Advanced Membrane Technologies
Stanford University, May 07, 2008

Membrane Types and Factors Affecting Membrane Performance

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Outline

Membrane filtration (low pressure applications)

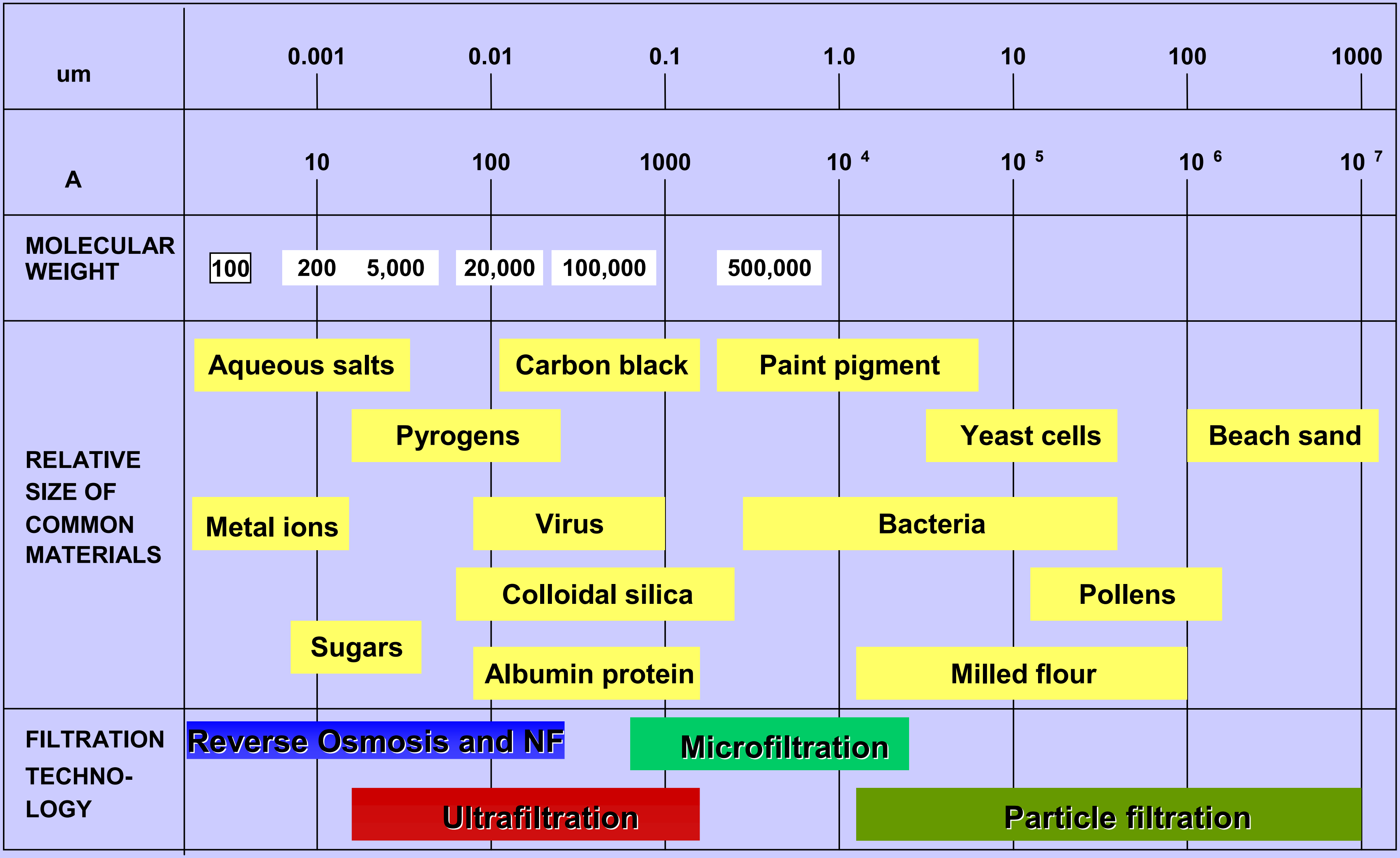
- **Membrane materials and modules configuration**
- **Modes of operation**
- **Relevant R&R directions**

Reverse osmosis and NF membranes (high pressure applications)

- **Membrane materials and modules configuration**
- **Modes of operation**
- **Relevant R&D directions**

Membrane filtration

THE FILTRATION SPECTRUM



UF/MF terms

TMP – trans membrane pressure

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

P_f = feed pressure

P_c = concentrate pressure

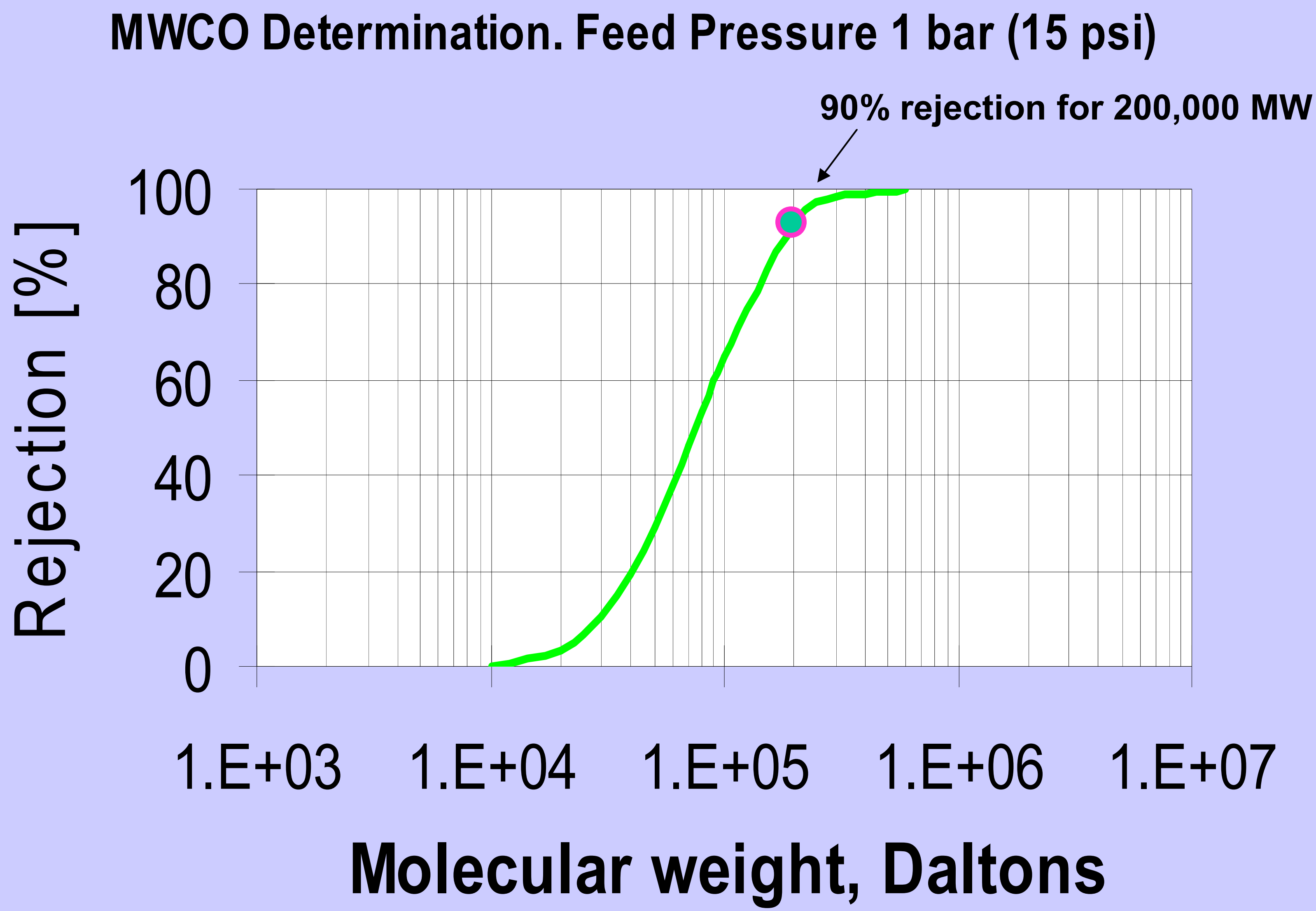
P_p = permeate pressure

SP – specific permeability

$SP = Q/(A_m * TMP)$

Q – filtrate flow rate

A_m – membrane area


MWCO Determination. Feed Pressure 1 bar (15 psi)
90% rejection for 200,000 MW
Rejection [%]
100
80
60
40
20
0
1.E+03
1.E+04
1.E+05
1.E+06
1.E+07
Molecular weight, Daltons

Commercial MF/UF membrane material

CA – Cellulose acetate

PS – polysulfone

PES – Polyether sulfone

PAN – Polyacrilonitrile

PVDF – Polyvinylidiene flouride

PP – Polypropylene

PE – Polyethylene

PVC – Polyvinyl chloride

Important membrane material property

High porosity

Narrow pore distribution or sharp MWCO

High polymer strength: elongation, high burst and collapse pressure

Good polymer flexibility

Permanent hydrophilic character

Wide range of pH stability

Good chlorine tolerance

Low cost

Preferred UF/MF membrane materials

High mechanical strength & durability

- **PVDF – Polyvinylidiene flouride**
- **PS – polysulfone**
- **PES – Polyether sulfone**
- **PAN – Polyacrilonitrile**

Low polymer cost

- **PE – Polyethylene**

Membrane manufacturing and configuration

Spinning – capillary

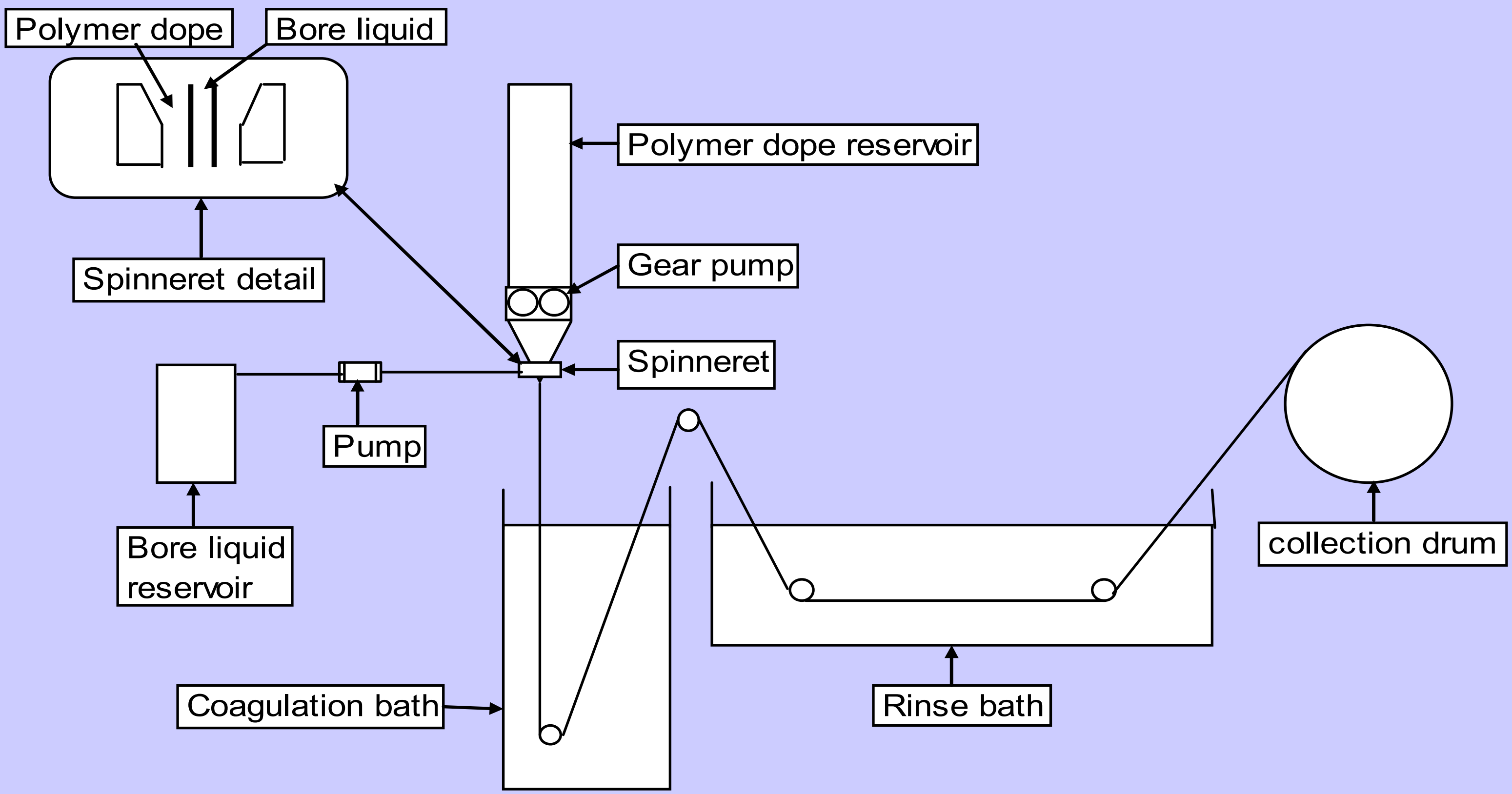
Casting – flat sheet

Extrusion and stretching – capillary, flat sheet

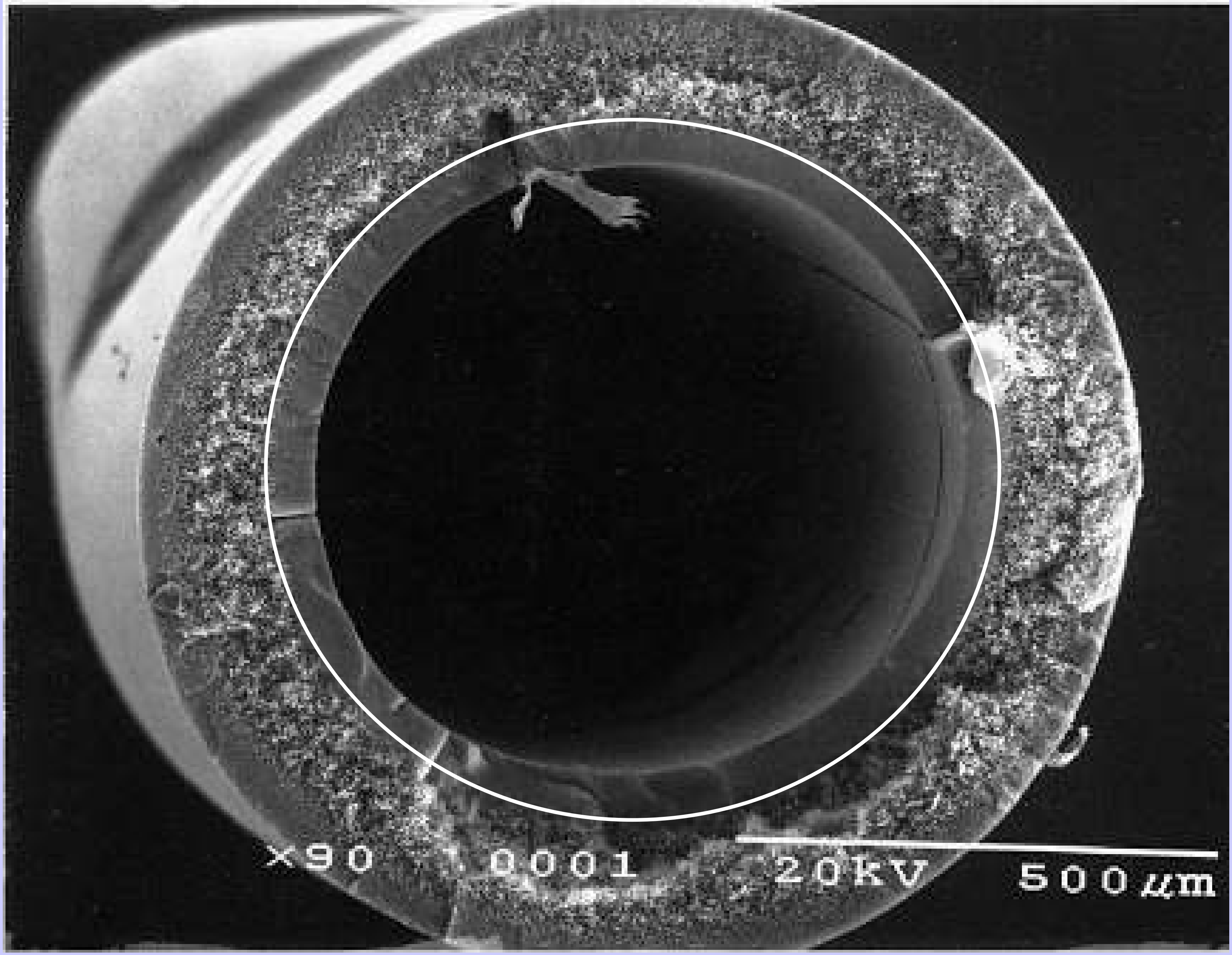
Thermally induced phase separation (TIPS)

