Electrodialysis Research Update

Mono-Valent Selective Ion Exchange Membranes for Saline Water Reuse and Desalination

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Acknowledgement

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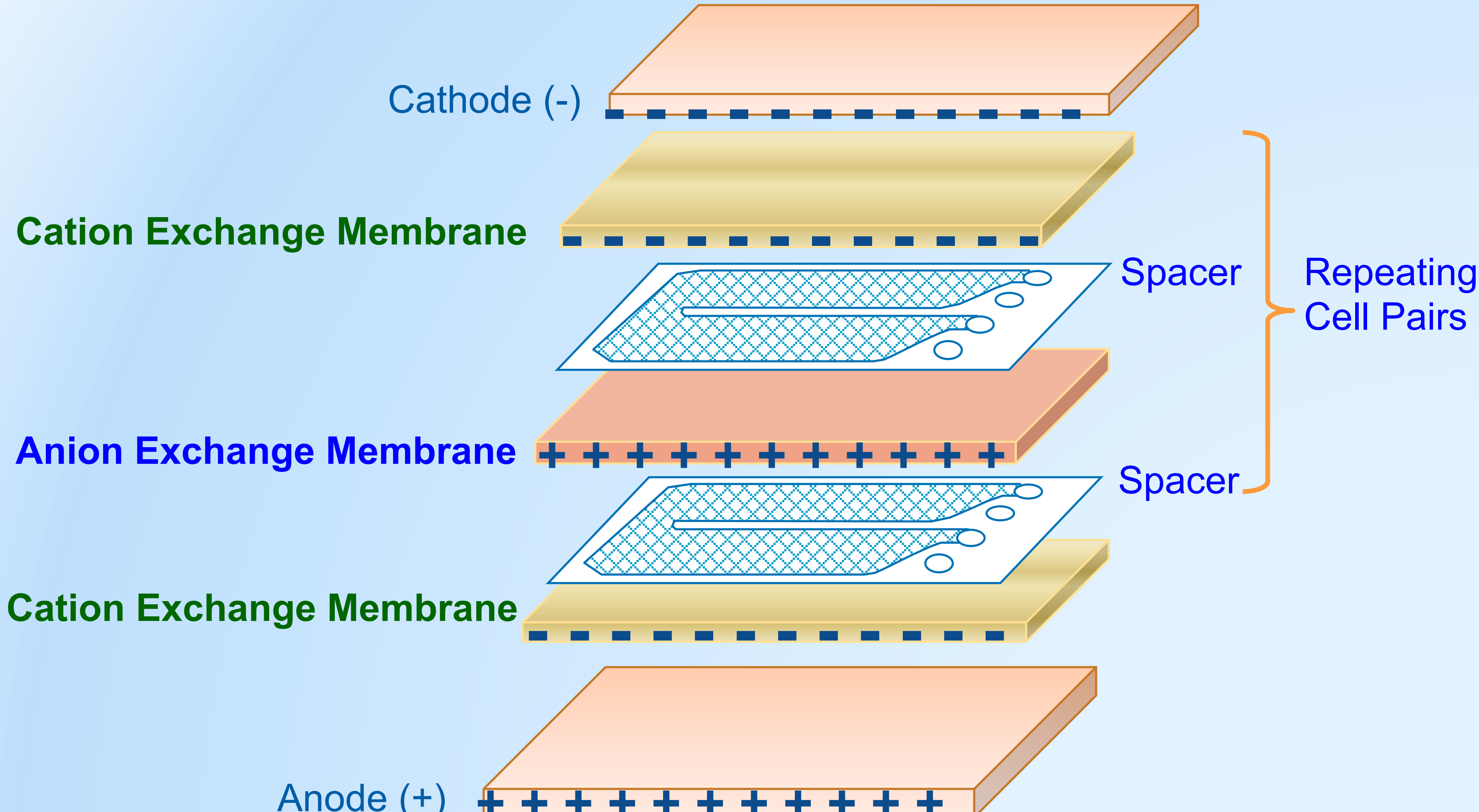
Presentation Outline

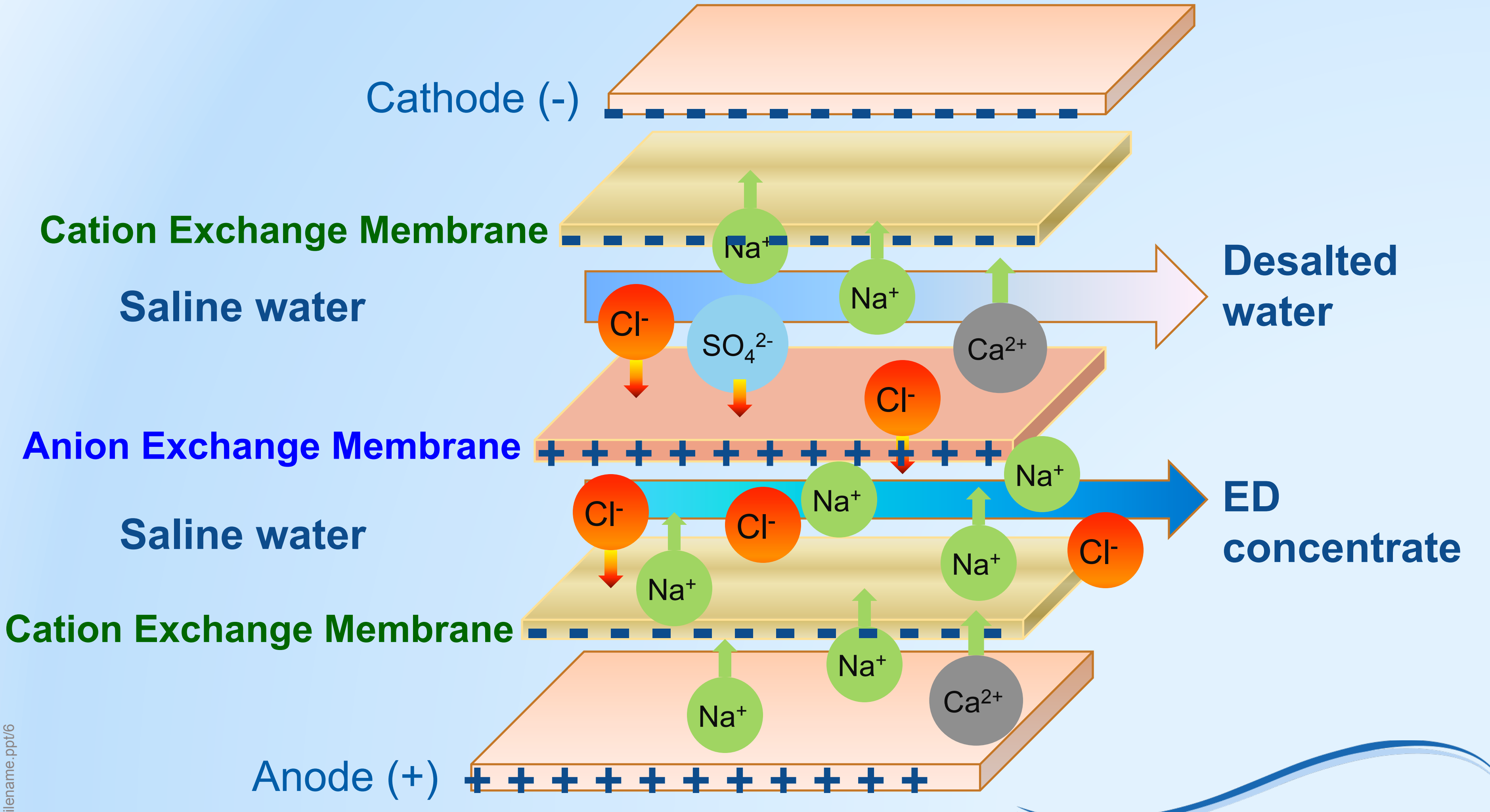
- ED/EDR Research Update
- Need of Selective Removal of Sodium
- Selected Testing Results
- Modeling and Blending Analysis
- Take Home Messages

ED/EDR Research Update

Electrodialysis Consists of Electrodes and A Stack of Membrane Cell Pairs



Electrodialysis with Normal Grade IX Membranes Remove All Cations and Anions



Electrodialysis, An Old Technology Finding New Applications

1948 - Ionics develops ion exchange membranes

1950-1959 – ED Technology is developed

1970 - Ionics introduces reversal process to Electrodialysis

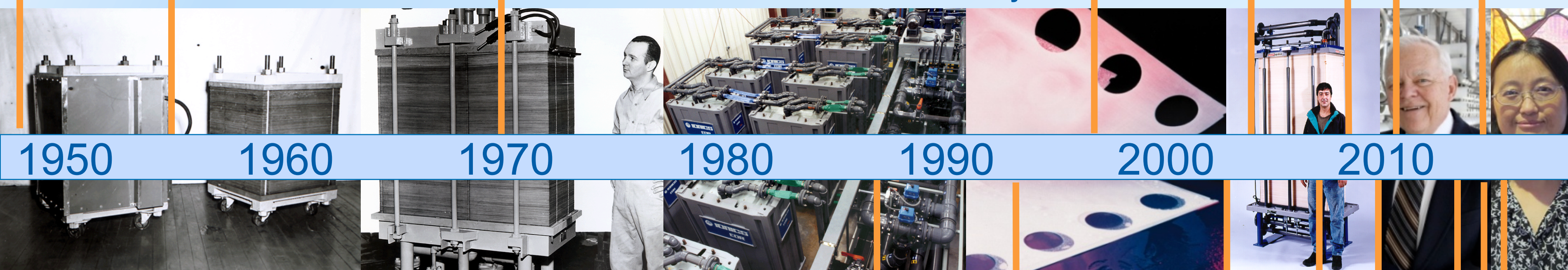
1997 – Introduction of Ionics EDR 2020 System

2005 – Ionics purchased by GE Water

2010 – GE High Reject and High Recovery EDR R&D

2011 – GE Announce New Non-Thermal Brine Concentrator (AquaSEL)

