Preparation of Ultra Pure Water

A focus on Membrane Separations

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Today's Presentation

- Introduction to pure water applications
- Pure water quality requirements
  - Semiconductor, Power, Pharmaceutical
- Water Contaminants
- Membrane Processes
  - MF, UF, RO
- Ion Exchange
  - EDI
- Semiconductor Industry Water
  - Water use Process Flow
  - UPW Process Flow
- High Efficiency RO (HERO)
- Q & A's

Introduction – Pure Water

- **Semiconductor Industry**
  - Ultra Pure Water (UPW) is used as an aggressive solvent to wash a wafer many times during its fabrication.
  - Trace amounts of impurities in UPW can result in increased defects and reduce yield
- **Power Industry**
  - Boiler feed water
- **Pharmaceutical Industry**
  - Purified Water
  - Wafer for Injection
  - GMP standards for production and quality
- **A continuous supply of consistently pure water is critical to the profitability of a company.**

Semiconductor UPW quality requirements

	Near-term								
Year of Production	*2005*	*2006*	*2007*	*2008*	*2009*	*2010*	*2011*	*2012*	*2013*
DRAM ½ Pitch (nm) (contacted)	*85*	*76*	*67*	*60*	*54*	*48*	*42*	*38*	*34*
Resistivity at 25 °C (MOhm-cm)	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2
Total oxidizable carbon (ppb) POE	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bacteria (CFU/liter)	<1	<1	<1	<1	<1	<1	<1	<1	<1
Total silica (ppb) as SiO_2 [Q]	<0.5	<0.5	<0.5	<0.5	<0.5	<0.3	<0.3	<0.3	<0.3
Number of particles > critical size (/ml) [A] POE	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dissolved oxygen (ppb) (contaminant based) [O] POE	<10	<10	<10	<10	<10	<10	<10	<10	<10
Dissolved nitrogen (ppm) [J]	8–12	8–12	8–18	8–18	8–18	8–18	8–18	8–18	8–18
Critical metals (ppt, each) [F]	<1	<1.0	<1.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Other critical ions (ppt each) [X]	<50	<50	<50	<50	<50	<50	<50	<50	<50
Temperature stability (° K) POE	+/- 1	+/- 1	+/- 1	+/- 1	+/- 1	+/- 1	+/- 1	+/- 1	+/- 1
Temperature gradient in K/10 min [V] POE for immersion photolithography	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Manufacturable solutions exist, and are being optimized

Manufacturable solutions are known

Interim solutions are known ◆

Manufacturable solutions are NOT known

- **Table values ("targets") generally are typical levels, not best available technology**
- **Tables should be used as guidelines only, not as specifications. Every parameter for each application should be reviewed and justified.**

International Technology Roadmap for Semiconductors (ITRS) 2006 www.public.itrs.net

Water Specifications: PW

Parameter	Units	USP	Eur. Ph.
TOC	ppm C	0.50	0.50
Conductivity	µS/cm	≤1.3 @ 25°C	≤4.3 @ 20°
Nitrate (NO_3)	ppm	-	≤0.2
Heavy metals	ppm as Pb	-	≤0.1
Bacteria	CFU/ml	≤100	≤100

Reference only – refer to USP and Eur. Ph. For up-to-date figures

Water Specifications: HPW

Parameter	Units	USP	Eur. Ph.
TOC	ppm C	n. c. st.	0.50
Conductivity	µS/cm	n. c. st.	≤1.1@ 20°
Nitrate (NO_3)	ppm	n. c. st.	≤0.2
Heavy metals	ppm as Pb	n. c. st.	≤0.1
Bacteria	CFU/100 ml	n. c. st.	≤10
Endotoxin	EU/ml	n. c. st.	≤0.25

n. c. st. = no comparable standard

Reference only – refer to USP and Eur. Ph. For up-to-date figures

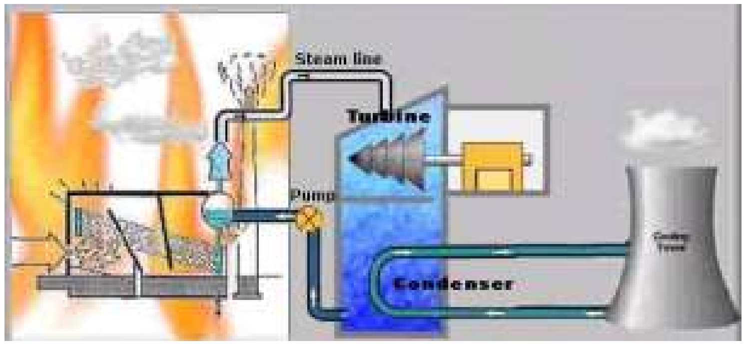
Water Specifications: WFI

Parameter	Units	USP	Eur. Ph.
TOC	ppm C	0.50	0.50
Conductivity	µS/cm	≤1.3 @ 25°	≤1.1 @ 20°
Nitrate (NO_3)	ppm	-	≤0.2
Heavy metals	ppm as Pb	-	≤0.1
Bacteria	CFU/100 ml	≤10	≤10
Endotoxin	EU/ml	≤0.25	≤0.25

Reference only – refer to USP and Eur. Ph. For up-to-date figures

Boiler Feed Water

- **Water contaminants must be limited to prevent scaling, corrosion and foaming.**
  - **pH, Hardness, Oxygen, Carbon dioxide, Silicates, Dissolved solids, Suspended solids, Organics**
- **Control limits**
  - **Conductivity is used as an indicator of total ion contaminants with an upper limit of 1 mOhm-cm but plants usually operate at 5 to 10 mOhm-cm and 10 to 20 ppb silica.**
  - **Other ionic contaminants listed above are usually < 2ppb**
- **Water Treatment includes**
  - **Reverse Osmosis**
  - **Ion Exchange**
  - **EDI**



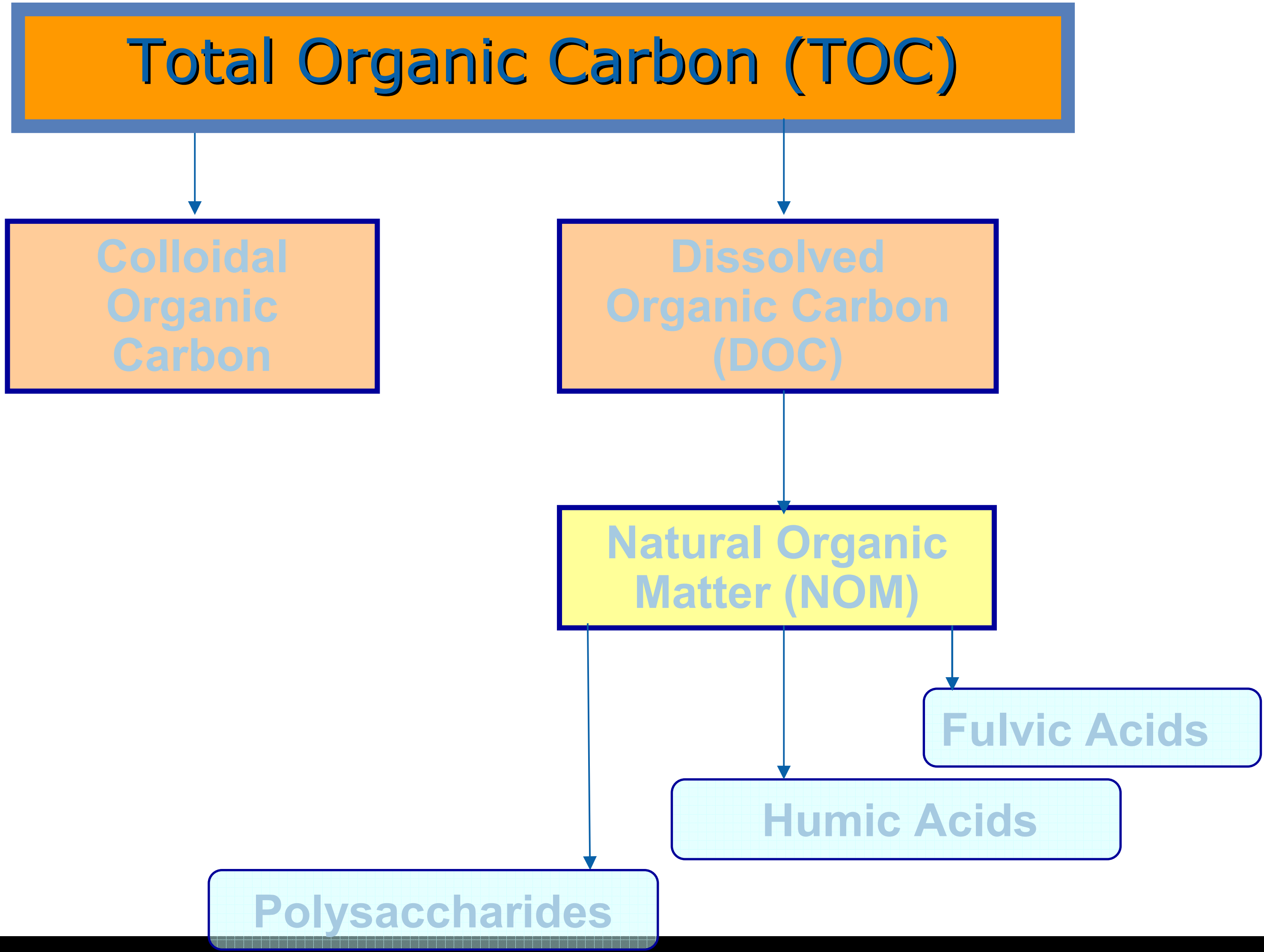
Water Contaminants (1)

			|-> S.E.M.		|-> OPTICAL MICROSCOPE		|-> VISIBLE TO NAKED EYE	
MICRON	0.0001	0.001	0.01	0.1	1	10	100	1000
ANGSTROM	1	10	100	1,000	10,000	100,000	1,000,000	10,000,000
MOLECULAR WEIGHT		200	20,000	200,000	2,000,000			
EXAMPLES	<-METAL IONS->	<-AQUEOUS SALTS->	<-COLLOIDS-> <-VIRUSES-> ->ENDOTOXIN, PYROGEN<-'		<-BACTERIA->	<-COAL DUST-> <-POLLENS->	|<-HUMAN HAIR->| <-BEACH SAND->	
FILTRATION TECHNOLOGY	<---HYPER---> -> RO'S	<---NANO---> -> LOW PRESS	<---ULTRA---> -> 0.01 PORES	<---MICRO---> -> 0.1 PORES	<-----------------------------PARTICLE-----------------------------> -> BAG FILTERS, CARTRIDGE	->CLARIFIERS, MEDIA FILTERS		
	<- DISSOLVED			-> SUSPENDED				