Supported, unsupported membranes

Hollow fibers modules, spiral modules, plate and frame modules, other configurations

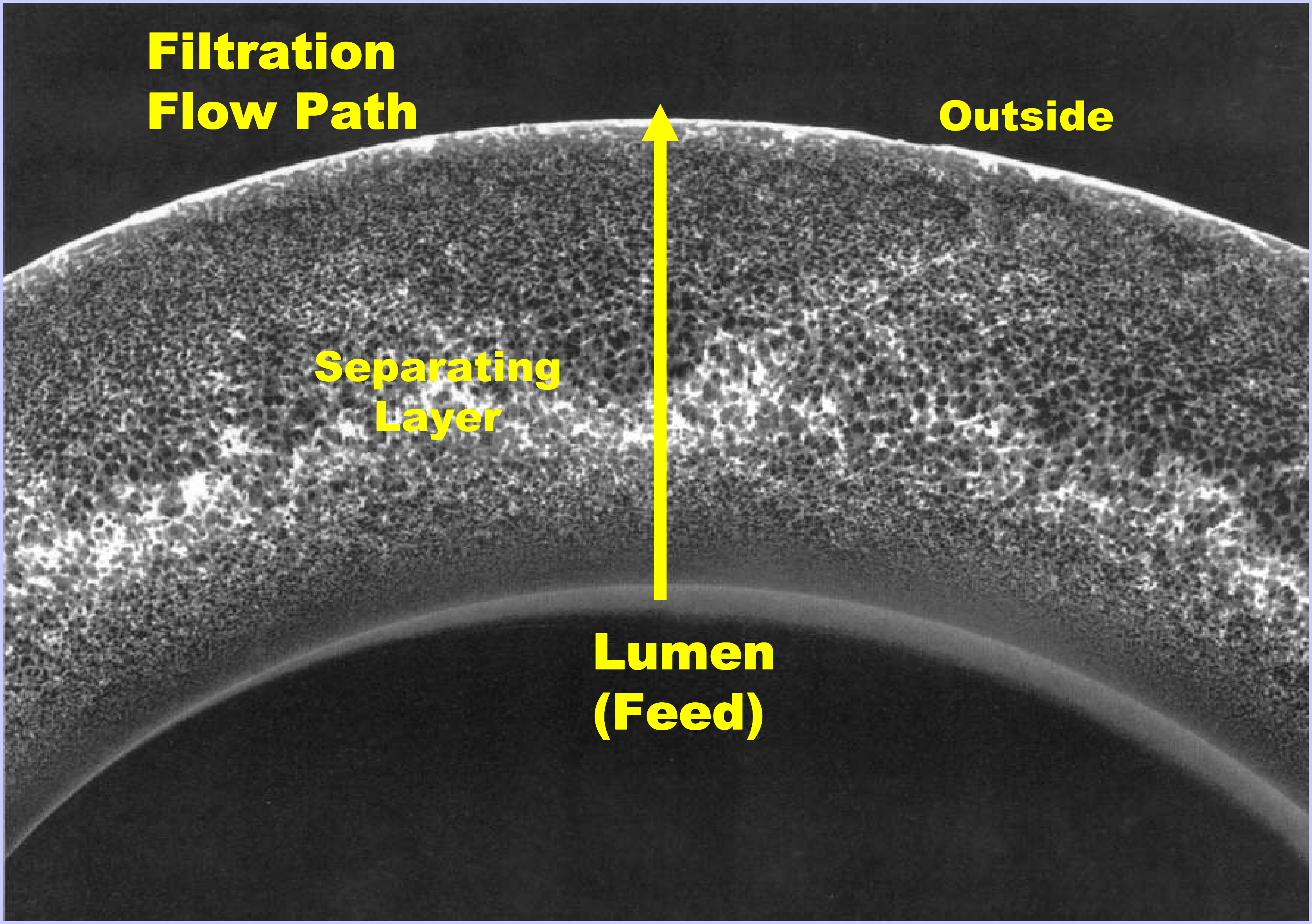


Capillary membrane manufacturing process

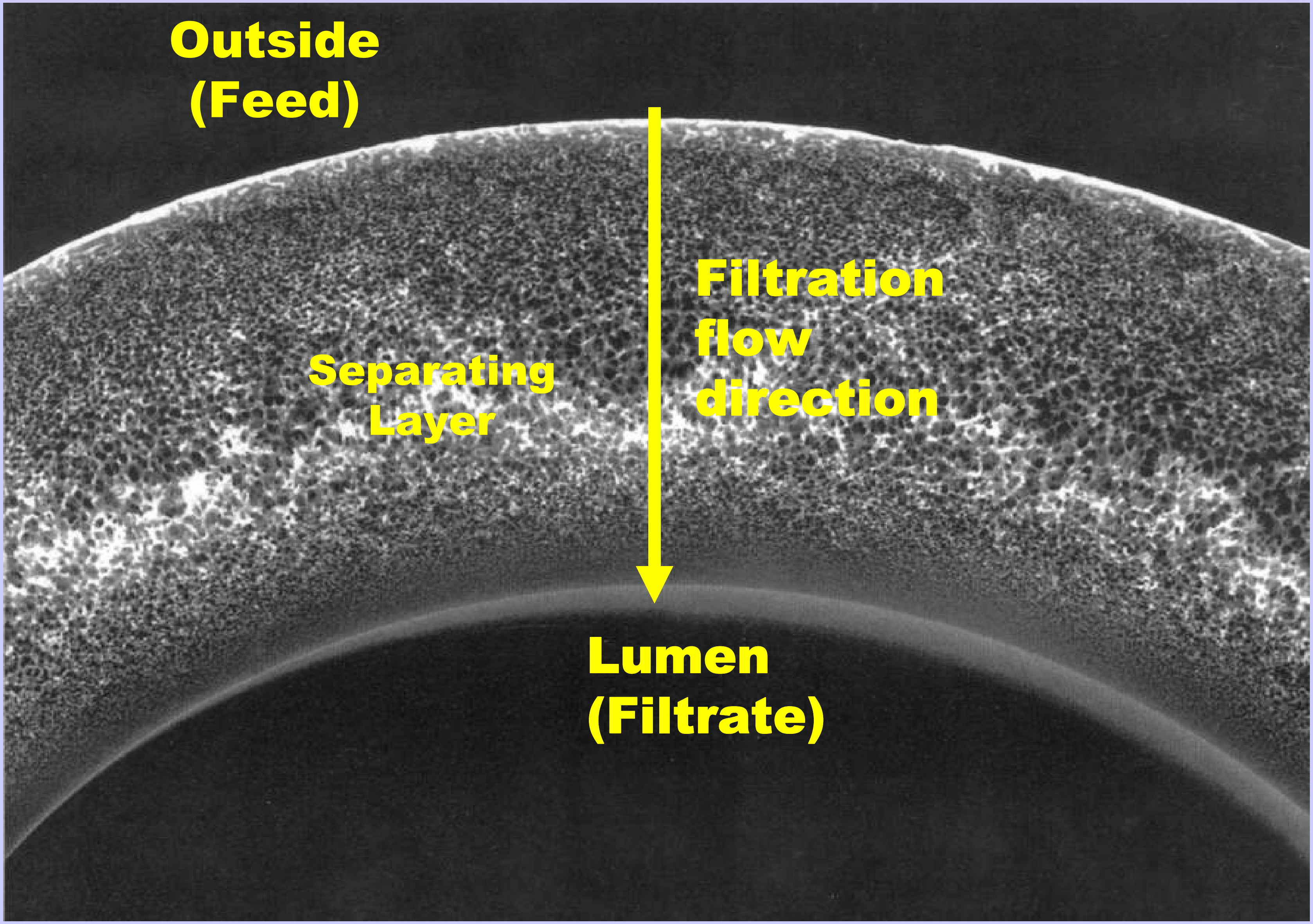

×90 0001 20kV 500µm

PRESSURE DRIVEN CAPILLARY TECHNOLOGY

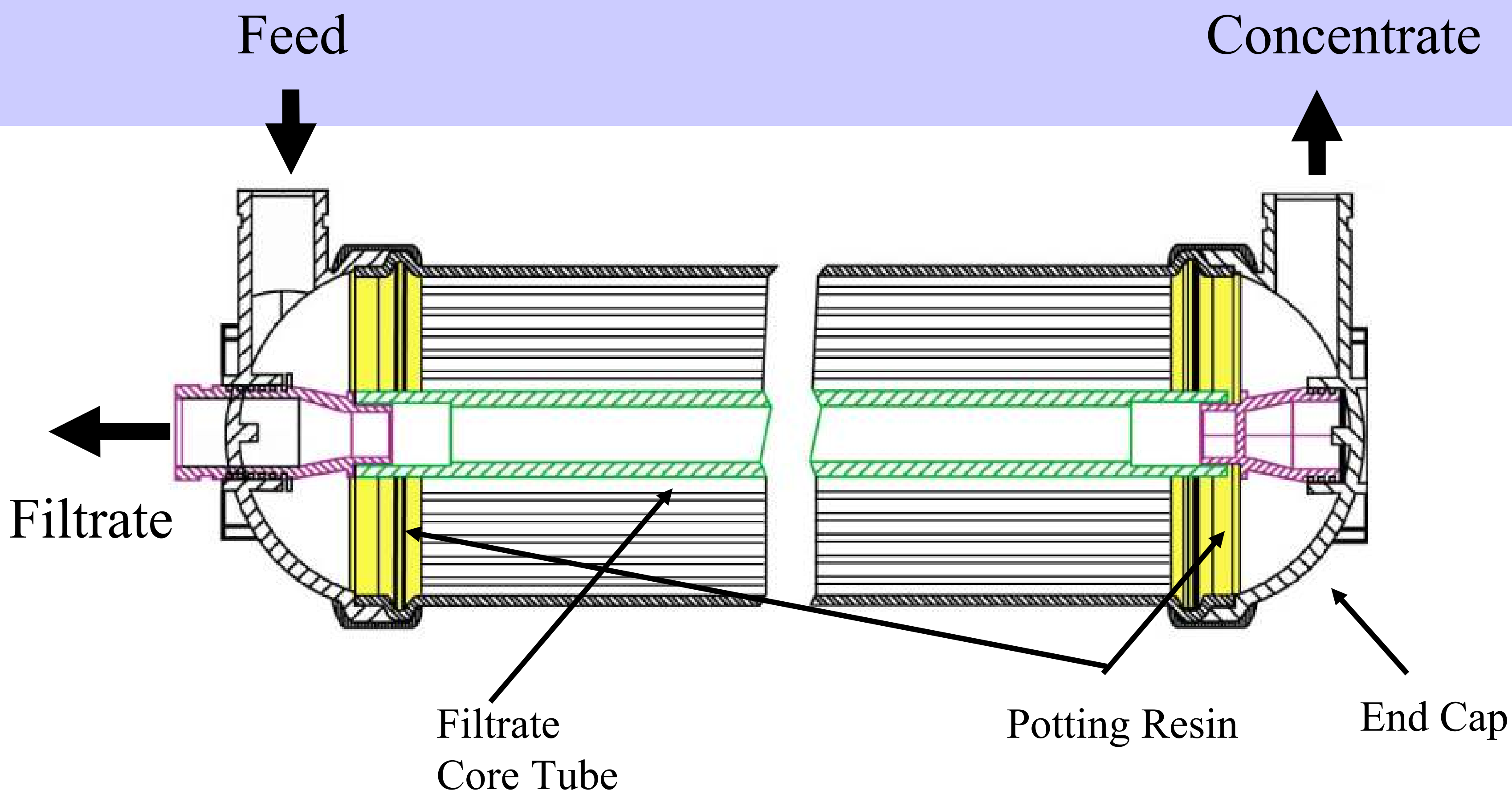
Pressure driven membrane cross section inside – out operation



Pressure driven membrane cross section outside – in operation

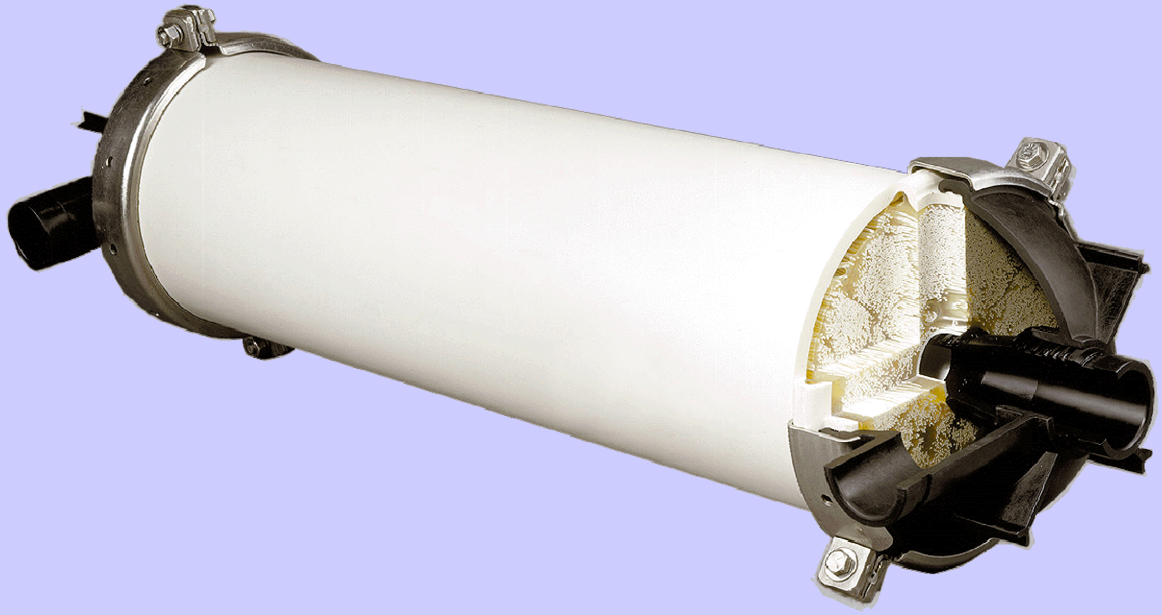


Configuration of pressure driven, capillary membrane module



- **Quick release end cap**
- **Maximize membrane area**
- **100% Hydraulic sealing**
- **Integral connection with filtrate core tube**
- **Light weight & streamlined design**

Example of pressure driven membrane module



	0.8 mm fibre	**1.2 mm fibre**
HYDRAcap 40:	30 m^2 (320 ft^2)	19 m^2 (200 ft^2)
HYDRAcap 60:	46 m^2 (500 ft^2)	30 m^2 (320 ft^2)

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

$SP = Q/(A_m * TMP)$

Example of permeability results

Test parameter	New membrane	Field conditions
P_f, bar (psi)	0.25 (3.6)	0.70 (10.1)
P_c, bar (psi)	0.15 (2.2)	0.60 (8.5)
P_p, bar (psi)	0.10 (1.5)	0.15 (2.2)
TMP, bar (psi)	0.10 (1.5)	0.50 (7.2)
Q, l/hr (gpd)	3,500 (22,000)	5,100 (32,300)
A_m, m^2 (ft2)	46.5 (500)	46.5 (500)
SP, l/m^2-hr (gfd/psi)	750 (29)	219 (8.9)

Integrity test procedure
(ASTM D6908-03)

Off line tests

- **Bubble point test**
- **Pressure hold test**
- **Diffusive air flow test**
- **Vacuum hold test**

Continuous (on line) tests

- **Particle passage counting/monitoring**
- **Marked particles passage**
- **Turbidity measurements**
- **Acoustic sensing**