Ongoing – Monovalent Selective Membrane Research



1950 1960 1970 1980 1990 2000 2010

1987 – CEDI Commercialized by Millipore

1995 – CDI Commercialized

2004 – BPED Commercialized by ASTOM

2009 – ZDD Commercialized

2010 – Therm-Ionic™ Commercialized

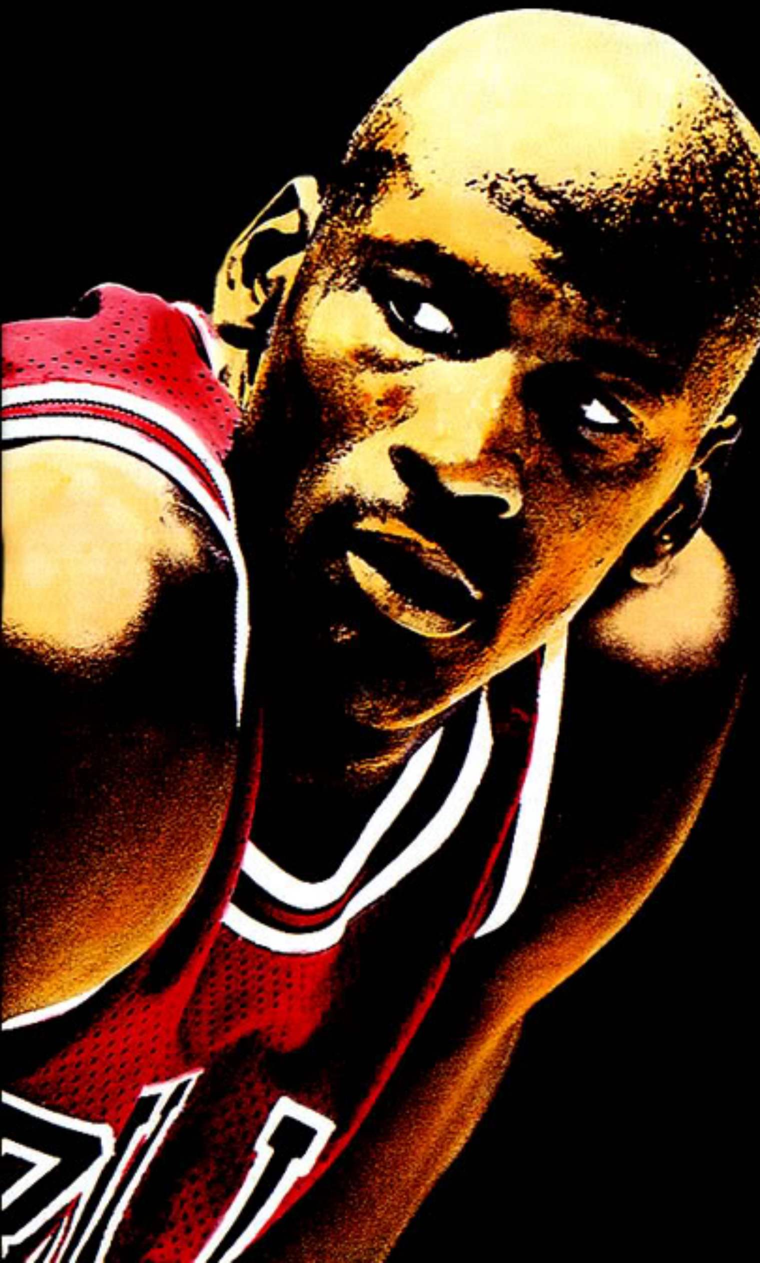
Ongoing – EDR IX & EDR SPARRO Pilot Testing

Ongoing – Lesico Modular ED

Ongoing – RED, MFC, MDC Research

Your Weakness Can be Your Strength

Disorganized	Creative
Inflexible	Organized
Inconsistent	Flexible
Stubborn	Dedicated
Emotionless	Calm
Unrealistic	Positive
Negative	Realistic



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Michael Jordan

My attitude is that if you push me towards something that you think is a weakness, then I will turn that perceived weakness into a strength.

Research and Engineering Expertise Turns Weakness into Strength

No Silica Removal	Silica limiting RO applications
Not efficient for TDS < 100	EDI Technologies
Electrode reactions and hazardous gas	New carbon electrode; Bipolar ED
Not an organic barrier	High tolerance to organics and particulates
Not suitable for high TDS?	Strong in brine treatment & high TDS applications
GE Proprietary	Innovative competitions
No Specialties?	Unique Selectivity
No ERD?	RED, MDC, Thermo-ionic, etc.

Selective Removal of Sodium

Selectively Removing Sodium is Desirable but Challenging – Ion Exchange & Softening

	Lime Softening	Ion Exchange
Sodium		x
Calcium	X	X
TDS		
Selectivity	No	Yes, but
Beneficial Selectivity	**No**	**No**

Selectivity Sequence for Typical Strong Acid Cationic Resin

$Ra^{2+} > Ba^{2+} > Pb^{2+} > Sr^{2+} > Cu^{2+} > \mathbf{Ca^{2+}} > Zn^{2+} > Fe^{2+} > Mg^{2+} > K^{+} > Mn^{2+} > NH_4^{+} > \mathbf{Na^{+}} > H^{+}$

Selectivity Sequence for Typical Strong Base Anionic Resin

$CrO_4^{2-} > SeO_4^{2-} > \mathbf{SO_4^{2-}} > HAsO_4^{2-} > HSO_4^{-} > NO_3^{-} > Br^{-} > SeO_3^{2-} > HSO_3^{2-} > NO_2^{-} > \mathbf{Cl^{-}} > HCO_3^{-} > OH^{-} > F^{-}$

Selectively Removing Sodium is Desirable but Challenging - Membranes

	Lime Softening	Ion Exchange	RO	NF	ED/EDR
Sodium		x	X	X	X
Calcium	X	X	X	X	X
TDS			X	X	X
Selectivity	No	Yes, but	No	Yes, but	Yes
Beneficial Selectivity	**No**	**No**	**No**	**No**	**No**

Sodium, Chloride	Calcium, Magnesium, Sulfate
Smaller ions, lower rejection	Larger ions, higher rejection

Selectively Removing Sodium is Desirable but Challenging - Membranes

	Lime Softening	Ion Exchange	RO	NF	ED/EDR
Sodium		x	X	X	X
Calcium	X	X	X	X	X
TDS			X	X	X
Selectivity	No	Yes, but	No	Yes, but	Yes
Beneficial Selectivity	**No**	**No**	**No**	**No**	**No**

	NF90	NF270
Description	Tightest (lower MWCO)	Loosest (higher MWCO)
NaCl Rejection	90-96%	50%
$MgSO_4$ Rejection	98+%	98+%

Selectively Removing Sodium is Desirable but Challenging - Membranes

	Lime Softening	Ion Exchange	RO	NF	ED/EDR
Sodium		x	X	X	X
Calcium	X	X	X	X	X
TDS			X	X	X
Selectivity	No	Yes, but	No	Yes, but	Yes
Beneficial Selectivity	**No**	**No**	**No**	**No**	**No**

Sodium	Calcium, Magnesium
Monovalent, lower charge, smaller ion	Divalent, higher charge, bigger ion

Selectively Removing Sodium is Desirable but Challenging – Innovative Membrane

	Lime Softening	Ion Exchange	RO	NF	ED/EDR	Monovalent Selective ED/EDR
Sodium		x	X	X	X	X
Calcium	X	X	X	X	X	X
TDS			X	X	X	X
Selectivity	No	Yes, but	No	Yes, but	Yes	Reported Yes
Beneficial Selectivity	**No**	**No**	**No**	**No**	**No**	**Reported Yes**

Defining Selectivity

- Selectivity based on ppm

$$\text{Selectivity}_{Ca/Na} = \frac{\text{Removal}_{Ca}}{\text{Removal}_{Na}} = \frac{(Ca_{feed} - Ca_{product}) / Ca_{feed}}{(Na_{feed} - Na_{product}) / Na_{feed}}$$

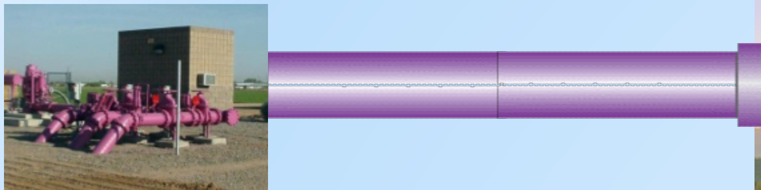
- Selectivity based on meq/L

$$\text{Selectivity}_{Ca/Na} = \frac{[Ca_{feed}] - [Ca_{product}]}{[Na_{feed}] - [Na_{product}]}$$

- Lower value means better removal of sodium

Problem Statement

For Scottsdale, Salinity Poses A Challenge to Irrigation Reuse



Water Reclamation Plant to Reuse

SAR = Sodium Adsorption Ratio

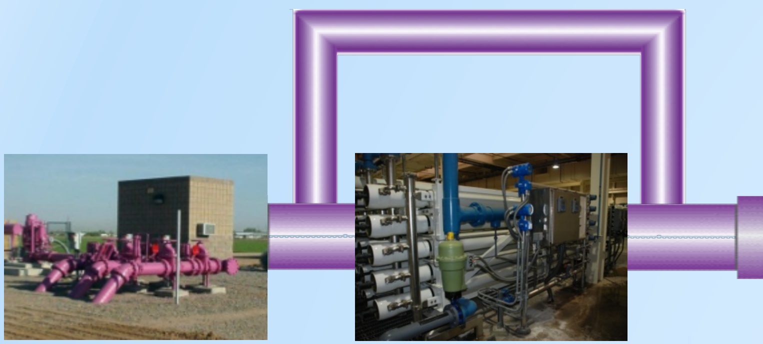
$SAR = [Na^{+}] / \{([Ca^{2+}] + [Mg^{2+}]) / 2\}^{1/2}$

[ ]: use meql units

- CAP Water — SAR ~ 5 on average
- Verde River — < 2 on average
- Salt River — > 9 on average
- Scottsdale Water Campus Effluent — 5-8

