr 25, July 26, Aug 28 and Sep 6
(a)
ETA 1
High pH cleanings for V2 on Aug 1 and 5
Feed pH switch
V1 E1 - CSM FE
V1 E2 - DOW XFR
V2 E1 - CSM CE
V2 E2 -TML10
Salt Transport Coefficient (10^{-6} m/s)
0.20
0.15
0.10
0.05
0.00
Feb-11
Mar-11
Apr-11
May-11
Jun-11
Jul-11
Aug-11
Sep-11
Oct-11
Long-term shut down events on Apr 25 & July 26
(b)
ETA 4
Feed pH switched from 5.8 to 6.0 on July 1
Flux increased to 18 gfd on Aug 26
V1 E1 - CSM FE
V1 E2 - DOW XFR
V2 E1 - CSM CE
V2 E2 -TML10
Salt Transport Coefficient (10^{-6} m/s)
0.20
0.15
0.10
0.05
0.00
Feb-11
Mar-11
Apr-11
May-11
Jun-11
Jul-11
Aug-11
Sep-11
Oct-11

Figure 6.36. Salt transport coefficient profiles for (a) ETA 1 and (b) ETA 4 during Round 2.

At the same time, ETA 4 was going through couple of feed condition changes, as well. The feed pH of MU 4 was increased from 5.8 to 6.0 on July 1, which also affected the performance of ETA 4 running in parallel to MU 4. The WTC values showed a significant increase during the two weeks following the pH adjustment. Since the membranes in this unit were performing very successfully, the flux was increased to 18 gfd from 15 gfd on August 26, resulting in a decreasing trend on WTC values. However, this left an unanswered question about the possibility of success of higher flux (18 gfd) with a more appropriate feed pH. Hence, a follow-up study was carried out with higher flux and the results are presented in Section 6.3.3.3.

The absolute values of initial salt transfer coefficients for all tested membranes were about 25% lower on Alternative 10 (ETA 4) relative to the ones on Alternative 17a (ETA 1). The same direct correlation between the WTC and STC of a membrane (meaning an element with a relative high WTC also had a relatively high STC) that was observed during Round 1 was also observed during Round 2 with the exception of DOW XFR. The DOW XFR had the lowest STC, whereas its WTC was higher than the CSM FE. Hence, having the lowest STC and a relatively higher WTC made the DOW XFR another good candidate for treating MODE water.

The only membrane that was in common for both rounds was Toray TML10. TML10 had matching WTC and STC during Round 1 and Round 2 in the two alternatives tested on MODE water, initially. The only main difference between the two rounds was the STC trend that TML10 had in ETA 1. Even though it started around 5 × 10-8 m/s in both rounds, the STC during Round 2 increased by more than 100%, while the STC during Round 1 stayed almost constant. This shows the water quality or pretreatment efficiency differed between the two rounds in Alternative 17a. In fact, the STC increase picked up mostly during summer 2011, which also matches with the observed water quality changes in MODE water during that time of the year that was mentioned earlier in the report. This makes direct comparison between the two rounds somewhat difficult. However, whatever the specific water quality changes that occurred in summer 2011, the effect differed significantly on the different element types (with the TML 10 most affected) and the effect was seemingly mitigated by the partial lime-softening pretreatment as seen in the more dramatic changes in WTC and STC in Alternative 17 than Alternative 10.

Table 6.8. Percent changes in STC for membranes tested in Round 2 ETA 1 and ETA 4. The values in parenthesis represent the percent changes in STC prior to any cleaning on ETA 1 and prior to a flux change on ETA 4.

	ETA 1 (Alt. 17a)		**ETA 4 (Alt. 10)**	
	% change	**% per 1000hr**	**% change**	**% per 1000hr**
CSM FE	37.43 (44.67)	8.90 (14.81)	17.80 (-2.59)	3.84 (-0.70)
DOW XFR	46.65 (39.03)	11.09 (12.94)	16.07 (5.82)	3.47 (1.57)
CSM CE	15.29 (28.36)	3.64 (9.40)	-7.60 (-8.10)	-1.64 (-2.19)
Toray TML10	34.17 (47.75)	8.13 (15.83)	-22.44 (-30.69)	-4.85 (-8.29)

The changes in the STC values during Round 2 are presented in Table 6.8. As presented in the table and also in Figure 6.36, ETA 4 membranes had a more stable run in terms of STC changes. STC of ETA 1 membranes started to increase in late June and early July. One reason for this increase might be the rising feed water TDS concentration. And since the constituents contributing to the TDS would be different in Alternative 17a than the ones in Alternative 10, this increase in TDS affected the two ETAs differently and at different scales. This increase slowed down significantly for Vessel 1 elements in about 10 days with the stabilized feed water TDS level. On the other hand, STC for the Vessel 2 elements, CSM CE and TML10, kept on increasing. As a matter of fact, the rate of overall increase reached to 10-15% per 1,000hrs, for the ETA 1 membranes. This motivated cleaning of vessel 2 elements to restore the membranes' performance. Two separate cleanings were performed on the 1st and 5th of August only on Vessel 2 elements to monitor and compare the efficiency. While they helped to restore the WTC values, they also helped to stabilize the STC until a feed pH adjustment for MU 3, affected ETA 1 operation. The feed pH for ETA 1 was dropped from 6.8 to 5.8 on August 26. WTC values for all the membranes in ETA 1 started to decrease following this pH change. However, STC values also started to decrease. And this simultaneous decline of both parameters continued until the end of Round 2. Based on the ETA results, the appropriate operating pH for the head elements of an array was between 5.8 and 6.8 for Alternative 17a.

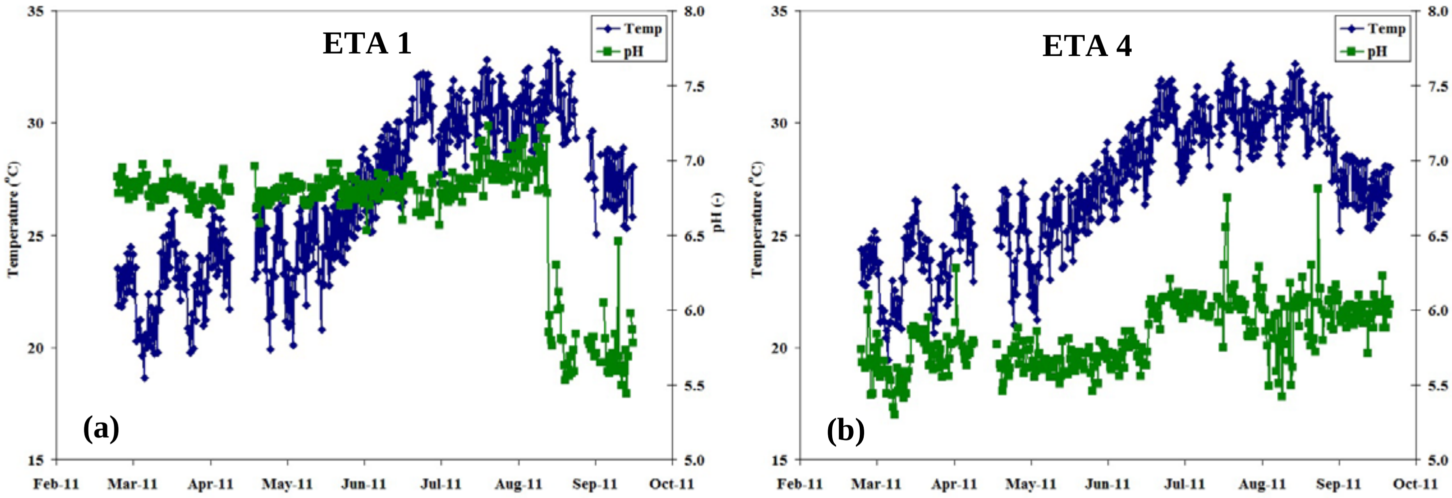


Figure 6.37. Temperature and pH profiles for (a) ETA 1 and (b) ETA 4 during Round 2.

During Round 1 testing, the feed pH for Alternative 10 (ETA 4) was dropped to 5.8 (from 6.8) on January 6, 2011. This change in the feed pH helped to stabilize the STC immediately and WTC in the long term. Therefore, Round 2 testing started with a feed pH of 5.8 for Alternative 10. The positive effect of this decision was clear on the STC since they started low and stayed steady. However, the initial loss on WTC was thought to be avoidable if the pH had started slightly higher. Hence, the feed pH adjustment on July 1 was performed, which did not have much effect on STC but stabilized and increased the WTC to some extent. Therefore, the appropriate operating pH for the lead elements was considered to be between 5.8 and 6.0 for Alternative 10.

A notable rise in the temperature of more than 10 Celsius degrees, with the ambient temperature reaching to above 30 ^{o}C, was observed during Round 2 (Figure 6.37). However, there was no clear correlation between the temperature and WTC or STC. As previously, all the parameters presented are temperature corrected as defined in the Methods and Materials section of the report.

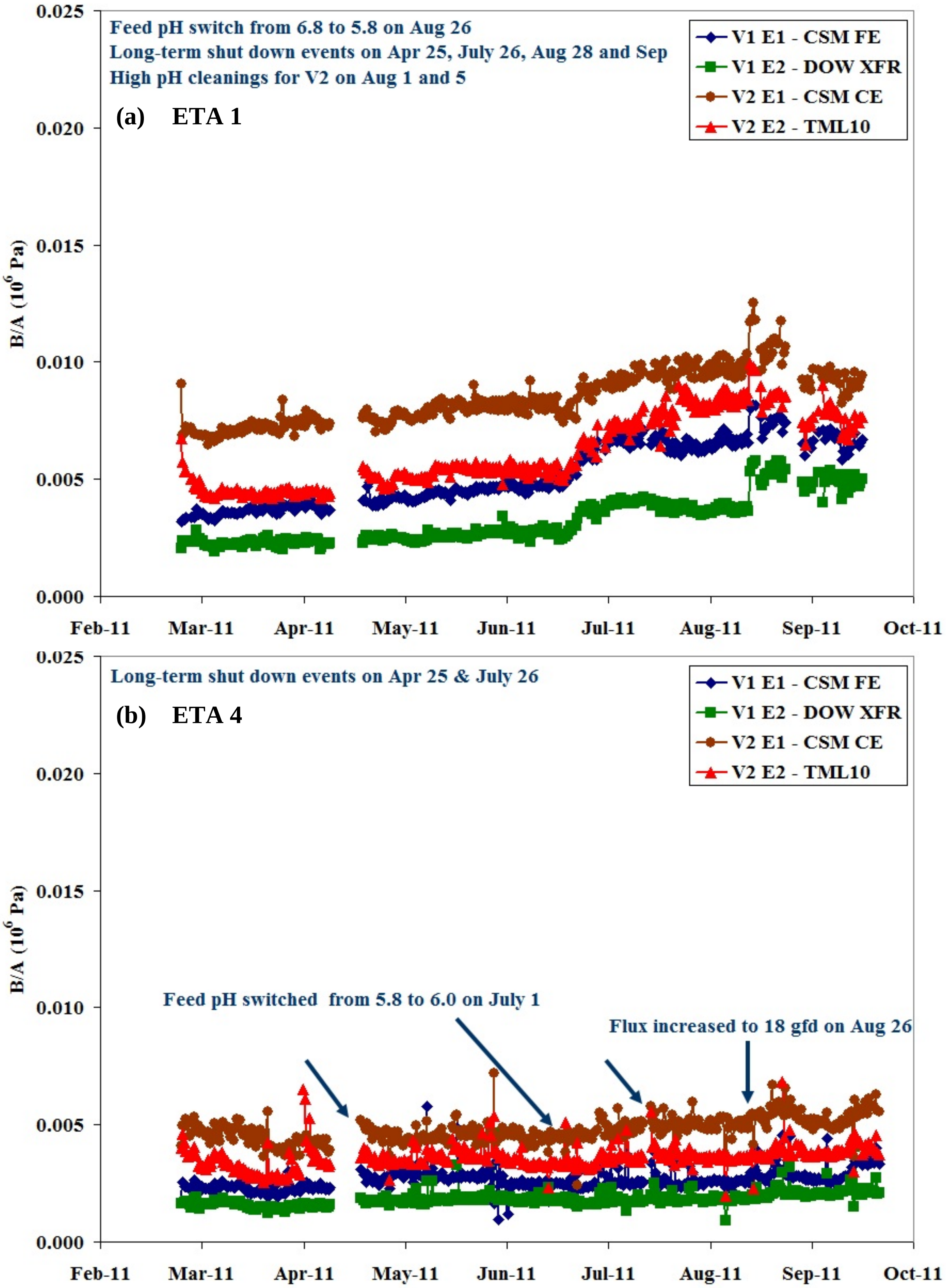

Feed pH switch from 6.8 to 5.8 on Aug 26
Long-term shut down events on Apr 25, July 26, Aug 28 and Sep
High pH cleanings for V2 on Aug 1 and 5
(a) ETA 1
V1 E1 - CSM FE
V1 E2 - DOW XFR
V2 E1 - CSM CE
V2 E2 - TML10
B/A (10^6 Pa)
0.025
0.020
0.015
0.010
0.005
0.000
Feb-11
Mar-11
Apr-11
May-11
Jun-11
Jul-11
Aug-11
Sep-11
Oct-11
Long-term shut down events on Apr 25 & July 26
(b) ETA 4
V1 E1 - CSM FE
V1 E2 - DOW XFR
V2 E1 - CSM CE
V2 E2 - TML10
B/A (10^6 Pa)
Feed pH switched from 5.8 to 6.0 on July 1
Flux increased to 18 gfd on Aug 26
0.025
0.020
0.015
0.010
0.005
0.000
Feb-11
Mar-11
Apr-11
May-11
Jun-11
Jul-11
Aug-11
Sep-11
Oct-11

Figure 6.38. B/A ratio profiles for (a) ETA 1 and (b) ETA 4 during Round 2.

The initial B/A ratios for all the membranes in ETA 4 were lower than the ones in ETA 1, and they stayed lower and relatively constant throughout Round 2 testing (Figure 6.38). The rising B/A ratio in ETA 1 could have been due to membrane degradation since it was accompanied with rising STC and WTC values. However, no event of high ORP or free chlorine concentration was recorded during Round 2. In addition, the high pH cleanings and the pH adjustment in August helped to stabilize and lower the B/A ratio. Therefore, the source water is most likely the cause of this increase and the partial lime softening before ETA 4 tended to buffer the impact of the source water change when compared to the impact of microfiltration on ETA 1.

The temperature corrected C_e calculated for each vessel is presented in Figure 6.39. Even though the Vessel 2 C_e values were very close to each other on the two MODE alternatives, Vessel 1 C_e was 20% higher on ETA 1. This was due to a 20% lower differential pressure (dP) on ETA 1. Lower feed pressure was needed on this unit, as well. The main difference came from Element 2 (DOW XFR) running on Vessel 2, which had higher product pressure in ETA 4. This difference might be due to the water composition. DOW XFR may need higher pressure to produce the same amount of water with lime-softened MODE water compared to microfiltered MODE water.

The element flow coefficient of ETA 4 showed a drop of about 1.5% per 1000 hours and 2.1% per 1000 hours for Vessel 1 and Vessel 2, respectively. Since this was accompanied with a WTC decrease, it is likely due to fouling. Neither the feed pH adjustment nor the flux increase changed this trend in C_e. On the other hand, the C_e of ETA 1 had a more stable run until late June 2011 with 1.15% per 1000 hours and 1.23% per 1000 hours for Vessel 1 and Vessel 2, respectively. After this point, a very sharp drop in C_e was observed for both vessels in ETA 1. Together with elevated HPC results, this was evidence of biofouling, and as a consequence, the feed total chlorine level was increased to almost 2.0 mg/L. Reducing the HPC was expected to increase the C_e. By mid July, the C_e values leveled off and started increasing slowly. The high pH cleanings on Vessel 2, as expected, restored the C_e significantly but not all, meaning that the foulant material can be removed partially by high pH cleaning. The detailed results of HPC

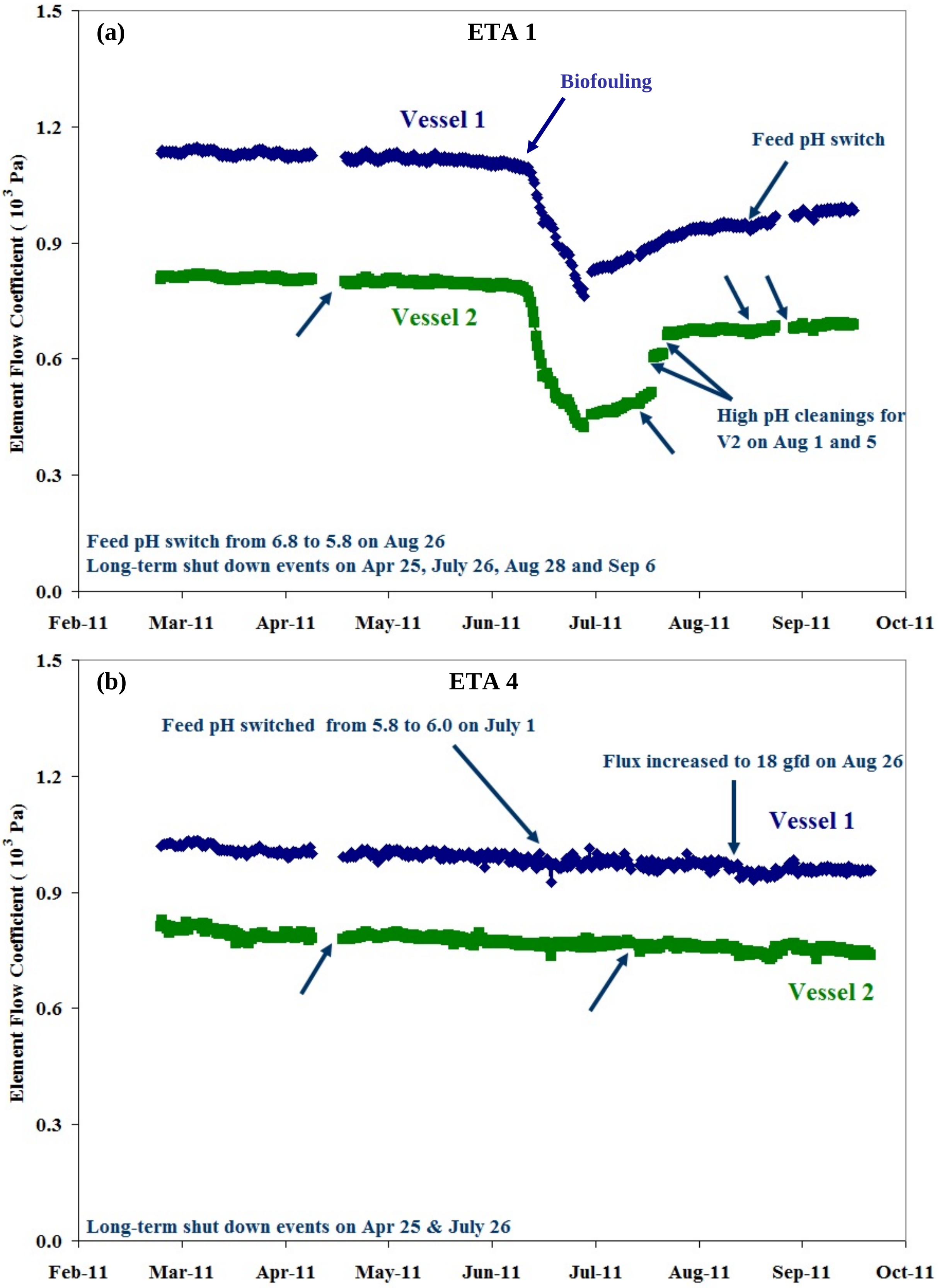


Figure 6.39 Element flow coefficient (C_e) profiles for (a) ETA 1 and (b) ETA 4 during Round 2.

In summary, based on the operating and the calculated parameters of the ETA units, a biofouling event was clearly indicated for ETA 1 running on Alternative 17a. Membrane degradation is possible, but could not be proved solely with the calculated parameters since the cleaning and feed pH adjustment restored the STC and WTC values. Increasing WTC and STC seemed most likely related to the operating pH and this was investigated in more detail in the MU testing (see later discussion). Just as in ETA 1, the decrease in the WTC and C_e values for ETA 4 were considered as indications of a possible fouling and material buildup. However, increasing the feed pH to 6.0 from 5.8 helped to restore these parameters and led to a more stable run, until the flux was increased on August 26, 2011. The flux of 18 gfd resulted in a falling WTC, while no other parameters were affected significantly. Before concluding on the feasibility of operating at a high flux (18 gfd versus normal 15 gfd) more data would be needed since both the run-time at high flux was too short for adequate evaluation and no opportunity was afforded for optimizing the operating conditions with respect to pH. Therefore, another short-term run of ETA 4 with only DOW XFR and TML10 was performed as a separate study. The results are presented in Section 6.3.3.3.

The rejection rates for the important water constituents, including major cations and anions, can not be calculated and presented for Round 2, because sampling of product water for each membrane for water quality analysis was discontinued at the end of Round 1. Please, see Appendix C-2 for the details of ETA feed and reject water quality analyses during Round 2.

6.3.2 RO Performance Testing (full-array and high-recovery)

Based on the results of Round 1 element screening testing and also on the availability of the membranes at the time, Hydranautics LFC3 was chosen for testing in the full-array and high-recovery equipment (MUs). Two MU units (MU 3 and MU 4) were used to evaluate the performance of the chosen membrane in treating the MODE water following the previously described pretreatment methods of Alternative 10 and 17a. 21 spiral wound 2.5-in by 40-in elements were used in 2-1 array formation in the two MU RO units. The 21 elements provided a total of about 525 ft^2 of total membrane area. The selected average flux of 12 gfd resulted in producing 6300 gpd of permeate water. The recovery was chosen as 80% for all the MUs, initially, so a feed flow of 7875 gpd was needed to run the MUs. The calculated performance parameters, such as WTC, water flux, etc., presented in this report for all the MUs that tested Hydranautics LFC3 were based on the average membrane area. The average membrane area for the LFC3 elements was calculated by taking the average of all the retired elements that went under post-mortem analyses based on actual measurement of the active area of each element's membrane leaves.

MU 3 and MU 4 were operated to evaluate the efficiency of the pretreatments for Alternative 17a and Alternative 10, respectively. The pretreatment for Alternative 17a consisted of gravity filtration followed by microfiltration. The pretreatment for Alternative 10, which represents the current pretreatment option of YDP, consisted of lime-softening (supplemented by ferric sulfate addition for enhanced organics and particulate removal) and gravity filtration. Round 2 for full-array testing lasted almost 6800 hours (9.5 months) for MU 4. On the other hand, this number stayed around 6500 hours (9 months) for MU 3 due to frequent shutdowns and issues with the West Pall MF unit. Even though the manufacturer suggested 0.5 mg/L and 0.8 mg/L as the concentration of anti-scalant, AWC A-102 Plus, for Alternative 10 and Alternative 17a, respectively, it was used 1.0 mg/L for both alternatives due to the pump and the dilution factor restrictions. The other benefit for this higher concentration of anti-scalant was to provide a safety factor.

WTC (A), STC (B), B/A ratio, water flux, net driving pressure, percent salt passage, water recovery, product total dissolved solids concentration, product flow rate and osmotic pressure for the lead and tail elements of the unit and also for the groups of three elements in the remainder of the unit were calculated and monitored daily by the Test Manager and the operators and weekly by the TAT members. Other parameters measured, calculated and monitored in the same manner included feed and interstage temperature, feed and reject pH, feed free and total chlorine concentrations, feed SDI, feed and reject flow rates, feed and reject total dissolved solids concentrations, feed and reject pressures, differential pressures for stage 1 and 2, element flow coefficients for each vessel and percent salt mass balance deviation for each stage, interstage and the whole unit. However, only feed temperature and pH of the units, WTC and STC for each vessel and for the whole unit and the C_e for each vessel are presented in the report. Please, refer to the appendix for the other results.

6.3.2.1 MU 3 Testing: Alternative 17a as Pretreatment

The RO unit, MU 3, started running on March 8, 2011 for Round 2 testing of Alternative 17a as the pretreatment option for a YDP operation on MODE water. MU 3 started running with a feed pH of 6.8. On June 17, the feed pH dropped to about 5.5 to achieve a reject pH of 5.8. On July 12, pH was increased to about 6.0 to achieve a reject pH of 6.3. The effects of these pH changes were observed for the next one and a half month, until August 26. However, the feed pH was decreased once again but slightly this time to a feed pH of around 5.8 to achieve a reject pH of 6.1. The reject pH was the main target to keep constant in the MU operations. Therefore, the reject pH was kept constant around 6.1 from August 26 until December 22. However, probably due to the changing water quality in the MODE canal, the feed pH dropped from 5.8 down to around 5.5 from August 26 until November, while the reject pH was successfully kept around 6.1-6.2.

The water temperature reached its peak value of 33.3 ^{o}C by late August. As the temperature of the water decreased in the canal, the microbial activity, hence the TOC level in the canal, decreased significantly. This drop in TOC is shown in Figure 6.2 of Section 6.1.2. It is well documented in literature that the TOC in natural waters is both a natural background source of acidity and a pH buffer in low alkalinity waters. Hence, the drop in TOC beginning in late August would decrease the buffering capacity of the RO feed water and, consequently, increase the pH difference between feed and reject pH as carbon dioxide is lost to the permeate. Therefore, this change in pH might, at least partially, explain the declining feed pH that was needed from late August onward in order to keep the reject pH constant. One should consider at this point that the operating pH was significantly decreased in summer 2011, which caused the MODE water to lose its carbonate buffering capacity (and alkalinity) by shifting the equilibrium reaction ($H_2CO_3 \leftrightarrow HCO_3^- + H^+$) to the left. As the water loses its carbonate buffering capacity, the buffering capacity of TOC gains more importance. Hence, the decrease in the TOC level after summer together with the drop in the temperature decreases the water's buffering capacity. As the buffering capacity of the water diminishes, a lower feed pH is required to keep the same level of pH in the reject stream. This also explains why there was less difference between the feed and reject pH when there was more TOC present in the water before August 2011, even after dropping the pH down to 5.8 in the reject stream. At this pH even though we decreased the carbonate buffering capacity, the high TOC level in the water probably kept the difference between the feed and reject pH small.

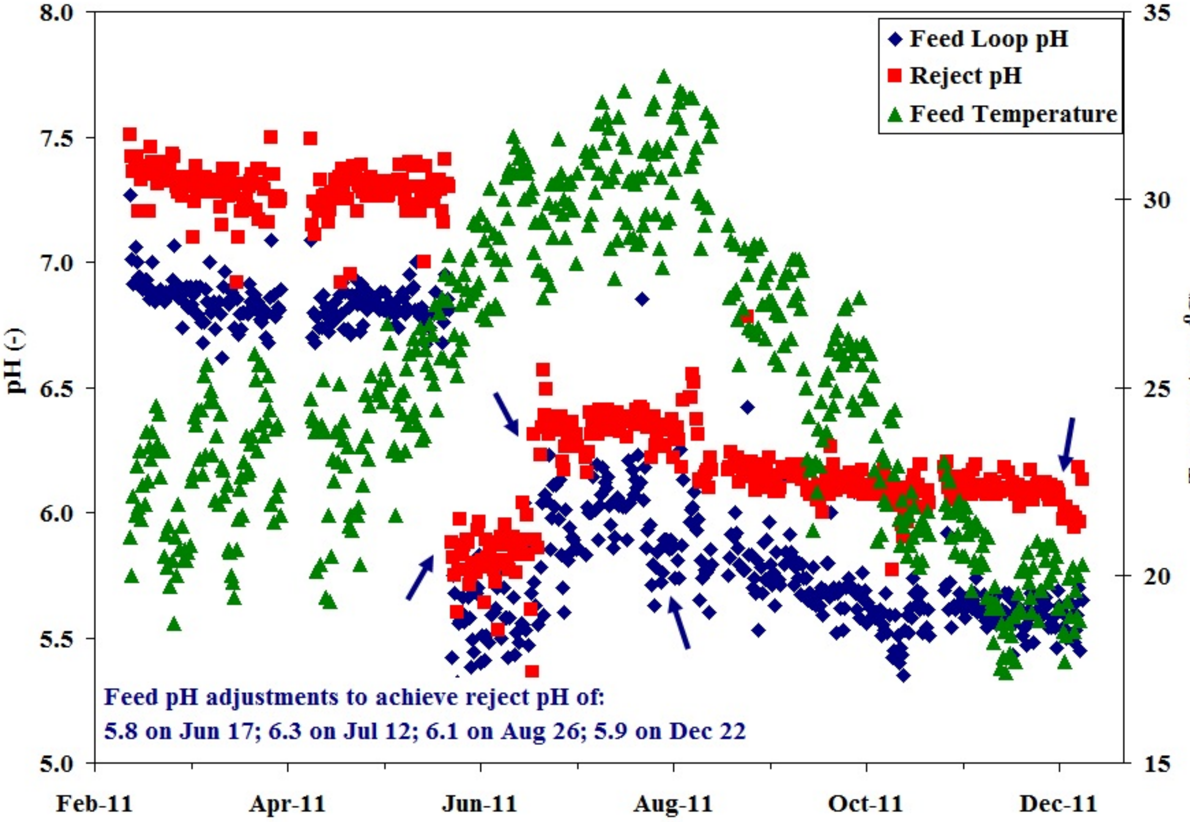


Figure 6.40. Feed and reject pH and temperature profiles for MU 3 during Round 2. Blue arrows indicate timing of reject pH adjustments. The thick marks on X-axis indicate the end of each month on the graph.

The feed pH was adjusted once again and for the last time during MU 3 operation on December 22 to around 5.3-5.4 to achieve a reject pH of 5.9. Only eight days of results were scrutinized with this new pH. The reasons and the outcomes of these pH adjustments are presented below in the paragraphs explaining the observed and calculated operating parameters, such as WTC and STC. The blue arrows in Figure 6.41 highlight the timing of the pH adjustments. The water temperature during Round 2 testing increased from low twenties to low thirties degrees Celsius between March (the beginning of testing) and late August. Thereafter, it dropped back to 17-18 ^{o}C by the end of the year, which was the end of Round 2 testing.

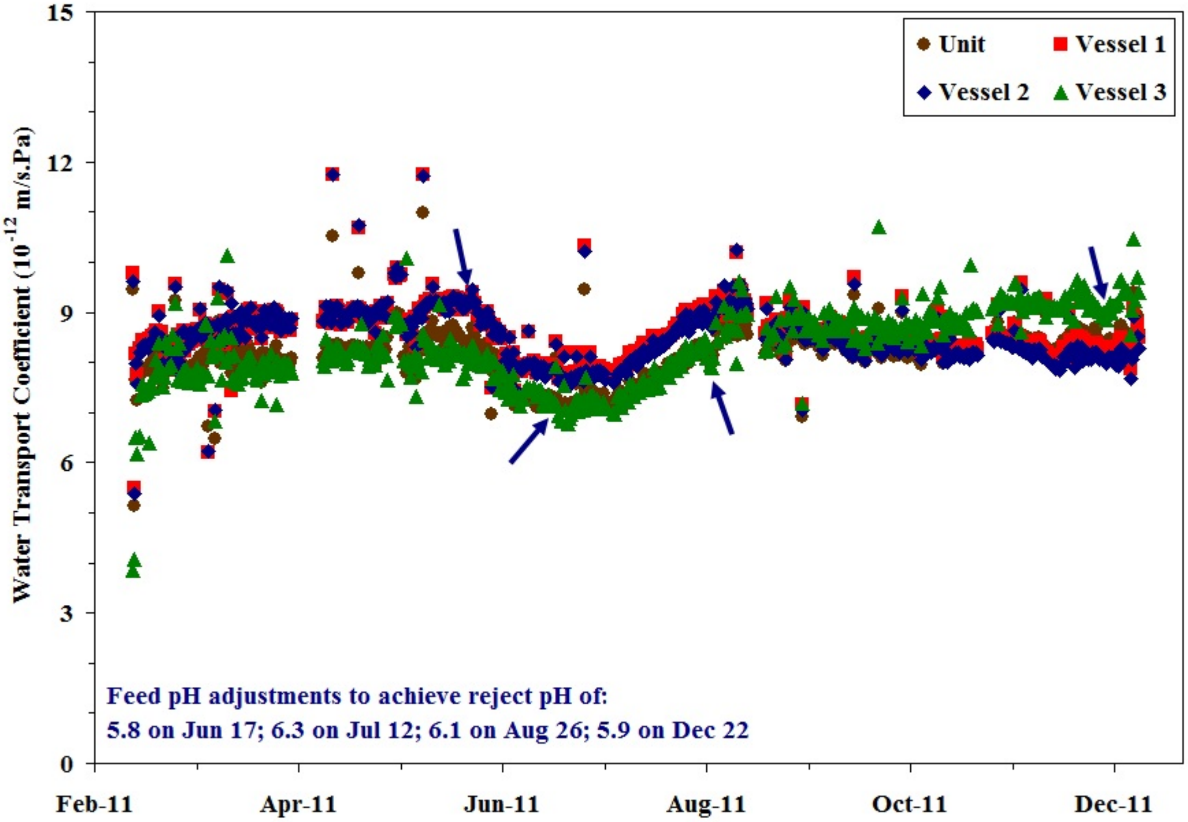


Figure 6.41. Water transport coefficient (WTC) profile for MU 3 during Round 2. Blue arrows indicate timing of reject pH adjustments. In addition, a high pH plus surfactant and a low pH cleaning were performed on May 23-24 and May 27, respectively. The thick marks on X-axis indicate the end of each month on the graph.

The early Round 2, MU 3 WTC values ranged between 7.3 and 8.2 × 10^{-12} m/s.Pa. This range matched almost perfectly with the observations of Round 1 testing of Hydranautics LFC3 on Alternative 17a. While running at the feed pH of 6.8, the average WTC for each vessel in both stages increased noticeably by about 0.8-1.0 × 10^{-12} m/s.Pa in three months. However, at the same time the STC for all vessels, especially in the second stage elements, was increasing rapidly, as well. A long-term shut-down event between April 25 and May 5 took place due to cleaning performed on the MODE intake structure. During this shut-down event, the membranes were flushed with RO permeate water at a pH of about 5.5 on a daily basis. No obvious impact was observed due to the shutdown event and the daily flushing routine. WTC and STC for all vessels continued from the same values prior to the shutdown event.

Because of the rising STC values, a high-pH (pH~11.5) cleaning with 0.03% sodium dodeclybenzene sulfonate was performed on May 23 for the first stage and on May 24 for the second stage. Please, see Appendix A-11 for the details of the cleaning procedure. No beneficial outcome of this high-pH cleaning was recorded. In fact, the increases in the WTC and STC for all three vessels were apparent after the cleaning. A low-pH cleaning on May 27 was performed. The low-pH cleaning brought the WTC and STC values back to pre-cleaning levels. However, the increasing trend immediately resumed after cleaning. The cleaning results suggest that (i) the changes in WTC and STC were not the result of fouling; (ii) the cleaning at high pH exacerbated the impact of higher feed/concentrate pH; (iii) the cleaning at low pH reversed the effect of neutral pH operation. This data suggested that there might be either membrane damage or changes in the surface morphology of the membranes (chemical bond/steric structure of the thin film layer) since both WTC and STC values kept increasing. WTC for Vessel 3 did not escalate as much as in the first stage vessels. However, its STC value increase was the highest, especially on the tail element of the second stage. This pattern reflected the results of studies conducted by Reclamation in the past. To eliminate the possibility of a faulty membrane causing the problem, the tail element (Element 7 in Vessel 3) was replaced on June 17. The retired element was taken to the University of Arizona for post-mortem analyses and to investigate if the element had any identifiable problems. The results of these analyses are presented in Section 8.0 but it is appropriate to mention here that there was no clear damage or fault observed on the membrane via either visual inspections or FTIR results.

Together with this switch of elements, a new acid injection point and two static mixers were installed and pH was decreased from 6.8 to 5.5 in the feed (5.8 in reject) water on June 17. In the older studies Reclamation conducted, it was observed that the WTC increases over time with a higher operating pH. This is probably due to how the organics and other foulants in the water bind to the membranes and change its behavior. When the units were operated at the lower pH, a decrease in both WTC and STC were observed. Hence, the pH for MU 3 was decreased to examine the pH effect on the performance of the membranes.

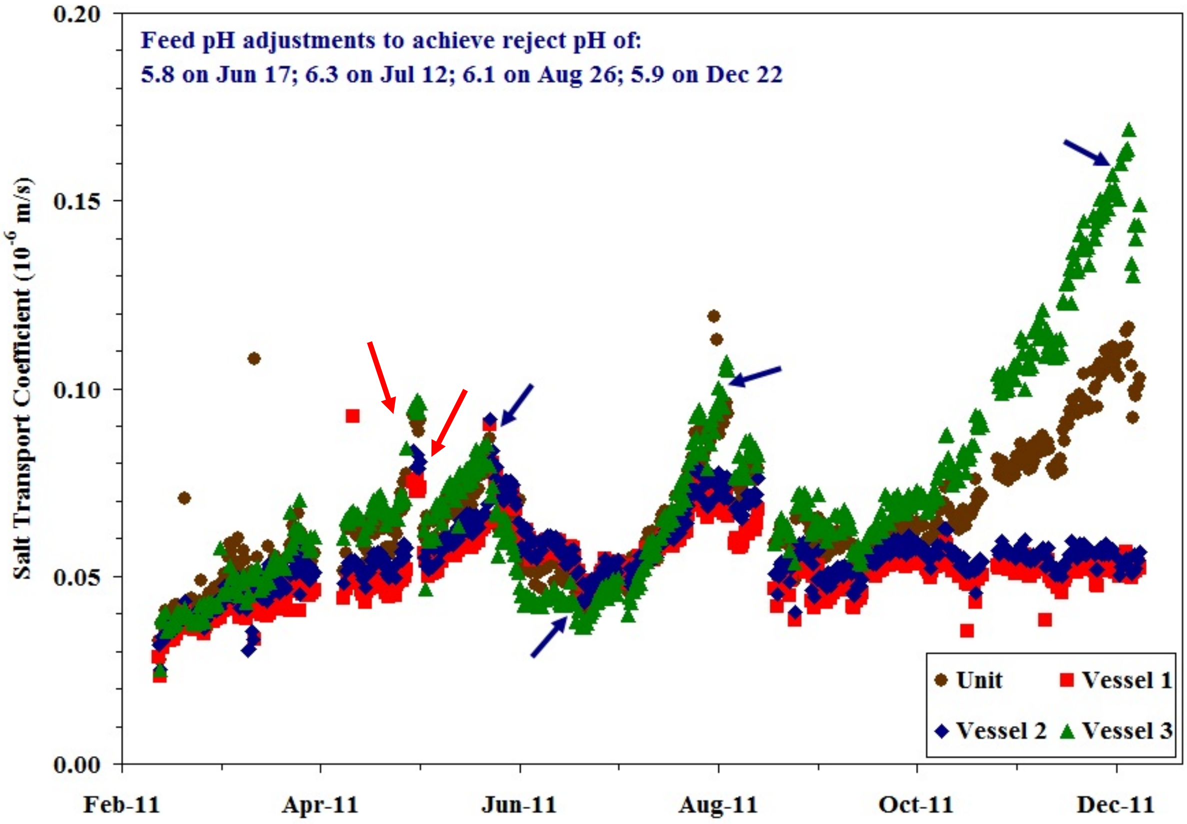


Figure 6.42. Salt transport coefficient (STC) profile for MU 3 during Round 2. Blue arrows indicate timing of reject pH adjustments. In addition, red arrows indicate a high pH plus surfactant and a low pH cleanings performed on May 23-24 and May 27, respectively. The thick marks on X-axis indicate the end of each month on the graph.

The decrease in the pH in June reversed the rising trend in STC values. As a matter of fact, the rate of decrease in STC was higher than the rate of increase prior to the pH change. However, the WTC for all the membranes started to decrease, as well. The rate of decrease for both parameters was highest in the first stage elements. Hence, the feed pH was adjusted to achieve an intermediate reject pH of 6.3 on July 12. This increase in the pH once again reversed the trends in both parameters. A rapid increase in STC accompanied by a relatively slower increase in WTC continued until the next pH adjustment in late August.

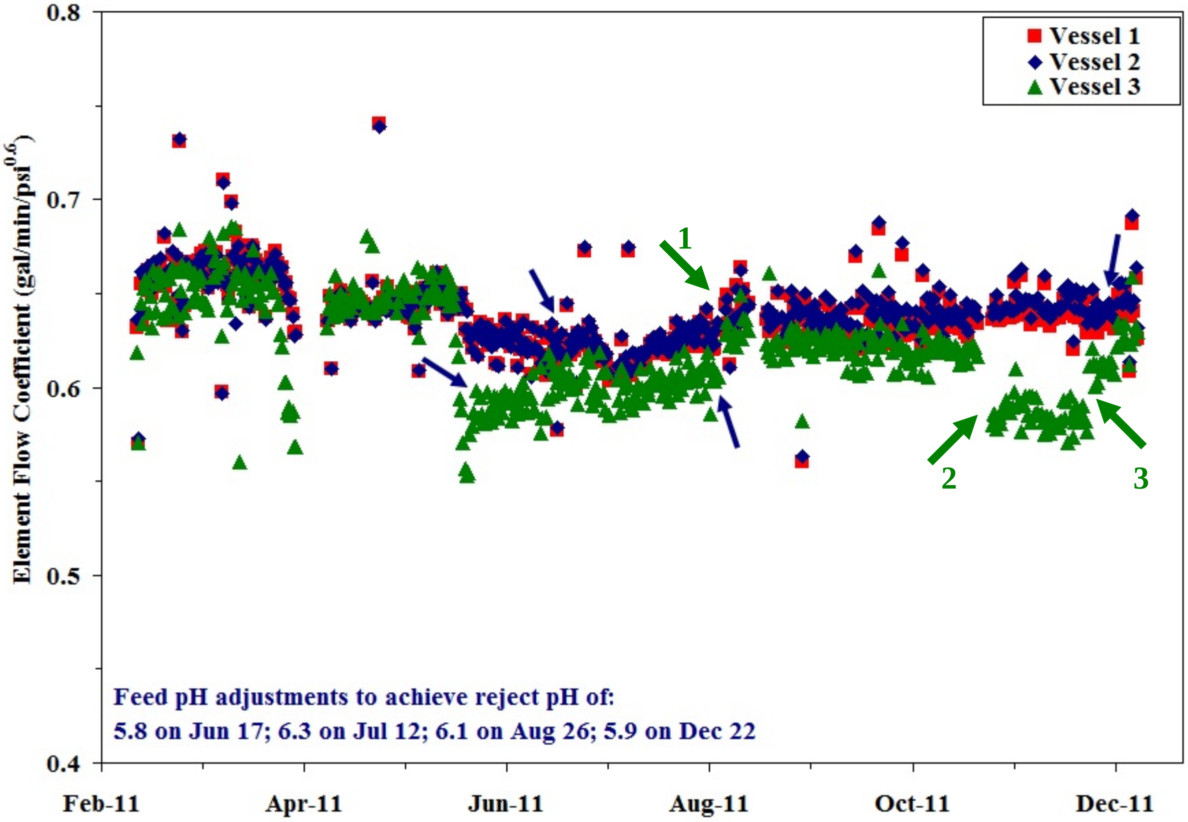


Figure 6.43. Element flow coefficient (C_e) profile for MU 3 during Round 2. Blue arrows indicate timing of reject pH adjustments, while green arrows indicate timing of unit shutdown and permeate flushing periods. In addition, red arrows indicate a high pH plus surfactant and a low pH cleanings performed on May 23-24 and May 27, respectively. The thick marks on X-axis indicate the end of each month on the graph.

The acid injection was adjusted again on August 26 to decrease the pH from 6.3 to 6.1 in reject. The beneficial effects of pH adjustment are unquestionable. However, the effects of shut-down events are obvious, as well. The two consecutive shut-down events on August 28 through 29 and September 6 through 10 had significant impacts on STC values. They both helped drop the STC values. This was probably due to a combination effect of lower operating pH and RO permeate flushing during the downtimes. After the pH change at the end of August all the parameters, including WTC, STC, C_e and B/A, were stable. The degree of the impact of such a small, 0.2 pH unit, change was impressive. However, the STC for second stage elements started increasing in early October. The increase slowed down for the lead elements (Elements 1-3) of the second stage after the shutdown event on November 12 (these results are not shown here, but refer to Appendix F-1). No change was monitored for the Elements 4-7. This result suggests an interstage acid injection might be beneficial for a sustainable run.

The element flow coefficients for both stages stayed constant until the beginning of June. The C_e for both stages started to decrease by June 10, prior to pH adjustment, for no obvious reason. While the element flow coefficients for first stage vessels (Vessel 1 and 2) were decreasing slowly, a step-drop was monitored in the C_e of Vessel 3. The June decrease in the pH appeared to help the Vessel 3 C_e but it did not alleviate the decreasing trend in C_e of vessels 1 and 2. By the end of July, the C_e for first stage vessels also started to increase. With the pH adjustment on August 26, all vessels' C_e values stabilized. The cleaning effect of RO permeate flushing during the August 28 shutdown event, probably helped to increase the C_e values for all the vessels. This jump is highlighted with green arrow number 1 in Figure 6.43.

The same impact was not seen with the next long-term shut down event on November 12, highlighted with the green arrow number 3. The C_e value dropped radically in Vessel 3, while no change in first stage vessels was observed. There was a strong storm that caused this shut-down event for all the MODE water alternatives. Large disturbances in the pretreatment performance (turbidity levels of 48.7 NTU and 4.6 NTU for PS 3 SCR effluent and PS 3 DMGF combined effluent, respectively) were observed following the storm. These results are presented and discussed in the results of PS 3 pretreatment. The next shut down event, which had an extensive impact on MU 3 performance, was on December 15 due to acid injection problems. The membranes were flushed with RO permeate water during this short-term shutdown event. A jump in the C_e of Vessel 3 is clear following this incident probably due to the cleaning effect of permeate flushing. By the end of Round 2, the element flow coefficients for both stages were almost back to their original starting values. It may need further discussions and testing to prove, but the permeate flushes and pH adjustments throughout the testing seemed to help maintain a sustainable run in terms of the C_e values.

In summary, lower WTC values and higher STC values were observed with high operating pH (> 6.5). The significant, rapid, and very beneficial effect of low pH on MU 3 salt passage was observed. Reject pH of 7.3 appears too high with increasing salt passage in all MU 3 elements. On the other hand, reject pH 5.8 appears too low, and probably too costly, with decreasing WTC value and decreasing salt passage of all MU 3 elements. The right pH to operate an RO unit on Alternative 17a, gravity-filtered microfiltered MODE water, is about 5.8 on the feed and about 5.9-6.0 on the reject. (However, it is also possible that a slightly different operating pH may be optimal as the MODE water quality changes seasonally.) In addition, an interstage pH adjustment might be beneficial for successful and sustainable operation, since the pH of the feed stream increases with passage through the element train and small changes in pH are observed to have large impacts on performance. However, the importance of organic content in the source water is also significant. It also appears that the increase in MU 3 salt passage at high pH apparently was not irreversible degradation, because low-pH rapidly reversed it.

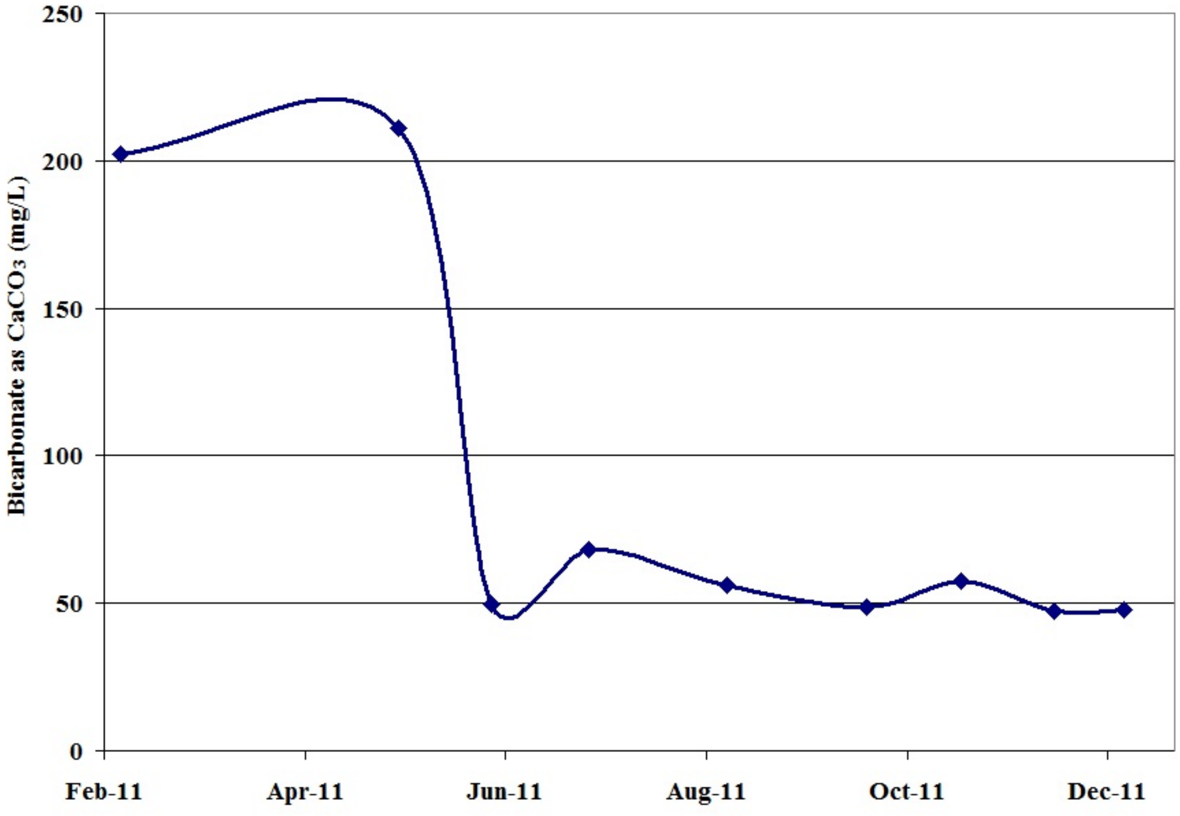


Figure 6.44. Bicarbonate (as $CaCO_3$) concentration profile for MU 3 feed during Round 2. The large decrease in May corresponds with a decrease in feed pH from 6.8 to 5.8.

Table 6.9. Water composition for feed and reject of MU 3 RO unit.

		MU 3 Feed				**MU 3 Reject**			
Parameter	**Units**	**Average**	**Minimum**	**Maximum**	**St. Dev.**	**Average**	**Minimum**	**Maximum**	**St. Dev.**
Barium	*mg/L*	0.03	0.03	0.04	0.00	0.16	0.14	0.18	0.01
Bicarbonate	*mg/L*	65.37	57.50	257.00	82.73	468.89	129.00	1,250.00	438.44
Calcium	*mg/L*	161.78	151.00	173.00	6.22	785.22	740.00	842.00	36.12
Chloride	*mg/L*	590.89	535.00	652.00	35.97	2,833.33	2,630.00	3,210.00	200.06
Conductivity	*µS/cm*	3,815.56	3,530.00	4,140.00	198.19	15,400.00	14,800.00	16,800.00	753.33
Iron	*mg/L*	0.124	0.075	0.294	0.070	0.445	0.189	0.672	0.155
Magnesium	*mg/L*	71.91	67.50	77.20	3.24	340.67	313.00	384.00	24.98
Manganese	*mg/L*	0.006	0.002	0.024	0.007	0.021	0.009	0.068	0.019
Nitrate as N	*mg/L*	5.34	4.30	6.30	0.78	20.28	16.80	24.90	2.53
pH	-	6.60	6.00	7.46	0.50	7.11	6.53	8.02	0.50
Potassium	*mg/L*	7.05	6.70	7.46	0.26	33.49	31.80	36.40	1.54
Silicon Dioxide	*mg/L*	17.59	11.80	20.80	3.69	82.18	61.10	96.90	13.33
Sodium	*mg/L*	573.78	533.00	601.00	23.68	2,724.44	2,560.00	2,940.00	121.46
Strontium	*mg/L*	2.24	1.84	2.58	0.22	11.06	9.31	12.60	1.10
Sulfate	*mg/L*	1,016.11	895.00	1,120.00	76.53	5,010.00	4,190.00	5,500.00	391.38
Sum of Anion	*meq*	40.14	37.70	43.20	1.86	193.89	183.00	213.00	9.98
Sum of Cation	*meq*	39.13	37.50	41.10	1.34	186.56	176.00	200.00	7.52
Tot. Alk. as CaCO3	*mg/L*	87.58	47.10	211.00	67.78	385.11	106.00	1,030.00	360.47
Tot. Hard. as CaCO3	*mg/L*	699.33	654.00	737.00	25.54	3,356.67	3,130.00	3,610.00	177.20
Total Organic Carbon	*mg/L*	2.51	2.07	3.01	0.30	9.24	7.43	12.30	1.70
Total Salt	*mg/L*	2,552.22	2,410.00	2,700.00	110.54	12,288.89	11,500.00	13,300.00	600.93

The results of the water quality analyses for MU 3 feed and reject are presented in Table 6.9, above. These results show very high standard deviations for both bicarbonate and total alkalinity levels. The reason is largely due to the large drop in the feed pH on June 17. The values measured prior to this drop were significantly higher than the ones measured after the pH adjustment, as mentioned in the earlier parts of this section, causing a big variation between the samples. This is illustrated in Figure 6.44, above, where the bicarbonate (HCO3-) concentration (mg/L as $CaCO_3$) for MU 3 feed throughout Round 2 is shown. The average concentration is presented in Table 6.9 as 82.73 mg/L as $CaCO_3$, which is a misleading value if the standard deviation is not considered properly. The bicarbonate concentration is assumed to be the same as total alkalinity at the pH levels for MU 3 feed and reject.

Table 6.10. Concentration and solubility data for MU 3 reject ion pairs that may contribute to membrane scaling. Ion products were based on the MU 3 reject average concentrations shown in Table 6.9, uncorrected for the ionic strength.

Precipitate	**Ion Concentration**	**log (ion product)**	**log K_{S0}[c]**	**Degree of Saturation [b]**
$BaSO_{4(s)}$	$[Ba^{+2}] = 1.15 \times 10^{-6}$ M $[SO_4^{-2}] = 5.21 \times 10^{-2}$ M	-7.22	-10.0	600.05
$CaSO_{4(s)}$	$[Ca^{+2}] = 1.96 \times 10^{-2}$ M	-2.99	-4.85	72.34
$CaCO_{3(s)}$	$[CO_3^{-2}] = 1.53 \times 10^{-5}$ M[a]	-6.52	-8.48	90.70

[a] based on 1000.00 mg/L carbonate alkalinity as HCO_3^- and reject pH = 7.30.

[b] calculated as Q_{SO}/K_{SO}. The value represents the approximate degree of oversaturation in the RO brine produced from MODE water.

[c] Benjamin, 2002.

The salts of barium and calcium are chemicals that might pose a problem while operating an RO unit at 80% or higher recoveries. The solubilities of calcium sulfate, calcium carbonate and barium sulfate, for example, are exceeded in brines derived from RO treatment of MODE water as shown in Table 6.10. The degree of saturation levels for barium sulfate, calcium sulfate and calcium carbonate in the feed water for MU 3 are calculated in the same manner as 25.77, 3.02 and 1.18, respectively, meaning that the concentrations of these salts are already higher than their saturation levels. The calculations for the degree of saturation are carried out for the initial conditions of MU 3 operation, i.e. feed pH of 6.8 and reject pH of 7.3. The bicarbonate concentration is assumed as 200 and 1,000 mg/L for feed and reject, respectively. These concentrations are very close to the average values of bicarbonate levels prior to any pH adjustment determined in the lab analyses. Feed pH of 6.8 (reject pH of 7.3) is chosen for the calculations since this operating condition is most likely to rise any scaling problem in the RO unit. However, no evidence of irreversible scaling, e.g. barium sulfate, was observed neither during the testing nor in the post-mortem analyses of the retired elements. The use of anti-scalant was likely important in this result and the use of anti-scalant is likely critical for a sustainable RO operation while desalting Alternative 17a pretreated MODE water.

Another component that may pose a problem in the RO operation is silicon dioxide. The solubility of silica is 120 mg/L at 25 ^{o}C and neutral pH. Even at the reject pH of MU 3, the level of silica is lower than this solubility limit. Another safety factor for the RO units treating water containing silica is the slow process of silica precipitation. On the other hand, decreasing the pH also decreases the solubility of silica. Therefore, it is more likely that silica problems will be experienced at lower operating pHs. The fact that silica was detected during the post-mortem analyses of the MU 3 retired elements might be an indication of that problem (or alternatively, that preformed silica solids (e.g., clays, quartz) were present in the MU feed). This topic is further discussed in the Autopsy Results section.

Iron and manganese levels were watched carefully not only for YMC water alternatives, but also for MODE water alternatives. Figure 6.45 shows the feed and reject concentrations of total iron and total manganese. Theoretical reject concentration is calculated for an RO running at 80% recovery. It is likely that these ions, especially iron levels with an average value of 0.124 mg/L in the feed water (0.445 mg/L in the reject) of MU 3, may cause performance problems while operating the RO unit. Iron and manganese detected on the surface of the membranes retired from MU 3 is evidence of this problem. Almost all the iron and manganese that reached MU 3 was considered as dissolved for two reasons. One is the microfiltration unit used in the upstream pretreatment train had a pore size of 0.1-µ and removes everything larger than this size. Second is that the lab analyses for the effluent of DMGF on PS 3 showed no difference in the concentrations of dissolved and total iron and manganese, suggesting that all the iron and manganese is in dissolved form at the effluent of DMGF.

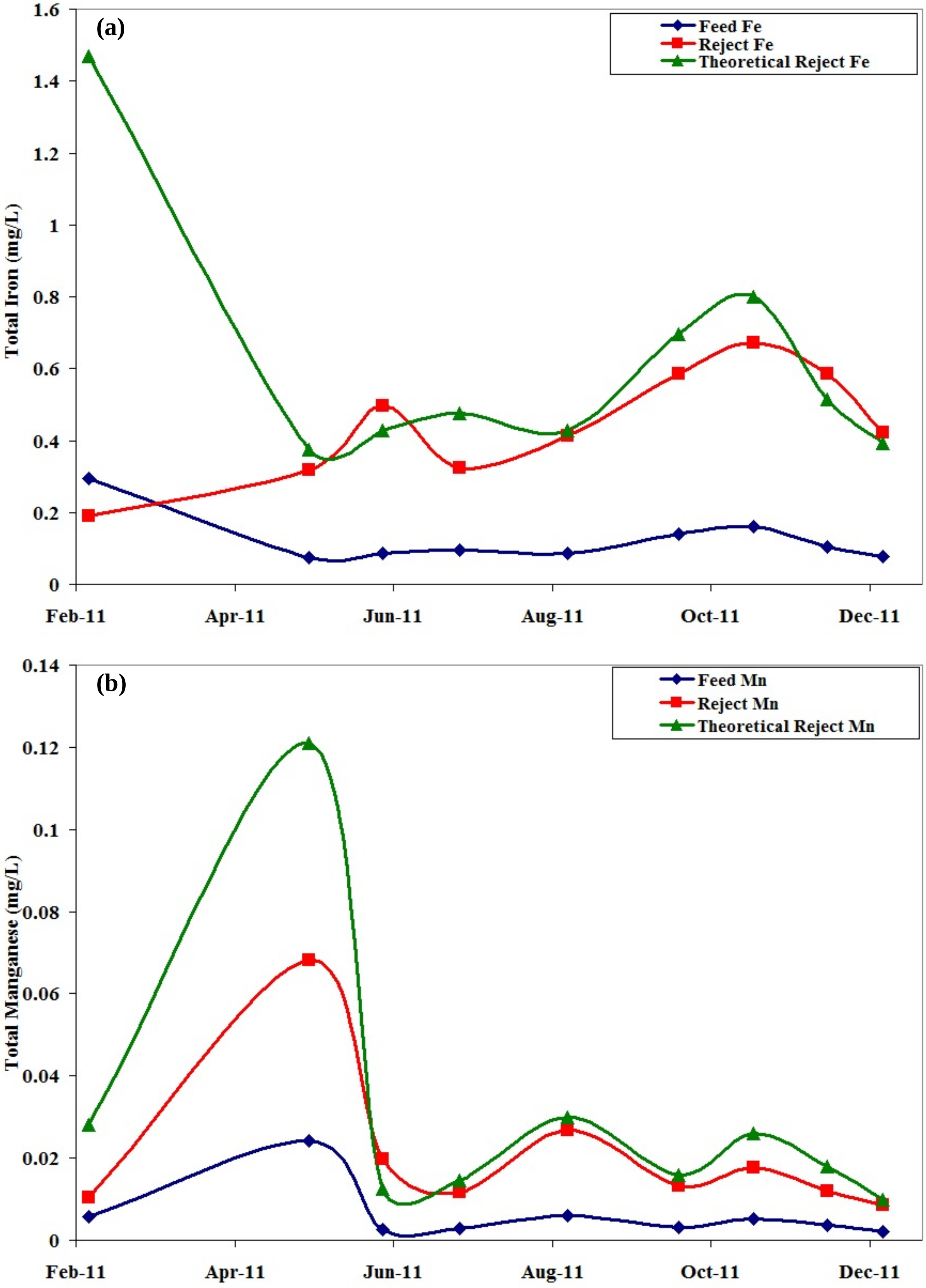


Figure 6.45. (a) Total Fe and (b) total Mn concentrations in MU 3 feed and reject streams during Round 2. Theoretical reject concentration is calculated for 80% recovery.