Water Contaminants (2)

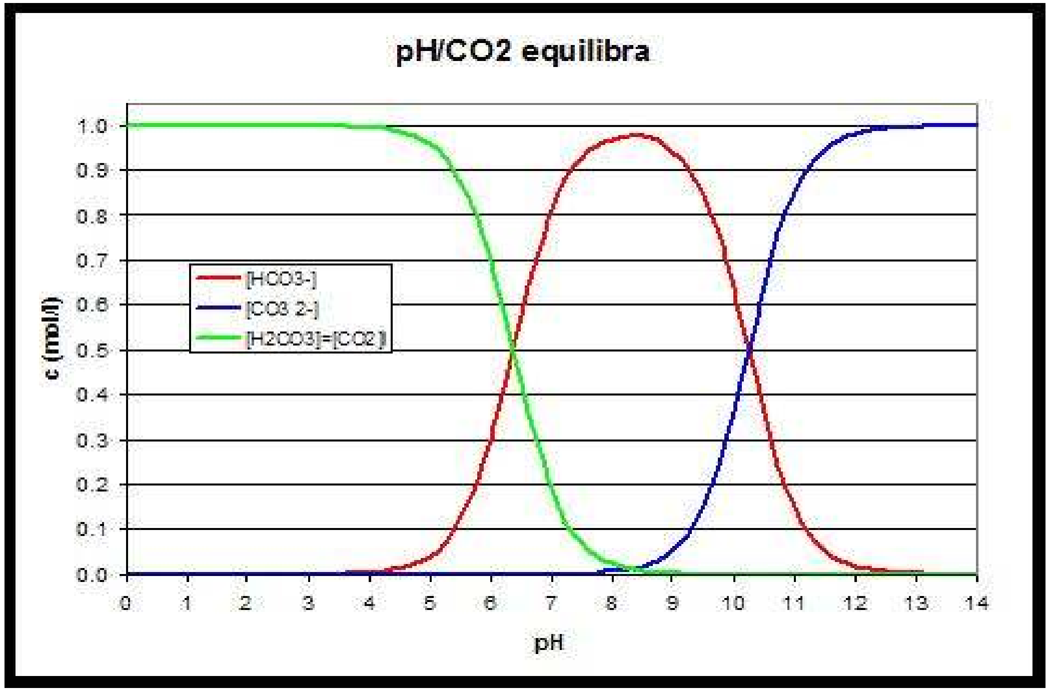
Dissolved		Suspended
<u>Charged</u>	<u>Uncharged</u>	
Ions		
Organics	Organics	Organics
Silica	Silica	Silica
	Gases	
		Living particles (Bacteria, Fungi, algae etc.)
		Non living particles (Sand, silt, precipitates)

Water Contaminants (3)



Water Contaminants (4)

- **Gases**
  - **Dissolved Oxygen – contributes to unwanted native oxide growth on silicon wafers and must be minimized in UPW.**
  - **Carbon Dioxide (Alkalinity)**
    - **Acts as a contaminant**
    - **Changes with pH**

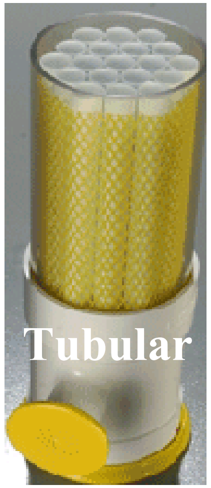


Membrane Processes

Used across industry in water purification

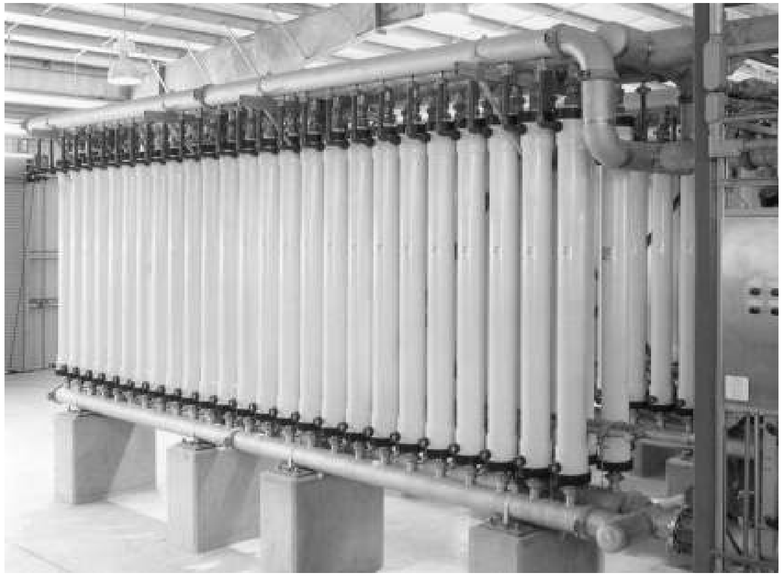
Process	Pore size/mol wt	Driving Force	Mechanism
Microfiltration	0.02-10μm	ΔP 0-1 bar	Sieving
Ultrafiltration	0.001-0.02μm mol wt 10^3 -10^6	ΔP 0-10 bar	Sieving
Nanofiltration	< 2nm mol wt 10^2 -10^3	ΔP 10-25 bar	Solution-Diffusion
Reverse Osmosis	non-porous	ΔP 10-100 bar	Solution-Diffusion
Gas separation	non-porous	ΔP 10-100 bar	Solution-Diffusion
Dialysis	10-30 A	Concentration difference	Sieving plus Diffusion
Pervaporation	non-porous	Partial pressure difference	Solution-Diffusion
Electrodialysis	mol wt <200	Electrical potential	Ion migration

Microfiltration/Ultrafiltration



- Membrane Material
  - polysulfones, polypropylene, and polyvinylidene fluoride (PVDF).
- Physical configurations
  - hollow fiber, spiral wound, cartridge, and tubular.
- Particle removal capability
  - MF down to 0.1- 0.2 microns.
  - UF down to 0.005-0.01 microns.
- Driving force
  - Pressure or vacuum.

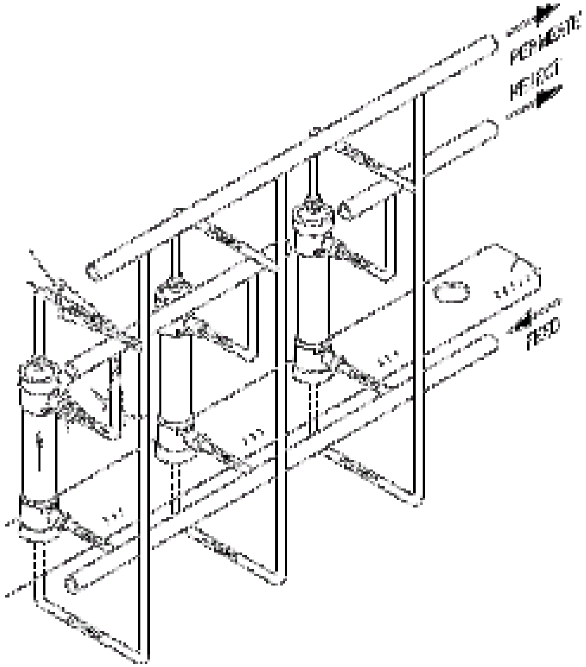
Microfiltration Modules



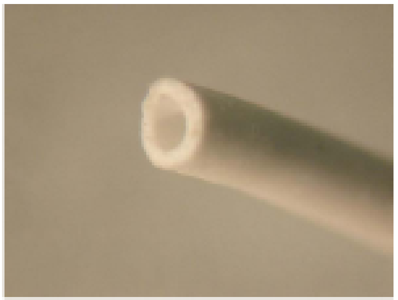
Water Quality	Multimedia	MF	UF
Turbidity (NTU)	0.5	< 0.1	< 0.1
SDI_{15}	3 - 5	< 3	< 2

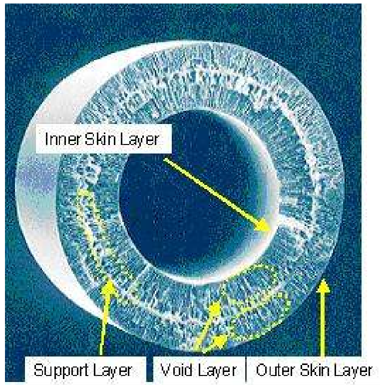
Filtrate Water Quality of membrane versus conventional pre-treatment