Integrity test procedure pressure or vacuum hold

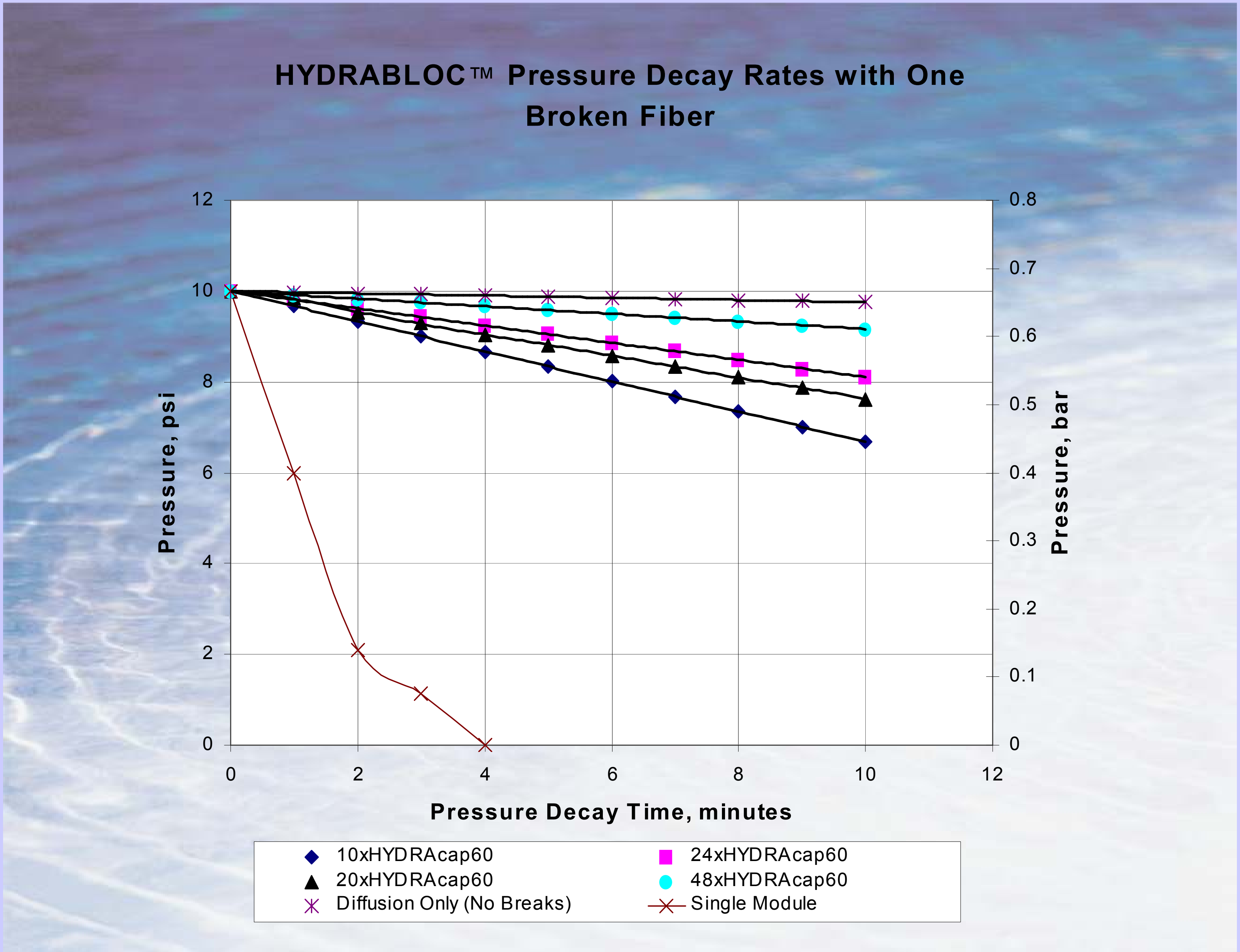
Pressure decay rate (PDR)

PDR = (Pi-Pf)/t
Pi – initial pressure
Pf – final pressure
t – time interval
PDR = PDR (measured) – rate of diffusion

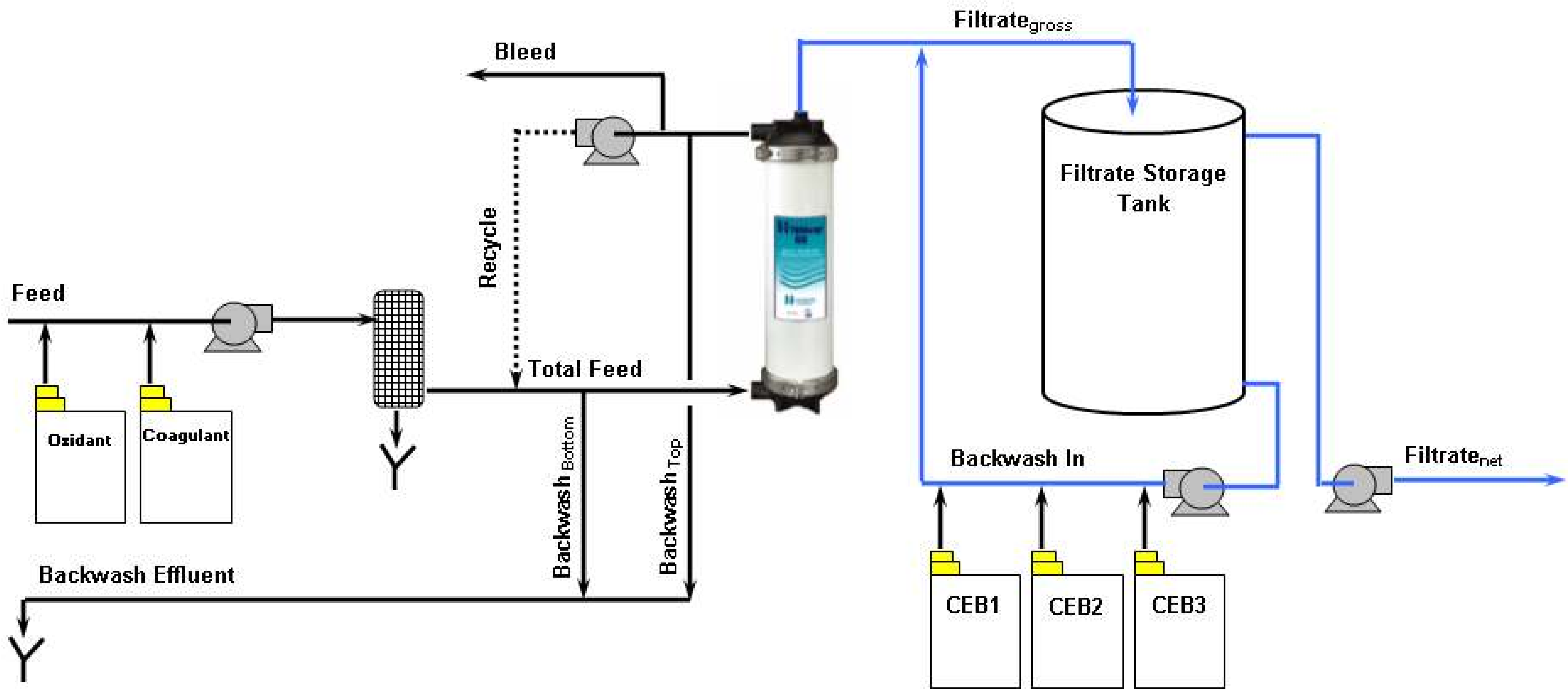
Vacuum decay rate (VDR)

VDR = VDR (measured) – rate of diffusion

Integrity test sequence



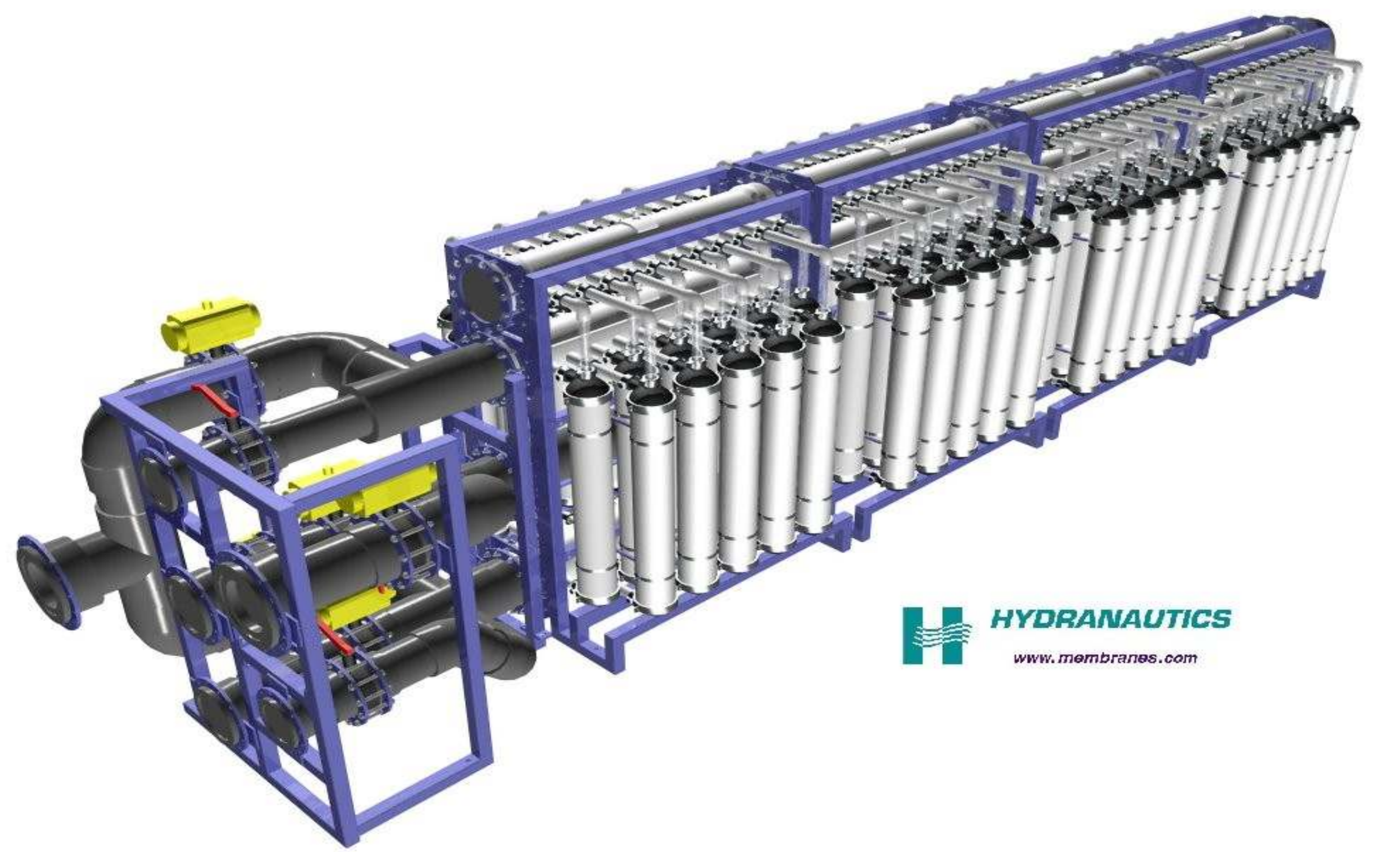
Schematics of pressure driven capillary unit



PRESSURE DRIVEN CAPILLARY SYSTEM

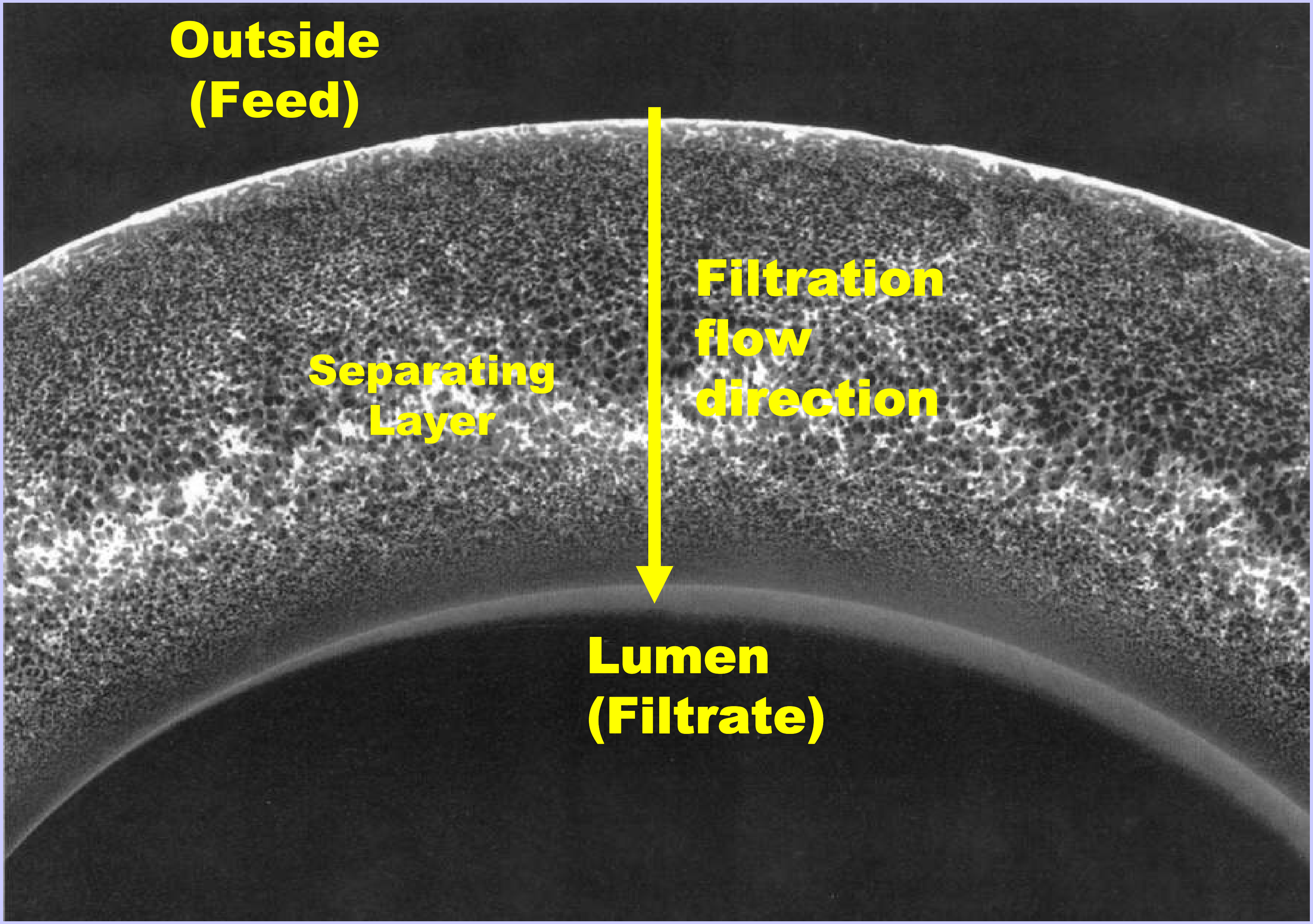
Process step	Objective	Duration	Frequency
Forward flow	Permeate production	15 – 60 min	Continuous
Backwash	Foulants removals	30 – 60 sec	Every 15 – 60 min
Chemicals enhanced backwash (CEB)	Foulanlts removal	1 – 15 min	Once – twice a day
Cleaning in place	Foulants removal	2 – 4 hr	Every 1 – 6 months
Integrity test	Verification of membrane integrity	20 min	Every 1 – 7 days

