NEW TECHNOLOGIES & BREAKTHROUGHS TO OLD DEIONIZATION APPLICATIONS

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STS AIChE March 2018 Monthly Dinner Meeting – Workshop

Thursday, March 1, 2018, 5:30pm-6:30pm CST

The Bougainvilleas, Houston, TX 77077, United States

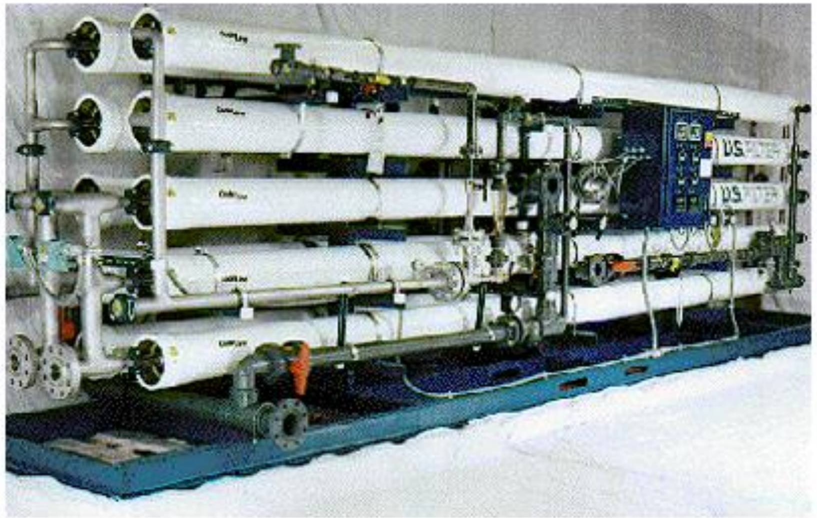
EQUIPMENT EXAMPLES SECTION

Basic water treatment methodologies

- Softeners
- Carbon
- Ultraviolet (UV) treatment
- Filtration
- Reverse Osmosis (RO)
- Deionization (DI)

Equipment: 72-inch skid-mounted dual filters

Application:	**Pretreatment OTSG (SAGD)**
Equipment:	**Omni w/ custom GS, Softeners, CL2 Inj, pH, O2 Scav**
Location:	**Canada**
Size:	**150gpm**



Reverse osmosis

Brine Concentrator
(mechanical vapor
recompression)

Application: Amine Makeup Water
Equipment: Pre-treat & RO
Location: Louisiana
Size: 20gpm

Application:	Potable water production
Equipment:	Sea water RO
Location:	North Sea oil platform
Customer:	Rosetti - Italy
Size:	20 gpm

Application: Process / Boiler Feed
Equipment: Counter Current IX
Location: Pasadena, TX
Size: Dual Trains – 90 gpm

Media, Softener, Carbon, and Chemical Feed
200-gpm Single Pass
100-gpm Double Pass

TOTAL DISSOLVED SOLIDS (TDS)

When reviewing water reports, the most important information to look for is the total dissolved solids or TDS. The TDS is the sum of all ions dissolved in the raw water. As seen in Table 4, the TDS is greater than the sum of all recorded minerals on the report. The conductance is also a good indicator of water quality 1.56 uS/cm (conductance) = TDS. Other ions can be present in water which are not shown on the report such as aluminum, boron, manganese, potassium, and many others.

CONDUCTIVIY VS RESISTIVITY

When the ionic concentration is very low (such as in high purity water), the measured conductivity falls below a value of one microsiemen per centimeter. In order to express this value as a whole number, as opposed to fractions, the resistivity scale are often used; conductivity and resistivity are inversely proportional. For example: the reciprocal of 0.10 μS/cm [or 1/(0.10 x 10^6 S/cm)] is then 10 x 10^6 ohms-cm (10 MΩ-cm). This is also commonly referred to as megaohms. Either unit of measurement can be used to state exactly the same value.

CONDUCTANCE

A convenient way to estimate the total amount of dissolved salts in water is to measure its electrical conductivity. A conductivity measurement can't distinguish between salts. Dissolved ions like sodium and chloride tend to have higher conductivities than other ions like calcium, magnesium and sulphate. Water with a higher proportion of sodium and chloride tends to have higher conductivity than water with the same amount of calcium, magnesium and sulphates.

Conductance		Resistance		Dissolved Solids		Status
Microsiemens	Micromhos	Ohms	Megaohms	PPM	GPG	
0.0500	0.0500	20,000,000	20.0	0.032	0.002	Stainless Steel Fill Valve Required
0.0556	0.0556	18,000,000	18.0	0.036	0.002	
0.0625	0.0625	16,000,000	16.0	0.040	0.002	
0.0714	0.0714	14,000,000	14.0	0.046	0.003	
0.0833	0.0833	12,000,000	12.0	0.053	0.003	
0.100	0.100	10,000,000	10.0	0.064	0.004	Brass Fill Valve with Stainless Steel Seat Acceptable
0.125	0.125	8,000,000	8.0	0.080	0.005	
0.167	0.167	6,000,000	6.0	0.107	0.006	
0.20	0.20	5,000,000	5.0	0.128	0.007	
0.25	0.25	4,000,000	4.0	0.160	0.009	
0.50	0.50	2,000,000	2.0	0.321	0.019	
1.00	1.00	1,000,000	1.0	0.641	0.037	
2.00	2.00	500,000	0.5	1.282	0.075	
4.00	4.00	250,000	0.25	2.564	0.150	
5.00	**5.00**	**200,000**	**0.2**	**3.205**	**0.187**	**Alarm**
6.67	6.67	150,000	0.15	4.274	0.250	Water Treatment Maintenance Required
8.00	8.00	125,000	0.13	5.128	0.300	
10.00	10.00	100,000	0.10	6.410	0.375	
12.50	12.50	80,000	0.08	8.013	0.469	
14.29	14.29	70,000	0.07	9.158	0.536	
16.67	16.67	60,000	0.06	10.684	0.625	
20.00	**20.00**	**50,000**	**0.05**	**12.821**	**0.750**	**Shutdown**

Table – Conductance, Resistance and Dissolved Solids

PH

pH is an approximate indication of the acidity or alkalinity of water. pH is a logarithmic expression of the inverse of the number of hydrogen ions (H^+) present in a solution. Low pH water often indicates increased corrosion potential or acidity in the sample. For drinking water pH should ideally be between 6.8 and 8.5.

TOTAL HARDNESS

Hardness is the amount of calcium and magnesium in the sample water. By convention hardness is given as amount of calcium carbonate ($CaCO_3$) although it actually measures magnesium as well.