Ultrafiltration modules



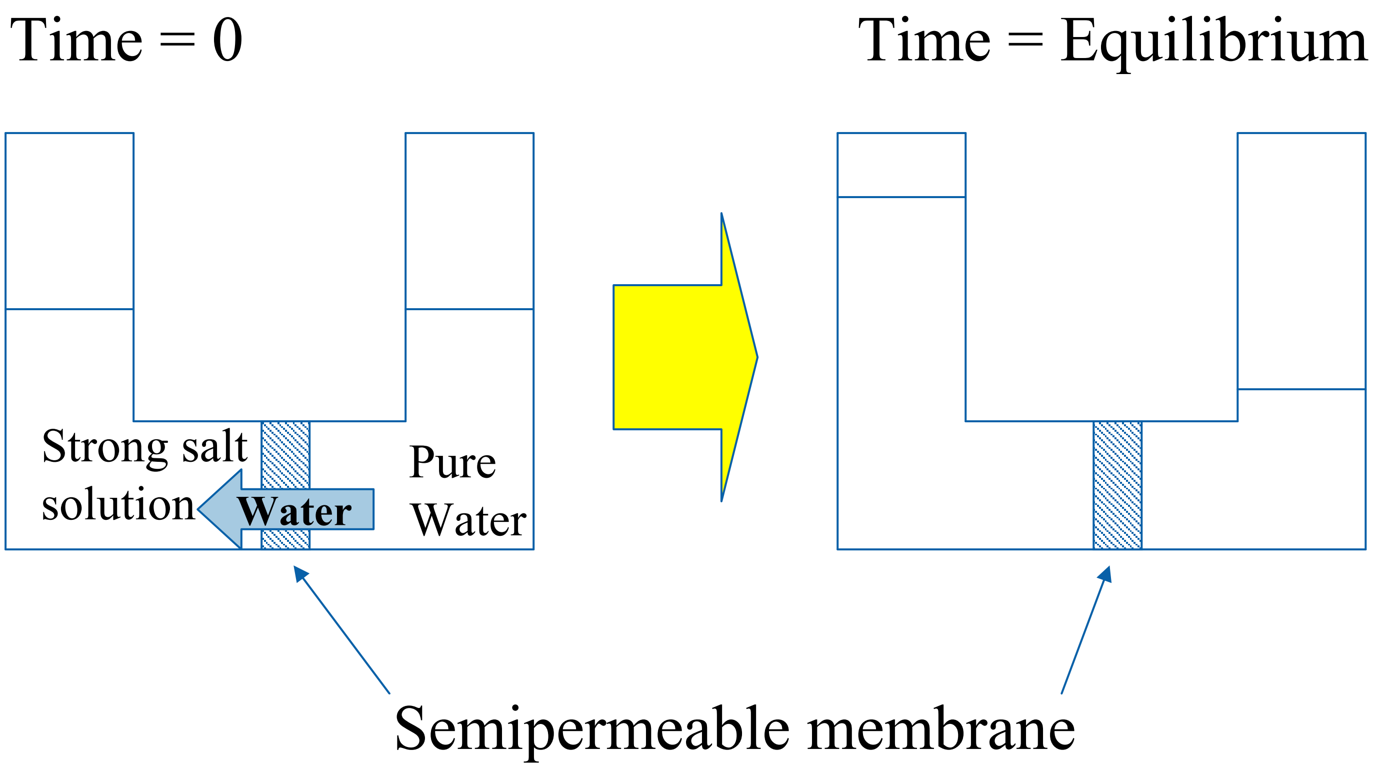
Cut end of loose fiber





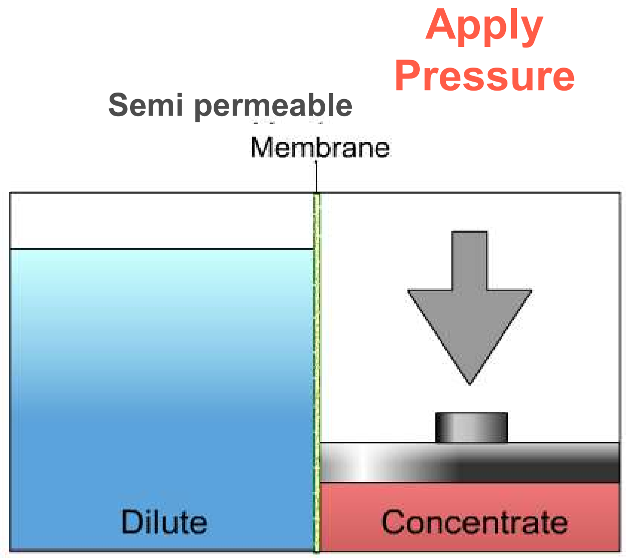
Osmosis

- **The tendency of water to pass through a semi-permeable membrane, into a solution of higher concentration.**



What is Reverse Osmosis?

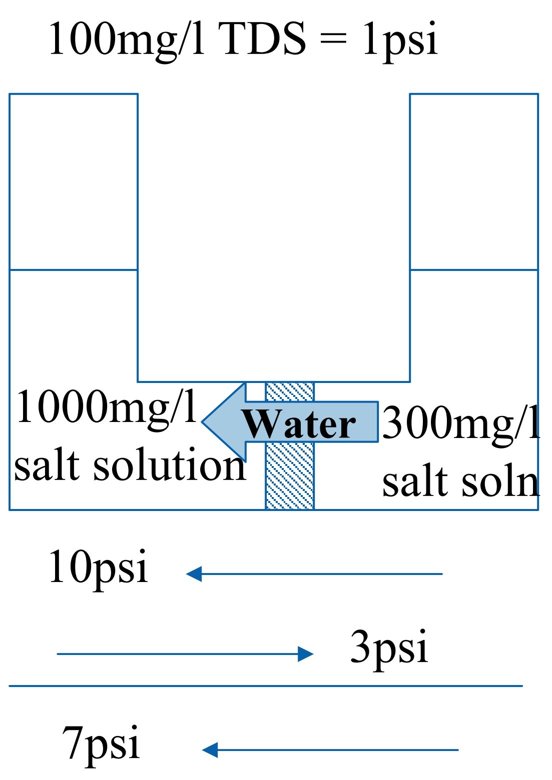
- Reverse osmosis is the reversal of the standard flow of materials in osmosis
- Pressure is applied to over come osmotic pressure, reversing osmosis
- Flow from higher salt concentration to lower salt concentration side.

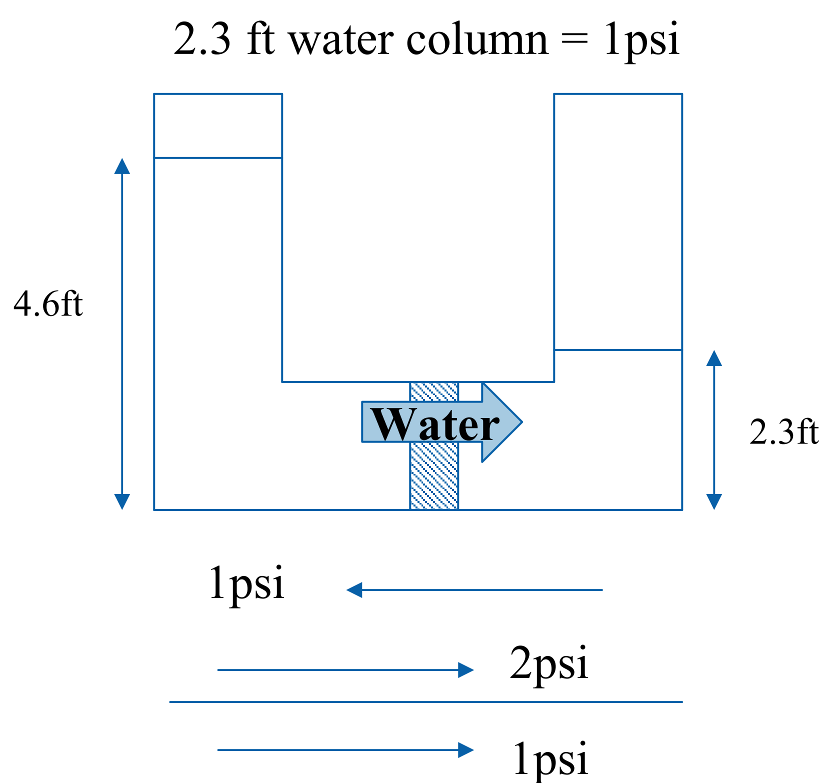


- Flow rate of water through the membrane is pressure dependent reducing the cconcentration of salts in the pure water side of the membrane will be lower
- RO membranes are effectively non-porous. The transport of a molecule across the membrane is diffusion controlled as described the solution-diffusion transport equation
- Salt passage through the membrane <u>is not</u> a function of pressure, <u>is only</u> a function of salt concentration