Theoretically calculated (5 times the feed concentration) iron and manganese concentrations in the reject stream is mostly higher than the measured reject concentrations. This might also suggest an accumulation of these ions in the elements. However, as all the iron and manganese is expected to be in dissolved form due to chelation with organics, it is not likely that MU 3 operation would be affected adversely due to problems associated with pre-formed iron and manganese. However, because both the concentration and pH increase as the feed moves through the MU element train, there is a possibility that some portion of the dissolved fraction precipitates and/or adsorbs and interacts with solids on the membrane surface. Thus, it is not a surprise to see evidence of these two metals on the membrane surface.

6.3.2.2 MU 4 Testing: Alternative 10 as Pretreatment

The RO unit, MU 4, started running on March 8, 2011 for long-term Round 2 testing of Alternative 10 as a pretreatment option for a possible YDP operation on MODE water. MU 4 started running with a feed pH of 5.6 to achieve a reject pH of 5.8 (Figure 6.46). On July 1, the feed pH was increased to about 6.0 to achieve a reject pH of 6.3. On December 8, it was increased once again to about 6.1 to achieve a reject pH of 6.5. The difference between the feed and reject pH increased as the operating pH was raised. Buffering capacity and the bicarbonate concentration is the most likely reasons for this behavior. As the authors increased the pH, water was gaining more buffering capacity with addition of bicarbonate. The increase in HCO_3:CO_2 ratio is the most likely reason for this behavior. As we increase the pH, less bicarbonate is converted to CO_2, which results in a greater concentration of bicarbonate in the reject and a greater HCO_3:CO_2 ratio, resulting in a greater reject pH. The reasons and the outcomes of these pH adjustments are presented below while explaining the observed and calculated operating parameters. The blue arrows in Figure 6.46 highlight the timing of the pH adjustments. The water temperature during Round 2 testing increased from the low twenties to low thirties degrees Celsius between March (the beginning of testing) and late August. Thereafter, it dropped back to 17-18 ^{o}C by the end of the year, which was the end of Round 2 testing.

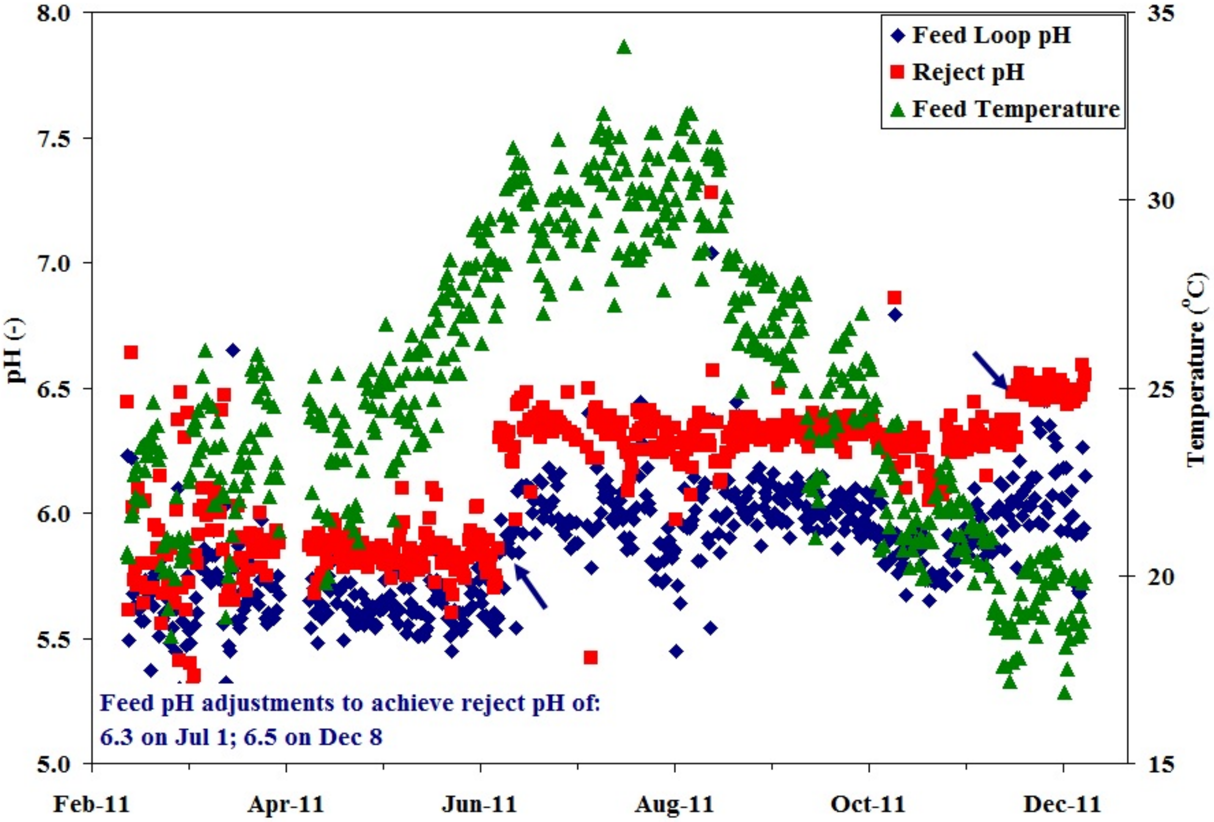


Figure 6.46. Feed and reject pH and temperature profiles for MU 4 during Round 2. The blue arrows indicate the timing of pH adjustments.

The early WTC values ranged between 7.5 and 8.7 × 10^{-12} m/s.Pa (Figure 6.47). As it was with MU 3 operation (Alternative 17a), these initial WTC values of the MU 4 elements matched almost perfectly with the observations during Round 1 testing of Hydranautics LFC3 on Alternative 10. During the first one and a half months of the testing (~1100 hours), WTC levels in all vessels dropped significantly by about ~1.5 × 10^{-12} m/s.Pa. The drop was slightly more in the first stage vessels, suggesting that it might be due to fouling by pre-formed solids. However, at the same time the STC for all vessels was decreasing (Figure 6.48). The drop was higher for the second stage elements for STC values. A long-term shutdown event between April 25 and May 3 took place due to cleaning performed on the MODE intake structure. During this shutdown, the membranes were flushed with RO permeate water at a pH of about 5.5 on a daily basis. No obvious impact was observed due to the shutdown event and the daily flushing routine. WTC and STC for all vessels continued from the same values prior to the shutdown event.

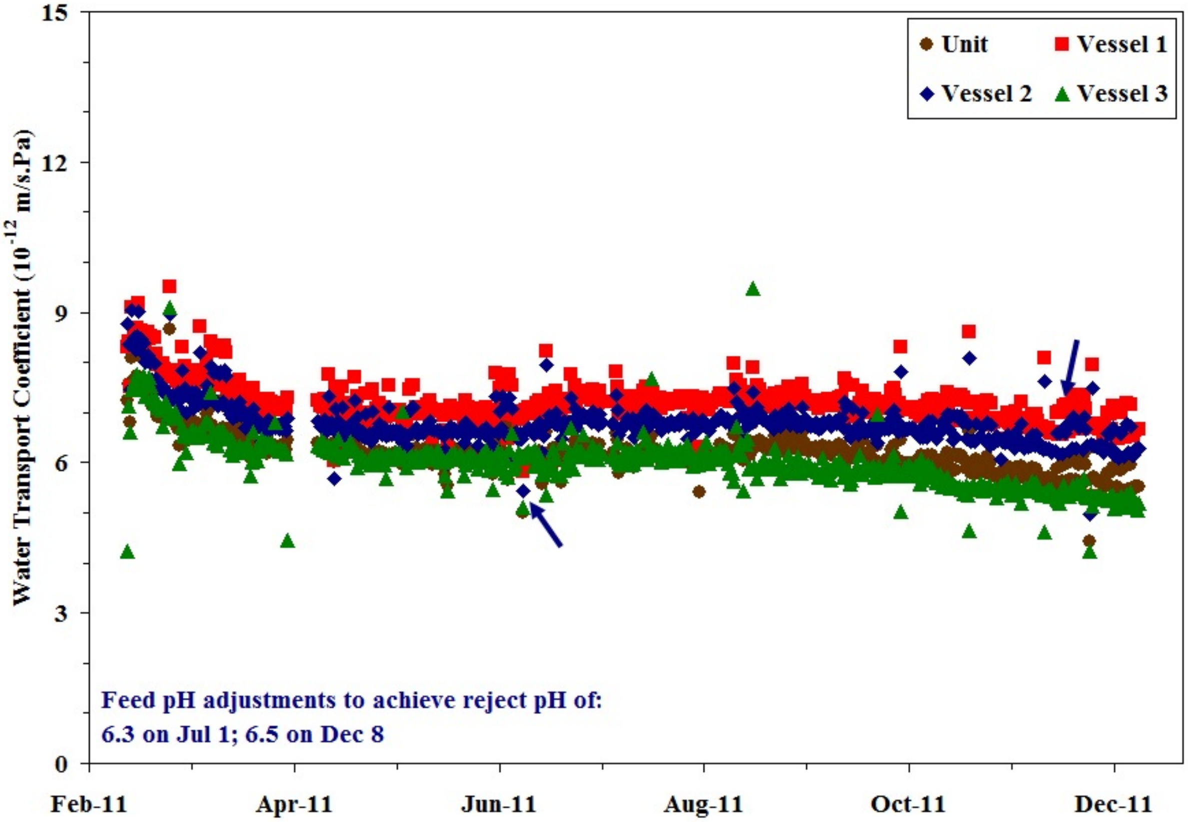


Figure 6.47. Water transport coefficient (WTC) profiles for MU 4 during Round 2. The blue arrows indicate the timing of pH adjustments.

Even though the STC values were very low and steady compared to Alternative 17a, the feed pH was increased to ~6.0 on July 1 to achieve a reject pH of 6.3 in an effort to increase MU 4 WTC values. The unit ran with stable but low WTC values during June. A minor increase by about 0.2 × 10^{-12} m/s.Pa in the WTC values was observed for all the membranes in both stages following the pH adjustment. This minor positive impact accompanied by a minor negative one as STC values increased very slightly after the pH increase. The influence was larger in the second stage (Vessel 3) elements. As observed in MU 3 elements, this jump was not followed by a continuous but slow decrease. The salt passage stayed rather constant after the pH change. WTC values for all the vessels stayed constant until mid-September to October. After this point, WTC for Vessel 3 elements, especially the tail element, started to decrease noticeably. The declines in the first stage elements were slower and not as drastic. This decrease in WTC values for both stages might be due to the decreasing temperatures, as the MODE water temperature dropped almost 10 °C between mid-September and early November (although a temperature correction is applied to all calculated values). On the other hand, it might also be due to fouling of the membranes, as the results of the post-mortem analyses of the retired membranes from this unit suggested. The steeper WTC decline in Stage 2 supported the latter idea. Therefore, the feed pH once again was raised by 0.2 to achieve a reject pH of 6.5 on December 8. However, this adjustment in pH did not help much for controlling the decline in WTC values and made little if any change on the STC values.

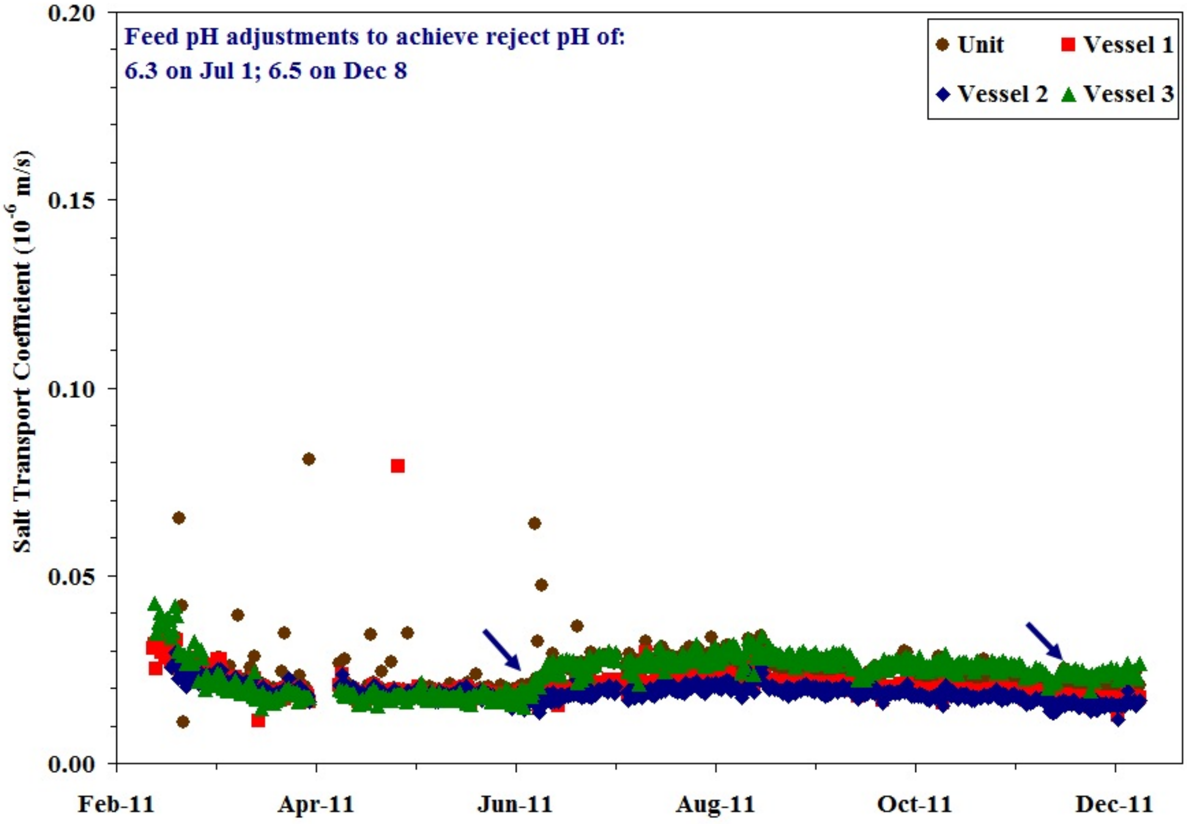


Figure 6.48. Salt transport coefficient (STC) profiles for MU 4 during Round 2. The blue arrows indicate the timing of pH adjustments.

A new element with lot # 10284524 (99.6% rejection during the wet test) was installed in Vessel 3 as Element 7 on July 2, 2011 (Figure 6.49), when the tail element was taken out for post-mortem analyses. The purpose was to determine if the loss of water flux was due to scaling or due to some other reason observable with the element autopsy techniques. The new element had a much higher salt passage of about 0.04 versus 0.02 x 10^{-6} m/s (Figure 6.50) and water transport coefficient of about 7 versus 6 x 10^{-12} m/s/Pa (Figure 6.49). Please, see Appendix F-2 for the detailed results. In response, the WQIC Operations Team performed troubleshooting and changed the o-rings and the connector for this element. They also checked the endcap of the vessel. No default was detected in any of the items checked. However, the high salt permeation and water transport of this element persisted. Therefore, the conclusion was that a bad element was loaded and it was replaced with a new LFC3 element on July 15. Even though the water flux came back up with the new element (indicated with arrow #2 in Figure 6.49), the salt passage stayed high. No explanation is obvious for this behavior.

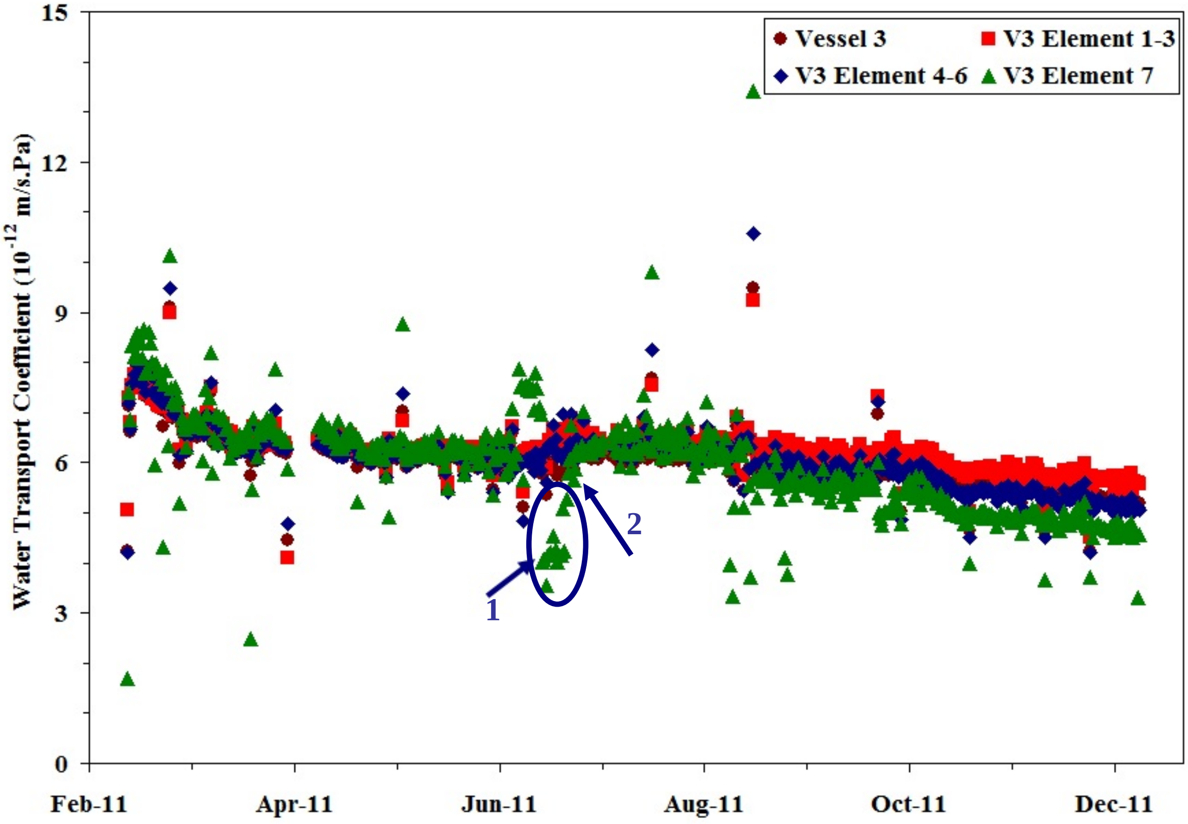


Figure 6.49. Water transport coefficient (WTC) profiles for MU 4 Vessel 3 (Second Stage) during Round 2. The blue arrow #1 indicates the timing of new "bad" element installation (Element 7) and arrow #2 indicates the timing of replacing the "bad" element with a new one. The green data points in the blue circle show the bad data collected by the faulty element.

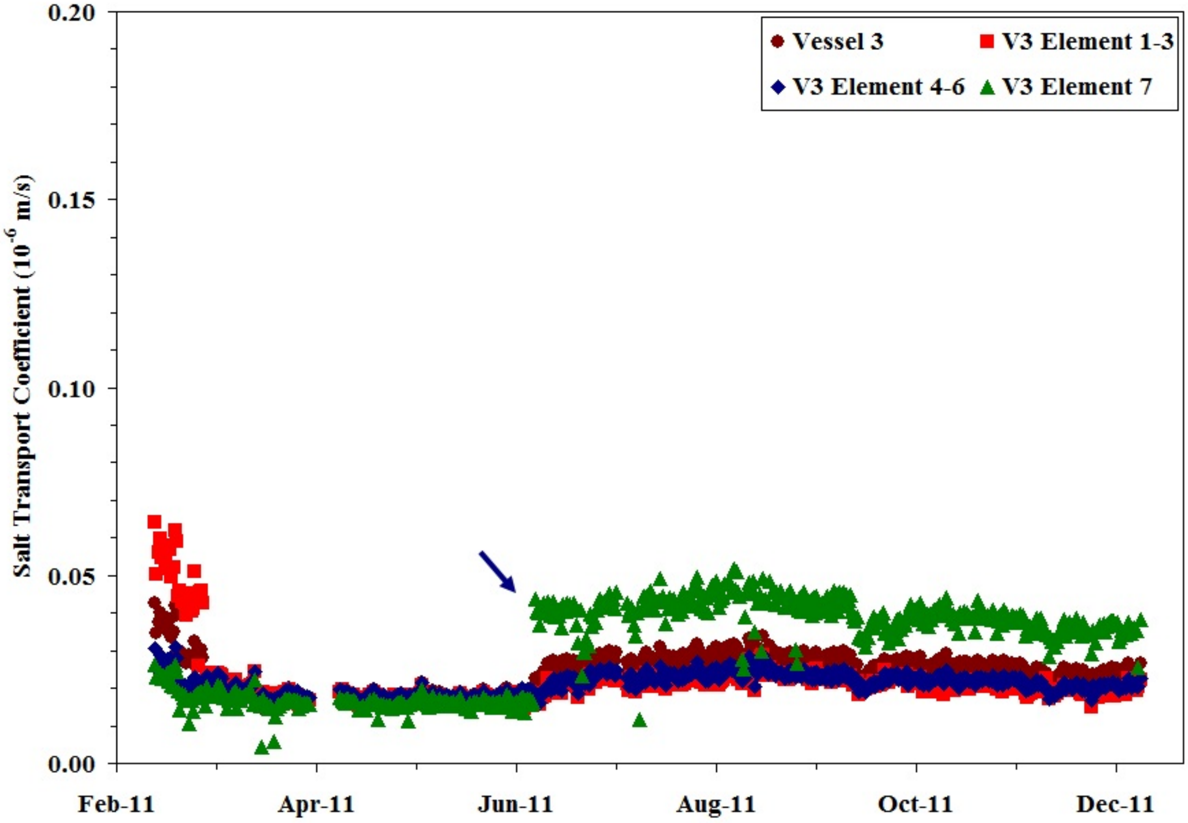


Figure 6.50. Salt transport coefficient (STC) profiles for MU 4 Vessel 3 (Second Stage) during Round 2. The blue arrows indicate the timing of new element installation (Element 7).

Initial values of element flow coefficients for MU 4 first stage vessels were the same as the ones in MU 3 ran on Alternative 17a. However, the C_e for Vessel 3 was more than 20% lower in MU 4 compared to MU 3 Vessel 3 C_e and it decreased slowly until the pH adjustment on July 1. Throughout the testing the C_e profile for MU 3 Vessel 3 was not as stable as observed for other vessels and MUs. However, it always stayed higher than the one in MU 4 Vessel 3. This low C_e value for Vessel 3 in MU 4 was due to the high differential pressure (dP) in the second stage of the RO unit. In fact, second stage dP was about 30 kPa higher than the first stage one. MU 4 was the only unit which had this situation. The first pH adjustment on July 1 helped to stabilize the C_e for Vessel 3. Conversely, when the next pH increase was carried out on December 8, all C_e values started to decrease slowly. This showed that operating at higher pH, may be more likely to cause fouling problems. Overall, the C_e looked good throughout Round 2 testing of MU 4. Cleaning the unit for this alternative might be advisable, based on the trends of

WTC and C_e profiles, although this was not done during the 9-month duration of MU 4 operation.

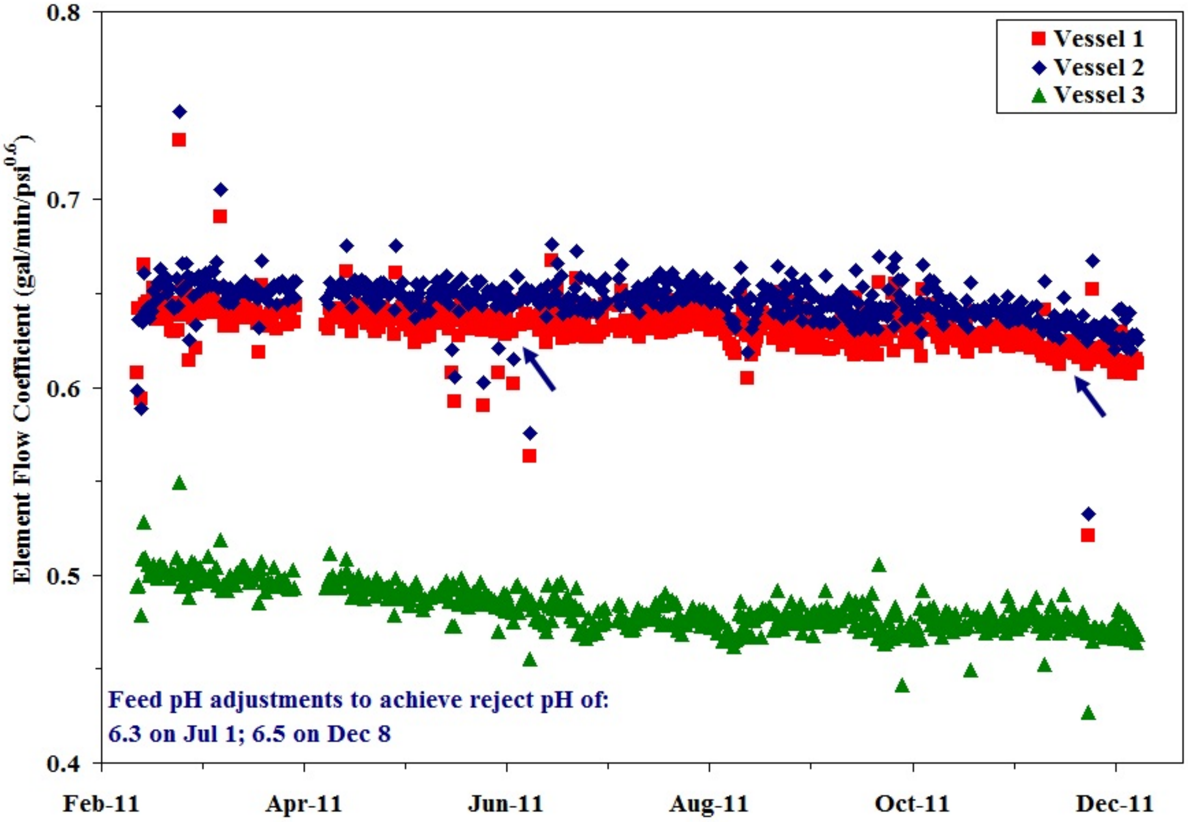


Figure 6.51. Element flow coefficient (Ce) profiles for MU 4 during Round 2. The blue arrows indicate the timing of pH adjustments.

In summary, the Hydranautics LFC3 membrane operated at 80% recovery with partial lime-softened, gravity filtered MODE water showed lower WTC values compared to all the other alternatives tested. However, the lower WTC values were associated with very low STC values. Both of these operational parameters stayed reasonably constant through Round 2. As the operating pH was increased, a slight decrease in WTC and a minor step increase in STC values were observed. After examining the autopsy results and physically observing the amount of material buildup (please, refer to Section 8), the immediate drop in WTC for all elements following the initiation of testing might suggest a fairly quick material buildup on the membrane surface. Although post-mortem analyses of the retired elements confirmed a larger build-up of material on the MU 4 than MU 3 elements, without conducting similar element autopsies after a much shorter runtime, the early buildup of material cannot be completely confirmed. However, the post-mortem analyses also demonstrated that the material that fouls the membranes is easy to scrape off the surface. Therefore, it might be reasonably conjectured that it would also be easy to clean *in-situ*. Further studies in lab and pilot scale testing are needed to confirm this theory. A feed pH of 5.6 (reject pH of 5.8) supplied a sustainable 9-month run in terms of WTC and STC values. At this operating pH, a slow but steady drop was observed in the C_e of the second stage vessel (Vessel 3). It is believed that this alternative, YDP current treatment, is overall a success, at least with respect to the LFC3 membrane chemistry and spacer configuration. A positive side of this alternative is that very little acid is needed to adjust the operating pH, since the carbonate system buffering capacity in the partial lime softened water is negligible.

The results of the water quality analyses for MU 4 feed and reject are presented in Table 6.11, below. One very important thing about lime-softening is that it removes almost all bicarbonate and carbonate alkalinity from the water. Therefore, it is very easy to decrease the pH of the water and requires minimal use of acid/base for pH adjustment. Reduced acid cost is counterbalanced by the significant amount of lime required for softening and the use of ferric sulfate for coagulation. Significant quantities of lime sludge are produced that require conveyance and disposal in drying beds. The average concentration of total alkalinity in the feed water of MU 4 is presented in Table 6.11 as 9.10 mg/L as $CaCO_{3.}$ The bicarbonate concentration is assumed to be the same as total alkalinity at the pH levels for MU 4 feed and reject.

Lime-softening also removes a very big portion of the divalent cations, i.e. Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+} and Mn^{2+}, via precipitation in the SCRs. Lower values for all these ions were detected during the MU 4 operation (Table 6.11).

Table 6.11. Water composition for feed and reject of MU 4 RO unit.

		MU 4 Feed				**MU 4 Reject**			
Parameter	**Units**	**Average**	**Minimum**	**Maximum**	**St. Dev.**	**Average**	**Minimum**	**Maximum**	**St. Dev.**
Barium	*µg/L*	9.8	7.3	12.4	1.6	43.8	13.1	59.5	13.8
Bicarbonate	*mg/L*	11.11	8.68	13.70	1.77	25.82	9.74	40.20	9.70
Calcium	*mg/L*	86.04	74.60	104.00	8.85	372.67	106.00	455.00	103.66
Chloride	*mg/L*	588.00	536.00	658.00	36.93	2,597.00	663.00	3,000.00	731.90
Conductivity	*µS/cm*	3,485.6	3,130.0	3,840.0	212.0	13,163.3	3,870.0	15,000.0	3507.4
Iron	*µg/L*	38.0	11.6	77.7	19.3	157.9	107.0	223.0	40.2
Magnesium	*mg/L*	57.98	53.30	63.30	3.40	251.08	57.70	306.00	73.97
Manganese	*µg/L*	1.4	0.6	3.4	0.9	3.2	1.3	8.2	2.1
Nitrate as N	*mg/L*	5.54	4.50	6.50	0.92	22.05	12.10	27.20	6.02
pH	-	6.36	6.10	6.61	0.17	6.81	6.39	7.25	0.27
Potassium	*mg/L*	7.04	6.64	7.46	0.29	30.96	7.42	36.80	8.97
Silicon Dioxide	*mg/L*	10.49	4.63	14.50	3.30	48.89	4.61	68.70	19.69
Sodium	*mg/L*	576.56	535.00	615.00	27.97	2519.78	628.00	2,890.00	714.42
Strontium	*mg/L*	1.32	1.02	1.69	0.20	5.69	1.62	7.47	1.64
Sulfate	*mg/L*	852.78	764.00	940.00	48.73	3,791.00	949.00	4,370.00	1,078.20
Sum of Anion	*meq*	35.10	32.30	38.90	1.93	154.59	39.30	176.00	43.54
Sum of Cation	*meq*	34.32	32.60	36.70	1.47	149.84	37.60	169.00	42.21
Tot. Alk. as CaCO3	*mg/L*	9.10	7.12	11.20	1.45	21.16	7.98	32.90	7.94
Tot. Hard. as CaCO3	*mg/L*	452.89	418.00	488.00	24.61	1,961.33	502.00	2,390.00	558.91
Total Organic Carbon	*mg/L*	1.79	1.50	2.08	0.23	6.85	2.91	11.30	2.35
Total Salt	*mg/L*	2,203.3	2,040.0	2,410.0	110.3	9,694.4	2,450.0	11,000.0	2,730.0

Table 6.12. Concentration/solubility data for MU 4 reject ion pairs that may contribute to membrane scaling. Ion products were based on the MU 4 reject average concentrations shown in Table 6.11, uncorrected for the ionic strength.

Precipitate	Ion Concentration	log (ion product)	log K_{S0}[c]	Degree of Saturation [b]
$BaSO_{4(s)}$	$[Ba^{+2}] = 3.19 \times 10^{-7}$ M $[SO_4^{-2}] = 3.95 \times 10^{-2}$ M	-7.90	-10.0	125.74
$CaSO_{4(s)}$	$[Ca^{+2}] = 9.30 \times 10^{-3}$ M	-3.44	-4.85	25.98
$CaCO_{3(s)}$	$[CO_3^{-2}] = 9.70 \times 10^{-9}$ M[a]	-10.04	-8.48	0.03

[a] based on 20.00 mg/L carbonate alkalinity as HCO_3^- and reject pH = 5.8.

[b] calculated as Q_{SO}/K_{SO}. The value represents the approximate degree of oversaturation in the RO brine produced from MODE water.

[c] Benjamin, 2002.

The salts of barium and calcium are among the chemicals that may pose a problem while operating an RO unit at 80% or higher recoveries, although partial lime softening is explicitly implemented to attempt to minimize this likelihood. Only the solubilities of sulfate salts, i.e. calcium sulfate and barium sulfate, are exceeded in brines derived from RO treatment of lime-softened MODE water as shown in Table 6.12. Calcium carbonate is much lower than its saturation level due to the removal of a substantial fraction of the divalent cations and bicarbonate via lime-softening. The degree of saturation levels for barium sulfate, calcium sulfate and calcium carbonate in the feed water for MU 4 are calculated in the same manner as 6.31, 1.35 and 0.002, respectively. The calculations for the degree of saturation are carried out for the initial conditions of MU 4 operation, i.e. feed pH of 5.6 and reject pH of 5.8. The bicarbonate concentration is assumed via lab analyses as 10 and 20 mg/L for feed and reject, respectively. The concentrations of bicarbonate (Table 6.12) in feed and reject streams show a concentration factor of ~2.5. As expected, this suggests that the rejection rate for bicarbonate is about 50%, while running at 80% recovery. At this recovery with 100% rejection, bicarbonate concentration would have been 5 times higher in the reject than feed. Feed pH of 5.6 (reject pH of 5.8) is chosen for the calculations since MU 4 operated successfully at this pH. Even though no scaling is expected regarding the calculations presented above, a considerable amount of fouling material was observed in the post-mortem analyses of the retired elements.

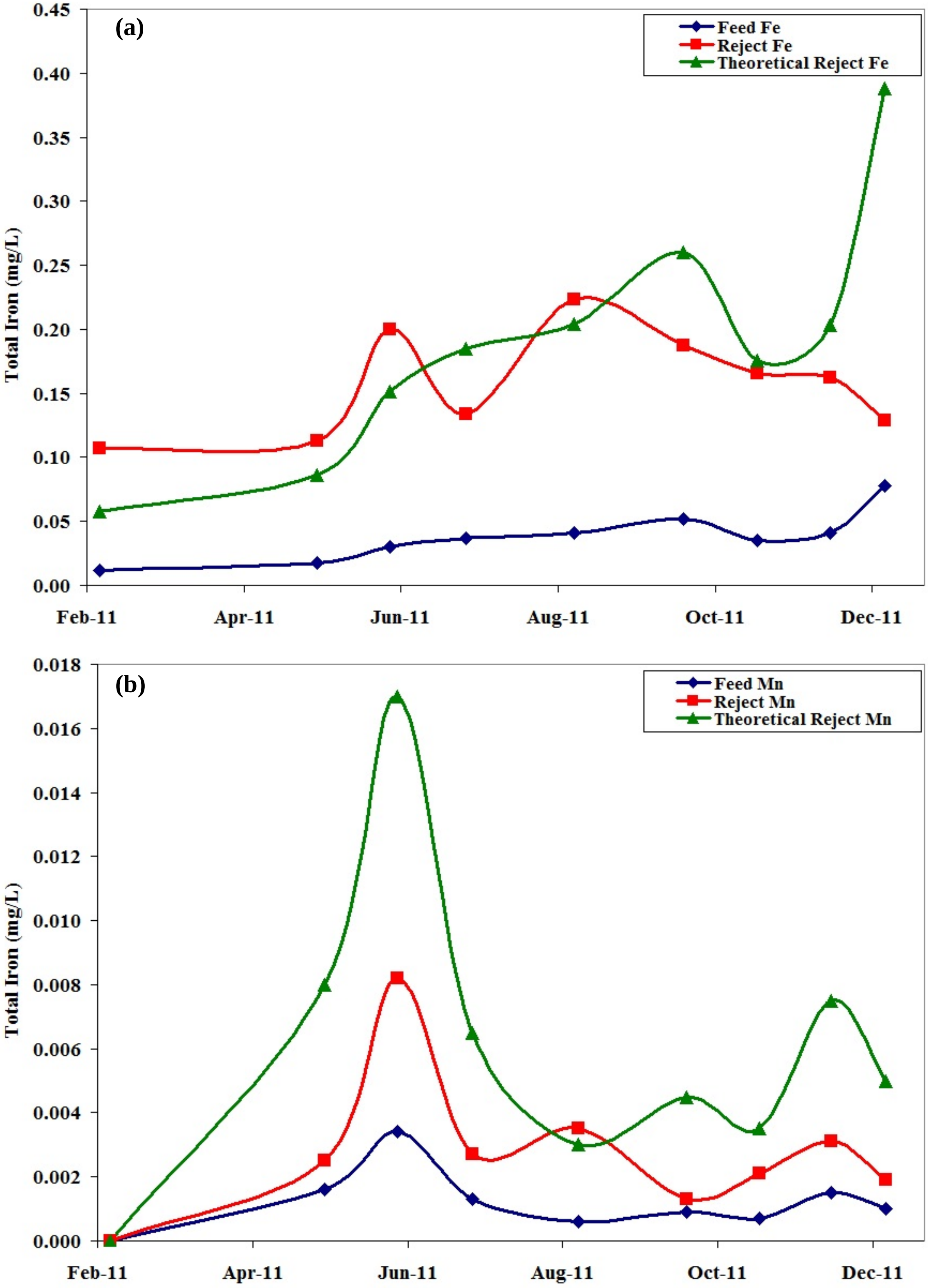


Figure 6.52. (a) Total Fe and (b) total Mn concentrations in MU 4 feed and reject streams during Round 2. Theoretical reject concentration is calculated for 80% recovery.

Figure 6.52 shows the feed and reject concentrations of total iron and total manganese. Iron and manganese had average values of 38.0 μg/L and 1.4 μg/L in the feed water (157.9 μg/L and 3.2 μg/L in the reject) of MU 4, respectively. These levels are much lower than the ones detected in the feed water of the RO units operated in Alternative 17a, reflecting their removal by lime softening. The pH changes will alter the way organics interact with the Fe and Mn. It is well known that lime treatment hydrolyzes organic matter into lower molecular weight compounds that are unlikely to complex with metals. This increases the removal efficiency of iron and manganese. However, they might still cause performance problems while operating an RO unit. Specifically, the theoretical Mn concentration calculated for the reject is almost always higher than the measured one (Figure 6.52(b)), suggesting the accumulation on the membranes. Correspondingly, minor levels of iron and manganese were detected on the surface of the membranes retired from MU 4.

6.3.3 The Effects of Flux and Membrane Type on RO Performance

Hydranautics LFC3 was chosen based on the results of Round 1 element screening tests and the availability of the membranes at the time of the procurement decision. Toray TML10 elements were initially chosen for Round 2 MU testing, however Toray was unwilling to supply the 109 (2.5” x 40”) elements required. The second choice by the TAT was the LFC3 membranes, which Hydranautics did supply. Initially, two MU units (MU 3 and MU 4) were used for evaluation of the performance of the chosen membrane in treating the MODE water following either Alternative 10 or 17a pre-treatment. The average flux and water recovery were selected as 12 gfd and 80%, respectively, for all the MUs. There were three main independent variables during the MU testing: (1) membrane type, (2) water flux, and (3) water recovery. Since these three factors critically affect the performance of an RO unit, testing variations on these factors was essential to arrive at a healthy decision at the end of the project.

The YMC water source was lost earlier than expected in early September 2011 after only about 5 months of operation, because YMC flows were diverted south to enable the U.S. to comply with its salinity and water treaty requirements to Mexico. This freed two extra MUs (MU 1 and MU 2) and an extra ETA (ETA 4) for extra testing that was not contemplated in the original project scope. Therefore, MU 1 started operating in parallel with MU 3 on Alternative 17a (MODE water) using Hydranautics LFC3 membranes on September 30, 2011. This trial was implemented to allow direct comparison between MU 1 and MU 3 behavior with the only variables being the difference in flux (15 gfd versus 12 gfd) for the period from 9/30-12/30, and recovery (85% versus 80%) together with the high flux for the period from 11/17-12/30. However, it is notable that MU 3 elements had already seen about 6 months of runtime, while MU 1 elements were new. On the other hand, MU 2 started operating in parallel with MU 4 on Alternative 10 on October 4, 2011 for testing the performance of two other membrane types, with Toray TML10 in the first stage and DOW BW30-XFR in the second stage. Just as with MU 4 which had been operating on the partial lime softened MODE water since early March, the average water flux of 12 gfd and water recovery of 80% were used for MU 2 operation during this testing. Thus, the direct comparison between MU 4 and MU 2 MODE operation was in the membrane types loaded in each stage. To test the fouling potential of these two membranes while operating at high-flux (15 gfd) on partial lime-softened MODE water, ETA 4 was loaded with two each of TML10 and BW30-XFR membranes and operated in parallel with MU 2 and MU 4. All three added RO tests were short-term, but very useful to address additional questions raised in the research. All other parameters, such as pH, chlorine dosing, anti-scalant dosing, etc., were kept the same as in their corresponding units. During these tests, the same parameters as for the other MU or ETA units were measured, calculated and monitored daily by the Test Manager and the operators and weekly by the TAT members. This period of testing is referred to as Round 2 Phase 2 testing.

6.3.3.1 MU 1 High-Flux High-Recovery Testing: Alternative 17a as Pretreatment

The RO unit, MU 1, started running on September 30, 2011 for Round 2 Phase 2 testing of Alternative 17a as the pretreatment option for a possible YDP operation on MODE water at elevated water flux. Again, 21 new Hydranautics LFC3 elements in 2-1 array were used for this unit. The flux was increased from 12 gfd by 25% to 15 gfd for this testing. During the first one and a half months of its operation, recovery was kept at 80% for direct comparison with MU 3 performance. On November 17, the recovery was increased to 85% while keeping the same high-flux. Since MU 1 ran in parallel with MU 3 and no separate pH or other adjustments were performed, it shared the same feed water as MU 3. Both ran at a feed pH of 5.6-5.8 to achieve a reject pH of 6.1 on MU 3. During this Round 2 Phase 2 testing, no pH changes were implemented. The total runtime for this testing was 2088 hours (almost three months).

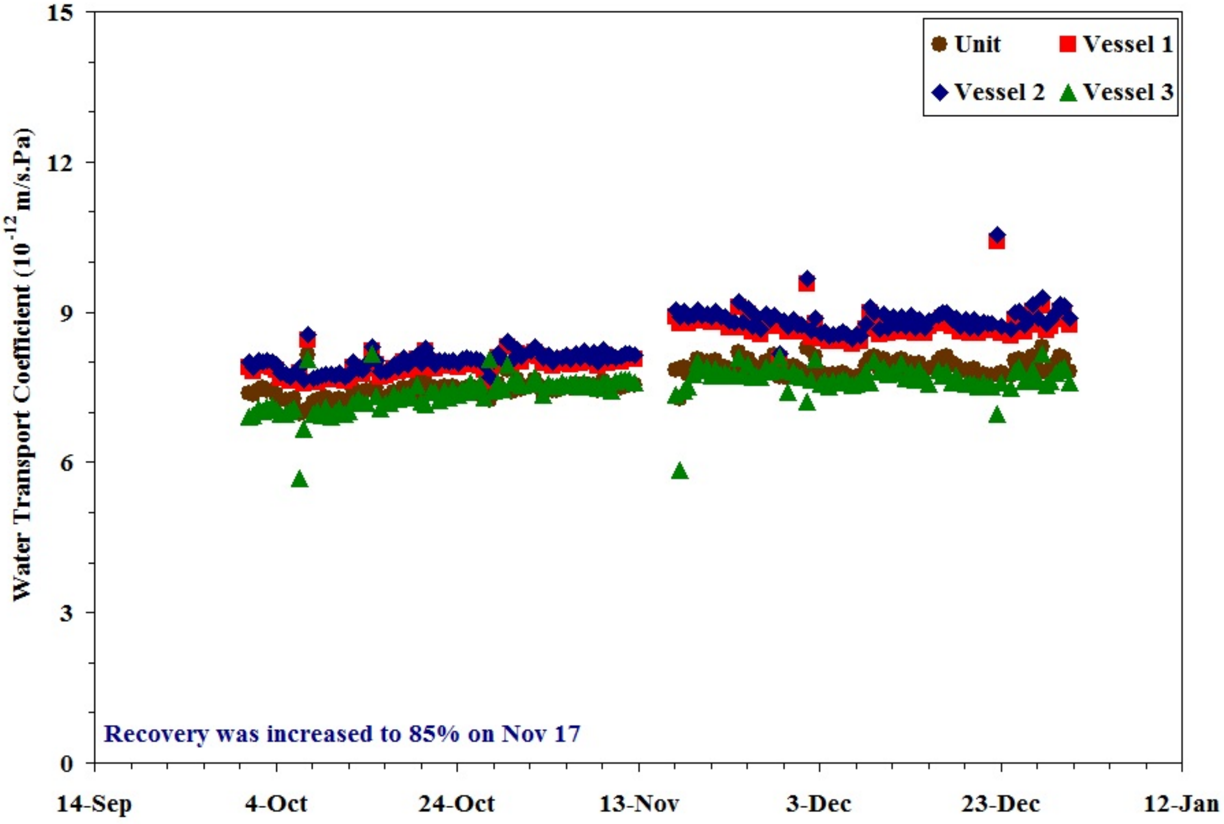


Figure 6.53. Water transport coefficient (WTC) for MU 1 on Alternative 17a during Round 2 Phase 2 (running with the reject pH of 6.1).

The initial values for WTC in both stages were lower than the ones recorded in MU 3 (meaning the increase in pressure necessary to increase the flux was greater than the increased volumetric flow rate of permeate through the membrane). Nevertheless, the same slow increase in WTC was observed as in MU 3’s first 1,035 hours of operation (almost one and a half months). Therefore, the increased flux decreased the initial WTC by 3-5% but it did not affect the trend of rising WTC for the LFC3 elements while operating on Alternative 17a at reject pH of 6.1. STC values for all elements increased slowly during the first month of operation until November 1. They appeared to stabilize after that.

Since the elements exhibited steady performance in the first one and a half months of high flux operation in terms of WTC and STC, the recovery was increased to 85% on November 17. Following this increase in recovery, WTC values for the first stage elements jumped up while Vessel 3 elements stayed at the same level. The STC values also jumped up as expected due to increased salt passage. However, a slow decline in STC was observed for all vessels following the initial jump. This matched with what was observed when the pH decreased to 6.1 on the reject stream of MU 3 operated with MODE water. However, by the second week of December, the STC for Vessel 3 started to increase, again. The rate of increase was similar to that at 80% recovery but considerably lower than the one observed at 80% recovery and baseline flux (see Figure 6.54). WTC values for both stages stayed stable after the recovery increase.

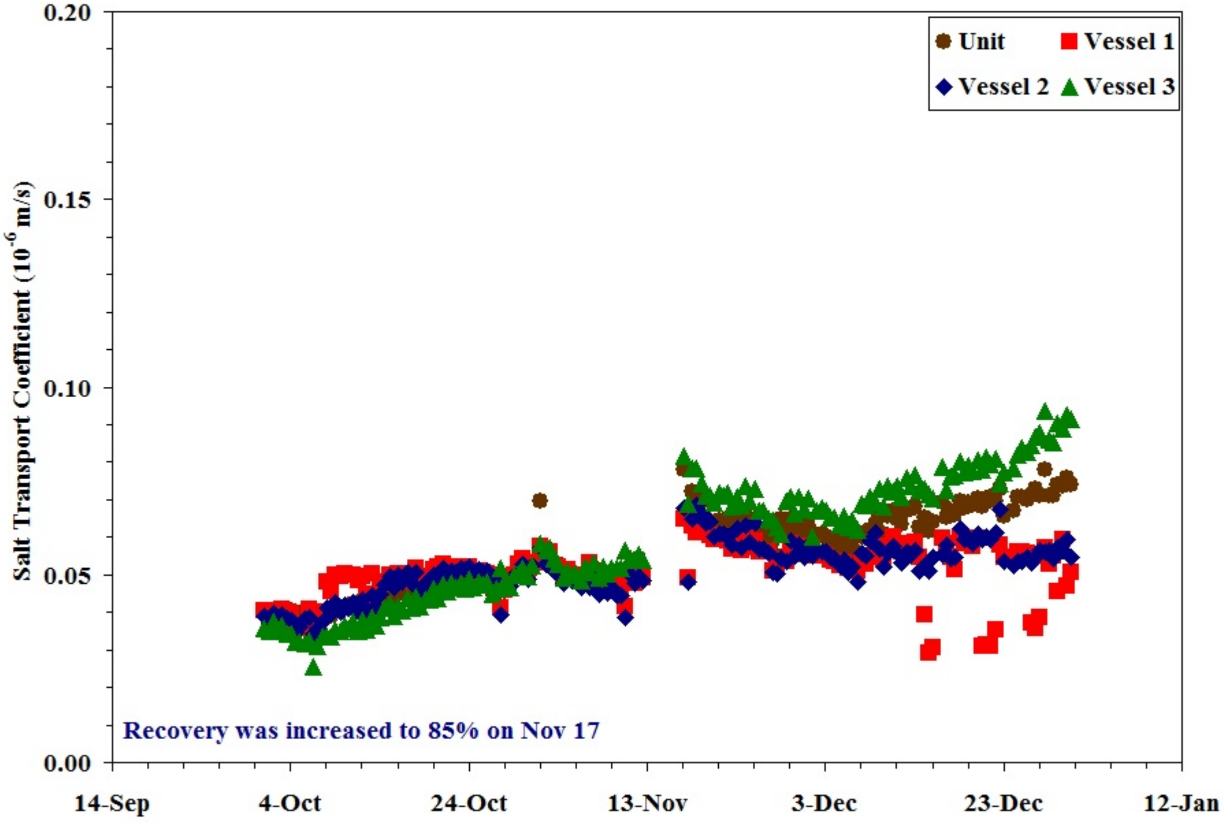


Figure 6.54. Salt transport coefficient (STC) for MU 1 on Alternative 17a during Round 2 Phase 2 (reject pH 6.1).

Overall, B/A values for Vessel 1 and Vessel 2 were stable throughout Round 2 Phase 2 testing (data not shown, but available in appendices). However, Vessel 3 B/A doubled during the three months of testing, but the rate of increase after switching to 85% recovery was lower than during 80% recovery. The STC values for the first stage membranes are also higher after increasing the recovery but the rates of increase are much lower. In fact, both STC and B/A values for the first stage can be interpreted as stable under the given conditions. The increase in the second stage STC and B/A values might be controlled by dropping the pH, except no change in pH was performed since other units were running on the same feed water. Additionally, the WTC values were high and very stable, so that this operating condition might be more favorable than lowering STC values and simultaneously lowering WTC values.

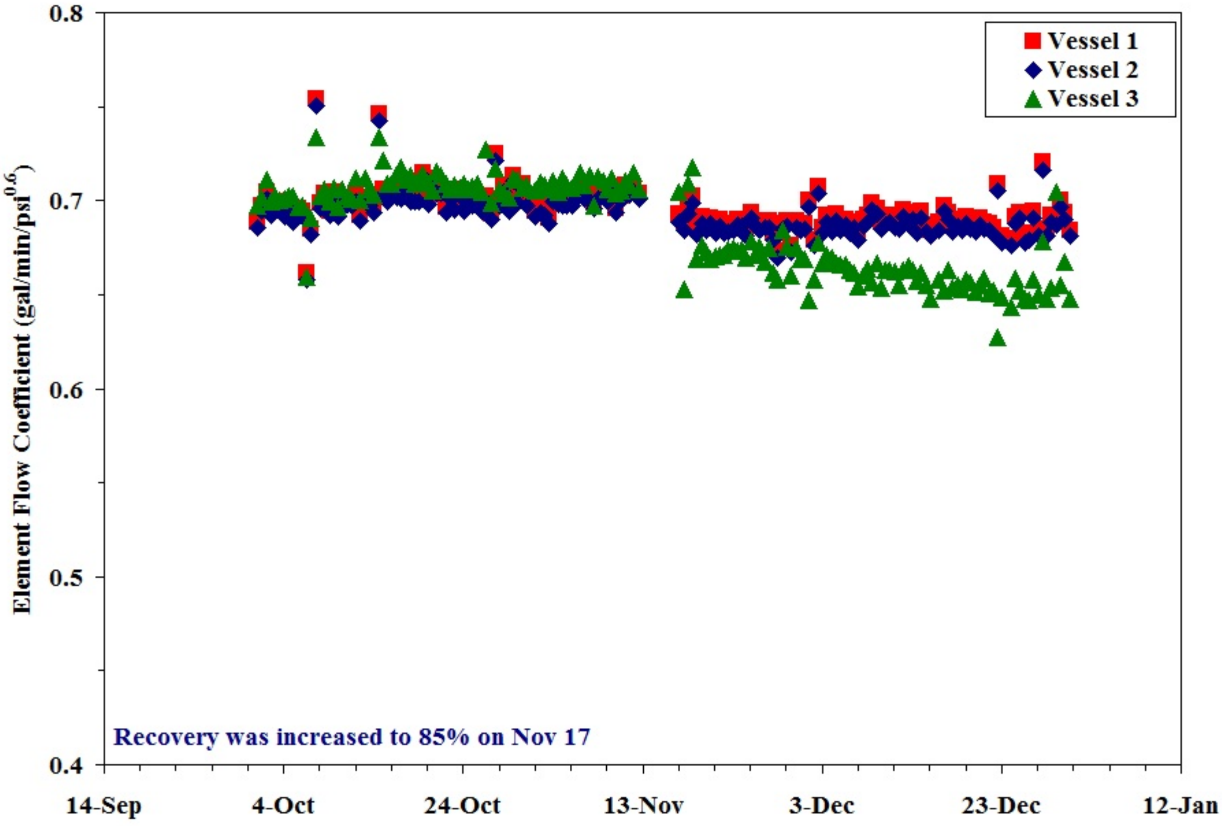


Figure 6.55. Element flow coefficient (C_e) for MU 1 on Alternative 17a during Round 2 Phase 2 (reject pH 6.1).

C_e dropped slightly after the recovery increase to 85% (Figure 6.55). Vessel 1 and Vessel 2 values stayed constant after the recovery increase until the end of testing. However, Vessel 3 *Ce* decreased slowly after the recovery increase. This decline is important if it indicates precipitation in the second stage. The autopsy results, which are discussed in more details in

Section 8, show higher amount of material buildup in high-flux high-recovery membranes compared to the ones ran with 12 gfd at 80% recovery. An expected increase in the second stage osmotic pressure was observed upon switching to the higher recovery, but no significant increase in the feed pressure required was recorded. Consequently, running an RO unit at 85% recovery with high-flux and PA membranes appears to be a feasible option for treating Alternative 17a water. Please, see Appendix H-3 for the remainder of the results.

6.3.3.2 MU 2 Different Membrane Types Testing: Alternative 10 as Pretreatment

The RO unit, MU 2, started running on October 4, 2011 for Round 2 Phase 2 testing of different membrane types on Alternative 10. Fourteen Toray TML10 elements in the first stage (Vessel 1 and Vessel 2) and seven DOW XFR elements in the second stage (Vessel 3) were used for this testing. TML10 and XFR were chosen based on their good performance in Round 2 ETA testing. An extra-foulant resistant (as claimed by the manufacturer) membrane, DOW XFR, was installed in the second stage rather than first stage because an insufficient number of XFR elements were available on-hand to fill stage 1 vessels and time restrictions did not allow additional elements to be ordered. The flux was 12 gfd for this testing. MU 2 operated in parallel with MU 4 during the Round 2 Phase 2 testing. Therefore, during the first two months of its operation, the feed pH was kept about 6.0 to achieve a reject pH of 6.3 on MU 4. For the last three weeks of the operation, the pH was increased by 0.2 units on December 8 to achieve 6.5 on MU 4 reject. Both MUs operated at 80% recovery. The total runtime for this MU 2 (Round 2 Phase 2) testing was 2,060 hours (almost three months).

The initial WTC values for Toray TML10 membranes in the first stage were almost 10% higher than the Hydranautics LFC3 membranes running in the first stage vessels on MU 4 at the same time, although at this point the MU 4 elements had been use for approximately 6 months while the MU 2 elements were new. On the other hand, DOW XFR membranes in the second stage had about 5-7% lower initial WTC values than the LFC3 membranes in second stage of MU 4. Although, this advantage of LFC3 membranes was lost in the first couple of weeks as LFC3 membranes lost the water flux significantly compared to the DOW XFR. TML10 membranes showed a steady decline in WTC throughout operation at the lower feed pH;

thereafter it was stable. Same behavior was observed for the LFC3 membranes in MU 4. Although, the rate of decline in LFC3 membranes was higher than the TML10. In contrast, XFR did not show any decline in WTC unlike the LFC3 membranes in second stage of MU 4. In fact, an increase was monitored prior to the pH adjustment on December 8 from 6.3 to 6.5 in the MU 4 reject. The WTC value for DOW XFR was higher than the LFC3 value after a month of operation. WTC for all membranes in both stages stabilized after the pH increase. The very different behavior of the different membranes running on the same water shows the importance of the membrane selection and finding the most appropriate operating conditions for the particular membrane chosen.

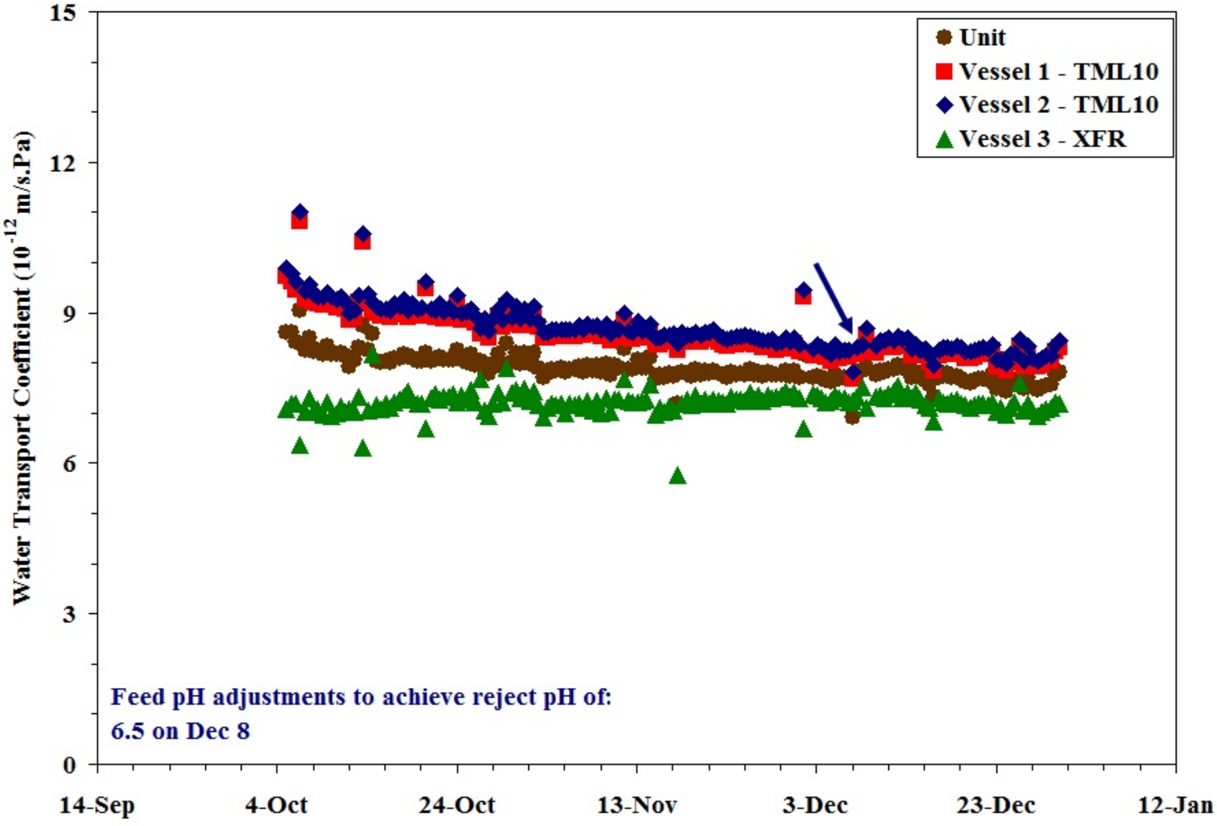


Figure 6.56. Water transport coefficient (WTC) for MU 2 on Alternative 10 during Round 2 Phase 2. The blue arrow indicates the timing of pH adjustment to achieve a reject pH of 6.5 (from 6.3) on MU 4 reject stream.

The initial STC value for TML10 was practically the same as the LFC3. In contrast, XFR had lower STC values than both LFC3 in the first and second stage and TML10 in the first stage.

This very low salt passage for XFR and relatively higher WTC values even when they were installed in the second stage make this membrane an attractive option to run on lime-softened water. Both MU 2 membranes showed a very minor decline in STC in the early period of testing and stayed extremely stable and low through Round 2 Phase 2. None of the MU 2 or 4 membranes showed a significant response in the STC to the pH increase in late December. The WTC and STC results for DOW XFR indicate that this membrane does better at the lower pH, as WTC appears to have declined after the pH increase while STC was stable. This is in contrast to results for TML10.