CALCIUM

Calcium (Ca) is the measure of calcium carbonate ($CaCO_3$) contained in the sample. Calcium carbonate is commonly found in ground water. Total water hardness is normally expressed as $CaCO_3$ on water quality reports.

MAGNESIUM

Magnesium (Mg) is expressed on most water hardness reports as $CaCO_3$. This expression is to normalize magnesium atomic number (12) to calcium atomic number (20), this is to express the total water hardness as parts per million of $CaCO_3$.

ALKALINITY

Alkalinity is a measure of the bicarbonates (HCO_3) and hydroxides (OH) that make water alkaline. The alkalinity in water comes partly from carbon dioxide dissolving in the water to form bicarbonate and H^+ ions. There is no acceptable or unacceptable level of alkalinity. Alkalinity gives an indication of the resistance the water has to changes in pH. It is also used along with carbon dioxide levels to calculate a theoretical pH.

NITRATE

The amount of nitrate (NO_3) in water is an important issue in many parts of the world due to nitrates entering groundwater and streams due to runoff of agricultural fertilizers or through organic pollution. High concentrations of nitrates may be a health problem. In unpolluted water nitrate is rarely above 1 ppm so higher levels may indicate contamination. If measurements are given as Nitrate-N this means the nitrogen contained in the nitrate compound is free nitrogen. Free nitrogen is unbound nitrogen which can form harmful nitires. To convert nitrate to nitrite, multiply by 4.4, so 1 ppm Nitrate-N (NO_3-N) is the same as 4.4 ppm nitrite (NO_2).

CHLORINE AND CHLORINATION

Chlorine gas (Cl_2) is widely used as a cheap and effective sanitizer for water. Bacteriological contamination is unlikely to occur if free chlorine levels are kept around 0.4 – 0.5 ppm. If used to treat drinking water, chlorine helps to offset the harmful effects of iron, manganese, sulphides and ammonia.

ORTHOPHOSPHATE

In natural waters orthophosphate (PO_4) ranges from about 0.005 – 0.02 ppm. Algae may become a problem in water with more than 0.05 to 0.09 ppm phosphate, depending on other conditions. Around 0.27 ppm phosphate is excessive in natural waters and may lead to over production of plants including algae. If water report is given as phosphorus, then multiply by 4.58 to get phosphate.

SILICA

Silica (SiO_2) can be present in water as silicic acid or silicate ions. This is known as reactive silica. It can also be present as insoluble or suspended particles in a polymeric or colloidal state. In general reactive silica levels are 20 ppm, and significantly higher in well water. The main problem with reactive silica is that it supports greater growth of algae in water.

IRON

Iron (Fe) is normally measured as dissolved and suspended. Dissolved iron levels for drinking water should not exceed 0.2 – 0.3 ppm, Iron in excess can foul pipes and fitting. Suspended iron occurs when water from wells and deeper dams is brought to the surface and mixes with air the iron becomes less soluble and suspends as reddish iron compounds. The iron becomes less soluble due to two factors; the water becomes more oxygenated and the pH usually rises because carbon dioxide dissipates.

COPPER

Normally copper (Cu) levels are around 0.03 ppm in natural waters but may rise to 1 ppm if copper contamination is present.

Levels are commonly around 0.05 ppm in reticulated supplies. Copper levels of 1.3 ppm or greater may cause staining and water may have a bitter taste. Water which is acidic normally contains higher copper levels due to dissolved copper from plumbing.

MOLYBDENUM

Molybdenum (MoO_4) is soluble in water and is a naturally occurring mineral. It is normally found in surface water supplies, such as water systems pulling water from rivers and reservoirs.

KEY INDUSTRIES SERVED BY D.I.

- Energy
- Oil & gas
- Chemical
- Food & beverage
- Industrial
- Pharma and Ultrapure
- Electronics and Plating operations

TOLYLTRIAZOLE

Tolyltrazole ($C_7H_6N_3$) or TTA is a rust and corrosion inhibitor. TTA is only found in a water systems where it has been added. TTA should only be found in closed loop systems. It is an irritant, to skin, eyes and is harmful if ingested.

MONO SODIUM NITRATE

Sodium nitrite ($NaNO_2$) concentrations are rarely over 0.1 ppm in natural water. Formation of nitrites is an intermediate step in the process that converts ammonium to nitrate. Normally nitrites are oxidized to less harmful nitrates in water if there is an adequate amount of oxygen. If there is too much nitrogenous waste to break down, the process may not have enough oxygen and nitrites will accumulate. Nitrite binds with sodium in a water system that contains insuficent oxygen to make nitrates. Sodium nitrite is used to prevent growth of bacteria; however in high amounts it is toxic to animals and humans.

Application: Ultrapure Water
Equipment: UF, RO, MB/DI
Location: Peru
Size: 3,840 m^3/day

Application: Ultrapure water
Equipment: Sand, SB, MB/DI
Size: 720 m^3/day

Application: Power Production
Equipment: RO / EDI
Location: US
Size: 150 gpm

Application: Boiler Feed – 926 Megawatts Natural Gas Power Plant

Equipment: Double Pass RO, PEDI, MCC, 16,000 gal tanks PLC

Location: Austin, Texas

Application: Diesel Fired Turbines
Equipment: Pretreat, RO (2 trains)
Location: Venezuela via Houston
Customer: Solar Turbines
Size: 5- 7 gpm

Application: Boiler Feed – Power
Equipment: Double Pass RO, MCC, Fully Automated PLC, MB DI
Location: Algeria
Size: 250 gpm