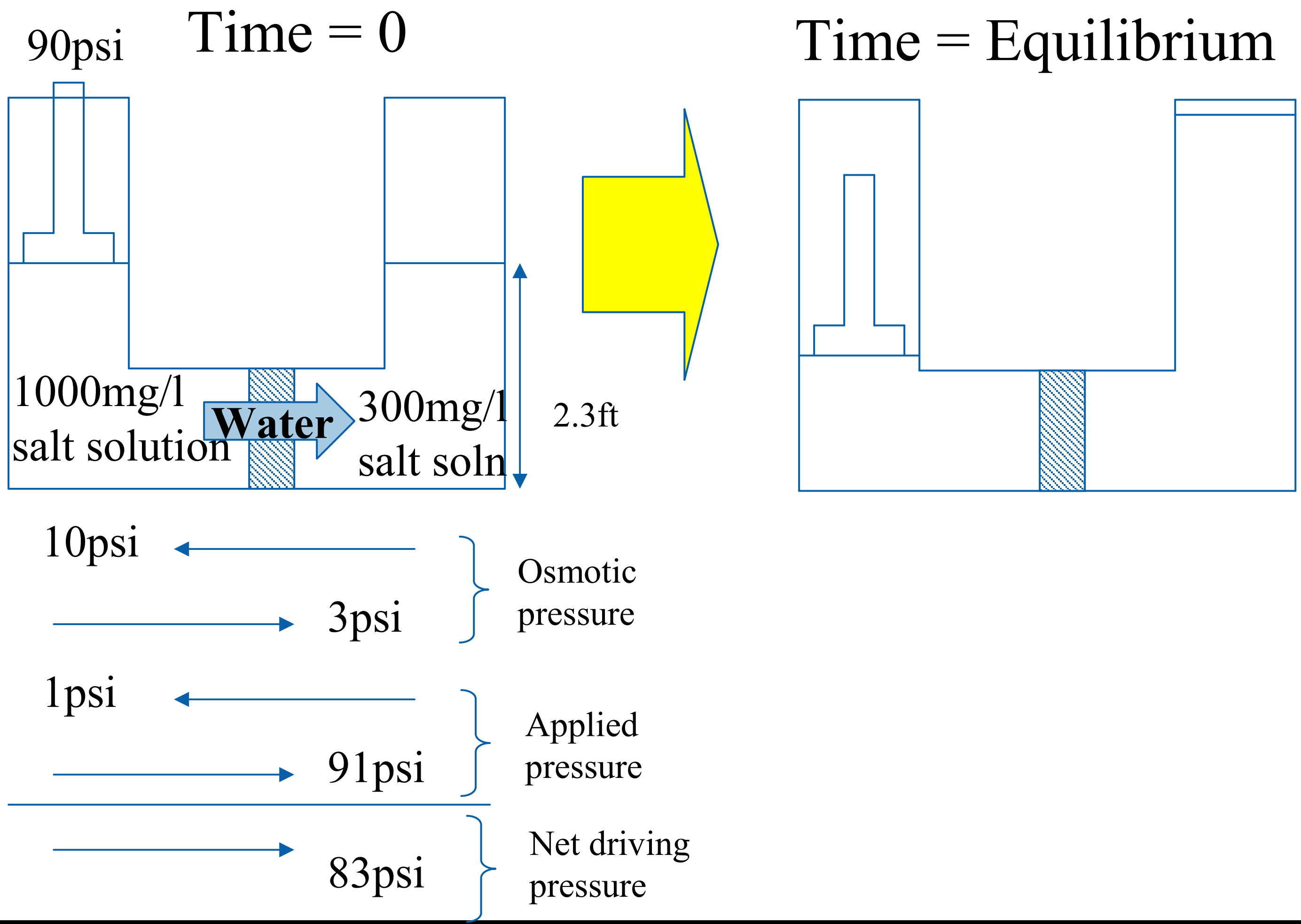
FORCES ACTING ON THE MEMBRANE

- **Osmotic Pressure: The pressure differential across a semi permeable membrane, due to the salt concentration gradient.**
- **Applied pressure: e.g. head pressure**

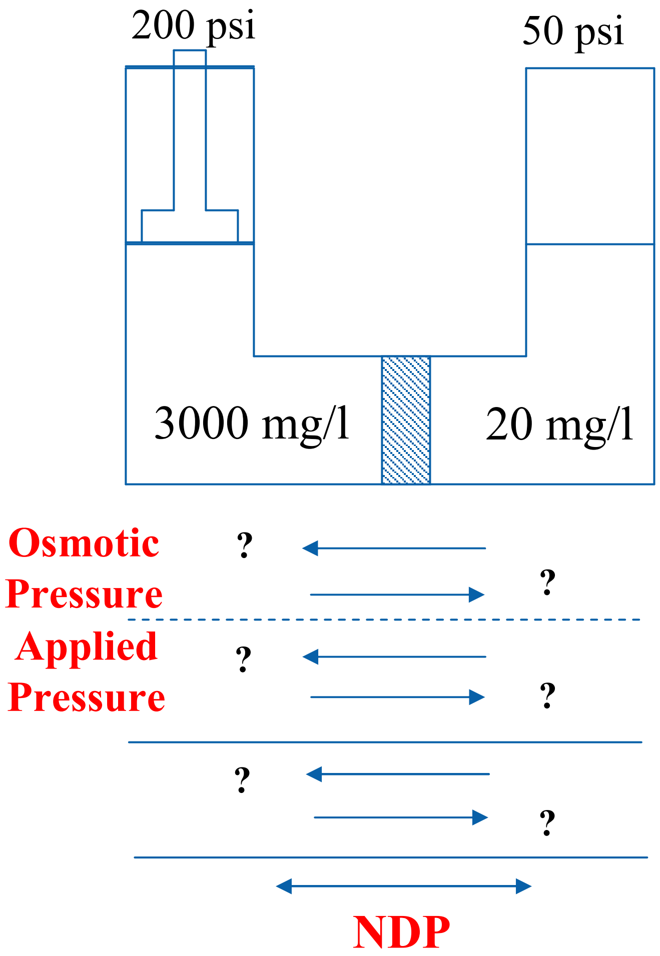




Applying pressure to reverse the natural process osmosis



Exercise



a) **Osmosis**

b) **Reverse Osmosis**

RO transport Equations 1a

- **RO membranes are effectively non-porous. The transport of a molecule across the membrane is diffusion controlled as described the solution-diffusion transport equation**

$$N_{Aw} = L(\Delta p - \Delta \pi)$$

  - **where N_{Aw} is the water flux through the membrane, Δp is the trans membrane pressure difference, $\Delta \pi$ is the difference in osmotic pressure between the feed and the permeate, and L is a constant describing the physical characteristics of the membrane itself**

- **Flow rate of water through the membrane is pressure dependent**
  - **Concentration of salts in the pure water side of the membrane will be lower**

RO transport Equations 1b

- **Within the context of the solution-diffusion model used to describe transport in nonporous films, L is given by**

$$L = \frac{DSV}{RTl}$$

  - **where D is the water diffusivity in the membrane, S is the water solubility in the membrane, V is the molar volume of water, R is the ideal gas constant, T is the ambient temperature, and l is the membrane thickness**

- **For an ideal solution, with complete dissociation of salt ions, osmotic pressure is defined as**

$$\pi = CRT$$

  - **where π is the osmotic pressure, C is the salt ion concentration, R is the ideal gas constant, and T is the solution temperature.**

RO transport Equations 2

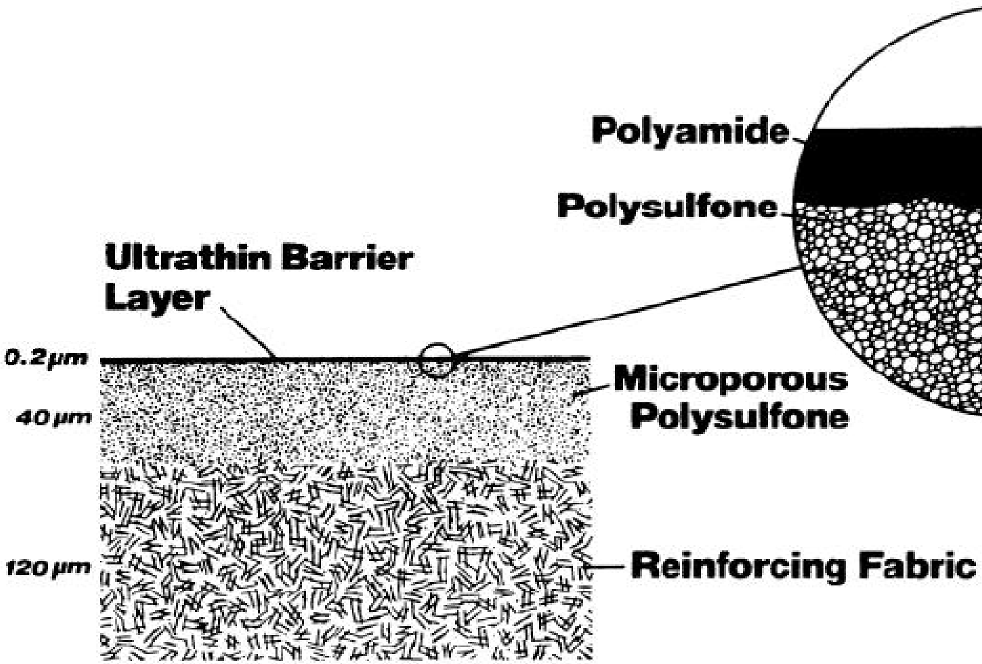
- **Salt passage through the membrane <u>is not</u> a function of pressure**
  - **The salt flux is only a function of salt concentration**

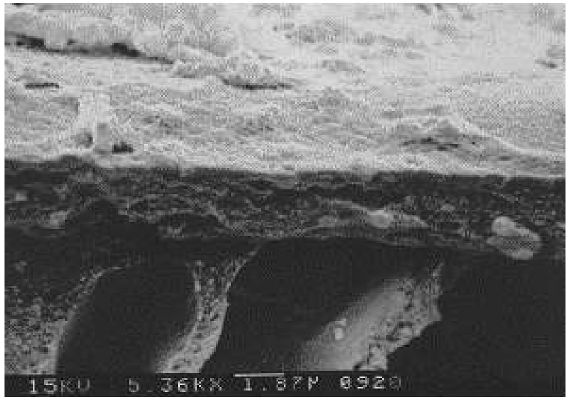
$$N_s = B(C_{feed} - C_{permeate})$$

  - **where N_s is the salt flux through the membrane, B is the salt permeability constant describing the physical characteristics of the membrane, C_{feed} is the salt concentration in the feed solution, and $C_{permeate}$ is the salt concentration in the permeate solution.**

RO transport summary

- **Thin Film Composite - give high flux, can operate at feed pressure up to 35 bar**
- **RO membranes are effectively non-porous. The <u>transport</u> of a <u>molecule</u> across the membrane is <u>diffusion controlled</u>**
- **<u>Flow rate</u> of water through the membrane is <u>pressure dependent</u>**
- **The <u>salt flux</u> is only a function of <u>salt concentration in feed</u>**

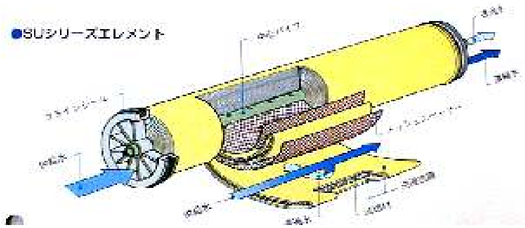




SEM image of cross-section of a thin-film composite membrane

Handbook of Industrial Membrane Technology, M.C.Porter, 1990

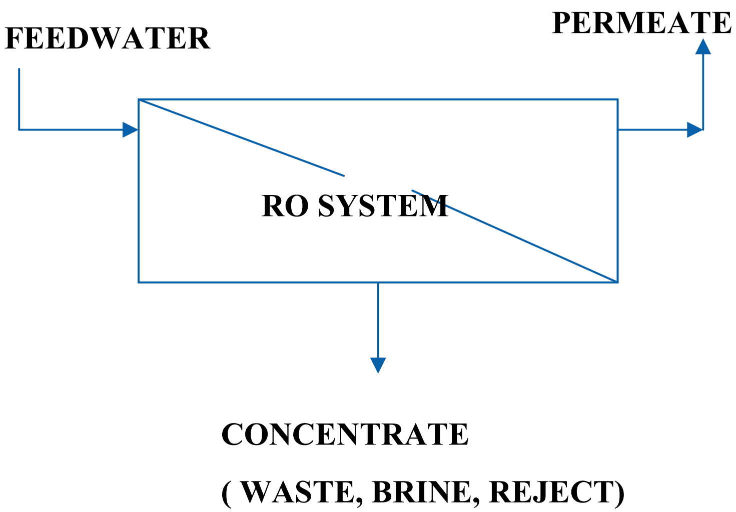
RO Equipment (1)