Advanced Treatment Using RO Solved The Problem, But …

Water Quality Goal
Contractual Limit: <125 ppm Sodium
Operating Target: <110 ppm Sodium

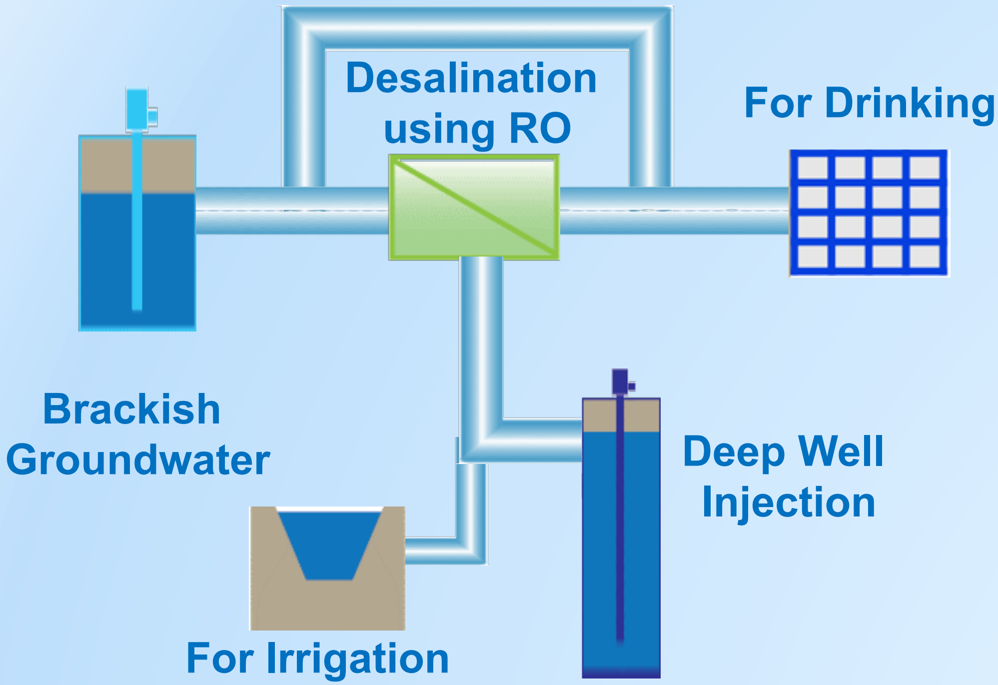


Water Reclamation Plant to Reuse

Advanced Water Treatment Plant

Concentrate Management

For El Paso, Brackish Groundwater Desalination Using RO is Successful. But Can We Do Better?



15 - 20% Water resource lost as concentrate; Limited deep well capacity.

Recovered Water Quality Goal
Based on Minimum Effluent Standard for Discharging into the American Canal Extension

TDS < 1,200~2,500 mg/L
SAR ≤ 29 – 6 logTDS

TDS (mg/L)	SAR
2500	8.6
2300	8.8
2000	9.2
1900	9.3
1500	9.9
1200	10.5

Reference: Texas Natural Resources Conservation Commission

Selected Testing Results

DWPR Funded Project Included Bench and Pilot Testing at Two Sites

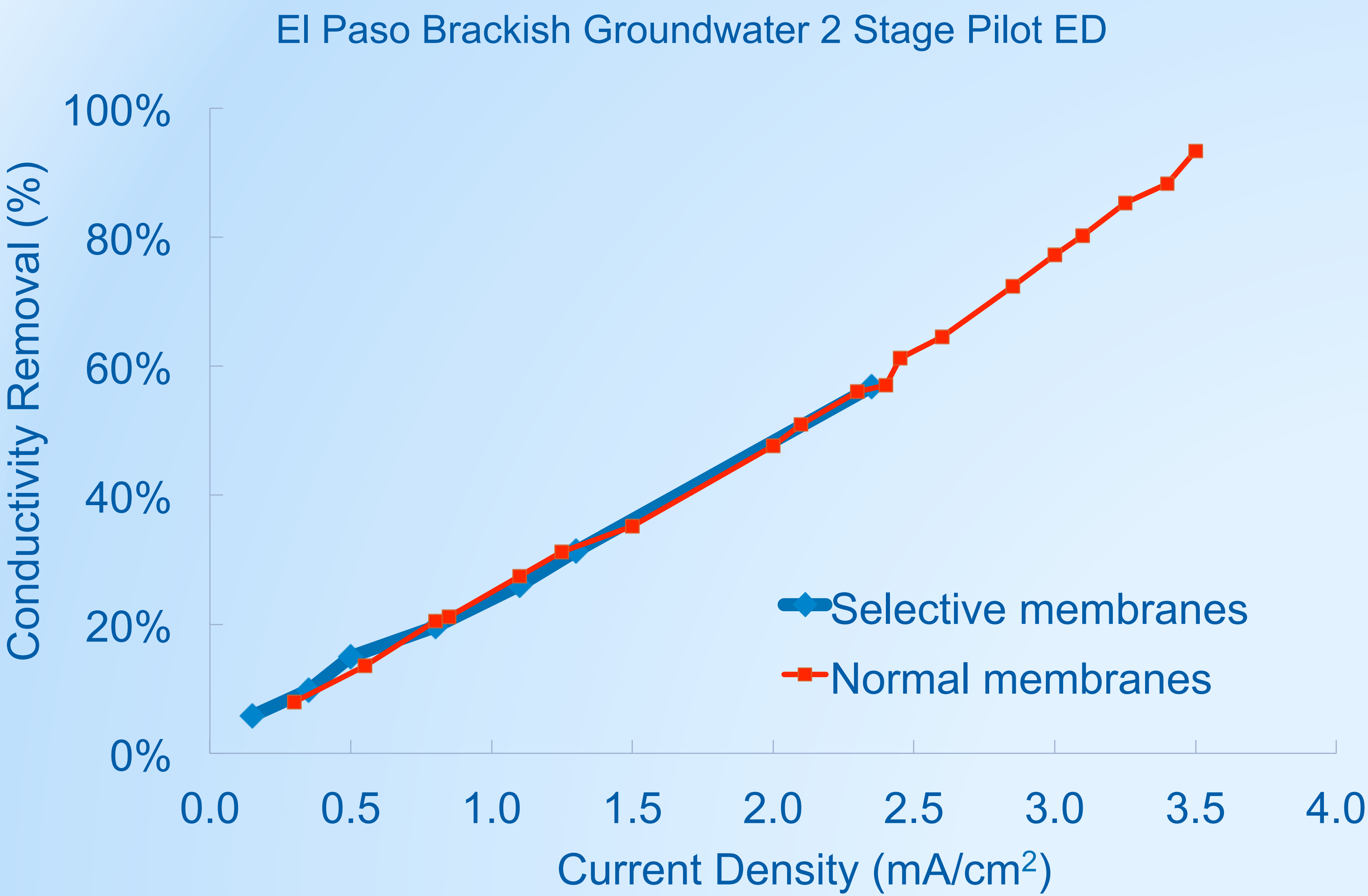
	Phase 1 - Scottsdale Water Campus	Phase 2 - El Paso KBH Desalination Plant	
Site	Scottsdale Water Campus	El Paso Kay Bailey Hutchison Desalination Plant	
Duration	July to December 2015	January to April 2016	
Objective	Saline Water Reuse	Concentrate Management	
Water Source	Reclaimed Water	Brackish Groundwater	Groundwater Brine
Feed TDS	1,150	3,252	11,000
Feed Sodium	235	738	2,900
Goal	125 mg/L Sodium in product	TDS < 1,200~2,500 mg/L SAR ≤ 29 – 6 logTDS	
Summary	**Unexpected low selectivity due to coating method**	**Improved Coating Method = Improved Selectivity**	