Isometric GA of HYDRAbloc 2D1288

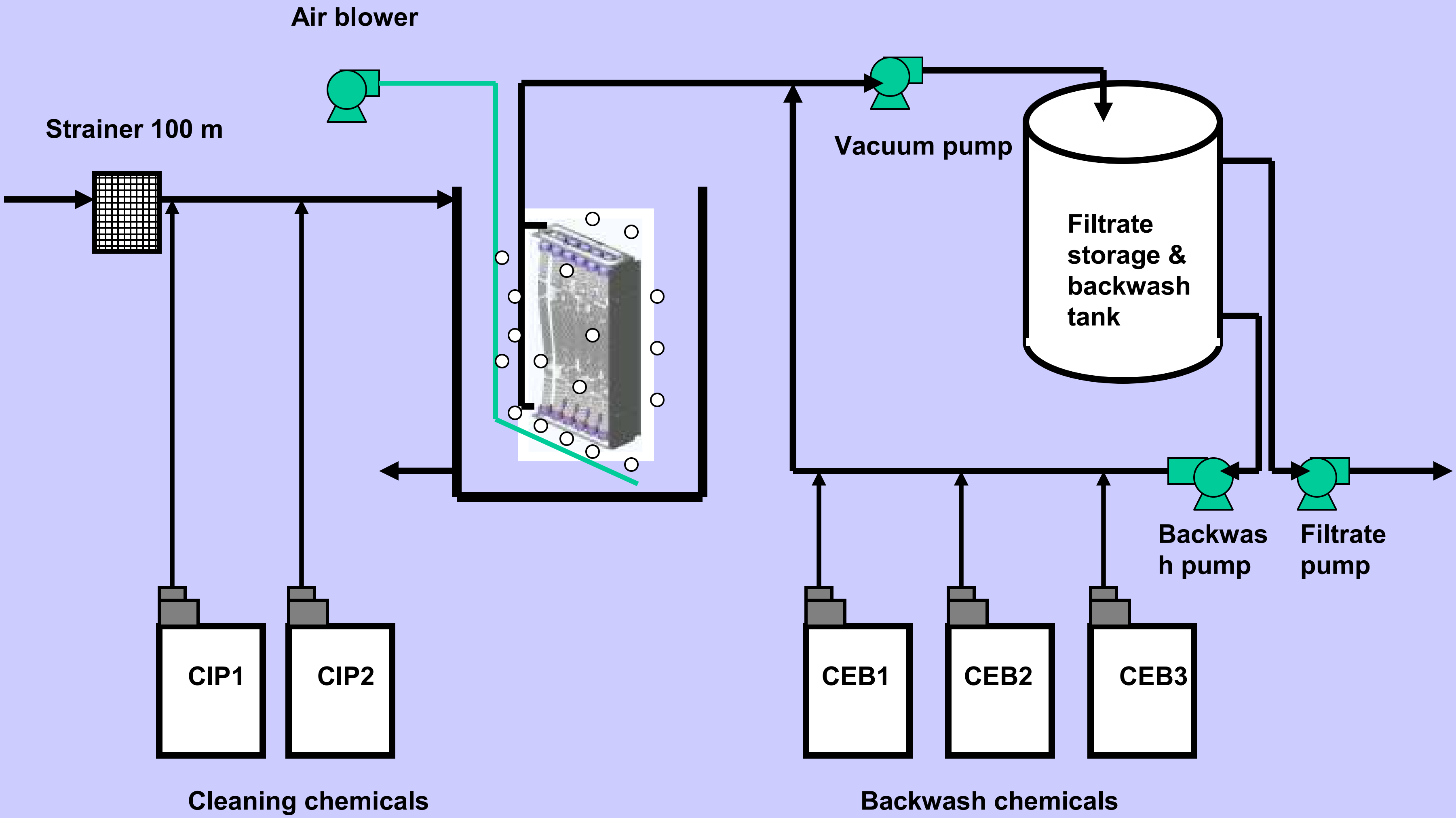


Pressurized UF train ~ 2MGD filtrate flow

Vacuum driven membrane cross section outside – in operation



Schematics of vacuum driven capillary unit

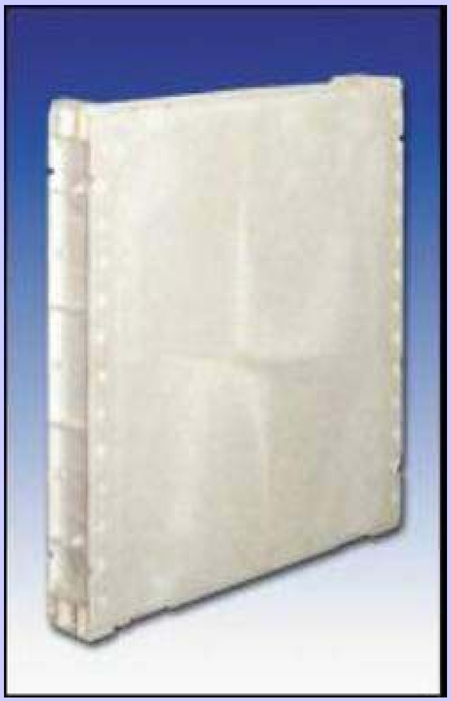


VACUUM DRIVEN CAPILLARY SYSTEM

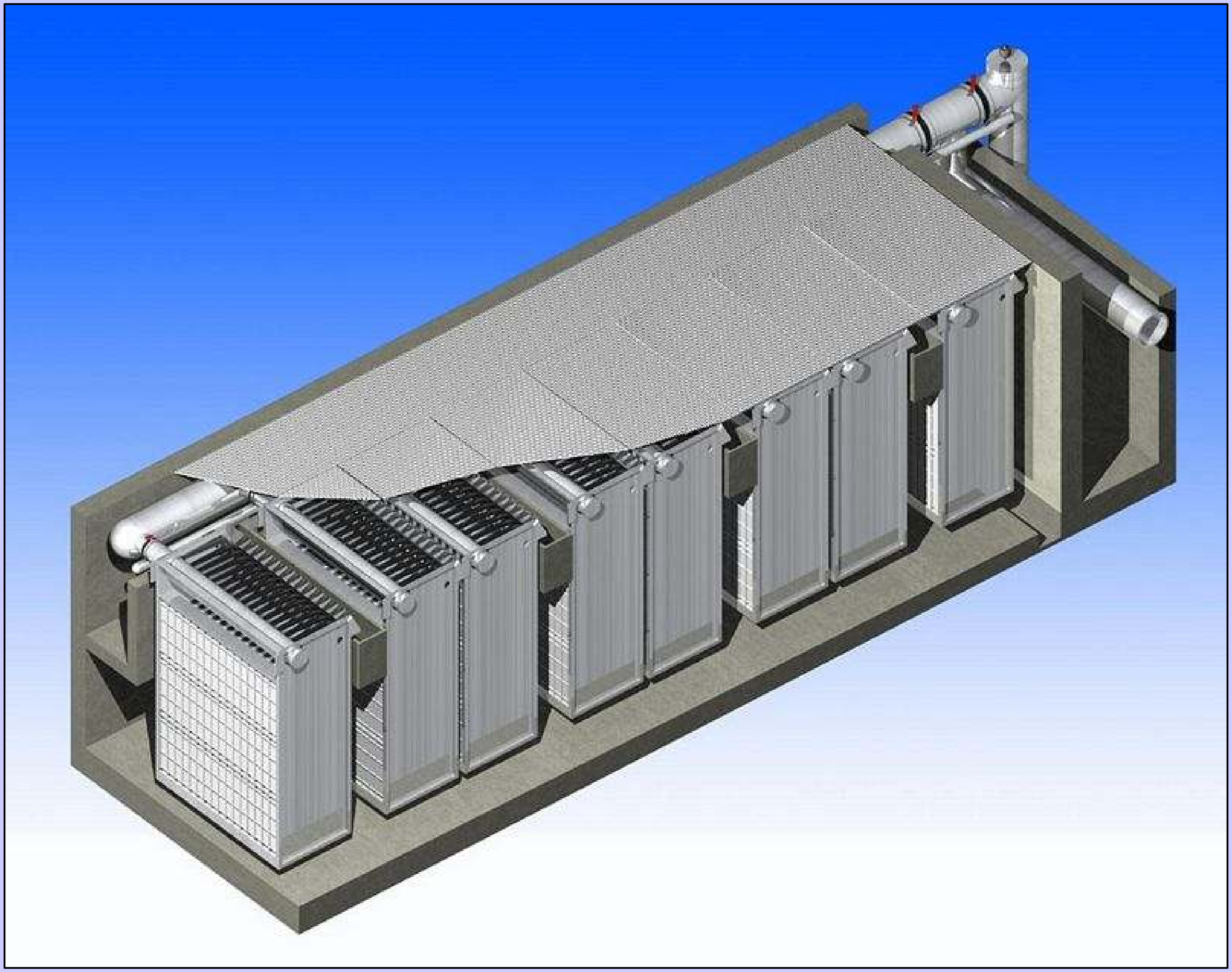
Process step	Objective	Duration	Frequency
Permeation	Permeate production	15 – 60 min	Continuous
Backwash & tank deconcentration	Foulants removals	15 – 60 sec	Every 15 – 60 min
Chemicals enhanced backwash (CEB)	Foulanlts removal	1 – 15 min	Twice a day – once per week
Cleaning in place	Foulants removal	2 – 5 hr	Every 1 – 6 months
Integrity test	Verification of membrane integrity	20 min	Every 1 – 7 days

ZeeWeed® 1000 Cassette for lower solids applications

Cassette capacity 1,500-2,000 m^3/d



Submersible membrane train configuration



ZeeWeed® 500 Cassette for High Solids Applications

Cassette capacity

750 - 1,000 m^3/d in MBR

2,500 - 3,500 m^3/d in water filtration

Application	Flux rate range, l/m2-hr (gfd)	Recovery rate range, %
Potable water	60 – 130 (35 – 75)	90 – 97
Tertiary filtration	34 – 85 (20 – 50)	85 – 92
Seawater filtration	42 – 70 (25 – 40)	85 – 92

Membrane filtration – commercial products

Aquasource

Membrane materials

CA

High hydrophilic, very wettable

Pore size 0.01 µm
35 to100kD

Fibre id 0.93 mm

Cl_2 resistance quite high

pH tolerance 3.5 – 8.5

Modified PS

Moderately hydrophilic, wettable

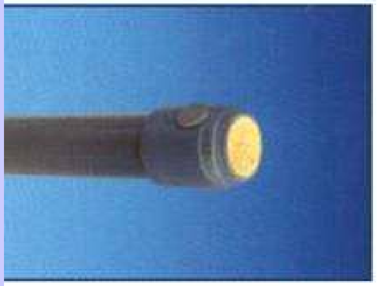
Pore size 0.01 µm
35 to100kD

Fibre id 0.96 mm

Cl_2 resistance quite high

pH tolerance 1 – 13

The Modules



DN100
7,2 m²

DN300
55 m²

DN300
64 m²

DN450
125 m²

AQUASOURCE

Inge

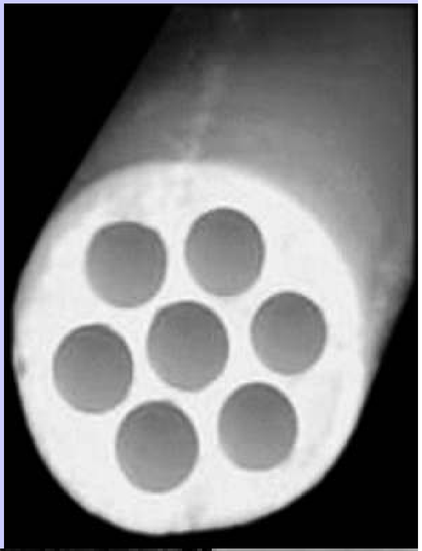
Membrane

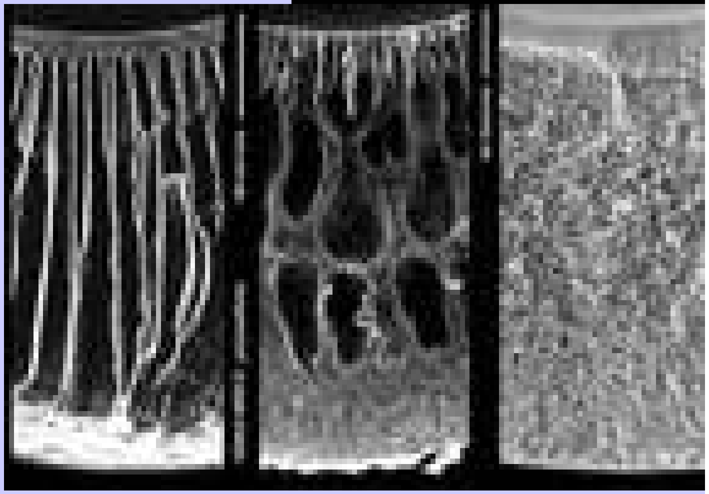
- Modified PES
- Moderately hydrophilic, easily wettable
- Pore size; UF 10 - 25 nm
- Fibre id, 0.9 mm; od 4.3 mm
- Cl_2 resistance moderately high
- pH tolerance 1.5 - 13

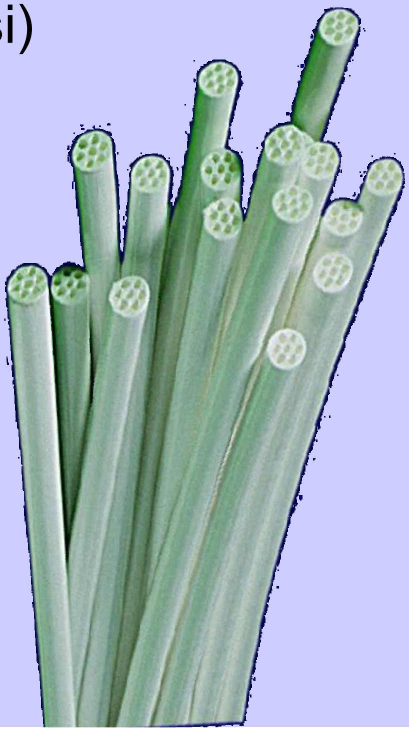
Multibore Membrane

Membrane

- 7 single capillaries combined into one fiber
- PES blended with a strong, hydrophilic polymer
- asymmetric membrane formed from polymer blend
- regular foam structure as active layer support
- burst pressure > 13 bar (190 psi)





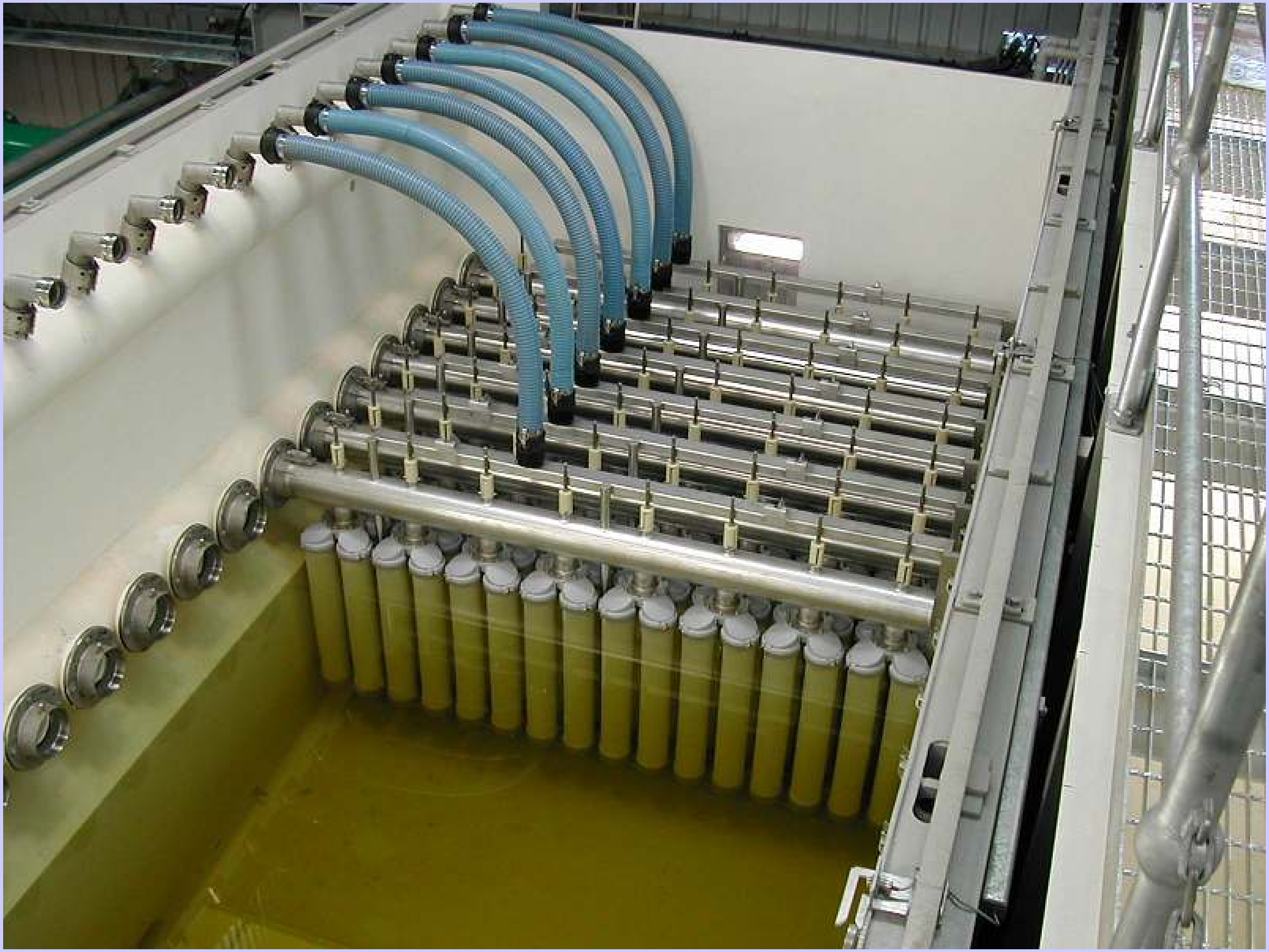


Norit

Membrane

- PES/PVP
- Hydrophilic, easily wettable
- Pore size; UF 20 - 25 nm
- Fibre id, 0.8 mm (1.5 mm); od 1.3 mm (2.5 mm)
- Cl_2 resistance moderately high
- pH tolerance 1.5 – 13
- Module diameter – 200 mm
- Membrane area – 40 m^2