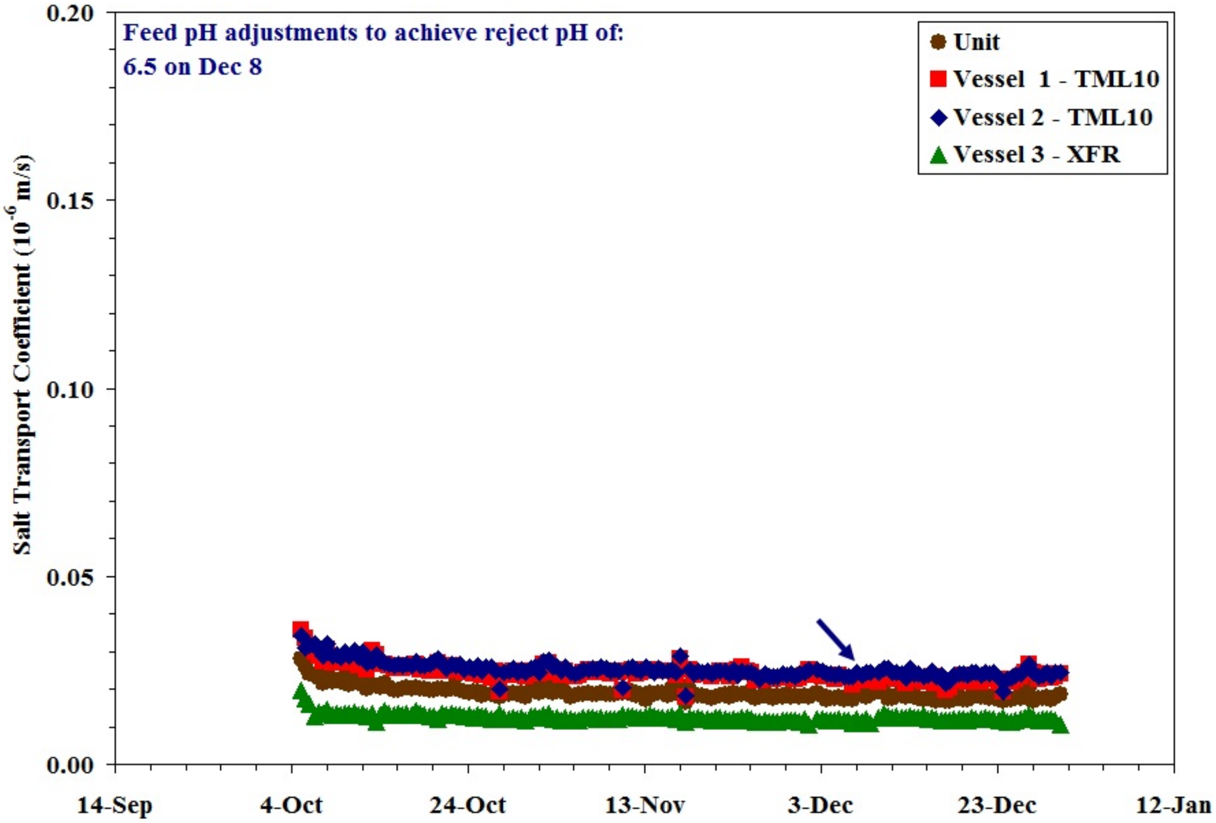


Figure 6.57. Salt transport coefficient (STC) for MU 2 on Alternative 10 during Round 2 Phase 2. The blue arrow indicates the timing of pH adjustment to achieve a reject pH of 6.5 (from 6.3) on MU 4 reject stream.

The C_e values for Vessel 1 and Vessel 2 stayed constant through the entire testing period (Figure 6.58). Nevertheless, Vessel 3 C_e value decreased steadily during both operating pHs. Differential pressures for both stages increased constantly during the entire testing period. These results indicate that all membrane types accumulate foulant in the feed/brine spacer and that such dP increases will require that chemical cleanings be performed on a regular basis to control, despite stable WTC and STC values. B/A values were exceptionally stable for all vessels.

As the salt passage decreased during the testing, the net driving pressure increased. This can be clearly seen in the TDS level of product water. No explanation is obvious for this. Decreasing salt passage is attributed to the formation of a semi-permeable dynamic foulant layer on the surface of the PA membrane. In response to the higher fouling in the TML10 elements, product flows increased for the XFR membranes in second stage and decreased for TML10 membranes in first stage.

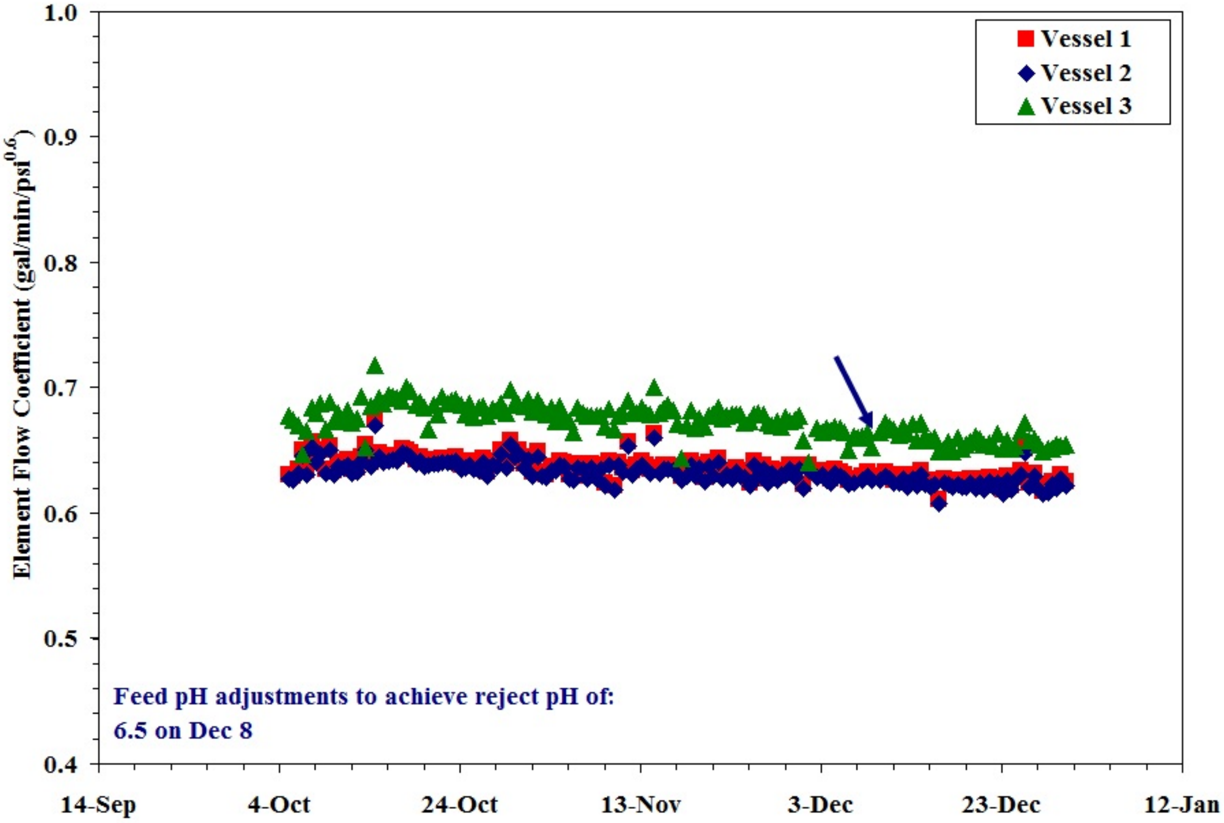


Figure 6.58. Element flow coefficient (C_e) for MU 2 on Alternative 10 during Round 2 Phase 2. The blue arrow indicates the timing of pH adjustment to achieve a reject pH of 6.5 (from 6.3) on MU 4 reject stream.

In summary, both TML10 and DOW XFR performed as well as the LFC3 for treating the lime-softened gravity-filtered MODE water on Alternative 10. Lower WTC values with Alternative 10 versus 17 were observed regardless of membrane type. Very low STC values and stable operating parameters are the main advantages of this alternative, again, regardless of membrane type.

6.3.3.3 ETA 4 High-Flux Element Screening Testing: Alternative 10 as Pretreatment

ETA 4 started running on November 14, 2011 for Round 2 Phase 2 testing of short-term fouling potential evaluation of Toray TML10 and DOW XFR membranes at high-flux operation on Alternative 10. Two DOW XFR elements in Vessel 1 and two Toray TML10 elements in Vessel 2 were tested for this phase. Because MU 2 Round 2 Phase 2 testing was performed with TML10 and XFR membranes, these membranes were chosen to test at high-flux operation. LFC3 was tested at high flux on the other alternative train treating MODE water. The flux was chosen as 18 gfd for this testing because the purpose was to simulate lead elements of an MU running at high flux. The average flux of an MU running at high flux is 15 gfd as it was in MU 1 operation. Therefore, the lead element of such an MU would treat the water at about 18 gfd, as it was measured in MU 1 operation (8.5×10^{-6} m/s). ETA 4 operated in parallel with MU 2 and MU 4 during the Round 2 Phase 2 testing. Hence, it shared the same feed water and its feed pH was about 6.0 to achieve a reject pH of 6.3 on MU 4 until December 8. For the last three weeks of the operation, the pH was increased by 0.2 units to achieve 6.5 on MU 4 reject. The total runtime for this testing was 1090 hours (exactly one and a half months).

The initial WTC values for Toray TML10 membranes in Vessel 2 were in the range of 10-10.5 × 10^{-12} m/s.Pa. The second element (downstream) had the higher value even though both elements were set to run at the same water flux, probably due to variations in the individual elements. This range of initial WTCs for ETA 4 was slightly higher than the one (9.7-9.9 × 10^{-12} m/s.Pa) observed for TML10 membranes in MU 2 first stage operation. On the other hand, the range was about 6.6-6.8 × 10^{-12} m/s·Pa for DOW XFR membranes in Vessel 2, which was slightly lower than the one (7.1-7.2 × 10^{-12} m/s.Pa) observed in MU 2 second stage operation. As it was monitored in MU 2, the WTC for TML10 membranes operated in ETA 4 started to decrease right after the initiation of the testing, while DOW XFR showed an increase in WTC. XFR stabilized at about the same WTC value in both ETA 4 and MU 2 units. However, TML10 kept the same difference between the two units (ETA 4 and MU 2) through the entire Phase 2 testing period. And again as it was observed in MU 2, WTC for the TML10 membranes became more stable (less rate of decline) after a slight increase following the pH adjustment on December 8.

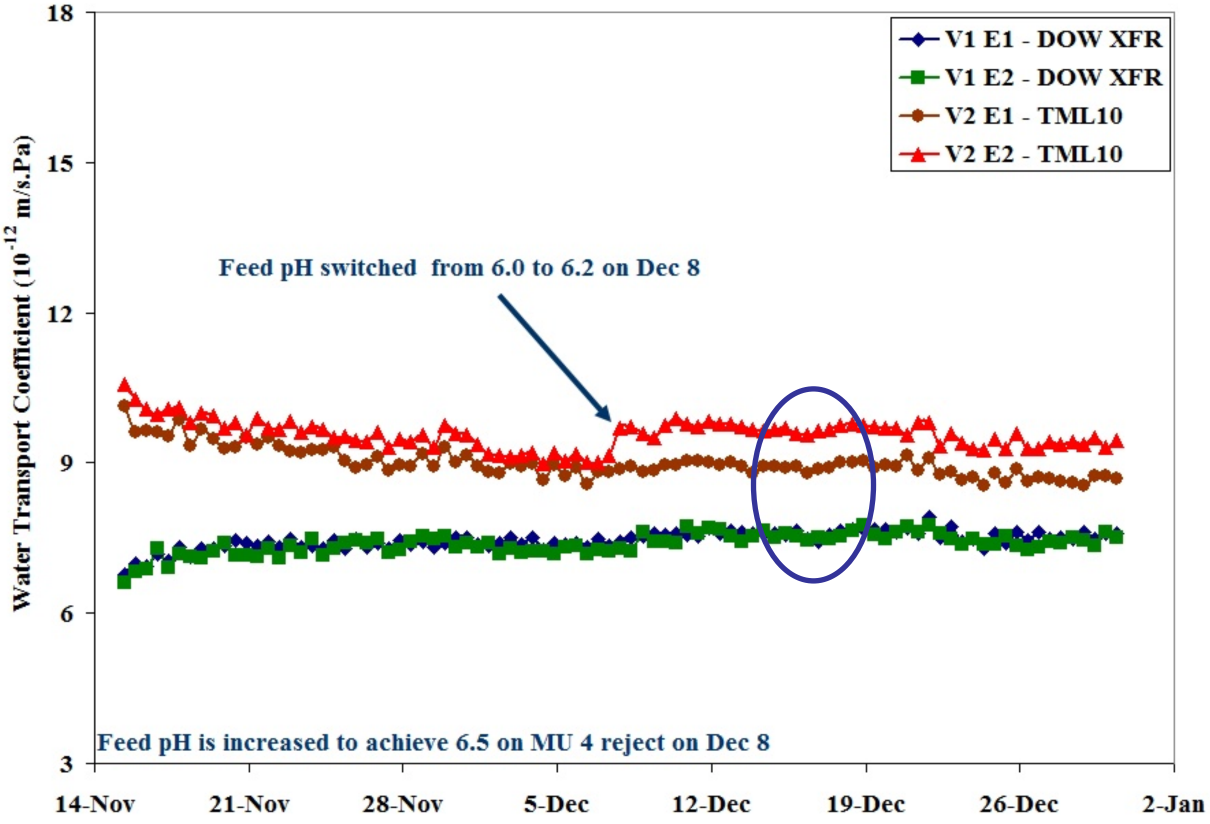


Figure 6.59. Water transport coefficient (WTC) for ETA 4 on Alternative 10 during Round 2 Phase 2. The blue arrow indicates the timing of pH adjustment to achieve a reject pH of 6.5 (from 6.3) on MU 4 reject stream. The blue circle highlights the period when the pH fluctuated due to MU 4 operation.

On lime-softened water, the WTC generally increased after the pH increased on December 8. When the feed pH dropped slightly due to the reasons explained in MU 3 and MU 4 operation results, on December 15 the WTC followed that pattern (highlighted by the blue circle in Figure 6.59). When the pH was brought back up later, WTC also followed.

The initial STC values for both elements were practically the same as the ones in MU 2. STC showed a step-increase, especially on TML10 elements after the pH adjustment on December 8. Both membranes showed a slight increase in STC by the end of testing probably due to the fluctuations in feed pH as described under the MU results section. Nevertheless, STC values, similar to the B/A values, for both membranes stayed very stable and low through Round 2 Phase 2.

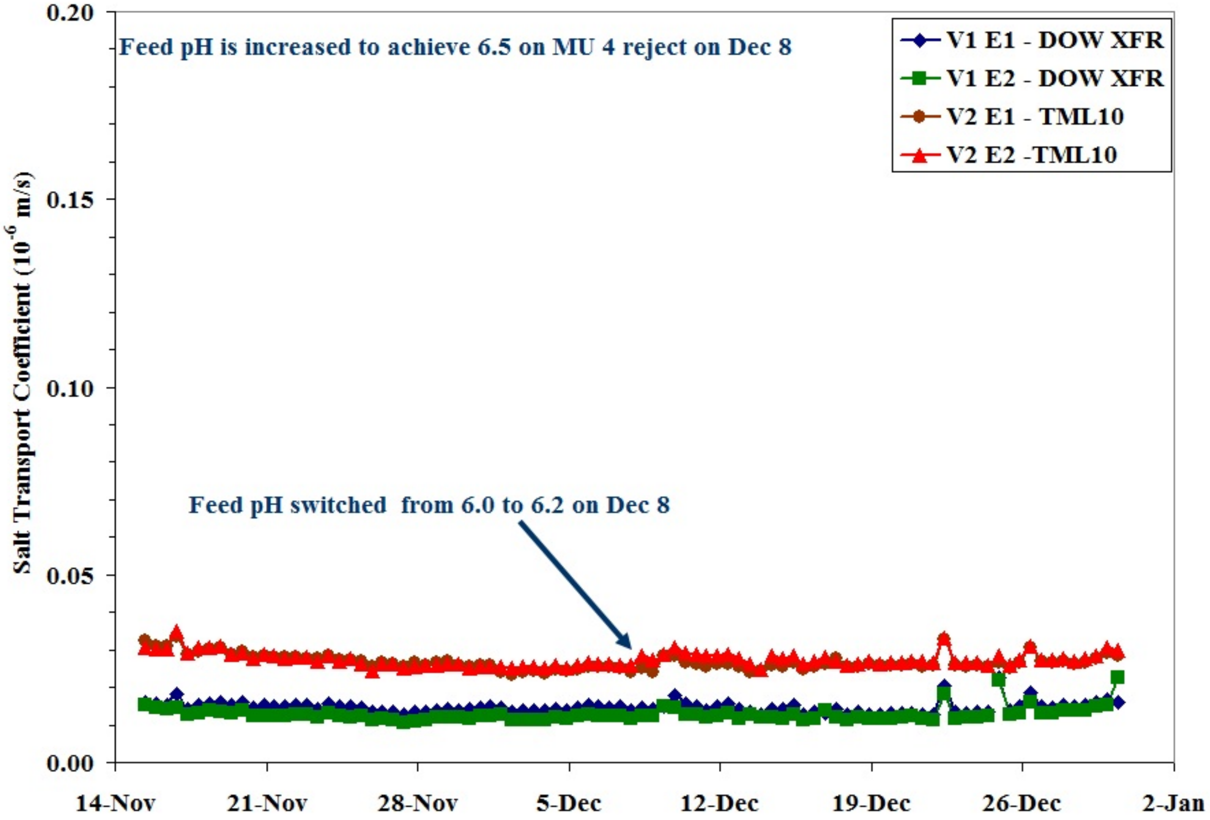


Figure 6.60. Salt transport coefficient (STC) for ETA 4 on Alternative 10 during Round 2 Phase 2. The blue arrow indicates the timing of pH adjustment to achieve a reject pH of 6.5 (from 6.3) on MU 4 reject stream.

The C_e values for Vessel 1 and Vessel 2 showed very minor decreases through the one and a half months of testing. The pH adjustment increased the values faintly but did not have any noteworthy effect on the declining trend. Differential pressures for both vessels increased constantly during the entire testing period as was observed in both stages of MU 2. In summary, the performance of both TML10 and DOW XFR was steady and showed a sustainable run at high flux (8.5×10^{-6} m/s ~ 18gfd) for one and a half months while treating the lime-softened gravity-filtered MODE water on Alternative 10. As was expected, lower WTC values were observed for both of the membranes tested at high flux on Alternative 10 pretreatment compared to the other alternatives in consideration. However, very low STC values and stable operating conditions were monitored for Alternative 10 during this Phase 2 testing. To the extent that it was tested, operation at 18 gfd water flux can be considered successful in terms of showing no clear evidence of fouling for lead elements on an Alternative 10 treatment train.

7. YMC RESULTS

7.1 Raw Water Quality

Table 7.1. YMC raw water quality between June 2010 and January 2012.

Parameter	Units	Average	Minimum	Maximum	St. Dev.
pH	-	8.0	7.7	8.6	0.3
Conductivity	*µS/cm*	2,437.5	1,249.0	3,470.0	527.3
Barium	*µg/L*	46.3	26.2	873.0	108.6
Calcium	*mg/L*	132.4	111.0	202.0	23.5
Iron	*µg/L*	140.2	17.2	1,900.0	266.7
Magnesium	*mg/L*	43.5	35.4	66.6	7.4
Manganese	*µg/L*	48.2	0.9	624.0	94.1
Potassium	*mg/L*	5.2	4.3	9.8	0.9
Sodium	*mg/L*	354.9	297.0	500.0	49.3
Strontium	*mg/L*	1.7	1.4	2.7	0.4
Sum of Cation	*meq*	24.8	23.2	29.0	2.1
Bicarbonate	*mg/L*	285.8	266.0	299.0	11.1
Chloride	*mg/L*	322.5	266.0	394.0	42.9
Nitrate as N	*mg/L*	ND	ND	ND	NA
Silicon Dioxide	*mg/L*	25.3	22.4	29.2	1.2
Sulfate	*mg/L*	537.5	510.0	639.0	50.5
Sum of Anion	*meq*	25.3	23.2	29.5	2.2
Tot. Alk. as CaCO3	*mg/L*	238.5	231.0	245.0	5.0
Tot. Hard. as CaCO3	*mg/L*	483.0	433.0	599.0	60.7
Total Organic Carbon	*mg/L*	1.0	0.9	1.2	0.1
Total Salt[1]	*mg/L*	1,670.0	1,550.0	1,940.0	138.4

[1] Total salt is measured gravimetrically by CEM AVC80 Microwave Moisture/Solid Analyzer.

Raw water quality for the YMC water is presented in Table 7.1, above. The sampling point is the Yuma Mesa Outlet Drain (YM MOD) at the YDP. Average, minimum and maximum values over one and a half years of sampling are shown with the standard deviation for more than 60 samples collected. Just like in MODE water, the major ions are calcium, magnesium, sodium, chloride and sulfate, which make up more than 80% of the total dissolved solids in YMC water. As expected prior to testing, iron and manganese concentrations in YMC water were substantial (refer to the iron and manganese results in Section 7.2.4). The average total salt concentration in

YMC water is more than 1,000 mg/L lower than in MODE water mainly due to sodium, chloride and sulfate ions. Almost all of the other ions detected had higher concentrations in YMC water than MODE water. Therefore, the pretreatment type and size and the operation of the RO system highly depend on the water source. Please, refer to Appendix C-1 for the details of Table 7.1 and Section 7.2.4 for iron and manganese results.

7.1.1 Seasonal Variations

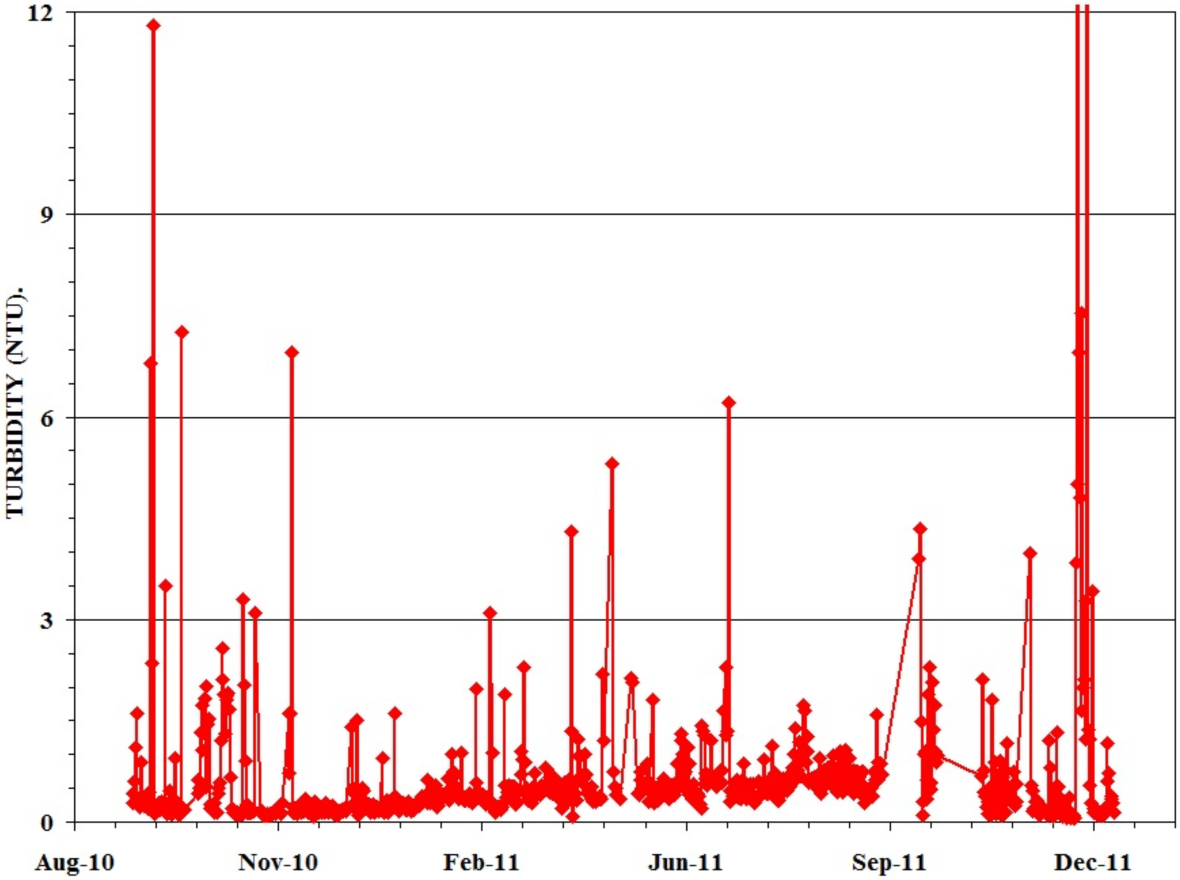


Figure 7.1. Manual turbidity measurements on the PS2 SCR effluent running on YMC water.

Although there is considerable variability in the concentration of many YMC constituents, there is no obvious seasonal variation in any water quality parameters during the testing period. The turbidity level in YMC water was quite low and almost constant for one and a half years, between September 2010 and December 2011. Turbidity of the YMC was typically in the 5-10 NTU range, whereas MODE waster was typically in the 5-15 NTU during the same period. The average pH of the raw YMC water was the same as the raw MODE water. However, all the major ion concentrations were considerably lower than in the MODE water.

The humps in the major ion concentrations observed during the last quarter of 2010 and 2011 (Figure 7.1), were probably due to the end-of-year diversions that Reclamation performed for meeting Minute No. 242 assurances. To help manage salinity in the Lower Colorado River, Reclamation diverts YMC water toward the Southerly International Boundary (SIB) (see Section 2.0). The total salt concentration in raw YMC water fluctuated between 1,500 and 2,000 mg/L, averaging ~1,670 mg/L, which is almost 1,000 mg/L less than MODE water.

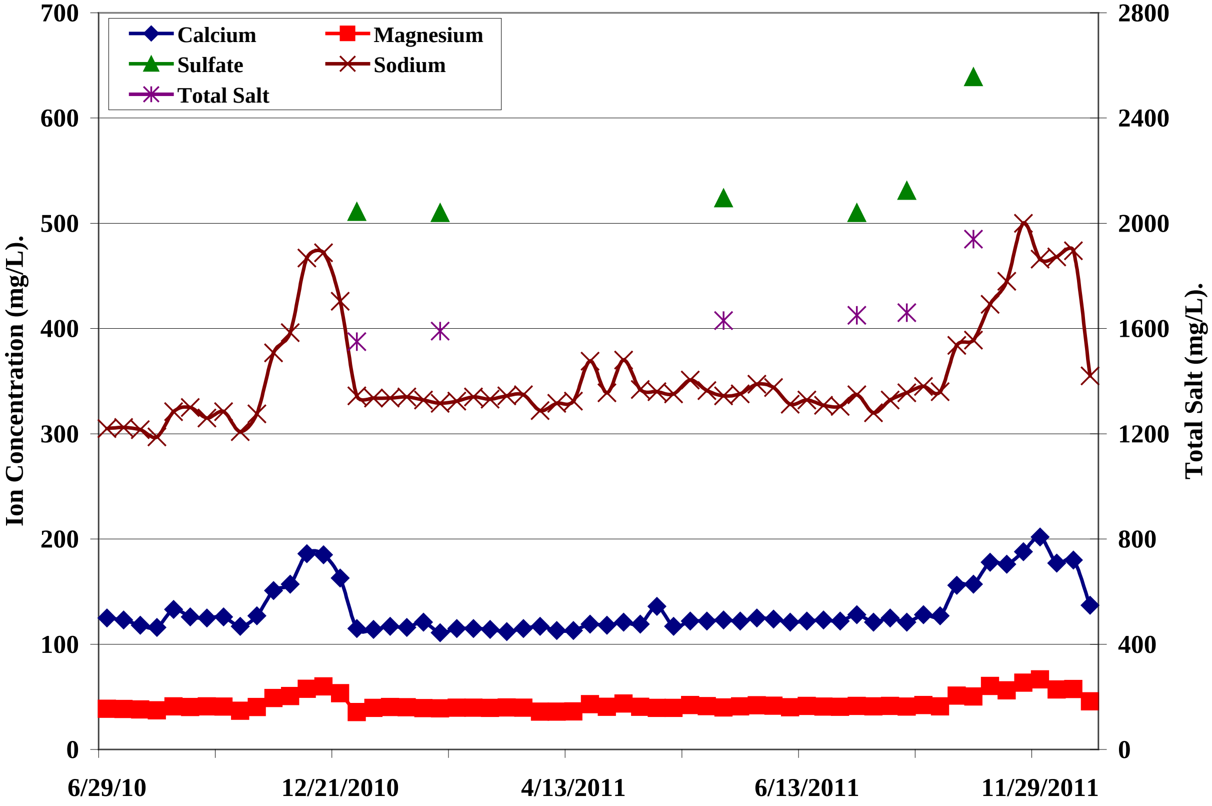


Figure 7.2. Major ions and total salt concentration in raw YMC water.

The concentrations of total iron and manganese in raw YMC water stayed constant throughout the sampling period, with the exception of a number of large, singular spikes. The spikes in iron typically coincided more closely with the spikes in manganese in YMC water than in MODE water. The time frame between August and October 2010 was the only period that elevated iron and manganese concentrations in raw YMC water were observed. All the YMC water at the time was diverted to the SIB and there was no continuous flow in the YMC to the YDP. The intermittent flow in the YMC and the frequent changes in the wells in operation were probably the reason for this anomaly. The samples analyzed and presented in the plot were taken when there was flow to the YDP. Not all the wells connected to the YMC have the same water quality composition. In fact, some wells have significantly higher iron and manganese levels. In addition, some wells have long intervals between their operational periods, so, once they are placed online, all the material deposited in their casing and pipelines is suspended and flows into the system. It is difficult to predict these effects since there is neither flow measurement nor adequate water quality data for the wells operating in the YMC system. More detailed analyses and discussion about iron and manganese levels in both MODE and YMC waters follows in relevant sections of this report.

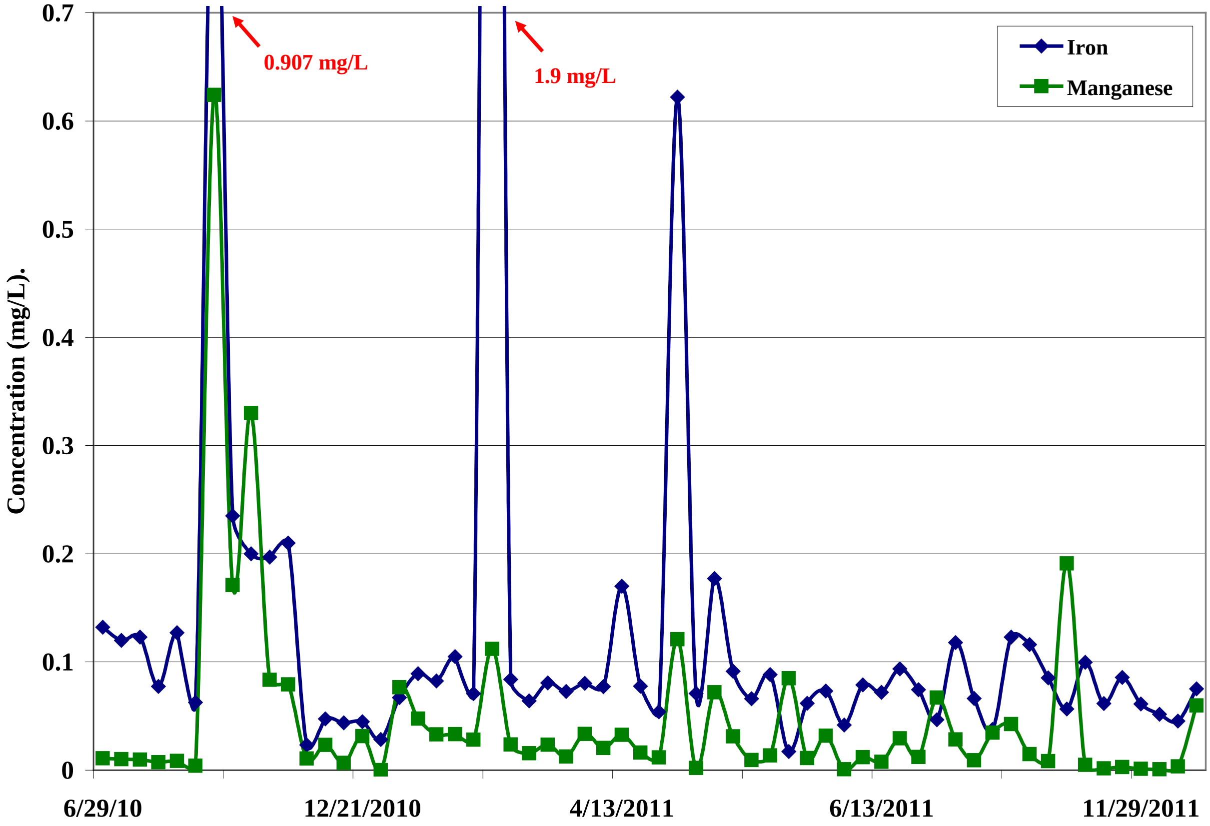


Figure 7.3. Iron and manganese concentrations in raw YMC water.

7.1.2 YMC Characterization

A YMC water characterization study was carried out by Dr. Peter Fox of Arizona State University (ASU) to supplement existing, but limited information that was available to provide a more complete characterization of key water quality constituents. Iron and manganese were considered as key constituents, which if not controlled, could have adverse impacts on RO. Since the YMC conveys groundwater from wells which provide drainage relief to the Yuma Valley and Yuma Mesa, iron and manganese concentrations were expected to be high enough to require special attention. Hence, five sampling points were selected along the YMC pipeline (Figure 7.4). It should be noted that the majority of flow was being diverted to the MODE during the first sampling event, May 2010, so the flow was low at Sampling Point 1. It was also difficult to sample from Sampling Point 4 and gas was pumped with the sample.

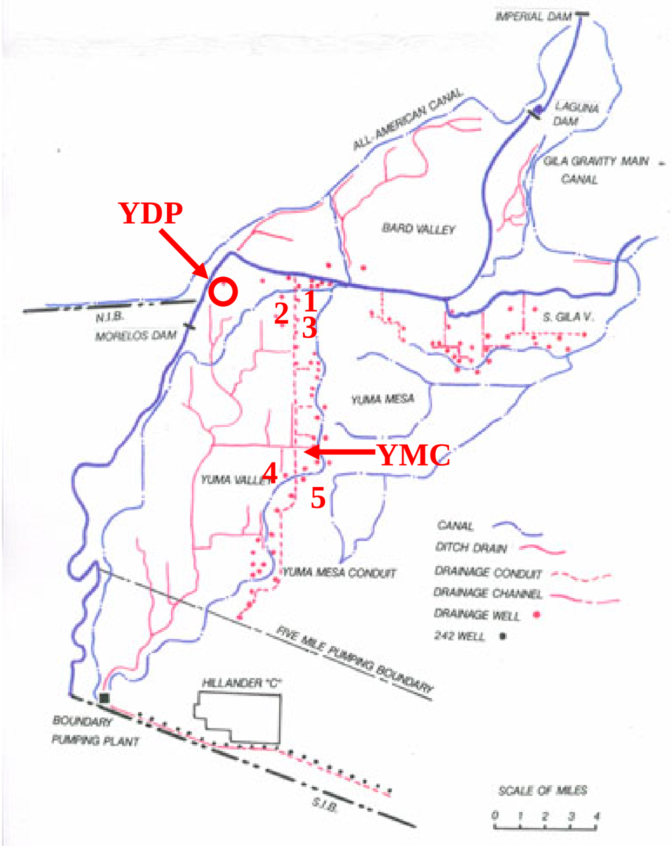


Figure 7.4. Approximate Yuma Mesa Conduit (red dotted line) sampling locations for iron, manganese and associated parameters. The red circle shows the approximate location of the Yuma Desalting Plant (YDP).

Sampling Point 1 – YMC air vent between MODE and Bifurcation Point (Point where water can be diverted to YDP)

Sampling Point 2 – Submersible pump at Bifurcation Point

Sampling Point 3 –YMC air vent on South Side of Canal (0.5 miles South of Bifurcation point before siphon under canal)

Sampling Point 4 –YMC air vent on Mesa at race track

Sampling Point 5 –YMC air vent on Mesa approximately 1 mile south of Sampling Point 4

Sampling Point 6 –YM-6 well

The results for YMC sampling on May 5, 2010 are summarized in Table 7.2, below. The approximate sampling locations are identified in red on Figure 7.4. Both dissolved iron and manganese concentrations decreased as water flowed northward (from point 5 to point 1), whereas the total iron and manganese concentrations tended to increase. Since there was significant dissolved oxygen in the YMC, it appeared that the dissolved iron and manganese were being oxidized within the YMC resulting in the observed shifts in concentrations. It was not clear why the total manganese increased so much between sampling points 3 and 2. There were no other wells in this region and the distance between sampling points 2 and 3 is less than 0.5 miles.

Table 7.2. Summary of the results for the May 2010 sampling along YMC flow path. Sampling locations are numbered from down- to up-stream.

Sampling Location	**1**	**2**	**3**	**4**	**5**
Total Mn (mg/L)	-	0.641	0.321	0.305	0.395
Dissolved Mn (mg/L)	0.149	0.195	0.195	0.245	0.293
Total Fe (mg/L)	-	0.434	0.326	0.222	0.124
Dissolved Fe (mg/L)	(0.003)	0.005	(0.001)	0.016	0.048
	EDL = 0.004		EDL = 0.004		
DO (mg/L)	5.9	2.5	3.2	2.7	3.2
pH (-)	7.40	7.21	7.16	7.20	7.08
Conductivity (µS/cm)	2290	2230	2300	2400	2390

Two more sampling events were carried out by the ASU researchers and the results of these analyses are presented in Table 7.3, below. All the data presented are in milligrams per liter. The same elevated concentrations observed in YDP sampling points (Figure 7.3 in Section

7.1.1) were detected in this element of the study, as well. However, these elevated concentrations can be considered as an indication of the inconsistent behavior of YMC and should not be generalized since lower and more stable concentrations of both iron and manganese were recorded throughout much of the research study (Figure 7.3 in Section 7.1.1). On the other hand, this does not change the fact that the downstream treatment processes must handle these elevated concentrations.

Table 7.3. Summary of the results for the three sampling campaigns for characterization of iron and manganese along the YMC flow path. Sampling sites are numbered from down- to up-stream.

	May				**August**				**September**			
Site	**Fe**		**Mn**		**Fe**		**Mn**		**Fe**		**Mn**	
	Diss	**Tot**	**Diss**	**Tot**	**Diss**	**Tot**	**Diss**	**Tot**	**Diss**	**Tot**	**Diss**	**Tot**
2	0	0.434	0.195	0.641	0	1.019	0.211	0.711	0	0.095	0.12	0.414
3	0	0.326	0.195	0.321	0	0.104	0.15	0.154	0	0.069	0.115	0.218
4	0.016	0.222	0.245	0.305	0.029	0.14	0.241	0.367	-	-	-	-
5	0.048	0.124	0.293	0.395	0.075	0.182	0.274	0.376	0.014	0.046	0.196	0.345
6	-	-	-	-	-	-	-	-	0.037	0.067	0.115	0.235

7.2 Pretreatment Performance

The two alternatives running on YMC water were Alternative 21a, dual media gravity filtration followed by microfiltration, and Alternative 22, dual media gravity filtration followed by cartridge filtration.

All PS2 dual media gravity filters operated initially with anthracite and silica sand combination until the installation of the greensand in three of the six PS2 gravity filters in June 2011. In both alternatives, anthracite was the top layer in the gravity filters throughout the study. Hence, both alternatives 21a and 22 were using the same gravity filtered water during Round 1, but differently treated water during Round 2. Even though the gravity filters were conditioned to remove manganese more efficiently in August and September 2010 prior to starting the Round 1 testing, the amount of manganese detected at the effluent of the DMGFs was enough to concern the TAT members that RO operation downstream might suffer. Therefore, the TAT decided to add a known and proven treatment, greensand filtration, as part of the pre-treatment for Alternative 22 in an attempt to further lower the concentrations of iron and manganese. This addition was expected to help especially in removal of the dissolved portion of the manganese concentration. A new filtrate collection tank was installed for Alternative 22 in early March 2011 and the flows of Alternatives 21 and 22 were separated at the effluent of the PS2 SCR. Greensand was installed on filters #4, #5 and #6. Greensand filter conditioning was performed in the second week of March. Due to the high chlorine demand of the greensand, the free chlorine level in the greensand filters effluent stayed undetectable until March 17, when it was recorded as 0.58 mg/L. Alternative 22 started running and producing data on that day. However, none of the RO units downstream were put online until mid-April. To be consistent within the alternatives, silica sand DMGFs running Alternative 21a were soaked with high-concentration chlorine solution on March 21 as part of the re-conditioning procedure. GF backwash flow rates were adjusted on both alternatives to get the best stratification. Since greensand is denser than silica sand, the same backwash flow rates could not be used. Please, see Section 5.7.2 for the details of the greensand gravity filters operation. Filtrate from either the silica sand or greensand was used for backwashing.

The purpose of these two alternatives was to test which pretreatment operates better on the given water source. Therefore in the following sub-sections, the results are presented as comparisons, such as silica sand vs. greensand and microfiltration vs. cartridge filtration.

7.2.1 Turbidity Removal on Alternatives 21a and 22

The average turbidity over the entire testing period at the PS2 SCR effluent was 0.74 NTU (Figure 7.5). Turbidity increased about 20% on average by January 2011. The average turbidity from September 2010 until January 2011 was 0.62 NTU, whereas this value was 0.78 NTU during Round 2. Hence, the removal efficiency of the DMGFs on PS2 also increased since the DMGFs effluent turbidity was a very consistent 0.15 NTU or less. There were no significant differences observed in the turbidity removal efficiency between the silica sand (blue line) and the greensand (red line) gravity filters (Figure 7.5).

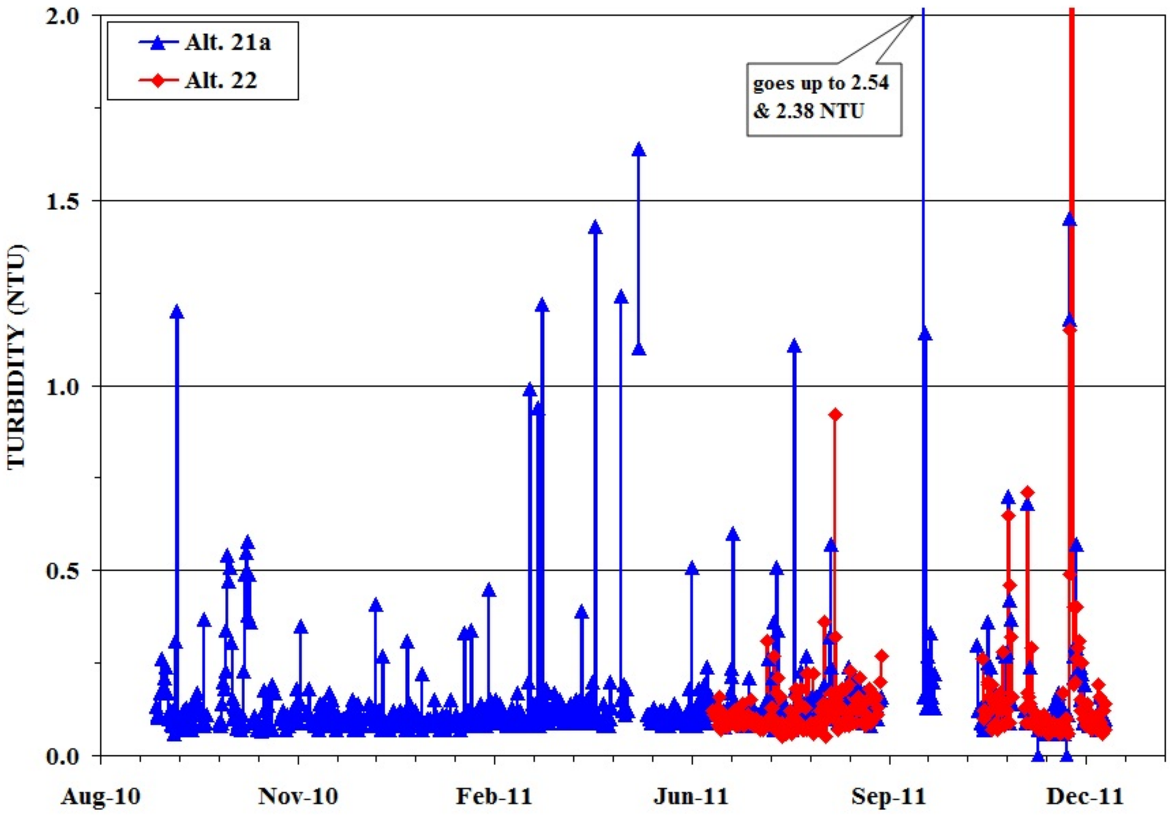


Figure 7.5. Turbidity profiles of Alternative 21a (silica sand) and Alternative 22 (greensand) effluents running on PS2.

The gravity filters on PS 2, before and after separation of the alternatives, supplied good quality water in terms of SDI to the downstream microfiltration and cartridge filtration units for Alternative 21a and Alternative 22, respectively. Even though, greensand had a media size (0.30-0.35 millimeters [mm]) almost three times smaller than the silica sand, no significant difference in SDI between the two alternatives was observed that might make a difference in the operation of the downstream units. The paired sample t-test performed on the SDI values showed that there is significant difference between the greensand filter (Mean=0.82; St.Dev.=0.45) and the silica sand filter (Mean=0.91; St.Dev.=0.47) with t= 1.96 and p=0.048. In other words, the greensand filters supplied slightly better quality of water in terms of SDI. However, the SDI values in this range (M<1.0) are considered optimal and the difference between the two alternatives is negligible.

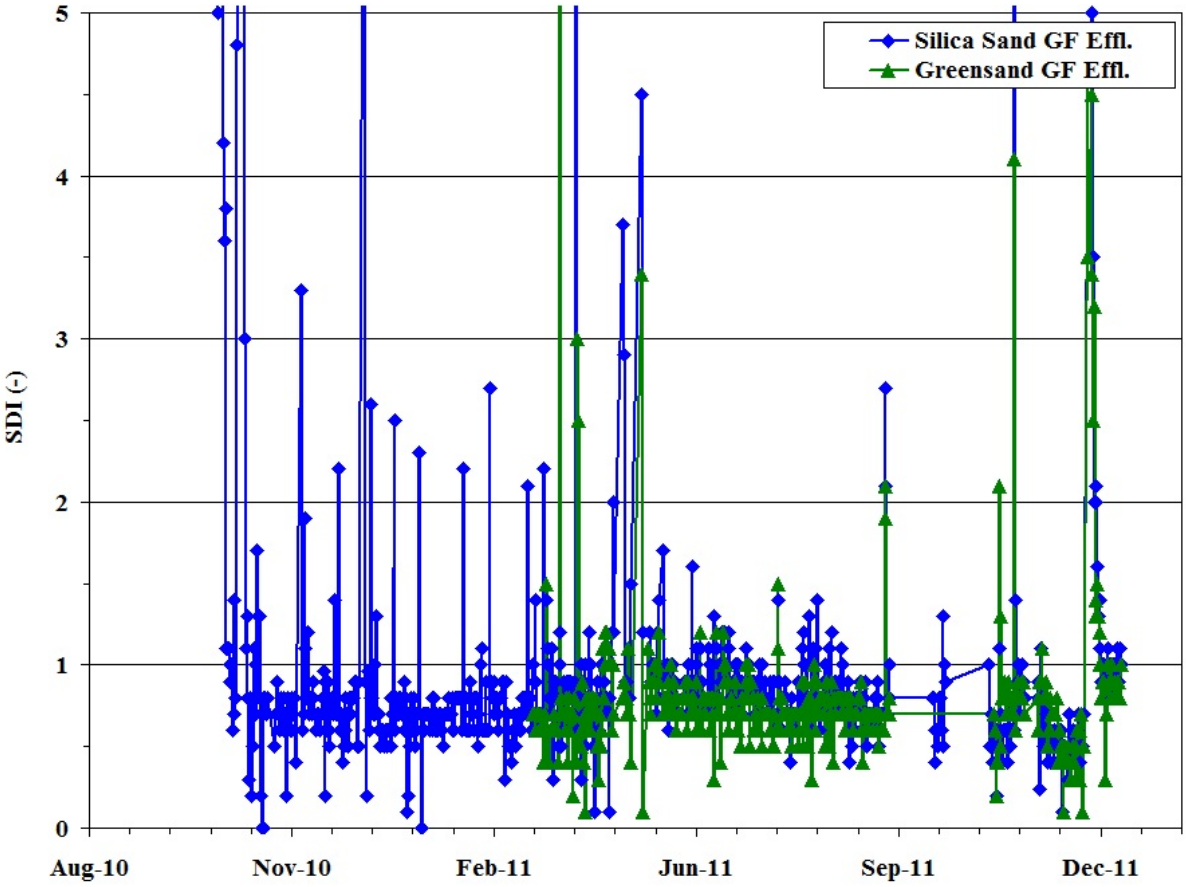


Figure 7.6. SDI profiles of Alternative 21a (silica sand) and Alternative 22 (greensand) running on PS2.

The chlorine demand in the YMC water stayed almost constant throughout the study. The demand was lower than for MODE water probably because of the lower TOC concentration in YMC water and in the warmer months, biological activity. YMC water had an average of 1.0 mg/L TOC, which was almost 60% less than MODE water (2.4 mg/L). A constant 1.0 mg/L of free chlorine was targeted at the gravity filter effluent for both alternatives to supply enough disinfection for the downstream filtration units as well as the RO units. Although there was only a minor difference between the free chlorine levels at the GF effluents of the alternatives, it was enough to produce a remarkable difference in their ORP levels (Figure 7.7). This difference might be due to the chlorine demand in the greensand, since there was only one injection point for both alternatives and the amount of feed chlorine entering each gravity filter was the same.

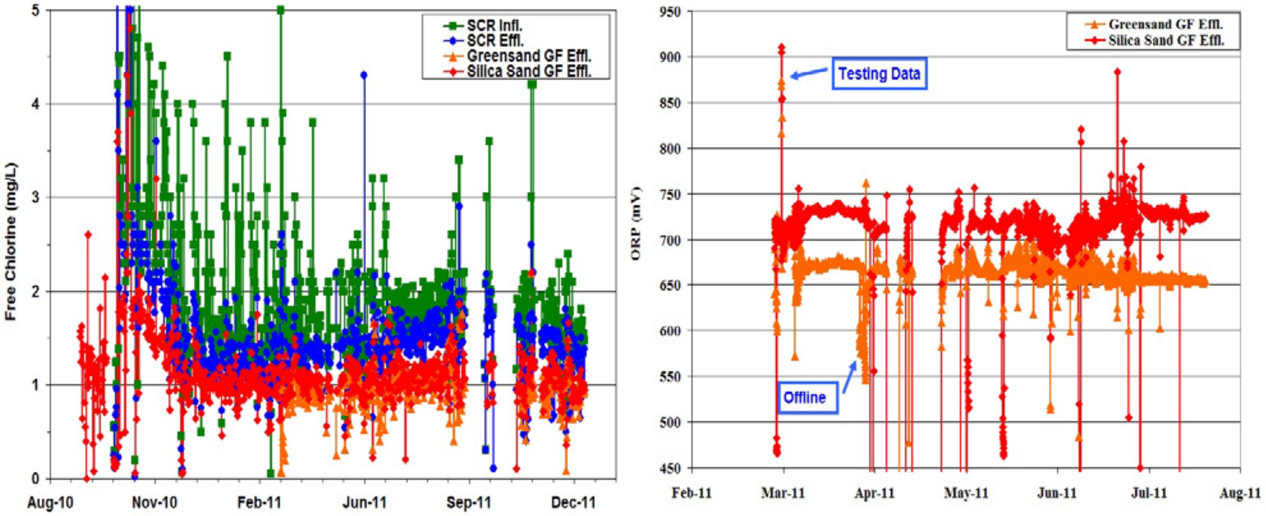


Figure 7.7. Free chlorine levels in PS 2 SCR and DMGFs and the ORP profiles for Alternative 21a (silica sand) and Alternative 22 (greensand) on PS 2.

7.2.2 Cartridge Filtration on Alternative 22

In both Round 1 and 2 the gravity filters on PS2, supplied good quality water in terms of detectable particulate matter, such as turbidity and SDI, to the downstream microfiltration and cartridge filtration units for Alternative 21a and Alternative 22, respectively. In fact, the original idea was that there would not be a need to use any other type of filtration other than DMGF on Alternative 22 because YMC water is a low-turbidity ground water source. And the SDI readings in the early stages of the study were mostly below 1.0 and supported this idea (Figure 7.6). However in fall 2010, the discoloration of the inside surface of the rotameter installed downstream of the DMGFs on Alternative 22 proved that iron was in the gravity filter effluent, based on iron staining in the effluent rotameter. This issue is explained in detail in Section 5.7.3 (Cartridge Filtration) of Methods and Materials. The same model rotameter installed downstream of the East Pall MF unit on Alternative 21a did not have any visible discoloration. Hence, a need to install cartridge filters on Alternative 22 was identified in October 2010 and they were installed and placed in operation on November 18, 2010.

This simple method of filtration, installed in most plants as a preventative technique, evolved into a more complex pretreatment assessment as the study progressed and ultimately a comparison study between it and microfiltration was implemented. Initially, 1-μ polypropylene Hytrex depth cartridge filters manufactured by General Electric Company were used. After installation of the cartridge filters on Alternative 22, the rotameter in downstream of the CF housing was cleaned and it stayed clean throughout the rest of the testing period, providing visual confirmation that residual iron present in the DMGF effluent was being effectively retained by the cartridge filter.

The two cartridge filters installed on Alternative 22 were 20 inches long and 4.38 inches in diameter, operating in parallel. They operated at a flux of 0.03 gpm/in^2 (16.5 gpm) mainly because of the downstream (RO feed) flow requirement on that alternative. CFs needed to be run at a rate that would produce enough water for both of the downstream RO units: one ETA and one MU. The feed pressure to the CFs until the end of August 2011 was between 7-9 psi. A new impeller for the pump was installed after this point to supply a higher feed pressure that would allow Reclamation to run the CFs longer. CFs were being changed as they became clogged. Once the flow requirement could not be met, a new set of CF was installed.

The first set of cartridge filters ran for 45 days with an average pressure difference increase rate of 0.013 psi/d. However, there was a shut down on December 21 for 40 hours. This shut-down affected the fouling rate significantly. Prior to the shut down, the average fouling rate was 0.042 psi/d. Nevertheless, after the shut-down, it dropped down to 0.014 psi/d. Besides, the differential pressure dropped down to 1.9 psi from pre-shut-down value of 2.7 psi. In almost every shut-down event occurring during the testing, a drop in the differential pressure was observed, whether or not it was accompanied by a change in the fouling rate. The reason for that is believed to be the relaxation and redissolving of the fouling material accumulated on the cartridge filter. The second set of cartridge filters installed ran about 52.5 days with a fouling rate of 0.019 psi/d. The vertical blue lines in Figure 7.8 indicate the dates for installation of a new set of cartridge filters. The fouling rate is calculated by the formula presented below.

$$\text{Fouling Rate} = [\Delta\text{Differential Pressure}] / \Delta\text{Time}$$

$$\text{Fouling Rate} = [(P_{t,in} - P_{t,out}) - (P_{t0,in} - P_{t0,out})] / (t - t_0)$$

where, $P_{t,in}$ and $P_{t0,in}$ is the inlet pressure of CF at times t and zero, respectively [psi]

$P_{t,out}$ and $P_{t0,out}$ is the outlet pressure of CF at times t and zero, respectively [psi]

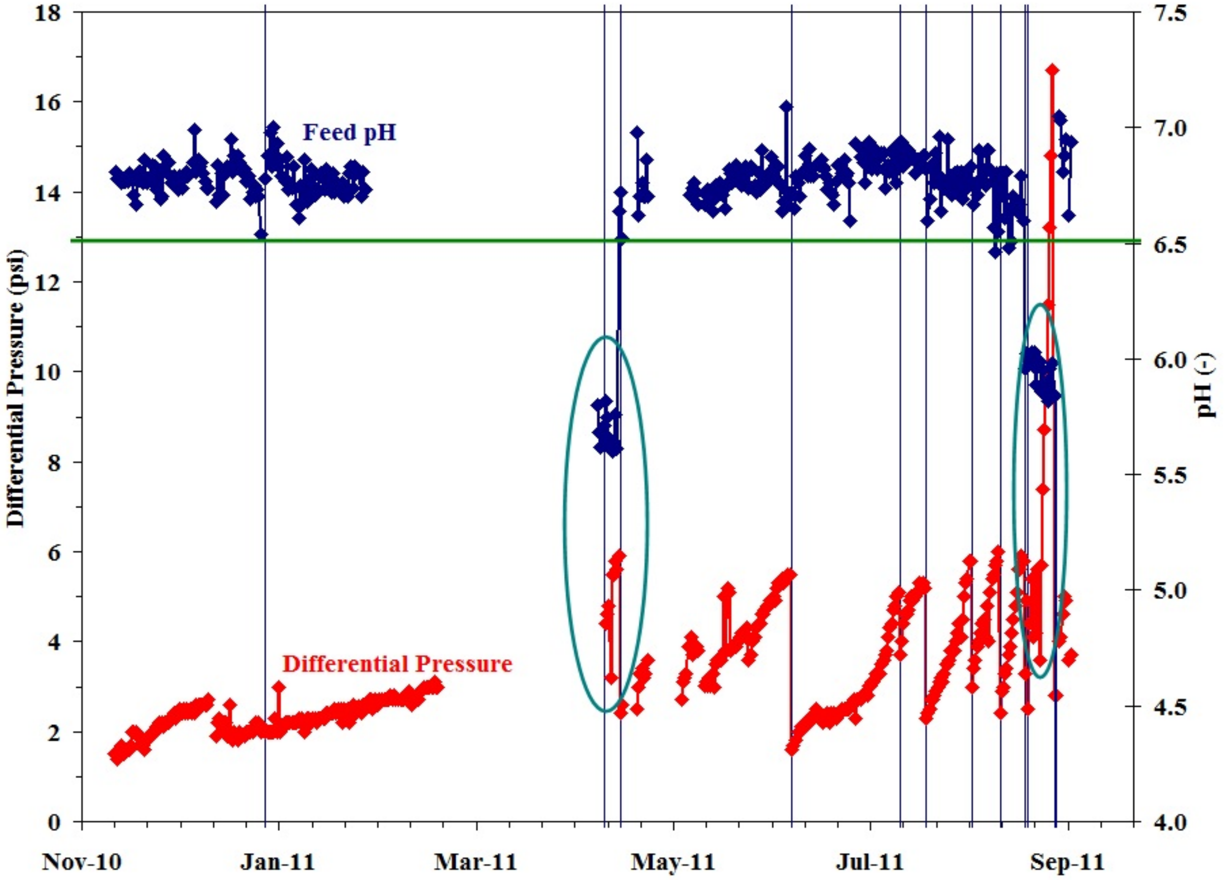


Figure 7.8. Differential pressure and the feed pH plot for the cartridge filters installed on Alternative 22. The vertical blue lines indicate the timing of cartridge replacement.

Based on the results of ETA Round 1 testing, the effect of the feed water pH on CF fouling rate was of interest to the TAT. Given that CF feed water pH was dictated by downstream RO feed pH, only limiting pH conditions could be trialed because a healthy operation of downstream RO units was the priority of this study. Normal RO feed during Round 1 was 6.8. During Round 2, two additional (lower) pH conditions were investigated with ETA 2 and MU 2 during the study, 5.8 between April 18 and April 24 and 5.9-6.0 between August 26 and September 4. Based on limited operating time at one ‘low pH’ condition (5.9-6.0) a higher fouling rate was observed (Table 7.4).

Table 7.4. Impact of pH and temperature on CF fouling rate.

Dates of Operation	**Fouling Rate (psi/d)**	**Feed pH (-)**	**Feed Temperature (^{o}C)**
April 21-April 25	*0.375*	*5.9-6.0*	*24.8*
April 25-June 16	0.060	6.8	25.1
June 16-July 19	0.108	6.8	27.6
July 19-July 27	0.200	6.8	28.7
July 27-August 10	0.259	6.8	29.0
August 10-August 19	0.375	6.8	28.8
August 19-August 26	0.486	6.8	28.9
August 26-August 27	*1.600*	*5.9-6.0*	*29.8*
August 27-August 28	*2.900*	*5.9-6.0*	*30.4*
August 29-August 29	*2.600*	*5.9-6.0*	*30.3*
August 30-August 30	*2.800*	*5.9-6.0*	*29.7*
August 31-September 4	*3.275*	*5.9-6.0*	*29.3*
September 4-September 9	0.180	6.8	29.5

Each row in the table represents a new set of CF installed on Alternative 22. The literature suggests that it is important to maintain the operating pH of greensand filtration higher than 6.5 to keep the manganese dioxide on the media oxidized. Operating conditions for greensand are reported to be pH between 6.2 and 8.5. However, the higher fouling rates observed during this research study cannot be explained by this fact, because the pH adjustment was made after the gravity filtration and before the cartridge filtration processes. The gravity filter effluent pH was between 7.6 and 7.9 for Round 2. In addition, lowering the pH should lower the fouling rate if it is directly related to iron or manganese in the feed water, unless they are in the form of organic or inorganic complexes. This is suspected as mentioned earlier in the report.

The effect of pH change on the CF fouling rate should not be ignored since immediate changes of the CF fouling rate coincided with major pH changes on August 26 and September 4. The drop of the feed pH on August 26 from 6.8 to 5.9 increased the fouling rate by more than three times, from 0.486 psi/d to 1.6 psi/d. Later the fouling rate dropped more than eighteen fold, from 3.275 psi/d to 0.18 psi/d, on September 4 when the pH was raised back to 6.8. The very rapid rate of fouling at pH <6.0 would result in a very short CF life and result in very high operating costs for a CF system if used in conjunction with a YDP upgrade. This strongly suggests a more detailed and extended study on this issue is appropriate before reaching a final conclusion on the extent and location of YMC water pH adjustment and the economic viability of using cartridge filters in lieu of or to augment microfiltration pretreatment.