advanced membrane technologies
that address the most demanding water challenges

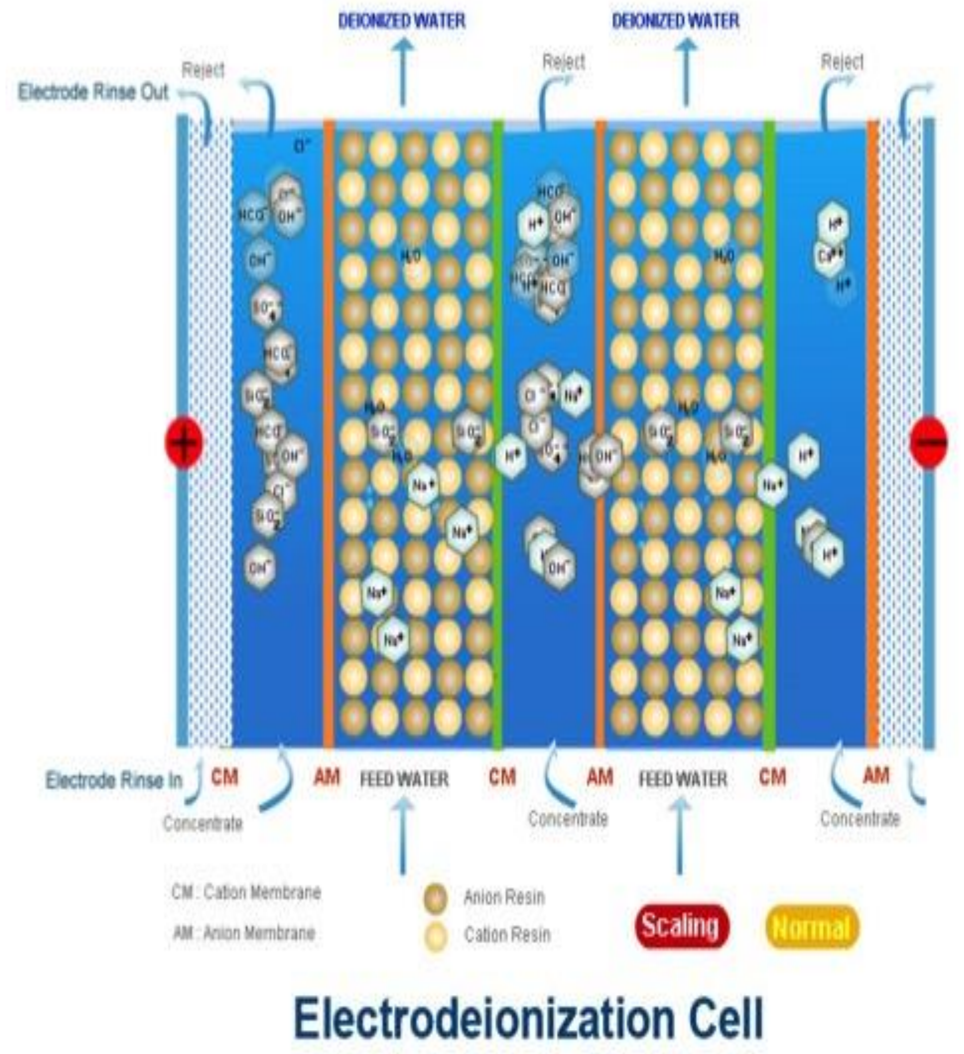
The next generation of EDI

FRACTIONAL ELECTRODEIONIZATION MODULES

- **Dual voltage process**
- **Higher hardness tolerance in feed water**
- **Quick startup**
- **Reduced cleaning**

FRACTIONAL ELECTRODEIONIZATION MODULES
Covered By Three Differentiating Patents:

•US Patent # **6,896,814 B2** for “Fractional Electrodeionization Process” (May 24, 2005)
•US Patent # **7,163,964 B2** for “Method of Preparing Ion Exchange Media“ (Jan 16, 2007)
•US Patent # **9,095,822 B2** for “Split Flow EDI Apparatus for Treating Second Pass RO Permeate Water with High Flow Rate” (Aug 4, 2015)
•CE Certified
•UL Certified
•FDA Certified for FEDI Rx

