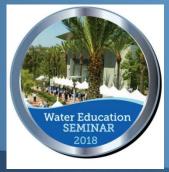
Maintaining Water Quality from Reverse Osmosis Systems in Advanced Treated Water Facilities

Presentation for





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The Membrane Technology Consultants



Orange County Water District















- 1. Introduction
- 2. Reverse Osmosis Basics
- 3. Reverse Osmosis Removal
- 4. Data Normalization
- 5. Monitoring RO Integrity
- 6. Pathogen Removal
- 7. Yucaipa Virus Testing Results
- 8. Summary



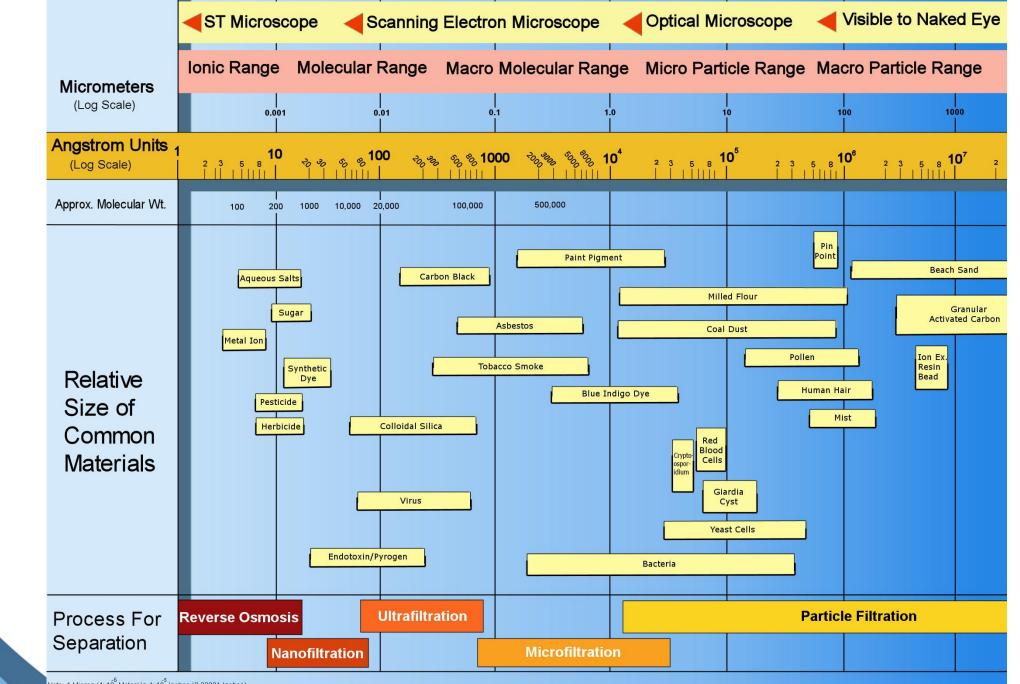






Introduction

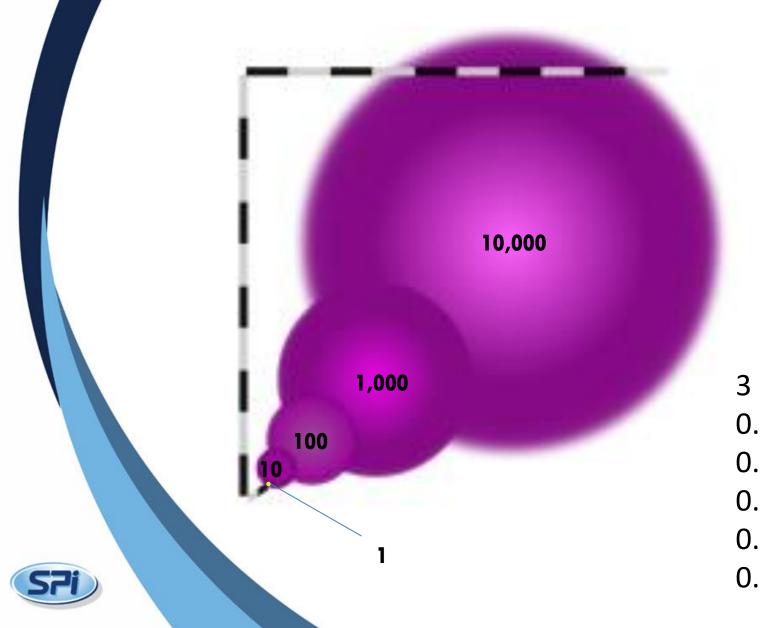




Note: 1 Micron (1x10⁶ Meters)≈4x10⁵ Inches (0.00004 Inches)

1 Angstrom Unit = 10 Meters = 10 Micrometers (Microns)

Volumetric Representation of Scale



Comparative Sizes

	microns = Cryptosporidium
.2	microns = smallest bacteria
.04	microns = virus
.002	microns = TOC
.001	microns = sulfate ion
.0002	e microns = sodium ion

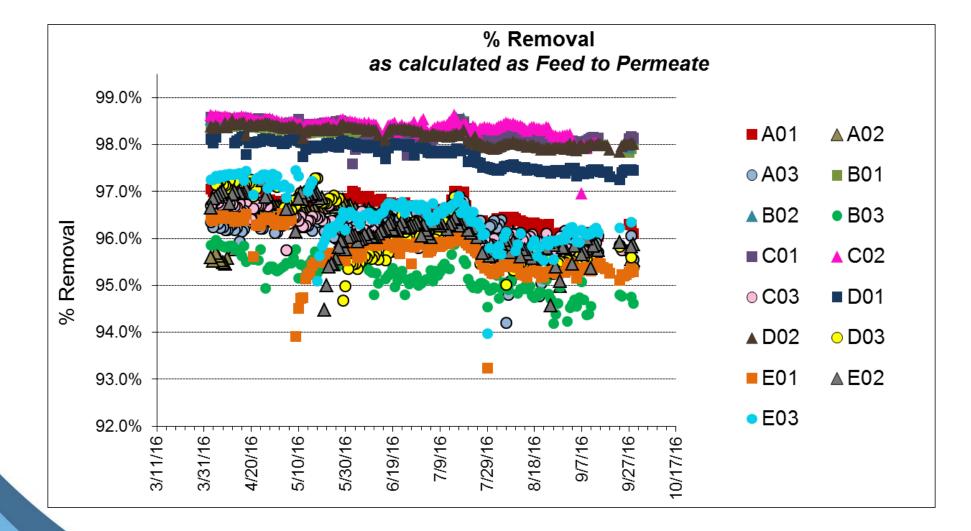
What are the Basics Reverse Osmosis?