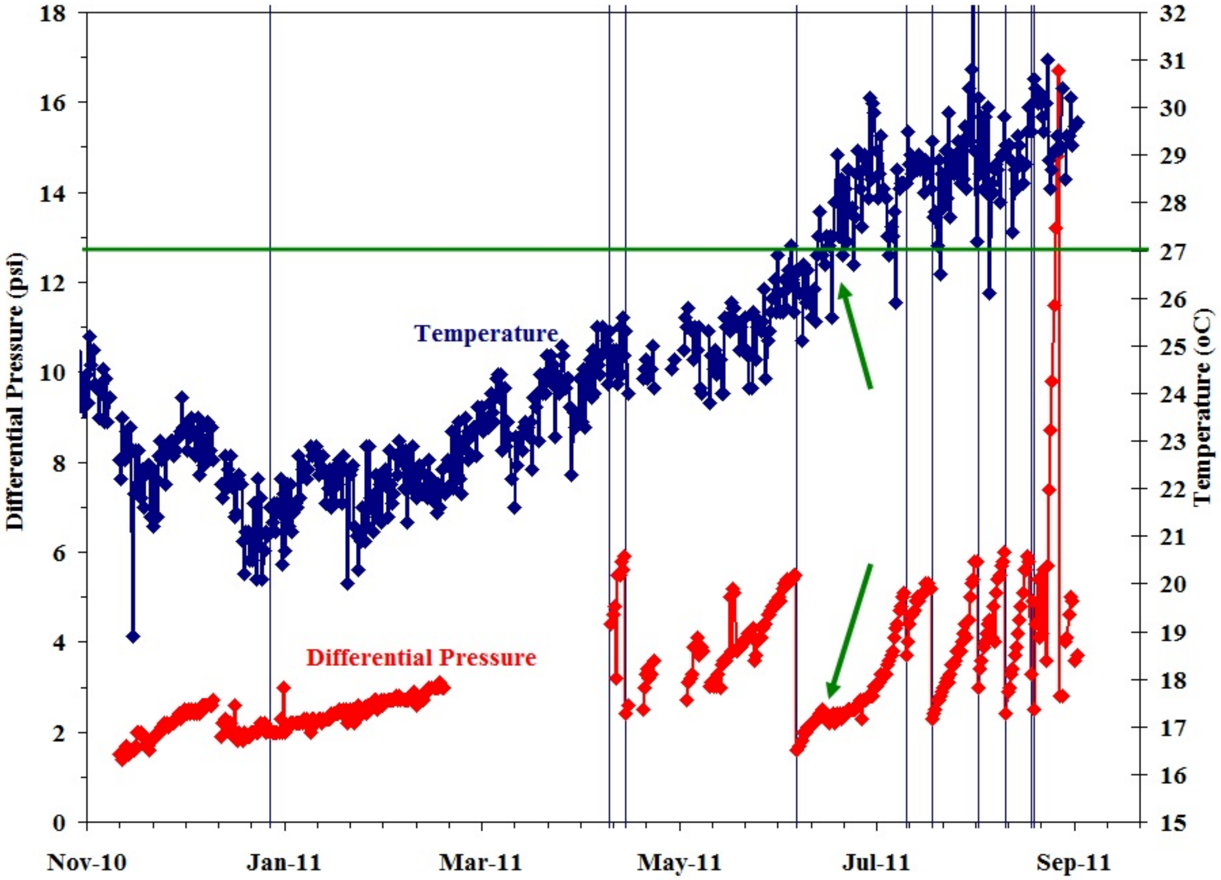


Figure 7.9. Differential pressure plot and the feed temperature for the CFs installed on Alternative 22. Green arrows indicate when the feed water temperature exceeded 27 ºC.

Another issue that is open to discussion is the relationship between the CF fouling rate and feed water temperature. It is reported that operating temperatures higher than 26.7 ^{o}C increase the possibility of greensand deterioration. As is illustrated in Figure 7.9, the temperature rising above 27 ^{o}C occurred at the same time as a shutdown on June 24 (green arrows). A noticeable change in the slope of the dP was recorded - probably due to the shut-down. If it was related to deterioration of the greensand, the expected change would be an increase in the slope of the dP, not a decrease as recorded and highlighted in Figure 7.9. That increase did not show up until early July. However, a noteworthy and continuous increase in the fouling rate was observed (Table 7.4) as the feed water temperature stayed above 27 ^{o}C throughout the summer. The fouling rate between April and June was calculated as 0.06 psi/d, whereas it reached 0.486 psi/d by the end of August. The other factors that might have affected the performance of greensand operation, such as silica and TDS concentrations, were not applicable to the YMC water situation since the water has greater than 20 mg/L of silica and 1,500 mg/L of TDS, which fall in the range of the optimum conditions.

If the problem was deterioration, with grains softening and the manganese oxide coating dissolving or flaking from the surface, as it is mentioned in the literature, then this should correspond with an increase in the manganese concentration in the greensand gravity filter effluent samples. However, the lab data shows no increase in the manganese concentration. Please, see section “Iron and Manganese Removal” for the total and dissolved manganese concentrations in PS2.

At this point, on the other hand, it should also be noted that the amount of samples collected were very small (250 ml) compared to the total amount of water passing through the cartridge filters daily. The amount of water passing through a single cartridge filter was almost 12,000 gallons per day. Therefore, a change in concentration too small to be discerned as a concentration change in the small grab samples could still cause significant accumulation of manganese on the cartridge filter (since cartridge filter is a dead-end filtration method). If the same deterioration of the manganese oxide coating (but now on silica sand) happened on Alt. 21a (silica-sand DMGF), it is possible the same effect would not be seen on the East Pall MF unit as increase in the TMP, due to the frequent (once in every half an hour) backwash schedule on this unit, thus washing out the particles that accumulate on the CF.

Comparison Study

After noticing the performance changes of the CFs running on greensand DMGF treated water without a coinciding increase in the TMP of the East Pall MF unit, it was decided to run cartridge filters on Alternative 21a, silica sand/anthracite DMGFs, for a comparison study. A second CF housing skid was constructed and operated in parallel with East Pall MF unit. The water treated with this CF skid was discarded without further use. Initially, 20 in long 1-μm and 10 in long 5-μm CFs were studied side by side on each alternative. Same flux, 0.03 gpm/in^2, was used for all the CFs. However, the depth factor of the CFs was ignored in this calculation as only the surface area was accounted for while calculating the operating flux. (This ignores that the CFs used are advertised as depth cartridge filters by the manufacturer, General Electric Company.) A feed pH of 6.8 was used throughout this comparison study.

Table 7.5. Fouling rates for different CF sizes and micron ratings.

CF Micron Rating	**1-μm**		**5- μm**	
CF Size	*20-in*	*10-in*	*10-in*	*10-in*
Experiment #	*1st*	*2nd*	*1st*	*2nd*
Alternative 21a	0.09	0.63	0.11	0.24
Alternative 22	0.13	0.79	0.18	0.21

* Alternative 21a uses silica sand; alternative 22 uses greensand.

SDI and turbidity values on the feed and filtrate streams of each CF in operation were monitored. However, no significant change in either of the values before and after the CFs was observed. Therefore, no solid conclusion could be reached regarding the impact on SDI and turbidity. The feed SDI and turbidity values for both alternatives were already lower than 1.0 and 0.2, respectively. At these values, measurement precision for these water quality parameters is reduced, making it difficult to discern statistically significant differences from cartridge filtration. Hence, the most reliable metric for determining the effect of the two media filtration approaches is via CF fouling rate.

The fouling rate for each CF tested was calculated by ignoring the rapid increase in the differential pressure during the last days or hours of its operation. Those rapid rises were observed probably due to the exponential loss of filtration area as the CF gets clogged. As the active filter area is lost on the CF during its operation, the nominal flux of the water, hence the flux of the fouling materials, passing through the CF increased. That, in turn, exponentially increased the differential pressure since the flow rate was kept constant (Figures 7.10 and 7.11).

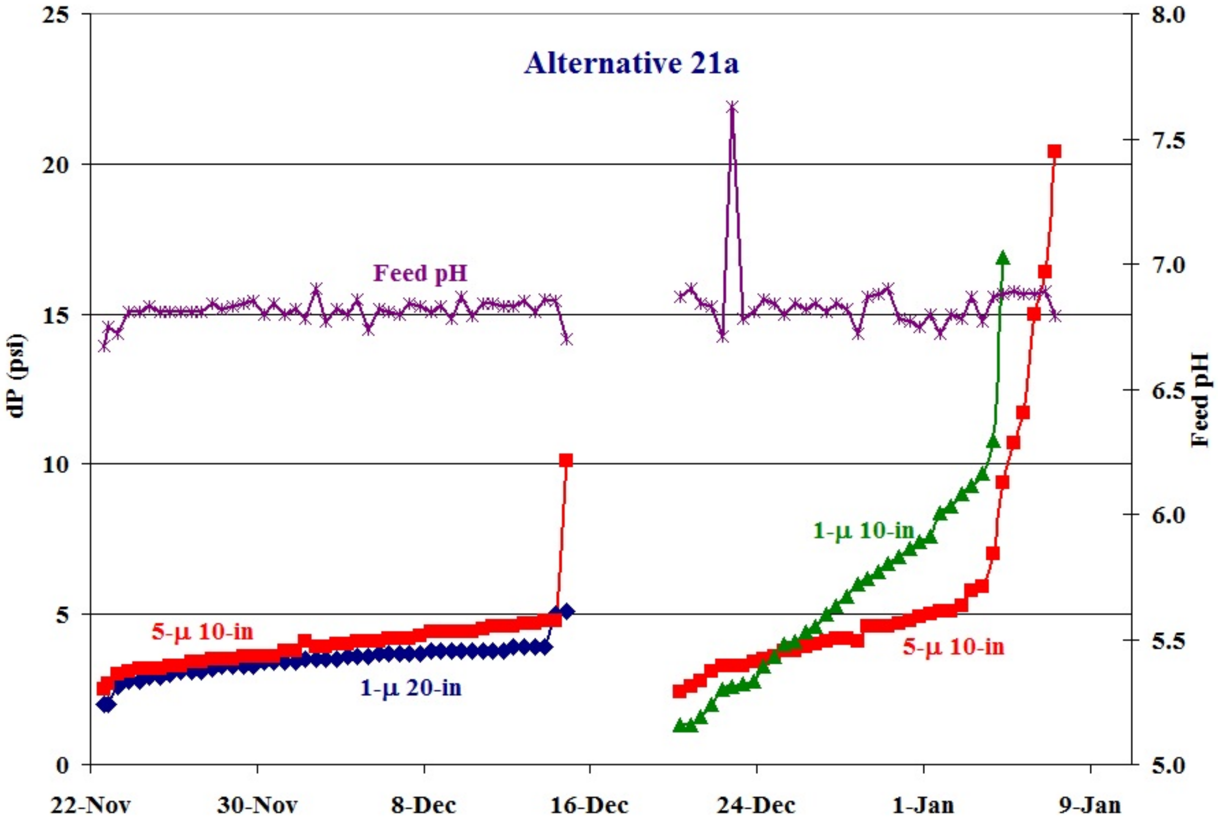


Figure 7.10. Differential pressure (dP) profiles for the CFs installed on Alternative 21a.

From Table 7.5 above, the fouling rate for all but the 5-μm filters in the second test was higher for the greensand than for the silica sand, noting that the fouling rate for the 2nd run on silica sand was significantly higher than for the first. The higher fouling rate on greensand filter effluent does suggest that the particle loading from the greensand filter is higher than the silica sand. As importantly, fouling rate of the 10 in, 1-µm filters was substantially greater than for the 20-in filter (by 6-7 times). It must be noted that the 20-in filter has a greater depth than the 10-incfilter and this most likely resulted in greater solids holding capacity. The change in the fouling rate needs to be investigated in more details and has to be taken into consideration while carrying out the economics analysis for the CF operation at the RO plant since the frequency of CF replacement (and associated cost) will be directly related to the fouling rate. At this point, it cannot be concluded whether the performance differences are differences in the filters themselves (i.e., variations between batches, filter sizes) or differences in the operation (i.e., water quality, flux as function of depth) of the filters.

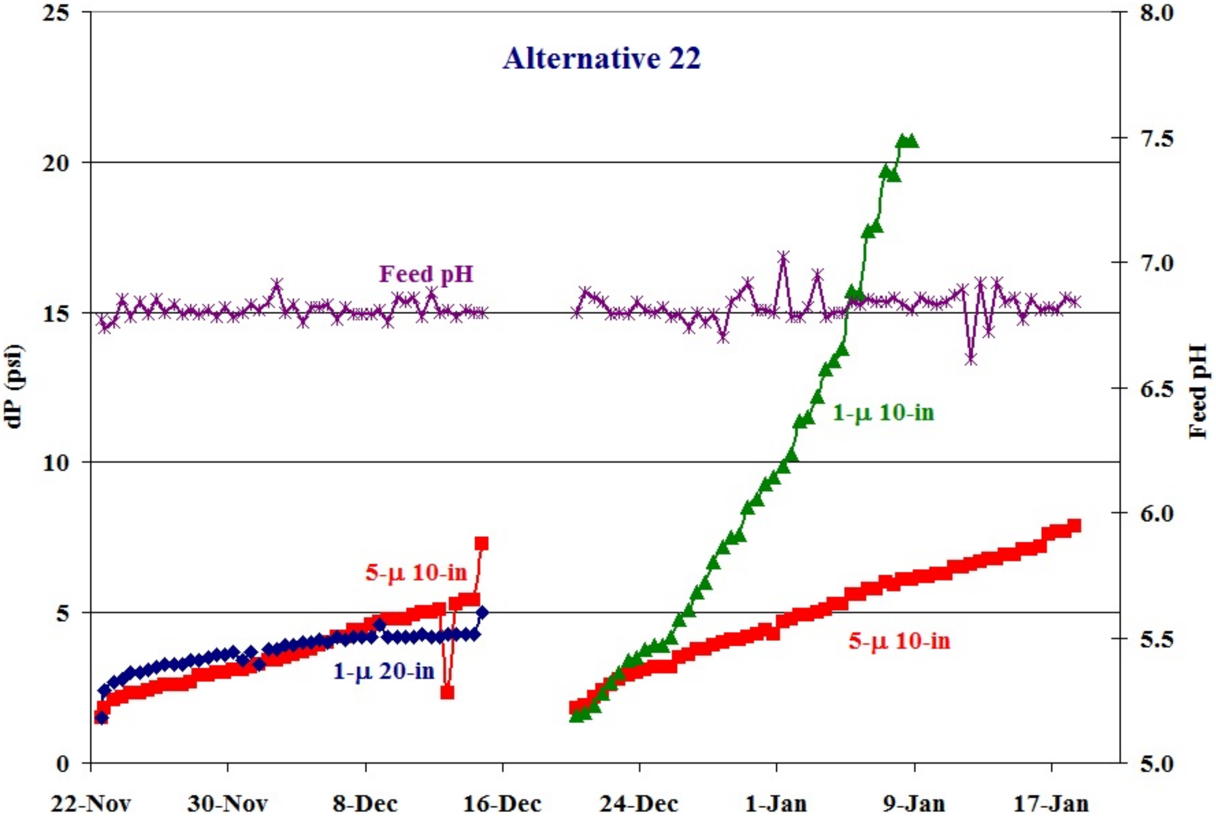


Figure 7.11. Differential pressure (dP) profiles for the CFs installed on Alternative 22.

7.2.3 Microfiltration on Alternative 21a

The East Pall MF Unit ran on Alternative 21a downstream of the PS2 silica sand/anthracite DMGFs. Initially, it ran at 50 gfd (18.7 gpm) with 97% water recovery. Due to the low rate of TMP rise, the flux was increased to 60 gfd (22.4 gpm) on September 4. The lower fouling rate experienced on YMC water compared to MODE water is due to the lower solids and organics loading in the YMC water based on its being a groundwater transported via closed pipeline. Transmembrane pressure is used as the primary metric to quantify performance as was done earlier in the report for the West Pall MF unit. TMP and specific flux were around 8-9 psi and 6-7 gfd/psi, respectively, when the East Pall MF was first placed in operation. The TMP profile for September 2010 is presented below as an example for the unit's initial performance.

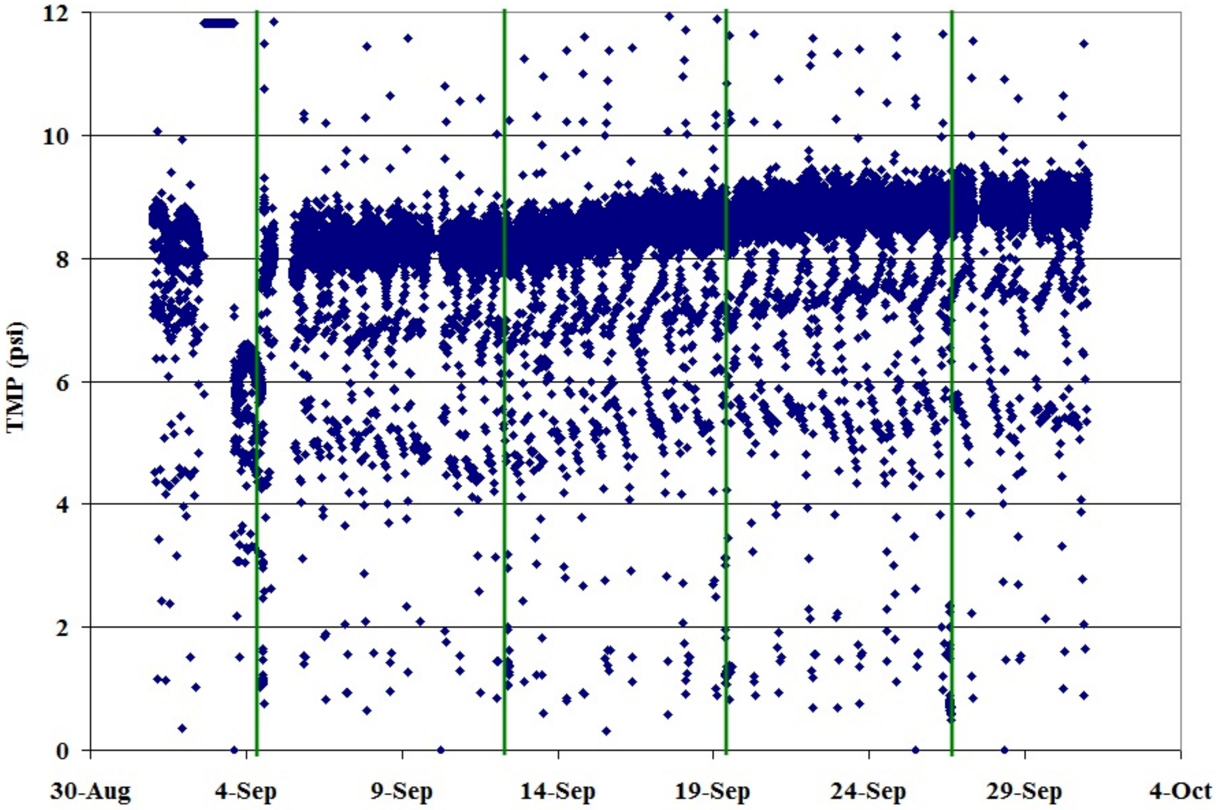


Figure 7.12. East Pall MF Unit TMP Profile for September 2010. The green lines denote the timing of high pH/bleach EFMs.

Analogous to initial West Pall MF unit operation, once-a-week bleach EFM was performed initially on the East Pall MF unit to inhibit any possible biological activity on the membrane surface. The bleach EFMs are indicated by the green lines on the plots. Citric acid EFMs were begun with bi-weekly frequency in early November as a precaution against build-up of inorganic fouling, such as iron and manganese.

The TMP stayed constant around 9-10 psi following the start up and throughout October 2010. There were extended periods of downtime during October due to YMC flow diversions. As a result, the idea of using a different well water, DW-8 locally located at the YDP, as a water source for Alternatives 21a and 22 was discussed, but the idea was discarded because DW-8 water was not a good representation of YMC water. Despite these issues, the East Pall MF unit supplied a consistent and high quality filtrate and operated at controlled TMPs. Hence, the flux was increased by 17% to 70 gfd on October 26. The TMP also increased by the same amount and jumped to 10-12 psi and stayed constant until the next flux increase. On January 12, 2011 the flux was increased by another 14% to 80 gfd and the TMP again jumped by 14% reaching 12-14 psi. The specific flux of the East Pall MF unit stayed quite constant around 6 gfd/psi and was unaffected by the flux changes.

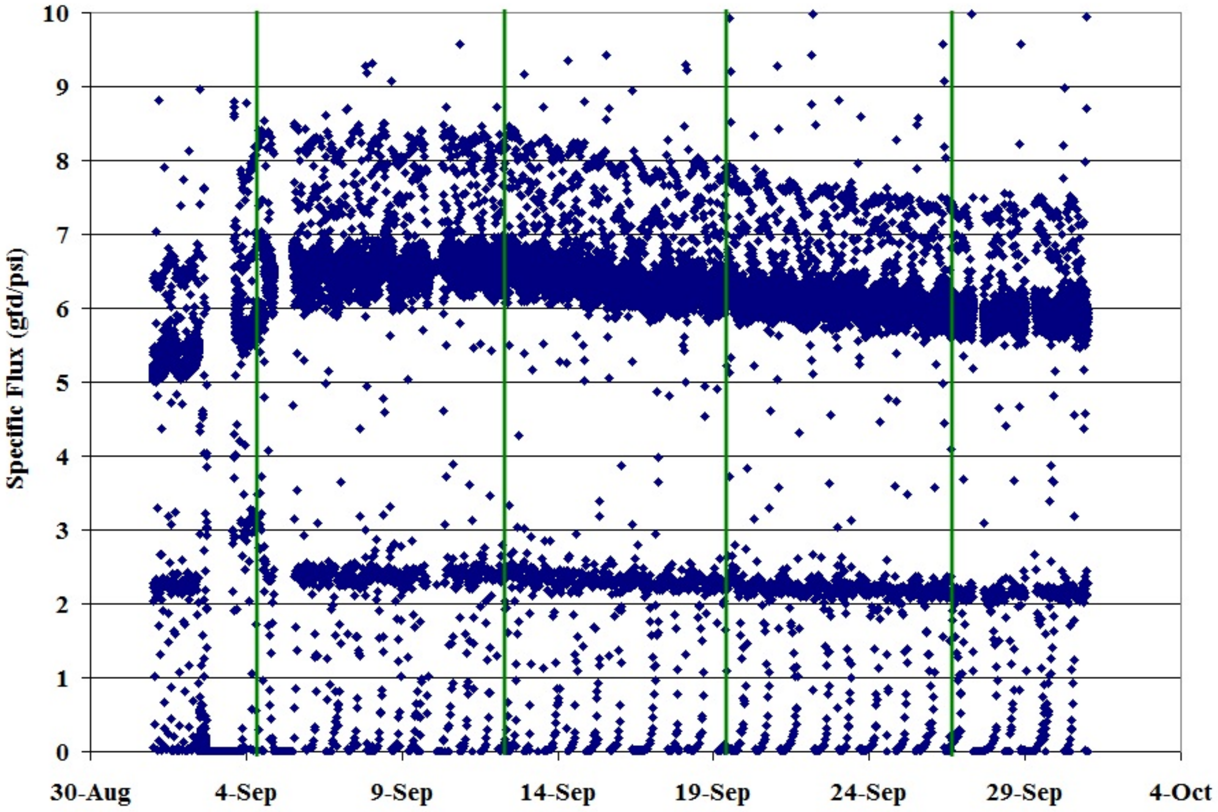


Figure 7.13. East Pall MF Unit Specific Flux Profile for September 2010. The green lines denote the timing of high pH/bleach EFMs.

Having a constant specific flux regardless of the unit's filtrate production rate is strong indication of sustainable and robust operation. The linear relation between the flux and the TMP it shows indicates that the unit is not losing active membrane area due to fouling. Both citric acid EFMs and bleach EFMs were performed on a biweekly schedule until the flux change in January. Since no indication of fouling had been observed before the change, the frequency of bleach EFM was dropped to once a month from that point forward. However, the citric acid EFM schedule was kept as biweekly until the unit's operation was discontinued on October 3, 2011.

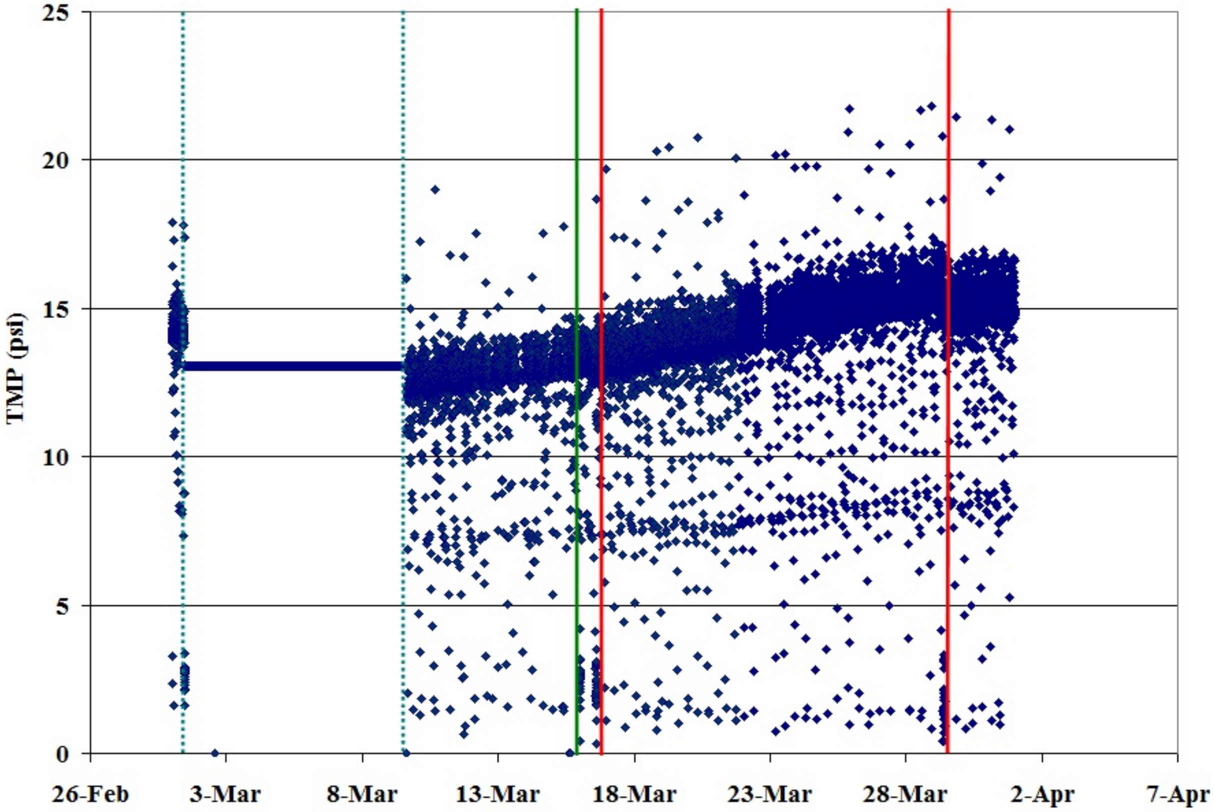


Figure 7.14. East Pall MF Unit TMP Profile for March 2011. The green and red lines denote the timing of high pH/bleach and citric acid EFMs, respectively.

The first time TMP rose above 15 psi was in late-March 2011, which lowered the specific flux to 5 gfd/psi and below. The two bi-weekly EFMs had previously dropped the TMP back down to around 12 psi, which was the TMP value immediately after the flux increase. On the other hand, the citric acid EFM performed on March 29 did not drop the TMP back to below 15 psi and the TMP kept increasing in early April, reaching almost 20 psi by mid-April. On April

12, even though the two EFMs performed on April 12 successfully dropped the TMP below 15 psi, it was decided to perform a CIP for the East Pall MF unit on April 22. The purpose was to check the efficiency of CIP on YMC water and investigate how the TMP profile would behave following the cleaning. The CIP dropped the TMP down to around 12 psi while restoring the specific flux to above 6 gfd/psi (Figure 7.15). Hence, the flux was increased one more time from 80 gfd to 85 gfd on April 25. No significant change in the operating parameters monitored and calculated was observed after this flux change and the performance of the unit stayed constant until mid-summer.

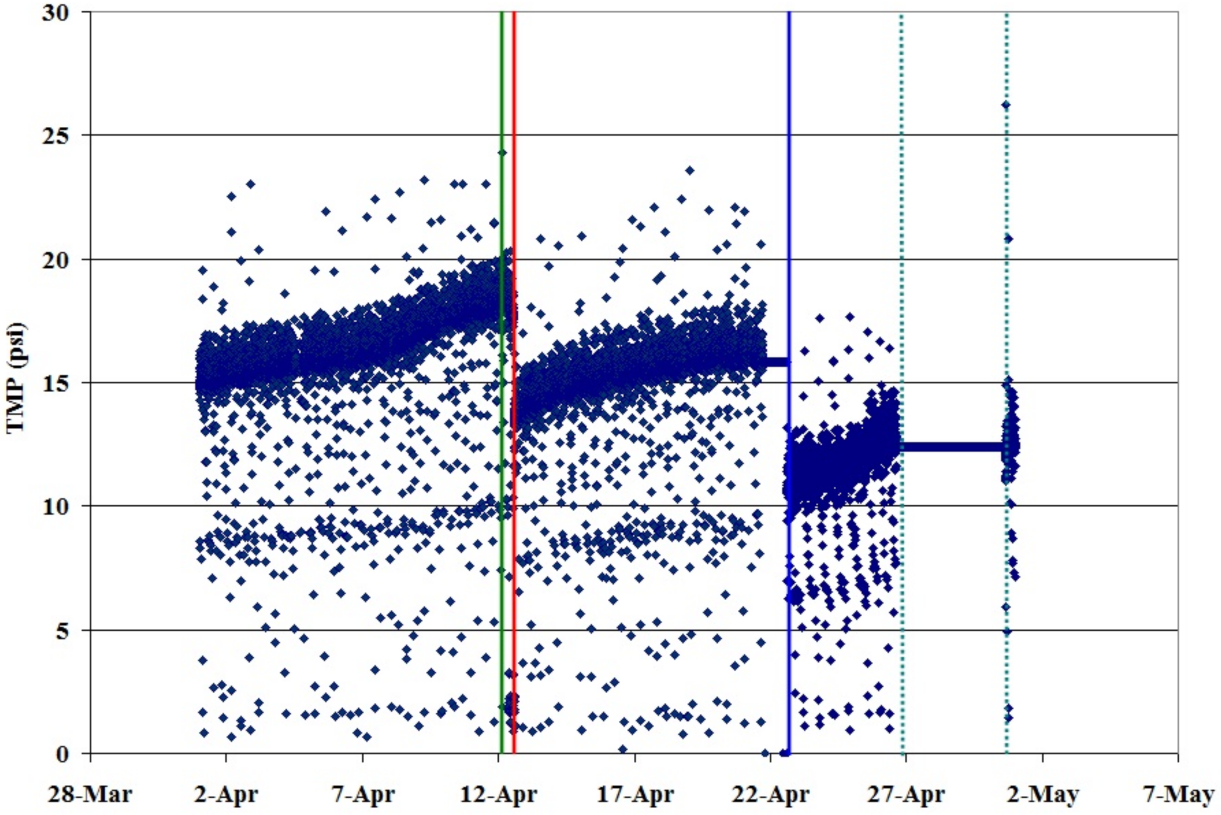


Figure 7.15. East Pall MF Unit TMP Profile for April 2011. The green, red, and solid blue lines denote the timing of high pH/bleach, citric acid EFMs, and CIP followed by the flux changes, respectively. The dotted blue lines indicate the time when YMC was not in operation.

Some minor loss in the performance of the unit was observed as the temperatures started to increase. Specific flux went down to 4 gfd/psi and below by late-summer. The TMP increased slightly and was fluctuating between 12 and 25 psi through the summer. Either citric acid EFM alone or the combination of bleach EFM followed by the citric acid EFM was doing a good job in cleaning the unit and dropping the TMP down to 12 psi. Therefore, at the end of summer, a higher flux of 93.5 gfd was tried for a couple of days prior to shutting the unit down on October 3. The reason for the discontinuation of the YMC water alternatives, hence the East Pall MF unit operation, was the loss of flow in the YMC due to the end-of-year diversions.

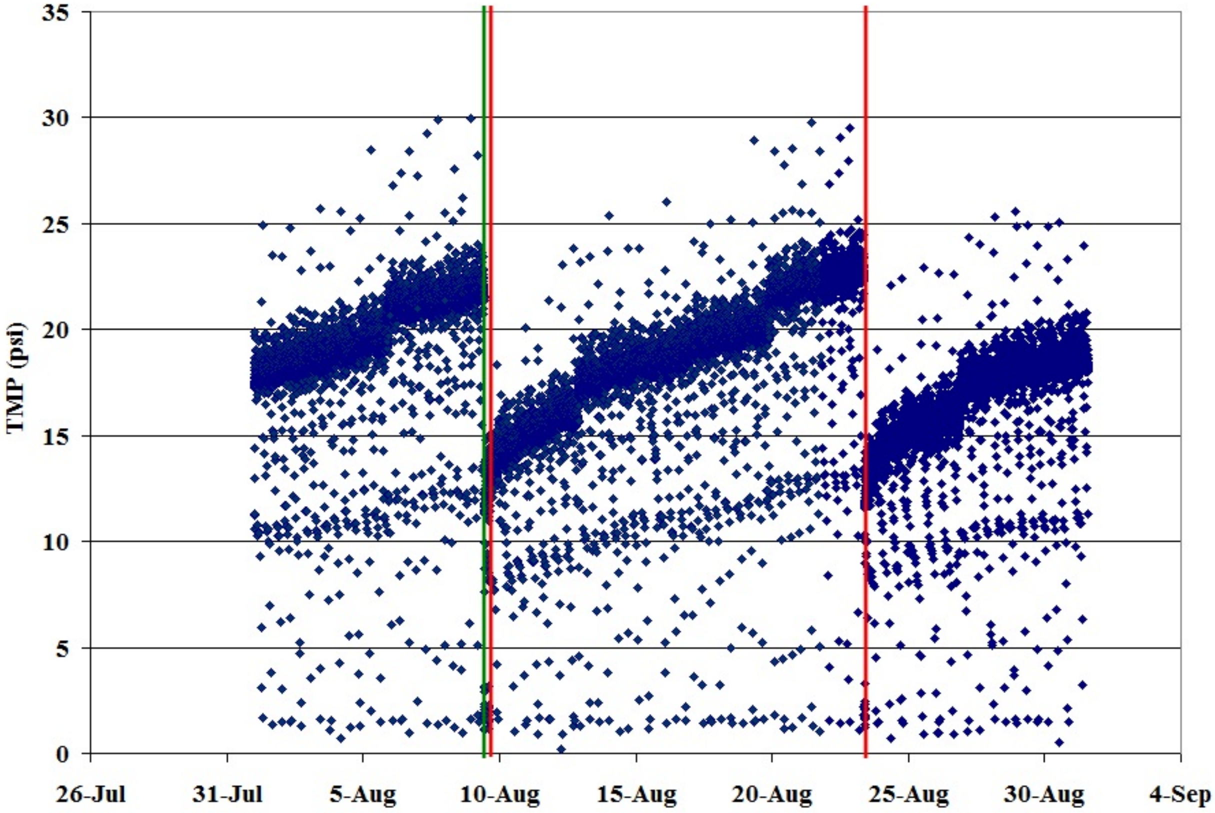


Figure 7.16. East Pall MF Unit TMP Profile for August 2011. The green and red lines denote the timing of high pH/bleach and citric acid EFMs, respectively.

7.2.4 Iron and Manganese Removal

In the Yuma Mesa Pipeline Evaluation Report published in 2008, the total pumping capacity of the YMC is estimated as greater than 80 MGD (125 ft^3/s), transferring the groundwater of Yuma Mesa wells that are 60 ft. higher than Yuma Valley ones. The YMC operates at 32 MGD continuous flow with an extra 19 MGD seasonal flow. Based on the level of manganese and TSS measured in these wells, an estimated 15 tons of manganese and 875 cubic yards (669 m^3) of sediment are being discharged from the wells into the conduit every year. Yuma Area wells have an average of 0.123 mg/L of iron and 0.571 mg/L of manganese concentrations. However, not all the iron and manganese reaches the YDP. Most is oxidized and precipitates in the pipeline. The pumping capacity for YMC could be increased if YMC water were to be used as the main source to supply water for YDP to operate at its design flow rate. However, this increase in the flow, due to the reduced detention time in the pipeline, would most likely result in higher dissolved manganese concentration reaching to the treatment plant compared to the concentrations measured during this research study.

The cleaning of the pipeline would also be necessary if the YMC were chosen to convey water to the YDP, since the deposited material in the pipeline would become suspended again as flow fluctuates. Furthermore, scheduled cleanings of the YMC would most likely be needed since the deposition of the material might still occur even at these higher flow rates due to seasonal flow fluctuations. The deposited materials during the low flow seasons will become suspended during the high flow seasons. Examples of this situation were observed during the research study.

Both iron and manganese concentrations were monitored closely during the pre-testing period as well as during Round 1. Alternatives 21a and 22 were running on the same silica sand/anthracite gravity filtration, before greensand/anthracite filtration was introduced at the start of Round 2 in Alternative 22 in place of silica sand/anthracite filtration. Hence, the sampling locations were somewhat different for Round 1 compared to Round 2. In addition, only total iron and total manganese concentrations were measured until the initiation of greensand filtration. The measured values of iron and manganese concentrations during this research study are presented in Figures 7.17-7.21, below.

Iron Removal

PS2 SCR and GFs started running more than two months earlier than the initiation of the research study testing period, Round 1. The purpose was to give enough time for the gravity filters to ripen for an increased removal efficiency of iron and manganese. Therefore, the iron concentration monitoring began by the end of June 2010. Total iron concentration was mostly below 0.2 mg/L during the following six-month period. However, a spike in mid-August reached a total iron concentration of more than 0.9 mg/L. In about two weeks, the concentration was again down to 0.2 mg/L. Prior to this event, the SCR running on PS 2 was not removing much iron. After the event, an increase in the iron removal efficiency of the SCR occurred as seen in Figure 7.17 where the gap between YMC raw water (blue line) and DMGF influent (green line) increases. This continued until almost December, showing the amount of particulate iron reaching the YDP increased after the August spike event and their sizes were large enough to be removed via sedimentation.

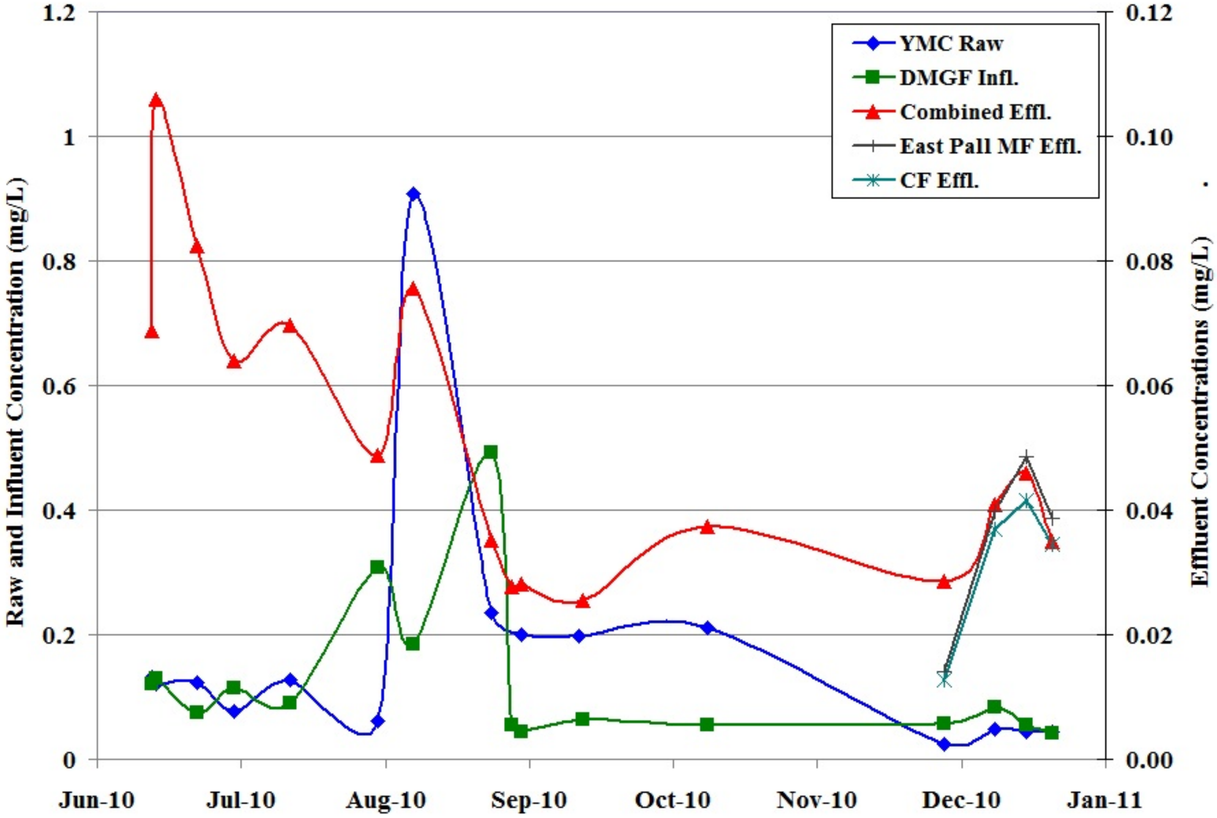


Figure 7.17. Total iron concentration profile for pre-testing period and Round 1.

It is notable that the iron concentration in the combined GF effluent (red line, Figure 7.17) gradually decreased during the first two months of the filters' operation. This was probably due to continued conditioning of the gravity filters and also better control in the oxidizing agent, chlorine injection. GFs supplied almost 45% removal efficiency on average for total iron during Round 1. In December, 2010, which is after the addition of cartridge filters on Alternative 22, several samples were taken of the effluent streams of MF and CF. The results of those samples showed that neither MF nor CF removed significant iron from the water (Figure 7.17). However even if the amount of iron and manganese removed via MF and CF was a very small fraction of the concentration present, because such a large volume of water is passed through the MF and CF units over the several months of a trial, the accumulated amount on the filter material may still have been big enough to cause MF and CF fouling problems. This is especially true for the dead end filtration style CFs, as was mentioned earlier (Section 7.2.2) in the report.

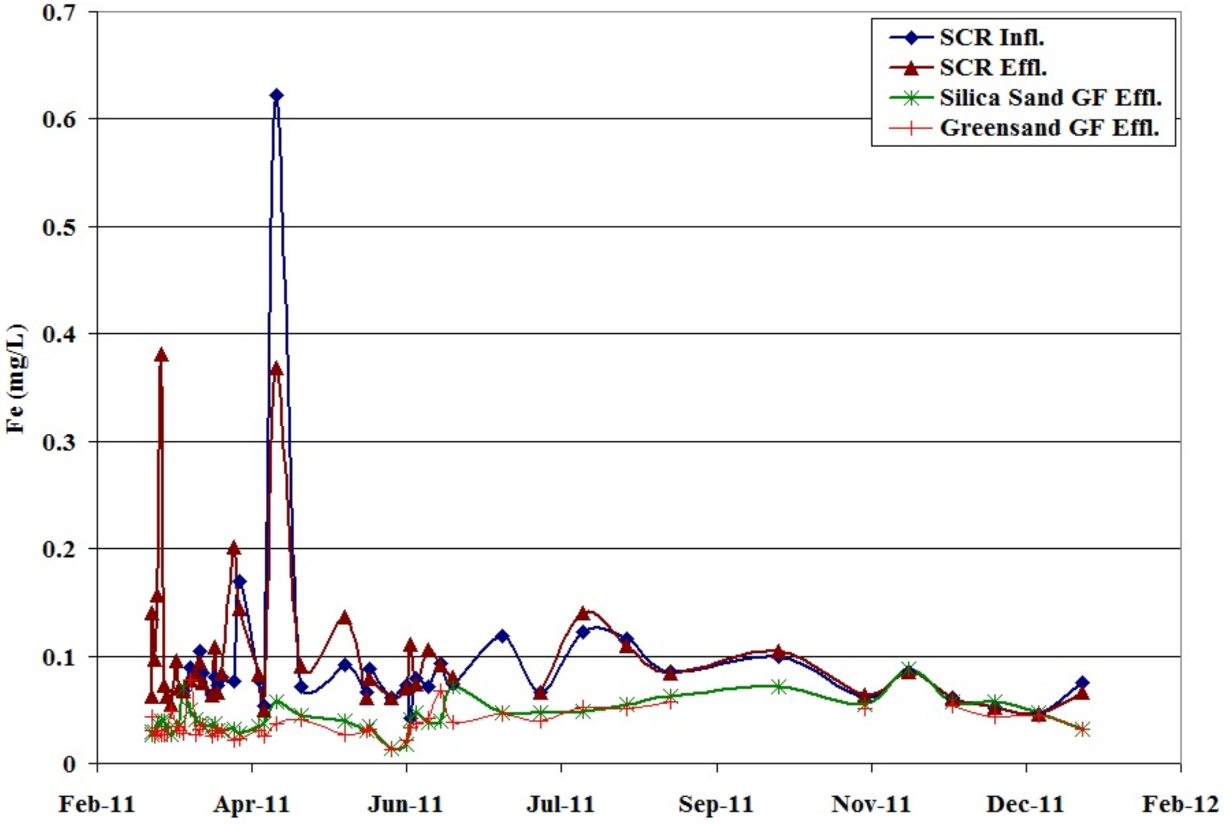


Figure 7.18. Total iron concentration profile for Round 2.

The total iron concentration in the YMC stayed around 0.1 mg/L or below through Round 2, other than the one spike that occurred in April 2011. Gravity filters on both alternatives, Alternative 21a with silica sand and Alternative 22 with greensand GFs, were successful in preventing this concentration spike from passing to the downstream treatment units. Silica sand GFs removed an average of 52% total iron, while greensand was slightly more successful in removing it with an average of 57% through Round 2. One major observation during this period was the lack of particulate iron concentration in November and December 2011. This was the same trend as observed in November and December 2010 (Figure 7.17). The removal rate of total iron during these periods in both years dropped significantly to levels of 0-10%. In Round 2, dissolved iron concentration measurements were initiated (Figure 7.19). The marked decrease of particulate iron concentration in November and December was identified in this way, because the total iron concentration became the same as the dissolved iron concentration during that time period. This shows that either the size of the iron particles were small enough to pass through 0.45 μ sized filter paper or all the iron in the water was in dissolved or complex form. November and December were the months that YMC water may be diverted the Southern International Boundary (SIB) due to Reclamation meeting IBWC Minute No. 242 assurances. Although it is unverified and the mechanism unidentified, this might be behind the reason for this water quality change that occurred in both consecutive years.

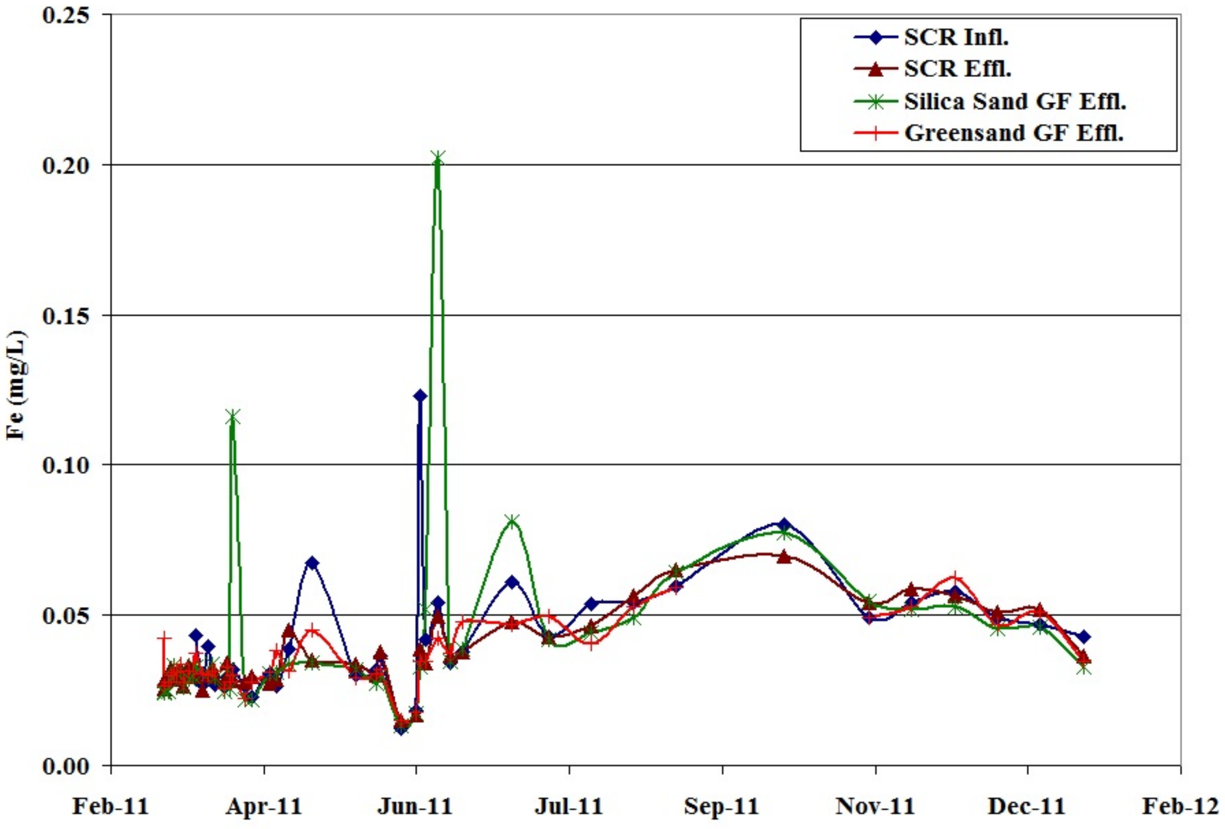


Figure 7.19. Dissolved iron concentration profile for Round 2.

The post-summer dissolved iron concentrations were higher than the pre-summer ones. This might be due to the seasonal variation in the water quality since the concentration started to decrease again after December, but the data record is insufficiently long to verify this conjecture. One other significant observation for this research study was that there was no removal of dissolved iron concentration in either alternative running on PS2. A more detailed study needs to be carried out to determine the real composition of this dissolved iron in YMC water and how to treat it more efficiently. However, no effect of the iron on the RO performance or signs of membrane deterioration due specifically to iron oxidation were detected on any of the downstream RO units. Please, refer to the RO and autopsy results sections for more details about this topic.

Manganese Removal

As was mentioned earlier, PS2 SCR and GFs started running more than two months earlier than the initiation of the research study with the purpose of conditioning the GFs, especially for a better removal of manganese. However, GF combined effluent monitoring showed that not all the manganese was removed from the water (Figure 7.20). Hence, it was decided at the end of August, 2010, to perform a special conditioning by depositing manganese dioxide (MnO_2) on the surface of the silica sand. Please, see Appendix A-6 for the details of the procedure. No significant improvement was recorded after this procedure.

The raw YMC water total manganese concentration was mostly below 0.1 mg/L during the six-month period of June-December, 2010 (Figure 7.20). However, the same spike recorded for iron concentration in mid-August was also observed for the manganese levels in YMC water, reaching to more than 0.6 mg/L. Unlike the iron concentration, which took only two weeks to return to pre-spike levels, manganese levels took almost one month to return to below 0.1 mg/L. The same effect of this spike that was observed for iron removal in SCR was detected also for manganese removal. After the August spike, an increase in the manganese removal efficiency of the SCR was monitored and it continued until almost December. As explained later along with the discussion of dissolved manganese observations, the increased amount of particulate manganese levels reaching the YDP increased in summer and then decreased to negligible levels by winter. The same trends in both 2010 and 2011 were observed for both particulate iron and particulate manganese levels in YMC water.

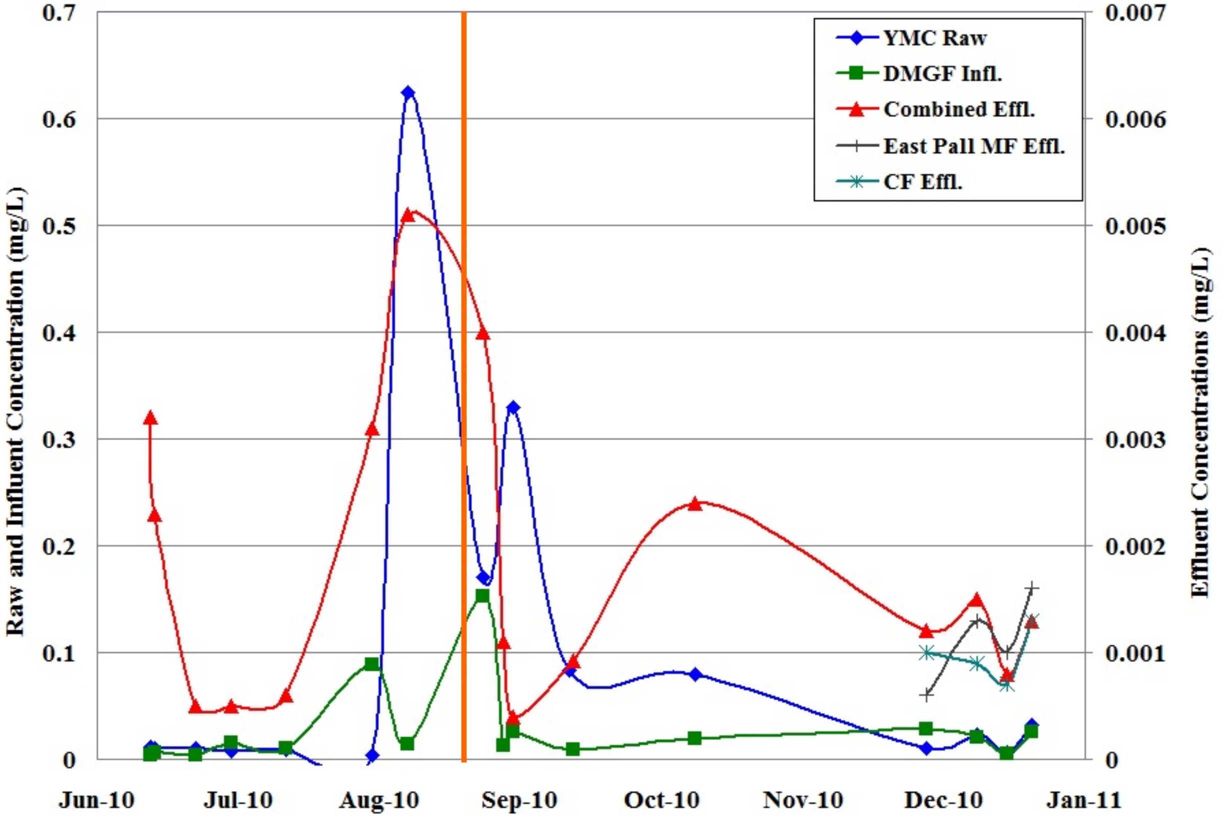


Figure 7.20. Total manganese concentration profile for pre-testing period and Round 1. Orange color line indicates the time for the special conditioning by depositing manganese dioxide (MnO_2) on the surface of the silica sand at the end of August, 2010.

Gravity filters removed the total manganese by almost 85% during Round 1. No significant difference in the manganese concentrations between the DMGF effluent and the effluent of East Pall MF and CF units were noticed (Figure 7.20). The concentration levels detected at the effluent of those two units were high enough to possibly trigger problems on the downstream RO units. Therefore, greensand filtration was decided to be implemented for Alternative 22 for Round 2 to achieve better manganese removal via gravity filtration. This strategy allowed comparison of manganese removal efficiencies by conditioned silica sand and greensand GFs, side by side, during Round 2.

The high concentration in the first couple of days after greensand GFs began running was probably due to wash out of some of the manganese used in the conditioning. The greensand GFs quickly started removing the manganese with a high efficiency following this period. The efficiency of silica sand DMGFs on Alternative 21a increased during Round 2 with an average of 90% manganese removal (which increased the average to 88% throughout the study). On the other hand, greensand DMGFs did only a slightly a better job in removing the manganese during Round 2 with an average of 94% efficiency. Hence, it was concluded that the conditioned silica sand media was as efficient as the greensand media in removing the total manganese concentration from YMC water. It should be noted that the silica sand GFs were specifically conditioned for dissolved manganese removal by depositing manganese dioxide (MnO_2) on the surface of silica sand and oxidizing it with potassium permanganate ($KMnO_4$) by the end of August 2010. After that and prior to installation of the greensand, they ran for more than six months with an effluent free chlorine level of 1.0-1.5 mg/L. This runtime should help them keep the manganese surface active, which consequently helps in removing dissolved manganese.

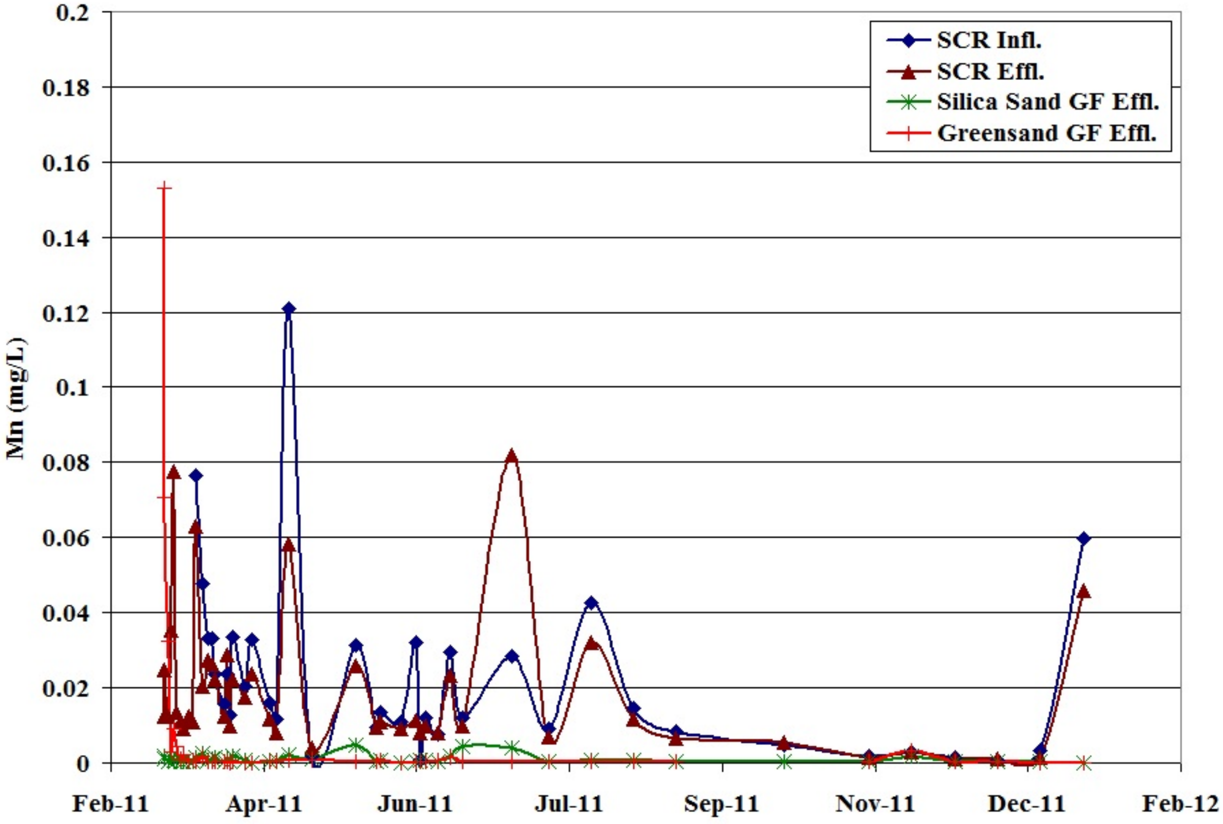


Figure 7.21. Total manganese concentration profile for Round 2.

The dissolved manganese concentration plots are not presented here. However, an average of 59% and 47% removal efficiencies were achieved during Round 2 for silica sand and greensand GFs, respectively. The overall removal rates during Round 2 for both silica sand running on Alternative 21a and greensand running on Alternative 22 are presented in Figure 7.22, below. Based on the lab data and the observations made throughout the research study, it could not be concluded that one alternative was superior to the other in the efficiency of iron and manganese removal.