Norit – UF train 7000m3/day (1.9 mgd)

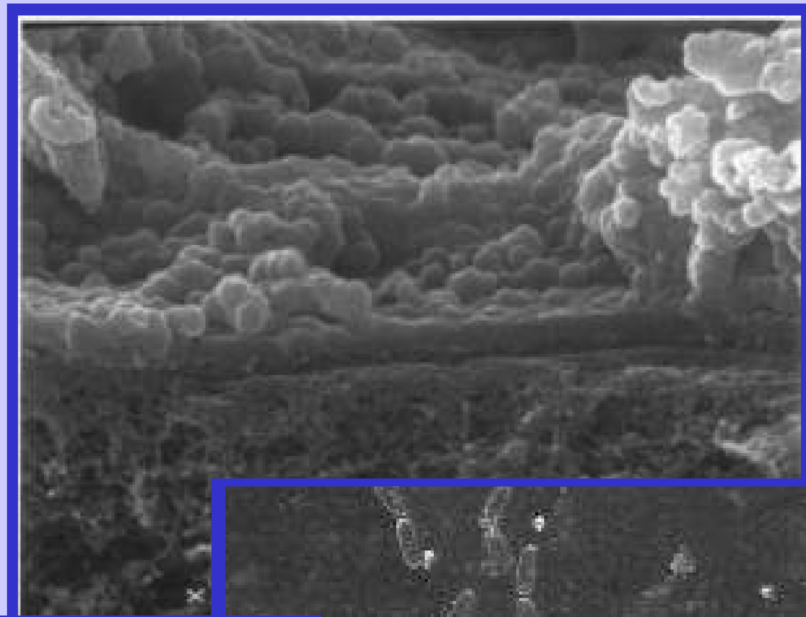


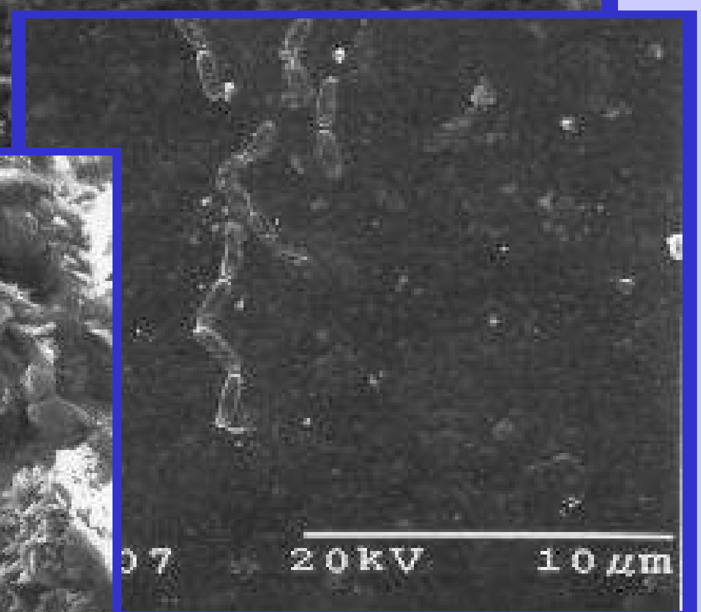
Memcor (Siemens) submersible – CMF S

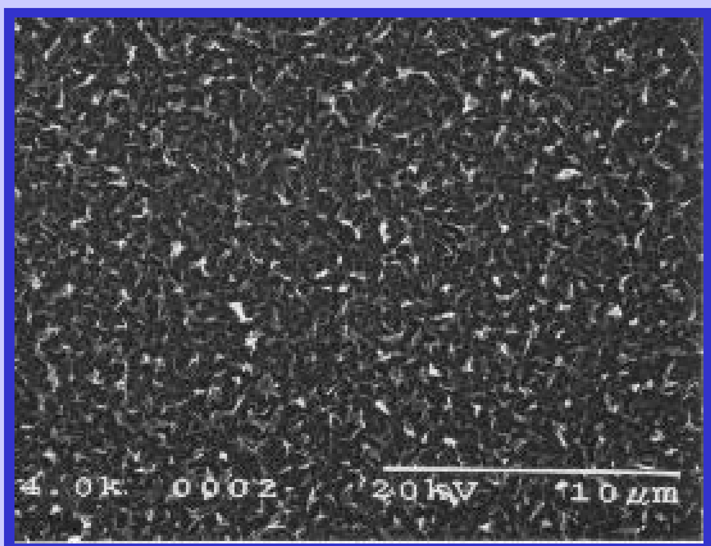
Memcor (Siemens) pressurized – CP

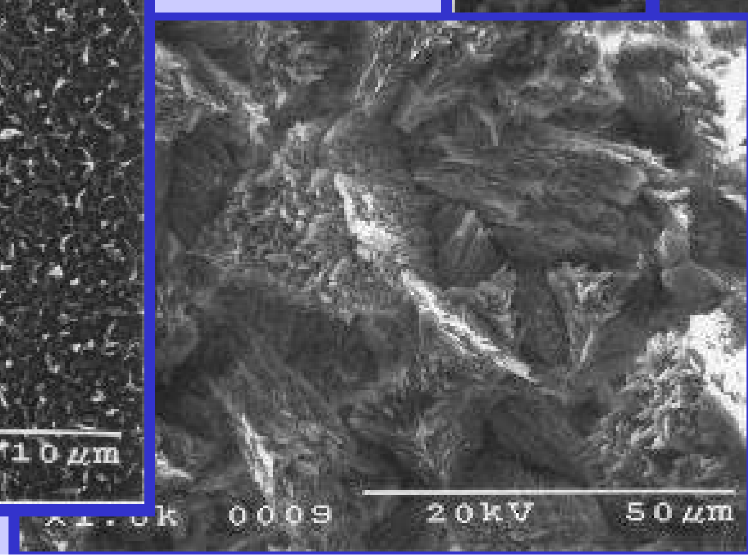
Membrane Fouling in Wastewater Reclamation

- Fouling Processes
  - Organic Adsorption
  - Colloidal Material
  - Biogrowth
  - Scaling