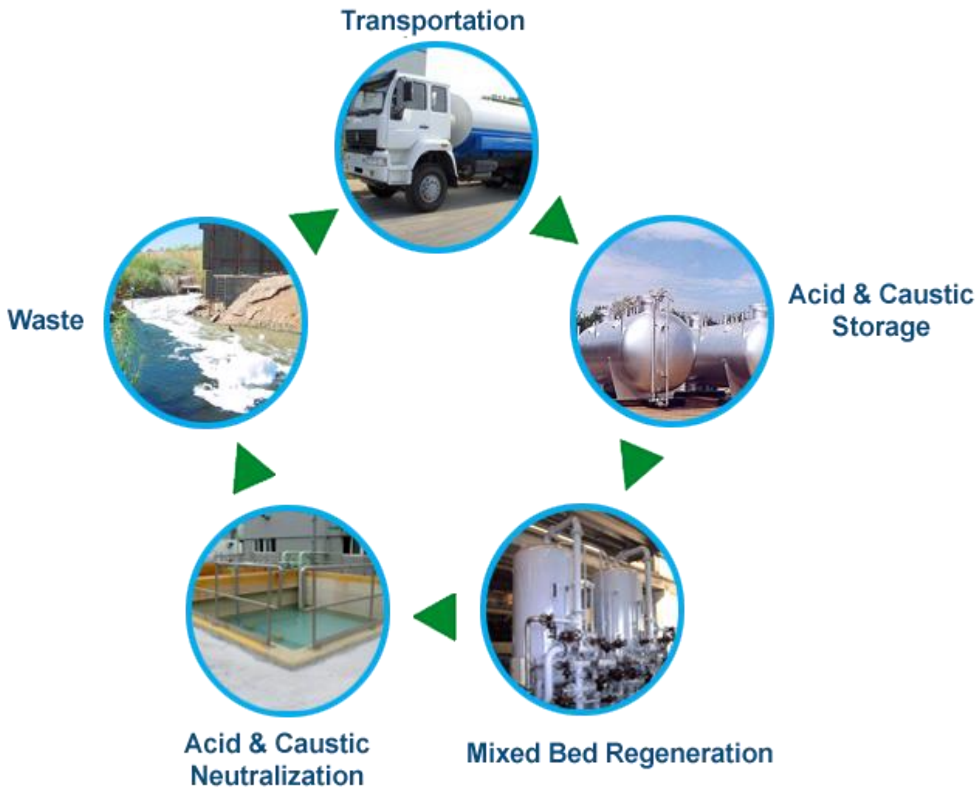


EDI OR ELECTRODEIONIZATION

Combines Electrodialysis & Ion Exchange

- Combination process
  - →Ion exchange resin media
  - →Ion selective membrane

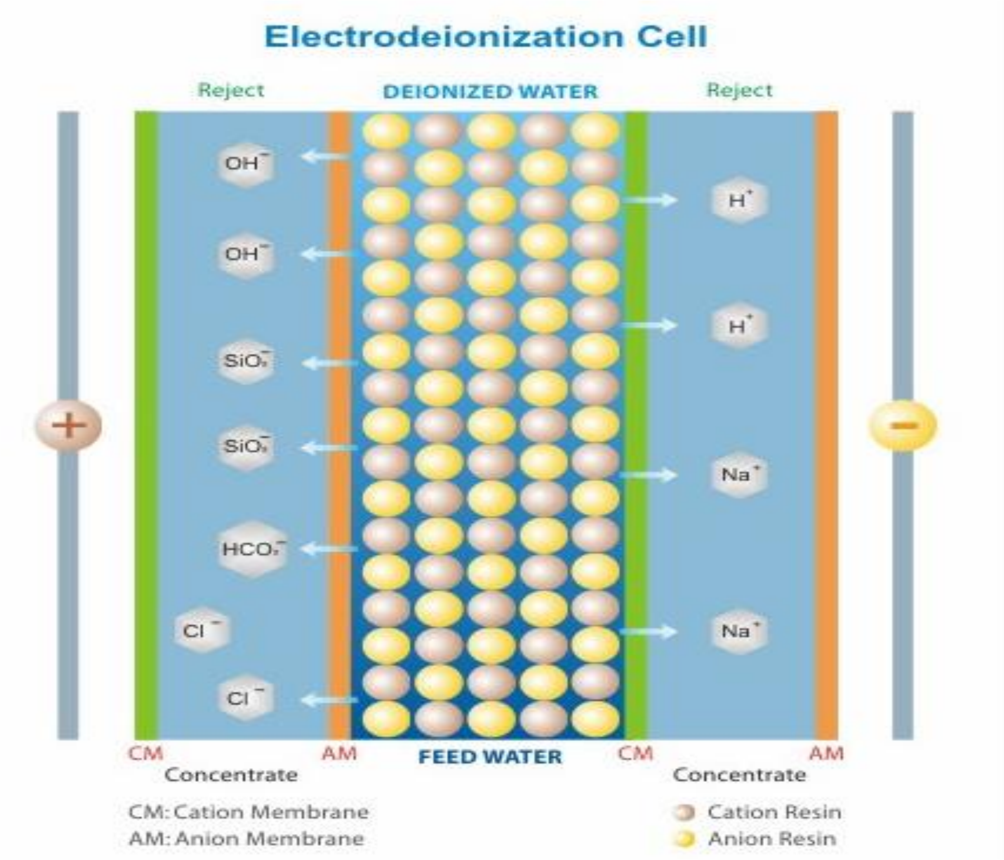
- Electric current used to
  - →Move ions uni-directionally across membrane
  - →Regenerate resin

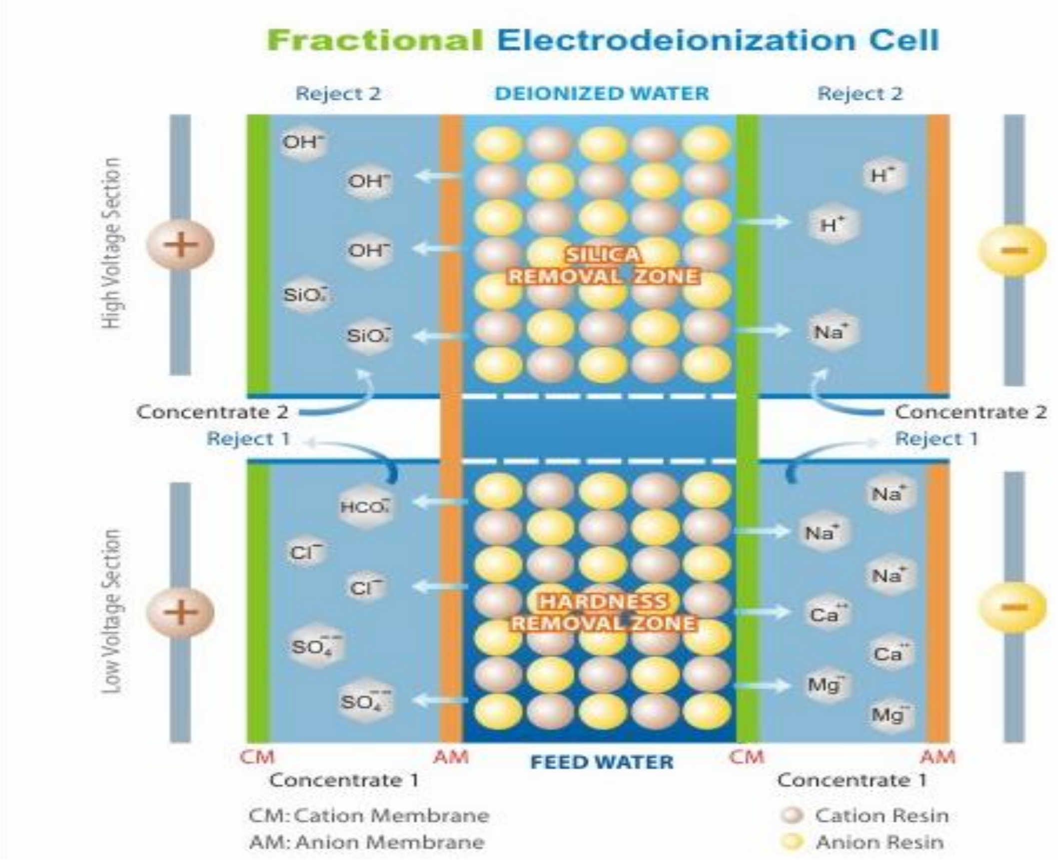


KEY EDI ADVANTAGES VS. MIXED BED

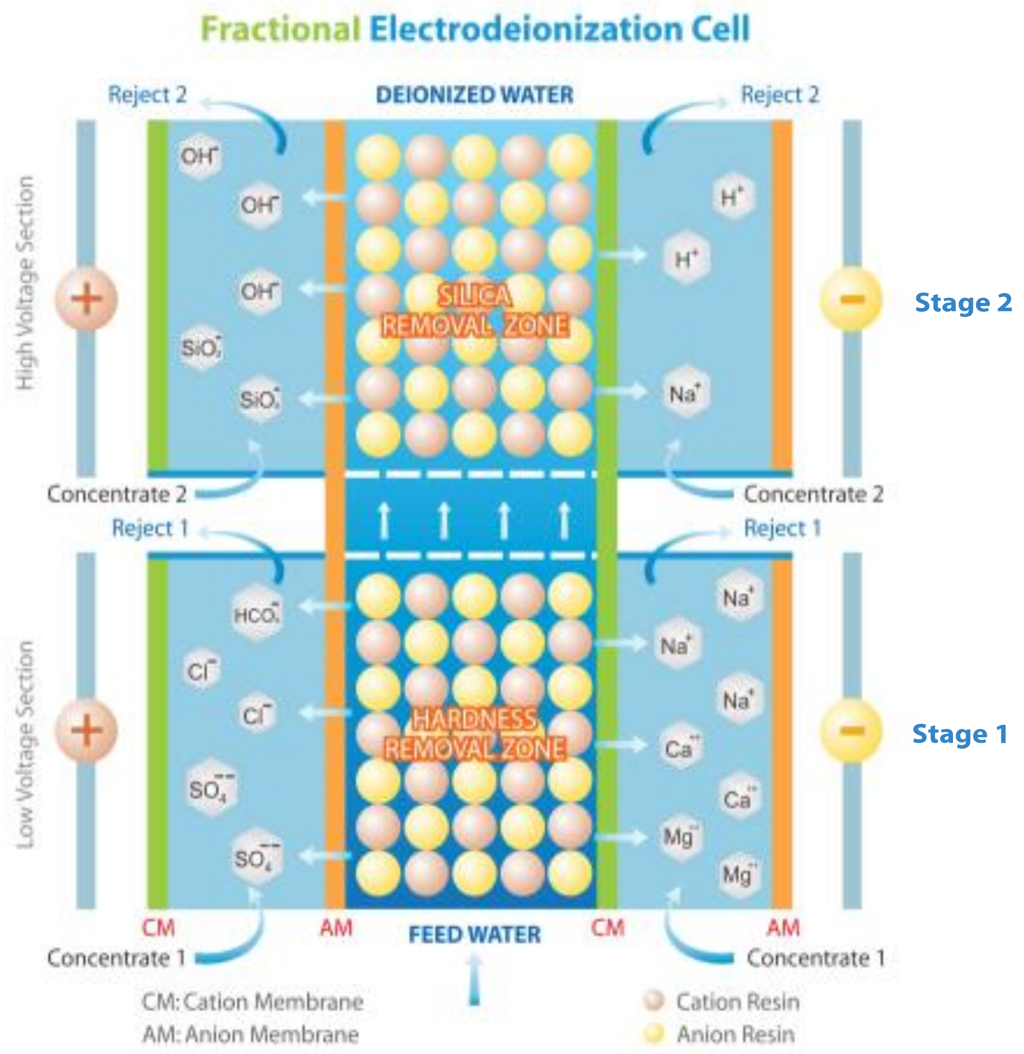
- **No Regeneration Chemicals**
- **No storage or handling of toxic chemicals**
- **Safe operation**