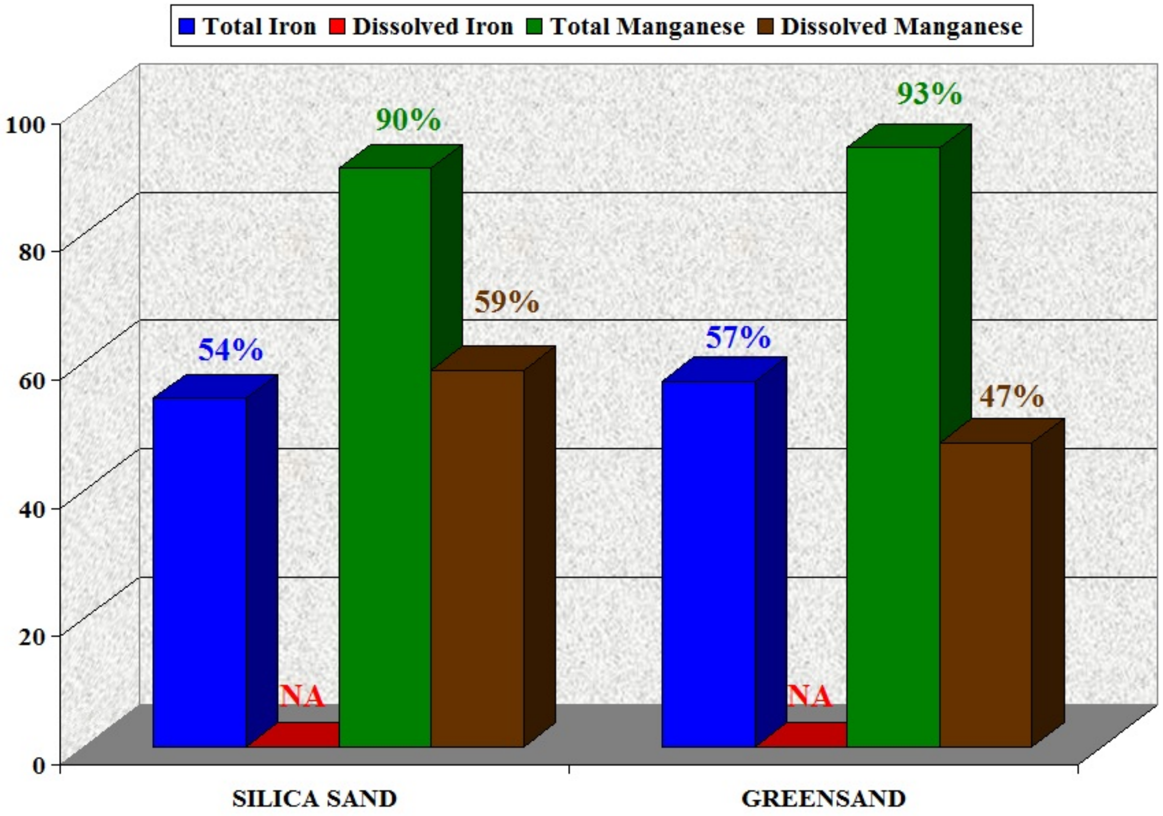


Figure 7.22. Iron and manganese removal efficiencies for silica sand on Alt. 21a and greensand on Alt. 22 during Round 2. No removal of dissolved iron was observed.

7.2.5 BDOC Analyses

During Round 1, BDOC samples were collected at three different locations on YMC alternatives running with YMC water: PS2 gravity filter effluent, and ETA 2 and ETA 3 RO feeds. ETA 2 had PS2 followed by cartridge filtration and ETA 3 had PS2 followed by East Pall

MF as pretreatment. There were no BDOC concentrations detected at any of the sampling locations. The DOC concentrations were also lower than MODE water (Appendix A-12). The higher DOC and BDOC concentrations observed at the effluent of West Pall MF unit running on MODE water were not detected in the effluent of the East Pall MF unit. All the samples analyzed had such consistently low levels that no further sampling was warranted on the YMC pretreatment units. Please, see Table 7.6 below for the average DOC and BDOC concentrations.

Table 7.6. DOC and BDOC concentrations in pretreatment units of MODE water.

Sampling Location	***DOC (mg/L)***	***BDOC (mg/L)***
PS2 GF Effluent	1.6	-0.03
ETA 2 Influent (cartridge filter effluent)	1.6	-0.03
ETA 3 Influent (East Pall MF unit effluent)	1.3	-0.08

7.3 RO Performance

The RO units running on YMC water successfully operated between September 2010 and December 2011. This report covers the RO performance results in two separate sections. The element screening (low recovery) results presented in Section 2.3.1 are investigated in two segments, for Round 1 and Round 2. The results of two-stage MU units running with standard fluxes (12 gfd in average) used in Round 2 full recovery testing are scrutinized in Section 1.3.2 following the element screening results. The effect of the operating pH and the HPC results for all the RO units are presented in separate sections.

7.3.1 Element Screening (low-recovery)

Four ETA units (ETAs 1-4) were used during the testing to evaluate seven different types of membranes in two different rounds. Round 1 that lasted almost 3,000 hours (4 months) tested four different types of membranes (Toray TML 10, Koch ULP, and Hydranautics LFC3 and ESPA2). Due to a combination of YMC flow disruptions and the time taken for gravity filter conditioning before starting the RO tests, ETA 2 on Alternative 22 had a lower runtime than the other three ETAs. Round 2, which lasted more than 3,500 hours, tested three more membrane types (DOW BW30 XFR, CSM FE and CE). The Toray TML 10 was kept the same for both rounds to allow direct comparison.

During Round 1 and Round 2, ETAs operated at an average 15 gfd and at approximately 13% water recovery. The average membrane area per element was assumed as 25 ft^2, initially, until the actual membrane areas were measured. Hence, the ETAs ran at a feed flow rate of 8.0 gpm. However, the performance results were updated with the actual membrane areas upon completion of the autopsies of the retired elements. The purpose for ETA runs (Round 1 and Round 2) was to test the relative performance, impact of type of pretreatment, and the fouling potential of different types of membranes manufactured by various companies.

The water transport coefficient (A), salt transport coefficient (B), B/A ratio, water flux, percent salt passage, percent water recovery, product flow rate, product total dissolved solids concentration and product pressure for each element in the units were calculated and monitored daily by the Test Manager and the operators and weekly by the TAT members. Other parameters measured, calculated and monitored in the same manner include temperature, feed and reject pH, feed free and total chlorine concentrations, feed SDI, feed and reject flow rates, feed and reject total dissolved solids concentrations, feed and reject pressures and percent salt mass balance deviation for each unit and differential pressure and element flow coefficients for each vessel. However, only feed temperature and pH of the units, water transport coefficient, salt transport coefficient, B/A ratio for each element and the element flow coefficient for each vessel are presented in the report. Please, refer to the appendices for the other results.

7.3.1.1 Round 1 Testing

ETAs 2 and 3 started running on September 29 and 28, 2010 for Round 1 testing, respectively. Operating on pretreated YMC water, both ETA 2 (Alternative 22) and ETA 3 (Alternative 21a) ran with a feed pH of 6.8 throughout the whole Round 1. The temperature and feed pH profiles for both of the units are presented in Figure 7.25, below. The early WTC values ranged between 6.5 and 12.5 × 10^{-12} m/s.Pa, Koch ULP and Toray TML10 had the highest, while Hydranautics LFC3 had the lowest WTC values for both of the alternatives (Figure 7.23).

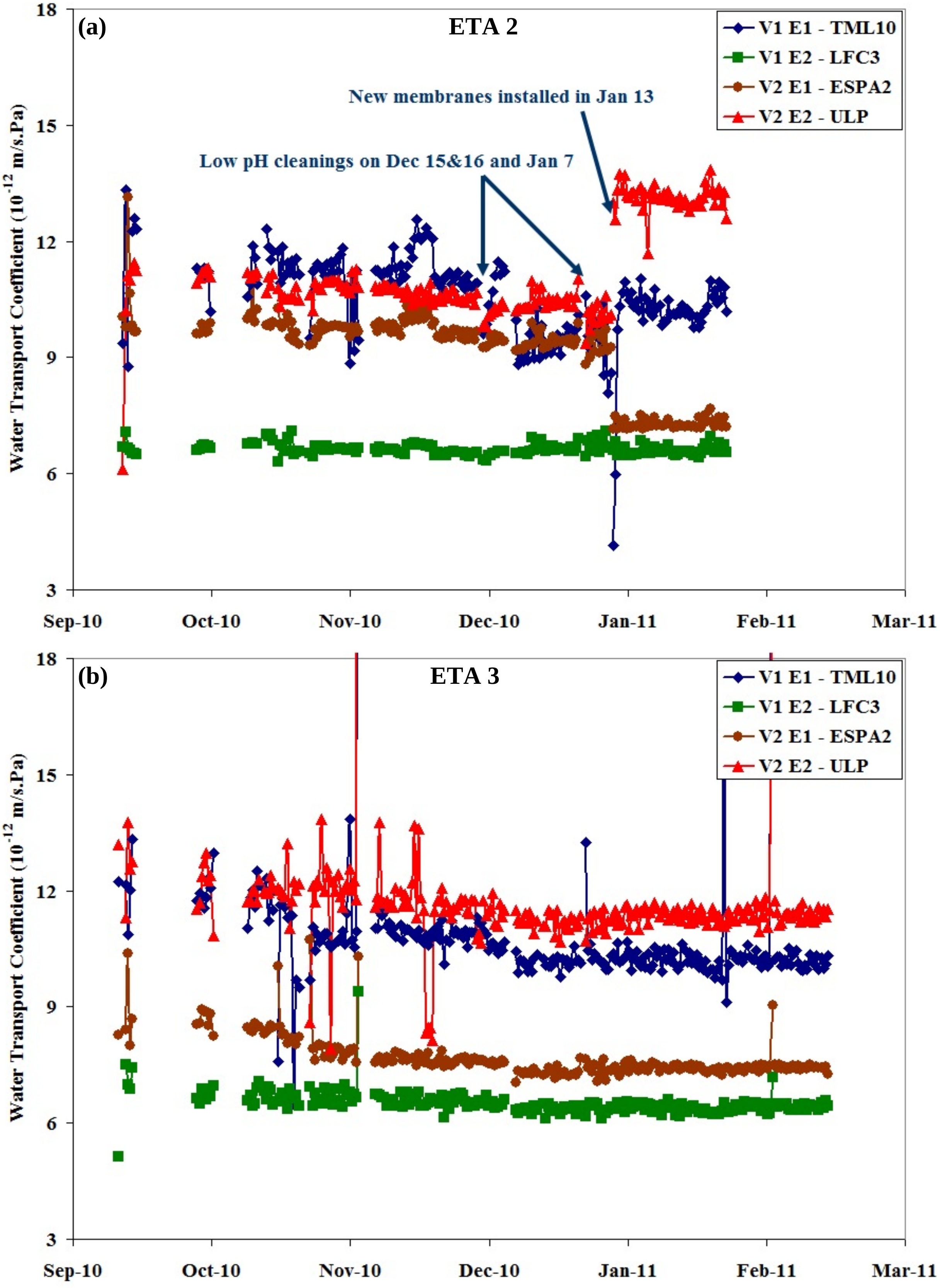


Figure 7.23. Water transport coefficient profiles for (a) ETA 2 and (b) ETA 3 during Round 1.

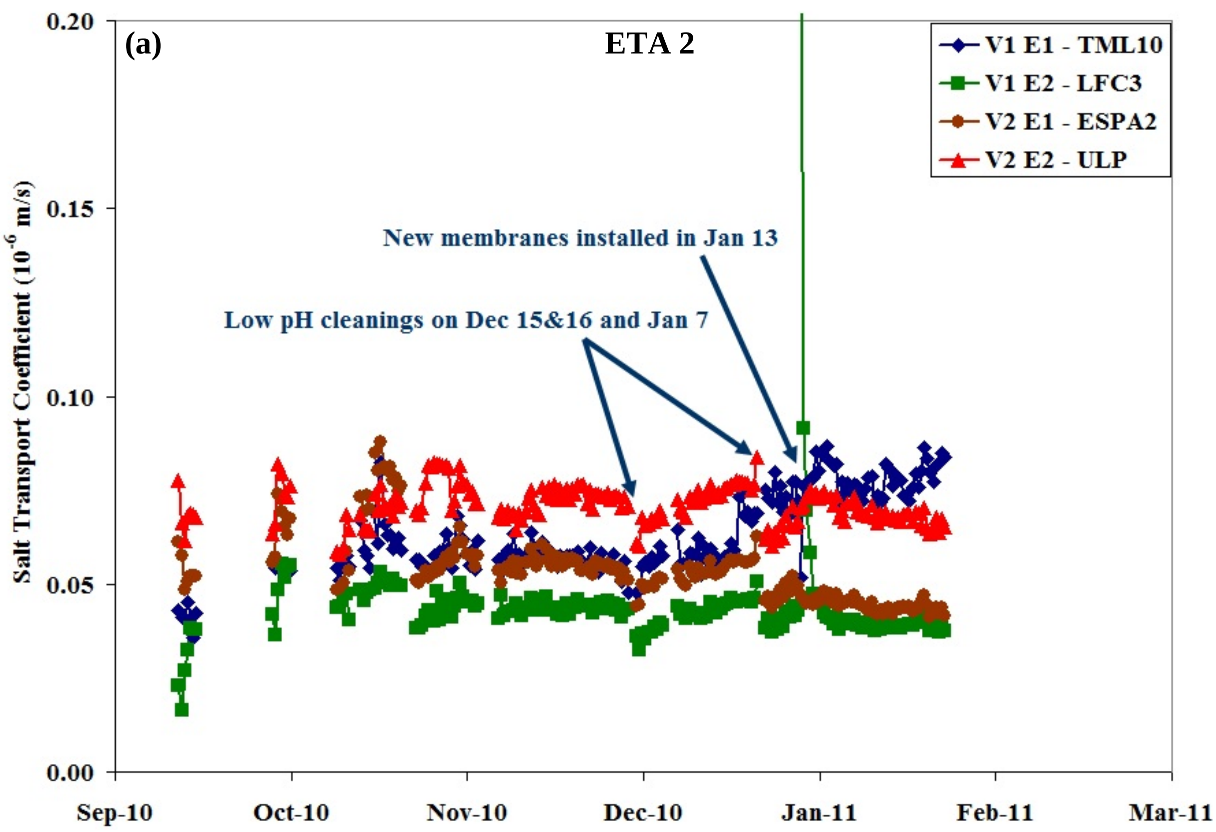
The initial WTC values for the membranes operating in Vessel 1 (Toray TML10 and Hydranautics LFC3) were very close to those for the same elements for both alternatives. On the other hand, the membranes in Vessel 2 (Hydranautics ESPA2 and Koch ULP) showed some variation in their early WTC values. ESPA2 had 9.8×10^{-12} m/s.Pa in ETA 2, whereas this value was about 8.5×10^{-12} m/s.Pa in ETA 3. Conversely, the initial WTC values for ULP were 11.2 and 12.5×10^{-12} m/s.Pa for ETA 2 and ETA 3, respectively.

This difference between the WTC values for the membranes running in Vessel 2 of the ETAs cannot be explained by source water composition difference since both vessels have the same source water. They both operated with the same feed pH, free and total chlorine concentrations and with the same antiscalant dosing. The only difference in the early period of Round 1 between the two alternatives was the microfiltration unit running on Alternative 21a. Hence, the only difference between the two alternatives was a physical pretreatment technique that removes all particles larger than 0.1 μ in size.

The loss of water transport in ETA 2 Vessel 2 membranes, Hydranautics ESPA2 and Koch ULP, in the first two months of its operation was thought to be possibly due to fouling. Hence, a low pH (pH ~2.5) cleaning was performed in mid-December. No effect of the cleaning was obvious regarding the WTC of the membranes. Therefore, another low pH cleaning was carried out on January 7. However, again no positive improvement was achieved. The two elements in Vessel 2 were changed for new elements a week after the second low pH cleaning. It was notable that the WTCs of the newly installed membranes were very close to the initial values for the same elements running in ETA 3 (and quite different than the initial values for these elements on ETA 2).

Cartridge filters were installed on Alternative 22 (ETA 2) on November 18, 2010 and were in operation for the balance of the project. It is difficult to say that the difference in WTC in the first few days of operation could be caused by the extra filtration provided by CF. However this is the only operational difference between the conditions at the start of the ETA 2 run and at the time of installation of the new elements. It is as likely the difference is due to high variability in individual element construction coming from the manufacturer or from other reasons not yet identified. Another reason for this behavior of the membranes ran in Vessel 2 can be explained by a faulty reading of the feed, reject and/or product pressure. Since the calculation of WTC is very sensitive to the pressure readings and related calculations, a very small error in any of these readings might give such a fault in the WTC values although this sort of variability should be equally seen for all elements (and it was not).

After the new membranes were installed on Alternative 22 (ETA 2), the relative order of the WTC values in both units running on YMC water as well as the ETA units ran on MODE water matched very well, with Koch ULP having the highest and Hydranautics LFC3 having the lowest. However, the WTC of the membranes tested during Round 1 showed some variations depending on the water source, even though their rank order stayed the same. The reason for the initial loss of the water transport properties of the membranes in both ETAs running on pretreated YMC water can be explained in (at least) two ways. First are the variations in the water quality of YMC water during the early stages of Round 1. The unexpected disruptions of YMC flows were the main reasons why there were multiple down time periods for both ETA 2 and ETA 3. In fact, only 11 days of runtime was achieved out of the first 32 days of operation. These frequent shutdown events may have caused some unexpected operational behaviors of RO membranes. Second is the lack of more complete iron and manganese removal by the PS 2 gravity filters. The average iron and manganese concentrations in the DMGF effluent during Round 1 were 35.8 μg/L and 1.7 μg/L, respectively. Another factor maybe the average iron concentrations in the feed waters of ETAs were 23 μg/L and 18 μg/L for ETA 2 and ETA 3, respectively, while the manganese levels were 0.7 μg/L and 0.3 μg/L, respectively. This shows that neither the DMGF nor the microfiltration on Alt. 21a or cartridge filtration on Alt. 22 could remove all the iron and manganese efficiently. Since the decrease in WTC was observed in both ETA 2 and 3, the declining WTC values cannot be explained by the lack of cartridge filters in the early period of Round 1. Although, the improvement in removal efficiency after CF installation was obvious (and explained in other parts of this report, such as the lack of coloration on the rotameter and the clear pipes downstream of CF after their installation and the autopsy results showing the evidence of iron and manganese on the cartridge filter material), because a similar decrease in WTC values was observed with ETA 3 on microfiltered YMC water, the lack of early cartridge filtration on ETA 2 feed water cannot be blamed solely for its WTC decline.



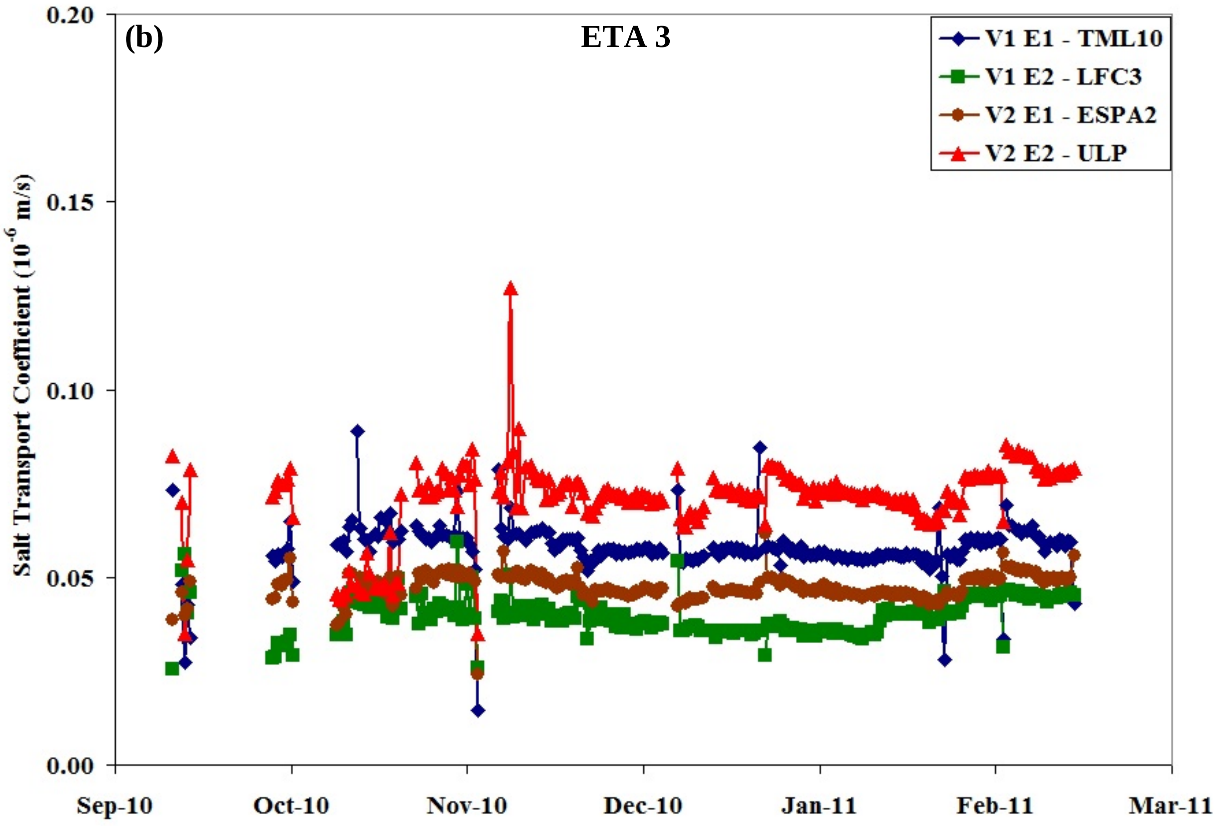


Figure 7.24. Salt transport coefficient profiles for (a) ETA 2 and (b) ETA 3 during Round 1.

The salt transport coefficients for both Alternatives 21 and 22 ranged between 4 and 8 × 10^{-8} m/s. Unlike the same elements run on the MODE water alternatives (where only the TML10 exhibited markedly different STC values from the other element types), the membranes started on YMC water showed a clear distinction between their STC values. STCs had the same rank order as the WTC values for both alternatives, ULP having the highest and LFC3 having the lowest ones. This was not surprising as there was no significant difference between the two feed waters, with regard to the chemical composition. Since the WTC decrease was accompanied by an STC increase in ETA 2, two separate low pH cleanings were carried out, one in mid-December and one in the first week of January. However, neither changed the trend of STC, even though both restored the STC values temporarily after the cleanings. The new membranes installed in Vessel 2 on January 13 had almost exactly the same STC values as the old ones. On the other hand, the new membranes did not show the previously observed trend of increasing STC.

Because of the numerous shutdown events early in Round 1 for the ETAs running on YMC alternatives and, as a consequence, the difficulty in calculating meaningfully accurate STC percent changes per 1,000 hours, no comments are made here on which membranes performed better regarding this parameter. Please, see Appendix D-13 for the calculated values.

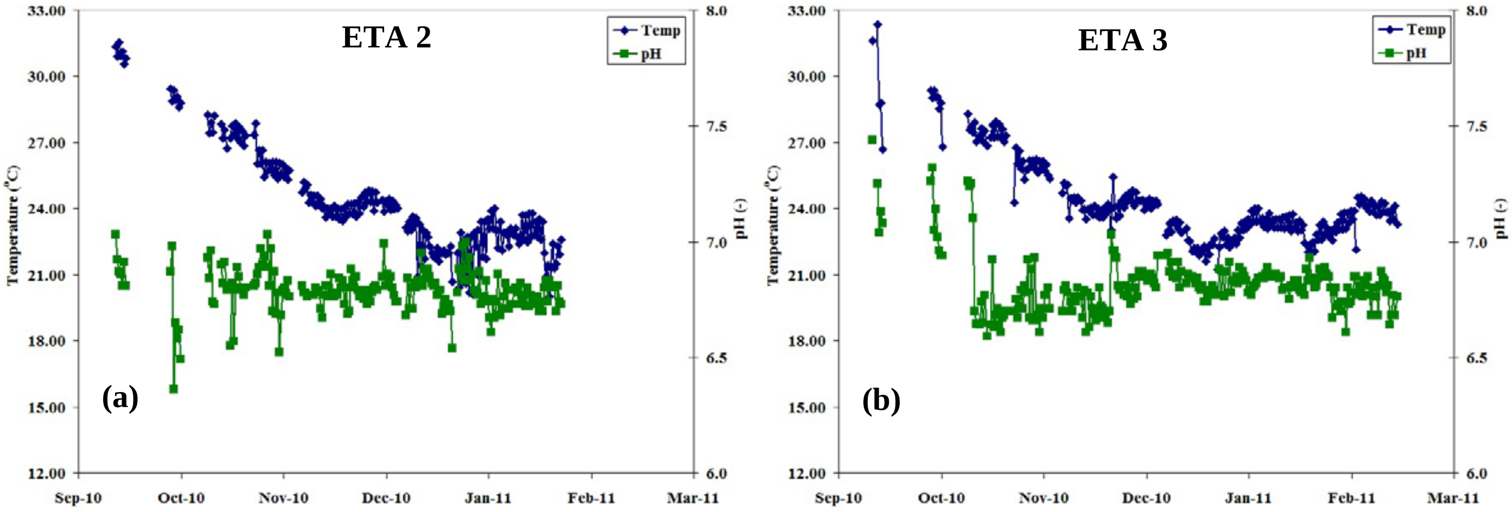


Figure 7.25. Temperature and pH profiles for (a) ETA 2 and (b) ETA 3 during Round 1.

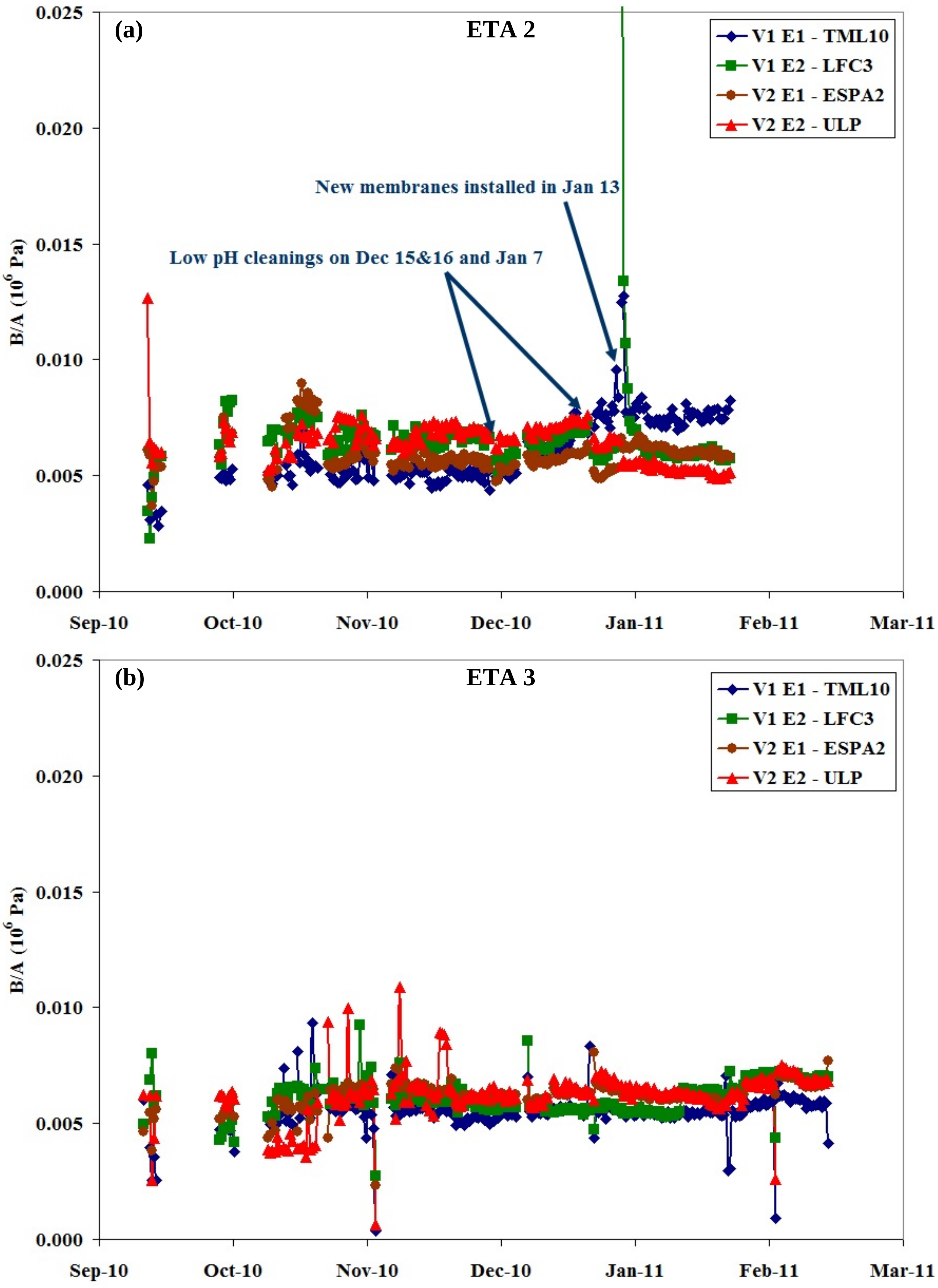


Figure 7.26. B/A ratio profiles for (a) ETA 2 and (b) ETA 3 during Round 1.

Even though it was not as much observed with the MODE water, a notable drop in the temperature from the low thirties to the low twenties degrees Celsius was observed in the YMC water during Round 1 as the run took place between September and February (Figure 7.25). However, all the parameters presented are temperature corrected as defined in the Methods and Materials section of the report. On the other hand, it can be argued that the TCF might be under-correcting the parameters since the higher the temperature, the easier the water passes through the membranes. In that case, a more intense TCF, meaning higher percent correction per degrees Celsius, might give more stable WTC values.

The B/A ratios for the membranes in ETA 3 were slightly lower than the ones in ETA 2 in the early period of Round 1 (Figure 7.26). However, after about 450 hours of operation, ETA 3 membrane B/A ratios caught up with the ones in ETA 2. And the membrane pairs running on each alternative stayed just about the same until about 900 hours of operation (early December). After this point, the B/A ratios in ETA 2 started to increase and kept this trend until the cleaning. Just like the STCs, the first low pH cleaning did not change the increasing trend of the B/A ratios. With the installation of the new membranes, the B/A ratios continued with the same absolute values but the rising trend stopped. On the other hand, ETA 3 membranes stayed constant until mid to late January and showed only a little increase by the end of Round 1. The most significant B/A ratio climb was with TML10 that ran on ETA 2 with about 54% increase through the whole Round 1. Not even the new membrane installation could stop this rise. The increase in the STCs, and hence B/A ratios, might be related with the YMC water composition, which showed considerable variations during Round 1. YMC had several shut down events and diversions during Round 1.

The pressure drop across each RO stage is a good indicator of possible fouling of the feed spacer channel. As with the MODE water alternatives, the temperature corrected element flow coefficient (C_e) is calculated for each vessel. C_e normalizes the pressure drop by flow rate and temperature (Figure 7.27).

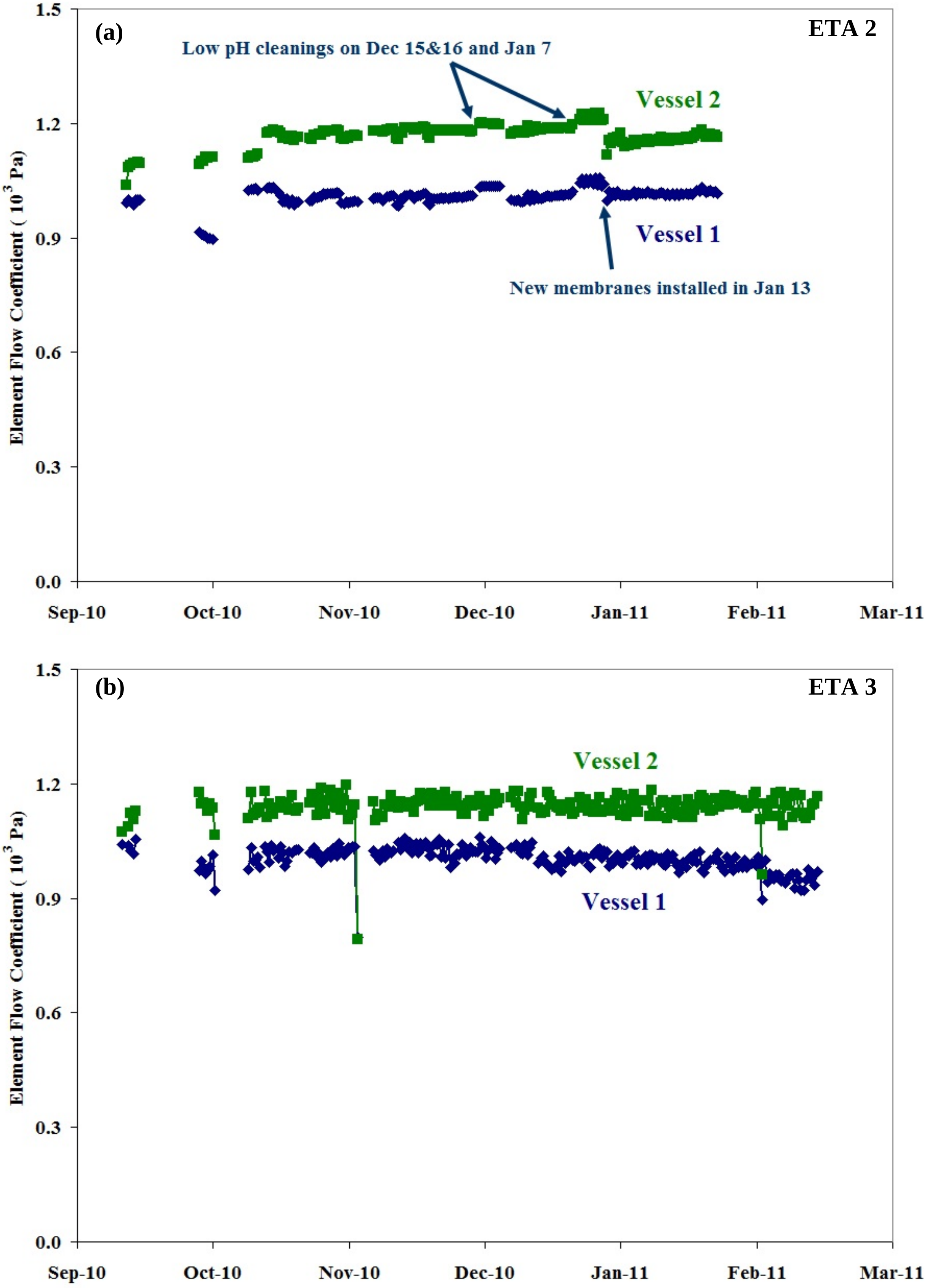


Figure 7.27 Element flow coefficient (C_e) profiles for (a) ETA 2 and (b) ETA 3 during Round 1.

After the fluctuation during the first month of operation, a constant increase in C_e was observed for both vessels in ETA 2. Vessel 1 stabilized with the installation of the new membranes. However, the increase continued on Vessel 2 even after the installation of the new membranes. Hence, no evidence of spacer channel fouling in ETA 2 was detected based on C_e values. On the other hand, very stable C_e values were observed in both vessels of ETA 3 until late January. A slight decrease occurred only in Vessel 1 after this point. The C_e values in the YMC water alternatives were very close to those in the MODE water alternatives, which is expected as the C_e value (initially, before any channel fouling can occur) is related primarily to the flow rates and the spacer thickness of the membranes (neither of which is a function of the water quality). As long as the same types of elements were operated in identical units with the same flow rates, then it is not a surprise to have the same C_e values.

In summary, based on the operating and the calculated parameters of the ETA units, no clear evidence of fouling was observed on Alternative 21a (ETA 3) during Round 1. Alternative 22 (ETA 2), on the other hand, showed some indication of fouling, being minor increase in the STC accompanied by minor decrease in WTC. This was most clearly observed with TML10. As it was on MODE water alternatives, Hydranautics LFC3 performed stably regardless of the pretreatment type with YMC water, even though it had again the lowest WTC. However, the LFC3's low STC value may still make it a favorable membrane for this type of water for extended operation. The most important outcome of Round 1 with YMC water was the positive effect of microfiltration exhibited on Alternative 21a, which highlighted the need for cartridge filter installation in the early period of the testing on Alternative 22. The need of using a more efficient pretreatment technology in removing iron and manganese, such as greensand filtration, also emerged during Round 1 testing.

The rejection rates for the important water constituents, including major cations and anions, are calculated using the feed and product concentrations of the relevant constituents that were measured in the lab by ICPMS (Table 7.7). Please, see Appendix C-2 for the detailed water quality analyses of the feed, product and reject streams of each ETA unit. Relatively low rejection rates compared to the other membranes in the same alternative are highlighted in yellow in the table. Hydranautics membranes (LFC3 and ESPA2) did somewhat better than the other two membranes tested during Round 1 with YMC water with respect to rejection of ions. This matches with the salt passage and STC values observed during Round 1. The overall salt rejection was equal to or lower than 99% for all the membranes in both alternatives. LFC3 stood out with the highest salt rejection rate in both alternatives.

Table 7.7. Rejection rates (in percentage) of important parameters for each membrane tested in ETA 2 and ETA 3 during Round 1. Low rejection values relative to other membranes for the same water constituent are highlighted in yellow.

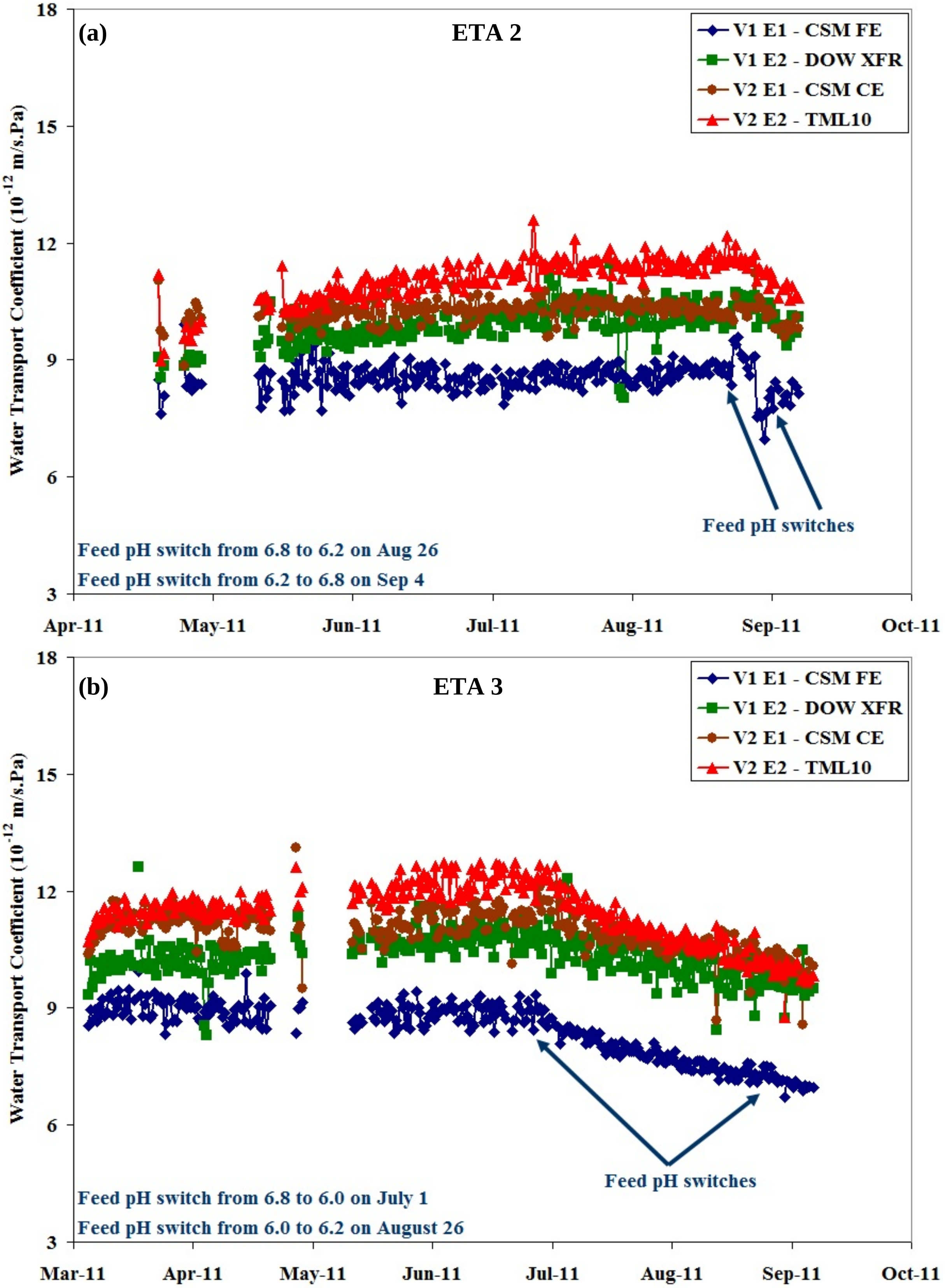
	ETA 2 (Alt. 22)				**ETA 3 (Alt. 21a)**			
	TML10	**LFC 3**	**ESPA2**	**ULP**	**TML10**	**LFC 3**	**ESPA2**	**ULP**
Bicarbonate	94.88	96.29	96.12	95.21	94.42	94.80	94.93	94.27
Calcium	99.88	99.97	99.96	99.90	99.84	99.95	99.91	99.78
Chloride	98.93	98.89	98.72	98.23	98.73	98.97	98.78	97.97
Conductivity	98.88	99.09	98.92	98.54	98.85	99.17	99.02	98.39
Iron	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Magnesium	99.88	99.98	99.97	99.89	99.85	99.96	99.94	99.76
Manganese	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Nitrate as N	NA	NA	NA	NA	NA	NA	NA	NA
Potassium	98.14	99.24	98.91	98.28	98.64	99.12	99.00	98.17
Silicon Dioxide	99.22	99.05	98.75	97.94	99.00	99.10	98.68	97.51
Sodium	98.53	98.82	98.59	98.10	98.55	98.92	98.76	98.00
Strontium	99.89	99.98	99.97	99.91	99.85	99.96	99.92	99.78
Sulfate	99.74	100.00	100.00	99.80	99.66	100.00	99.83	99.71
Sum of Anion	98.64	98.81	98.68	98.33	98.59	98.83	98.70	98.15
Sum of Cation	99.06	99.29	99.16	98.82	99.06	99.34	99.22	98.69
Tot. Alk. as CaCO3	94.96	96.35	96.18	95.29	94.52	94.89	95.02	94.37
Tot. Hard. as CaCO3	99.88	99.97	99.96	99.90	99.84	99.96	99.92	99.77
Total Organic Carbon	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total Salt	98.74	99.00	98.87	98.52	98.73	98.99	98.89	98.39

7.3.1.2 Round 2 Testing

During Round 1, the desired level of iron and manganese removal was not achieved via silica sand DMGFs. The loss of water transport coefficient and the increase in the STC levels through Round 1 led to discussion about the efficiency of the DMGF on YMC water. High enough levels of iron and manganese were measured in the feed of the ETAs that greensand was installed on three PS2 gravity filters between Rounds 1 and 2 of testing. The purpose was to investigate the removal efficiencies of iron and manganese along with other ions that may cause fouling, scaling or membrane deterioration via greensand. The results of Round 2 are presented in the following section. Installation and conditioning of the greensand however took time out of the Round 2 schedule, so ETA 2 ran for a shorter duration in Round 2 than ETA 3.

ETAs 2 and 3 started running on April 18 and March 11, 2011 for Round 2 testing, respectively. As with MODE water alternative testing, the main purpose of Round 2 testing with YMC alternatives was to evaluate three additional membrane types from two different manufacturers on two different pretreatment systems. Operating on greensand and CF pretreated YMC water, ETA 2 (Alternative 22) ran with a feed pH of 6.8 until August 26. The pH was dropped to 5.8 for the next 10 days and then increased back to 6.8 for the 5 more days until the end of Round 2 testing. On the other hand, ETA 3 (Alternative 21a with silica sand and MF pretreatment) ran with a feed pH of 6.8 until July 1. The pH was dropped to 6.0 for the next two months until August 26 and then increased back to 6.2 for the 10 days until the end of Round 2 testing. Again, none of these pH adjustments were done for improving the ETA performances. They were carried out to improve either the MU performances running on the same alternatives or testing the impact of pH on cartridge filter operation. However, the changes, as expected, affected the ETAs. The effects of these modifications are discussed in detail, below. Temperature and feed pH profiles for both of the units are presented in Figure 7.30, below.

ETA 2 and ETA 3 operated about 2,965 hours and 3,763 hours during Round 2, respectively. These durations, especially for Alternative 22 (ETA 2), are much lower than for the MODE alternatives in Round 2. The reason for this shorter runtime for the YMC water alternatives is mainly the frequent and long-term shut down events for YMC system. In addition, installation of greensand in Alternative 22 prevented ETA 2 having the same amount of operation time as ETA 3. However, both units ran as long as the Round 1 ETA testing, which was about 3,000 hours.



Feed pH switch from 6.8 to 6.2 on Aug 26

Feed pH switch from 6.2 to 6.8 on Sep 4

Feed pH switch from 6.8 to 6.0 on July 1

Feed pH switch from 6.0 to 6.2 on August 26

Figure 7.28. Water transport coefficient profiles for (a) ETA 2 and (b) ETA 3 during Round 2.

The early WTC values ranged between 8.5 and 10.5 × 10^{-12} m/s.Pa. These values were practically the same as the ones recorded in MODE water alternatives for Round 2. Similar to MODE water alternatives, Toray TML10 and CSM CE had the highest, while CSM FE had the lowest WTC values in both alternatives for YMC water (Figure 7.28). Even though the starting WTC values of each membrane pair running on two different alternatives were very close to each other, a different trend was observed for each alternative. This was again similar to the MODE water observations. The WTC of the membranes in ETA 3, running on microfiltered YMC water, showed a rapid increase in the early stage but then stabilized and stayed constant until the feed pH adjustments. On the other hand, the increase in ETA 2 was slow but steady and continued until the feed pH adjustment. One important observation was that the membranes that ran on microfiltered YMC and MODE waters demonstrated similar WTC trends. When the feed pHs of the units were dropped on July 1 for ETA 3 and August 26 for ETA 2 from 6.8 to 6.0 and 6.2, respectively, WTC for all the membranes showed a steep decline. This trend in WTC of the ETA 2 membranes was stopped when the feed pH was increased back to 6.8 on September 4. However, no restoration was recorded to the original WTC values (although the run-time of only 5 days after the pH increase was likely insufficient to see full restoration). The slight increase in ETA 3 feed pH (from 6.0 to 6.2) on August 26 neither stopped nor changed the rate of decrease in WTC values.

A very important observation during Round 2 YMC water element (fouling potential) testing was the magnitude of the impact that the changes of feed water pH had. In the literature, there are many studies presented about the importance of the operating pH on the RO treatment, including the effects on the solubility of the salts, on the rejection rates and on the membrane structure. The feature that distinguishes the results of this study from others presented in the literature is the size of the impact of the pH fluctuations. There was an increasing trend in the STC values for the membranes run on ETA 2, other than DOW XFR, prior to the feed pH adjustment. On the other hand, the STC values were variable but relatively constant on average for the membranes running on ETA 3.

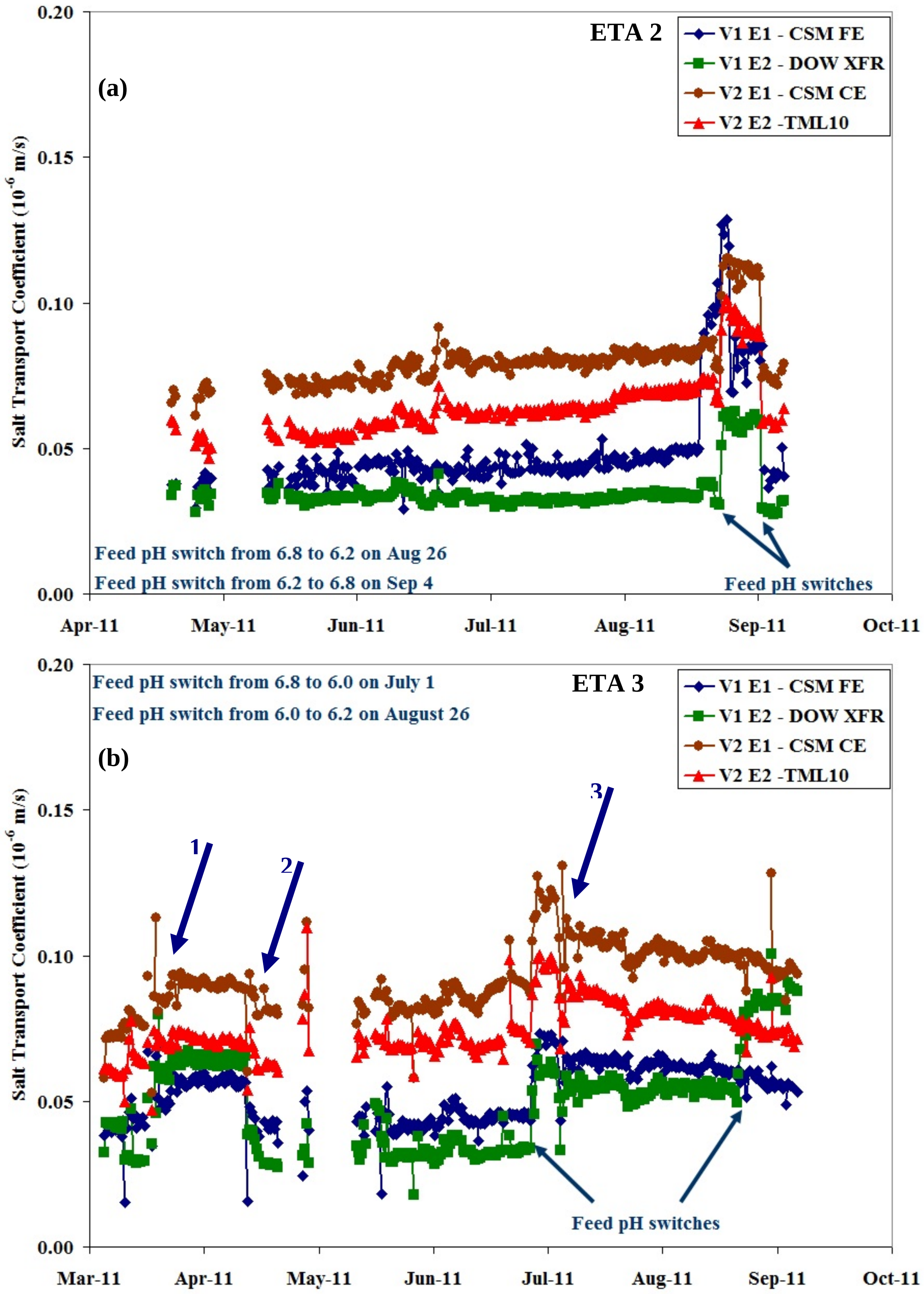


Figure 7.29. Salt transport coefficient profiles for (a) ETA 2 and (b) ETA 3 during Round 2. The numbered arrows indicate the timing of unintentional pH changes to the ETA 3 feed water.

The initial values of salt transfer coefficients for each pair of membranes tested on the two YMC water alternatives were very close to each other. CSM CE had the highest and DOW XFR had the lowest ones in both alternatives. This order was the same as that observed in MODE water alternatives. This supported the idea of DOW XFR being a good candidate for long-term treatment, since it had the lowest STC and a relatively high WTC.

One thing very clear is that the feed pH had a significant effect on the STC values. The feed pH dropped from 6.8 to 6.5 on ETA 3 unintentionally between March 22 and March 28. The reason for this unintentional decrease in the feed pH was due to some operational issues with the acid injection and pH control units. Because there were several shutdown events during that time, it was difficult to keep the pH at its desired level. The shutdown events occurred on a daily basis (March 22-25) because of chlorine residual problems, pump problems, computer updating and ORP testing. Notwithstanding the cause, in response to the pH drop from 6.8 to 6.5, the STC values of the membranes showed a jump as indicated with a blue arrow (number 1) in Figure 7.29, above. Later, the problem was realized and the feed pH was adjusted back up to 6.8 around April 20, indicated with the blue arrow numbered as 2 (Figure 7.29). This corresponds exactly with the timing of a drop back to near pre-March 22 values. These lower STC values continued until the feed pH was changed from 6.8 down to 6.0 on July 1, 2011. This pH change was to test the pH effect on MU 1. However, it had an effect on ETA 3 as well, since they both used the same feed water.

With the drop of pH on July 1, the ETA 3 STC values for all the membranes jumped up. However, the feed pH was around 5.8, which was below the actual targeted value. When this problem was realized, the pH was increased slightly. This event is indicated with the blue arrow numbered as 3 in Figure 7.29. This slight increase had again affected the STC values of the membranes and they all dropped a little. Following these pH adjustments, dropping the feed pH from 6.8 down to 6.0 showed its impact on the membrane performances. The STC values for all membranes tested in ETA 3, except DOW XFR, showed noticeable declines in their STC values through July and August. No change in STC was observed with feed pH of 6.0 on DOW XFR. The next feed pH adjustment was on August 26, increasing it from 6.0 up to 6.2. However, this time the only effect was observed on DOW XFR. All the other three membranes performance kept declining with the same rate as previously until the end of Round 2 testing. On the other hand, the STC value of DOW XFR jumped up with this pH adjustment and stayed high until the end of testing.

ETA 2 membranes showed the same kind of behavior as the ETA 3 membranes to feed pH adjustments on August 26 and September 4, 2011. When the feed pH was dropped from 6.8 to 6.2 on August 26, the STC values for all the membranes tested in the unit showed a jump by 50% or more. When the feed pH was increased back up to 6.8 on September 4 to test the effect of this on cartridge filters, a momentous impact on the STC values of the membranes running in ETA 2 downstream was observed. All the values came below where they were prior to any pH adjustment. In fact, they were very close to the starting STC values. There was not enough runtime afterwards to see the effect of increasing the pH. However, a faster increasing rate in the differential pressure of the cartridge filters was observed during the low pH operation, between August 26 and September 4, on Alternative 22 (see details in earlier section). This shows that the change in the pH does not solely (if at all) affect the structure of the polyamide membranes, but also the composition of the feed water. A more detailed investigation needs to be carried out to detect the exact changes and underlying mechanisms occurring with varying pH. The effect of operating pH is discussed further in the results section for the MU operations.

The only membrane that was in common for both rounds was Toray TML10. The significant differences in performance results between Round 1 and Round 2 for this membrane showed that one or more of the following factors must have occurred: i) there was something different with the way that the units were operated, ii) there was something different in the water composition, or iii) there were variations between the specific TML10 membranes tested. Because the Toray TML10 tested in ETA 2 during Round 1 had a higher initial WTC value compared to the one tested during Round 2, there is reason to suspect that individual membranes may differ markedly. The Round 1 membrane showed a decreasing trend in WTC, while the latter showed an increasing trend. Finally, the one tested in Round 2 ended with a higher WTC value than the one tested in Round 1. Similarly, the WTC value for the Toray TML10 tested in ETA 3 during Round 1 was slightly higher but showed a decline, while the one tested during Round 2 started with a lower WTC compared to Round 1 but showed an increase. In conclusion, the increasing trend for the WTC values of TML10 elements tested during Round 2 was different than the decreasing trend observed during Round 1. The most likely (but certainly not only) explanation is different water composition in both rounds.

Table 7.8. Percent changes in STC for membranes tested in ETA 2 and ETA 3 during Round 2. The values in parenthesis represent the percent changes in STC prior to any pH adjustments on ETA 2.

	ETA 2 (Alt. 22)		**ETA 3 (Alt. 21a)**	
	% change	**% per 1000hr**	**% change**	**% per 1000hr**
CSM FE	2.47 (21.56)	0.93 (9.65)	25.71	7.07
DOW XFR	-19.13 (-0.22)	-7.18 (-0.10)	52.46	14.42
CSM CE	4.57 (14.44)	1.72 (6.46)	22.66	6.23
Toray TML10	12.56 (26.87)	4.72 (12.02)	16.10	4.43

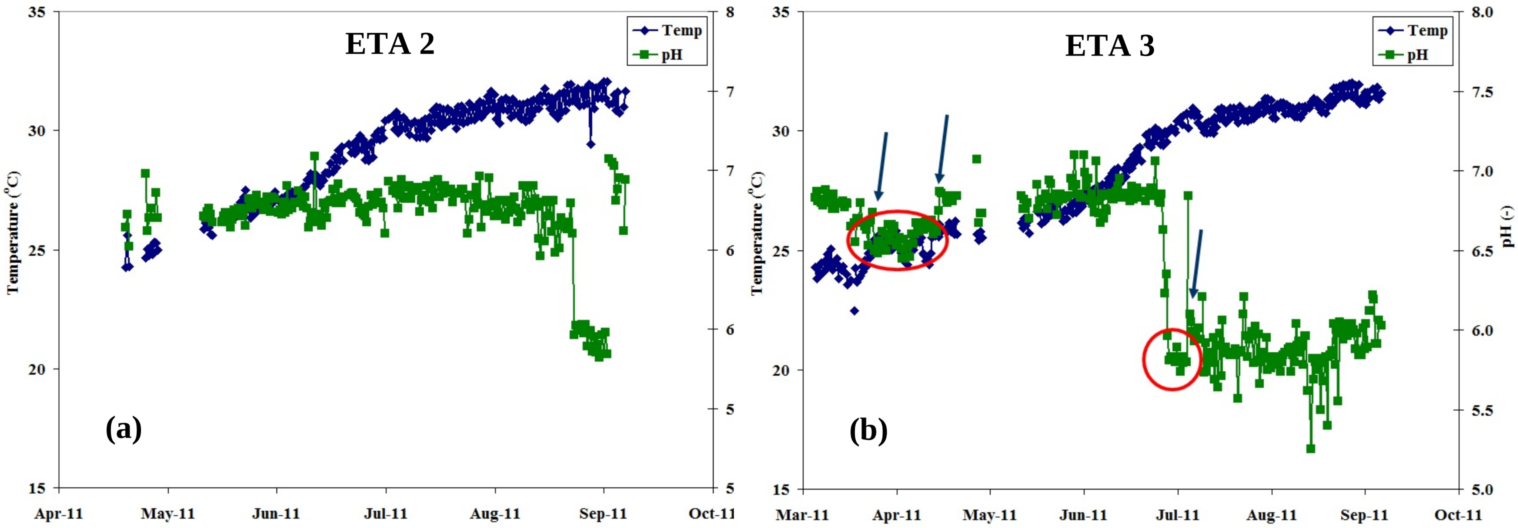


Figure 7.30. Temperature and pH profiles for (a) ETA 2 and (b) ETA 3 during Round 2. The red circles (b) represent the unintentional pH fluctuations on ETA 3.

The changes in the STC values during Round 2 are presented in Table 7.8. As presented in the table and also in Figure 7.29, ETA 2 membranes had a more stable run in terms of STC. The values presented in the parenthesis represent the percent changes of STC prior to any pH adjustments on the unit. It is clear that the salt passage was increasing in all the membranes tested, except DOW XFR. The XFR was stable until the pH adjustment on August 26. Prior to this pH change, the rates of increase for the other membranes were 6.5, 9.7 and 12.0 % per 1000 hours for CSM CE, CSM FE and Toray TML10, respectively. Feed pH adjustments helped to drop the STC values by one third or more for CSM FE.

Both ETA 2 and 3 were running with a feed pH of 6.8 initially for Round 2, just as in Round 1. The feed pH on ETA 2 was dropped to 5.8 on August 26, but was brought back to 6.8 a short time later. The purpose, as it was mentioned earlier in the report, was to test the pH effect on the cartridge filters that were running upstream of ETA 2. The red circles in Figure 7.30(b) represent the unintentional pH fluctuations on ETA 3. These fluctuations probably occurred due to shutdown events that made the pH control harder. These shut down events were caused by operational issues, including computer updating, chlorine level excursions and ORP testing. The consequences of these pH fluctuations were discussed and explained earlier in this section. The temperature for the YMC alternatives during Round 2 increased from 25 ^{o}C to 32 ^{o}C between March and September, 2011. As with the MODE and earlier YMC ETAs, there was no clear correlation between the temperature and WTC or STC values of any of the ETAs. All the parameters presented in this section are temperature corrected as defined in the Methods and Materials section of the report.

The initial B/A ratios for the membrane pairs in ETAs 2 and 3 were practically the same. Other than the pH fluctuations and pH adjustment sections of the round, they all showed stable B/A ratios. Based on this parameter, there was no reason to believe that there was fouling or membrane degradation on the membranes running on YMC water alternatives. On the other hand, the B/A ratio step changes, reflecting increased salt passage at that operating pH, occurred either because of the membrane structure changes or because of the water composition changes or both. However, to the degree that the objective was to achieve stable B/A ratios, regardless of the pretreatment types for YMC water alternatives, this was achieved.