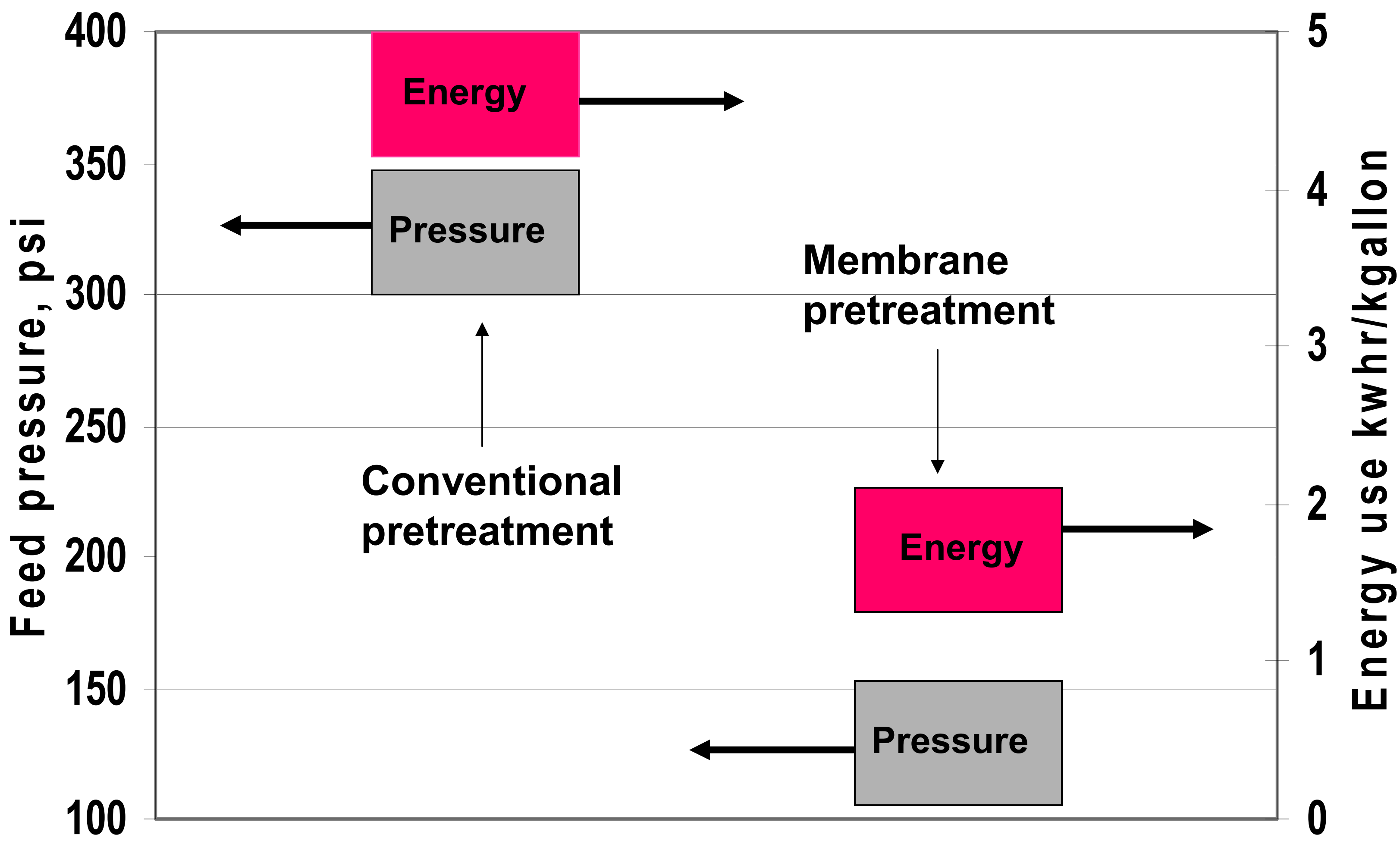


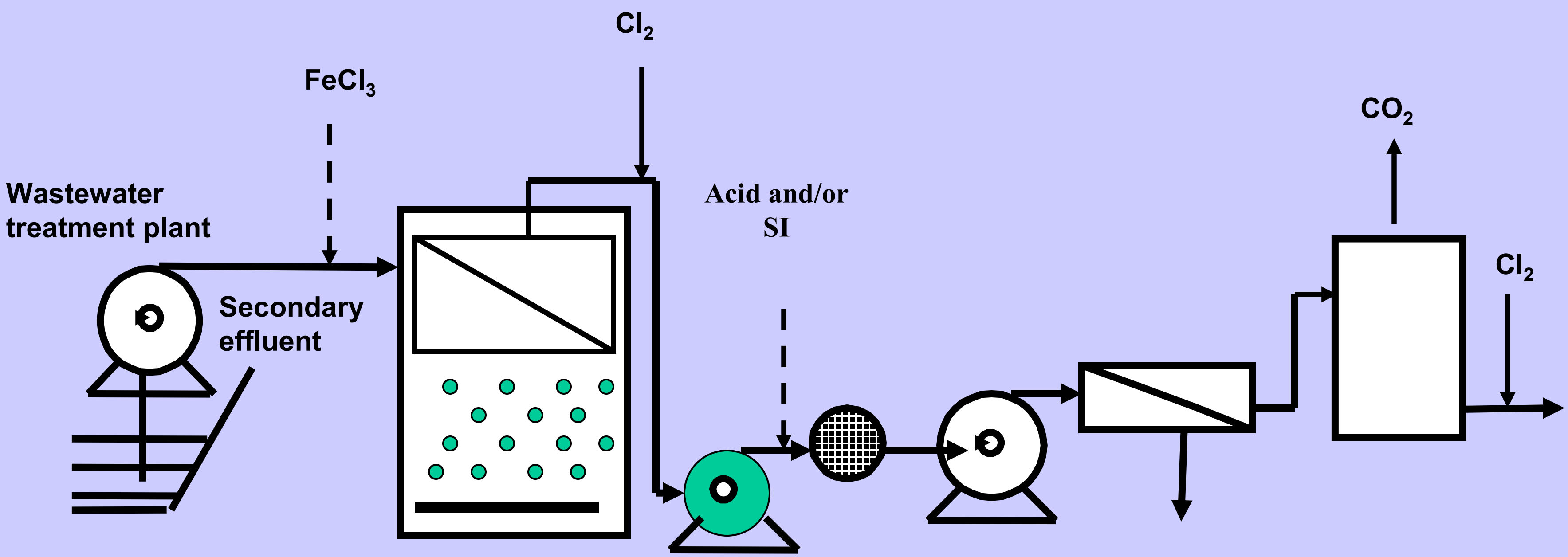






Effect of pretreatment on operating parameters in wastewater reclamation systems

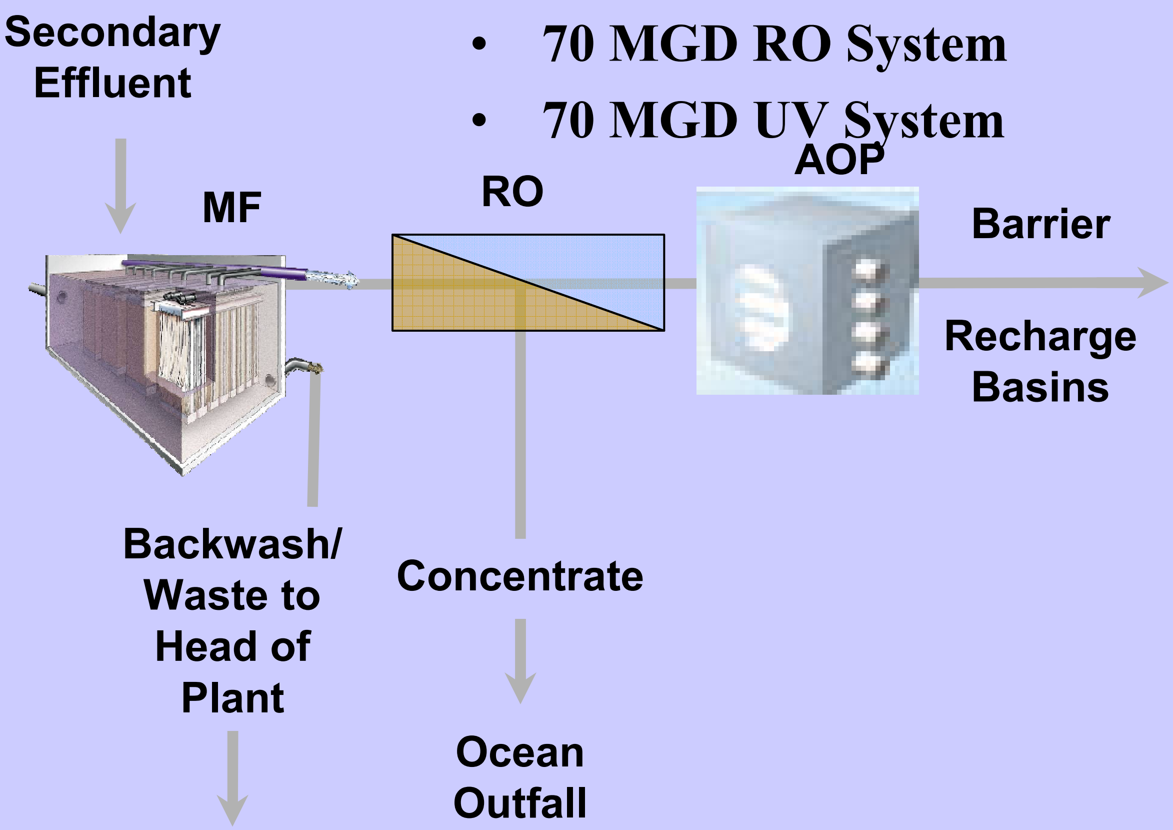




RO wastewater reclamation with membrane pretreatment

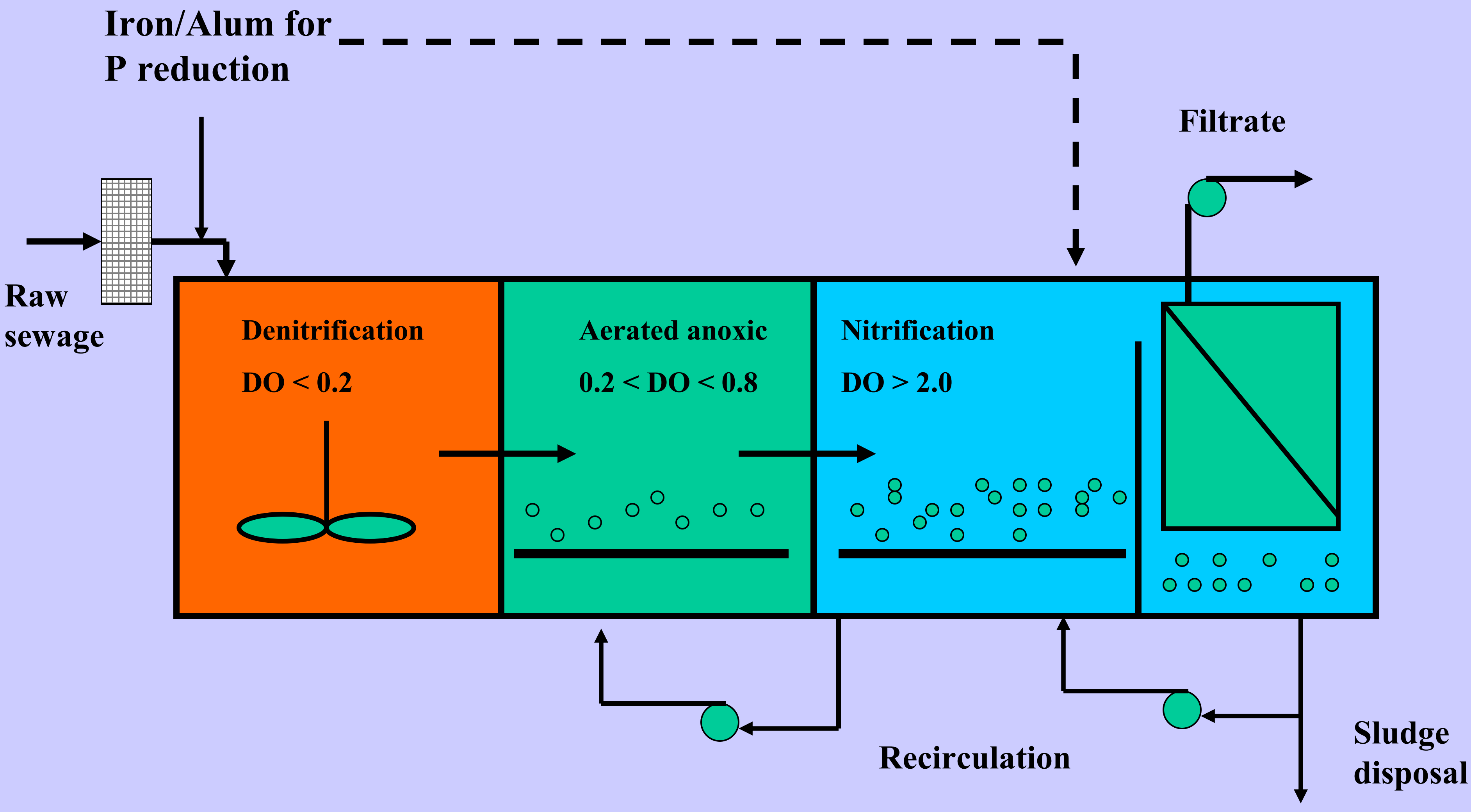
Orange County, CA GWR System

- 86 MGD MF System
- 70 MGD RO System
- 70 MGD UV System

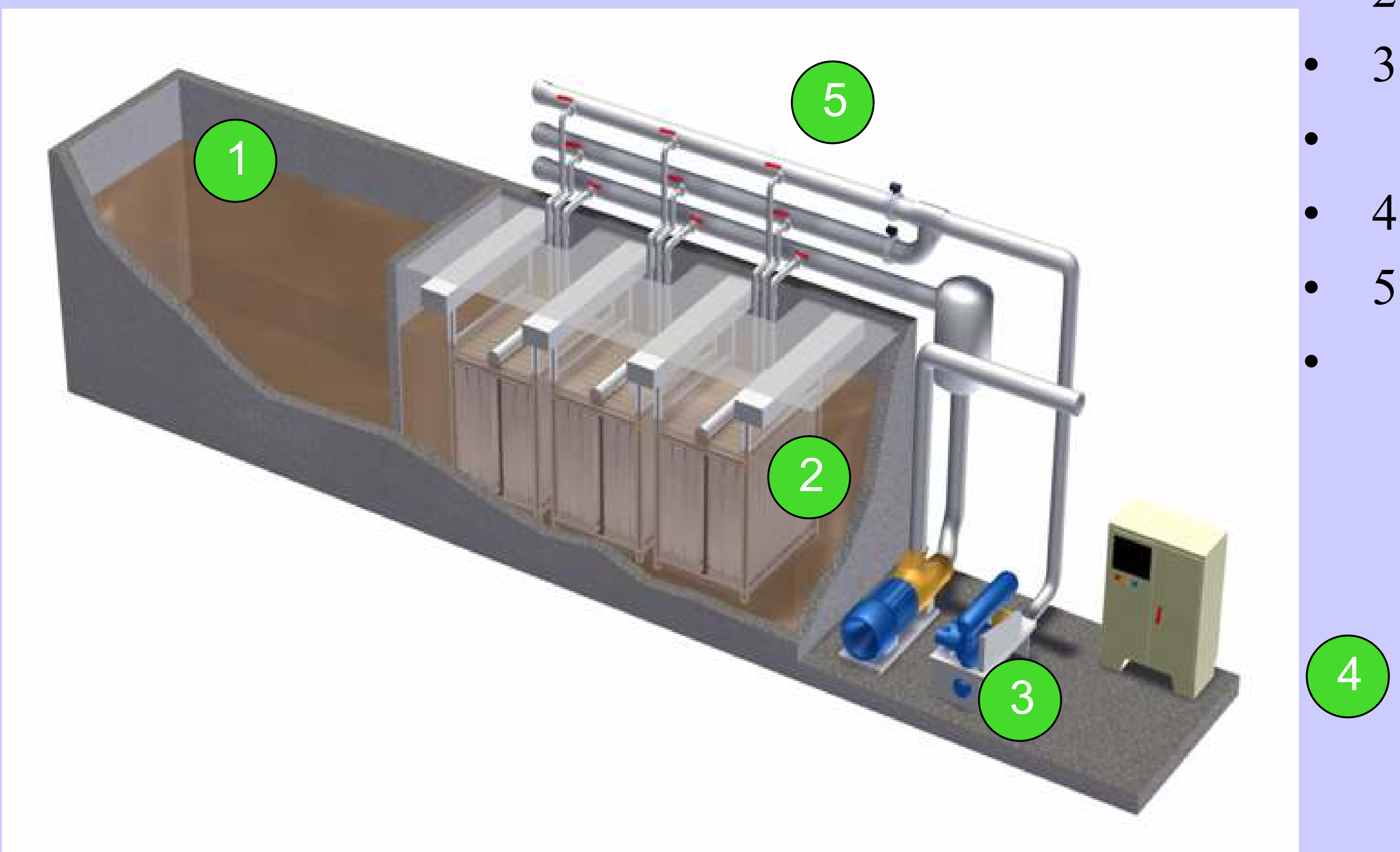


- MF System
  - Recovery: 90%
  - 0.2 micron pore
- RO System
  - Recovery: 80% - 85%
  - 5 mgd per train
  - Flux rate: 12 gfd
- UV System
  - Low Pressure/High Output
  - 8 trains with 3 vessels per train
  - Hydrogen peroxide

Nitrogen and phosphorus reduction process (three stages)



A Basic MBR Production Train



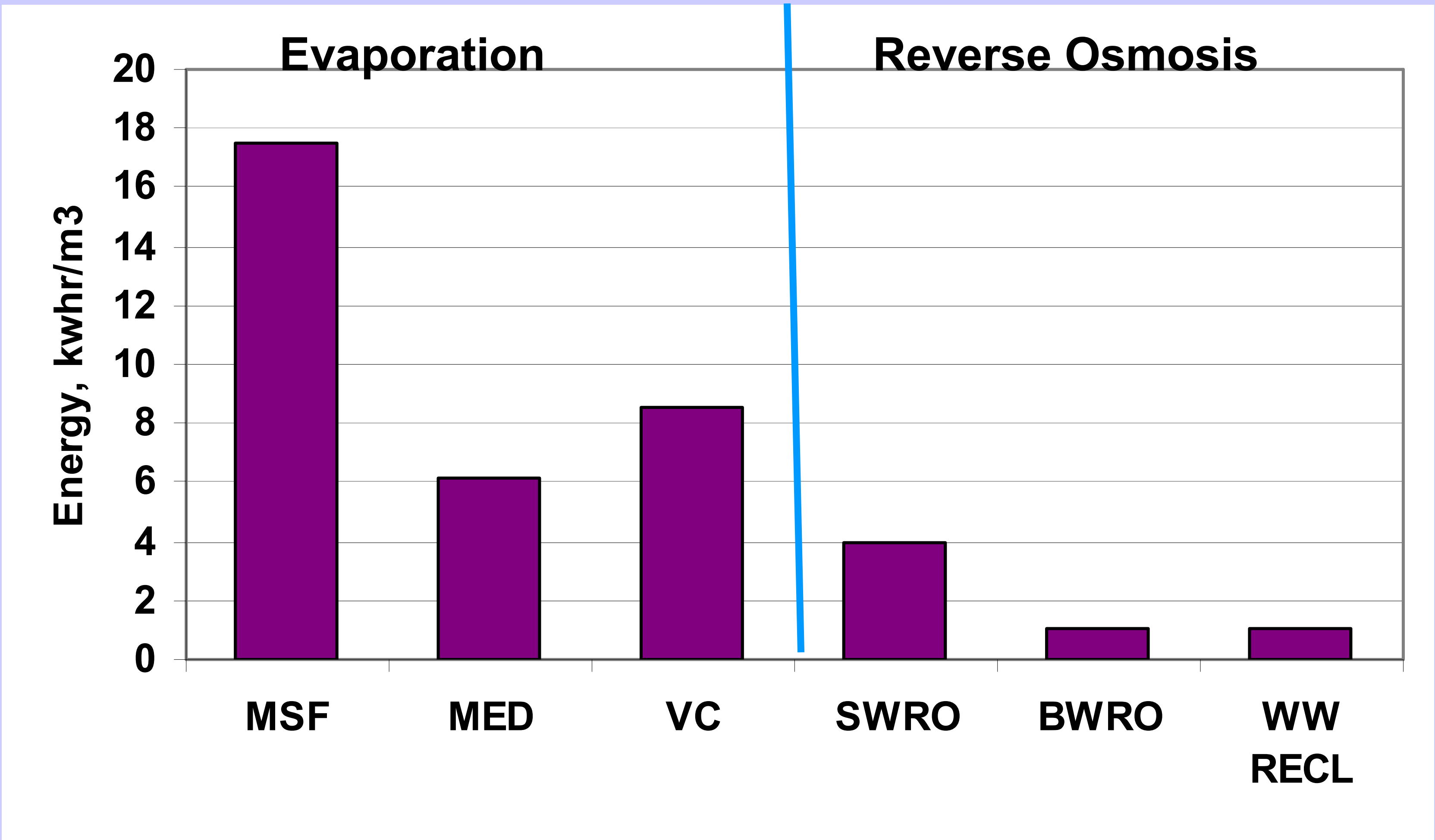
- 1.Biological reactor
- 2.Membranes
- 3.Permeate pump &
- air blower
- 4. Control panel
- 5. Permeate & air
- piping

R&D directions – membrane filtration

- Lower cost of membrane products
- Reduction of energy requirement
- Permanent hydrophilic membranes
- Reduction of fouling tendency
- Easy identification of integrity breach
- Simplified system configuration
- Replacement of chemical membrane cleaning with biological processes

Desalination

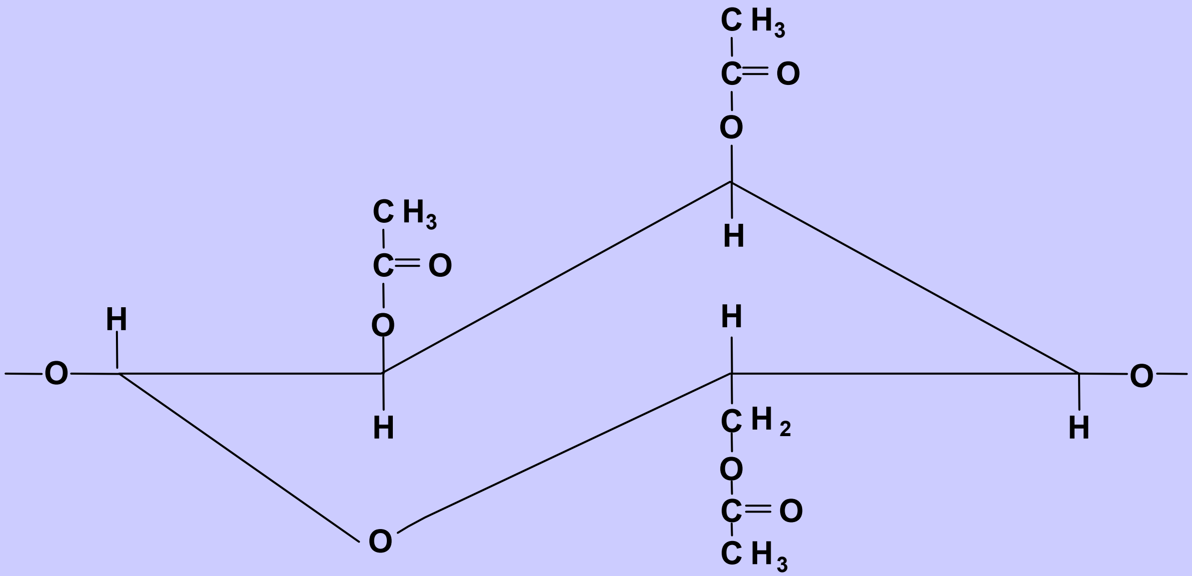
Energy usage in desalination processes



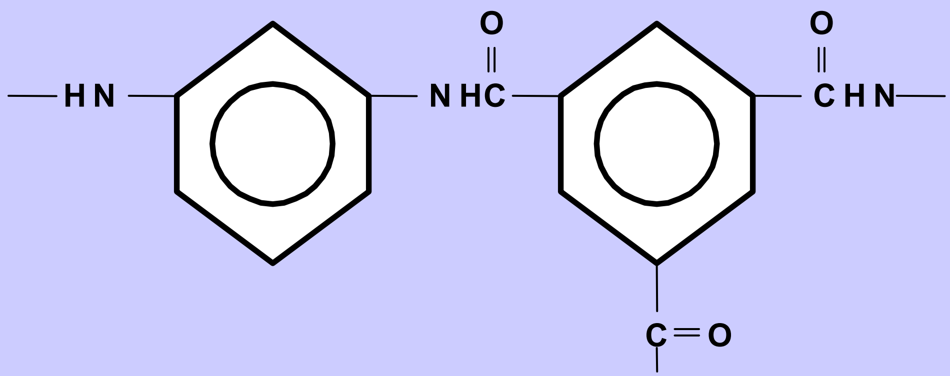
MSF – Multistage flash, MED – Multieffect distillation, VC – Vapor compression, SWRO – Sea water RO, BWRO – Brackish water RO, WWRECL- Wastewater reclamation