Several Types of Conventional & Innovative Membranes Were Used for the Testing

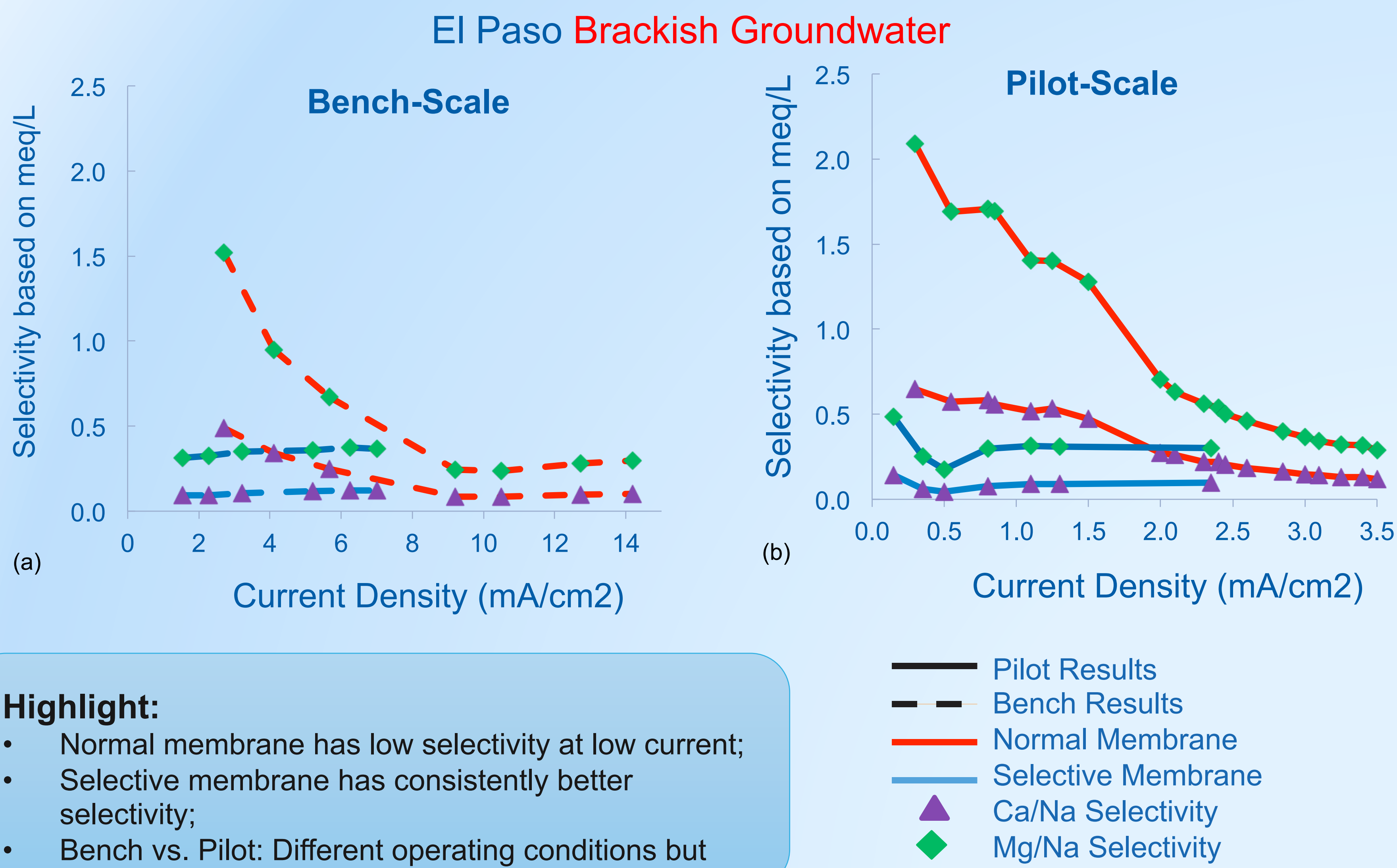
Membrane	AR204	CR67	AR112	CR671
Manufacturer	Ionics/GE	Ionics/GE	Ionics/GE	Ionics/GE
Characteristics	Normal grade	Normal grade	Mono – anion permselective	Mono – cation permselective
Thickness (µm)	500	560-580	580-690	560-580
Water content (g H_2O/g dry membrane)	46% of wet resin	46% of wet resin	20-25% of wet resin	46% of wet resin
Electrical resistance (Ω-cm^2 in 0.01N NaCl)	8	12	22-26	12
Ion exchange capacity (meq/g dry membrane)	2.40	2.10	1.6-1.8 Strong base 0.3-0.6 weak base	2.0-2.1

Note: NEOSEPTA membranes are also used in bench testing: normal grade membranes (AMX and CMX-SB) and NEOSEPTA monovalent permselective membranes (ACS and CMX-S).

Selective and Normal Membranes Demonstrates Same Desalination Efficiency



Selective Membrane Demonstrates Better Selectivity of Divalent Cations over Monovalent than Normal Membrane

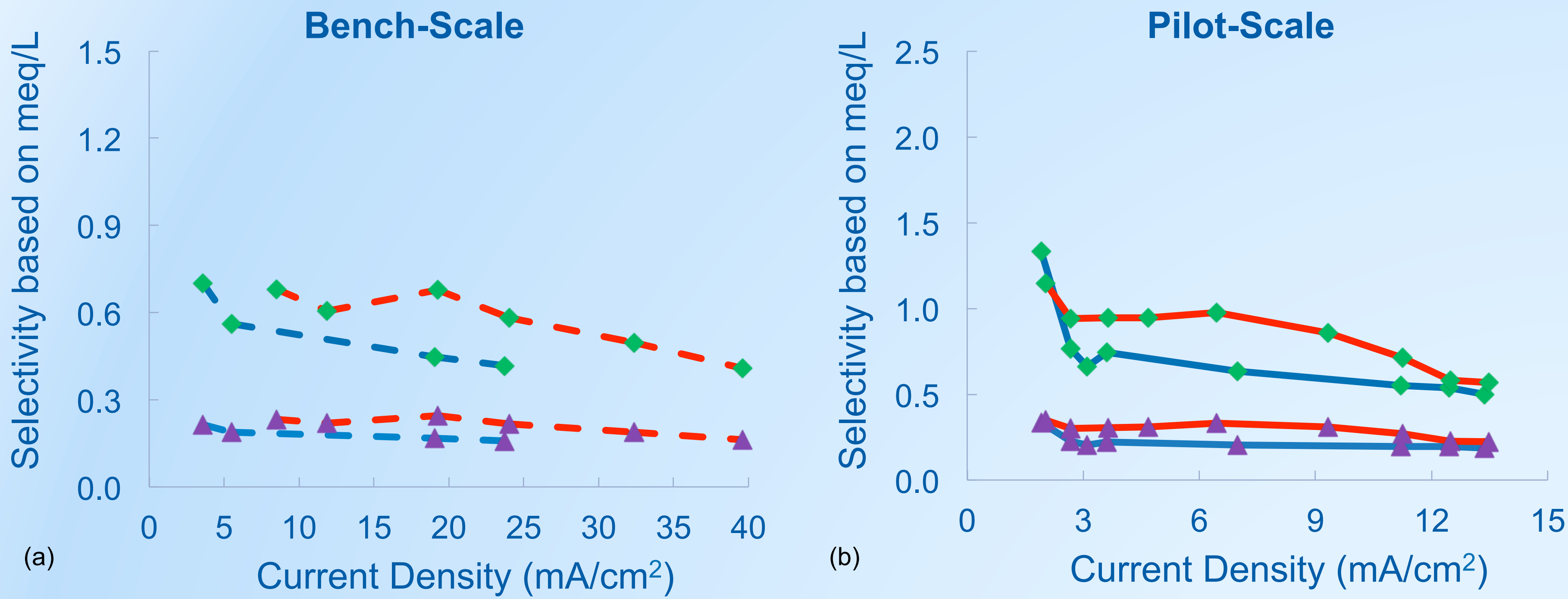


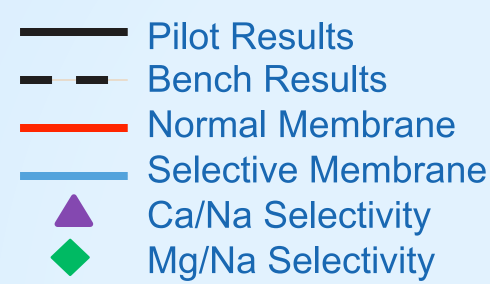
Highlight:

- Normal membrane has low selectivity at low current;
- Selective membrane has consistently better selectivity;
- Bench vs. Pilot: Different operating conditions but same trends.

Selective Membrane Demonstrates Better Selectivity of Divalent Cations over Monovalent than Normal Membrane

El Paso RO Concentrate



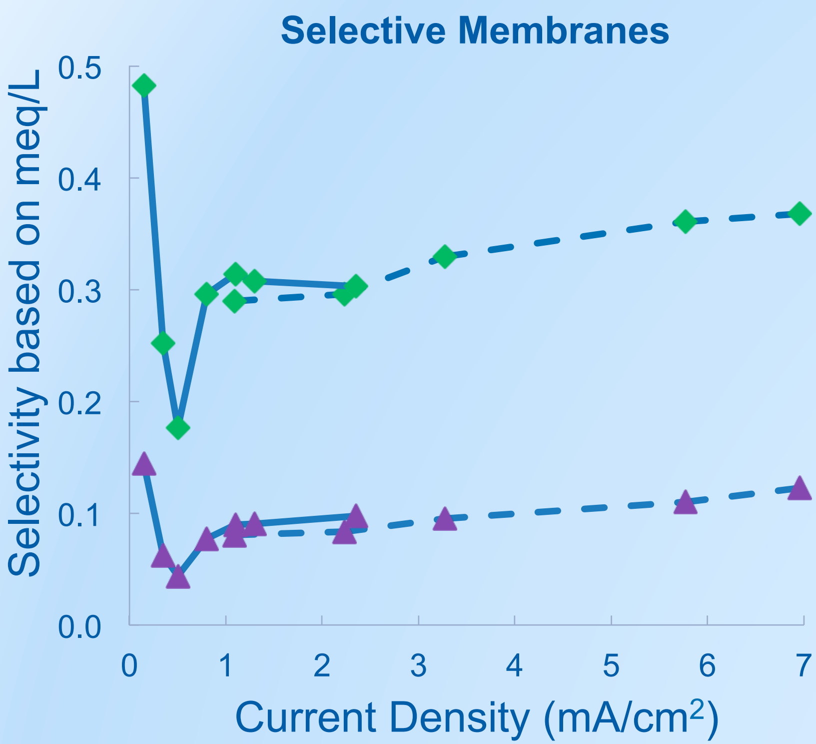


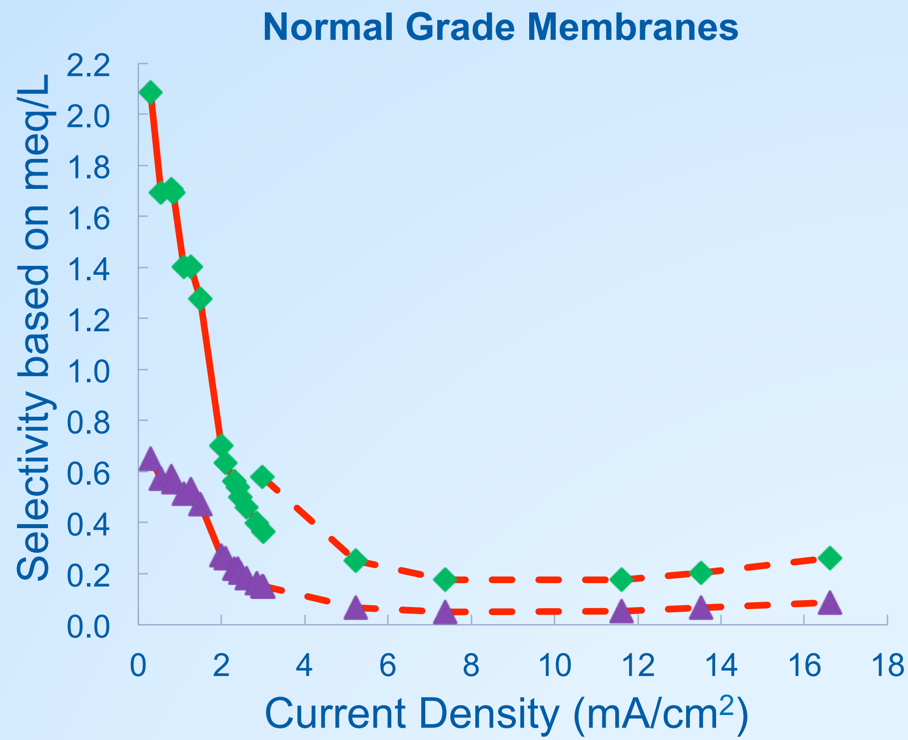
Highlight:

- Similar to previous slide
- Selectivity reduced with increase in feed water TDS

Bench Testing Data Matches Well with Pilot Testing Results

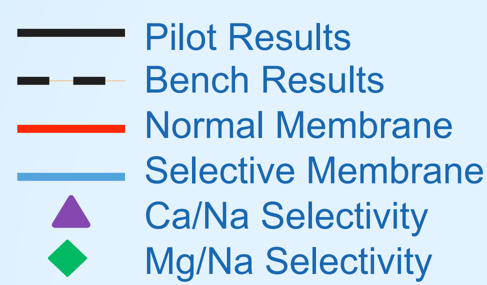
El Paso Brackish Groundwater



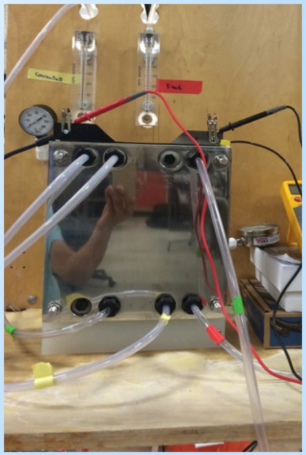


Highlight:

- Bench and pilot operates under different conditions
- Bench testing can be used for pilot or full scale performance projections



Value Adding Research Links Bench Testing, Pilot Testing, Modeling, and Full Scale Design



Bench Testing

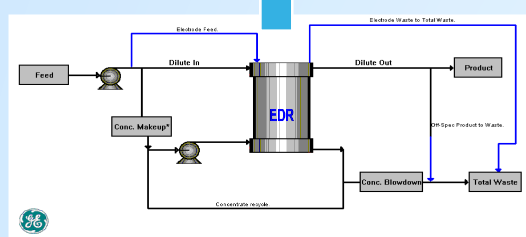
Pilot Testing

Minitab 17

Data Fitting and Mathematical Modeling

BLUE PLAN-IT™
DECISION SUPPORT SYSTEM

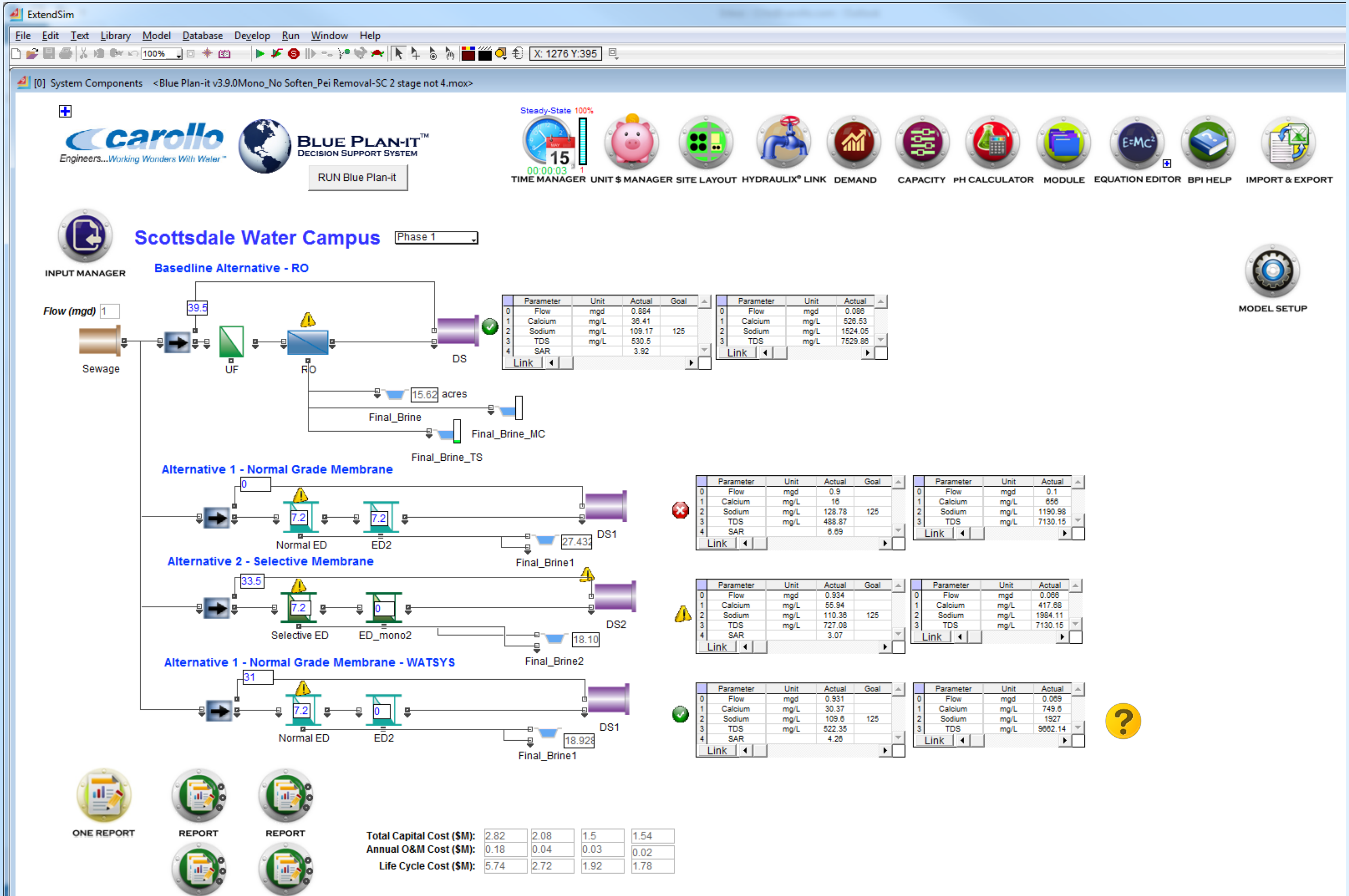
Water and Salt Balance, Process Modeling
Cost Analysis



WATSYS: Specialty EDR Projection Model by GE
(Normal Grade Membrane Only)

Full Scale Design

Scottsdale Blending Analysis and Cost Comparison



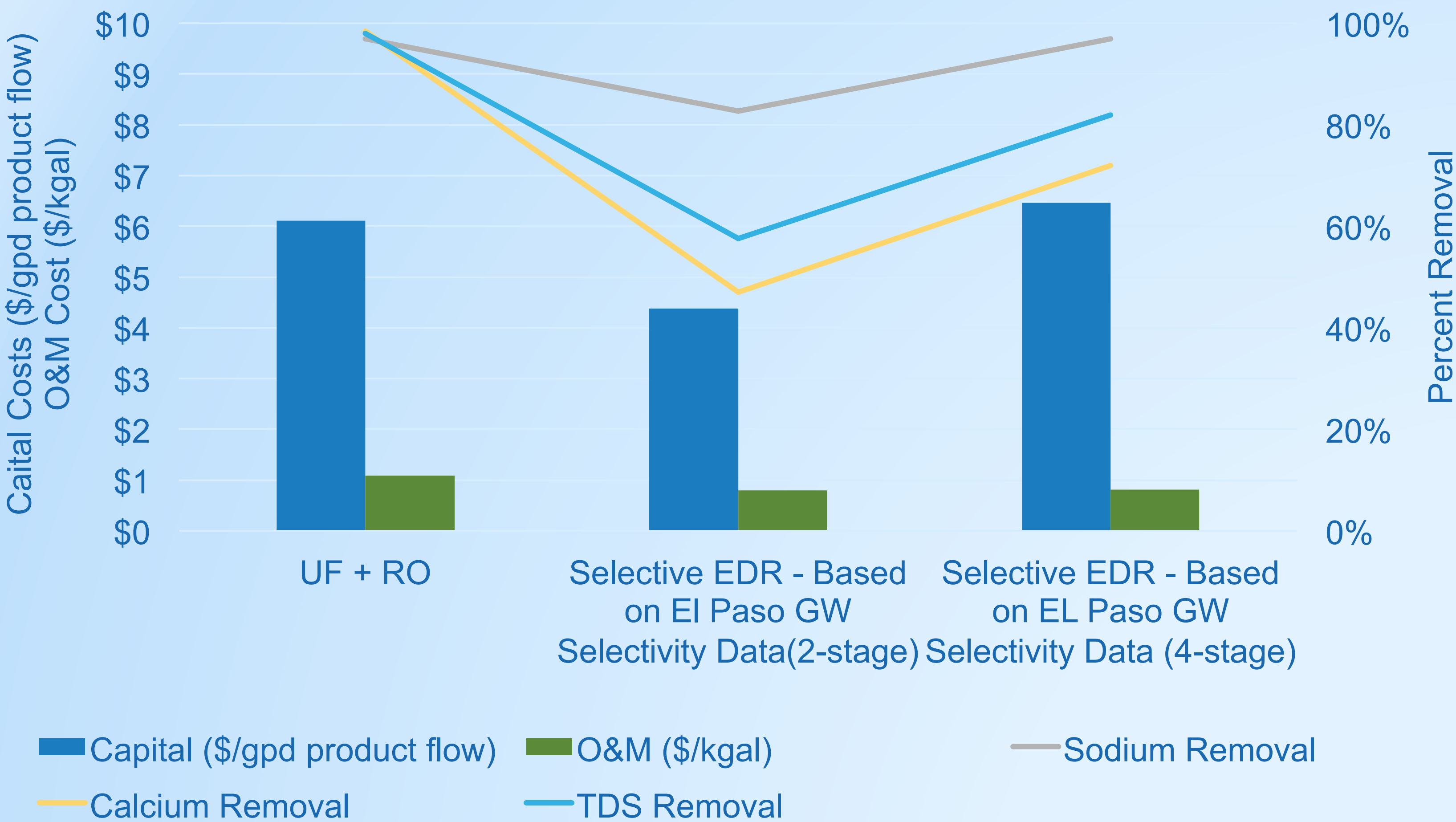
Scottsdale Blending Analysis and Cost Comparison – 1 MGD Reclaimed Water (2-stage)