- Removes constituents in water including:
 - Inorganic Ions (sodium, chloride, calcium, sulfate)
 - Total Organic Carbon (TOC)
 - Synthetic Organic Compounds (SOC)
 - Unregulated Constituents of Emerging Concern (CEC)
 - Personal Care Products
 - Pharmaceutical Compounds
 - Endocrine disrupting compounds
- RO permeate is essentially free of most contaminants of regulatory concern with the exception of:
 - Nitrosamines (NDMA)
 - 1,4-dioxane





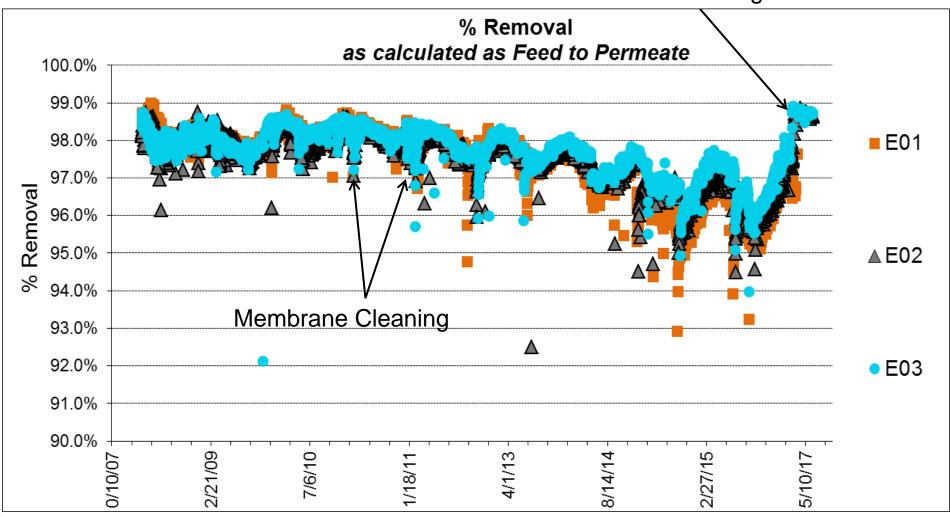
GWRS Reverse Osmosis Removal Performance (Trains A-E)



SZI

GWRS Train E Percent Removal 2007-2017 (Raw Data)

Membrane Change



SZI



RO Basics



RO Membranes

- RO membranes are non-porous.
 - Thin-Film Composite Membrane
 - Membrane is coated on the surface of a Polysulfone UF Membrane
 - Underlying non-woven support layer
- Thickness and Evenness of Membrane layer are important
- Pin holes are defects.
- Sealing of the membrane has improved over the years.
- Oxidants and improper cleaning can destroy the membrane



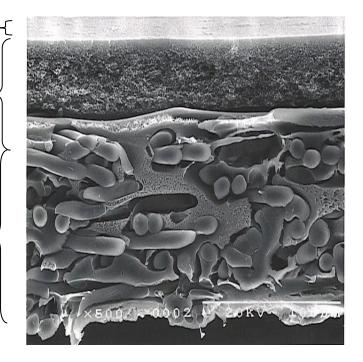


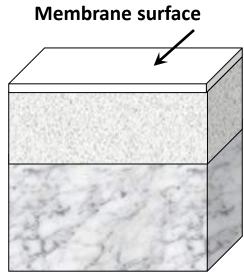
Thin Film Composite Membrane Cross Section

Polyamide 0.04 - 0.1 microns

Polysulfone 75 - 100 microns

Polyester Fabric 2000 microns







Reverse Osmosis Theory and Principals

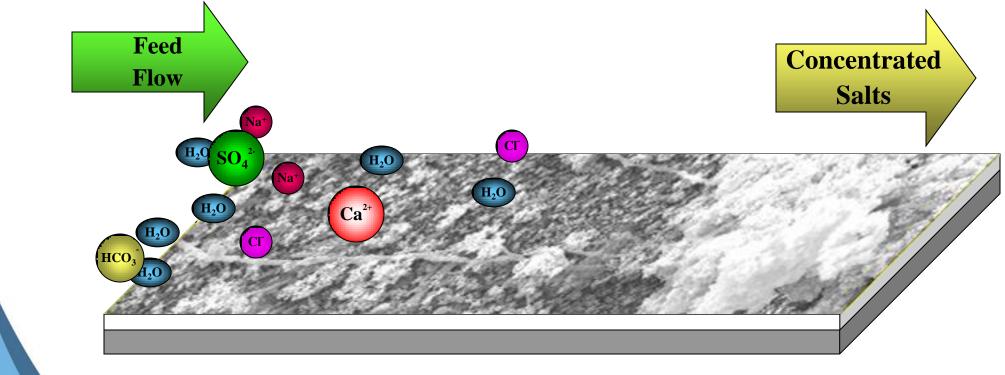
- Water and Salt pass through interstitial (molecular) spaces
- Solution-Diffusion Model is most commonly used
- Water Flow is controlled by the Net Driving Pressure (NDP)
 - NDP is the Average Pressure Differential minus the Osmotic Pressure
- Salt Flow is controlled by diffusion
 - Concentration Difference across the membrane.







RO Removal Mechanism = Solution-Diffusion



Permeate



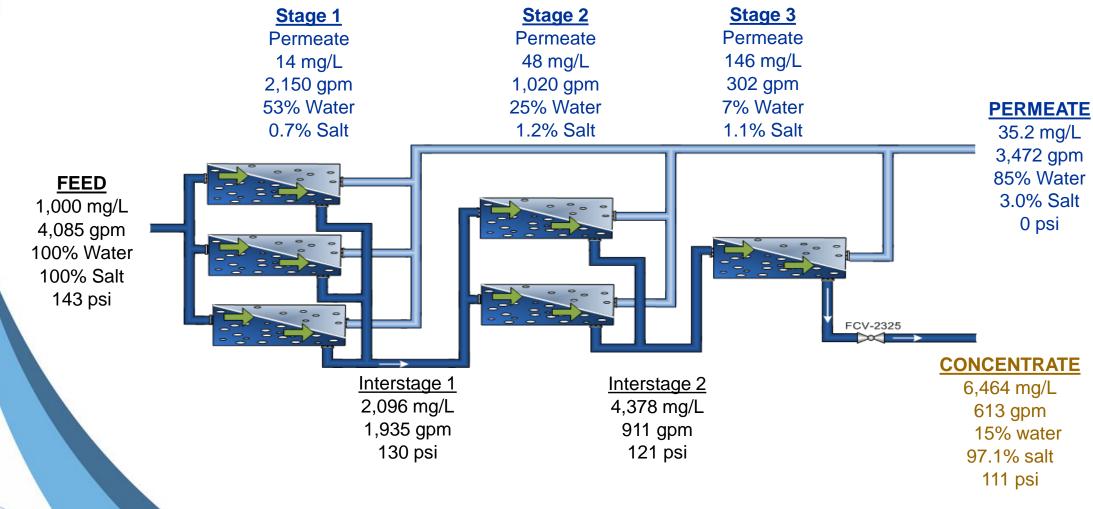
Practical Points about Reverse Osmosis

- Membrane Performance is local to the element under consideration.
- Osmotic pressure can be viewed as a threshold pressure that must be overcome to obtain flow.
- The flow of water through a membrane is a function of the localized net driving pressure
- The flow of salt through a membrane is a function of the localized concentration difference.
- The osmotic pressure increases as salts are retained, lowering the net driving pressure
- Increasing water temperature will decrease feed pressure and increase salt flow.



How are water and salts separated through a RO Unit?