COMMERCIAL MEMBRANES AND MEMBRANE MODULE CONFIGURATIONS

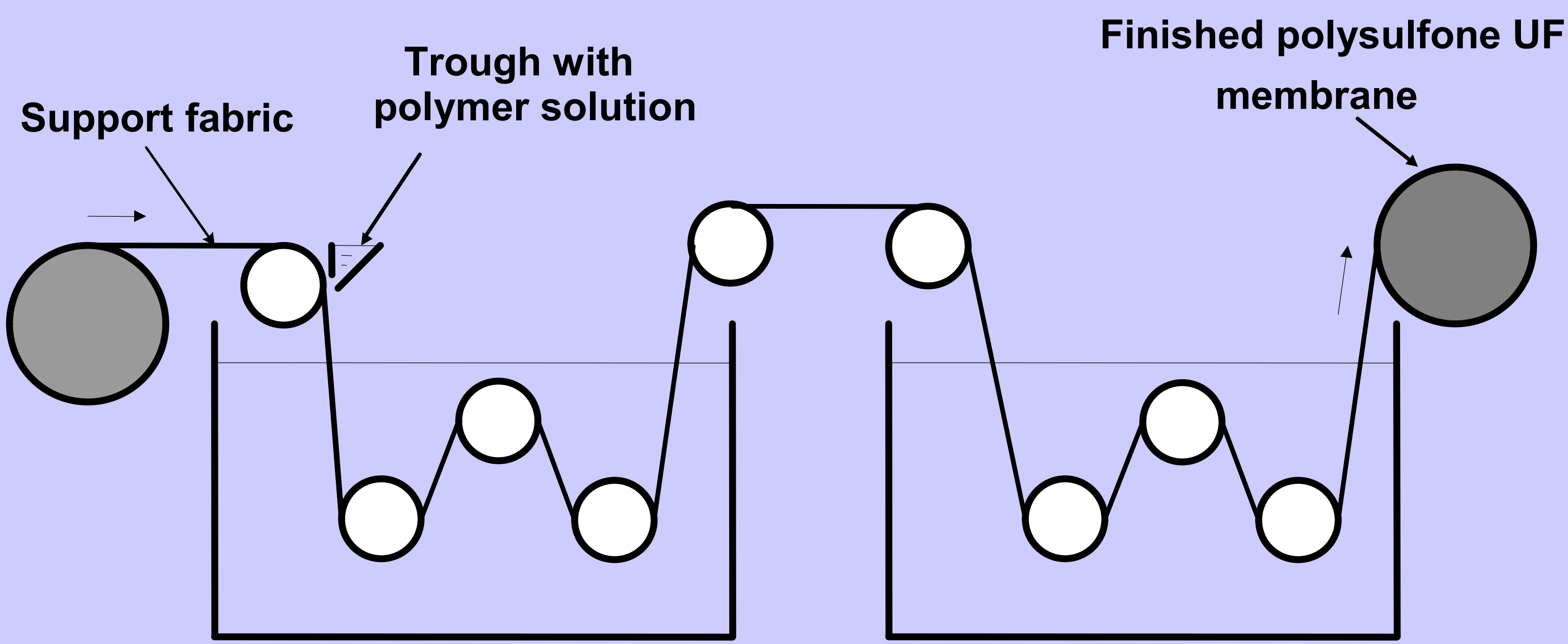
A



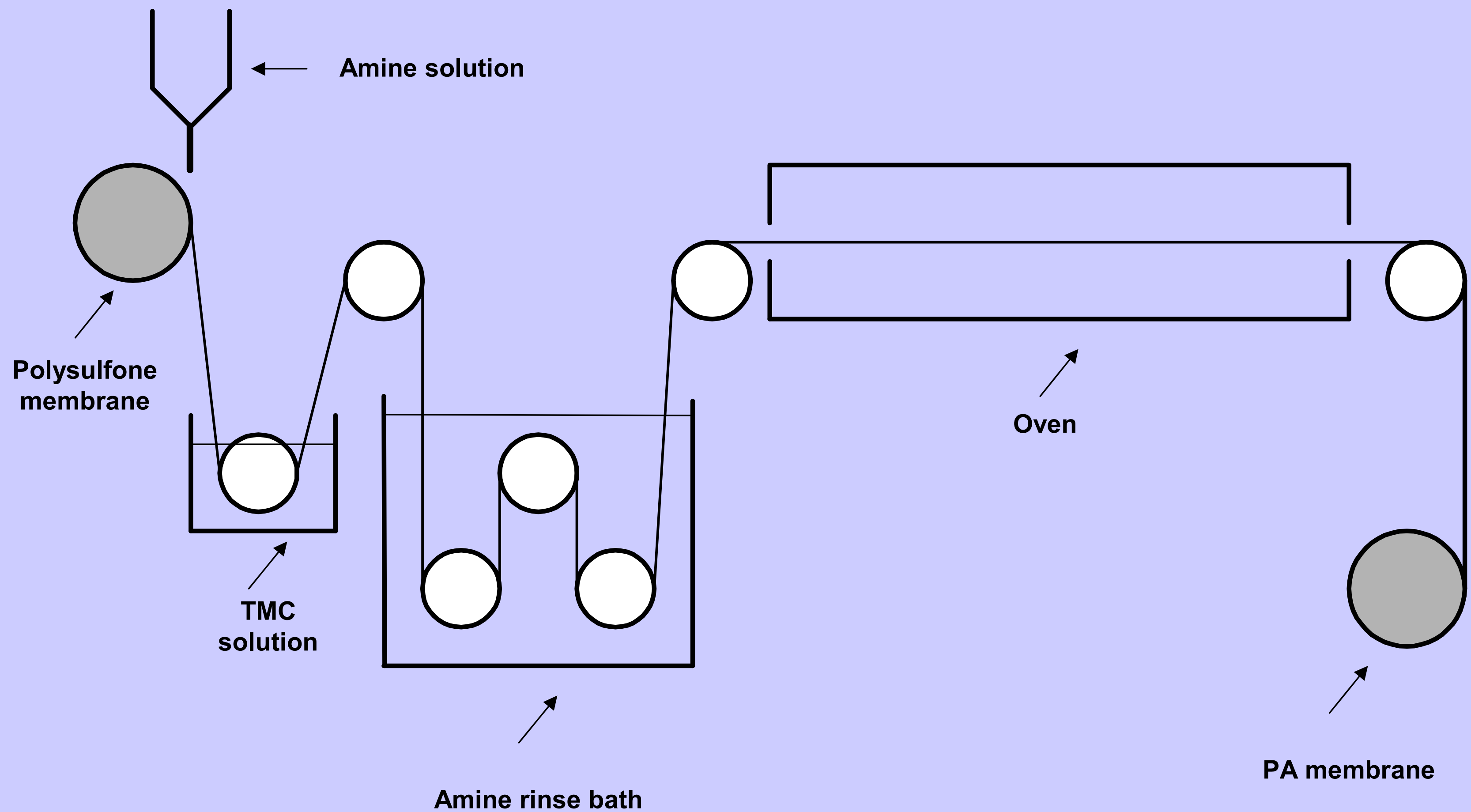
B



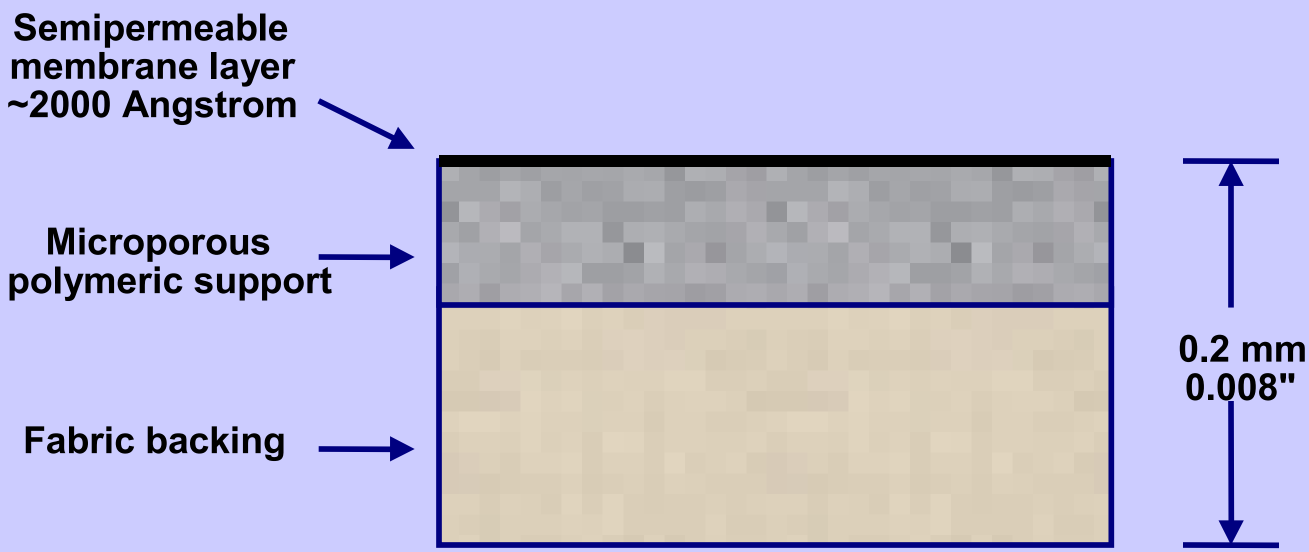
Chemical structure of cellulose triacetate (A) and polyamide (B) membrane material