	Baseline Alternative	Alternative 1A	Alternative 1	Alternative 2
	UF + RO	Normal EDR - WATSYS	Normal EDR - Testing	Selective EDR (Based on EP GW Testing)
Feed Water Flow (mgd)	1			
Feed Water Sodium (mg/L)	235			
% Flow Treated	60.5%	69.0%	100.0%	66.5%
Overall Recovery	88%	93%	92%	93%
Unit Recovery	**85%**	**90%**	**90%**	**90%**
Blended Water Flow (mgd)	0.88	0.93	0.92	0.93
Product Water Sodium (mg/L)	110	110	129	110
Product TDS (mg/L)	530	522	489	727
Concentrate Flow (gpm)	60	48	69	46
Concentrate TDS (mg/L)	**7530**	9662	7130	**7130**
Concentrate Sodium (mg/L)	**1524**	2136	1715	**3940**
Number of Product Line	-	7	8	6
Number of Stages	-	**2**	**2**	**2**
Capital ($/gpd product flow)	$6.1	$5.0	$5.6	$4.4
O&M ($/kgal)	$1.09	$0.82	$0.80	$0.79
Note	Blending based on RO Projection Model	Based on Modeling	Based on Pilot Testing	Based on El Paso GW Testing

Scottsdale Blending Analysis and Cost Comparison – 1 MGD Reclaimed Water (4-stage)

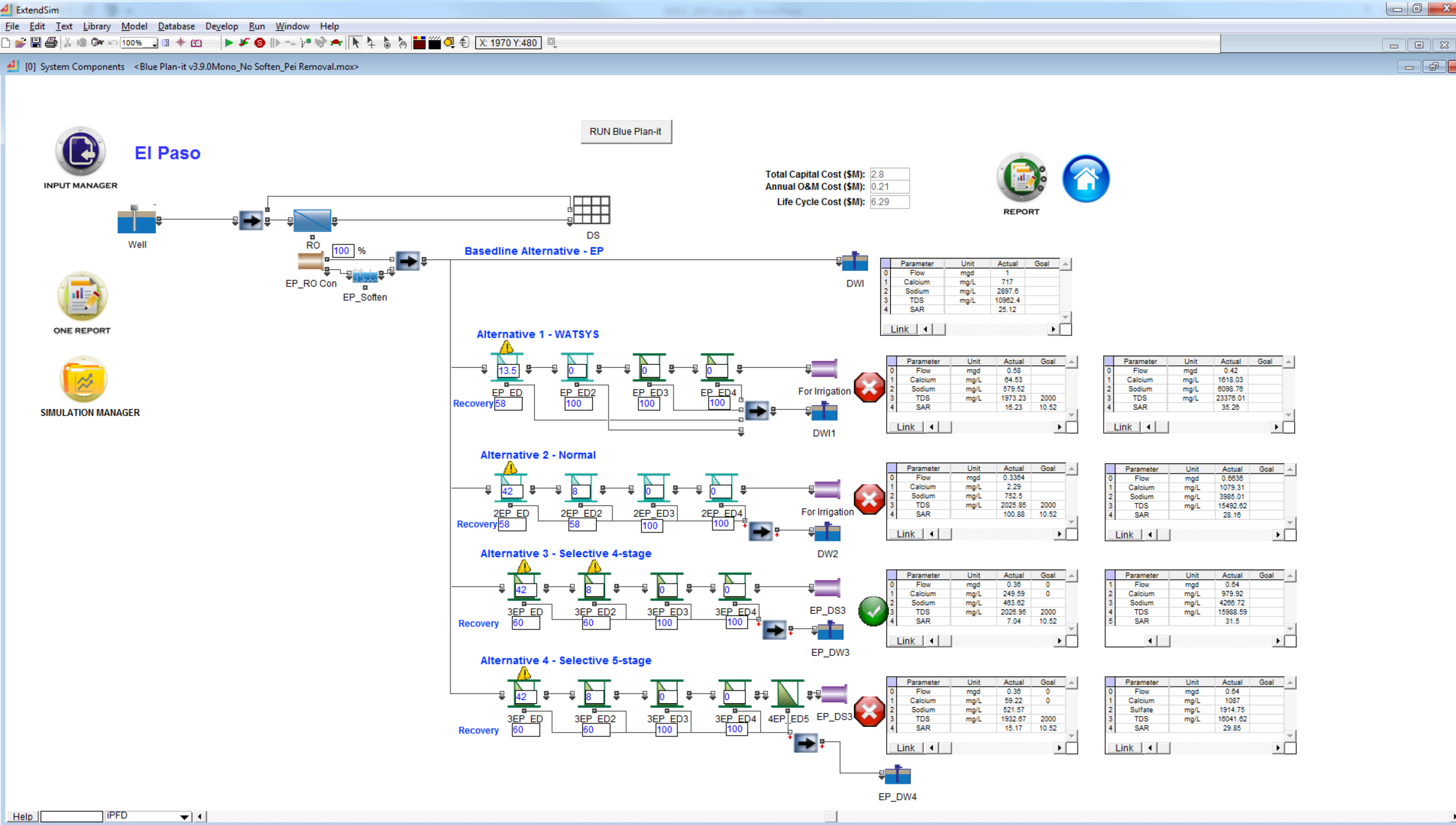
	Baseline Alternative	Alternative 1A	Alternative 1	Alternative 2
	UF + RO	Normal EDR - WATSYS	Normal EDR - Testing	Selective EDR (Based on EP GW Testing)
Feed Water Flow (mgd)	1			
Feed Water Sodium (mg/L)	235			
% Flow Treated	60.5%	69.0%	78.0%	57.5%
Overall Recovery	88%	93%	92%	94%
Unit Recovery	**85%**	**90%**	**90%**	**90%**
Blended Water Flow (mgd)	0.88	0.93	0.92	0.94
Product Water Sodium (mg/L)	✓ 110			
Product TDS (mg/L)	530	522	433	634
Concentrate Flow (gpm)	60	48	54	40
Concentrate TDS (mg/L)	7530	9662	9662	9662
Concentrate Sodium (mg/L)	1524	1927	1715	2287
Number of Product Line	-	7	6	6
Number of Stages	-	4	4	4
Capital ($/gpd product flow)	$6.1	$6.5	$7.6	$6.5
O&M ($/kgal)	$1.09	$0.88	$0.83	$0.81

Scottsdale Cost Estimates (UF RO vs. 2-stage and 4-stage Selective EDR)



Note: Costs include full system with residuals handling, chemical, and 30% contingency, 18% OH, admin & engineering. Does not include evaporation pond or other final concentrate disposal costs.

El Paso Blending Analysis and Cost Comparison



El Paso Blending Analysis and Cost Comparison – 1 MGD RO Concentrate

	Alternative 1A	Alternative 2	Alternative 3	Alternative 3A
	WATSYS	Normal Grade	Selective (Condition 1)	Selective (Condition 2)
RO Concentrate Water Flow (mgd)	1			
RO Concentrate Sodium (mg/L)	2898			
RO Concentrate Calcium (mg/L)	717			
RO Concentrate SAR|	25.1			
RO Concentrate TDS (mg/L)	10962			
% Flow Treated	100%	100%	100%	100%
Unit Recovery	**58%**	**34%**	**36%**	**37%**
Recovered Water Flow (mgd)	0.58	0.34	0.36	0.37
Product Water Sodium (mg/L)	580	753	522	485
Product Calcium (mg/L)	65	2	59	124
Product Water SAR	16.2	101	15.1	10.2
Product TDS (mg/L)	1973	2026	1933	2323
Concentrate Flow (gpm)	291	461	444	439
Concentrate TDS (mg/L)	23376	15493	16042	15976
Concentrate Sodium (mg/L)	6099	3985	1915	4297
Number of Product Line	8	10	10	10
Number of Stages	4	4*	4*	4*
Capital ($/gpd product flow)	$4.1	$10.9	$9.2	$9.2
O&M ($/kgal)	$5.62	$7.44	$8.25	$8.25

* Line and stage design is specially configured. This table shows a 4-stage equivalent.

Take Home Messages

- Selective electrodialysis membrane removes more monovalent cations (i.e., sodium) than normal grade membranes
  - Good selectivity under wide range of current
  - Similar power consumption compared to normal grade membrane
  - Better selectivity for low TDS water than for concentrate
- Selective membrane can meet the required water quality for Scottsdale (Based on El Paso GW Selectivity with improved coating method)
- Very close, but may not achieve SAR goals for recovering El Paso RO concentrate due to low Ca:Na ratio and high Na removal goal

Questions?