TECHNICAL SPECS


Electrodeionization Cell
Reject
DEIONIZED WATER
Reject
OH⁻
SiO₃⁻
HCO₃⁻
Cl⁻
H⁺
Na⁺
CM
AM
FEED WATER
CM
AM
Concentrate
Concentrate
CM: Cation Membrane
AM: Anion Membrane
Cation Resin
Anion Resin


Fractional Electrodeionization Cell
Reject 2
DEIONIZED WATER
Reject 2
High Voltage Section
Low Voltage Section
SILICA REMOVAL ZONE
HARDNESS REMOVAL ZONE
Concentrate 2
Reject 1
Concentrate 2
Reject 1
CM
AM
FEED WATER
CM
AM
Concentrate 1
Concentrate 1
CM: Cation Membrane
AM: Anion Membrane
Cation Resin
Anion Resin

EDI VS. FEDI



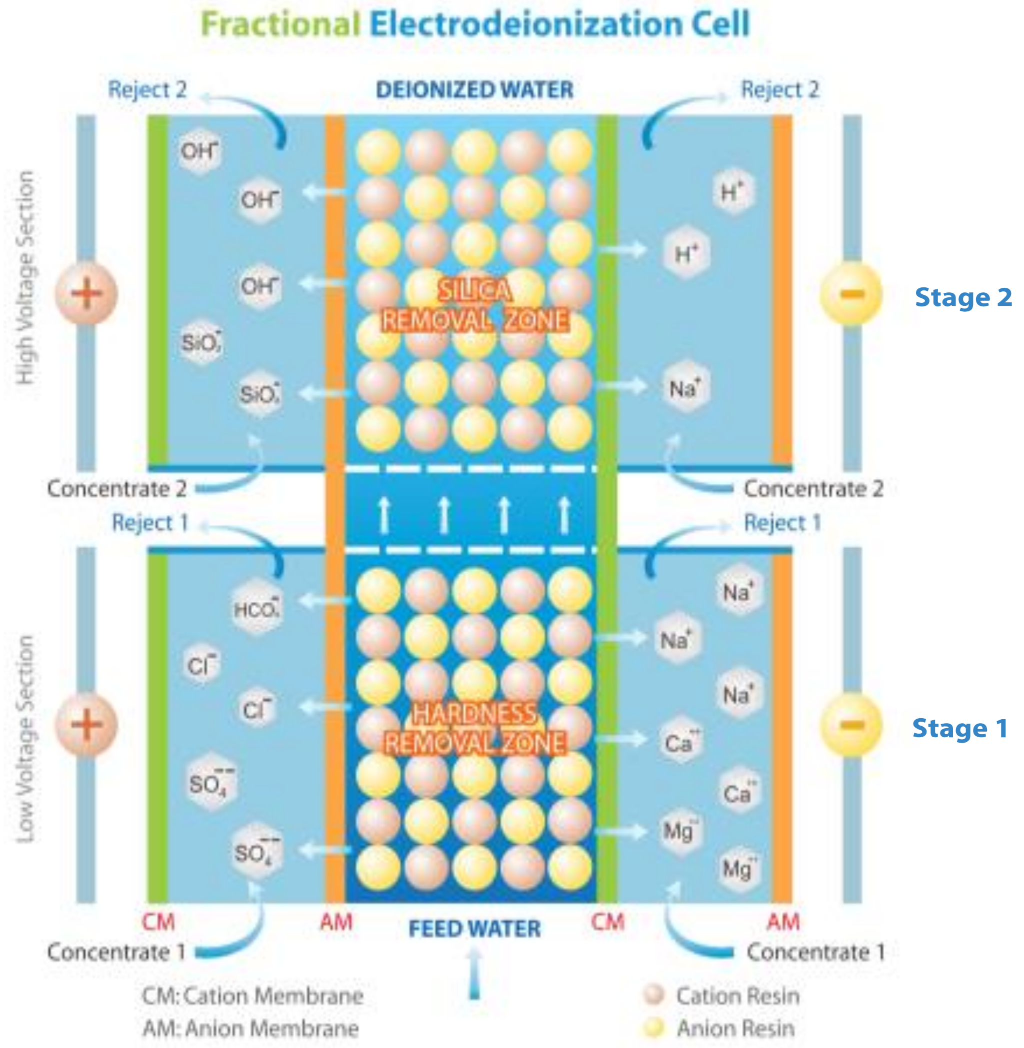
FEDI® - DIFFERENTIATED SEPARATION TECHNOLOGY