77:49:24 ARRAY - 85% RECOVERY



All membranes are the same



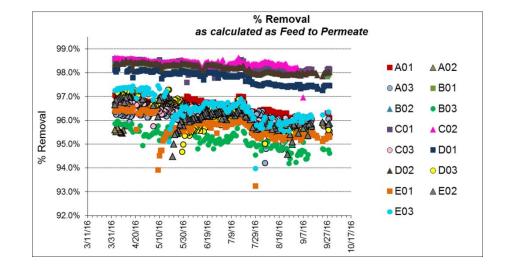
RO Removal



Train/Unit Rejection (Feed to Permeate)

% Removal =
$$\frac{C_F - C_P}{C_F} \times 100\%$$

where : C_F = Conductivity of Feed (μ S/cm) C_P = Conductivity of Permeate (μ S/cm)



Membrane Rejection (Avg. Feed to Permeate)

% Removal =
$$\frac{C_{FB} - C_P}{C_F} x 100\%$$

where : $C_{F} = \text{Log Mean Average Conductivity of Feed/Brine (<math>\mu$ S/cm) C_{P} = Conductivity of Permeate (μ S/cm)



Removal of Constituents by RO

	Feed mg/L	Permeate mg/L	% Rejection*
Ca ²⁺	93	0.01	100.0%
Mg ²⁺	24.9	0.01	100.0%
Na ⁺	214	6.38	97.0%
NH4 ⁺ (as N)	30.2	1.24	95.9%
Cl-	236	3.64	98.5%
HCO ₃ -	287.7	16.45	94.3%
SO ₄ ²⁻	298.5	0.48	99.8%
тос	11.1	0.18	98.4%
SiO ₂	23.7	0.10	99.6%
Total Nitrogen (as N)	33.5	1.53	95.4%
TDS	991	19.86	98.0%

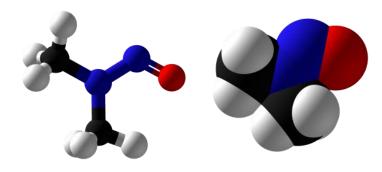
* System Rejection: 11gfd @ 85% Recovery



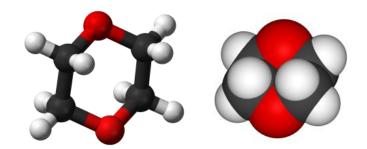
% Rejection =
$$\left(1 - \frac{\text{Permeate TDS}}{\text{Feed TDS}}\right) \times 100$$

Chemical Constituent Factors that Effect Membrane Rejection

- Molecular Weight (size)
 - higher weight, higher removal
- Ionic Charge (valence)
 - Higher charge, higher removal
- Molecular Structure (shape)
 - Nitrogen Compounds have higher diffusion (e.g. ammonium, (MW 17,+1), NDMA (MW 74)) and can "align" with polyamide membranes
 - 1,4-dioxane (MW 88)



NDMA

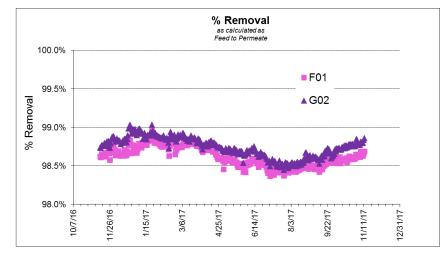


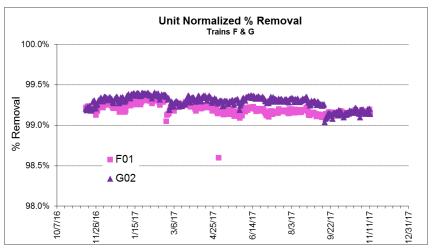
1,4-Dioxane



Operational Factors also Effect Membrane Rejection

- Temperature (higher diffusion, lower removal)
- Membrane Flux (higher dilution, higher removal)
- Boundary Layer and other Concentration Effects (higher concentration, lower removal)
- Calculation Method
 - feed (lower concentration, lower removal)
 - average (higher concentration, higher removal)
 - Normalized Performance Calculations
- Ionic Equilibrium between feed and permeate
 Chemical Cleaning and Age (years in service)





Why is my rejection less than the published values?

- Membrane Test Conditions
 - 10,000 gpd = 25 gfd
 - Typical Design Flux is 12 gfd
- Test Data Normalization
 - Average Feed Brine Concentration
 - Higher than Feed Concentration
 - Temperature Correction to 25 degrees C.

Nitto		YDRANAUTICS Nitto Group Company	
	Membrane Element	ESPA2-LD (Low Fouling Technology)	
Performance:	Permeate Flow: Sait Rejection:	10,000 gpd (37.9 m ³ /d) 99.6% (99.5% minimum)	
Туре	Configuration: Membrane Polymer: Membrane Active Area: Feed Spacer:	Low Fouling Spiral Wound Composite Polyamide 400 ft ² (37.1m ²) 34 mil (0.864 mm)	
Application Data*	Maximum Applied Pressure: Maximum Operating Temperature: pH Range, Continuous (Cleaning): Maximum Feed-water Turbidity: Maximum Feed-water SDI (15 mins): Maximum Reed Flow: Minimum Ratio of Concentrate to Permeate Flow for any Element: Maximum Pressure Drop for Each Element:	600 psig (4.14 MPa) < 0.1 PPM 113 *F (45 *C) 2-10.6 (1-12)* 1.0 NTU 5.0 75 GPM (17.0 m ³ /h) 5:1 15 psi	

Test Conditions

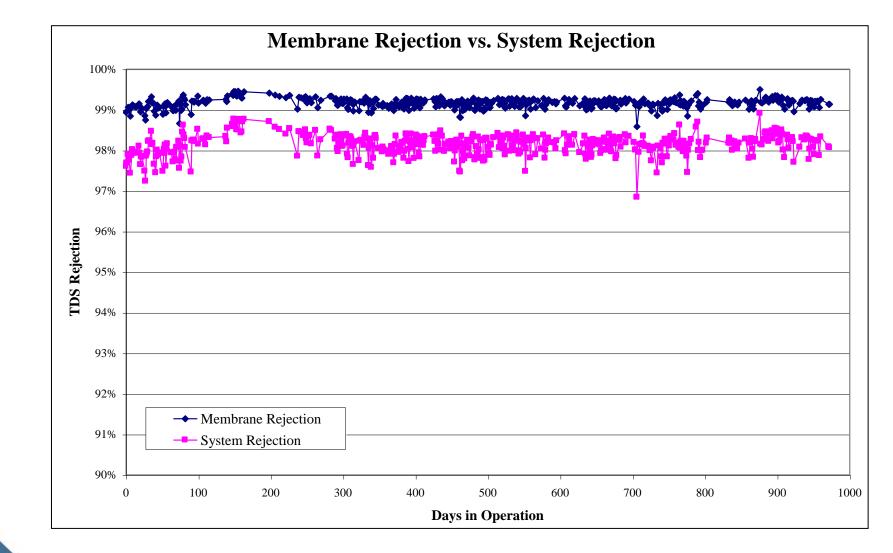
The stated performance is initial (data taken after 30 minutes of operation), based on the following conditions

1500 PPM NaCI solution
 150 psi (1.05 MPa) Applied Pressure
 77 °F (25 °C) Operating Temperature
 15% Permeate Recovery
 6.5 - 7.0 pH Range