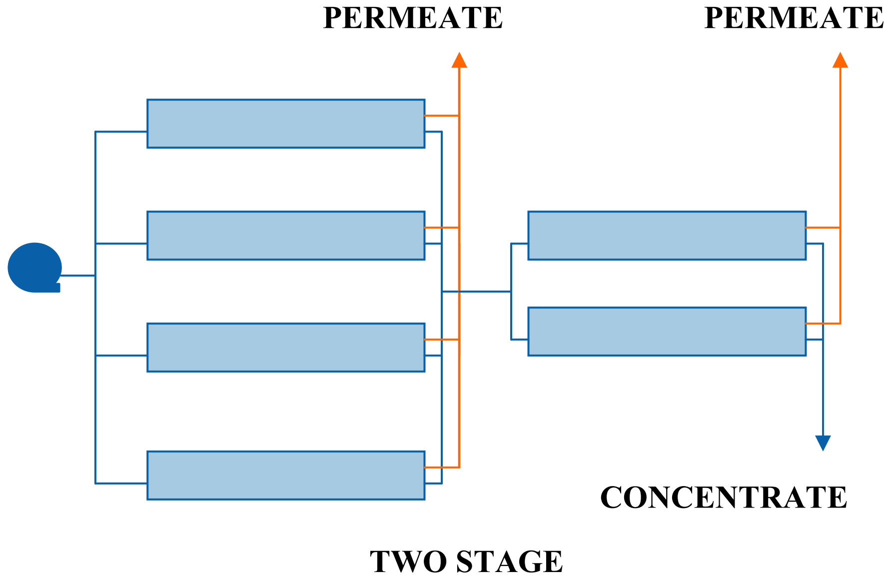


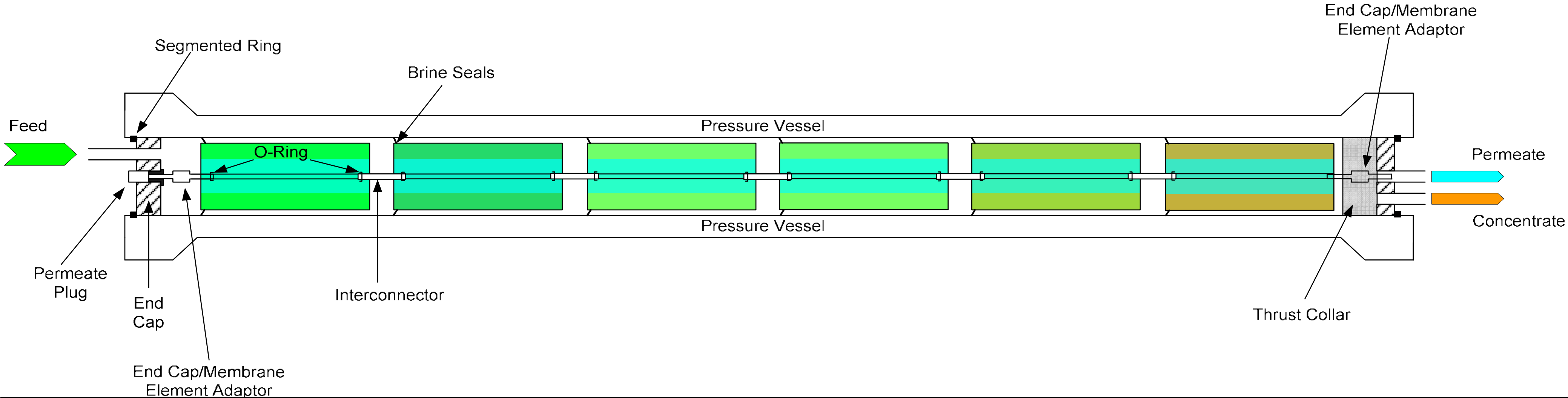
- **Water Quality Impacts**
  - Removal of dissolved solids (TDS reduction)
  - Removal of organics
  - Removal of silica (total SiO2 reduction)
  - Removal of other trace contaminants (i.e., boron, metals)

- **Application Limitations**
  - Is not an "absolute" treatment technology such as ion-exchange (>99% for most ions, ~ 70-80% TOC)
  - Requires downstream treatment for contaminants (TDS, TOC, SiO2, etc.) to achieve "ultrapure" water
  - Polymer membranes cannot tolerate oxidizers such as chlorine, biocides, ozone
  - Reject stream (~ 25% of the feed) is near-saturation and non-reclaimable
  - Chemical injection required: antiscalant, biocide, oxidant reduction (bisulfite)
  - Periodic on-site membrane cleaning using aqueous chemicals

RO Equipment (2)







RO membrane manufacture

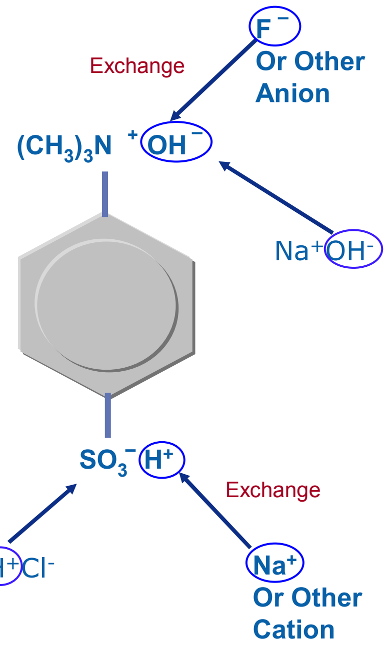
- **Hydranautics video of spiral wound membrane manufacture**
  - **http://www.membranes.com/**
    - **Downloads**
      - **Download RO animation**
- **Dow Filmtec video of iLEC Interlocking Endcaps**
  - **http://www.dow.com/liquidseps/service/lm_install.htm**
    - ***iLEC* Interlocking Endcaps Video**

Ion Exchange (1)

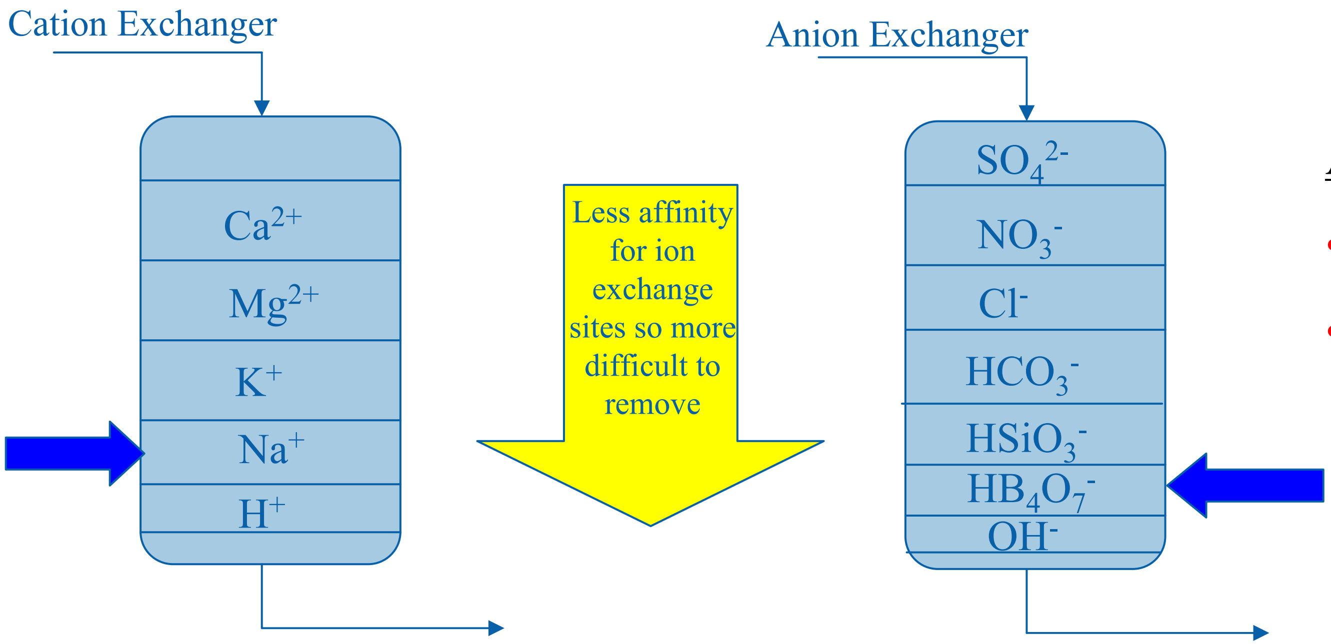
- **Water Quality Impacts**
  - Removal of dissolved solids (TDS reduction) as ionic species
  - Removal of ionized organics (TOC reduction)
  - Removal of silica (dissolved SiO2 reduction)
  - Removal of other trace contaminants (i.e. boron/borate)

- **Application Limitations**
  - Is an "absolute" technology, completely removes ionic species until resins "exhaust." Requires frequent regenerations in high TDS applications (i.e. water softeners, primary beds)
  - Because of leakage/exhaust issues, requires two IX mixed beds in series between the RO system and wafer Fab users for UPW, either one in primary and one in polish systems, or two in polish systems. Use of EDI can replace primary beds.
  - Polymeric resins cannot tolerate oxidizers such as chlorine, biocides, ozone

Ion Exchange Beds (2)



- **Resin beads are made of Styrene and Di-vinyl-benzene with functional groups attached.**
- **Upon exhaustion all exchange sites are occupied by ions from solution and the bead is unable to remove additional ions.**
- **Regenerate with HCl and NaOH**
- **Analyse for Sodium, Silica and Boron – signal ion breakthrough and resin exhaustion.**