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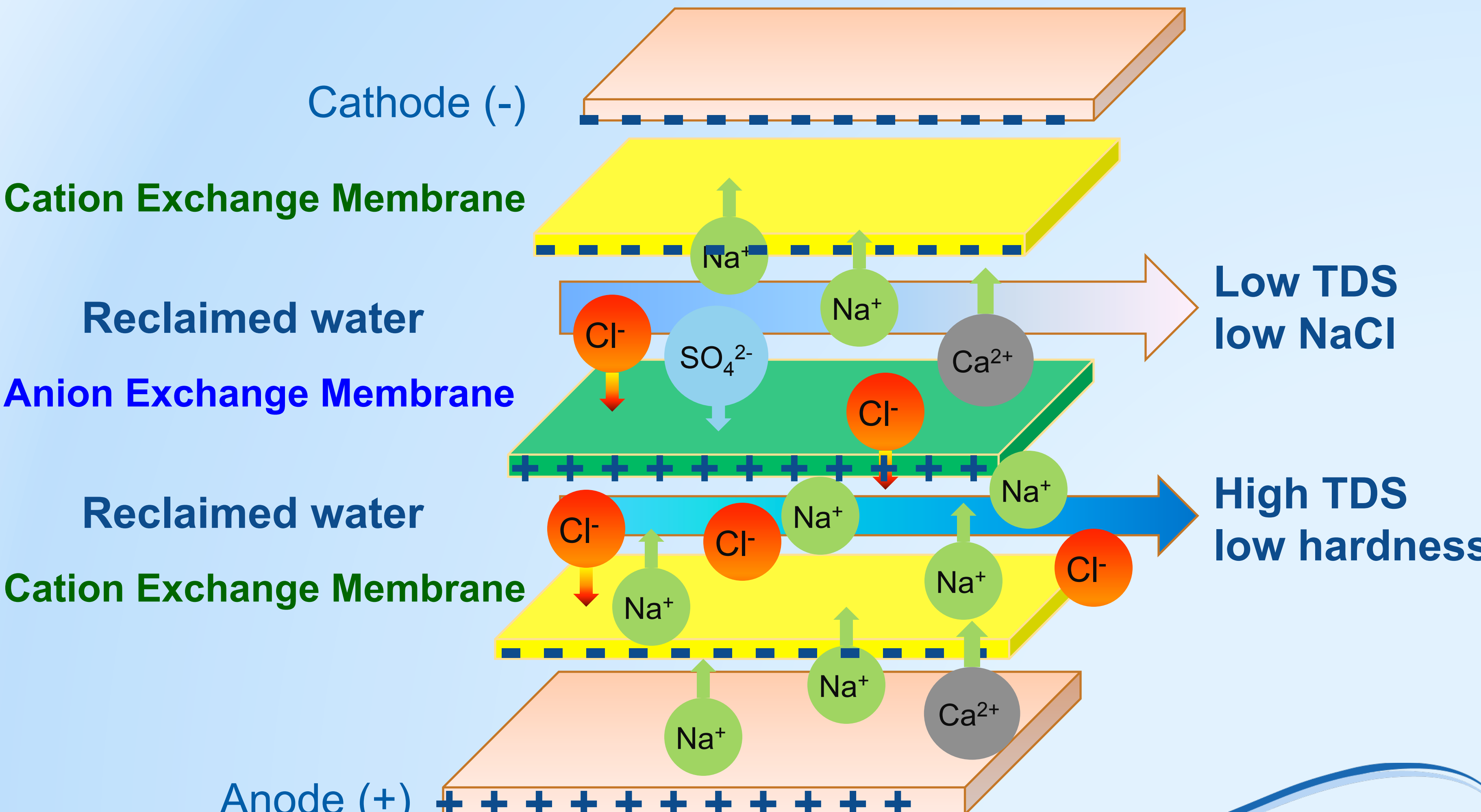
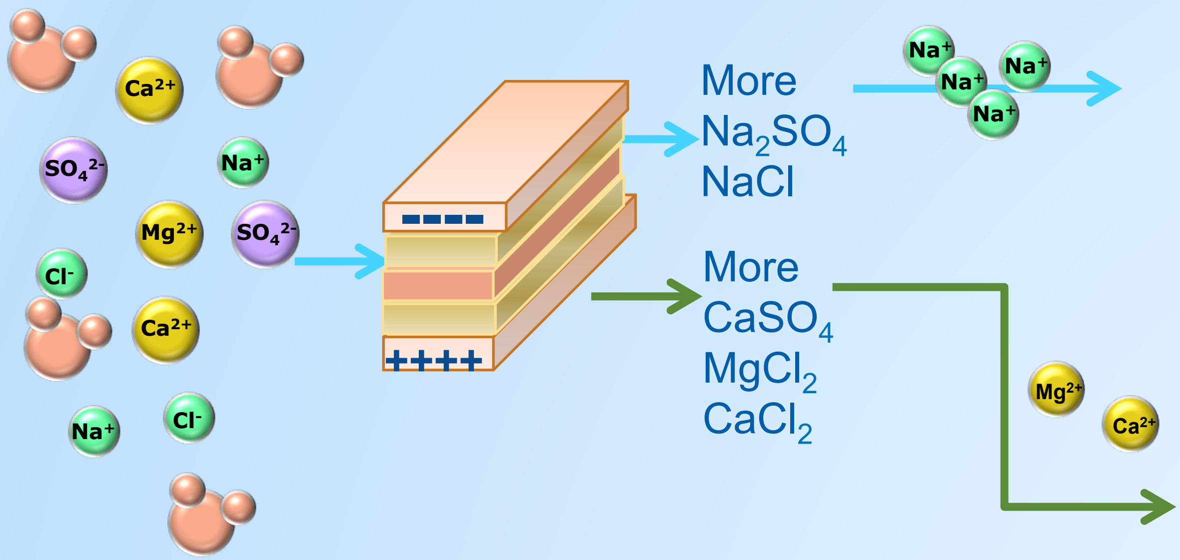
Electrodialysis with Selective IX Membranes Remove Monovalent Ions Preferably



Ion Switcher Concept Was Proposed to Solve Reclaimed Water Sodium Problem without Generating a Brine

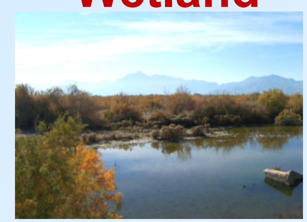
Salty Reclaimed Water
1150 mg/L TDS
215 mg/L Sodium
80 mg/L Calcium

Not a brine
Reclaimed Water
with higher TDS
relatively low hardness

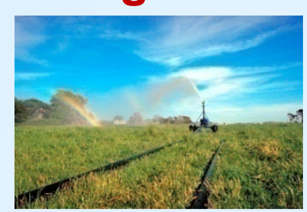


Cooling Water

Wetland



Irrigation



Product Water
<125 ppm Sodium
Reclaimed Water
with lower TDS and sodium

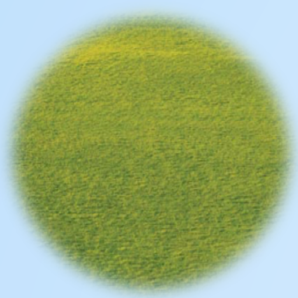
High Sodium to Hardness Ratio Resulted in Reuse Challenges

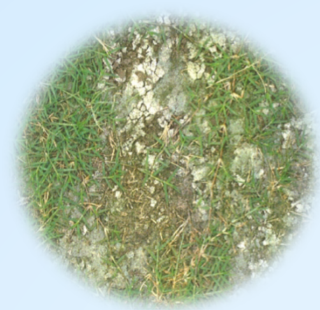
- SAR = Sodium Adsorption Ratio

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

[ ]: use meql units

≤3	6 to 9	> 9





- CAP Water SAR ~ 5 on average
- Verde River < 2 on average
- Salt River > 9 on average
- Scottsdale Water Campus Effluent 5-8

Monovalent Anions Such As Chloride Also Pose A Compliance Challenge

Whole Effluent Toxicity
Permit Action Level:
Toxic Unit 2.0 or less

Fathead Minnow (Pimephales promelas) 7-day larval survival and growth test

Water Reclamation Plant

Discharge to River

Water flea Ceriodaphnia dubia 3-brood survival and reproduction test

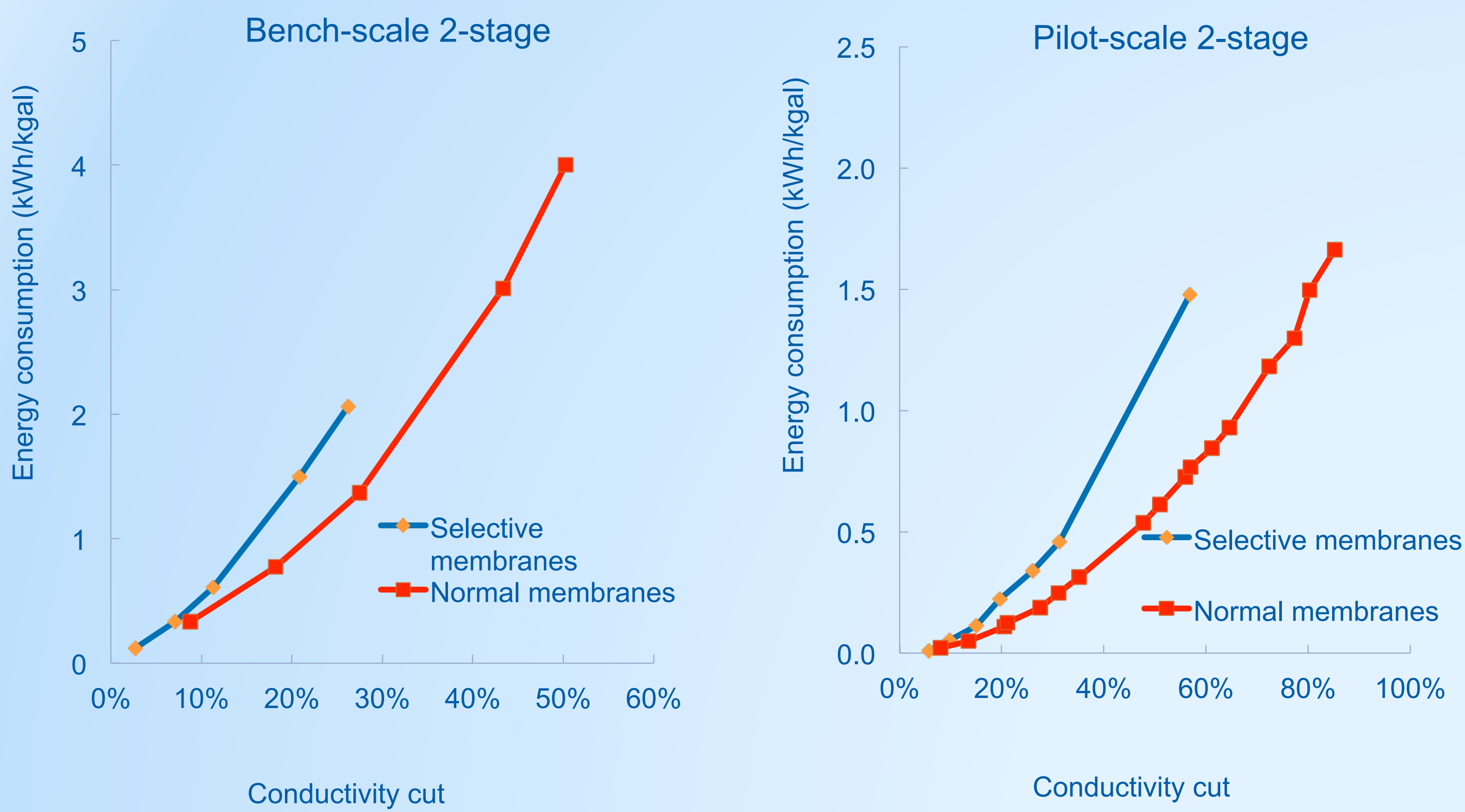
Selenastrum capricornutum Green Algae, 4-day growth test