•Advanced two stage process

•Designed to fractionate & separate

•Creates ideal conditions for removal

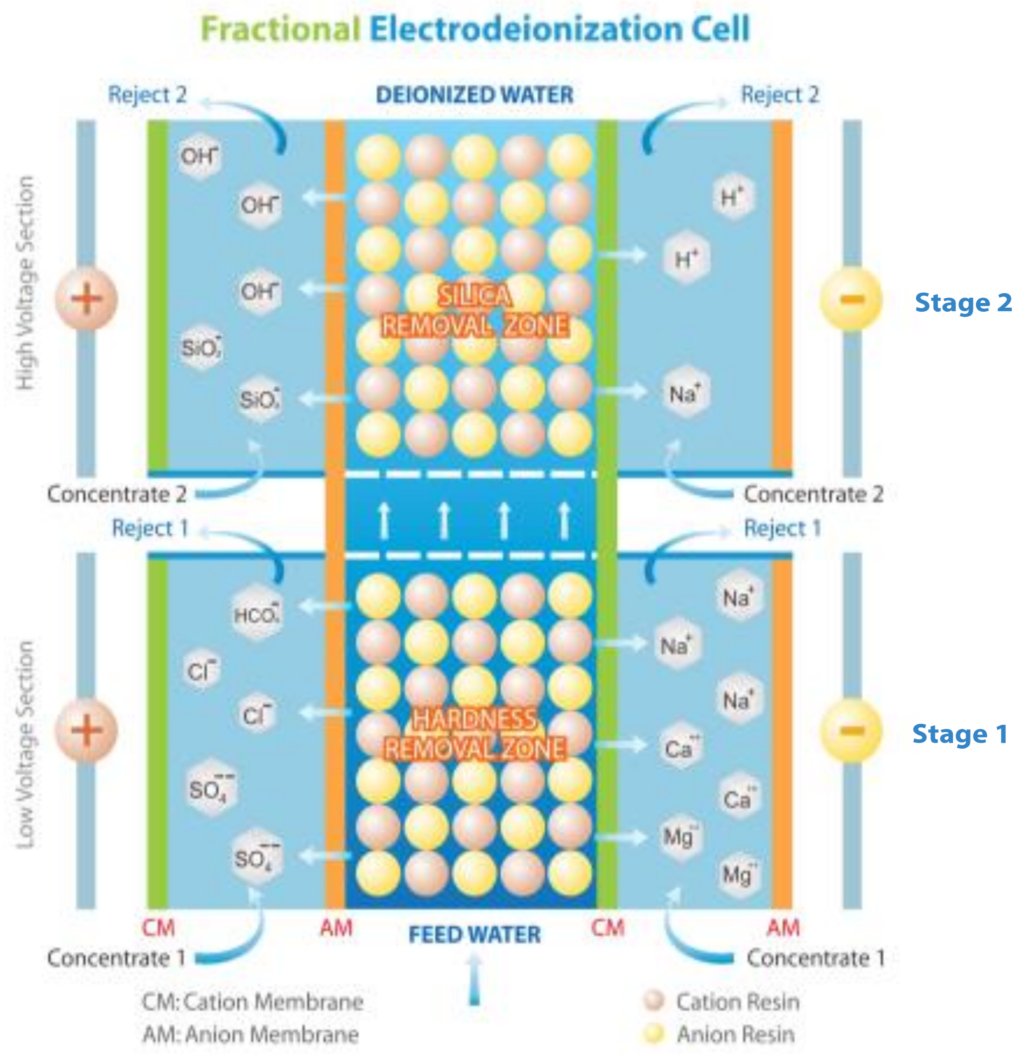
- Strong & weekly ionized impurities
- Using varying electrical driving force



FEDI® TWO-STAGE PROCESS

Hardness Removal Zone

- Low electrical driving force
- Strongly ionized impurities removed
- - (Ca^{++}, Mg^{++}, Na^{+}, SO_4^{--}, Cl^{-})
- Reject pH acidic, eliminates scaling
- Prepares weekly ionized impurities for Stage 2 removal



FEDI® TWO-STAGE PROCESS

•Silica Removal Zone

- Higher electrical driving force
- Creates water splitting
  - - Results in highly regenerated resin
  - - Results in alkaline reject pH
- Balance monovalent & weakly ionized impurities removed (Silica, Boron, CO_2)

ADVANTAGES OF TWO-STAGE SEPARATION

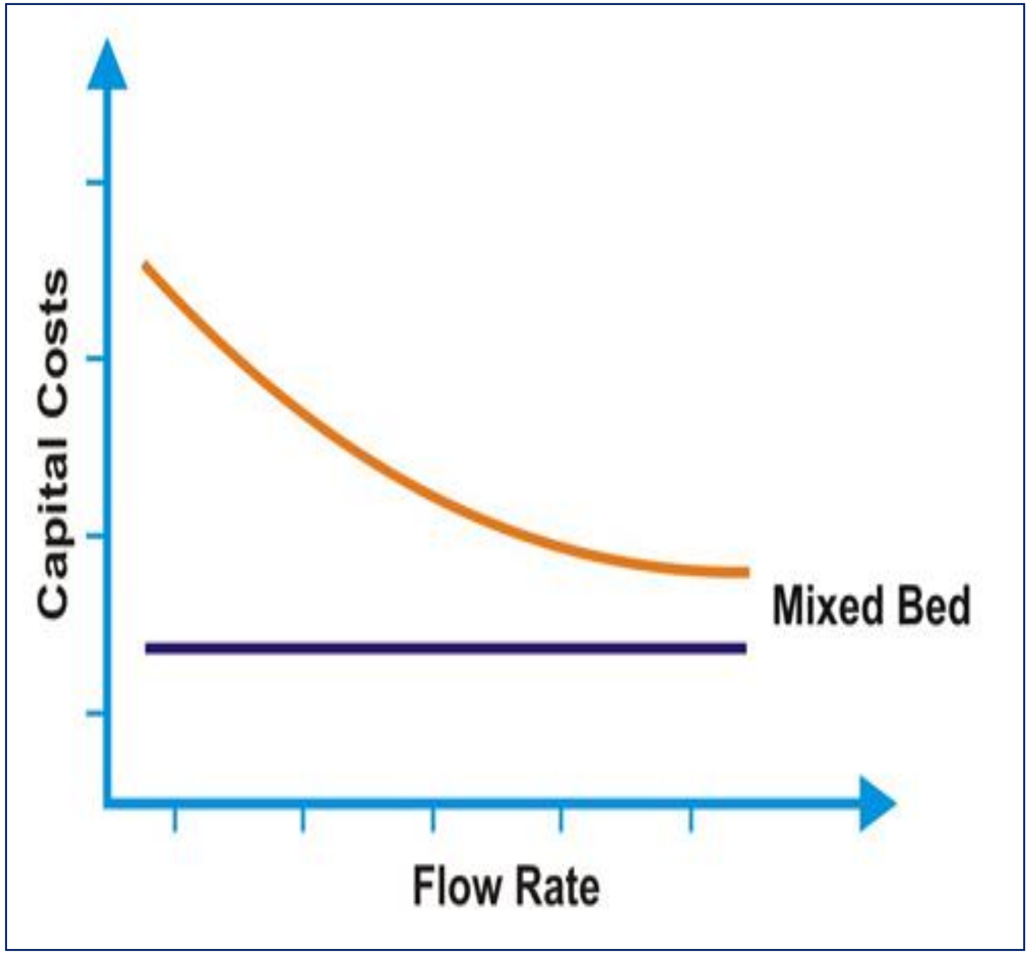
- Two distinct voltage and pH operating zones
- Working zone to take primary load
  - →High hardness tolerance due to low pH
- Regenerated zone for polishing mode
  - →Ideal condition for silica removal at high pH
  - →High removal of ionic TOC
- Optimized power consumption
  - Low voltage for primary load
  - Higher voltage for secondary load / polishing
  - Better control for process optimization