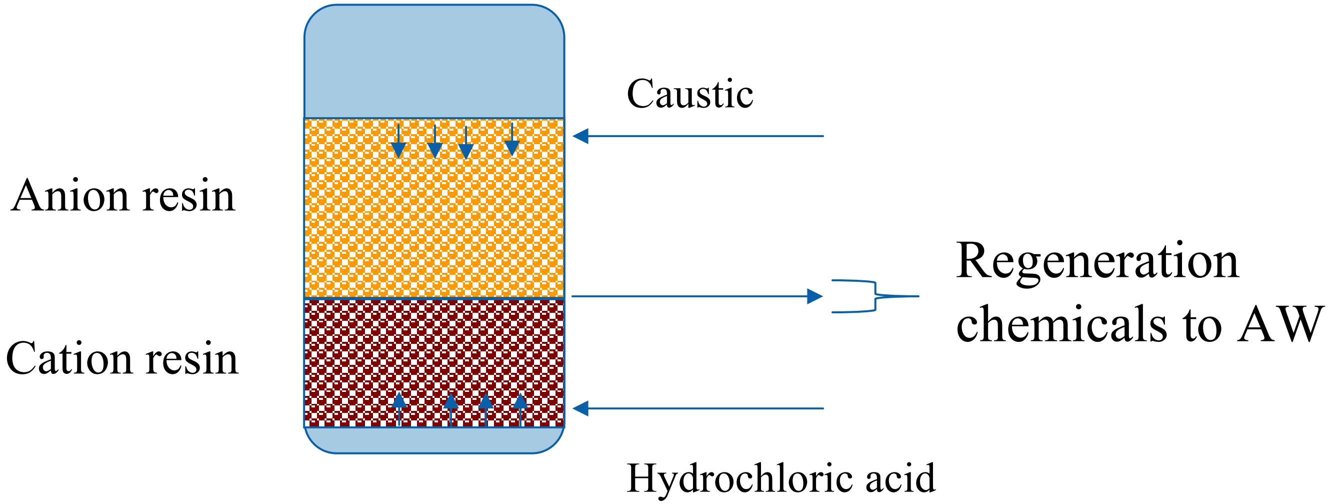
Affinity of ions

- Higher valence
- Higher MW

Product Water >18 mOhms

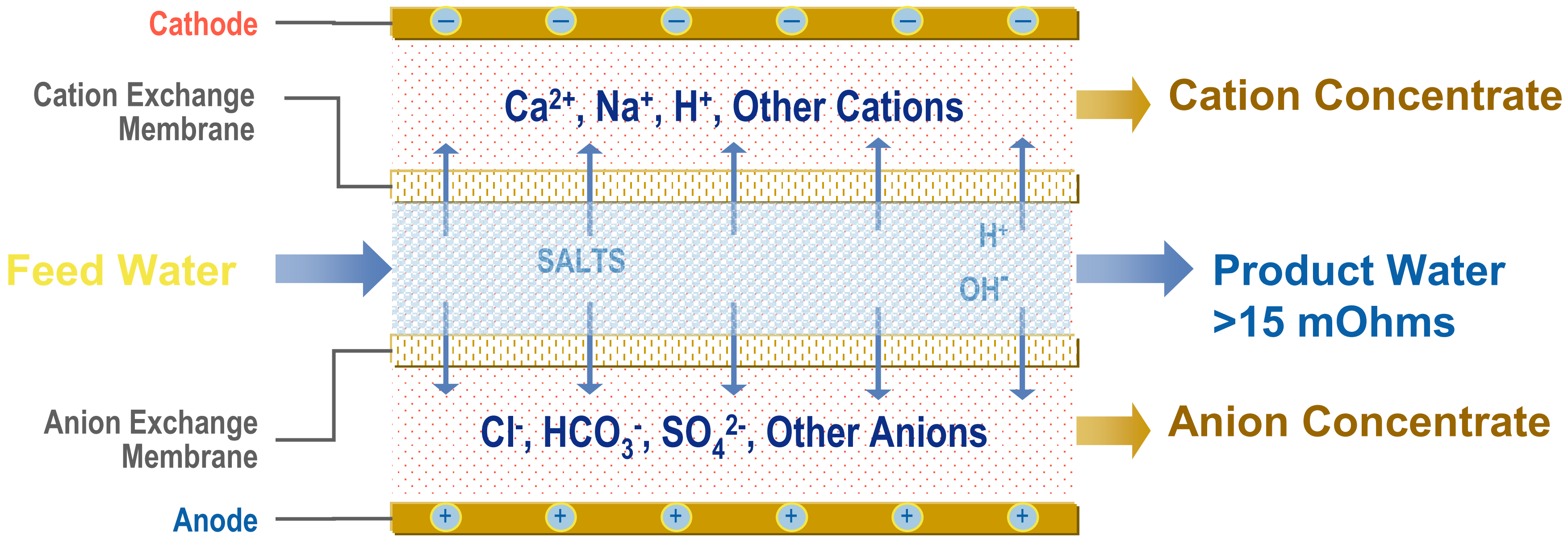
Ion Exchange Beds (3)

- Mixed bed ion exchange resins i.e. they each bed has anion and cation resin (60:40 ratio – anion has less capacity).
- Separate resin based on different densities

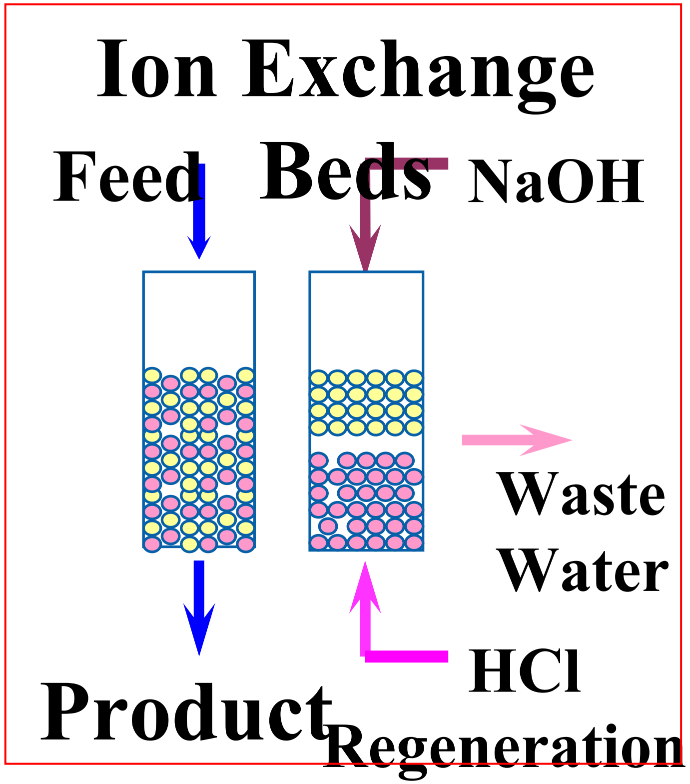


Electrodeionistation (EDI)

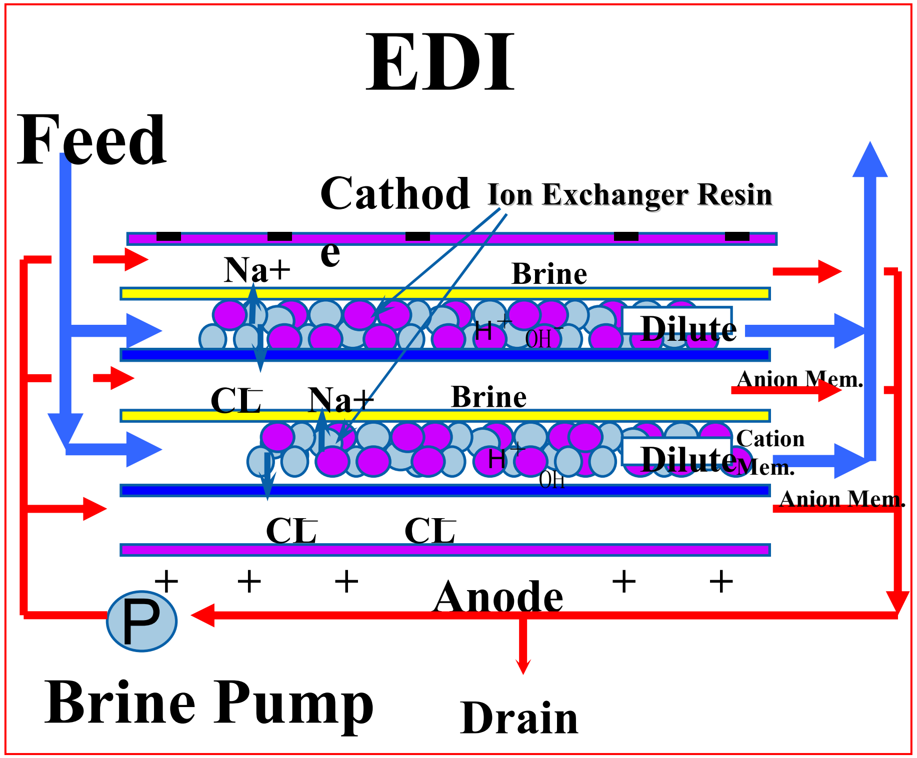
- Water flows through the IX resin in the dilute chamber.
- Normal IX occurs to produce high purity water in the dilute chamber.
- Positive ions are drawn to the cathode through the cation selective membrane
- Negative ions are drawn to the anode through the anion selective membrane.
- The large electric potential between the electrodes cause water in the dilute chamber to split into H+ and OH- ions which regenerate the resin.