Unit Staging



TDS Rejection



SZI



Data Normalization



Data Normalization

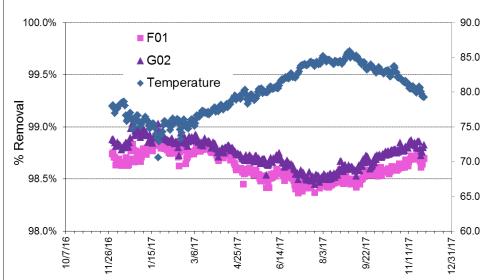
- Calculation of values that describe membrane performance at design conditions even when system is not operated at design conditions (flow, temperature, recovery, etc.)
- Allows the user to make an approximation of membrane performance despite changes in operating conditions to determine if the system performance is stable or developing problems
 - Unit Specific General Idea
 - Stage Specific Better for detailed analysis



Basics of Normalized Data

- Accounts for Multiple Variables of Interest
 - Feed Conductivity
 - Temperature
 - Flow
 - Pressure
- Used as a tool to manage
 - Energy
 - Cleaning
 - Membrane Replacement
 - Maintenance
- Monitor both Unit and Stage Performance
 - Specific Flux
 - Normalized Differential Pressure
 - Normalized Percent Removal

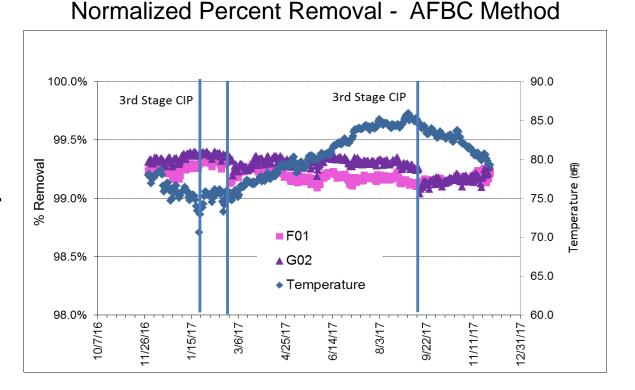
Percent Removal – Feed to Permeate





Why do we use Normalized Data?

- When Data is Normalized, variations are attenuated.
- Membrane Cleaning has a significant but temporary effect on removal.
- The duration is typically a week or so.
- Average Feed/Brine Conductivity
 - ASTM Standard
 - higher removal than feed to permeate



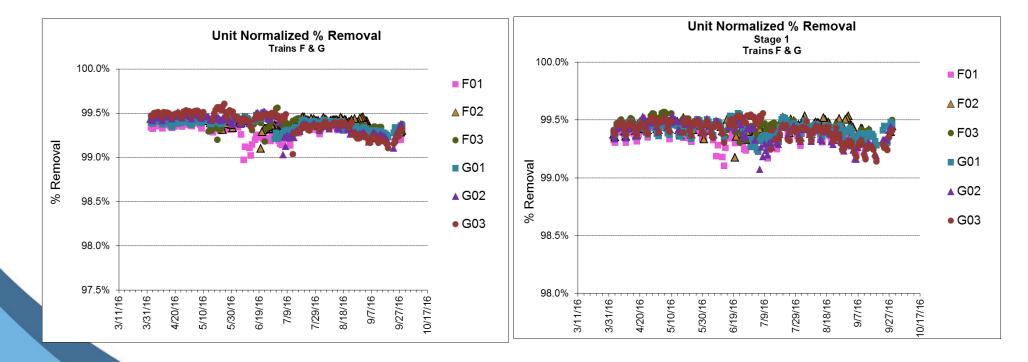
Impact of Membrane Cleaning Becomes More Obvious

Normalized Percent Removal

% Normalized Removal =
$$\frac{C_{FBS} - C_{PN}}{C_{FBS}} x 100\%$$

 $C_{FBS} = AFBC$ Conductivity at Standard conditions (μ S/cm)

 C_{PN} = Normalized Permeate Conductivity (µS/cm)







Monitoring RO Integrity

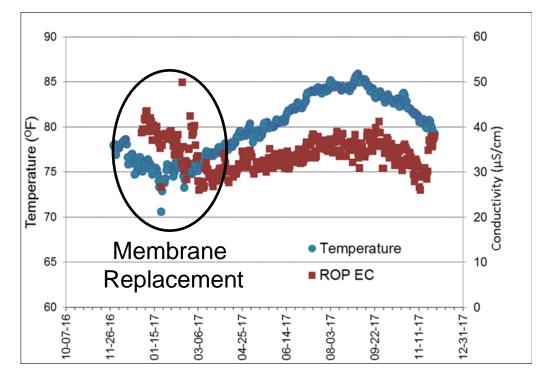


Compliance Monitoring & Reporting is beginning to approach the Drinking Water Standards

- For IPR facilities,
 - The percentage of time of non-compliance is determined
 - Must be reported to the State
 - Failure of greater than 10 percent requires corrective action.
- Operational Monitoring
 - SCADA Historians normally collect data at 1 to 5 minute intervals.
 - SCADA Operational Data contains transitional /nuisance vents
 - start up, shut and analyzer issues
- Compliance Monitoring (Key Elements)
 - Prepare the Compliance Report after the data is formatted in accordance with proceedure
 - A time basis is established (15 min, 3 hour, daily)
 - A singular event cannot be the basis of a compliance violation.
 - Instrumentation used for regulatory compliance is designated
 - verification and calibration protocols established

RO Permeate Water Quality is Very Stable

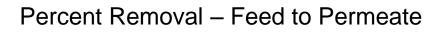
- Combined permeate conductivity is very low.
- Recent membrane replacement in 6 units lowered the overall system permeate conductivity.
- Conductivity removal is in the range of 97 to 98 percent.
 - There are temperature effects.

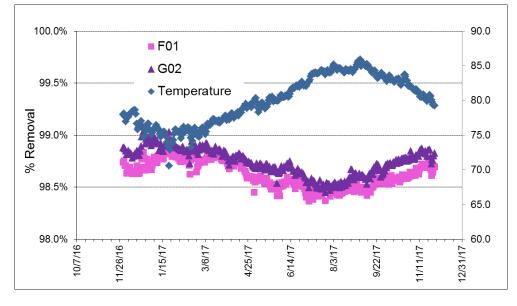


GWRS – Combined Permeate

RO Membrane Issues and 12-10-10

- For IPR Facilities, meeting LRV 12-10-10 brings a new challenge to operations
- RO systems are being used to obtain LRV credit for virus, Giardia and Cryptosporidium. (e.g. 2-2-2)
- EC (Conductivity) and TOC are not the best indicators for microbial integrity
- There is an challenge with going above 3 log because of Membrane Filtration Guidance Manual precedence for Cryptosporidium Removal and the Direct Integrity Test Requirement.