FEDI APPLICATIONS

- **Power and Oil & Gas Industries**
  - Demineralized water with conductivity < 0.1 - <1.0 microS/cm
  - Reactive Silica < 10 / < 20 ppb
  - Sodium (Na): <5 ppb, Chloride <3 ppb
- **Pharmaceutical Industry**
  - High purity product water < 1.0 MicroS/cm
- **Semiconductor/ Microelectronics Industries**
  - Ultrapure product water > 16 Megaohm.cm or better
- **Industrial Water**
  - High purity product water

- **Replacement of existing Mixed Bed Polisher with FEDI® after RO system**
- **Replacement/Retrofits of Other EDI based system with FEDI®**
- **Condensate polishing (Ambient Temperature)**

FEDI SYSTEM



COST EFFECTIVE AT ALL FLOW RATES

•Cost-Competitive With Primary Mixed Beds

•Cost-Competitive At All Flow Rates

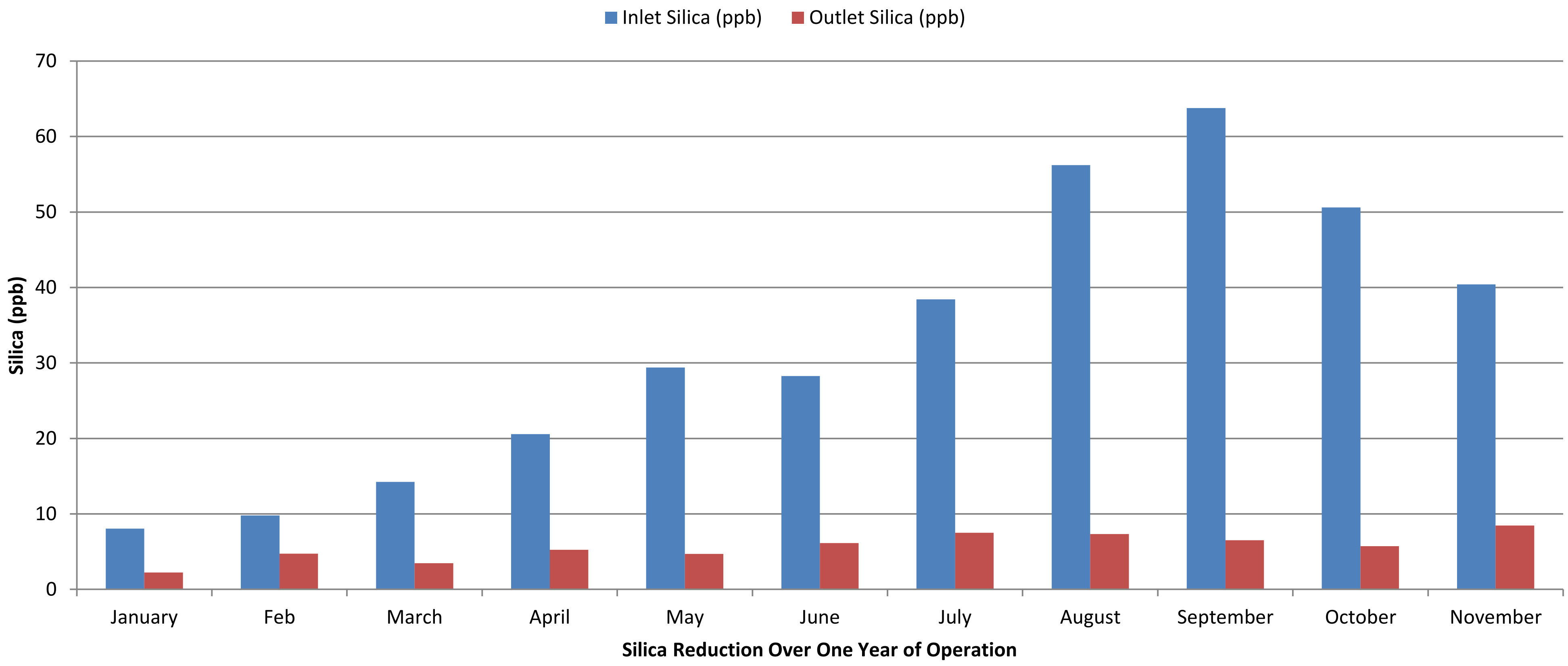
CASE STUDY: ELECTRIC GENERATION FACILITY

- Commissioned in 2010, still running very well after 6 years of performance
- FEDI Dual Voltage stacks – 2 trains of 165 gpm.

FEDI stacks treating Single pass RO water to produce less than 0.07µS/cm Conductivity and less than 10ppb Silica