EDI (2)



EDI → Chemical Free , Stand-by Bed Free



Advantages

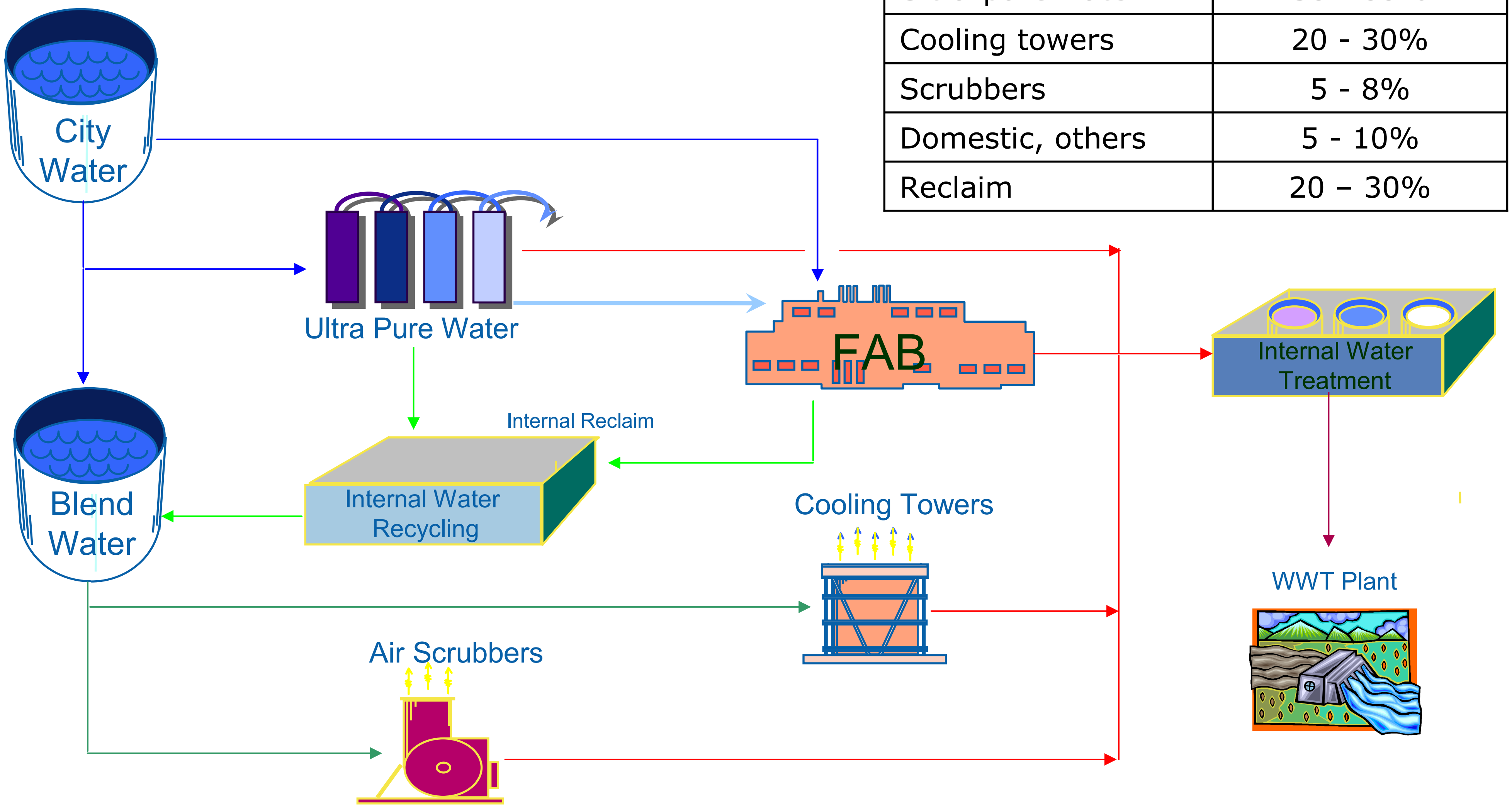
- Replaces regeneration chemicals
- Continuously regenerates resin system
- Robust mechanical systems.
- High performance and low maintenance
- Easily expandable.

Disadvantages

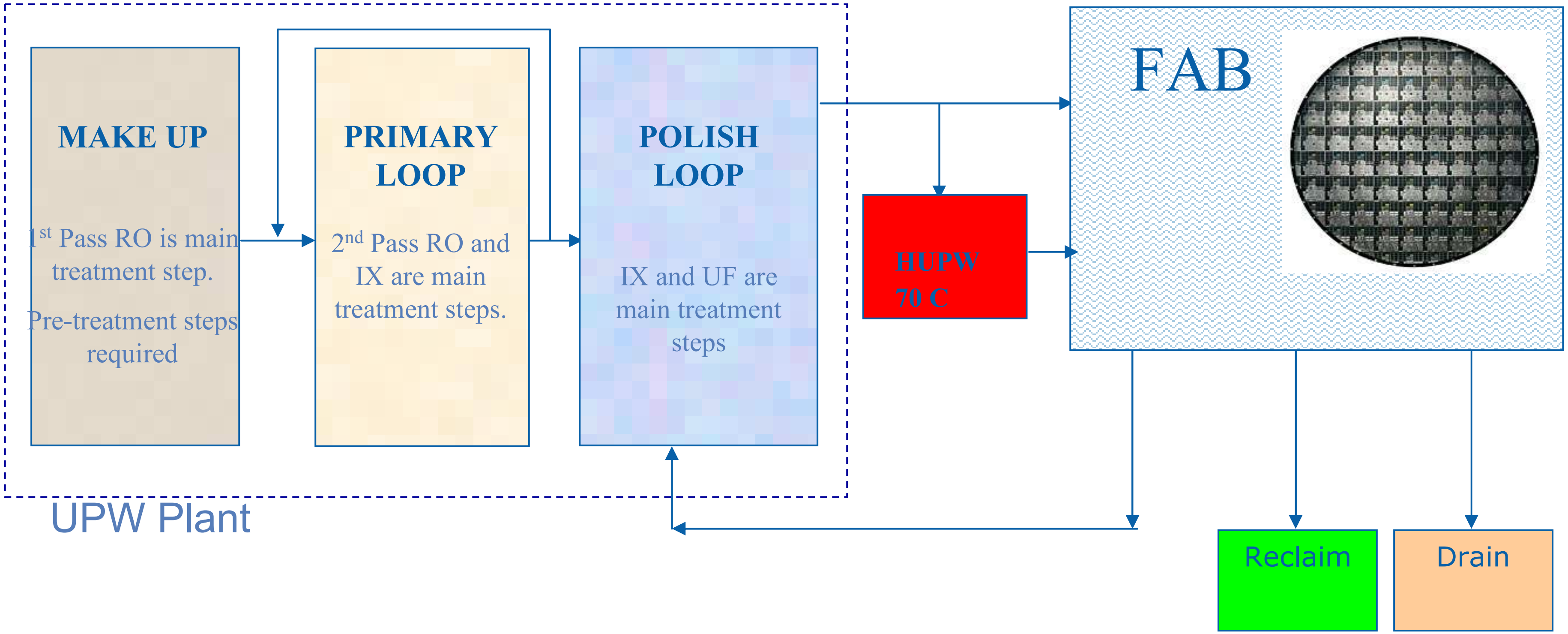
- Consumes high amount of power.
- Lots of piping involved in process, prone to leaks.
- Lots of parameters to monitor during operations.
- Difficult trouble shooting

Typical Semiconductor Plant water use

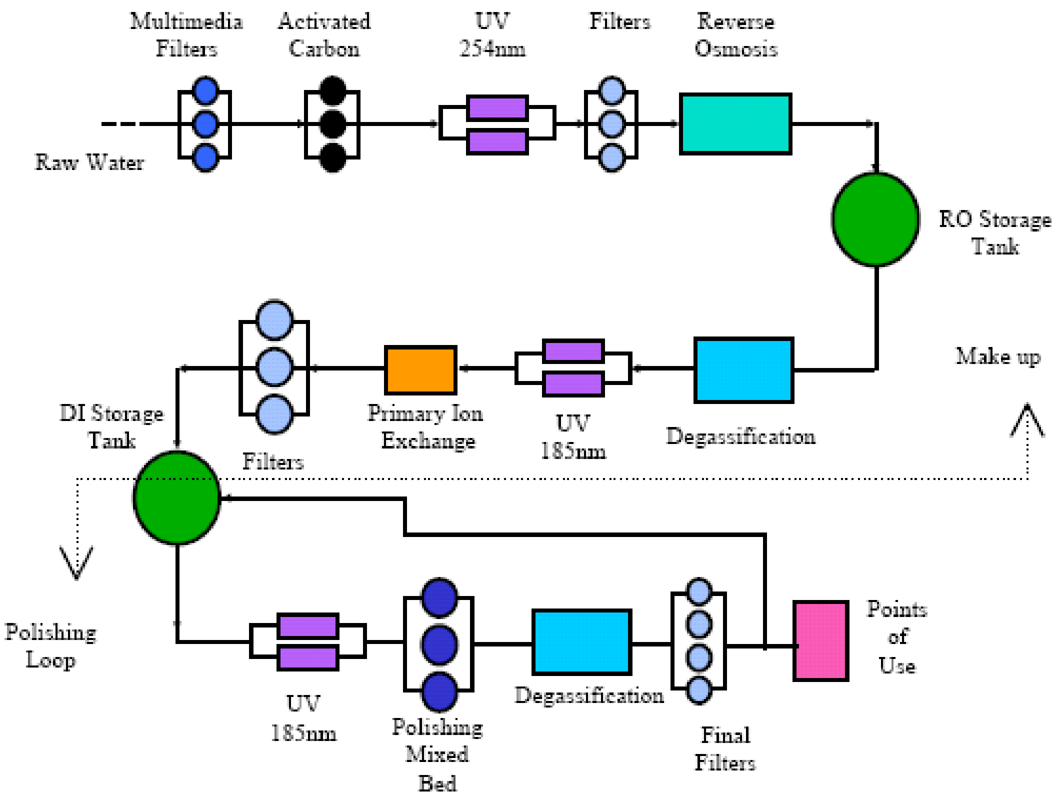
Application	Water Use
Ultra-pure water	50 - 60%
Cooling towers	20 - 30%
Scrubbers	5 - 8%
Domestic, others	5 - 10%
Reclaim	20 – 30%