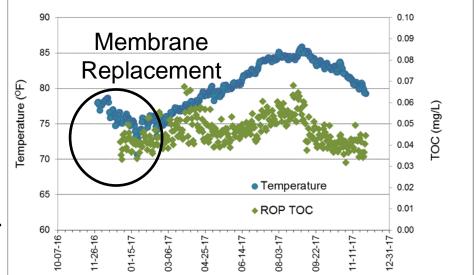




Permeate Water TOC is Significantly less than 0.5 mg/L (BDL/BRL)

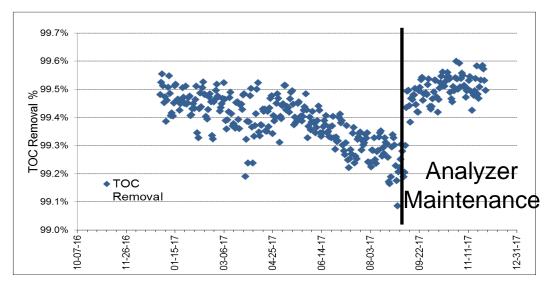
- Operationally, TOC is monitored sensitive equipment with a RDL of 0.05 mg/L.
- The lower range of the analyzer is 0.04 mg/L and is more accurate with lower conductivity water (35 µS/cm maximum).
- Technically this can a compliance issue
- Overall TOC removal is only slightly higher than 99 percent but approaches 99 percent (2 log) during summer.

GWRS – Combined Permeate TOC



The quandary – use of TOC as "surrogate" indicator for virus removal credits

- OCWD uses RO for log virus, Giardia, and Cryptosporidium removal credit (2-2-2).
- Salts and Organic removal is controlled by diffusion.
- Diffusion is a temperature and concentration controlled parameter.
- Virus removal is governed by the principal of size exclusion.



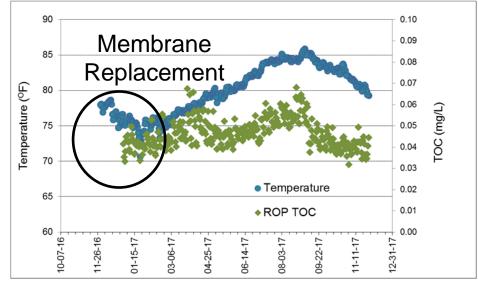




Factors that Affect TOC Removal

- Amount of TOC in Feed Water
 - Secondary 12-16 mg/L
 - Nitrified 7 to 10 mg/L
 - Nitrified/Denitrified 4-7 mg/L
- Ozonation Pretreatment to reduce MF Fouling creates smaller TOC fragments.
- The 0.25 mg/L (First 20 weeks) and 0.5 mg/L TOC requirements may pose challenges to facilities that use ozone or have low TOC.

GWRS – Combined Permeate TOC

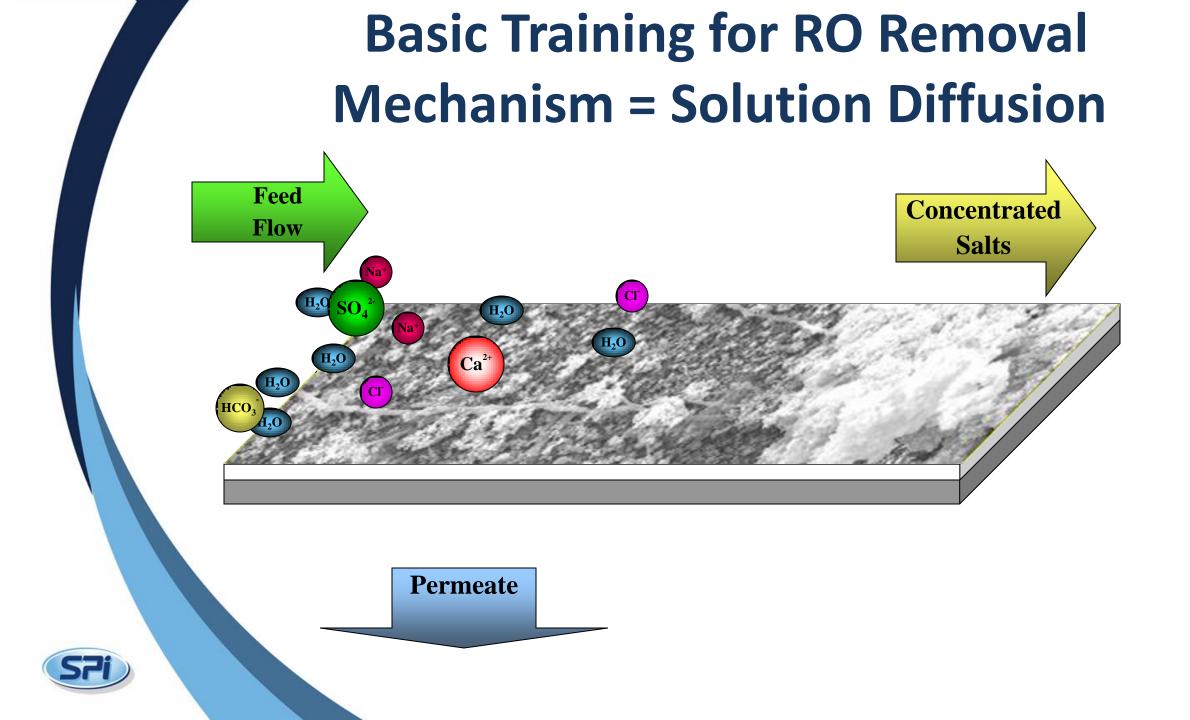






Pathogen Removal





Feed Flow Virus, Giardia and Cryptosporidium

Concentrated

Salts

Are Orders of Magnitude larger in Size

Permeate

H₂O

HCO



What are the types of defects that would create a loss of microbial integrity?

- Missing or deteriorated o-rings on interconnectors and end adapters. (Some types of EPDM)
- Vessel sagging creating stress on vessel and interconnectors
- Broken Glue line (rarer occurrence than previously)
- High Feed Side Differential Pressure (telescoping)
- Permeate Backpressure Incident (catastrophic)

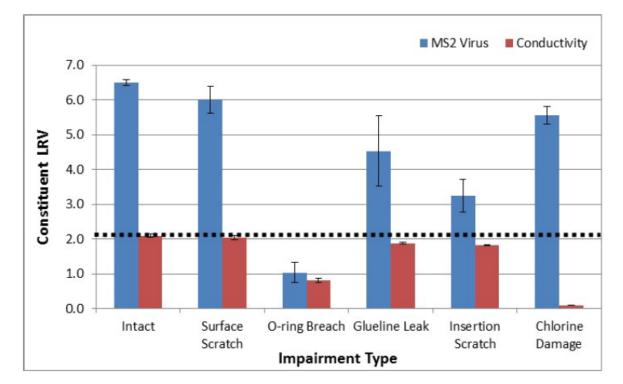
Most integrity occurrences are easily identifiable. Integrity issues for RO are relatively uncommon





What causes an increase in permeate conductivity and is unrelated to integrity?