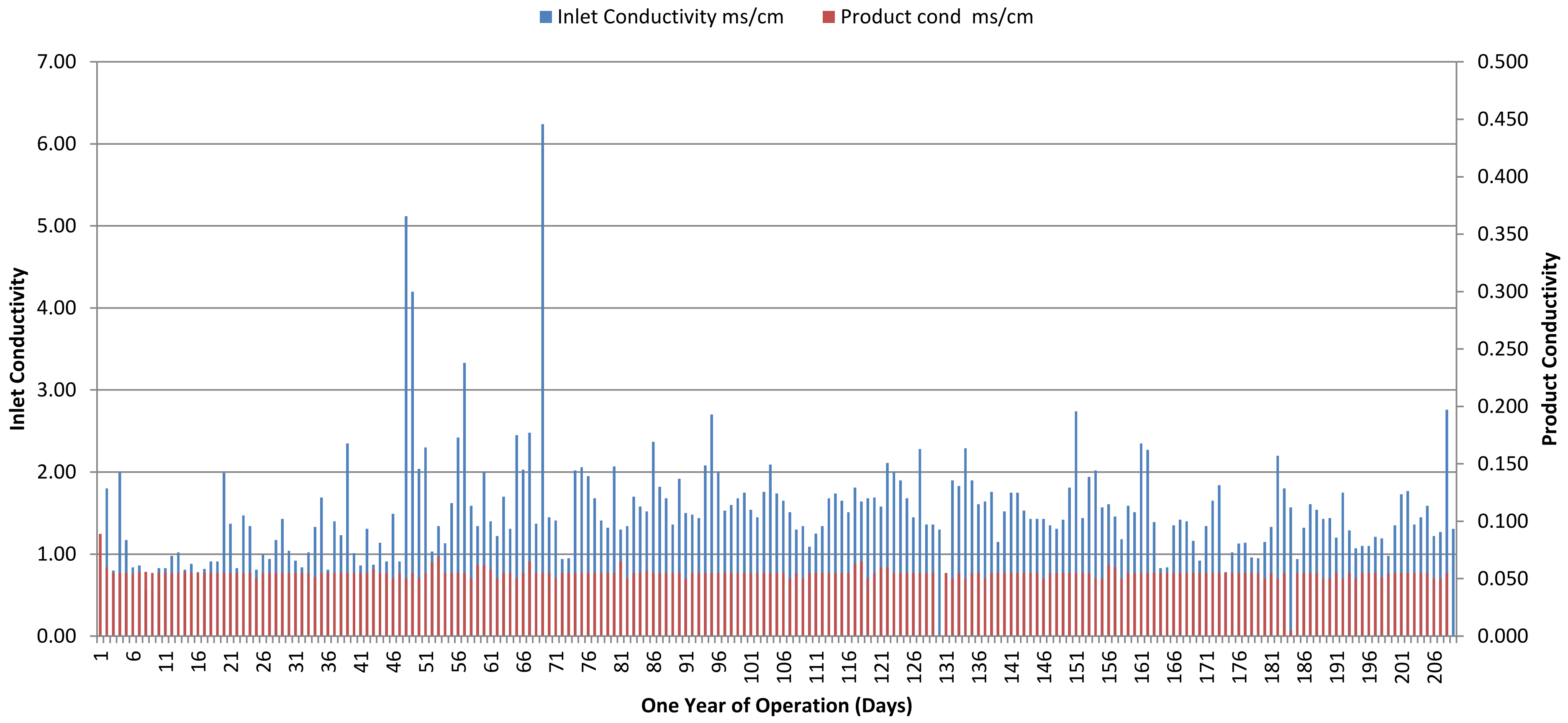
Feed water characteristics	Product water characteristics
Silica up to 70ppb	Silica less than 10ppb
Inlet cond up to 6 to 7µS/cm	Prod cond less than 0.07µS/cm

CASE STUDY: ELECTRIC GENERATION FACILITY



- Despite rises in inlet silica, consistent removal to below 10 ppb

CONDUCTIVITY PERFORMANCE FOR ONE YEAR

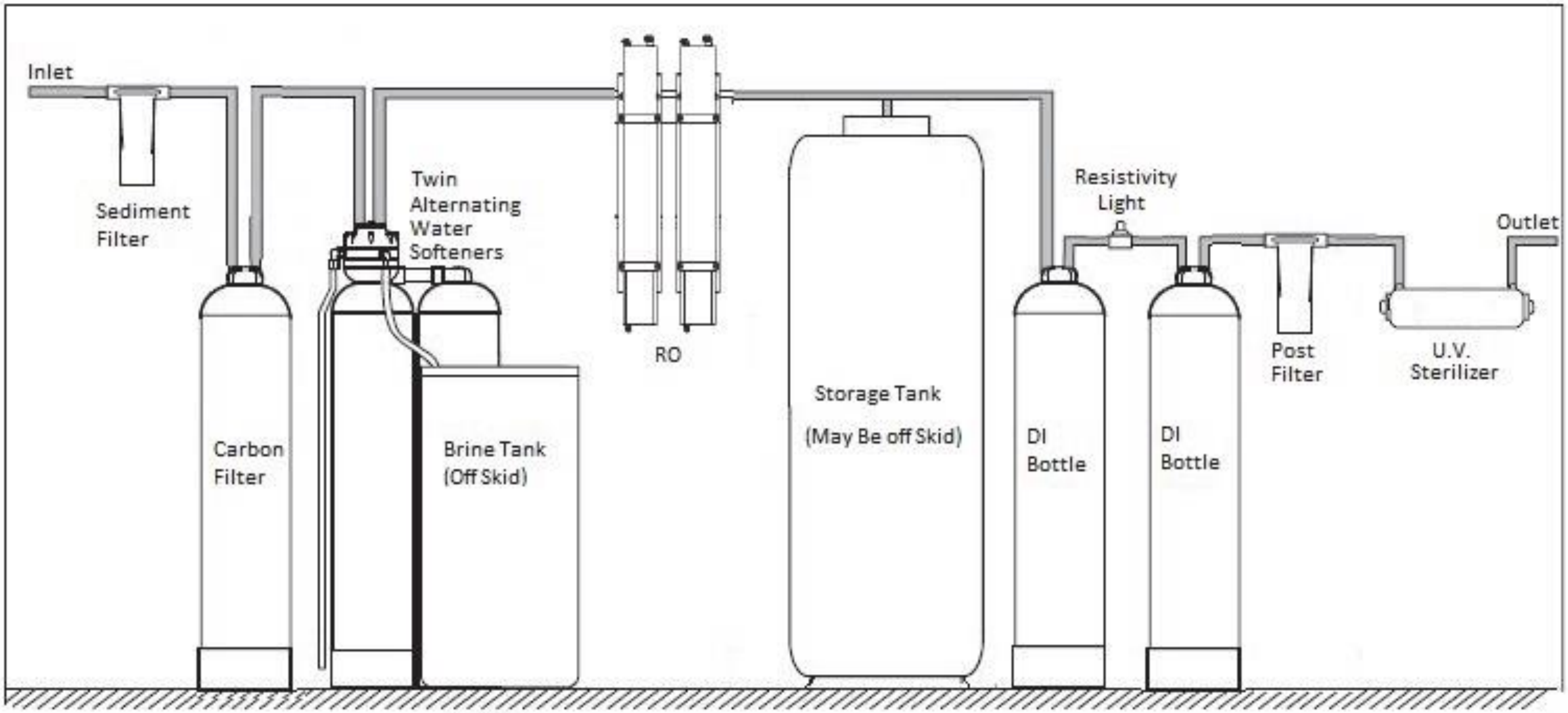


- Conductivity consistently below 0.1 µS/cm, despite spikes

Demi Cabinet

RO Cabinet

Large RO Skid



RO Skid Process Diagram

QUESTION & ANSWER SECTION

Culligan Water

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- Customized treatment solutions