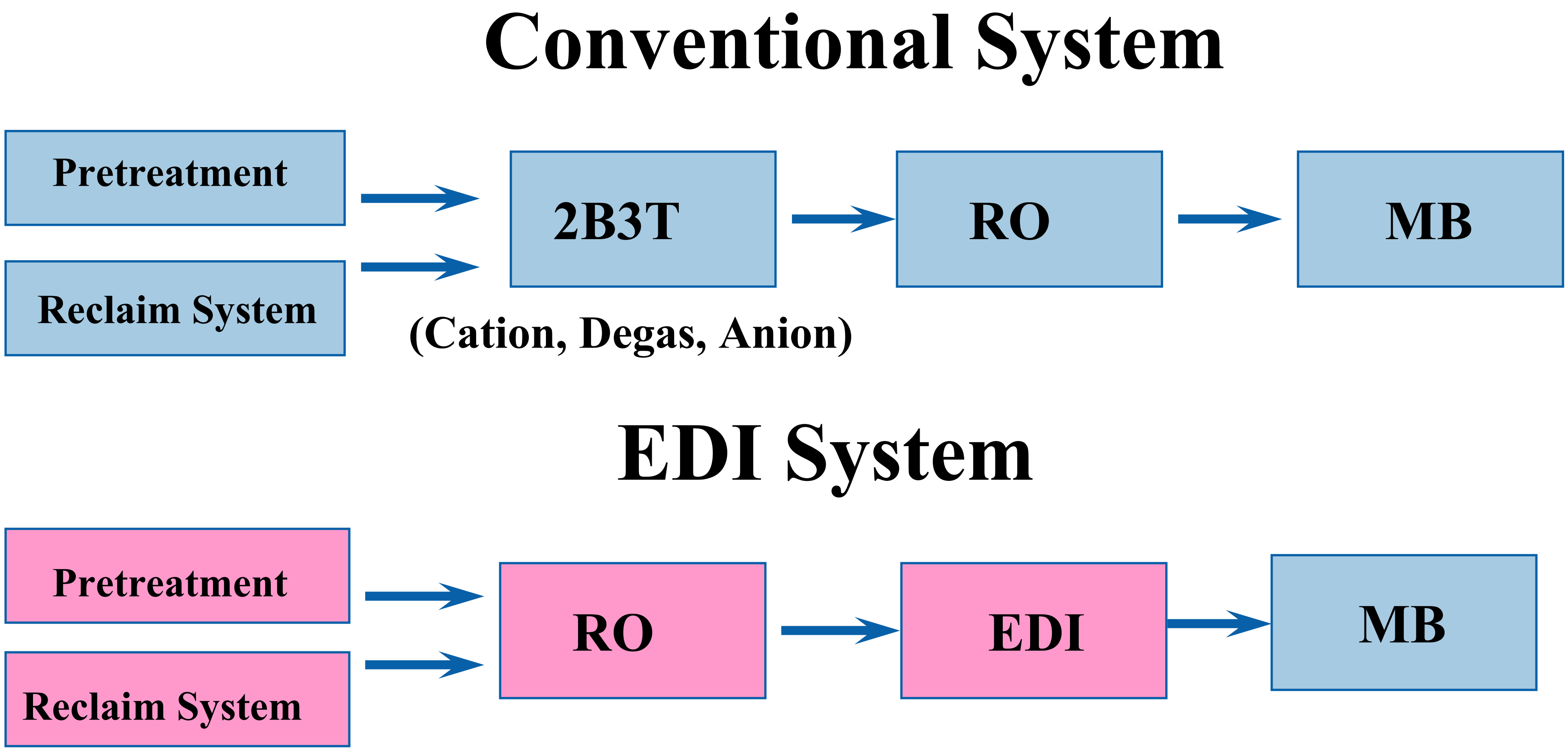
Typical UPW system – block diagram



Typical UPW Plant Process Flow

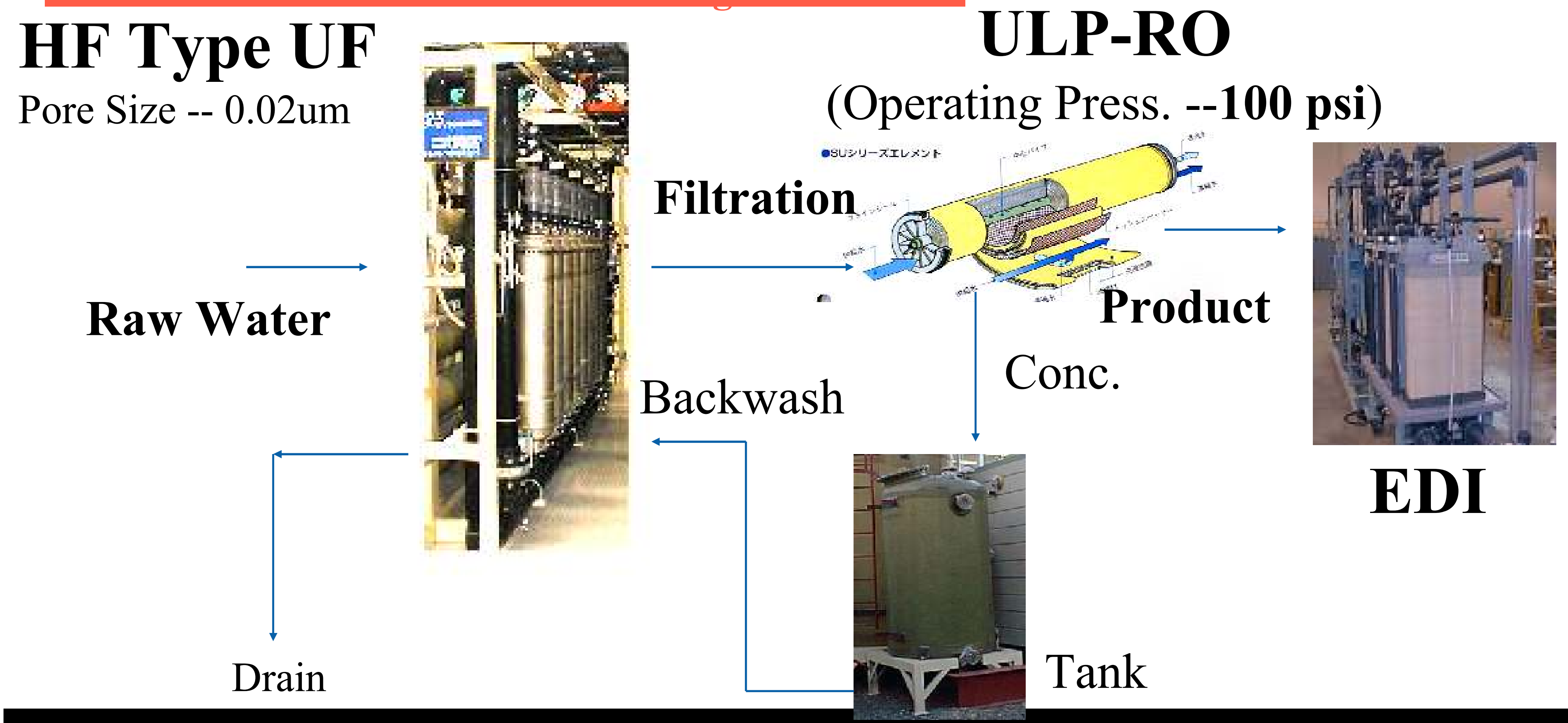


Flow Diagram of Primary System



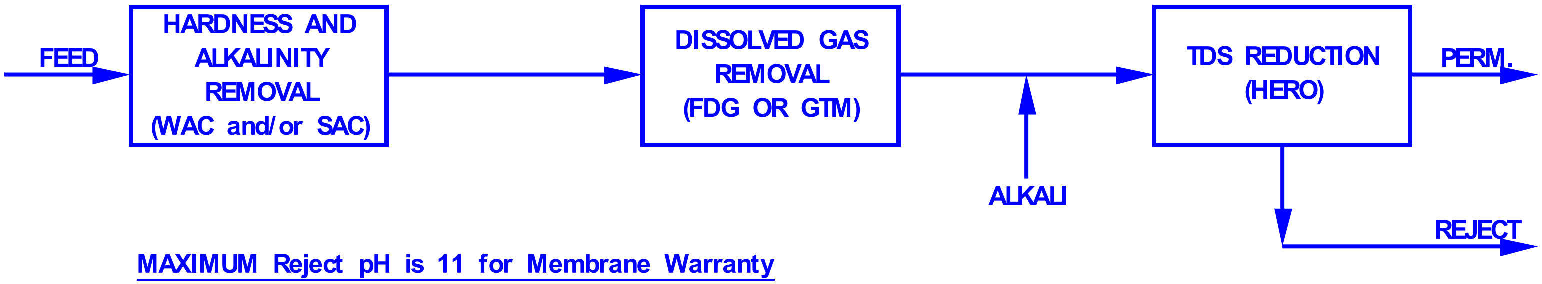
EDI System - pre-treatment

Perfect Pretreatment — **Free RO Cleaning**
Ultra Low Pressure RO — **Low Power Cost**
Chemical Free — **No IX Regeneration**



UPW process efficiency improvement

- **High Efficiency RO (HERO™)**



- **Operating at high pH (~ 11) is the significant increase in rejecting weakly ionised anions such as organics, silica and boron.**
- **Strongly ionised species are also better rejected at high pH levels resulting in lower ionic loads on ion exchange beds.**
- **Pretreatment of the HERO™ feed water to remove hardness (Ca2+, Mg2+) and alkalinity (CO2) eliminates the potential for scale forming on the RO membrane allowing operation at high recoveries and flux.**

Criteria	Conventional	HERO
pH, Typical Operating Range	6.5-7.5	10+/-
Recovery Rate	≤75%[1]	90-98%
Flux (Gallons per Square Foot per Day)	12-15[2]	25-30
Membrane Replacement, Typical Frequency	3 years	5-10 years
Cleaning, Typical Frequency	6-20 times per year	Once every several years
Fouling Susceptibility: Particulate, Organic & Bio-Fouling	Highly Susceptible	Virtually None

Patent holder – Deb Mukhopadhyay

List of References

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