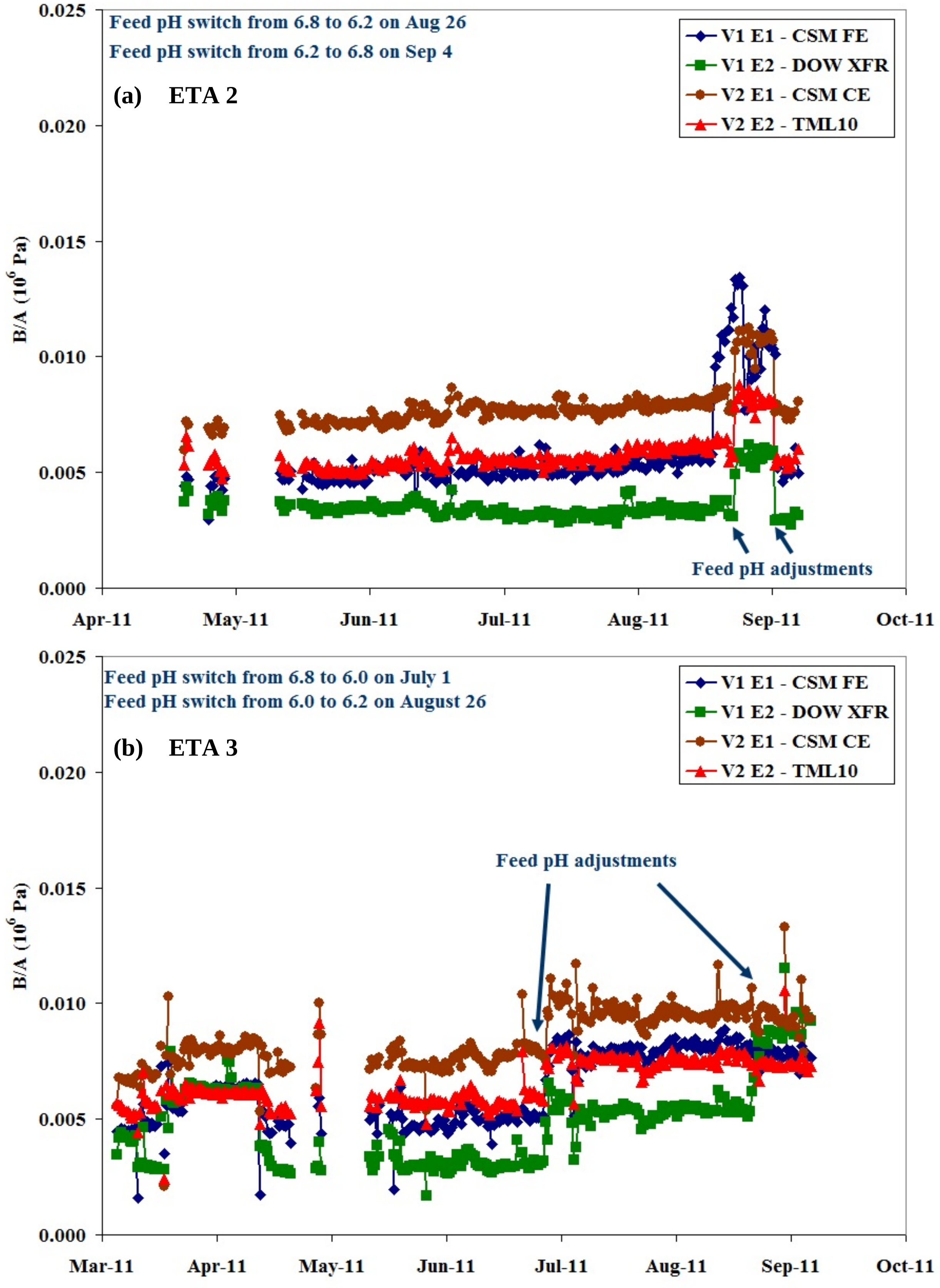


Figure 7.31. B/A ratio profiles for (a) ETA 2 and (b) ETA 3 during Round 2.

The temperature corrected element flow coefficient (C_e) calculated for each vessel is presented in Figure 7.32 for both units. Even though Vessel 2 C_e values were very close to each other on the two different alternatives, Vessel 1 C_e values were 8-10% higher on ETA 3. The differential pressures for vessels 1 and 2 were significantly different in each unit. ETA 2 Vessel 1 dP was about 20% higher than the Vessel 1 dP in ETA 3 and it stayed like that throughout Round 2. In contrast, the dP for Vessel 2 was lower in ETA 2 by about 8-9% compared to the one in ETA 3. The C_e values for both vessels in ETA 2 showed a decline during Round 2 testing and this trend was not affected by the pH adjustments, suggesting that there might be some fouling in ETA 2. The rate of decrease was about 1.80% per 1000 hours and 1.96% per 1000 hours for Vessel 1 and Vessel 2, respectively. Similarly, the C_e values for both vessels in ETA 3 dropped throughout the Round 2 testing. But the declines observed in ETA 3 were less than the ones observed in ETA 2, with 0.75% per 1,000 hours and 1.28% per 1000 hours for Vessel 1 and Vessel 2, respectively. The ETA 3 values also were not affected by the pH fluctuations and adjustments. Hence, microfiltration appeared to work better than cartridge filtration in terms of keeping the C_e values stable.

In summary, based on the operating and the calculated parameters of the ETA units, no evidence of fouling or scaling was observed. However, there was some behavior consistent with membrane degradation, since both WTC and STC values were increasing in the early period of Round 2 testing for both units. Nevertheless, this suspicion is not supported when examining the effect of pH adjustments. All membranes tested in YMC Round 2 ETAs showed increases in both STC and WTC when pH was adjusted down. The sensitivity of STC values for all four membrane types tested during Round 2 was clear. In general, a jump in the STC values accompanied a step decrease in pH and this was followed by a slow but continuous decline in STC. Likewise, an increase in pH induced a drop in the STC values, regardless of the membrane type. This suggests that the reason for the sensitivity of STC to the operating pH might be the water composition rather than changes in membrane structures.

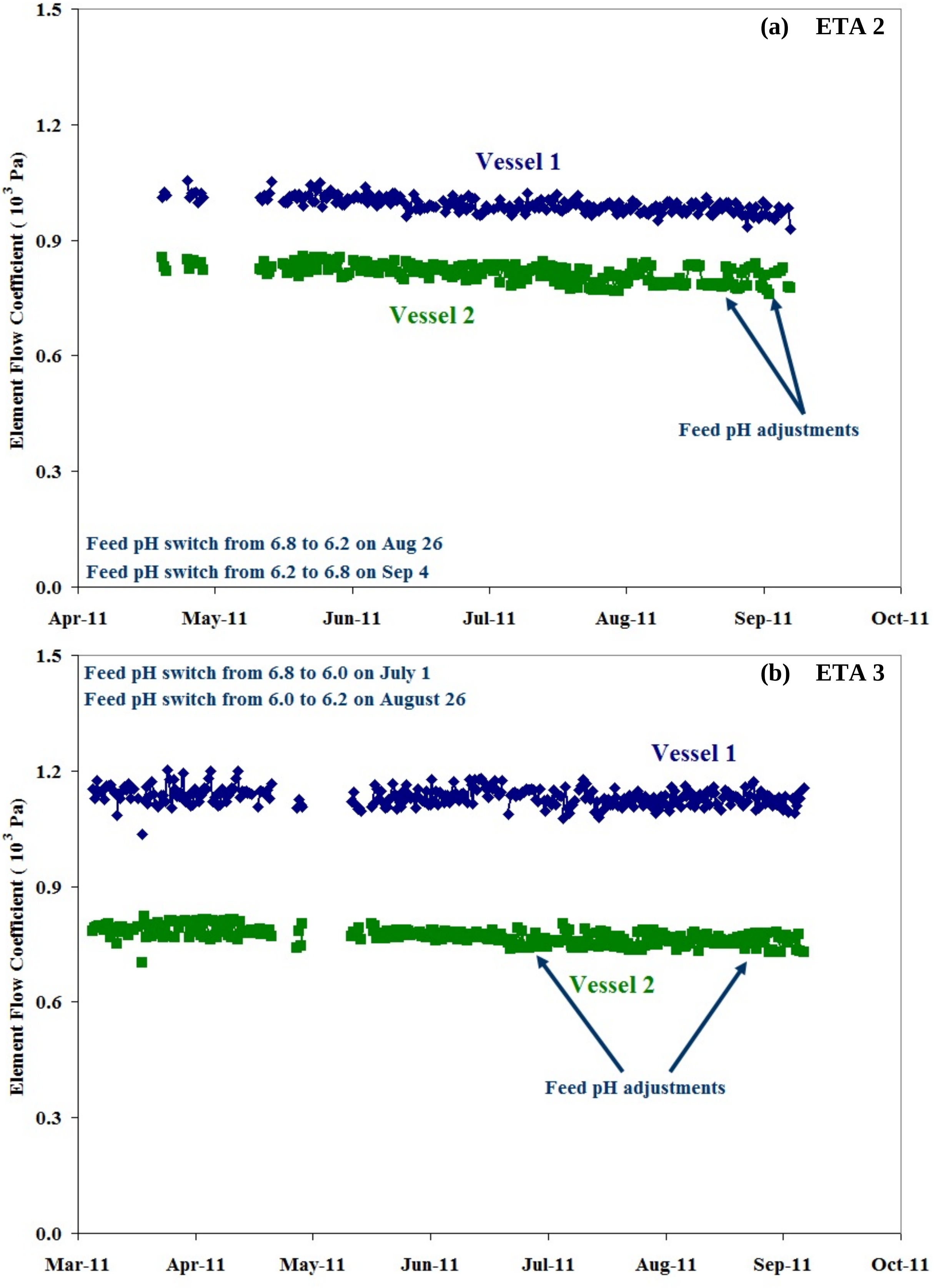


Figure 7.32 Element flow coefficient (C_e) profiles for (a) ETA 2 and (b) ETA 3 during Round 2.

The rejection rates for the important parameters, including major cations and anions, cannot be calculated and presented for Round 2, because sampling of product water from each membrane for water quality analysis was discontinued at the end of Round 1. Please, see Appendix C-2 for the details of ETA feed and reject water quality analyses during Round 2.

7.3.2 RO Performance Testing (full-array and high-recovery)

Hydranautics LFC3 was chosen for Round 2, MU testing based on the results of Round 1 element screening tests and the membranes available for the start of Round 2 testing. Two MU units (MU 1 and MU 2) were used to evaluate the performance of the chosen membrane in treating the YMC water following the two applied pretreatment methods of silica sand filtration and MF, or greensand filtration and CF. Twenty-one spiral wound 2.5-in by 40-in elements were used in 2-1 array formation in the two MU RO units. The 21 elements supplied an estimated total of 525 ft^2 of total membrane area. The selected average flux of 12 gfd resulted in producing 6300 gpd of permeate water. The recovery was chosen as 80% for all the MUs, initially. Hence, a feed flow of 7,875 gpd was needed to run the MUs. However, the calculated performance parameters, such as WTC, water flux, etc., presented in this report for all the MUs that tested Hydranautics LFC3 were based on the average measured membrane area. The average membrane area for the LFC3 elements was calculated by taking the average of all the retired elements that underwent post-mortem analyses.

MU 1 and MU 2 RO units were operated to evaluate the efficiency of the pretreatments for Alternative 21a and Alternative 22, respectively. The pretreatment for Alternative 21a consisted of gravity filtration with silica sand followed by microfiltration. And the pretreatment for Alternative 22 consisted of gravity filtration with greensand followed by cartridge filtration. Round 2 for full-array testing lasted almost 3790 hours (5.3 months) for MU 1. On the other hand, this number stayed around 2900 hours (4 months) for MU 2. The difference was mainly due to the late initiation of MU 2 operation. The need to install greensand, to achieve better removal of manganese, in the filters of Alternative 22 and their conditioning delayed the operations on this alternative. Moreover, frequent shut-downs and operational problems were experienced with the YMC system, in general. The loss of YMC water as a source in early

September prevented these two RO units reaching the 9 months of total runtime originally planned. The manufacturer suggested 2.0 mg/L of anti-scalant, AWC A-102 Plus, was used for both Alternative 21a and Alternative 22.

As in MODE water alternatives, the water transport coefficient (A), salt transport coefficient (B), B/A ratio, water flux, net driving pressure, percent salt passage, water recovery, product total dissolved solids concentration, product flow rate and osmotic pressure for the lead and tail elements of the unit and also for the groups of three elements in the remainder of the unit were calculated and monitored daily by the Test Manager and the operators and weekly by the TAT members. Other parameters measured, calculated and monitored in the same manner include feed and interstage temperature, feed and reject pH, feed free and total chlorine concentrations, feed SDI, feed and reject flow rates, feed and reject total dissolved solids concentrations, feed and reject pressures, differential pressures for stage 1 and 2, element flow coefficients for each vessel and percent salt mass balance deviation for each stage, interstage and the whole unit. However, only the feed temperature and pH of the units, water transport coefficient and salt transport coefficient for each vessel and for the whole unit and the element flow coefficient for each vessel are presented here. Please, refer to the appendix for the additional results.

7.3.2.1 MU 1 Testing: Alternative 21a as Pretreatment

The RO unit, MU 1, started running on March 10, 2011 for long-term Round 2 testing of Alternative 21a as a pretreatment option for YDP operation on YMC water. MU 1 started running with a feed pH of 6.8. It fluctuated during the first two weeks of April due to control issues with acid injection. However, it was stable after resolving the issue. On July 1, the feed pH was dropped to about 5.8-5.9 to achieve a reject pH of 6.3. On August 26, it was increased to about 6.0-6.1 to achieve a reject pH of 6.5. For this and the other MU units, the reject pH was the target to keep constant and the pH of the feed was adjusted accordingly and as necessary. The reasons and the outcomes of these pH adjustments are presented below in the paragraphs showing the observed and calculated operating parameters, such as WTC and STC. The blue arrows in Figure 7.33 highlight the times of the pH adjustments. The water temperature continuously increased in YMC water through Round 2 testing reaching to its peak value of 32 ^{o}C by late August. The testing was finalized before the temperature started to decrease (Figure 7.33).

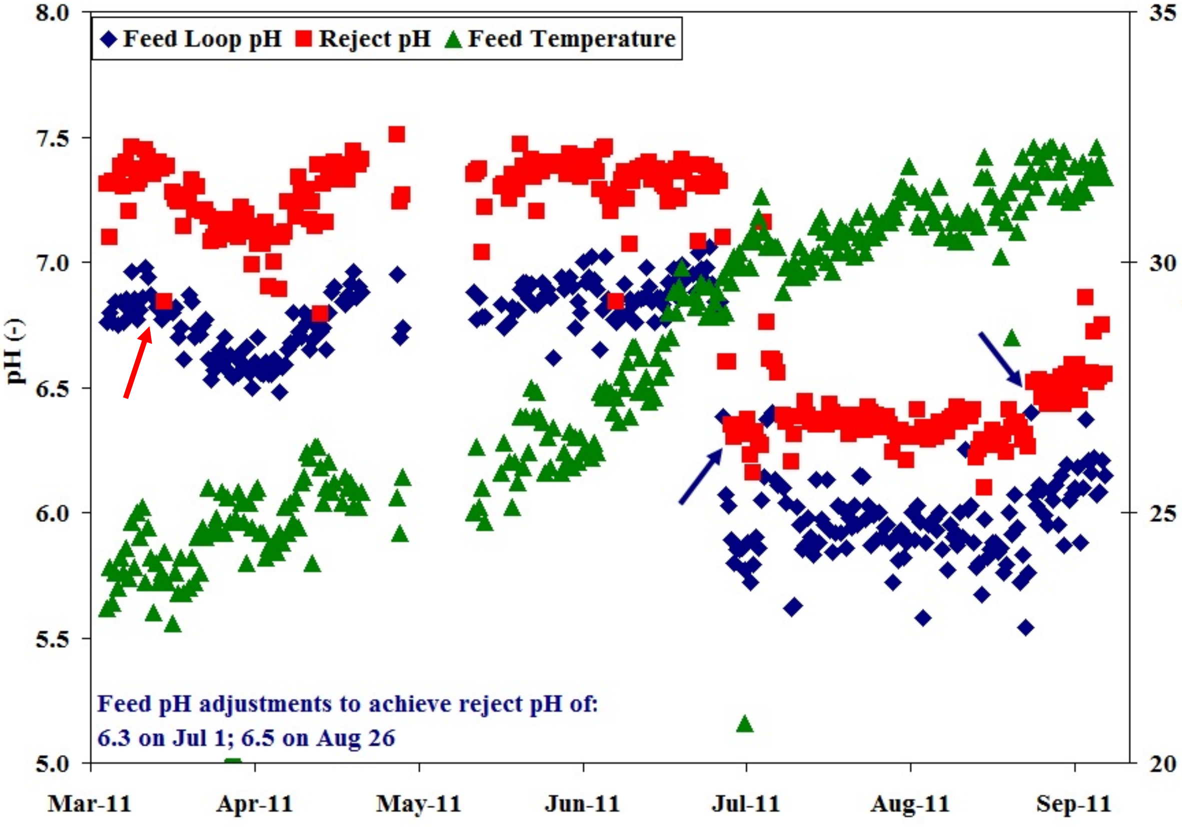


Figure 7.33. Feed and reject pH and temperature profiles for MU 1 during Round 2. The blue arrows indicate the timing of reject pH adjustments. The red arrow indicates the time, in early April, when the feed pH dropped unintentionally from 6.8 down to 6.5-6.6.

The early WTC values were very close to each other in all vessels and ranged between 8.5 and 8.7 × 10^{-12} m/s.Pa (Figure 7.34). This range, on average, was almost 20% higher than the WTC values during Round 1 testing of Hydranautics LFC3 on Alternative 21a, where the average initial WTC for ETA 3 was 7.2 × 10^{-12} m/s.Pa. As observed in the other MUs, except MU 4 running on Alternative 10 (lime-softened MODE water), the average WTC for each vessel in both stages increased by about 0.5 × 10^{-12} m/s.Pa in the first one and a half month while running at the feed pH of 6.8, and then stayed constant until the first pH adjustment on July 1. At the same time the STC for all vessels, especially in the second stage elements, was increasing rapidly (Figure 7.35). This motivated the pH adjustment on July 1. Decreasing the pH was expected to lower the STC values.

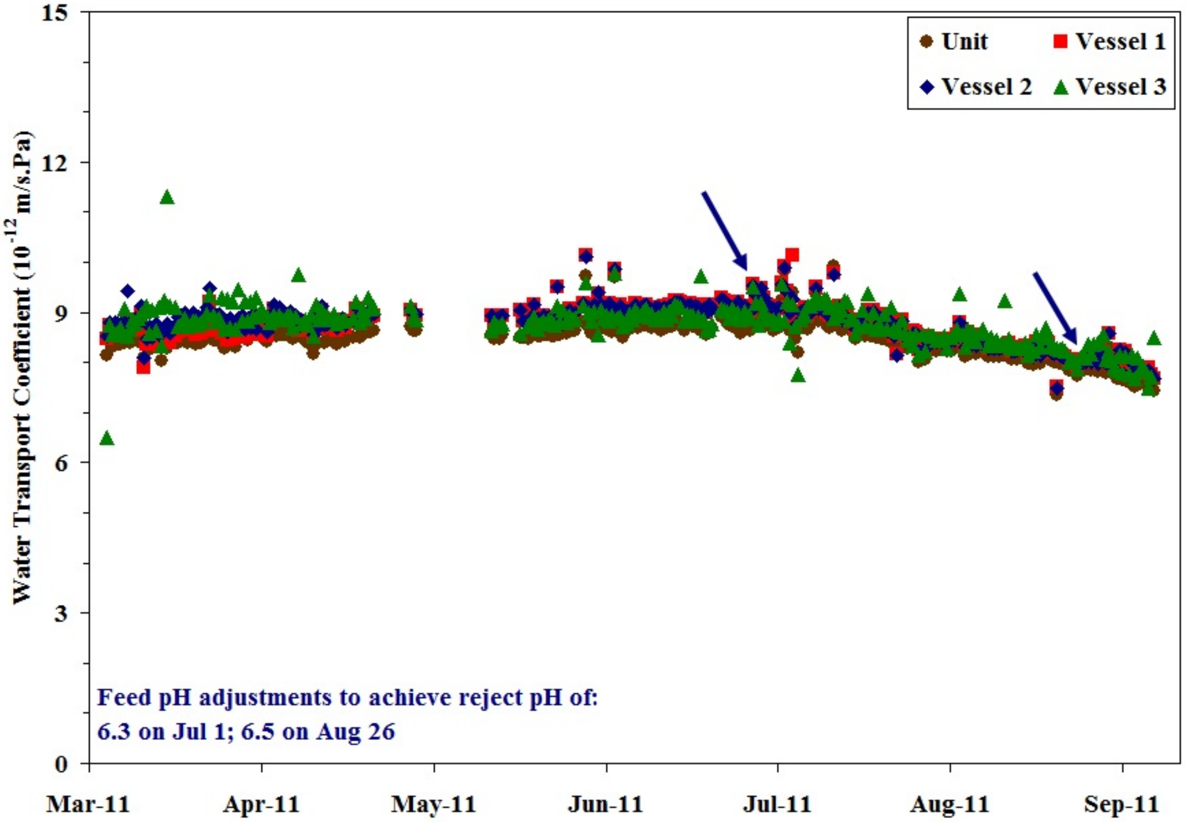


Figure 7.34. Water transport coefficient (WTC) profile for MU 1 during Round 2. The blue arrows indicate the timing of reject pH adjustments.

Prior to discussing this pH adjustment and its effects, two other important events and their impacts must be considered. In early April the feed pH dropped from 6.8 down to 6.5-6.6 and the reject pH followed. Mainly, the WTC values stayed untouched by this pH fluctuation. On the other hand, STC values were clearly affected (Figure 7.35). While there was no significant effect on Vessel 3 STC values, first stage elements had an increase in salt passage and STC values during this decrease in pH. The same effect was observed in all the ETA 3 membranes. When the pH went down, the STC jumped, followed by a slow but continuous decline in the lead elements. The other interesting part of this observation was that the tail elements were largely unaffected. It appears that more than one process was playing a role in this incident. If it was only a pH effect on membrane structure, all vessels should exhibit the same behavior with this event as they did when the reject pH was dropped to 6.5-6.6 in August. Therefore, it is expected a component in the water was also playing an important role.

A second important event was the long-term shut-down between April 26 and May 21 due to lack of available YMC flows. The main reason was that the pumps that deliver YMC water to YDP went down. There were a couple of attempts to restart the YMC alternatives during this period but they only supplied five more days of data. The membranes were flushed with RO permeate water at a pH of about 5.5 on a daily basis while the units were down. No noticeable effect was observed due to the shutdown event and maintenance flushing. WTC and STC values for all vessels resumed from those prior to the shutdown event.

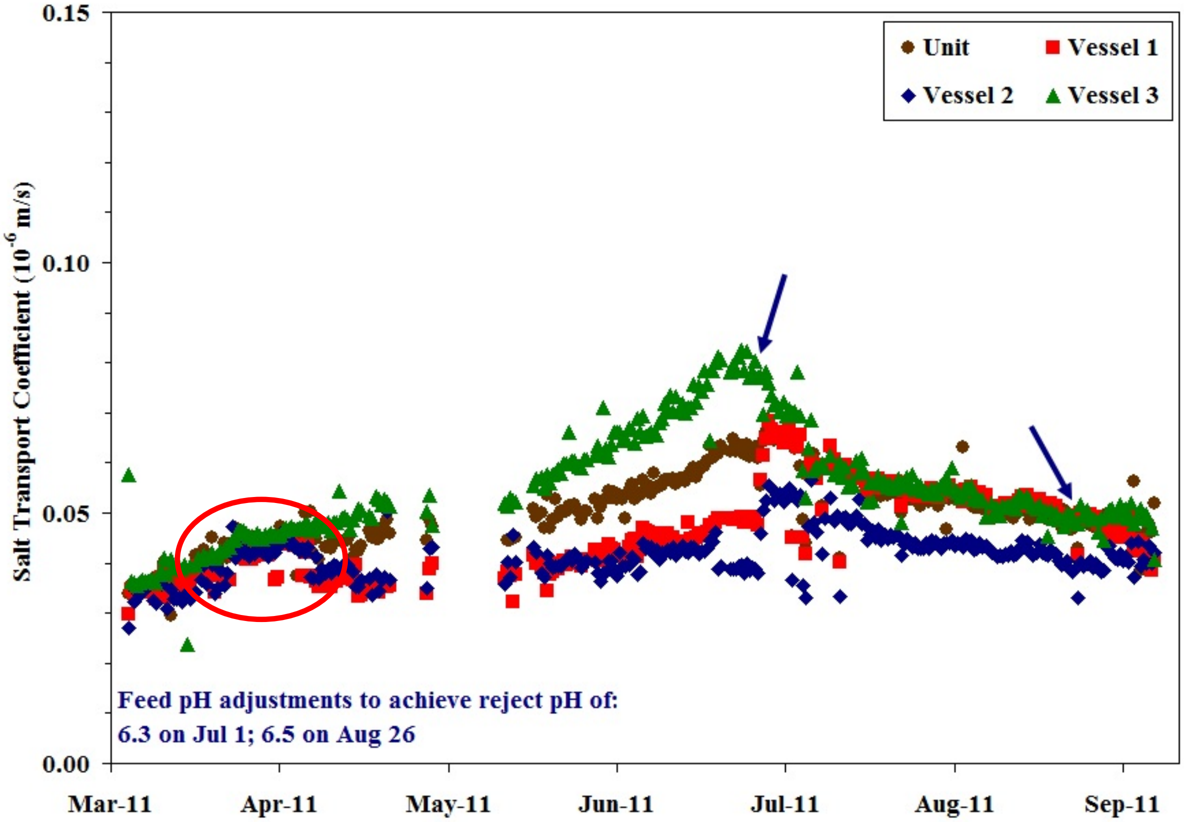


Figure 7.35. Salt transport coefficient (STC) profile for MU 1 during Round 2. The blue arrows indicate the timing of reject pH adjustments. Red circle indicates the time, in early April, when the feed pH dropped unintentionally from 6.8 down to 6.5-6.6.

As mentioned earlier, on July 1 the feed pH was decreased to achieve a reject pH of 6.3 to counteract rapidly increasing STC values, especially in Vessel 3 elements. Immediately prior to the pH adjustment, the tail element (Element 7 in Vessel 3) was taken out for post-mortem analyses and replaced with a new LFC3 element. The purpose was to find out if there was any scaling on the membrane and, if there was, to find out the type of scaling. The retired element was taken to the University of Arizona. Detailed results of these analyses are presented in Section 8.0, but it is appropriate to mention here that there was no observable damage to the membrane, no material build-up on its surface, and the membrane was not faulty. As observed during the pH fluctuation in April, a jump-up in the STC values of the first stage elements was witnessed, followed by a slow but steady decline. On the other hand, the jump was not observed for the second stage elements and they showed a slow and steady decline right after the pH drop. The results obtained for the first stage elements matched the results of ETA 3 elements (all different types than the LFC3) running in parallel with MU 1 on Alternative 21a. This fact supports the theory of the water source being, at least partially, the reason for this effect.

Another observed, but unexplained change in MU 1, is the divergence of the STC values between vessels 1 and 2 in mid-late June. Prior to this time the STC values for the two vessels tracked one another as is expected for two identical vessels seeing the same feed water and operating in parallel. However, in mid-late June, the vessel 2 STC dropped suddenly and then subsequently began to track the vessel 1 STC again. Although this sort of change is indicative of an instrumentation maladjustment, no such problem was identified. The element flow coefficient for the first stage vessels, Vessel 1 and Vessel 2, declined very slowly (by about 3%) until the July 1 pH adjustment, while the C_e for Vessel 3 stayed constant until then (Figure 7.36). This might suggest fouling in the first stage. The new, lower operating pHs during the following two months did not appreciably change the decline with the exception of a sharp rise in C_e just prior to the MU shutdown.

The July 1 decrease in the pH reversed the rising STC value trend, showing that the reason for the increase was not damaged membranes, but either the water composition or the pH effect on membrane structure. WTC for all the membranes decreased with the lower pH. The falling WTC was not the desired outcome despite achieving the desired outcome of falling STC. Hence, the pH was adjusted slightly up on August 26 in an effort to find a pH for sustainable RO operation in terms of stable WTC and STC. Feed pH was increased by 0.2 units to achieve a reject pH of 6.5. The pH increase appeared to stabilize both the WTC and the STC values. Moreover, stable B/A values were achieved with the new pH (data not shown). Although, the runtime after the last pH increase was only about 10 days and this makes it difficult to see the long-term outcome of the pH adjustment.

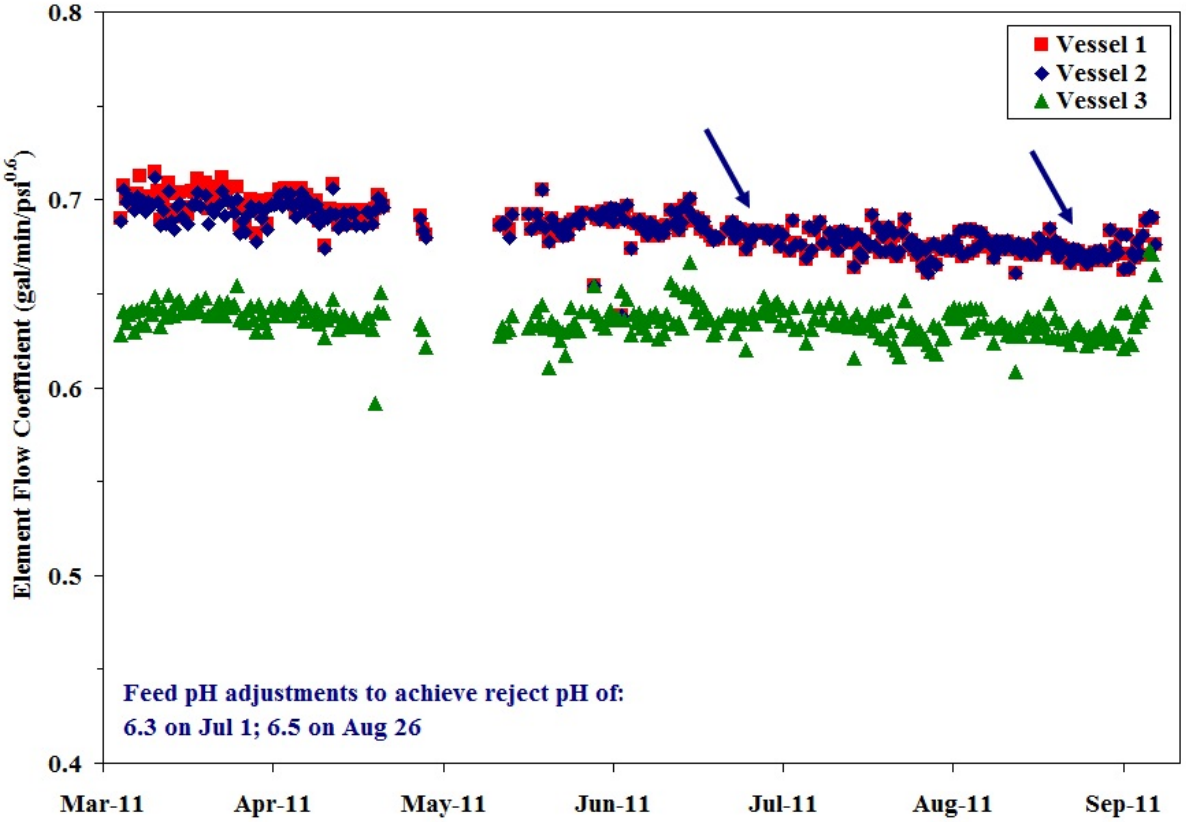


Figure 7.36. Element flow coefficient (C_e) profile for MU 1 during Round 2. The blue arrows indicate the timing of reject pH adjustments.

In summary, WTC values were relatively higher during the operation of MU 1 on Alternative 21a compared to the MODE alternatives. STC values were almost the same as with the other alternatives, except of course the ones scrutinized in Alternative 10 (lime-softened MODE water). A significant and rapid effect of lower operating pH on MU 1 salt passage was monitored. A reject pH of 7.3 appears too high with increasing salt passage of all MU 1 elements. On the other hand, reject pH 6.3 was too low for sustaining stable WTC values. The right pH to operate an RO unit on Alternative 21a, gravity-filtered microfiltered YMC water, is in the range of 6.0 and 6.8 on the feed. No obvious effect of the pH was observed on the element flow coefficient. No clear observation of fouling was monitored on the unit and during the post-mortem analyses of the retired membranes, suggesting that the pretreatment for this alternative successfully protected the downstream RO units. It was also learned that the increase in MU 1 salt passage at high pH was not irreversible, because lower feed pH rapidly reversed the effect.

The results of the water quality analyses for MU 1 feed and reject are presented in Table 7.9, below. As in MU 3 results, both bicarbonate and total alkalinity levels have very high standard deviations. Again, the reason for that is the large drop in the feed pH on July 1. As expected due to first acidity constant of carbonic acid being about 6.3, the values measured prior to this drop for these two parameters were significantly higher than the ones measured after the pH adjustment. This caused a big variation between the samples as illustrated in Figure 7.37, below. Presented is the bicarbonate (HCO3-) concentration (mg/L as $CaCO_3$) for MU 1 feed throughout the Round 2 Phase 1 testing. The average concentration is presented in Table 7.9 as 160.35 mg/L as $CaCO_3$, which might be a misleading value if the standard deviation is not considered properly. The bicarbonate concentration is assumed to be exactly the same as total alkalinity at the pH levels for MU 1 feed and reject.

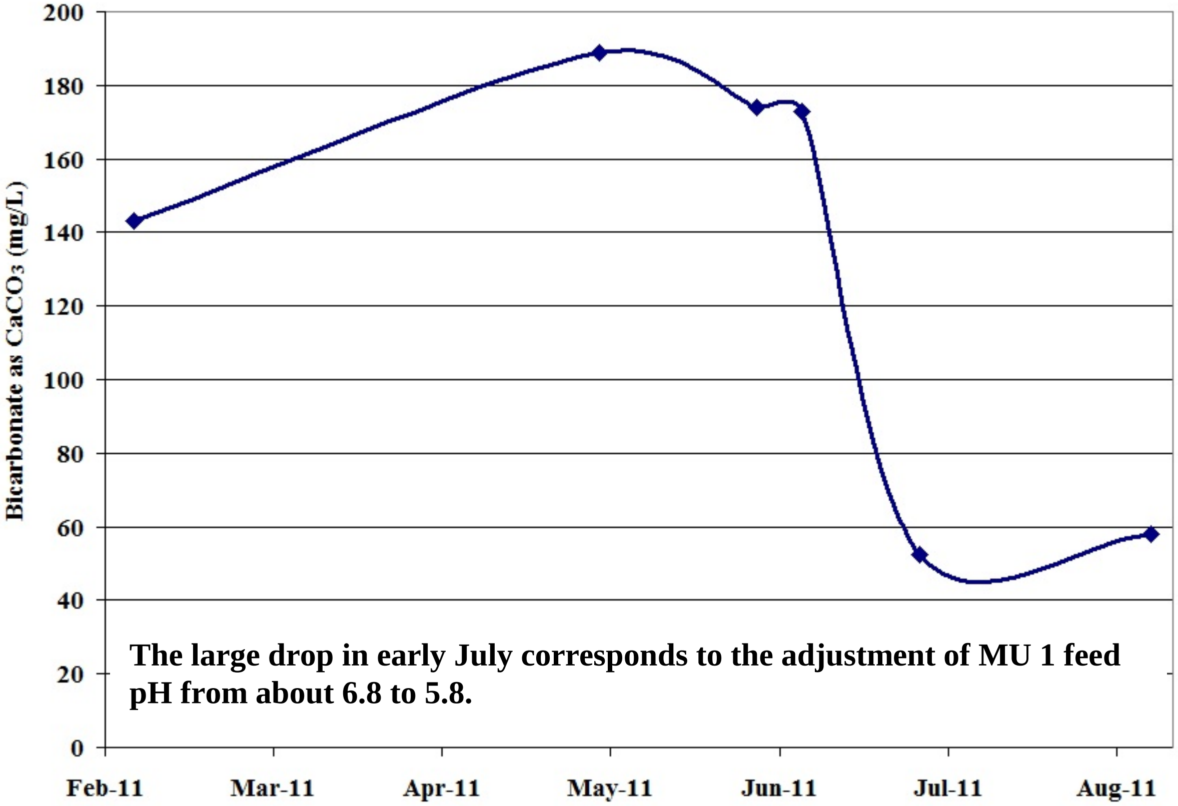


Figure 7.37 Bicarbonate (as $CaCO_3$) concentration profile for MU 1 feed during Round 2Phase1.

Table 7.9. Water composition for feed and reject of MU 1 RO unit.

		MU 1 Feed				**MU 1 Reject**			
Parameter	**Units**	**Average**	**Minimum**	**Maximum**	**St. Dev.**	**Average**	**Minimum**	**Maximum**	**St. Dev.**
Barium	*mg/L*	0.032	0.029	0.035	0.002	0.164	0.149	0.179	0.011
Bicarbonate	*mg/L*	160.35	64.20	230.00	74.18	882.83	248.00	1760.00	568.62
Calcium	*mg/L*	129.17	112.00	158.00	16.15	644.50	586.00	760.00	68.02
Chloride	*mg/L*	341.33	312.00	394.00	29.85	1645.00	1490.00	1890.00	141.67
Conductivity	*µS/cm*	2508.33	2390.00	2830.00	161.79	10305.00	9870.00	11400.00	558.63
Iron	*mg/L*	0.043	0.012	0.064	0.023	0.219	0.108	0.294	0.087
Magnesium	*mg/L*	42.50	39.20	50.50	4.31	213.33	193.00	249.00	20.61
Manganese	*mg/L*	0.0014	0.0006	0.0023	0.0007	0.0047	0.0026	0.0071	0.0020
Nitrate as N	*mg/L*	ND	ND	ND	ND	ND	ND	ND	ND
pH	-	7.15	6.37	7.74	0.50	7.62	6.96	8.10	0.46
Potassium	*mg/L*	5.08	4.42	5.79	0.47	24.72	21.40	27.40	2.08
Silicon Dioxide	*mg/L*	25.17	23.40	27.00	1.45	120.50	113.00	125.00	5.21
Sodium	*mg/L*	350.83	337.00	395.00	22.42	1693.33	1620.00	1840.00	84.77
Strontium	*mg/L*	1.65	1.39	2.08	0.23	8.12	7.01	9.76	0.91
Sulfate	*mg/L*	649.67	573.00	823.00	101.59	3230.00	2850.00	4030.00	467.03
Sum of Anions	*meq*	26.00	24.70	29.60	1.81	128.83	120.00	142.00	8.50
Sum of Cations	*meq*	25.33	23.60	29.40	2.12	124.17	117.00	139.00	8.42
Tot. Alk. as $CaCO_3$	*mg/L*	131.62	52.60	189.00	60.96	579.80	204.00	904.00	340.92
Tot. Hard. as $CaCO_3$	*mg/L*	497.17	441.00	602.00	57.73	2486.67	2280.00	2920.00	252.32
Total Organic Carbon	*mg/L*	1.09	1.05	1.13	0.03	3.59	3.44	3.81	0.16
Total Salt	*mg/L*	1686.67	1600.00	1900.00	108.57	8360.00	7840.00	9090.00	518.77

Table 7.10. Concentration and solubility data for MU 1 reject ion pairs that may contribute to membrane scaling. Ion products were based on the MU 1 reject average concentrations shown in Table 7.9, uncorrected for the ionic strength.

Precipitate	Ion Concentration	log (ion product)	log K_{S0}[c]	Degree of Saturation [b]
$BaSO_{4(s)}$	$[Ba^{+2}] = 1.19 \times 10^{-6}$ M $[SO_4^{-2}] = 3.36 \times 10^{-2}$ M	-7.40	-10.0	400.73
$CaSO_{4(s)}$	$[Ca^{+2}] = 1.61 \times 10^{-2}$ M	-3.27	-4.85	38.28
$CaCO_{3(s)}$	$[CO_3^{-2}] = 1.26 \times 10^{-5}$ M[a]	-6.69	-8.48	88.59
$CaCO_{3(s)}$	$[CO_3^{-2}] = 4.07 \times 10^{-7}$ M[d]	-8.18	-8.48	1.98

[a] based on 1190 mg/L carbonate alkalinity as HCO_3^- and reject pH = 7.30 (feed pH = 6.8).
[b] calculated as Q_{SO}/K_{SO}. The value represents the approximate degree of oversaturation in the RO brine produced from YMC water.
[c] Benjamin, 2002.
[d] based on 265.5 mg/L carbonate alkalinity as HCO_3^- and reject pH = 6.30 (feed pH = 5.8).

As with the MODE water alternatives, the salts of barium and calcium are potential precipitates that might pose a problem while operating an RO unit at 80% or higher recoveries on YMC water. The solubilities of calcium sulfate, calcium carbonate and barium sulfate, for example, are exceeded in brines derived from RO treatment of YMC water as shown in Table 7.10. The degree of saturation levels for barium sulfate, calcium sulfate and calcium carbonate in the feed water for MU 1 (prior to pH adjustment on July 1) are calculated in the same manner as 15.99, 1.54 and 0.99, respectively. Therefore, the sulfate salts (barium and calcium) are already higher than their saturation levels, whereas calcium carbonate is at its saturation level at the given operating pH (feed pH of 6.8) and alkalinity. The calculations for the degree of saturation are carried out for both the initial conditions of MU 1 operation, i.e. feed pH of 6.8 and reject pH of 7.3, and the conditions after pH adjustment on July 1, i.e. feed pH of 5.8 and reject pH of 6.3. For the initial conditions, the bicarbonate concentration is assumed as 210 and 1,190 mg/L for feed and reject, respectively, which are the average values of bicarbonate levels determined in the lab analyses prior to any pH adjustments. Feed pH of 6.8 (reject pH of 7.3) is the operating condition that is most likely to raise any scaling problem in the RO unit (Table 7.10). However, no evidence of irreversible scaling, e.g. barium sulfate, was observed either during the testing or in the post-mortem analyses of the retired elements. The supersaturation values show the use of anti-scalant is critical for a sustainable RO operation while desalting Alternative 21a pretreated YMC water.

Another component that may pose a problem in the RO operation while treating YMC water is silicon dioxide. As was mentioned earlier, the solubility of silica is 120 mg/L at 25 ^{o}C and neutral pH. The level of silica is very close to its solubility limit in the reject stream of MU 1. However, the slow kinetics of silica precipitation is an advantage in controlling the silica scaling, since the silica concentration would reach its solubility limit in the concentrate stream only near (or after) the tail-end elements and hence have only a short residence time in which to precipitate. Nevertheless, silica scaling might occur prior to the reject pH adjustments, because temperature and the reject pH were suitable for this process and the precipitation kinetics are difficult to predict. Since decreasing pH decreases the solubility of silica, it was more likely that silica problems would occur after the downward adjustment of reject pH in July. Hence, another problem might be created while trying to balance the WTC and STC values by decreasing the pH. The fact that silica was detected (albeit in only small amounts) during the post-mortem analyses of the MU 1 retired elements might be an indication of that problem. Microfiltration should be effective in controlling the feed water's particulate silica. Thus, all the silicon dioxide detected in the MU 1 feed was likely dissolved or smaller than 0.1-μm size colloids.

Iron and manganese levels were watched carefully in the YMC water alternatives as potentially high levels of these ions were expected in this water. Figure 7.38 shows the feed and reject concentrations of total iron and total manganese for MU 1. These ions, especially iron levels with an average value of 0.043 mg/L in the feed water (0.219 mg/L in the reject water) of MU 1, are high enough to cause performance problems in an RO unit. All the iron and manganese detected in the feed of MU 1 is expected to be dissolved (or colloidal below 0.1 μm size) as the upstream microfiltration unit has a pore size of 0.1 μm. However, there might be in colloidal forms having smaller sizes than the MF pore size or there might be organic or inorganic complexes in the dissolved fraction. Nonetheless, both the iron and manganese concentrations are lower than those detected in the MUs running on MODE water alternatives. This was not expected prior to the project.

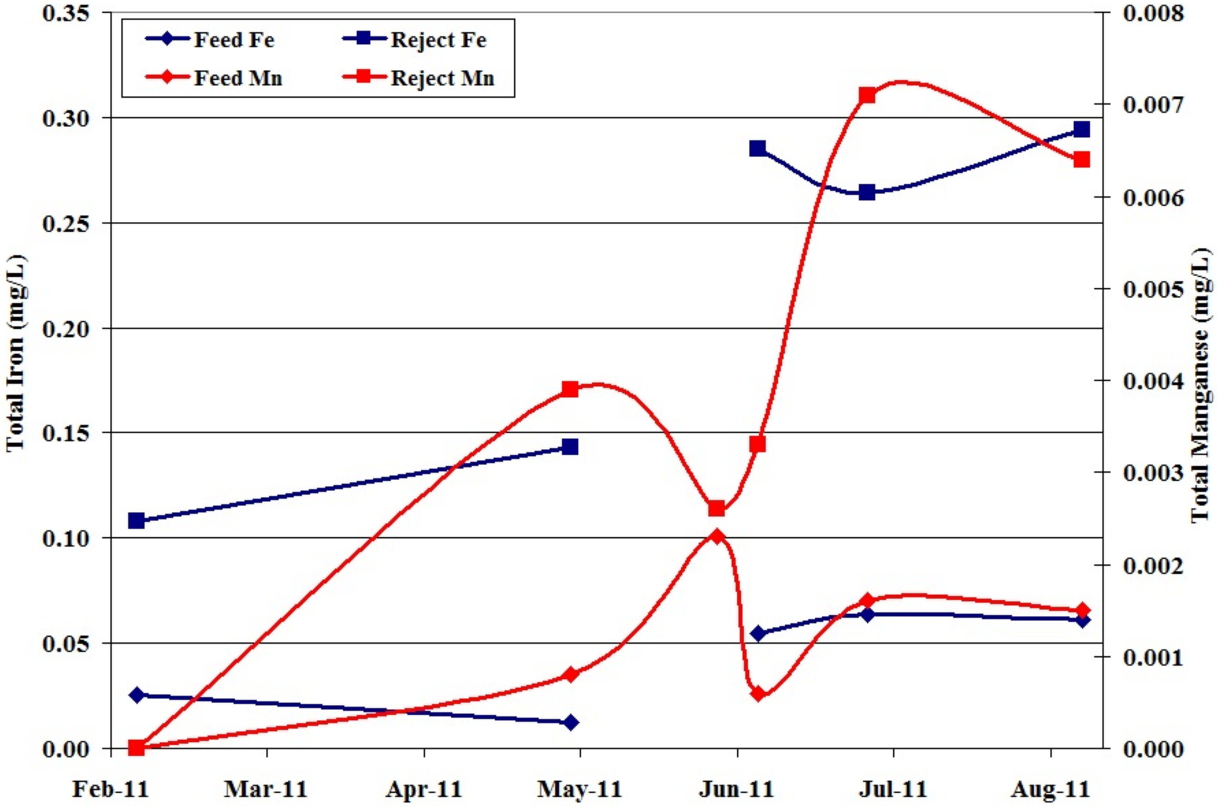


Figure 7.38. Total iron and total manganese concentrations in MU 1 feed and reject during Round 2 Phase 1.

Although the resolution of the measurements and precision of the recovery calculations do not allow high accuracy calculation of the mass of iron and manganese retained in the MU unit, the reject concentrations measured are approximately five times the feed concentrations which is consistent with low retention by the RO elements operating at an overall recovery of 80%. Iron and manganese were detected on the surface of the membranes retired from MU 1, although like silica in small amounts. The amount detected was not enough to affect the MU 1 operation adversely. However because the run length was much shorter than a normal membrane's expected useful life and the possibility of iron catalytically leading to membrane degradation, it is still important to consider the form of pretreatment that decreases the concentration of these two ions as much as possible.

7.3.2.2 MU 2 Testing: Alternative 22 as Pretreatment

The RO unit, MU 2, started running on April 21, 2011 for Round 2, long-term testing of Alternative 22 as a pretreatment option for possible YDP operation on YMC water. The reason for this late start was the greensand installation and conditioning on three of the PS2 gravity filters. MU 2 started running with a feed pH of 6.8. On August 26, it was decreased to about 6.2 to achieve a reject pH of 6.5. The reject pH was the criterion to keep constant in the MU operations. The blue arrows in Figure 7.39 highlight the times of the pH adjustments. The water temperature continuously increased in YMC water throughout Round 2 testing from 25 ^{o}C reaching its peak value of 32-33 ^{o}C by late August. The testing was finalized before the temperature started to decrease.

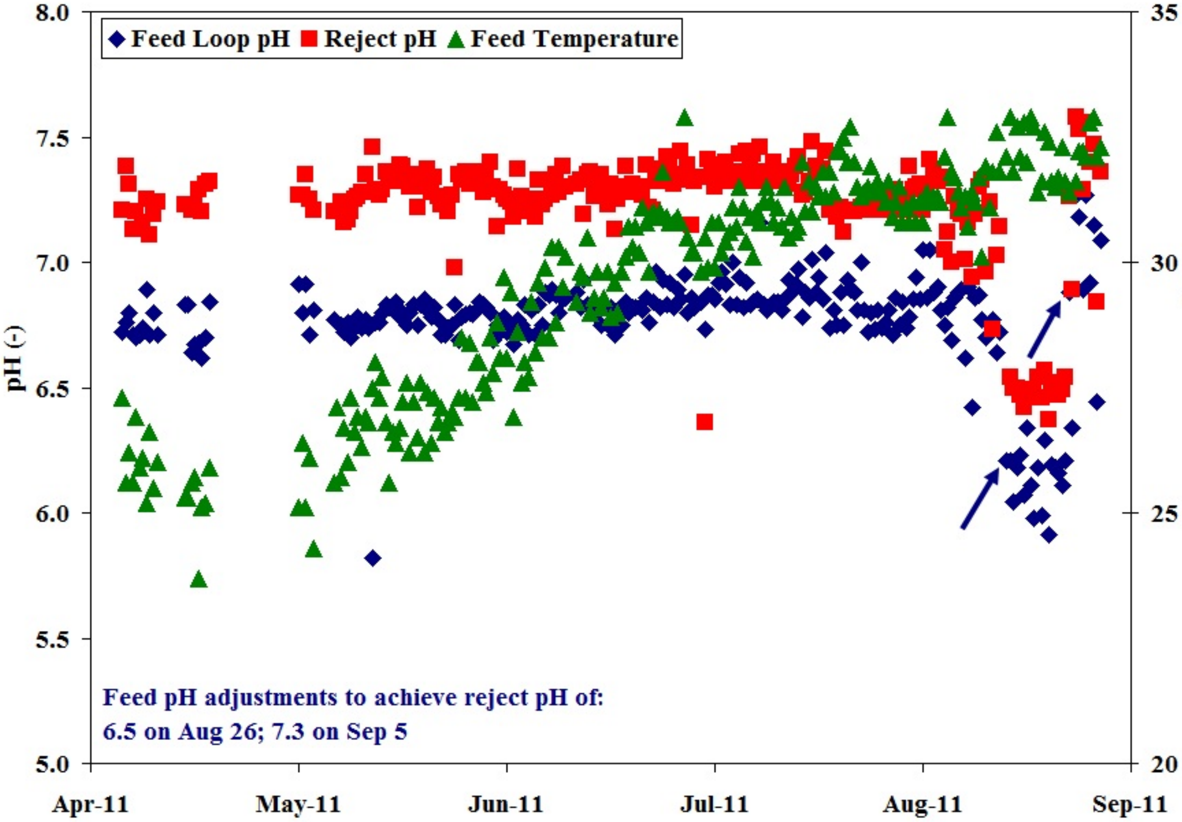


Figure 7.39. Feed and reject pH and temperature profiles for MU 2 during Round 2. The blue arrows denote the timing of pH adjustments.

The initial WTC values in MU 2 Stage 1, ~8.5-8.6 × 10^{-12} m/s.Pa (Figure 7.40) were very close to the values observed in MU 1. However, the main difference between MU 1 and MU 2 was the second stage WTC values. While MU 1 Vessel 3 elements performed very similar to its first stage elements, MU 2 Vessel 3 elements had about 0.5 × 10^{-12} m/s.Pa lower WTC values than its first stage elements. Furthermore, this difference between the two stages' WTC values stayed almost constant throughout the Round 2 testing. The initial average WTC value was 7.4 × 10^{-12} m/s.Pa for Vessel 3 (tail element having the lowest). These WTC values, on average, were about 10% (for second stage) and 25% (for first stage) higher than the average initial values observed during Round 1 testing of Hydranautics LFC3 on Alternative 22 (~6.7 × 10^{-12} m/s.Pa). As observed in the other MUs, except MU 4 running on Alternative 10 (lime-softened MODE water), the average WTC for each vessel in both stages increased noticeably. This increase was about 0.7 × 10^{-12} m/s.Pa during the first four months while running at the feed pH of 6.8. However, at the same time the STC for all vessels, especially in the second stage elements, was increasing rapidly (Figure 7.41). The WTC and STC trends in MU 2 were similar to those in MU 1 when operating at a feed pH of 6.8.

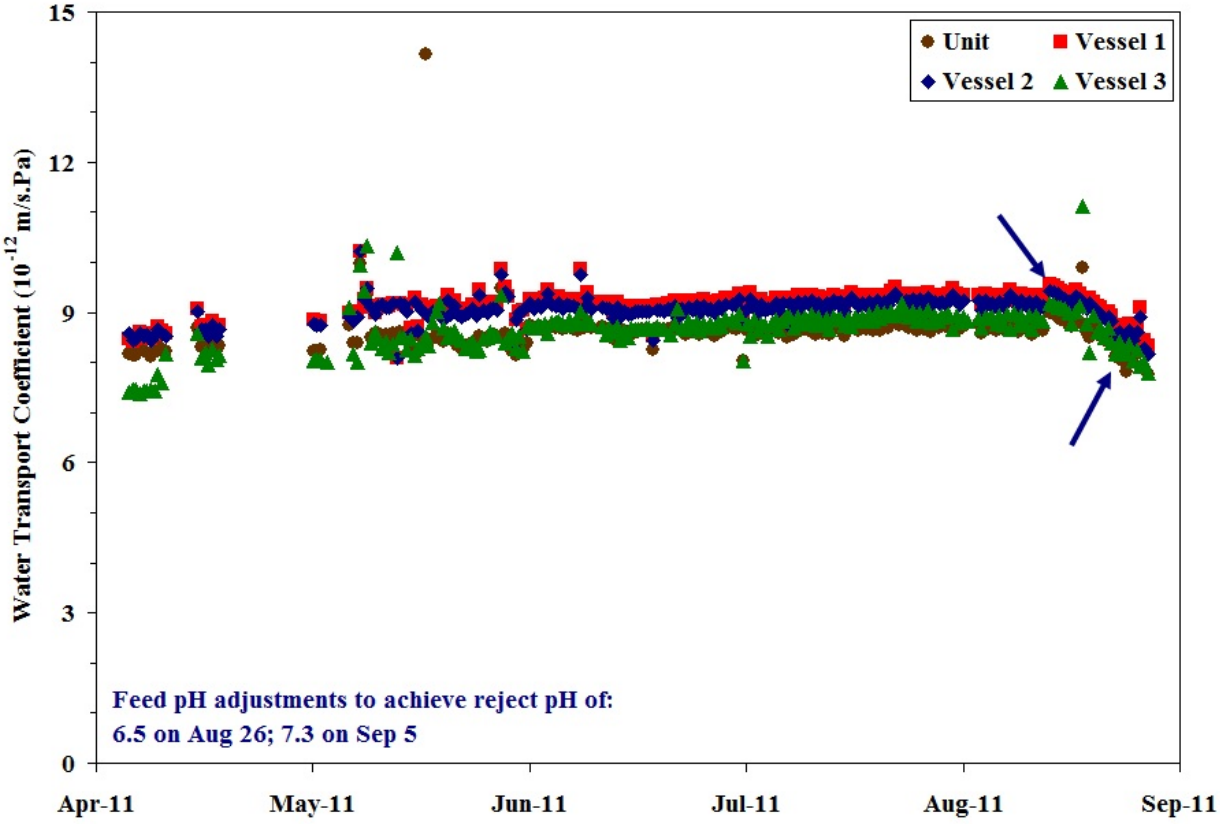


Figure 7.40. Water transport coefficient (WTC) profile for MU 2 during Round 2. The blue arrows denote the timing of pH adjustments.

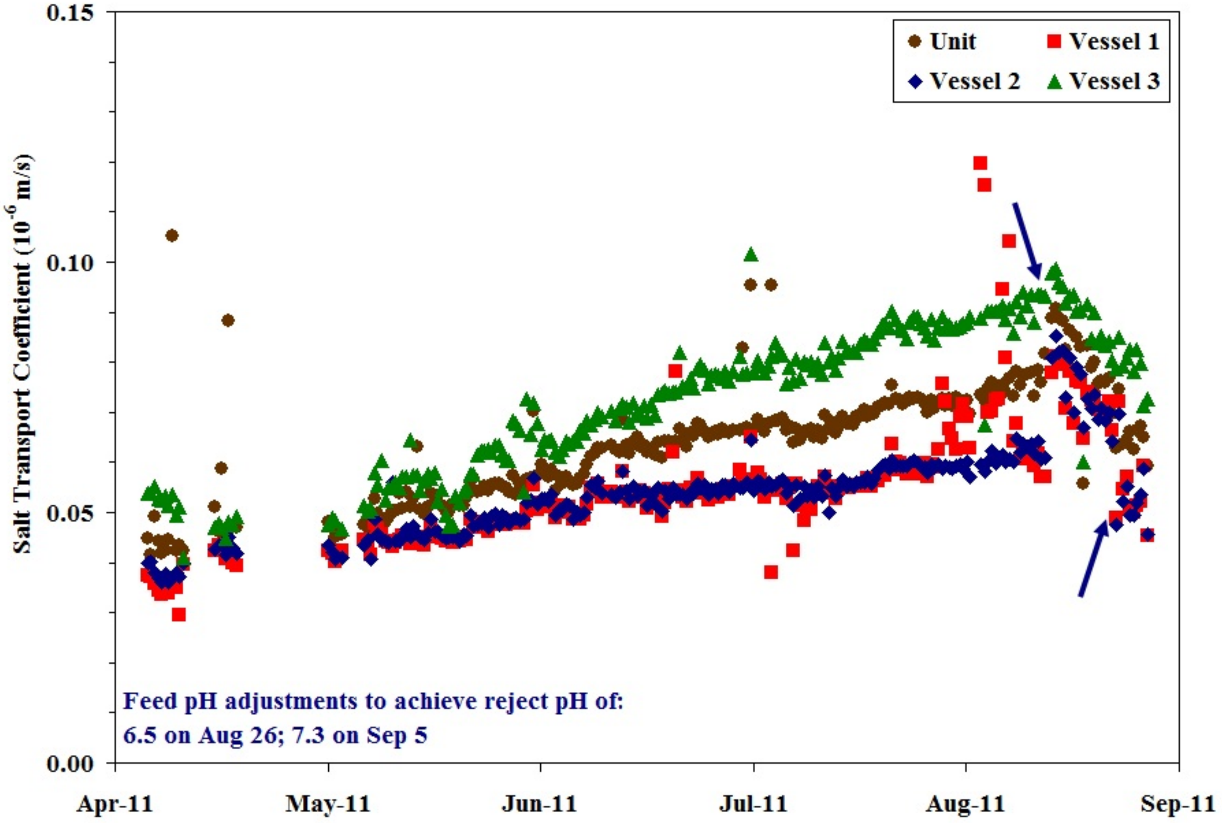


Figure 7.41. Salt transport coefficient (STC) profile for MU 2 during Round 2. The blue arrows denote the timing of pH adjustments.

Operation at higher pHs (closer to the raw water pH) decreases the cost of acid, which is a primary operational cost component in most desalination plants. Thus, for MU 2 it was decided to continue operation at reject pH of 7.3 for an extended period, even though operation at a lower pH was expected (and later verified) to reverse the rising STC trend seen at reject pH 7.3. Since STC values at 0.1 x 10^{-6} m/s (and even above) still allow a very high blending ratio, the rising STC of MU 2 had not reached a point of practical concern (Figure 7.41). There was some expectation that the STC might stabilize after extended operation at reject pH 7.3. However, by late August there was no indication that the STC rise rate was diminishing, so the TAT decided to decrease the feed pH to achieve a reject pH of 6.5 to verify that the expected response to a pH drop would indeed occur. The main purpose was to gather information about how the unit would run at different pH. As it was observed in the other MUs and ETAs, the pH decrease caused a sudden increase in the STC values of the first stage elements followed by a steep decline.

Furthermore, this sudden step-increase effect was not observed for the second stage elements yet they again showed the steep decline right after the pH drop. The results obtained for the first stage elements matched the results of ETA 2 elements running in parallel with MU 2 on Alternative 22, regardless of the membrane type.

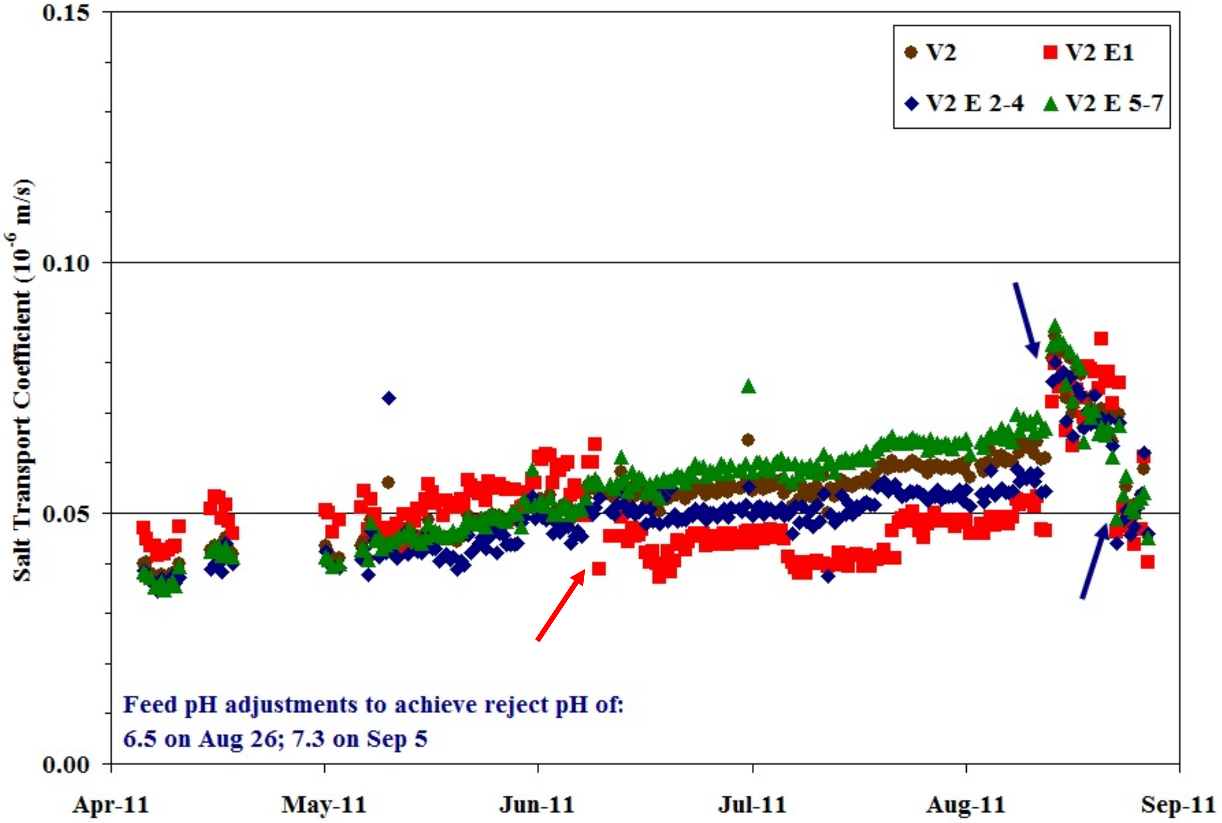


Figure 7.42. Salt transport coefficient (STC) profile for MU 2 Vessel 2 during Round 2. The blue arrows denote the timing of pH adjustments. The red arrow denotes the timing of 27-hour shutdown event on June 24.