- Membrane Oxidation in Chloramines
- Aggressive Membrane Cleaning
- Scaling of Membranes
- Temperature Variations
- Increased Recovery

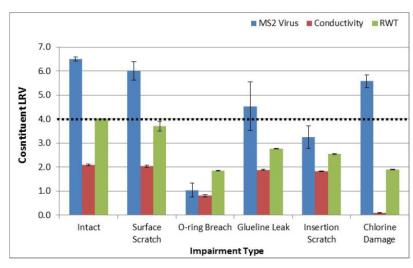


WateReuse -2015

What are the emerging methods that can be used to determine RO Membrane Integrity

- Fluorescence Marker Based Testing
 - Trasar (MW 610)
 - Uranine (MW 376)
 - Rhodamine WT (MW 440)
- All makers are relatively low molecular weight
- Higher Sensitivity because the compounds are Fluorescent at various wavelengths.
- Requires fluorometer and approach to the application
- Data suggests that sensitivity is increased to greater than 4 log.
- A combined permeate measurement does not tell us where the integrity is located.





WateReuse -2015



What are the other methods that can be used to determine RO Membrane Integrity

- Ions such as Strontium and Sulfate
 - Naturally present in water
 - Instrumentation exists from power plants
- Microbial ATP
 - Molecular marker that is associated with wastewater
 - Reduction across RO



Measurement	
Range	0-500 ppb
Limit of detection	0.5 ppb
Accuracy	Chloride: \pm 5% of reading \pm 0.5 ppb, typical
	Sulfate: ± 5% of reading ±1 ppb, typical
Measurement cycle time	45 min typical, programmable between 15 minutes and 1 hour
Sample flowrate	25-50 mL/min
Sample temperature	10-45 °C (50-113 °F)
Sample pressure	0.3-7 bar (5-100 psig)
Grab sample measurement	100 mL capacity

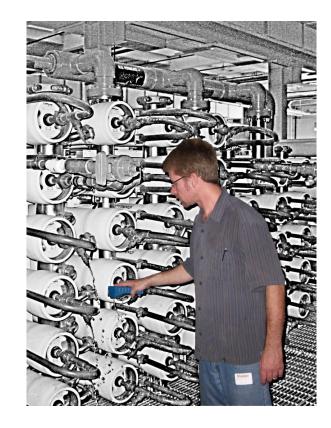


Conductivity Profiling



Historical RO Integrity Monitoring Tools

- Conductivity profiles
- Vessel Probing
- Individual Element Testing
- Used as part of commissioning of a RO system to verify that all membranes are integral and performing similarly
- Routinely performed by most facilities to assure vessels are operating properly.



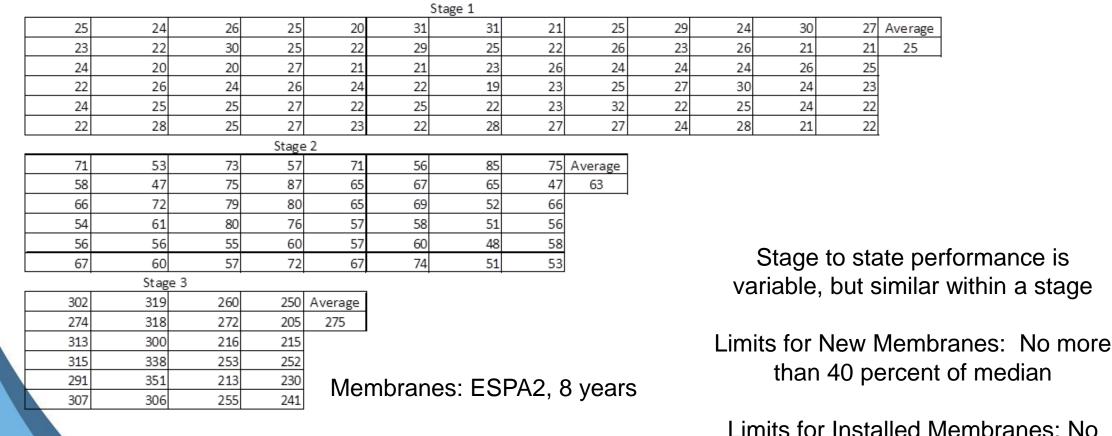


Conductivity Profiling – Fast and Reliable

- Always use the same handheld meter and do not use any values from unit conductivity meters.
- Write down conductivity values along with system flow and pressures.
- Vessels from each stage should have similar conductivity.
- Conductivity is lowest in the first stage, and highest in the third.
- Once per week initially, then once per month.
- Vessels that exhibit higher than normal conductivity should have their seals checked or the elements in the vessel profiled by probing.
- Review data from prior or similar testing to identify outliers



At the GWRS Integrity Defects are Identified by Conductivity Profiling

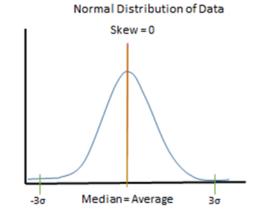


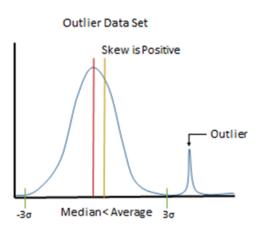
more than 50 percent of median

Routinely monitored

Principals associated with a Conductivity Profile

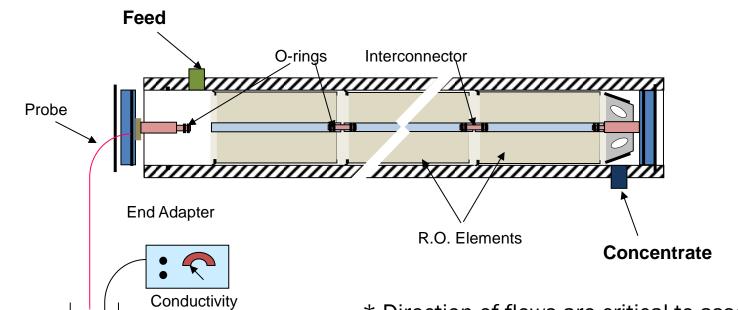
- Diffusion is an intrinsic property of RO Operation
 - Water Temperature
 - Membrane Age and Flux
 - Concentration Difference / Staging
- There is conductivity that is associated with normal operation, and conductivity (outliers) that would be associated with a defect.
- Parsing the data has been left to operators for interpretation, but statistical methods are available. (JAWWA August 2018)