Discussion:

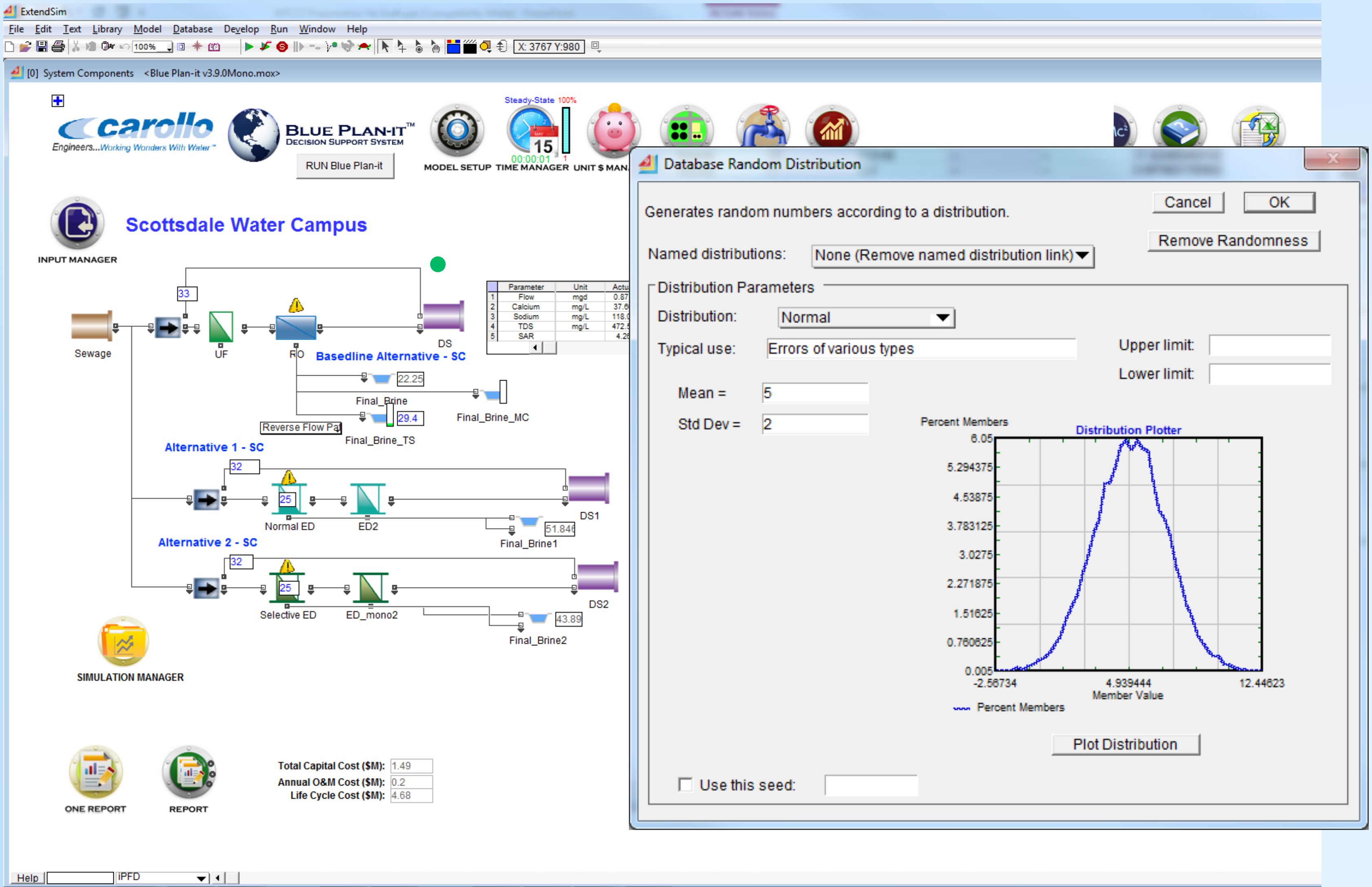
	Scottsdale	El Paso RO Concentrate
Feed Water Sodium (ppm)	235	2898
Feed Water Calcium (ppm)	80	717
Feed Sodium : Calcium Ratio	0.34	0.25
Product Water Sodium Target (ppm)	110	~464
Target Sodium Removal %	53%	84%

Selective Membrane Consumes More Power than Normal Membranes, Especially at High Conductivity Cuts

El Paso Brackish Groundwater
Power Consumption



Insert a video on model runs and misc. screens



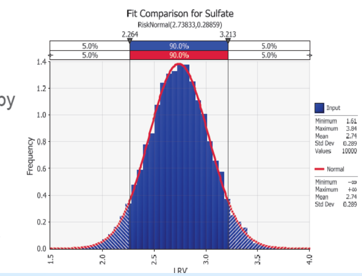
BPI Monte Carlo Simulation Have Many Applications for Desalination and Reuse

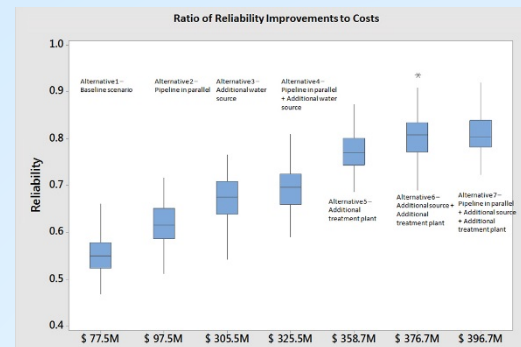
- Water System Resilience to Earthquake
- Hurricane Impact on SWRO Siting and Operation
- Microbial Risk Assessment and DPR Reliability
- Security and Vulnerability Assessment
- Pond sizing considering randomness in climate changes

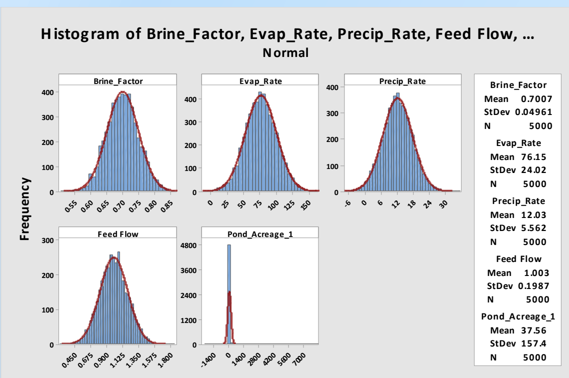
RO Membranes: Sulfate as Surrogate for Giardia and Crypto

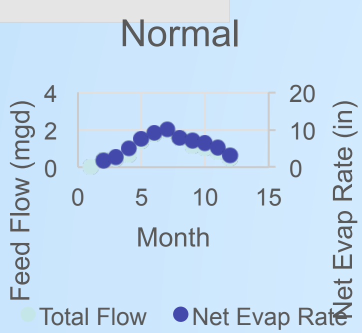
Limited short term test data available on virus removal by RO

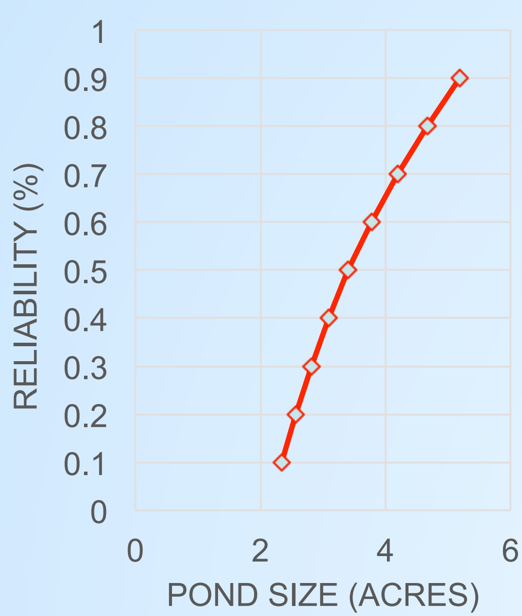
Necessitated long-term surrogate data use

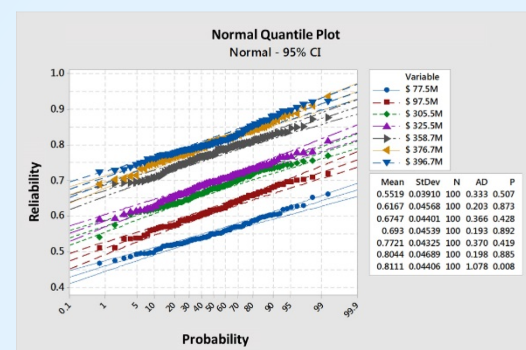












Scottsdale Cost Estimates (2 Stage Ion Switcher vs. UF RO)