One interesting observation during the MU 2 testing occurred after a shutdown event on June 24. Both of the lead elements of the first stage (Vessel 1 and Vessel 2) had a sudden drop in their STC values when the unit came back online following the 27-hour shutdown event (Figure 7.42). As it happened in both of the lead elements, the possibility of instrument error was essentially discarded. And after this sudden-drop, the increase in the STC values for these two elements stopped and they stayed practically constant until the pH adjustment on August 26. A guess for the reason behind this anomaly was that there was a material build-up on the lead elements during the early stages of the run and the RO permeate flush during this shutdown event cleared off the material that caused the build-up. This begs the question as to why the following elements in stage 1 (and stage 2) were not affected by this shutdown event (or if the material build-up/flushing is true, why the material was not either deposited further down stream or flushed from downstream elements).

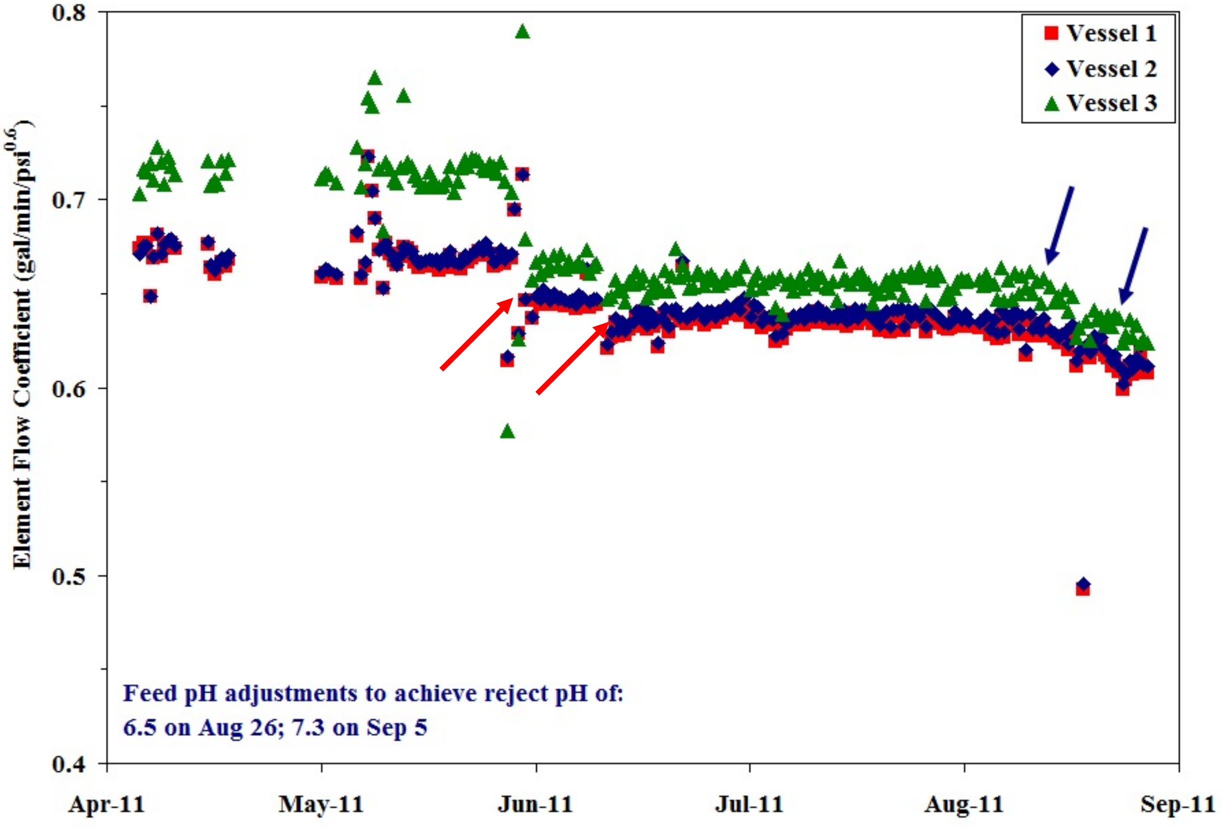


Figure 7.43. Element flow coefficient (C_e) profile for MU 2 during Round 2. The blue arrows denote the timing of pH adjustments. The red arrows denote the timing of step changes on June 14 and June 24.

Another interesting observation during this testing were two step-changes in element flow coefficients observed for all vessels in MU 2 (Figure 7.43). The element flow coefficients of all vessels stayed steady up to the pH adjustment on August 26 with the exception of these step changes in mid- and late-June. The first and larger step occurred on June 14 and was followed by the second one on June 24. The latter may have been due to the shutdown event on that day, however there was no shutdown event on June 14 that might explain the first C_e change.

The water flux and net driving pressures record shows some fluctuations suggesting that there might be adjustments performed on the unit (but not recorded) by the operators to keep the desired operating values. Hence, this step change in C_e values should not be considered as fouling.

The decrease in the pH on August 26 helped to decrease the rising STC values. Yet, the WTC values as well as the C_e for all the membranes also started to decrease with the lower pH. An even greater impact of the feed pH decrease to 5.9-6.0 was a several fold increase in the fouling rate of the cartridge filters upstream of MU 2 (Table 7.4). The TAT decided to increase the feed pH back to 6.8 on September 5to determine if the pH shift was indeed the cause of the increased fouling rates of the cartridge filters on Alternative 22. The renewal rate of the cartridge filters with the feed pH of 6.2 (6.5 on the reject of MU 2) was not sustainable. Unfortunately, YMC water was lost as a water source on September 9 until September 27. Since it was not known when the YMC would be back online, it was decided to stop the MU Round 2 Phase 1 testing for the units on the YMC water alternatives. The MUs were moved to MODE alternatives for Round 2 Phase 2 testing (see earlier description of configurations and results). Hence, further investigation of pH effect on RO operation with YMC water could be achieved. Nonetheless, during the last four days of the MU 2 testing all the STC and C_e values and first stage WTC values appeared to be stabilizing after the pH was increased back to 6.8. The only parameter that did not change was the WTC values of the second stage elements.

In summary, practically the same initial WTC values were observed for the first stage elements of MU 2 on Alternative 22 and MU 1 on Alternative 21a and they were both higher than the ones in the MODE alternatives. Nevertheless, the elements in the second stage of MU 2 had lower initial WTC values. Furthermore, higher STC values accompanied the lower WTC values in the second stage of MU 2. One prominent observation for MU 2 operation was the rate of increase in STC values. While the rates of increase (in % per 1000 hours) in the first stage elements were significantly lower in MU 1, the rates of increase in the second stage elements were significantly lower in MU 2 (Table 7.11). That might indicate more scaling on the MU 1, whereas fouling had more impact on MU 2. Considering the pretreatment differences in the two alternatives, with MU 1 having microfiltration upstream of the RO units, this observation is consistent with expectation.

Table 7.11. Percent changes in STC values per 1000 hours for MU 1 and MU 2 RO units. The percent changes were calculated prior to any pH adjustments. See Appendices G-1 and G-2 for the details of the calculations.

RO Unit	Vessel 1				Vessel 2				Vessel 3			
	Avg	**E1**	**E2-4**	**E5-7**	**Avg**	**E1**	**E2-4**	**E5-7**	**Avg**	**E1**	**E2-4**	**V3 E7**
MU 1	-19.06	-1.97	-14.40	-26.77	-5.44	1.20	2.85	-14.41	-57.69	-46.63	-60.34	-64.11
MU 2	-60.13	-4.99	-34.46	-93.99	-26.37	-5.83	-21.04	-34.93	-30.34	-25.91	-31.77	-28.15

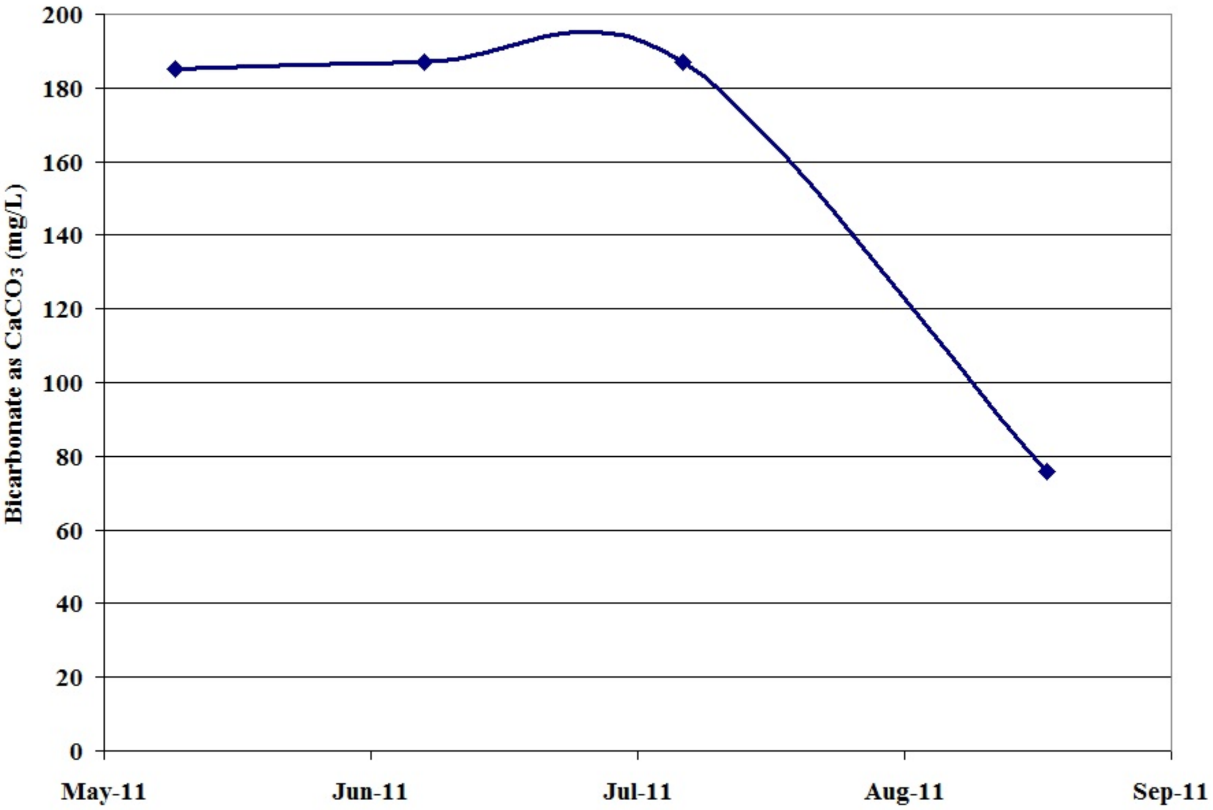


Figure 7.44 Bicarbonate (as $CaCO_3$) concentration profile for MU 2 feed during Round2 Phase1.

A significant and rapid effect of lower operating pH on MU 2 salt passage was observed. As was witnessed also in MU 1 operation, the reject pH of 7.3 was too high to sustain a low salt passage of all MU 2 elements. On the other hand, a reject pH of 6.5 was too low and to keep stable WTC values. Furthermore, the higher fouling rate of cartridge filters at a reject pH of 6.5 prevented viable continuous operation of the pretreatment and would likely influence the long-term operation of the downstream MU (see Section 8.0 on membrane autopsies). Therefore, it is very important to find the correct operating pH for a long and healthy running RO unit on Alternative 22, greensand and cartridge filtered water. The most appropriate operating pH seems to lie between the two tested ones. A more precise pH could be obtained with a short period of experimental run. Unlike with Alternative 21a, a very clear and significant effect of the pH was observed on the MU element flow coefficient with Alternative 22 pretreatment. The decreasing Ce values after the pH adjustment might indicate fouling with this alternative, which was not observed on the microfiltered YMC water. As was observed with the other MUs, the increase in MU 2 salt passage at high pH was reversible, by lowering the feed pH.

The results of the water quality analyses for MU 2 feed and reject are presented in Table 7.12, below. As it was in MU 1 and MU 3 results, both bicarbonate and total alkalinity levels have very high standard deviations. And again, the reason for that is the large drop in the feed pH on August 26. The values measured prior to this drop for these two parameters were significantly higher than the ones measured after the pH adjustment. This caused a big variation between the samples as illustrated in Figure 7.44. The bicarbonate (HCO_3^-) concentration (mg/L as $CaCO_3$) is shown for MU 2 feed throughout the Round 2 Phase 1 testing. The average concentration is 193.68 mg/L as $CaCO_3$ (Table 7.12). The bicarbonate concentration is assumed to be the same as total alkalinity at these pH levels for MU 2 feed and reject.

Table 7.12. Water composition for feed and reject of MU 2 RO unit.

		MU 2 Feed				**MU 2 Reject**			
Parameter	**Units**	**Average**	**Minimum**	**Maximum**	**St. Dev.**	**Average**	**Minimum**	**Maximum**	**St. Dev.**
Barium	*mg/L*	0.032	0.029	0.038	0.004	0.161	0.144	0.179	0.015
Bicarbonate	*mg/L*	193.68	92.70	228.00	67.32	941.75	367.00	1150.00	383.37
Calcium	*mg/L*	132.25	120.00	157.00	16.92	650.00	600.00	766.00	77.82
Chloride	*mg/L*	343.50	316.00	396.00	36.16	1660.00	1560.00	1870.00	144.45
Conductivity	*µS/cm*	2532.50	2430.00	2810.00	185.18	10380.00	9720.00	11400.00	721.30
Iron	*mg/L*	0.048	0.021	0.078	0.023	0.273	0.166	0.372	0.092
Magnesium	*mg/L*	42.98	40.10	50.40	4.98	215.00	199.00	252.00	24.81
Manganese	*mg/L*	0.0011	0.0006	0.0020	0.0006	0.0048	0.0024	0.0085	0.0029
Nitrate as N	*mg/L*	ND	ND	ND	ND	ND	ND	ND	ND
pH	-	7.22	6.37	7.72	0.60	7.74	6.94	8.19	0.55
Potassium	*mg/L*	5.22	4.92	5.84	0.43	25.03	23.90	27.30	1.54
Silicon Dioxide	*mg/L*	25.68	24.00	26.50	1.16	119.00	113.00	122.00	4.08
Sodium	*mg/L*	354.50	338.00	393.00	25.96	1695.00	1590.00	1840.00	108.47
Strontium	*mg/L*	1.72	1.53	2.09	0.25	8.36	7.70	9.95	1.07
Sulfate	*mg/L*	634.00	557.00	808.00	116.78	3167.50	2790.00	3980.00	546.95
Sum of Anions	*meq*	26.28	25.00	29.70	2.29	128.75	123.00	142.00	8.88
Sum of Cations	*meq*	25.70	24.20	29.20	2.35	124.75	118.00	140.00	10.31
Tot. Alk. as $CaCO_3$	*mg/L*	158.75	76.00	187.00	55.17	772.50	301.00	943.00	314.53
Tot. Hard. as $CaCO_3$	*mg/L*	506.75	464.00	599.00	62.62	2507.50	2340.00	2950.00	295.79
Total Organic Carbon	*mg/L*	1.09	1.07	1.12	0.03	3.63	3.50	3.82	0.17
Total Salt	*mg/L*	1715.00	1650.00	1910.00	130.00	8380.00	8020.00	9110.00	494.97

Table 7.13. Concentration and solubility data for MU 2 reject ion pairs that may contribute to membrane scaling. Ion products were based on the MU 2 reject average concentrations shown in Table 7.12, uncorrected for the ionic strength.

Precipitate	Ion Concentration	log (ion product)	log K_{S0}[c]	Degree of Saturation [b]
$BaSO_{4(s)}$	$[Ba^{+2}] = 1.17 \times 10^{-6}$ M $[SO_4^{-2}] = 3.30 \times 10^{-2}$ M	-7.41	-10.0	387.18
$CaSO_{4(s)}$	$[Ca^{+2}] = 1.62 \times 10^{-2}$ M	-3.27	-4.85	37.86
$CaCO_{3(s)}$	$[CO_3^{-2}] = 1.73 \times 10^{-5}$ M[a]	-6.64	-8.48	84.84

(a) based on 1130 mg/L carbonate alkalinity as HCO_3^- and reject pH = 7.30 (feed pH = 6.8).

(b) calculated as Q_{SO}/K_{SO}. The value represents the approximate degree of oversaturation in the RO brine produced from YMC water.

(c) Benjamin, 2002.

The solubilities of calcium sulfate, calcium carbonate and barium sulfate were again exceeded in brines derived from RO treatment of YMC water on Alternative 22 as shown in Table 7.13. The degree of saturation levels for barium sulfate, calcium sulfate and calcium carbonate in the reject of MU 2 are very close to the ones calculated for MU 1. The feed water values are 15.61, 1.54 and 1.11 for barium sulfate, calcium sulfate and calcium carbonate, respectively. They are already higher than their saturation levels at the given operating pH (feed pH of 6.8) and alkalinity. The calculations for the degree of saturation were again carried out for the initial conditions of MU 2 operation, i.e. feed pH of 6.8 and reject pH of 7.3. The bicarbonate concentration is assumed as 230 and 1130 mg/L for feed and reject, respectively, which are the average values of bicarbonate levels determined in the lab analyses prior to any pH adjustments. Feed pH of 6.8 (reject pH of 7.3) was chosen as it was for the other MUs for calculating the saturation degrees since scaling problem is more likely to be observed with the highest operating pH. However, minimal evidence of irreversible scaling, e.g. barium sulfate, was observed during the testing and in the post-mortem analyses of the retired elements. Knowing that some ion pairs were significantly supersaturated and yet observing minimal scaling indicates the use of anti-scalant is necessary for a sustainable RO operation while desalting Alternative 22 pretreated YMC water.

With respect to a possible silicon dioxide problem, it is more likely to be observed in this unit compared to the one operated in Alternative 21a due to the lack of tighter filtration technique, i.e. microfiltration. Even though cartridge filters appeared to perform as effective as the microfiltration unit based on WTC values, they did not produce as robust performance as microfiltration. The amount of build-up and the fouling materials detected during the post-mortem analyses of the retired cartridge filters and of the MU 1 versus MU 2 elements provides strong evidence that they do remove significant amount of substance from the source water and help to protect the downstream RO units, but do not remove as much material as the MF unit. As it was in the MU 1 operation, silicon dioxide concentrations close to the solubility levels of silica (120 mg/L at 25°C and neutral pH) were measured. Hence, caution shall be taken while treating Alternative 22 pretreated YMC water in terms of silica scaling prevention.

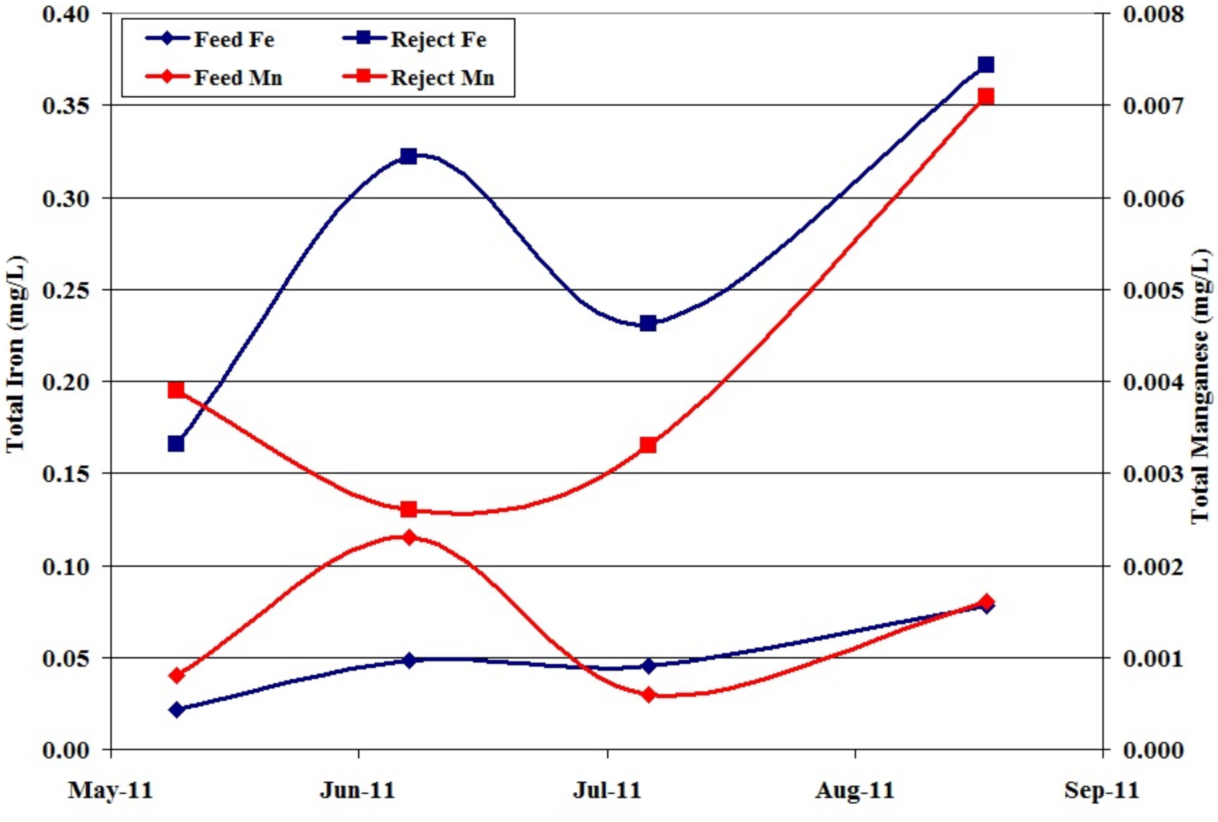


Figure 7.45 Total Fe & total Mn concentrations in MU 2 feed and reject during Round 2 Phase1.

As expected, very similar iron and manganese levels were detected in MU 1 and MU 2 feed waters. Figure 7.45 shows the feed and reject concentrations of total iron and total manganese for MU 2. No significant difference was observed between the two alternatives (21a and 22) tested on YMC water in terms of iron and manganese levels in feed water of the MUs. This suggests that the conditioned silica sand performs as effectively as (or even better than) the greensand in terms of removal of these two ions from YMC water. Although the resolution of the measurements and precision of the recovery calculations do not allow high accuracy calculation of the mass of iron and manganese retained in the MU unit, the reject concentrations measured are approximately five times the feed concentrations which is consistent with low retention by the RO elements operating at an overall recovery of 80%.

7.4 Heterotrophic Plate Count (HPC) Results

Table 7.14. HPC results for the PS 1 SCR (PISCRE), PS 2 (P2ET1) and PS 3 gravity filters (P3ET3) effluents in colony forming units (cfu) per ml.

Date	P1SCRE	P2ET1	P3ET3
9/8/2010	<2	-	-
9/15/2010	6	23	59
9/22/2010	<2	62	<2
9/29/2010	6	6	10
10/6/2010	62	74	65
10/13/2010	4	<2	2
10/20/2010	<10	160	6
10/25/2010	-	<2	-
11/3/2010	2	2	-
11/10/2010	2	<2	8
11/16/2010	6	<2	2
11/23/2010	2	-	4
11/30/2010	2	<2	<2
12/7/2010	<2	4	560
12/14/2010	<2	2	2
12/21/2010	1	0	1
12/28/2010	43	<2	97

Weekly water samples were collected for heterotrophic plate count (HPC) analysis during both Round 1 and Round 2 testing. However, the location of the sampling points varied between the two study periods. During Round 1, samples were collected at the pretreated water sources of the four alternatives and at the feed and reject streams of the ETAs. On the other hand, samples were collected only from the reject streams of ETAs and MUs during Round 2 and Round 2

Phase 2 testing, because concentrations of concern were detected neither in the effluents of the pretreatment units nor in the feed of ETAs.

Table 7.15. HPC results for the ETAs during Round 1 in colony forming units (cfu) per ml.

	Date	**F A**	**F B**	**V1 R**	**V2 R**
ETA 1	**10/6/2010**	43	17	140	30
	10/20/2010	170	21	160	160
	11/10/2010	2	2	10	6
	11/16/2010	10	8	8	4
	11/23/2010	4	12	10	56
	11/30/2010	6	2	8	38
	12/7/2010	26	48	4	30
	12/14/2010	300	100	738	738
	12/21/2010	34	4	28	60
	12/28/2010	740	2	200	2

	Date	**F A**	**F B**	**V1 R**	**V2 R**
ETA 2	**11/10/2010**	17	2	2	2
	11/16/2010	2	2	2	2
	11/30/2010	2	2	2	2
	12/7/2010	12	2	4	2
	12/21/2010	0	0	2	3
	12/28/2010	2	2	2	2

	Date	**F A**	**F B**	**V1 R**	**V2 R**
ETA 3	**11/10/2010**	2	2	4	2
	11/16/2010	8	2	2	2
	11/30/2010	2	2	2	2
	12/7/2010	2	2	2	2
	12/14/2010	10	2	2	2
	12/21/2010	4	4	1	0
	12/28/2010	370	2	74	360

	Date	**F A**	**F B**	**V1 R**	**V2 R**
ETA 4	**10/6/2010**	8	10	10	15
	10/20/2010	23	21	19	15
	11/10/2010	4	2	2	2
	11/16/2010	2	4	6	2
	11/23/2010	2	2	6	4
	11/30/2010	12	2	2	2
	12/7/2010	2	17	4	2
	12/14/2010	6	2	28	6
	12/21/2010	0	1	2	2

The HPC results for the PS1 solids contact reactor effluent, PS2 gravity filters combined effluent and PS3 gravity filters combined effluent are presented in Table 7.14. The primary drinking water standard for HPC is 500 cfu/ml. During Round 1 testing of pretreatments, only one sample at the effluent of PS3 gravity filters reached above that number with 560 cfu/ml out of 17 sampling occasions. All these sampling locations are after chlorine injection, meaning that the pretreatment and disinfection techniques for all the alternatives worked properly during Round 1 testing. Please, see below for the HPC results of ETAs during Round 1 testing. FA, FB, V1R and V2R stand for feed water prior to antiscalant addition, feed water after antiscalant addition, vessel 1 reject water and vessel 2 reject water samples, respectively. There are only two occasions on December 14 and 28, 2010 where the number of coliform forming bacteria exceeded 500 cfu/ml on ETA 1 reject and feed waters, respectively. No adverse effect of these incidents was observed on the performance of ETA 1.

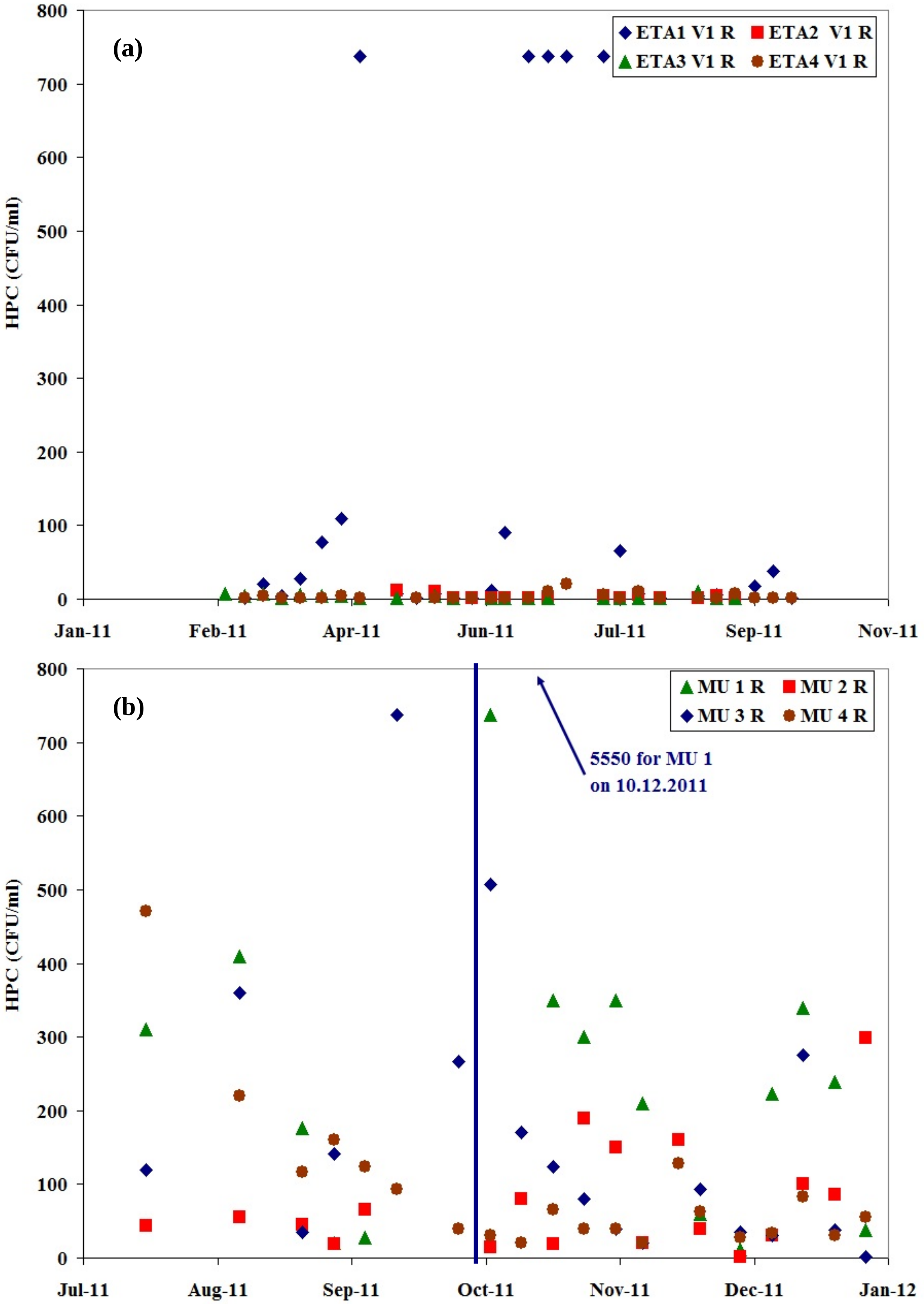


Figure 7.46. HPC results for (a) ETAs Vessel 1 reject waters during Round 2 and (b) MUs reject waters during Round 2 and Round 2 Phase 2 testing.

The HPC results for MU reject waters are presented in Figure 7.46. The blue line in Figure (b) represents the time that MU 1 and MU 2 moved to Alternative 17a and Alternative 10, respectively. MU 1 had high counts after moving to the MODE water alternative. However, no adverse effect on the operational parameters was recorded. On the other hand, ETA 1 during Round 2 (operating on MODE water parallel to MU 1) had high HPC results during June and July, which affected the unit's performance significantly. (ETA 1 and MU 1, Round 2, Phase 2, operational results are in the earlier MODE section of this report.)

8. POST-MORTEM ANALYSES RESULTS

8.1 Bacterial Contamination

Heterotrophic plate counts were conducted from a measured area of surface for each membrane element autopsied. In general for the MODE MUs, it was found that the HPC was highest in the tail rather than lead elements for each treatment train (Table 8.1). This suggests both that viable bacteria were not filtered out in the feed spacer passages as feed/concentrate progressed through the elements in series and that the bacterial population was highest where the concentrate (and presumably organic matter substrate) was strongest. In addition, the Alternative 17 (microfiltration) tail elements had much higher HPCs than the analogous elements in Alternative 10 (partial lime softening). This corroborates the conjecture that bacterial growth was occurring in Alternative 17 RO units from mid-summer 2011 when the total chlorine in the feed decreased to 1.5 mg/L. Other evidence included rising net driving pressure to maintain a constant product flow rate and high HPCs in the reject water from ETA 1, MU 3 and MU 1 (after it was moved from YMC to MODE water). In response the total chlorine was increased to 2.0 mg/L. The high pH of ca. 10 attendant with partial lime softening in Alternative 10 may also act to disinfect the feed water.

Table 8.1. Heterotrophic plate counts (HPCs) for lead and tail elements of MUs operated on MODE water. HPCs are expressed in [cfu/in^2] units.

Alternative 17	HPCs	Alternative 10	HPCs
MU3, Vessel 1, Element 1	4.62E+01	MU4, Vessel 1, Element 1	8.39E+02
MU3, Vessel 2, Element 1	0.00E+00	MU4, Vessel 2, Element 1	1.38E+03
MU3, Vessel 3, Element 7	1.10E+05	MU4, Vessel 3, Element 7	1.18E+02
MU1, Vessel 1, Element 1	4.46E+02	MU2, Vessel 1, Element 1	5.33E+01
MU1, Vessel 2, Element 1	4.85E+03	MU2, Vessel 2, Element 1	3.78E+01
MU1, Vessel 3, Element 7	1.61E+06	MU2, Vessel 3, Element 7	1.80E+02

8.2 MODE, Partial Lime Softening versus Microfiltration

Figures 8.1a and 8.1b show scanning electron microscope (SEM) images of the surface of TML and LFC membranes used in round 1, on partial lime softened MODE water (alternative 10, ETA 4). Material build-up was observed also on ULP and ESPA 2 membranes, but to a lesser degree.

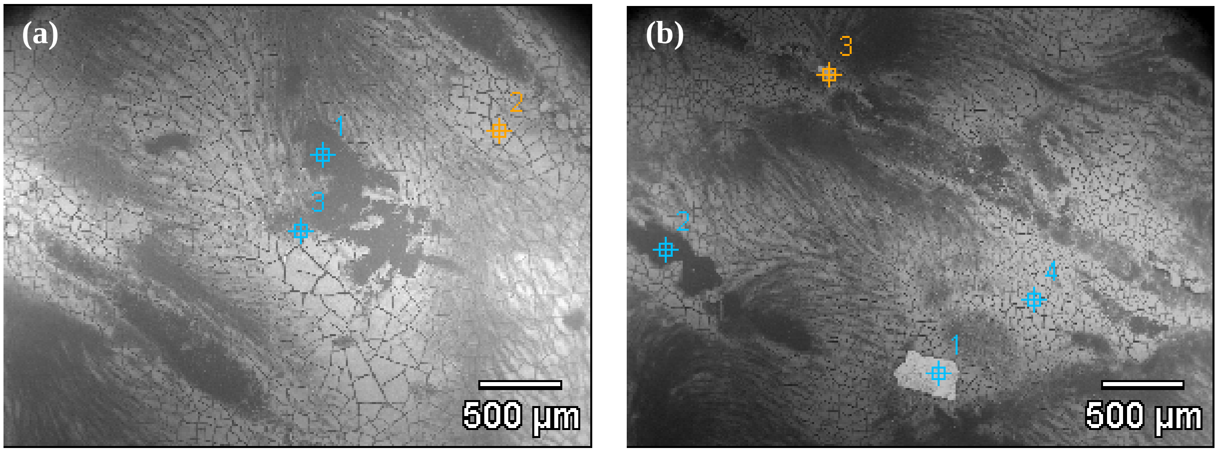


Figure 8.1. Scanning Electron Microscope (SEM) images of the surface of (a) Toray TML10 and (b) Hydranautics LFC3 membranes used in Round 1 on partial lime softened MODE water (Alternative 10, ETA 4).

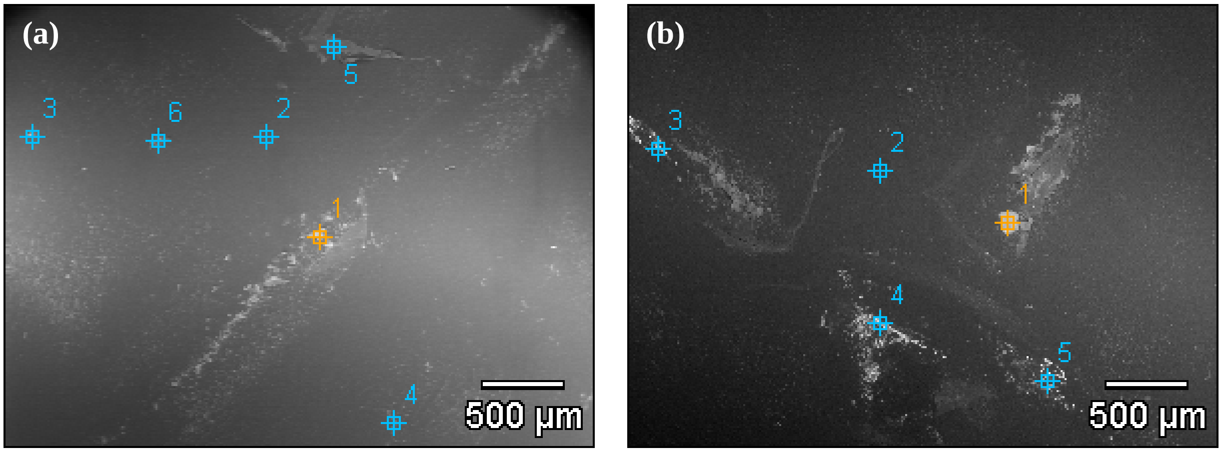


Figure 8.2. Scanning Electron Microscope (SEM) images of the surface of (a) Toray TML10 and (b) Hydranautics LFC3 membranes used in Round 1 on microfiltered MODE water (Alternative 17a, ETA 1).

In contrast, the membranes receiving microfiltered MODE water at the same time showed no or very little material build-up. Figure 8.2a shows an SEM image of the TML membrane and the representative amount of build-up observed on alternative 17 round 1 membranes. The FTIR spectra of round 1 MODE water elements supports the visual and SEM observations of greater material build-up following partial lime softening than microfiltration. Figure 8.3a and 8.3b show FTIR spectra of round 1 TML10 and LFC3 membranes after air drying.

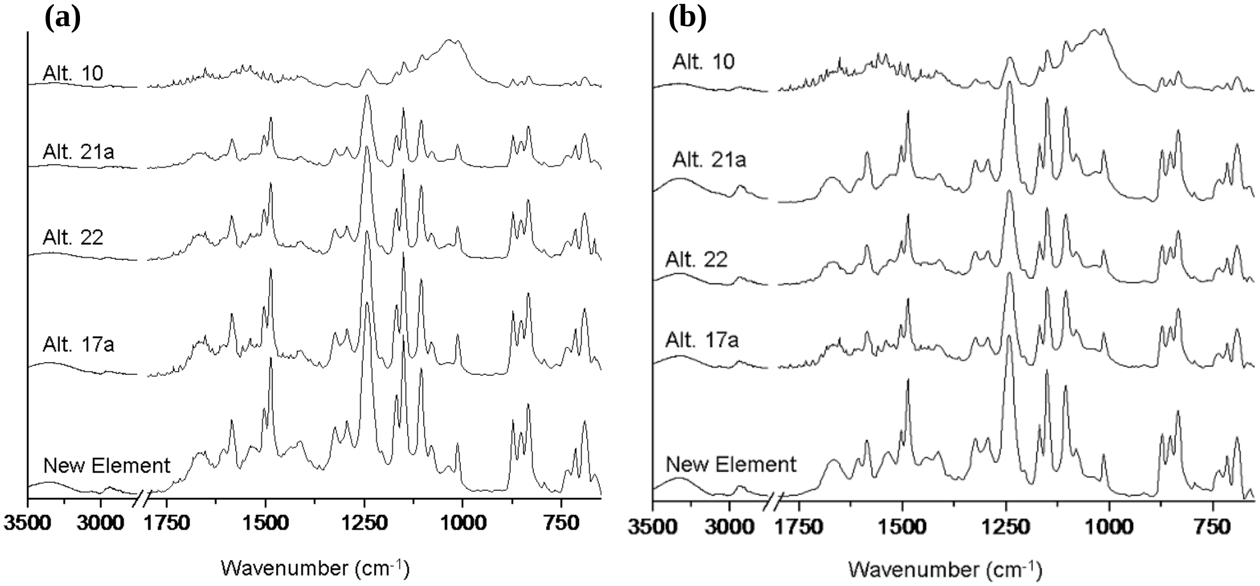


Figure 8.3. Fourier transform infrared spectroscopy (FTIR) spectra of (a) Toray TML10 and (b) Hydranautics LFC3 membranes used in Round 1 after air drying. Y-axis on the graphs presented is “absorbance”.

Both alternative 10 membranes show clear evidence of biofouling with polysaccharide build-up (wavenumber 1,150-950 cm^{-1}) and/or abiotic fouling with silicon-oxide materials (e.g. alumina silicates) (1,040 cm^{-1}), and general attenuation (by surface coating) of the polyamide and polysulfone structures of the membrane in the 1,700-1,500 cm^{-1} and 1,350-1,100 cm^{-1} ranges, respectively. In contrast the alternative 17 (microfiltered water) membranes show little if any polysaccharide or general surface build-up in the FTIR spectra. SEM-EDS (energy dispersive spectroscopy) and XRD (x-ray diffraction spectroscopy) of the material on the surfaces of both alternative 10 and 17 membranes indicate aluminum-silicates (anorthite clay), silicon oxide and iron oxide as the primary inorganic constituents of the surface materials. The Alternative 10 SEM revealed a number of diatoms on the membrane (Figure 8.4) and, consistently, the SEM-EDS showed the surface particles to generally have high fractions of silicon (in the range of 30% by weight) likely of both biotic (diatoms) and abiotic (clays) origin.

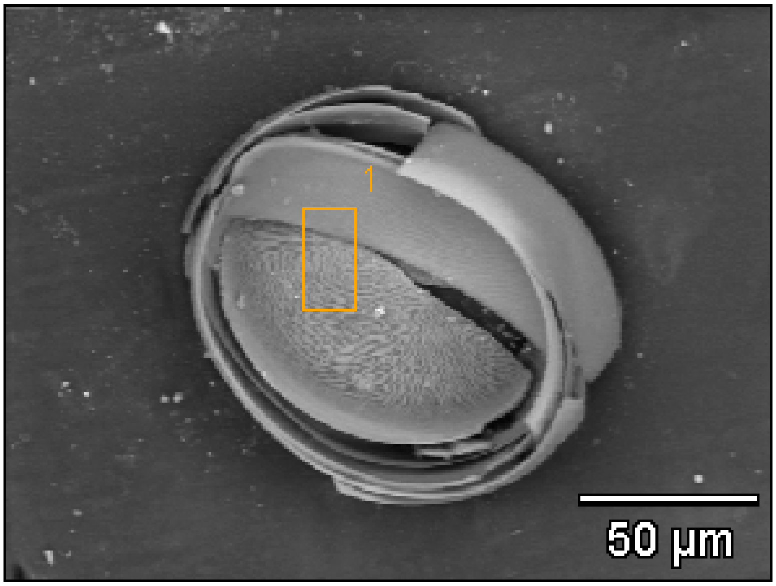


Figure 8.4. SEM image of a diatom on ESPA2 membrane used in Round 1 lime softened MODE water (Alternative 10, ETA 4).

Similar results with respect to material accumulation on the alternative 10 and 17 membranes were observed in the round 2, high recovery testing in which the feed/concentrate passed through 14 elements in series (as opposed to the round 1 use of low recovery testing with 2 elements in series). The high recovery testing allowed insight into lead versus tail element accumulation that was not possible in the round 1 and 2 low recovery testing. Figures 8.5a and 8.6a show that both lead and tail elements of alternative 17 have very little polysaccharide (wavenumber 1,150-950 cm^{-1}) build-up compared to alternative 10 elements. Even though there is a slight decrease in polysaccharide accumulation between lead and tail elements, there is a very substantial increase in spectra indicative of palmitate salts (e.g., $Ca(CH_3(CH_2)_{14}COO)_2$, particularly with alternative 10. Palmitic acid is the most common fatty acid in biological tissue and is a strong indicator of organisms or their residual tissues. The spectra for palmitate includes peaks at 2,920 and 2,850 cm^{-1} (CH_2 stretching), 1,470 cm^{-1} (CH_2 bending), and 1,575 and 1,540 cm-1 (COO$^-$ stretching). It is interesting that for alternative 10 high recovery elements the thickness of surface coating, although easily observable, was not as much as had been observed in the shorter duration, round 1 low recovery tests.

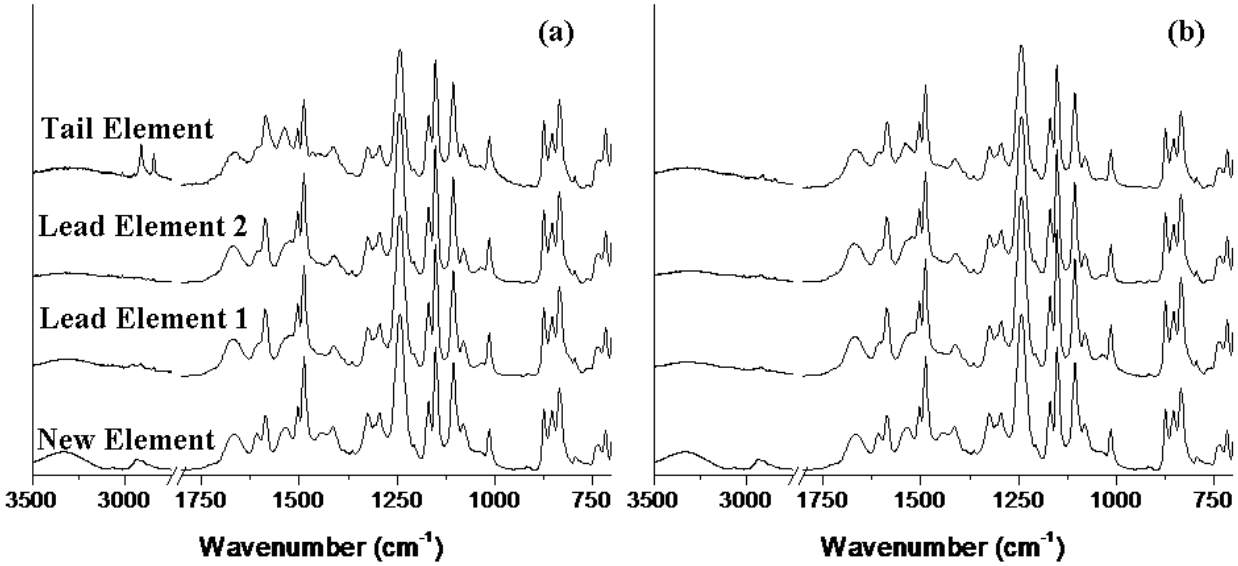


Figure 8.5. Fourier transform infrared spectroscopy (FTIR) spectra of LFC3 elements retired from MU 3 operated with microfiltered MODE water (Alternative 17a); (a) original elements and (b) surface precipitate removed elements by scraping with a soft plastic spatula. Y-axis on the graphs presented is “absorbance”.

It is worth noting that the material deposited on the high recovery membranes was easily removed by simply scraping with a soft plastic spatula and the near-original surface features reappeared (Figures 8.5b and 8.6b). This gives some support to the conjecture that the material might be removed from the membranes in situ without aggressive cleaning, although this was not verified as cleaning studies were beyond the scope of the present work.

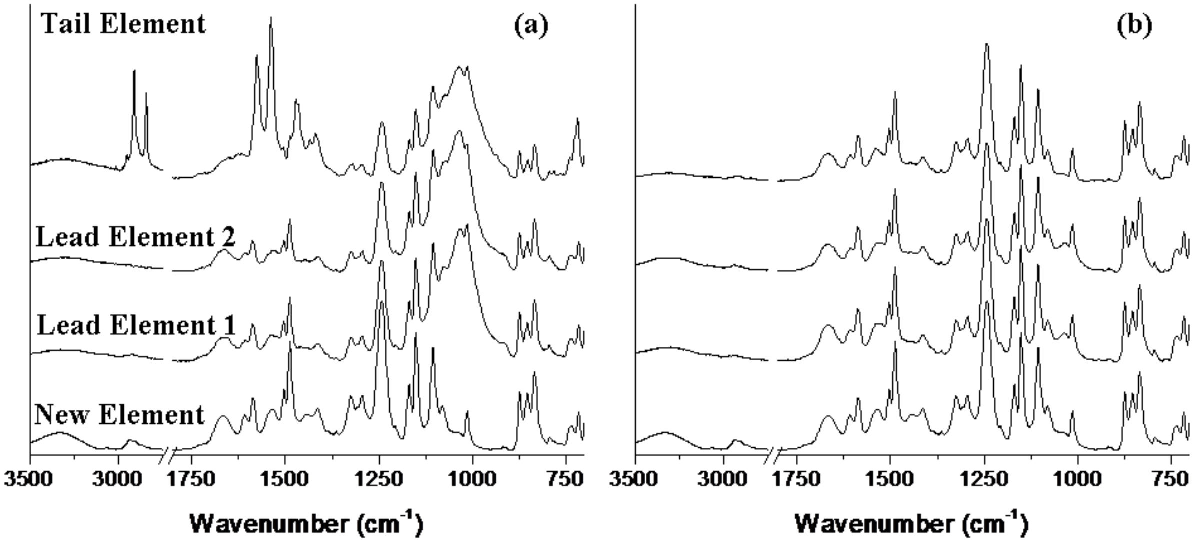


Figure 8.6. Fourier transform infrared spectroscopy (FTIR) spectra of LFC3 elements retired from MU 4 operated with lime softened MODE water (Alternative 10); (a) original elements and (b) surface precipitate removed elements by scraping with a soft plastic spatula. Y-axis on the graphs presented is “absorbance”.

8.3 MODE, High Flux and Recovery

From September 30 until December 30, 2011, a second 21-element high recovery unit was operated in parallel with the high recovery unit operating since March 8, 2011 on the microfiltered MODE water. This second unit also contained Hydranautics LFC membranes, but was operated at an increased average flux of 15 gfd (rather than 12 gfd) for the full three months and at an increased recovery of 85% (rather than 80%) from November 17 to December 30, 2011. Although only operating for approximately one third of the time, the high flux/recovery (HFR) elements showed considerably greater accumulation of surface material than the normal flux/recovery (NFR) elements (compare Figure 8.7a to Figure 8.7b). SEM-EDS and XRD analysis of the material on the HFR surface indicated a large proportion of elemental sulfur (see discussion below) as well as smaller amounts of clay constituents (aluminum silicates).

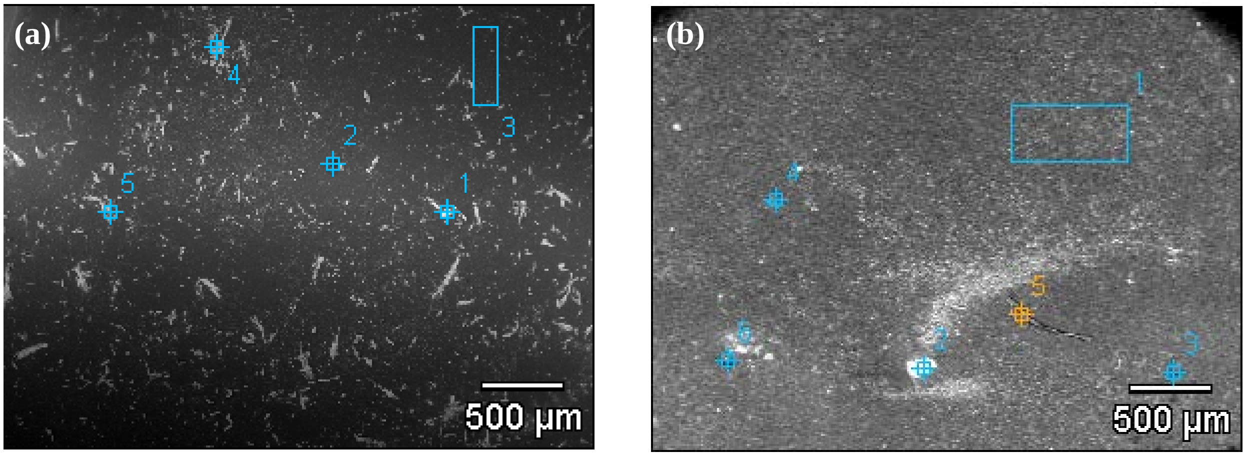


Figure 8.7. Scanning Electron Microscope (SEM) images of the surface of LFC3 elements retired from (a) MU 1 (Round 2 Phase 2 – HFR) and (b) MU 3 (Round 2 – NFR). Both units operated with microfiltered MODE water (Alternative 17a). Both elements were tail elements located in Vessel 3 Element 7.

The surface accumulation is further evidenced in the FTIR spectra (Figure 8.8a). Comparing the HFR FTIR spectra to that of the NFR FTIR spectra (Figure 8.5a) the tail element shows a general coating over the entire HFR spectra and the appearance of distinct palmitate peaks between 3,000 – 2,500 cm^{-1}. The fouling is particularly pronounced in the HFR tail element, but biofouling is evident also in the lead elements in the 1,200 – 1,000 cm^{-1} range. As was seen with the fouling material on the other membranes operated on MODE water, the foulant on the HFR membranes was readily removed with light scraping with a soft plastic spatula (Figure 8.8b).

As previously discussed with respect to the fouling observed with the partial lime softened MODE water, FTIR peaks in the 1,200 – 1,000 cm^{-1} range are indicative of polysaccharides (biofouling). However, the silicon-oxygen stretching peak also occurs at about 1,040 cm^{-1}. The 1,040 cm^{-1}peak in the HFR tail element is qualitatively more singular (sharper) than that for tail and lead elements in the partial lime softened case (compare Fig 8.8a to Fig. 8.6a). This may indicate more inorganic (silicates) fouling for the HFR case, while the fouling of the latter case is more mixed organic (polysaccharides) and inorganic (silicates). More elemental and compound specific analysis would be needed to verify or deny this hypothesis.

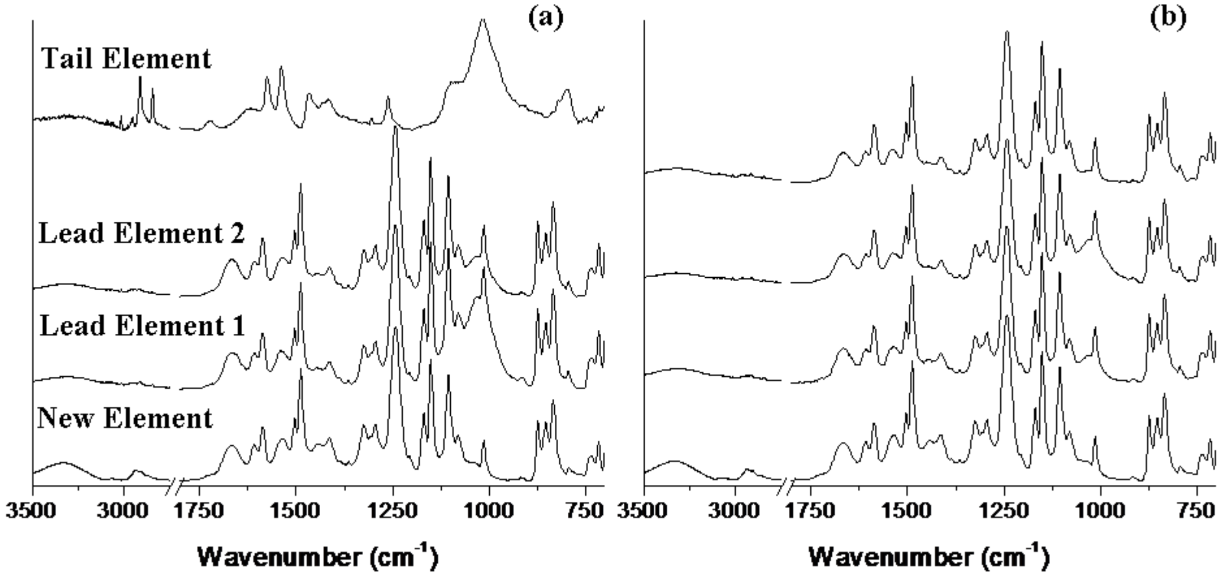


Figure 8.8. Fourier transform infrared spectroscopy (FTIR) spectra of LFC3 elements retired from MU 1 operated with microfiltered MODE water (Alternative 17a) at high flux/recovery (HFR); (a) original elements and (b) surface precipitate removed elements by scraping with a soft plastic spatula. Y-axis on the graphs presented is “absorbance”.

8.4 MODE, Elemental Sulfur Deposition

Unexpectedly, the tail membrane elements (vessel 3, element 7) of both of the high recovery arrays operated on microfiltered MODE water (alternative 17) and the high recovery array operated for nine months on partial lime softened MODE water showed elemental sulfur as either the only or a major constituent of the surface material. Figures 8.9, 8.10, and 8.11 all show high sulfur content in SEM–EDS spot analysis on the tail elements of the arrays. The sulfur weight percent in spots on surface particles is commonly in the 10-50% range.

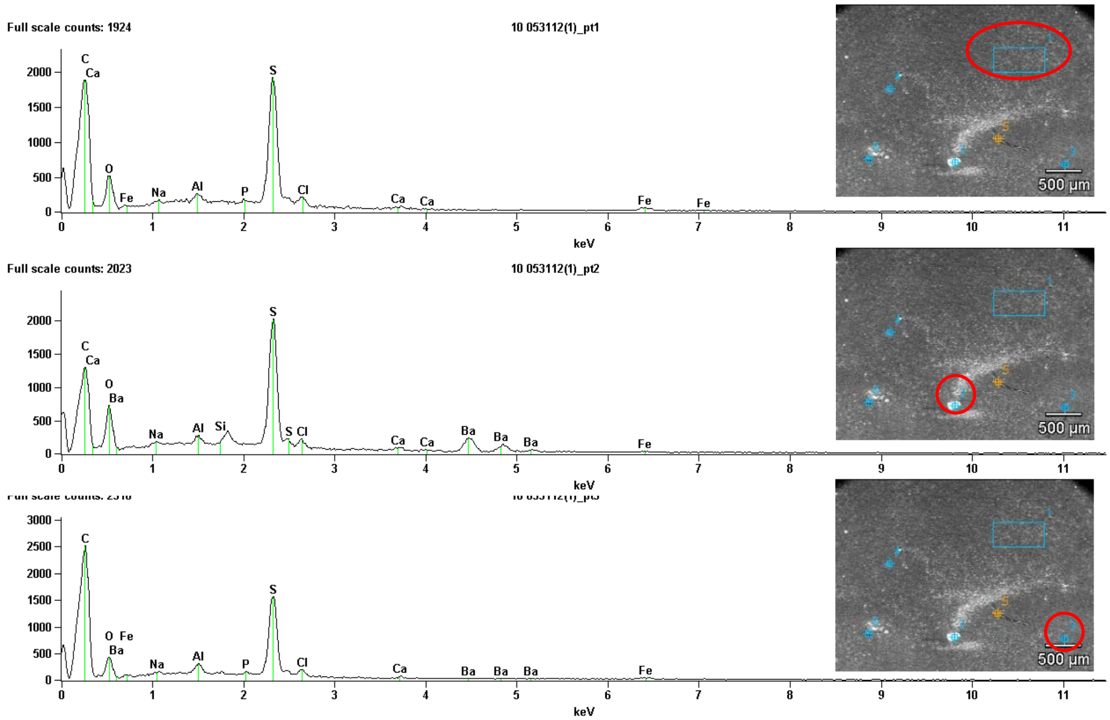


Figure 8.9. SEM-EDS images of LFC3 element (located as Vessel 3 Element 7 – tail element) retired from MU 3 operated with microfiltered MODE water (Alternative 17a) at normal flux/recovery (NFR) during Round 2. Red circles highlight the points for EDS readings.

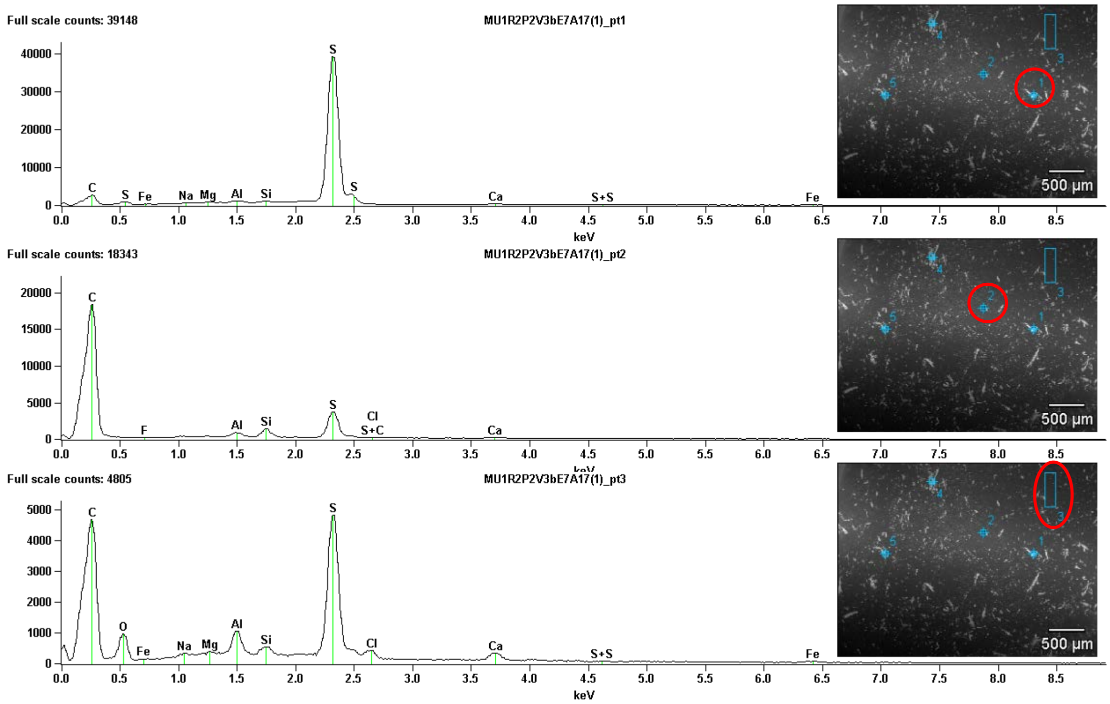


Figure 8.10. SEM-EDS images of LFC3 element (located as Vessel 3 Element 7 – tail element) retired from MU 1 operated with microfiltered MODE water (Alternative 17a) at high flux/recovery (HFR) during Round 2 Phase 2. Red circles highlight the points for EDS readings.