RO Vessel Probing



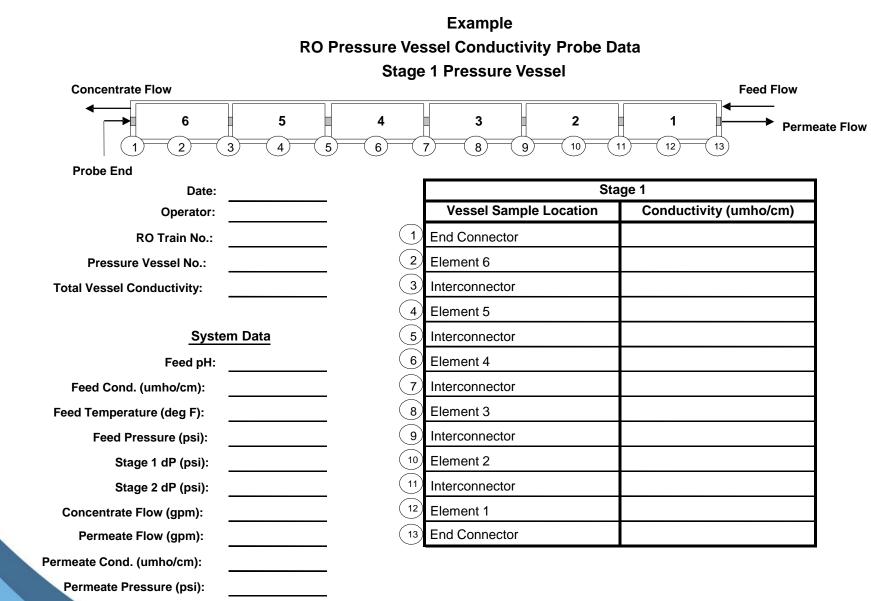
Meter

* Direction of flows are critical to assessing the data





RO Vessel Probing







Yucaipa Virus Testing Results



Yucaipa Valley UV/RO MS-2 Virus Testing

- Full Scale MS-2 virus testing was required for open channel UV System to update to the 2012 NWRI Standard (Spot Check Bio-Assay)
- Partial RO is used to reduce salinity in order to comply with Groundwater Basin Plan
- Single RO Unit
 - 52:20 array
 - 1650 gpm unit
 - 85 percent recovery
 - CSM RE-8040-FE Membranes (2013)
- A retest was required for the UV System, so the RO system was tested as well.
- RO system was operating under normal conditions
 - no special preparation

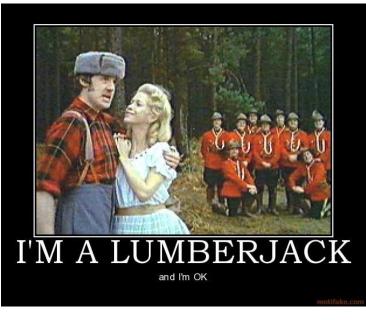






Rationale Behind Yucaipa Work

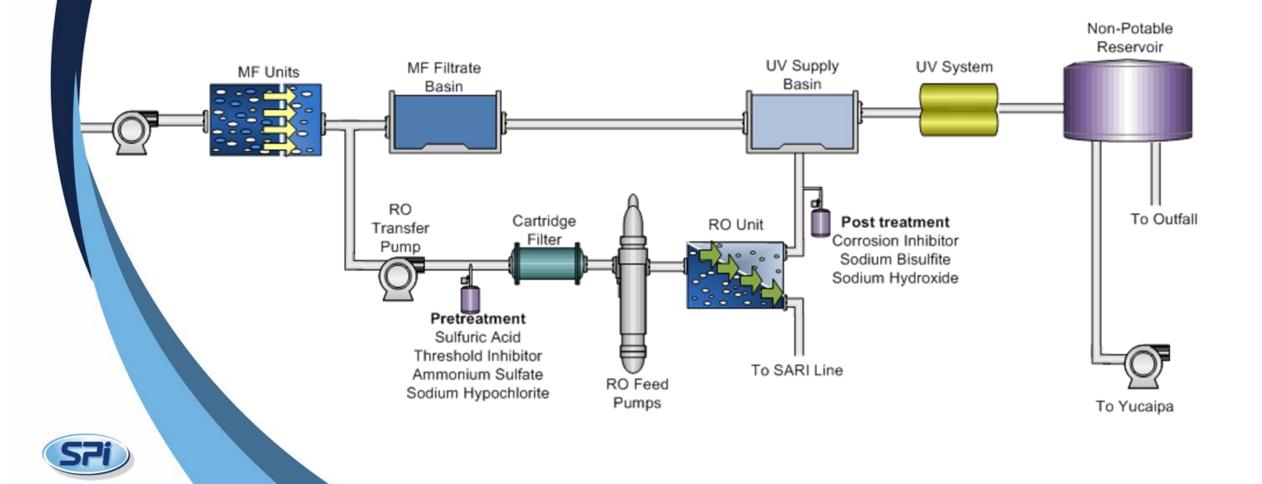
- Changes in IPR regulations (aka 12-10-10) means that RO will be operated for virus removal credits.
- WateReuse and State of California suggest LRV's of 1.5 to 2.0 (although the actual range is broader)
- Water Reuse Project 12-07 suggests on a lab/pilot level RO removal is above 5.0.
- Fluorescence Testing (WateReuse Project 09-06b) indicates that LRV's are above 4.0 based on RO pilot studies.
- Information on full scale system RO performance is limited (or non-existent).
- Because we wanted to find out for ourselves as the information is missing.







Yucaipa Valley Water District Process Flow Diagram



Our Questions to be addressed

- How does the feed concentrate?
- Is there different performance between vessels and stages?
- Is Removal Flow/Flux dependent?
- Do chloramines make a difference in performance (inactivation/disinfectant effect)
- Can a Loss of Integrity be detected by Conductivity Profiling
- Does permeate water quality change as a result of "osmotic shock"
 1/16
 - MS-2 die-off in permeate (aka inactivation)
 - Laboratory Confirmed that MS-2 would not survive overnight shipment in RO Permeate, so buffer was necessary.







Testing Matrix – Spiked Challenge Testing

Flux Characterization (w/o chloramine)

- Test 1: 10 gfd @ 85 percent Recovery
- Test 2: 12 gfd @ 85 percent Recovery

Chloramine Effect

Test 3: Chloramines Dosed At 2-3 mg/L

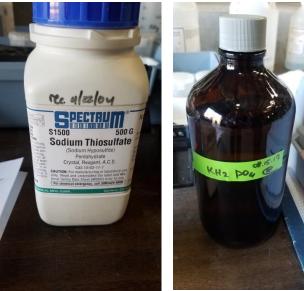
Integrity (w/o chloramine)

• Test 4 : Compromised interconnector

Buffer Effect - Parallel Sampling

- Immediately into Buffer (KH₂PO₄)
- Wait 5 minutes before adding buffer







YVWD Initial Conductivity Profile

								18	18	18	17	7
				20	19	18	17	17	18	18	19	6
51	42	48	43	19	18	18	20	19	18	18	18	5
43	53	43	45	19	20	21	18	18	20	19	18	4
46	42	39	45	19	19	18	18	18	18	20	19	3
43	45	46	46	17	19	20	19	21	19	18	18	2
39	39	40	43	17	19	20	20	18	19	21	21	1
2-4	2-3	2-2	2-1	1-8	1-7	1-6	1-5	1-4	1-3	1-2	1-1	



Yucaipa Valley Water District

August 2017

YVWD Conductivity profile with Compromised Interconnector

								15	15	15	15	7
				17	16	16	15	15	16	16	16	6
40	42	37	33	16	15	15	18	16	16	16	15	5
33	33	33	35	16	15	17	16	15	16	16	16	4
35	32	30	35	16	16	16	15	16	15	34	16	3
34	35	36	36	15	16	17	17	27	15	15	15	2
30	29	30	32	15	16	17	17	15	16	17	17	1
2-4	2-3	2-2	2-1	1-8	1-7	1-6	1-5	1-4	1-3	1-2	1-1	



Yucaipa Valley Water District

August 2017

MS2 Testing – Spiked Feed Concentrations

Feed
1.04-1.45 x 10 ⁶
<u>Interstage</u>
2.19-5.55 x 10 ⁶
<u>Concentrate</u>

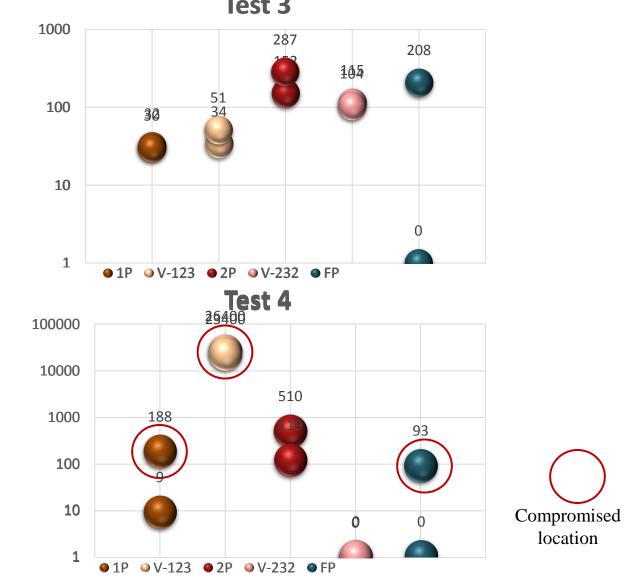
4.3-7.3 x 10⁶

	Feed	Interstage	Concentrate
Test 1 (10 gfd)	1.22*10 ⁶	2.44*10 ⁶	5.70*10 ⁶
Test 2 (12 gfd)	1.21*10 ⁶	2.55*10 ⁶	6.10*10 ⁶
Test 3 (Total Cl2)	1.45*10 ⁶	5.55*10 ⁶	5.70*10 ⁶
Test 4 (Integrity)	1.33*10 ⁶	2.22*10 ⁶	4.30*10 ⁶

	Feed	Interstage	Concentrate
Test 1 (10 gfd)	$1.04^{*}10^{6}$	3.08*10 ⁶	7.30*10 ⁶
Test 2 (12 gfd)	1.10^*10^6	2.44*10 ⁶	5.35*10 ⁶
Test 3 (Total Cl2)	1.38*10 ⁶	2.91*10 ⁶	6.30*10 ⁶
Test 4 (Integrity)	1.21*10 ⁶	2.19*10 ⁶	4.65*10 ⁶

Permeate Virus (pfu/mL) – combined results Test 1



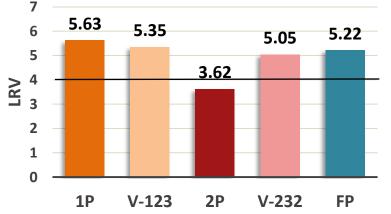


location

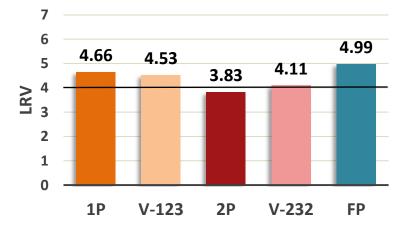
Average is Geometric Mean

LRV (Avg. Feed to Avg. Permeate)

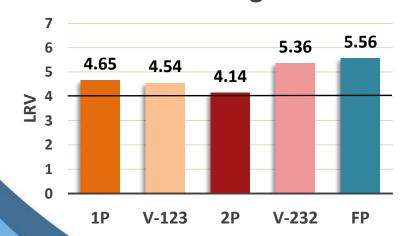
Test 1 - 10 gfd

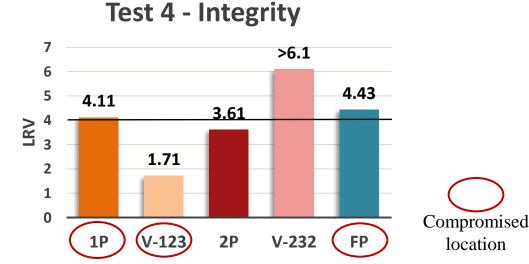


Test 3 - Total Cl2



Test 2 - 12 gfd

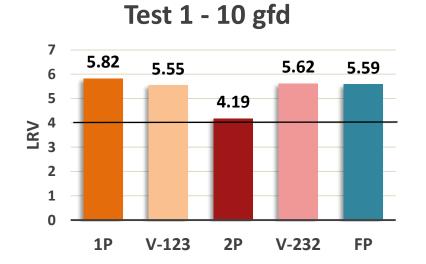




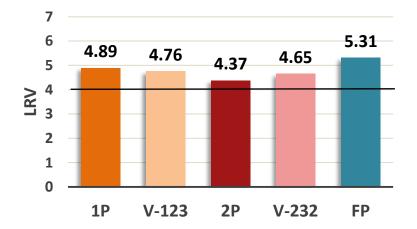
SZI

Average is Geometric Mean

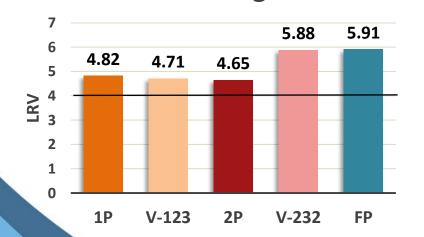
LRV (AFBC Avg. Feed to Avg. Permeate)

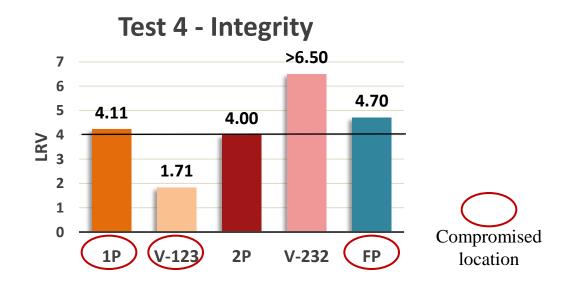


Test 3 - Total Cl2



Test 2 - 12 gfd







What did we learn from the testing?

- Scatter in the data results, take multiple samples.
- Results of testing at 10 gfd and 12 gfd membrane flux were similar and greater than 5 log.
- We could identify a compromised vessel with a conductivity profile, and the vessel LRV as reduced from ~5 to less than 2.
- Overall reduction from the system remained above 4 LRV even with a compromised vessel.





Summary



Summary (1)

- RO Removal is diffusion based and affected by the feed composition/concentration and process conditions.
- Normalization of data is useful in characterizing RO system performance and diagnosing operational problems (temperature, conductivity, TOC, flow).
- Water Quality Indicators (Conductivity, TOC) are influenced by diffusion and unless considered, underestimate the removal of regulated virus, Giardia and Cryptosporidium.
- Fluorescence (marker) measurement is useful and provides higher sensitivity, and is useful for pilot testing and may be applied to full scale systems.

Summary (2)

- For full scale systems, integrity issues can be identified by conductivity profiling and subsequent diagnostic testing.
- Recent challenge studies suggests that virus removal through a RO unit is significantly higher than removal credits currently awarded.
- Membrane cleaning has a temporary effect upon salt removal performance.
- In the future, individual vessel integrity will require monitoring to obtain higher pathogen removal credits.
 - Approved Compliance methods will be needed to obtain higher Log Removal Values for RO if used on combined permeate.



Questions?