The XRD spectra from material scraped from the surface of these same tail elements show elemental sulfur as the sulfur-bearing mineralogic species present (Figure 8.12a, 8.12b and 8.12c). No elemental sulfur (S^0) was detected by any of the autopsy analytic techniques in the lead elements of any of the MODE water high recovery arrays. This suggests that the deposition of the S^0 is concentration-related whereby the feed/concentrate stream reaches a threshold concentration in S^0 somewhere within the array's sequence of elements at which point precipitation of S^0 onto the membrane begins.

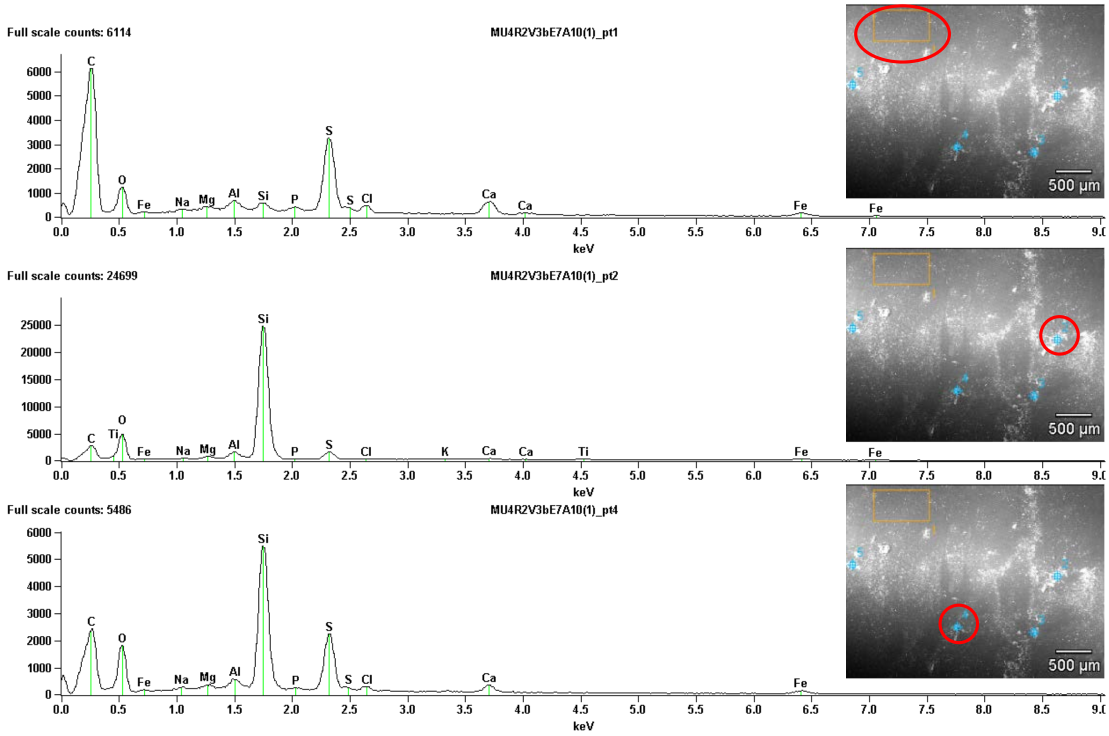


Figure 8.11. SEM-EDS images of LFC3 element (located as Vessel 3 Element 7 – tail element) retired from MU 4 operated with microfiltered MODE water (Alternative 17a) at normal flux/recovery (NFR) during Round 2. Red circles highlight the points for EDS readings.

Elemental sulfur (S^0) can be generated in the environment from sulfate (SO_4^{2-}) under anaerobic conditions as a two-step process. Sulfate is reduced to sulfide (S^{2-}) by sulfur reducing bacteria and then the sulfide is oxidized abiotically (or in some instances, biotically) to S^0 in the presence of an electron donor such as Fe^{3+} or Mn^{4+}. The sulfate concentration in MODE water is high (~850 mg/L) and both oxidized iron and manganese are present, so if anaerobic conditions occur then it is expected elemental sulfur could be generated.

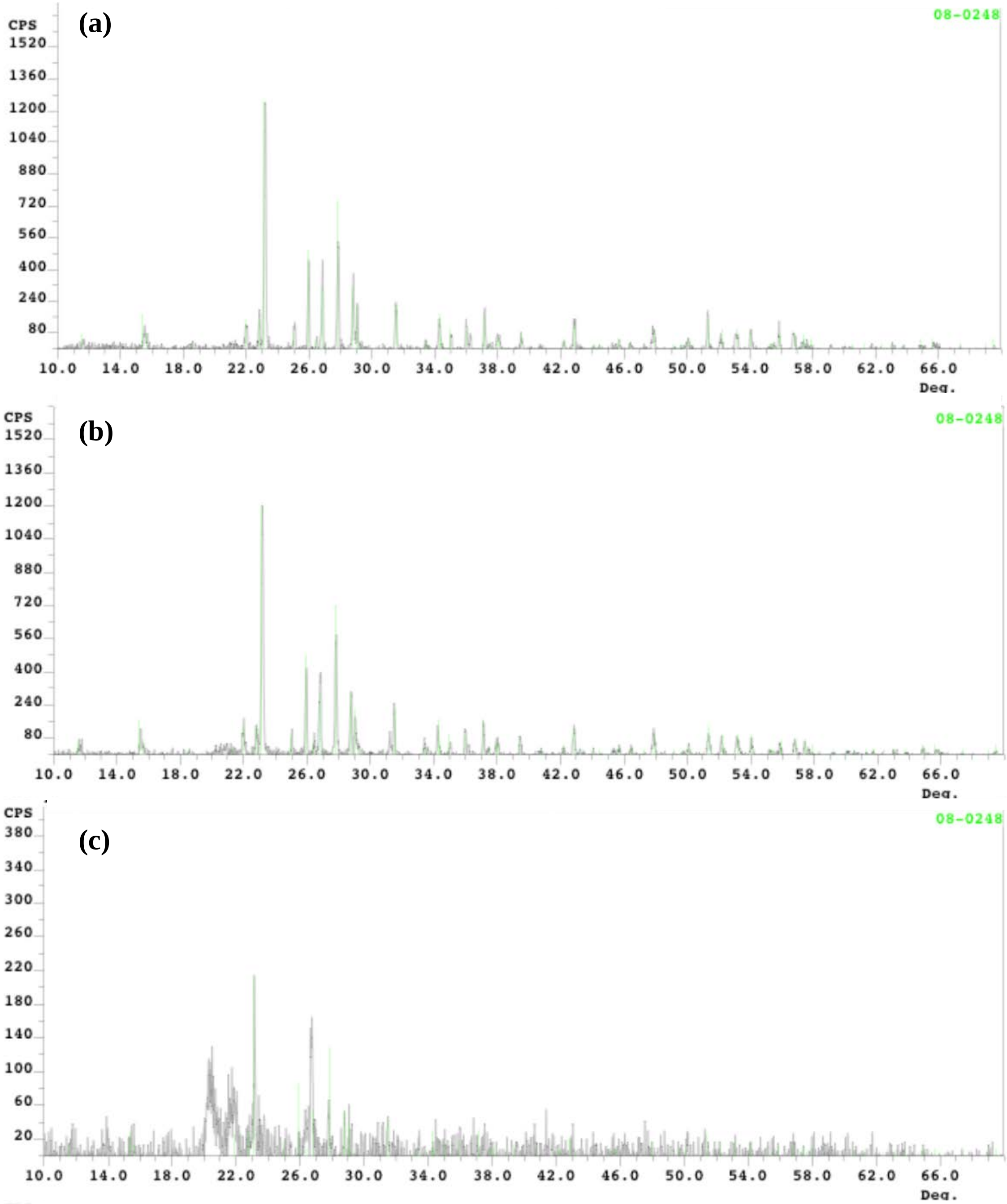


Figure 8.12. The XRD spectra from material scraped from the surface of the tail elements (Vessel 3 Element 7) showing elemental sulfur as the sulfur-bearing mineralogic species present for (a) MU 3, (b) MU 1 – HFR operation during Round 2 Phase 2, and (c) MU 4. MU 3 and MU 1 were operated on Alternative 17a, whereas MU 4 was operated on Alternative 10.

Anaerobic conditions probably exist in sediment layers and accumulation areas in the MODE canal and the products could become mobilized into the YDP feed during storm events or when flow in the canal is perturbed. Alternatively, anaerobic conditions could occur locally at YDP in MODE water operations if the chlorine disinfectant feed is lost or inadequate to meet demand. It is impossible to determine with the information available, which of these two potential sources (or some other source) of S^0 generation led to the S^0 observed on the MODE water membranes. There is no literature to suggest that elemental sulfur is more deleterious to membrane performance than any other mineral scalant. However, the presence of S^0 is significant in that it indicates there were periods of sub-oxic conditions in the water source. This is a red flag that other highly reduced species (e.g., Fe^{2+}, Mn^{2+}) may be present, which do have documented negative impacts on membrane material integrity, and that sufficient oxidation potential may not have been continuously maintained to keep microbial growth on the membranes completely in check.

8.5 YMC, Micro- versus Cartridge Filtration

In all cases the high recovery array (MU) membranes operated on YMC water showed less accumulation of surface materials than those operated on MODE water. However, it is not clear to what degree this is because YMC alternatives were operated for less time than the MODE alternatives as opposed to the YMC pre-treated water being of better quality than that of MODE water. Consequently, although the operational results (reported in other parts of this report) and the autopsy results both suggest that membrane fouling/scaling is less problematic with YMC than MODE water, direct, conclusive comparisons cannot be made because of the difference in duration of operation between the alternatives on the two source waters. However, direct comparison between the autopsy results of the two pretreatments, microfiltration (MF) and cartridge filtration (CF), used on YMC water is appropriate and indicates that CF is not as efficient as MF for protecting downstream membranes from particulate build-up. Visual inspection and SEM imaging of membranes fed microfiltered YMC water showed the least particle accumulation of all membranes analyzed.

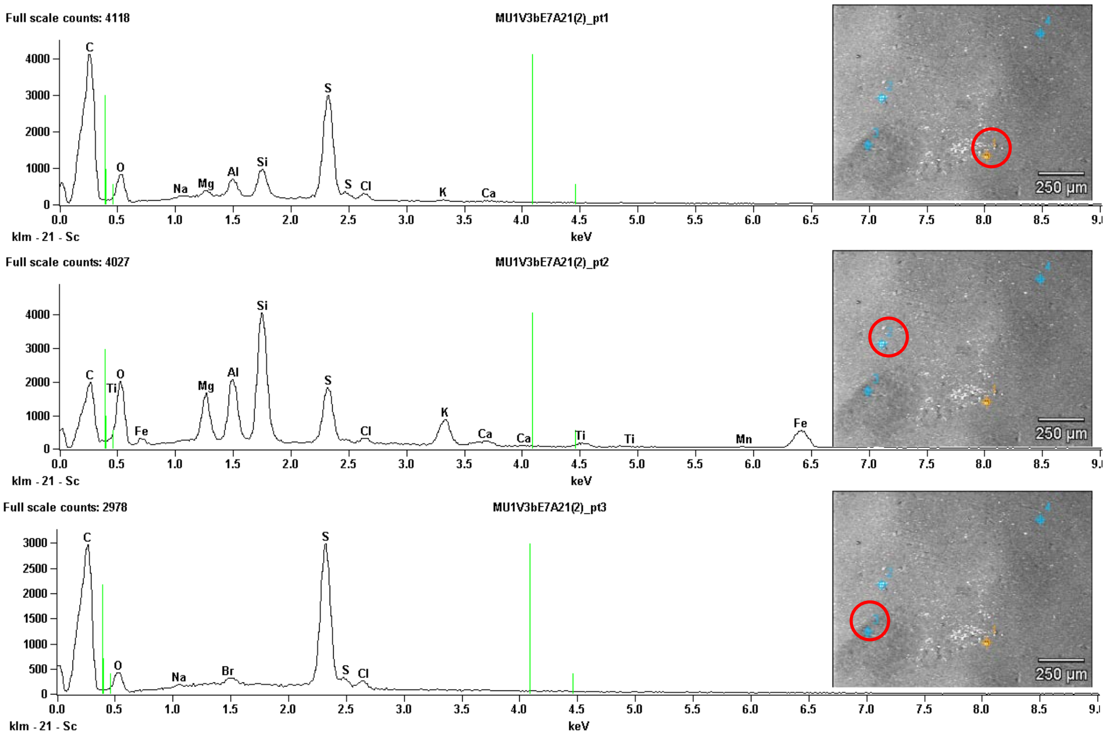


Figure 8.13. SEM-EDS images of LFC3 element (located as Vessel 3 Element 7 – tail element) retired from MU 1 operated with microfiltered YMC water (Alternative 21a) at normal flux/recovery (NFR) during Round 2 Phase 1. Red circles highlight the points for EDS readings.

For these membranes, even at SEM resolution, large areas of the membrane surface were free of particles. Figure 8.13 shows a patch of particles imaged on the surface of the tail (vessel 3, element 7) membrane of the array receiving MF water. Based on SEM-EDS, the particles are primarily either aluminosilicates (clays) or metal sulfates (e.g., calcium sulfate). In comparison, Figure 8.14 shows particles on the surface of the tail element of the array receiving CF water as being more concentrated but also primarily composed of aluminosilicates and metal sulfates, with the addition of some metal chlorides. SEM-EDS also indicates some iron on the CF membrane surface. For neither of these YMC water alternatives was there sufficient material on the membrane surface to allow XRD analysis and more specific identification of minerals species.

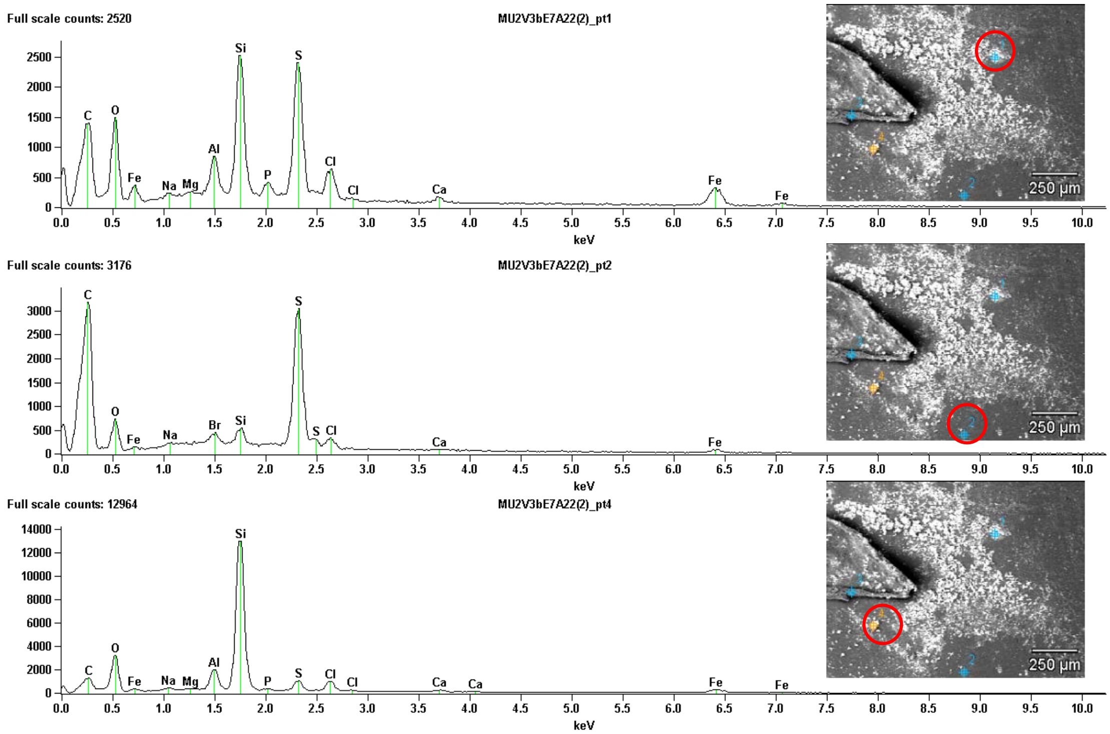


Figure 8.14. SEM-EDS images of LFC3 element (located as Vessel 3 Element 7 – tail element) retired from MU 2 operated with cartridge-filtered YMC water (Alternative 22) at normal flux/recovery (NFR) during Round 2 Phase 1. Red circles highlight the points for EDS readings.

The FTIR spectra for the YMC water exposed membranes corroborate the SEM analysis indicating CF was less efficient at particle removal than MF. Figure 8.15 and 8.16 are the FTIR spectra for the new, two lead elements and one tail element in the high recovery arrays operating on microfiltered and cartridge filtered YMC water, respectively. The loss of all spectral peaks in the 1750-1250 cm^{-1} range and the broad, undifferentiated peak in the 1250-850 cm^{-1} range indicate a substantial surface layer (greater than 300 nanometers (nm) thickness) overlying the membrane surface of the CF water tail element while there is little if any change in the peaks of the MF water tail element (relative to the new element). The broad peak in the 1250-850 cm^{-1} range (CF water) is most likely from silicon-oxygen stretching and/or carbon-carbon stretching which indicates the layer is composed of clays, polysaccharides (biological detritus) or a combination of these.

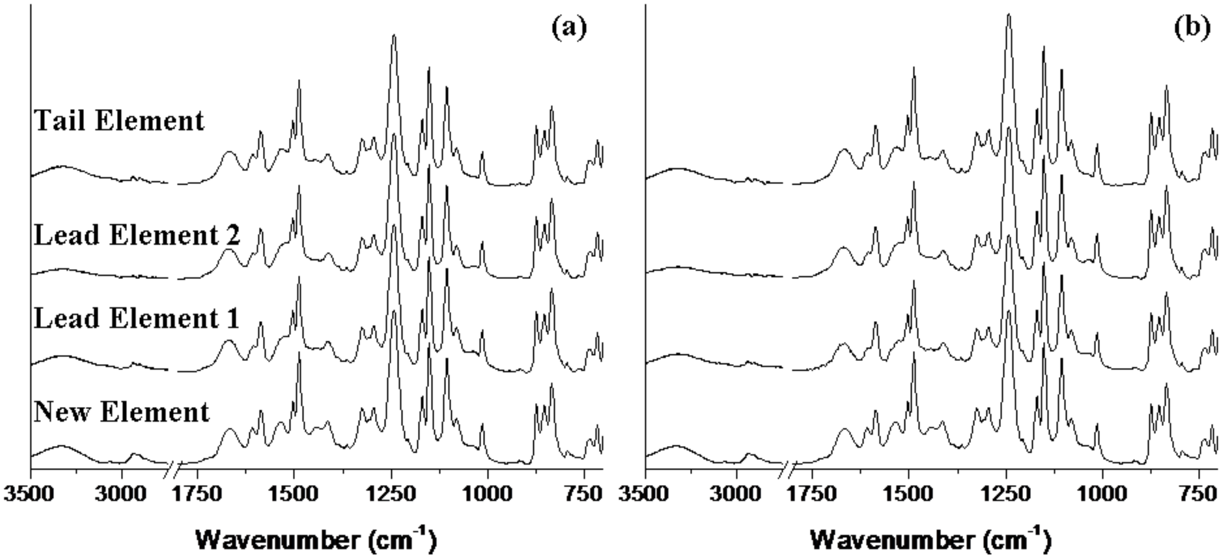


Figure 8.15. Fourier transform infrared spectroscopy (FTIR) spectra of LFC3 elements retired from MU 1 operated with microfiltered YMC water (Alternative 21a) at normal flux/recovery (NFR); (a) original elements and (b) surface precipitate removed elements by scraping with a soft plastic spatula. Y-axis on the graphs presented is "absorbance".

The lead elements of the CF treated water array shows considerably less particle accumulation than the tail element, however the slight loss of definition and increase in the spectra around 1,050 cm^{-1} suggests these elements are not entirely free from accumulation. Furthermore, comparing the scraped and unscraped spectra in Figure 8.16, it can be seen that the material on the lead elements is easily removed (by the light scraping with a rubber spatula), whereas the material on the tail element is more tightly bound to the membrane and is not as easily removed. This may be because the material on the lead and tail elements is different, the degree of compaction and hence adhesion is greater on the tail element, or some other as yet unidentified reason.

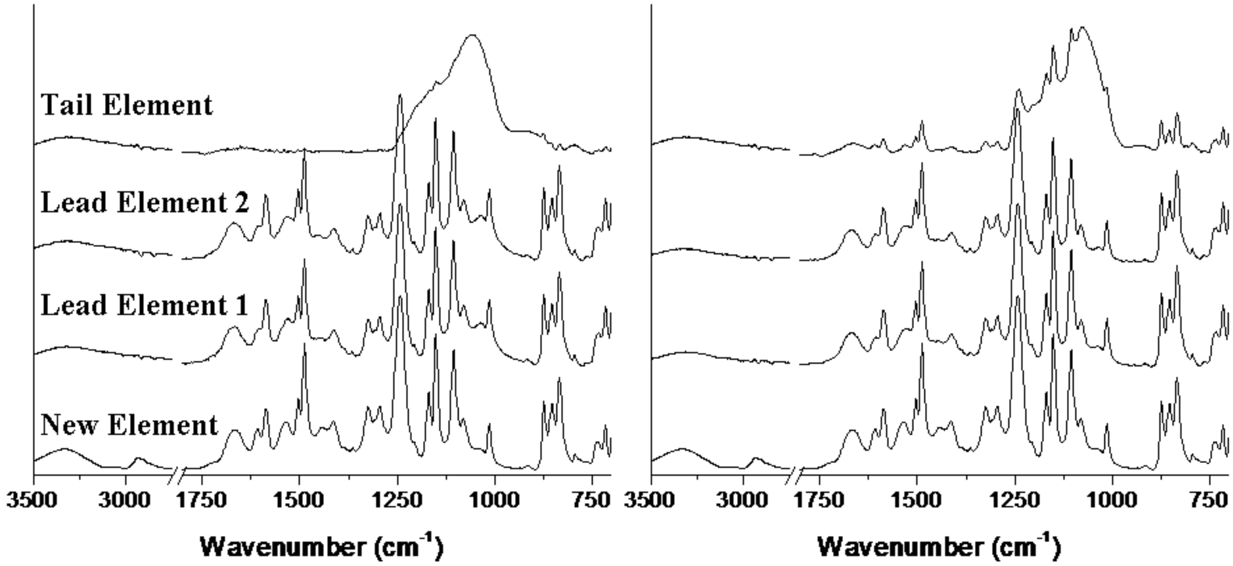


Figure 8.16. Fourier transform infrared spectroscopy (FTIR) spectra of LFC3 elements retired from MU 2 operated with cartridge-filtered YMC water (Alternative 22) at normal flux/recovery (NFR); (a) original elements and (b) surface precipitate removed elements by scraping with a soft plastic spatula. Y-axis on the graphs presented is “absorbance”.

8.6 YMC and MODE, Chlorination of Polyamide Structure

The presence of an amide II peak at 1,540 cm^{-1} in the FTIR spectra for the virgin Hydranautics LFC membranes used in the round 2 high recovery array tests indicates the polyamide functional, thin film, surface layer is a fully aromatic polyamide as shown in the top structure in Figure 8.17. As shown lower in this same figure, attack by free chlorine can result in either ring chlorination or chlorine substitution in the amide group of the polyamide polymer chain. Ring chlorination is evidenced by a decrease in the C=C ring vibration peak at 1,610 cm^{-1}, whereas proton substitution with chlorine in the amide group causes a decrease in the (amide II) N-H bending peak at 1,540 cm^{-1}. Figure 8.18a illustrates the spectra change seen in Hydranautics ESPA2 membranes operating in the Round 1 low recovery apparatus study due to both ring and amide group chlorination. Comparable levels of chlorination were seen in all membranes operated in the low recovery apparatus in both rounds 1 and 2. Chlorine substitution into the polyamide polymer is masked when materials build-up on the surface of the membrane. Therefore, to investigate the degree of chlorination in the round 2, high recovery arrays it is best to consider the FTIR spectra for elements in the array experiencing the least accumulation of particles on the membrane.

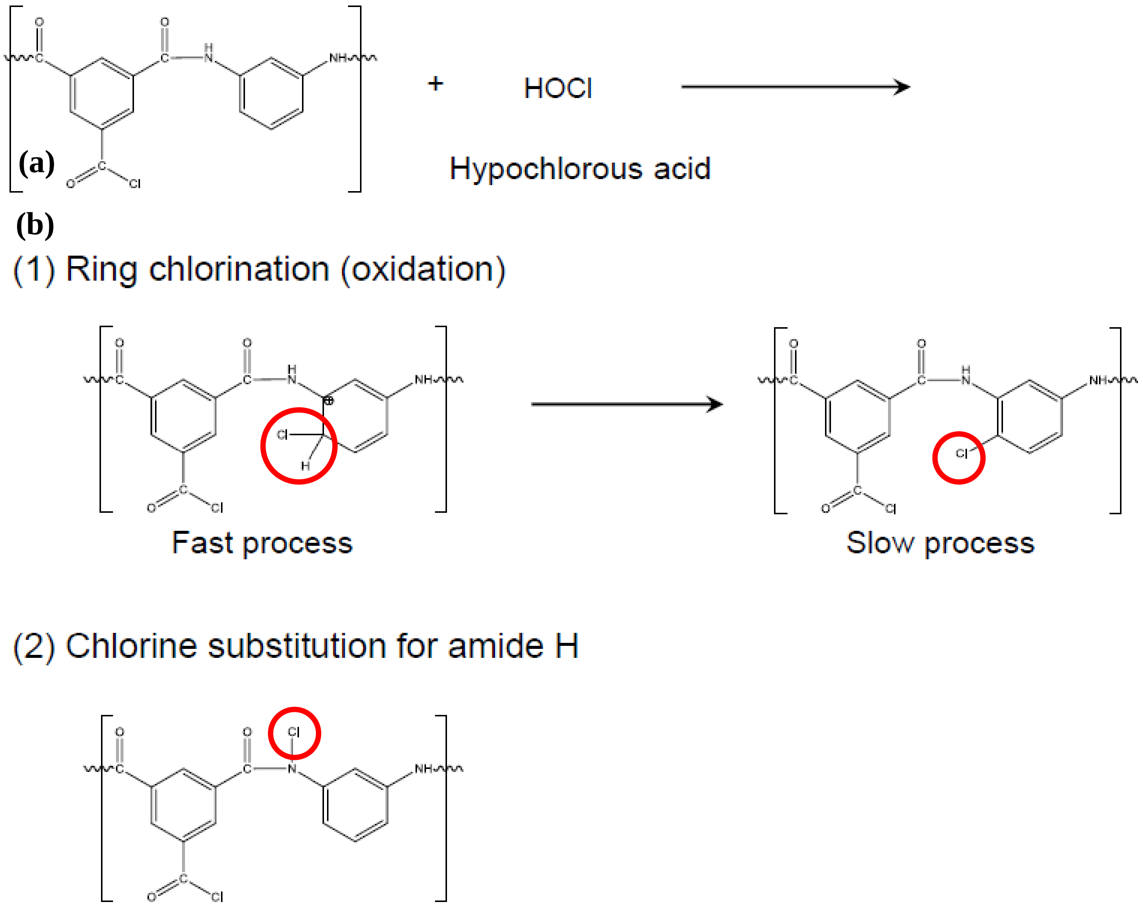


Figure 8.17. (a) The polyamide functional (thin film) surface layer, a fully aromatic polyamide and; (b) the ring chlorination (1) or chlorine substitution (2) in the amide group of the polyamide polymer chain are illustrated via attack by free chlorine. The chlorine substitutions are highlighted by red circles.

Consequently, the membranes in the array receiving MF pre-treated YMC water are shown in Figure 8.18b. In this figure it can be seen that despite ring and amide chlorination taking place in both lead (vessels 1 and 2, element 1) and tail (vessel 3, element 7) membranes, the degree of chlorination is greater in elements at the front of the array chain. To the degree that surface accumulation of materials did not make the determination impossible, this same decrease in chlorine substitution from lead to tail elements was seen in all arrays operating on both YMC and MODE water.

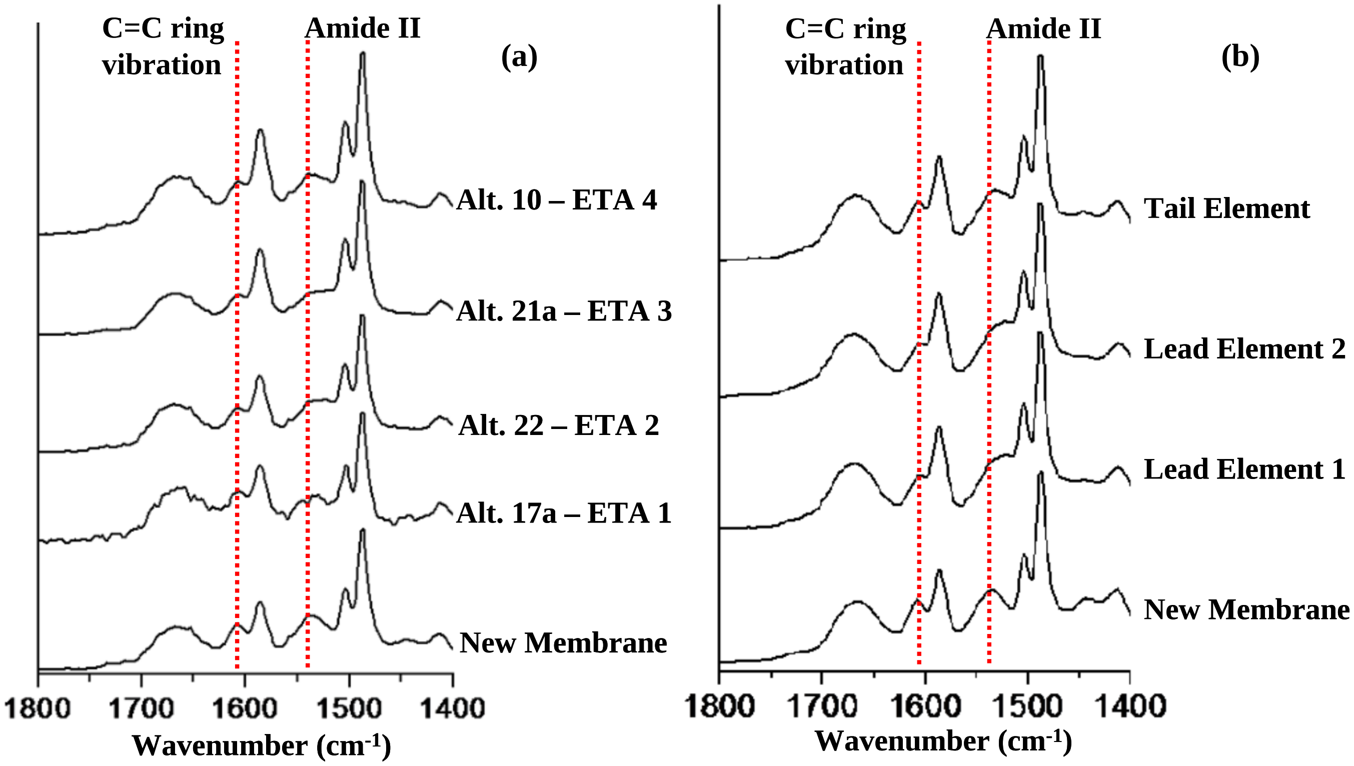


Figure 8.18. Fourier transform infrared spectroscopy (FTIR) spectra changes seen in (a) Hydranautics ESPA2 membranes operated in the Round 1 low recovery apparatus study and (b) Hydranautics LFC3 membranes operated in the Round 2 Phase 1 (Alternative 21a – MF treated YMC water) high recovery apparatus study due to both ring and amide group chlorination. Y-axis on the graphs presented is “absorbance”.

8.7 Summary of Primary Autopsy Results

Comparing the post-mortem results for membranes treating partial lime softened MODE water (Alternative 10) and microfiltered MODE water (Alternative 17), the following general conclusions can be drawn: i) deposition of polysaccharides (indicative of general biofouling) is much greater with Alternative 10 than Alternative 17; ii) deposition of inorganics is greater for Alternative 10 and for both alternatives is dominated by aluminum silicates (clays) and silicon oxides with traces of iron; and iii) palmitate deposits (indicative of degraded organic tissues) are significant on Alternative 10 and slight on Alternative 17. The autopsy results suggest that YMC water leads to less deposition of material on the membrane surface than MODE water, but this result is not conclusive since the YMC water alternatives operated for a significantly shorter duration than the MODE water alternatives. For the YMC water pre-treatment alternatives, MF versus CF, there was significantly greater material build-up with CF pre-treatment, particularly on the tail element in the high recovery array. Finally, for both source waters and all pre-treatment alternatives, the low recovery, single element testing showed chlorine substitution (both ring and amide group) with all membrane types evaluated. In the high recovery membrane arrays (Round 2), the chlorine substitution was evident in both lead and tail elements, but decreased from lead to tail element.

9. DISCUSSION OF RESULTS

Alternative Water Sources

Two distinct water sources, both unique to the Yuma region, were selected for this research program; the Main Outlet Drain Extension (MODE) water – pumped agricultural drainage from the Wellton-Mohawk Irrigation & Drainage District (WMIDD) – and brackish groundwater conveyed by the nearby Yuma Mesa Conduit (YMC), which collects agricultural drainage pumped from the Yuma Mesa and Yuma Valley. There were specific concerns with each water source on the basis of historical data and the characteristics of the source. The MODE is an open canal. Throughout the study, complications related to this feature of the source were experienced. These complications were both due to environmental and artificial events, such as severe storm events and agricultural usage and diversions on the canal (e.g. from DPOC to MODE), which changed the water quality in the canal. The severity of the event, for example the change in the flow rates, determined the intensity of the water quality change. Furthermore, MODE water had a higher fouling potential (than the YMC alternative) due to higher levels of particulate and organic matter. The average TOC level was 2.4 mg/L through the research project. The MODE water is also susceptible to annual fluctuation in the temperature. The biological activity in the MODE canal affects both organic and inorganic contaminant levels. Concentrations of iron and manganese during the research were up to 0.15 and 0.3 mg/L, respectively, which were much higher than expected prior to the initiation of the study. Fluctuation of TDS was a final factor to be considered with MODE as a water source. All of these issued notwithstanding, MODE was a more reliable water source in terms of consistent availability during this research study compared to the YMC alternative. There was only one extended MODE water outage (due to annual canal cleaning) during the study period.

On the other hand, the YMC is a closed pipe conveyance and was considered as an alternative water source for a possible operation of YDP. The TDS concentration of YMC water ranged from 1,400-1,700 mg/L, and its particulate and organic matter concentrations were lower than those for water in the MODE. The average TOC level was 1.0 mg/L through the research project. However, the YMC was expected to contain elevated levels of iron and manganese that required special removal techniques, such as greensand or conditioning on the silica sand, prior to RO treatment. Nevertheless, the main problem that became evident with using the YMC as the possible water source for YDP operation turned out to be its availability during testing. The YMC's primary function is to serve as an operational tool to help Reclamation manage the salinity of the lower Colorado River, thus enabling the United States to meet requirements to Mexico (IBWC Minute No. 242 assurances) regarding the quality of water delivered. As a result, at some times during the year, flows in the YMC are diverted to the south rather than the north, which affected the availability of YMC flows for testing at the WQIC. At times during testing, the limited availability of YMC water at the WQIC affected operations.

For both the MODE and YMC waters, pretreatment options were identified and tested, which would provide a water quality for satisfactory operation of downstream RO units.

Alternative Pretreatments

There were four different alternative pretreatment trains, two on each water source, tested during this research study. The main purpose of all the alternatives was to remove the particulate matter with high efficiency and decrease the concentrations of iron and manganese to levels that are harmless for RO operation. A common unit operation for all the alternatives was gravity filtration. All gravity filters were initially composed of silica sand and anthracite. However, greensand was installed on Alternative 22 (YMC water with DMGF and CF) to evaluate its relative removal efficiency for iron and manganese compared to manganese-conditioned silica sand (which was initially installed for both YMC alternatives). The installation of cartridge filters, as a precautionary particulate removal technique on this alternative, also provided enough data to compare the efficiency of cartridge filters with microfiltration. Alternatives 17a and 21a had microfiltration downstream of gravity filters to boost the removal efficiency of particulate matter, whereas Alternative 10 removed not only particulate matter, but also divalent cations and alkalinity via lime-softening.

No significant difference was monitored between the greensand and silica-sand alternatives on YMC water in terms of turbidity removal and iron and manganese removal.

However compared to cartridge filtration, microfiltration was more efficient at removing particulate matter, including iron and manganese, and providing a sustainable and reliable operation on treating YMC water. The pH played an important role in determining the fouling rate of cartridge filters (lower pH increased the fouling rate) and this issue needs to be studied in more detail. A cost/benefit analysis should provide enough data to decide which filtration technique will be more cost effective to apply when treating YMC water. Twenty-in long 1-μm CFs and 10-in long 5- μm CFs performed better than 10-in long 1-μm CFs in terms of fouling rate. The explanation for this may be in differences in the manufacturing, in different hydraulic flow paths in the two size elements with the same pore size, or some other reason yet to be identified. Regardless of the reason, if CF is recommended for use, then on-site testing of the actual, full-size CF species is advisable as extrapolation from performance of CFs with other pore size and vessels may lead to large errors. A sustainable run was achieved for the East Pall MF unit on YMC water operating at a flux of 90 gfd and above. Regular biweekly citric and bleach EFMs kept the TMP low without any need for CIPs. However, based on Pall Corporation recommendations and the observed behavior of the West Pall MF unit operating on MODE water, scheduled semi-annual or similar duration CIPs are advised for sustainable operation.

Considering MODE water pretreatment, Alternative 10 (lime-softening and gravity filtration) removes divalent cations up to 95%. PS 1 was also successful in removing substances that might possibly cause scaling or fouling problems in RO treatment, such as iron, manganese and silicon dioxide by 75%, 95% and 46%, respectively. More than 80% of the total alkalinity and almost all bicarbonate were removed, so this alternative would have the lowest acid demand if pH adjustment is required. Examining the performance results of the RO operations, we can conclude that lowering the feed pH probably down to ~6.0 will be necessary for a sustainable operation. Alternative 10 at feed pH of 6.0 compared to a feed pH of 6.8 requires an additional 6.5 mg/L of 100% sulfuric acid. This, at $220/ton (in February 2011 dollars) and 80% recovery, adds $2.40/af to cost of RO product water. However, Alternative 17a at feed pH of 6.0, compared to pH of 6.8, requires an additional 138 mg/L of 100% sulfuric acid and adds $52/af to the cost of RO product water with the same assumptions. The difference between the costs is almost 22 fold. Nonetheless, the lower WTC and lower STC values of Alternative 10 versus 17a RO units would also have to be accounted in the choice of MODE water pretreatments.

Another important issue with Alternative 17a was the performance of microfiltration unit. West Pall MF unit operated at a flux of 66 gfd for over six months successfully. However, the performance deteriorated during summer 2011 probably due to a combination of reasons, such as higher iron and manganese concentrations, diversions of DPOC water to the MODE canal, higher TOC levels during the summer and the effect of operating pH on fouling rate. A higher MF fouling rate was observed with lower pH (~5.7-5.8) compared to a feed pH of 6.8. Even though it is difficult to say what the real reason for this behavior is, a suggestion would be to move the acid injection to after the filtration units to protect their sustainable operation. (This however begs the question if the materials causing the increased MF fouling rate seen at lower pH would then foul the RO elements if the acid injection point were moved to between the MF and RO units. Analyzing the results of the MF cleaning and autopsy studies conducted in early 2012, it could be concluded that the stronger CIPs performed during the cleaning study were partially successful and could likely be further improved to obtain a better cleaning efficiency. The EFM efficiency could likely be improved, as well, (e.g. by adding a soaking period, using different chemicals or different concentrations of the same chemicals, or passing the cleaning solution through the fibers' pores rather than just recirculating on the outside of the fibers as it was done during the cleaning study . These parameters are extremely important not only for the operation point of view but also during the economic analyses.

Membrane Performances

Four ETA units (ETAs 1-4) were used for this study and seven different types of membranes over two different rounds were evaluated in each unit. The ETAs operated at an average 15 gfd and approximately at 13% water recovery during the testing. Round 1 lasted almost 3000 hours (4 months) and tested Toray TML 10, Koch ULP, and Hydranautics LFC3 and ESPA2 membranes. Round 2 lasted more than 3500 hours and tested DOW BW30 XFR, and CSM FE and CE membranes. Toray TML 10 was kept the same for both rounds for the purpose of direct comparison. Comparing the TML 10 performance for the same alternative between rounds, there was a considerable difference in the initial WTC values for YMC alternatives, whereas the initial STC and *Ce* values for TML 10 varied less between rounds. This suggests that either the water quality of the YMC varied substantially between Round 1 and Round 2 or (and less likely) that there was considerable variation between the individual membranes in the batch obtained from Toray, the manufacturer of TML 10. Assuming a water quality change caused the difference in performance observed between rounds, then it is more correct to normalize the performance of each membrane against the TML 10 performance for its respective round, rather than directly comparing the values of a performance metric for membranes used in different rounds. Therefore, in the following discussion not only are the absolute values of performance metrics compared for the membranes, but the normalized (against TML 10 value) performance metrics are compared.

Even though the performance of a single membrane type varied as a function of the pretreatment alternative, the relative performance of the different membrane types was not a function of the pretreatment alternative. That is to say that if one membrane type exhibited the lowest WTC among the membrane types for one alternative, then it generally exhibited the lowest WTC for all alternatives even though the value of its WTC might vary between alternatives.

In selecting a membrane type, there is a clear trade-off between WTC and STC, since membranes with high WTCs also tended to have high STCs. Thus, a choice needs to be made on the relative weighting to put on the value of high specific flux (i.e., lower energy use per unit of water produced) versus high salt rejection (i.e., higher blending ratio potential). Hydranautics LFC3 had the lowest WTC but also had some of the lowest STC values of all the elements tested in all alternatives. In addition, it exhibited equal or less variable operation (meaning least change in WTC and STC over the duration of the study) compared to the other types of membrane, regardless of the pretreatment method. LFC3 was the only membrane that did not show any initial decline on Alternative 10 during the ETA testing. In contrast, Koch ULP had the highest WTC, but also the highest STC values among the membranes tested regardless of the alternative. Although each membrane’s initial values were normalized against the Toray TML10 values, the CSM CE and TML 10 had nearly equal specific fluxes to the ULP and each exhibited better salt rejection characteristics than the ULP (Table 9.1). DOW XFR and Hydranautics ESPA2 also had relatively high WTC values.

Table 9.1. WTC and STC comparison for all membranes tested during Round 1 and Round 2 element testing studies.

Water Transport Coefficient Comparison

	Round 1							
	Absolute Values[1]				Normalized Values[3]			
	Alt. 10	Alt. 17a	Alt. 21a	Alt. 22	Alt. 10	Alt. 17a	Alt. 21a	Alt. 22
Toray TML10	10.69	11.11	11.78	11.20	1.00	1.00	1.00	1.00
Hydranautics LFC3	7.71	7.35	6.65	6.68	0.72	0.66	0.56	0.60
Hydranautics ESPA2	10.33	7.37	8.45	9.69	0.97	0.66	0.72	0.87
Koch ULP	13.90	7.90	11.84	11.13	1.30	0.71	1.01	0.99

	Round 2							
	Absolute Values[1]				Normalized Values[3]			
	Alt. 10	Alt. 17a	Alt. 21a	Alt. 22	Alt. 10	Alt. 17a	Alt. 21a	Alt. 22
Toray TML10	11.13	11.00	11.26	9.67	1.00	1.00	1.00	1.00
CSM FE	8.01	8.70	8.94	8.69	0.72	0.79	0.79	0.90
CSM CE	11.15	11.08	10.86	9.79	1.00	1.01	0.96	1.01
DOW XFR	9.17	9.68	9.91	9.00	0.82	0.88	0.88	0.93

Salt Transport Coefficient Comparison

	Round 1							
	Absolute Values[2]				Normalized Values[3]			
	Alt. 10	Alt. 17a	Alt. 21a	Alt. 22	Alt. 10	Alt. 17a	Alt. 21a	Alt. 22
Toray TML10	0.032	0.050	0.056	0.055	1.00	1.00	1.00	1.00
Hydranautics LFC3	0.023	0.037	0.031	0.047	0.72	0.75	0.55	0.85
Hydranautics ESPA2	0.029	0.045	0.042	0.064	0.91	0.91	0.75	1.16
Koch ULP	0.108	0.090	0.046	0.073	3.38	1.82	0.82	1.33

	Round 2							
	Absolute Values[2]				Normalized Values[3]			
	Alt. 10	Alt. 17a	Alt. 21a	Alt. 22	Alt. 10	Alt. 17a	Alt. 21a	Alt. 22
Toray TML10	0.042	0.053	0.060	0.053	1.00	1.00	1.00	1.00
CSM FE	0.018	0.030	0.040	0.037	0.43	0.57	0.67	0.70
CSM CE	0.055	0.077	0.072	0.067	1.31	1.45	1.20	1.26
DOW XFR	0.015	0.024	0.042	0.033	0.36	0.45	0.70	0.62

[1] $\times 10^{-12}$ m/s.Pa

[2] $\times 10^{-6}$ m/s

[3] Absolute values are normalized to Toray TML10 values. Toray TML10 was the only common membrane in both rounds.

When comparing effect of pretreatment and water type on membrane performance, Alternative 10 had the highest fouling potential among all the alternatives based on the autopsy results. Nevertheless, it was the alternative that led to a very low salt passage regardless of the membrane type, with the exception of the Koch ULP. On lime-softened gravity-filtered MODE water alternatives, a sudden initial drop in WTC was followed by a stable run for all the membranes tested. Low and stable STC values are the advantages of this alternative.

Effect of pH

MU and ETA RO performances demonstrated a strong dependence on pH for both MODE and YMC waters. Feed pH of 6.8 causes an increase in STC values, salt passage and B/A values as observed during the first three months of Round 1 ETA 4 testing. However, when the pH was decreased (by a log unit) to reverse the rising STC values, a decline in WTC values at pH values of 5.8 or less was experienced. The same initial drop in WTC values was detected for Round 2 membranes. All four WTC values in ETA 4 during Round 2 partially recovered when the feed pH was increased to 6.0 and they remained stable at 15 gfd, until a decline in WTC accompanied the flux increase to 18 gfd. A very minor increase in STC and B/A values was detected while operating at the feed pH of 6.0 for all membranes regardless of the flux. The same behavior for WTC and STC values was detected during MU 4 operation, as well. Therefore, the best operating pH range for Alternative 10 was at a feed pH of 6.0 to 6.2 and a reject pH of 6.3 to 6.5 based on ten months of MU 4 operation. The expected long-term WTC value for LFC3 membranes is about 6×10^{-12} m/s.Pa based on the observations of ten months of MU 4 operation. Since the fouling rate observed during the testing was high, the estimated membrane life may be lower than the manufacturer suggested 5 years, but the feasibility of periodic membrane cleaning to increase membrane life was not fully evaluated in this study. Alternative 10 offers a very easy transition from the existing treatment schematic, i.e. CA membranes, to the new one with PA membranes. The lowest detected WTC value during this testing was still almost 50% higher than the ones for CA membranes.

On the other hand, LFC 3 membranes fed MF treated MODE water (Alternative 17a) showed higher WTC values than with partially lime softened water. However, rapidly increasing

STC values raised questions as to whether or not this could be effectively mitigated with improved pH choice and control. MU 3 RO performance demonstrated a strong dependence on pH. A reject pH greater than 6.0 caused an increase in salt passage. Salt passage increased significantly at feed pH 6.8 (reject pH 7.3), at feed pH 5.9-6.0 (reject pH 6.3), and again (although only for stage 2) at feed pH 5.6-5.7 (reject pH 6.1). pH values less than 5.8 caused a decline in WTC values for both stages. The WTC values decreased about 15% during the one month operation at feed pH 5.5 (reject pH 5.8). Therefore, the best feed pH range is 5.8 to 6.0 in terms of maintaining high WTC values and low salt passages.

MU head and tail elements behaved differently to feed water pH changes. For example, the head elements, including the membranes tested in the ETAs, first showed a jump in their STC values when the feed pH was decreased. Then a slow decline followed this jump. This behavior was very clear for the units running on YMC water, both MUs and ETAs, and especially for the elements in the first stage (Vessels 1 and 2). Hence, the elements running on ETAs had the same type of reaction regardless of who the manufacturer of the element was. It appears that this pH change effect loses its magnitude as it moves down the MU unit. The second stage elements did not show the same drastic reaction. In fact, the jump following the pH adjustment was hardly, if at all, observed in the tail element of the MU units. Since no pH adjustment was performed during Round 1, no comments can be made about the response of membranes tested in Round 1.

The effect of the operating pH was a little different for the MODE water alternatives. In ETA 4 and MU 4, the RO units running with lime-softened gravity-filtered MODE water, no clear effect was observed for the lead elements, including all the ETA 4 membranes, when the feed pH was adjusted. A slight jump was noticed when the feed pH for the MU 4 was increased from 5.6-5.7 to ~6.0. On the other hand, for the RO units running on gravity-filtered and microfiltered MODE water, MU 3 and ETA 1, the jump was not as significant as the ones observed in YMC alternatives, but the decline following the jump was quicker and more effective in taking the STC below where it was prior to the pH adjustment. The effect on the lead elements, including all the membranes tested in ETA 1 during Round 2, was milder compared to the LFC 3 elements installed in the second stage of MU 3. This was obvious especially during the last month of the MU 3 run (December 2011). While the STC value for the elements 1, 2 and 3 of the second stage (Vessel 3) was stabile during that month, both of the STC values for the elements 4-6 and element 7 were increasing. This is probably due to the effect of pH on a constituent of water that concentrates through the MU unit. The STC values for the elements in Stage 1 (Vessel 1 and Vessel 2) and for the lead elements of Stage 2 (Elements 1-3 of Vessel 3) stabilized, whereas the increase for the tail elements of Stage 2 continued.

Based on the foregoing, interstage acid injection might be advantageous for a sustainable RO operation, because RO operation appeared stable for two months at feed pH of 5.6-5.7 (reject pH 6.1), while stage 2 salt passage increased at the rate of ~1% per month. With a feed pH 5.5-5.6 (reject pH 5.9), as tested during the last days of operation, stage 2 STC values decreased immediately. This suggests using a feed pH of 5.6-5.7, and then an interstage acid injection to force a stage 2 reject pH of 5.9, might well allow the high WTC (relative to Alternative 10) to be maintained without incurring rapidly increasing stage 2 STC values.

High and stable or rising WTC values were observed for both YMC water alternatives tested at feed pH of 6.8. Alternative 21a had slightly higher values than Alternative 22. Slight increases of STC values in the ETA membranes and the first stage elements for both MU units were monitored at the feed pH of 6.8. However, the rate of increase was higher on the second stage elements for YMC alternatives, unlike the MODE alternatives. On Alternative 21a, decreasing the feed pH to 5.8-5.9 (reject pH of 6.3) dropped the STC values significantly, but also dropped the WTC values for both stages. The feed pH of 6.0-6.1 (reject pH of 6.5) helped to stabilize the STC values. Not enough data was collected to make a clear comment about the long-term effect of this pH on WTC values. For Alternative 22, the same feed pH of 6.0-6.1 (reject pH of 6.5) dropped the WTC values as well as the STC values. Therefore, the best operating pH for YMC alternatives lies in the range of feed pH 6.1 and 6.8, but further study would be required to fine tune this range and to determine if interstage pH adjustment would be advantageous for YMC water desalination. It is clear that a lower pH (5.8-6.0) causes higher fouling rates with YMC water based on the MU, ETA and CF results.

A pH decrease on YMC water alternatives caused a jump in STC values. At the same time, the cartridge filters' fouling rate increased significantly with the lower operating pH. The reason for the effects observed in the lead elements might be the same reason for the high fouling rates of the cartridge filters. However, whatever was fouling the cartridge filters did not have any significant and observable effect on the East Pall MF unit. The TMP level and the rate of increase in TMP for this unit stayed almost the same regardless of the operating pH. This shows that the fouling material probably has a particle size larger than 0.1µm, which is the smallest size of the cartridge filters. Furthermore, it is removed off the MF filter almost completely with the filter's backwash cycles.

RO Operation at High-Flux and High-Recovery

High flux and high recovery of MODE water were tested during this study in two units, i.e. ETA 4 and MU 1. ETA 4 was operated on partial lime-softened water and MU 1 on MF treated water. The flux increase from 15 to 18 gfd (without any other operational changes) on ETA 4 running on Alternative 10 caused decreased WTC values for all membrane types tested during Round 2; while no significant effect on STC values was detected. MU 1 also had a period of high-flux operation during Round 2 Phase 2 testing. With similar behavior to ETA 4, MU 1 WTC values were slightly lower with the increased flux, especially on Vessel 3 (second stage), and no clear differences were observed in the initial STC values and the STC trends between the high-flux and regular-flux MUs. Increasing the recovery on MU 1 after almost one and a half months of high flux operation resulted in a 20% step-change increase in WTC values of the first stage and STC values for both stages. The STC values came down right after that but increased again later during the testing.

After completing the trial with the four round 2 membranes originally specified in the CRADA, two DOW XFR and two Toray TML membranes were installed in ETA 4 Vessel 1 and Vessel 2, respectively, and it continued to operate on partial lime-softened water (Alternative 10). The purpose was to test the high-flux operation on Alternative 10 with the same membranes that were being tested in MU 2 after it was moved from YMC water to MODE water. Interestingly in ETA 4, the DOW XFR membranes showed an increase in WTC values while the

TML10, like the LFC 3 membranes, had a decline. Both membranes' initial WTC values were lower than the ones tested during Round 1 on Alternative 10. Even by the end of the testing, the values were still lower than those at regular flux. The STC values were very close to the ones monitored during the regular-flux testing. Hence it is concluded that high-flux high-recovery operation is feasible with the appropriate operating pH, although a slightly lower WTC value will be experienced.

MU Performance with Alternative Membranes

As was mentioned earlier, the best operating pH range for Alternative 10 was at a feed pH of 6.0 to 6.2 and a reject pH of 6.3 to 6.5 based on the MU 4 data. Two months operation of MU 2 (on Alternative 10) at feed pH of 6.0 and reject pH of 6.3 and 3 weeks at feed pH of 6.2 and reject pH of 6.5 corroborated this selected operational pH range using two alternative membranes, Toray TML10 in the first stage and DOW XFR in the second stage. In fact, while TML10 WTC values were decreasing in the first stage, DOW XFR showed an increase in the second stage. Comparing this observation with the one in ETA 4 Round 2 Phase 2, the authors saw that regardless of the location of the membrane and the flux, WTC values for XFR increased initially while TML10 decreased. Again regardless of the location and the flux of the membrane, the same STC values were observed in both ETA 4 and MU 2 units for both of the membranes. The observations indicate the DOW XFR is the preferred membrane (relative to LFC3 and TML10) for desalting the partial lime softened MODE water.

10. RECOMMENDATIONS FOR FURTHER STUDY

Extended Testing of Chosen Alternative

Because the YMC, as operated and configured, suffered from flow disruptions and the MODE water alternatives operated with success, if a cost/benefit analysis determines that MODE water treatment is attractive, then running two MODE alternatives with modifications is recommended. This alternative testing should last long enough to analyze the effects of seasonal variations. Alternative 10 operating at a feed pH of 6.0 to 6.2 and a reject pH of 6.3 to 6.5 should be tested for an extended period at regular-flux and at high-flux with high-recovery. Likewise, Alternative 17a should be tested for extended duration at feed pH of 5.6-5.7 and interstage adjustment to give an optimum reject to be determined during testing. (This optimum stage 2 reject pH will be below 6 based on this study’s results.)

If extended testing is undertaken, different locations for acid injection should be considered to improve each unit operation’s efficiency. For example, moving the acid injection or adding another one after the MF unit on Alternative 17a should help to obtain more sustainable MF operation as well as lower STC values while keeping the WTC values stable. Comparison of different types of microfiltration units should be considered for this alternative, as well.

MF and RO Cleaning Tests

Because the MF unit on Alternative 17a showed operational variations, its performance deteriorated late in the CRADA study, and a post-CRADA cleaning study showed significantly improved cleaning could be achieved; a more appropriate cleaning scheme (both EFM and CIP) should be tested for sustainable operation of this unit. Permeate recirculation, higher concentrations of cleaning chemicals, different cleaning chemicals (including Iron-Off), and soaking periods for both EFM and CIP cleanings should be considered to improve the cleaning efficiencies.

Because the WTC values on Alternative 10 decreased near the end of testing and autopsies on Alternative 10 membranes showed significant material build-up, cleaning studies on RO units on this alternative should be conducted. In addition, if extended testing of Alternative 17a shows the STC increase persists despite improved pH adjustment and MF performance, a cleaning study should also be conducted on this train.

RO on Cartridge Filter Testing

Because the cartridge filters were tested without any downstream units and because they were proven to operate efficiently on YMC water following gravity filtration, they should be tested also on MODE water alternatives. RO units should be tested as well to compare the fouling potentials on different sizes of cartridge filters. The flux of cartridge filters needs to be experimented with to find out which works best. As a control unit, one RO should be tested without any upstream filtration other than gravity filters (no MF and no CF).

Further Investigation of Operating pH

Because the pH effects were so pronounced and affected different pretreatment types differently, and because the chemical reactions and components causing the effects were not identified with any certainty, a more detailed study is needed for pH. Detailed organics analysis and lab experiments identifying the fouling rates at different pHs and the chemical compounds behind it should be carried out, particularly for MODE water.

Economic Analysis

As is planned, a detailed economic analysis for the alternatives tested with the identified operating conditions should be performed.

REFERENCES

Amjad, Z. Applications of Antiscalants to Control Calcium Sulfate Scaling in Reverse Osmosis Systems. 1985, Desalination, 54, pp. 263-276.

Antony, A., How Low, J., Gray, S., Childress, A.E., Le-Clech, P., Leslie, G. Scale formation and control in high pressure membrane water treatment systems: A review. 2011, Journal of Membrane Science. 383, pp, 1-16.

Baker, R. W. *Membrane Technology and Applications*. Second edition. 2004, John Wiley & Sons, Ltd, Chichester, UK.

Benjamin, M.M. Water Chemistry. 2002, New York, New York: The McGraw-Hill Companies, Inc.

Brahims, E., et al. Microfiltration system as a pretreatment for RO units: Technical and economic assessment. 1997, Journal of Desalination. Vol. 109, No.2, pp. 165-175.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G. *Water Treatment: Principles and Design*. 2005, Hoboken, New Jersey: John Wiley & Sons, Inc.

Fritzmann, C., et al. State-of-the-art of reverse osmosis desalination. 2007, Journal of Desalination. Vol. 216, No. 1-3, 5, pp. 1-76.

Hargate, A.C. and W.R. Knocke, Assessment of Fate of Manganese in Oxide-Coated Filtration Systems. 2001, J. Environ. Eng., 127:10, 1132-1138.

Hydranautics Design Limits. 2011, URL http://www.membranes.com/docs/trc/Dsgn_Lmt.pdf

Hydranautics Element Specifications Sheets for ESPA-2450. 2011, URL http://www.membranes.com/docs/2inch/ESPA%20-%202540.pdf

Knocke, W.R., L. Zuravnsky, J.C. Little and J.E. Tobiason, Adsorptive Contactors for Removal of Soluble Manganese during Drinking Water Treatment. 2010, Journal AWWA, 102:8, 64-75.

Knocke, W.R., S. Occiano, and R. Hungate, Removal of Soluble Manganese from Water by Oxide-Coated Filter Media. 1990, AWWA Research Foundation, Denver, CO.

Merkle, P.B, W.R. Knocke, and D.L. Gallagher, Method for Coating Filter Media with Synthetic Manganese Oxide. 1997, J. Environ. Eng., July, 642-649.

Moody, C., Garret B., and Holler E. Pilot Investigation of Slow Sand Filtration and Reverse Osmosis Treatment of Central Arizona Project Water. 2002, U.S. Department of the Interior, Bureau of Reclamation, Science and Technology Program Advanced Water Treatment Research Program Report No. 90.

Moody, C., et al. Reverse Osmosis Treatment of Central Arizona Project Water for the City of Tucson. 2004, U.S. Department of the Interior, Bureau of Reclamation, Science and Technology Program Advanced Water Treatment Research Program Report No. 36.

Sincero, A. and Sincero, G. *Physical-Chemical Treatment of Water and Wastewater*, 2003, IWA Publishing, London.

Voros, N.G., Maroulis, Z. B., Marinos-Kouris, D. Salt and water permeability in reverse osmosis membranes. 1995, Journal of Desalination. Vol. 104, pp. 141-154.

LIST OF APPENDICES

Appendix A - Appendices for Introduction, Background and M&M