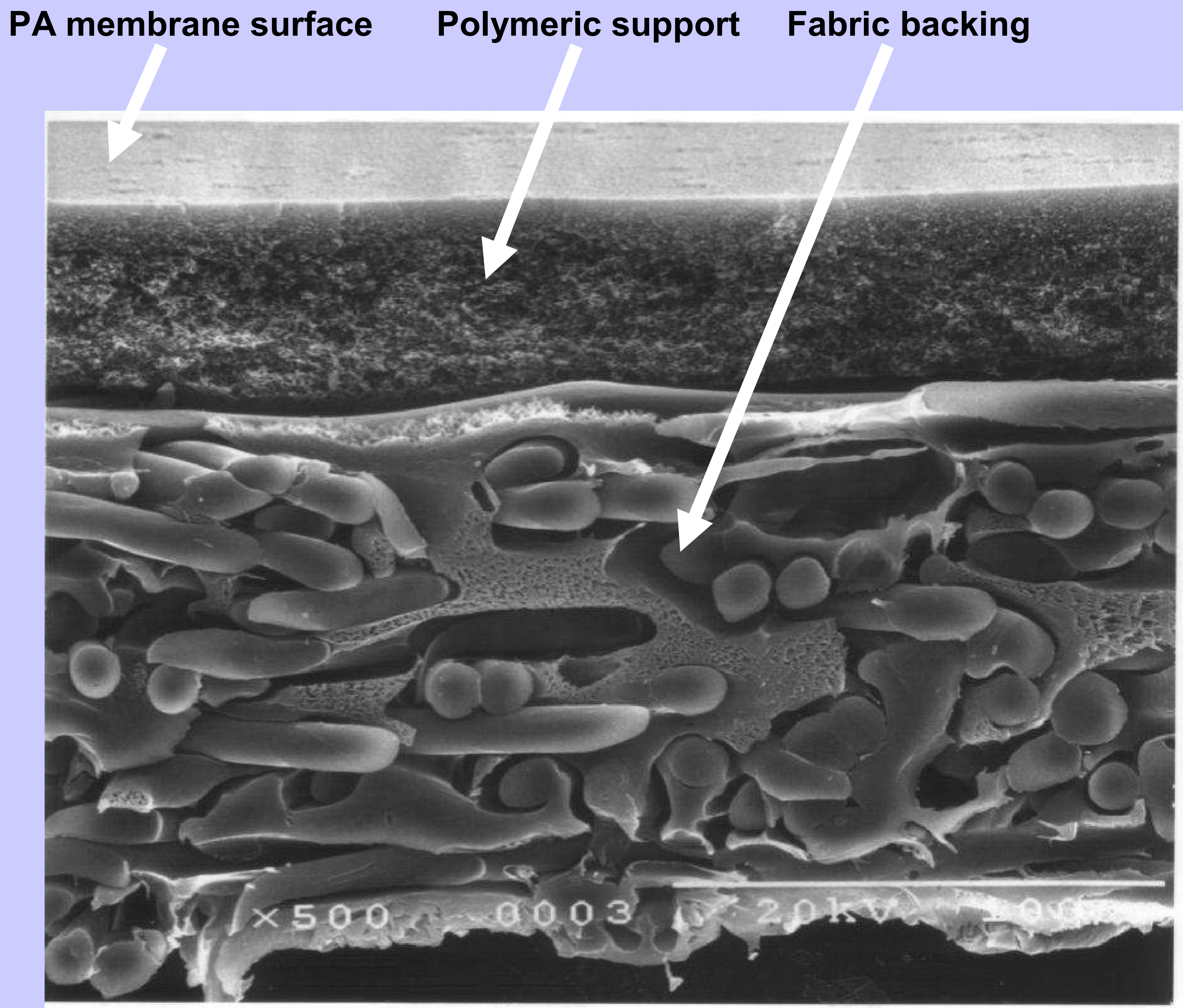


Manufacturing process of polysulfone membrane support

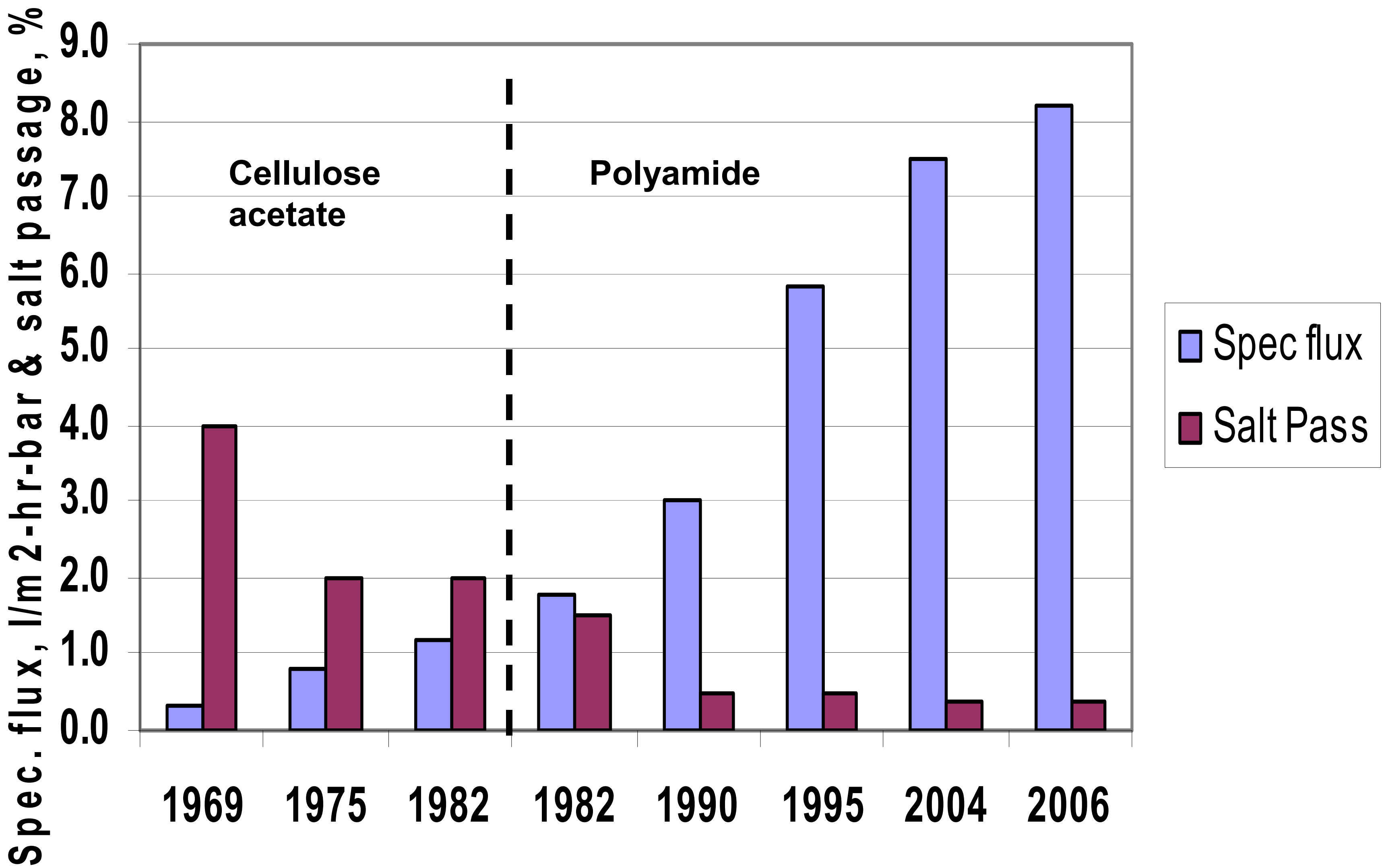


Manufacturing process of polyamide membrane barrier on polysulfone support

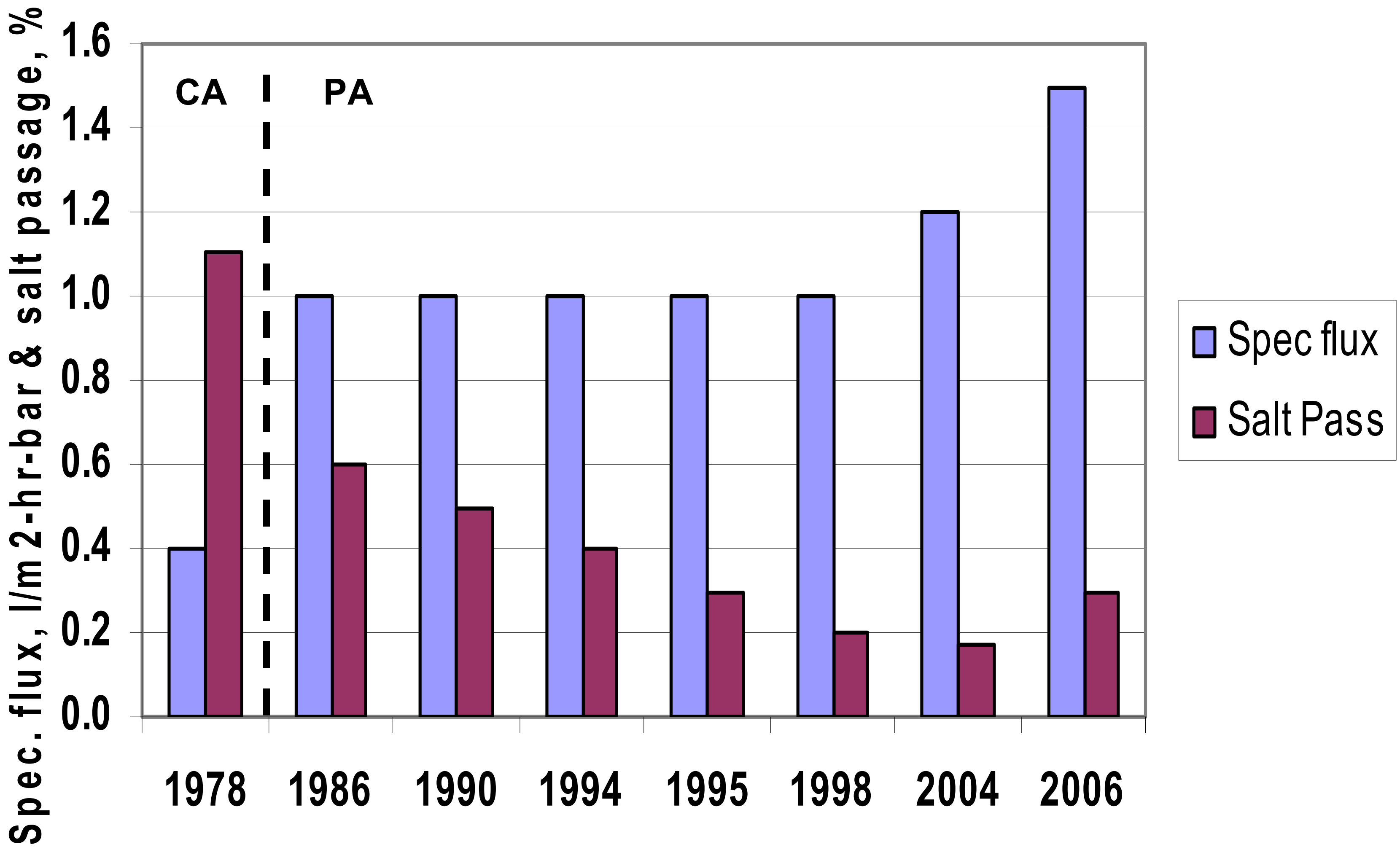

Semipermeable membrane layer ~2000 Angstrom
Microporous polymeric support
Fabric backing
0.2 mm
0.008"

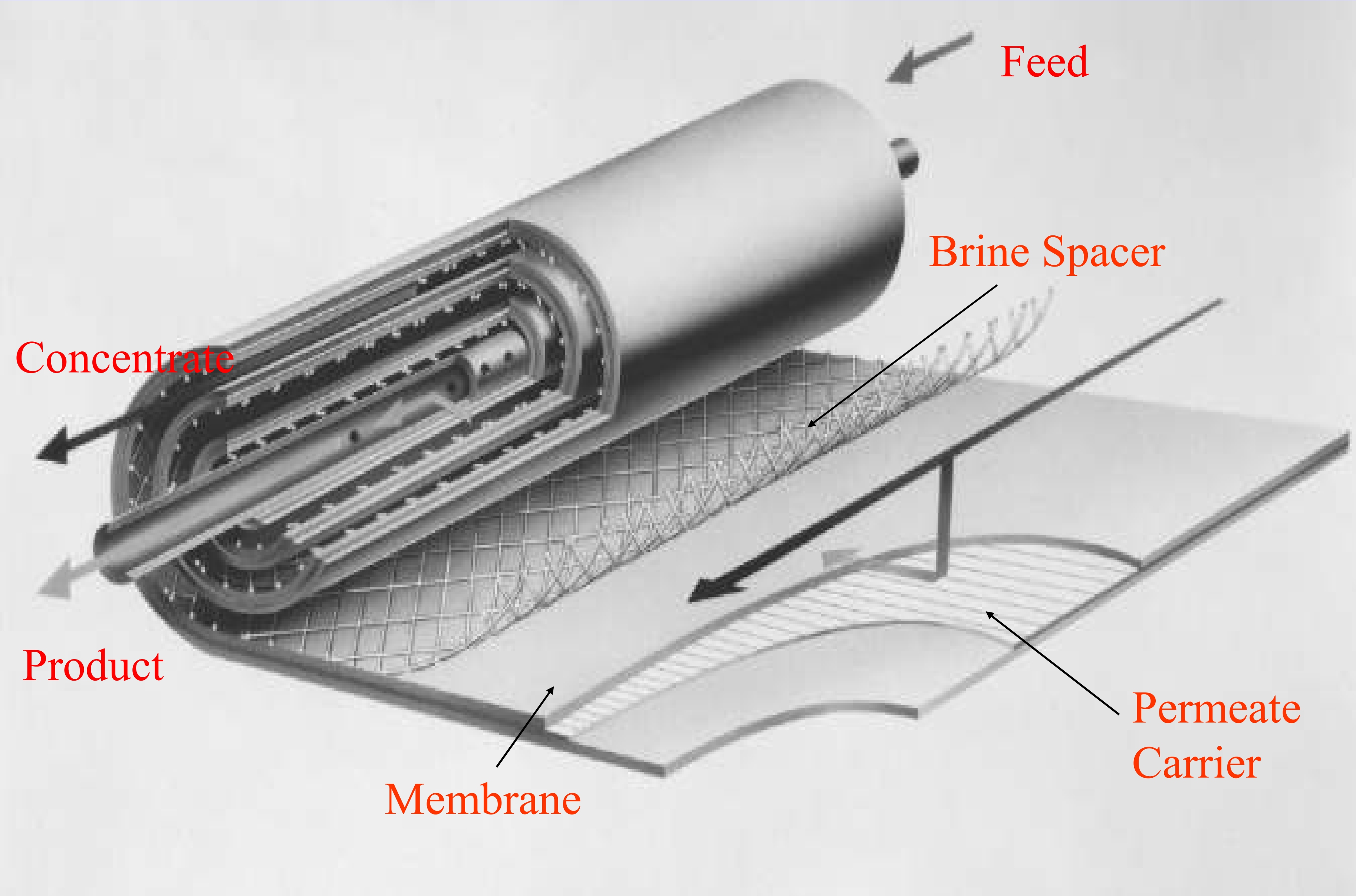

PA membrane surface
Polymeric support
Fabric backing
×500
0003
20kV

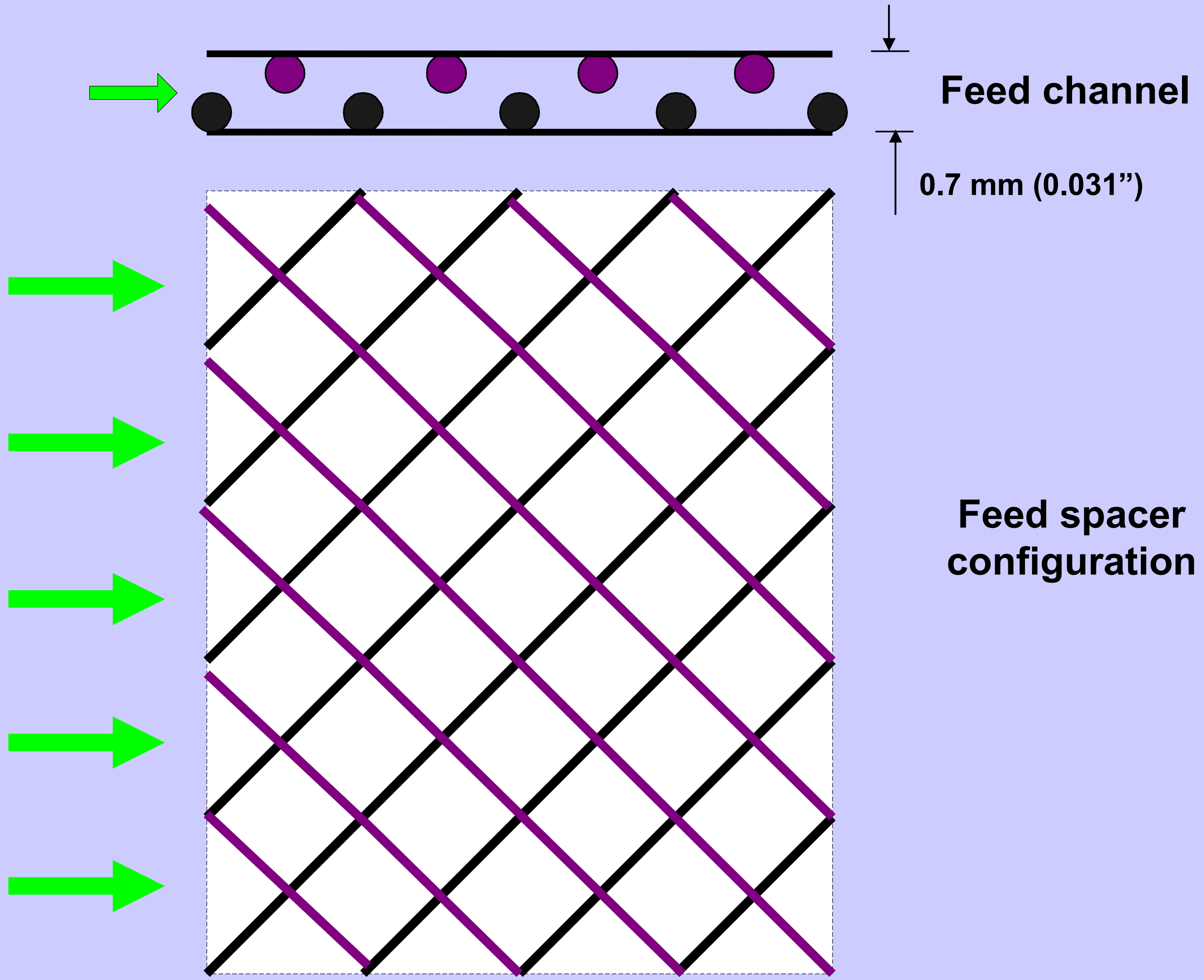
Evolution of performance of brackish membranes



Evolution of performance of seawater membranes




Feed
Brine Spacer
Concentrate
Product
Membrane
Permeate
Carrier



Configurations of feed channel and feed spacer net

Osmotic pressure is function of concentration and temperature

Salinity, ppm TDS	5,000	20,000	35,000	70,000	80,000
π @ 30C (86 F)	3.3 bar (48 psi)	13.9 bar (201 psi)	25.7 bar (372 psi)	51.3 bar (744 psi)	59.0 bar (856 psi)
π @ 15C (59 F)	3.2 bar (46 psi)	13.2 bar (191 psi)	24.5 bar (355 psi)	48.8 bar (708 psi)	56.1 bar (813 psi)

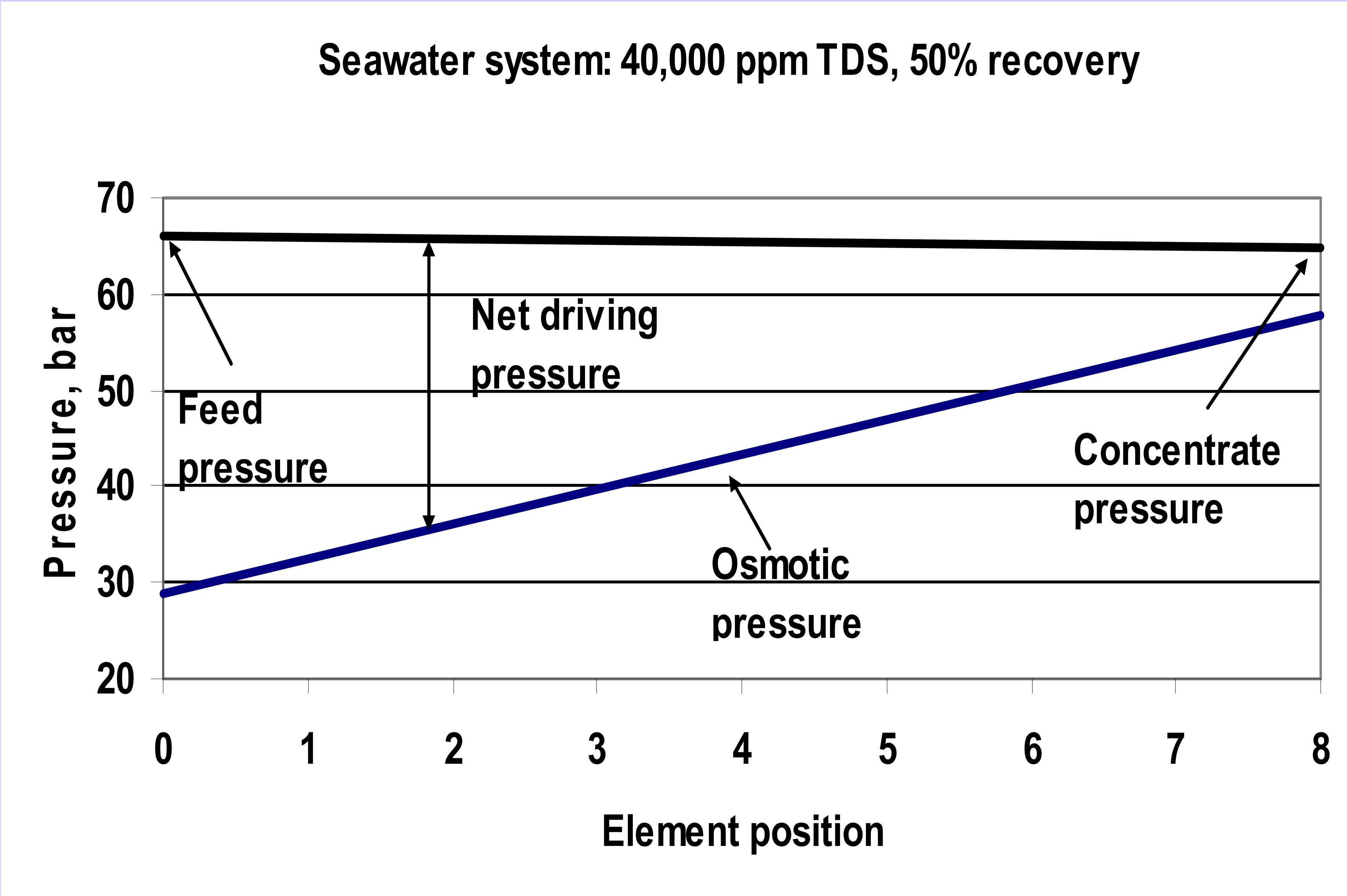
RO TERMS

NDP - net driving pressure

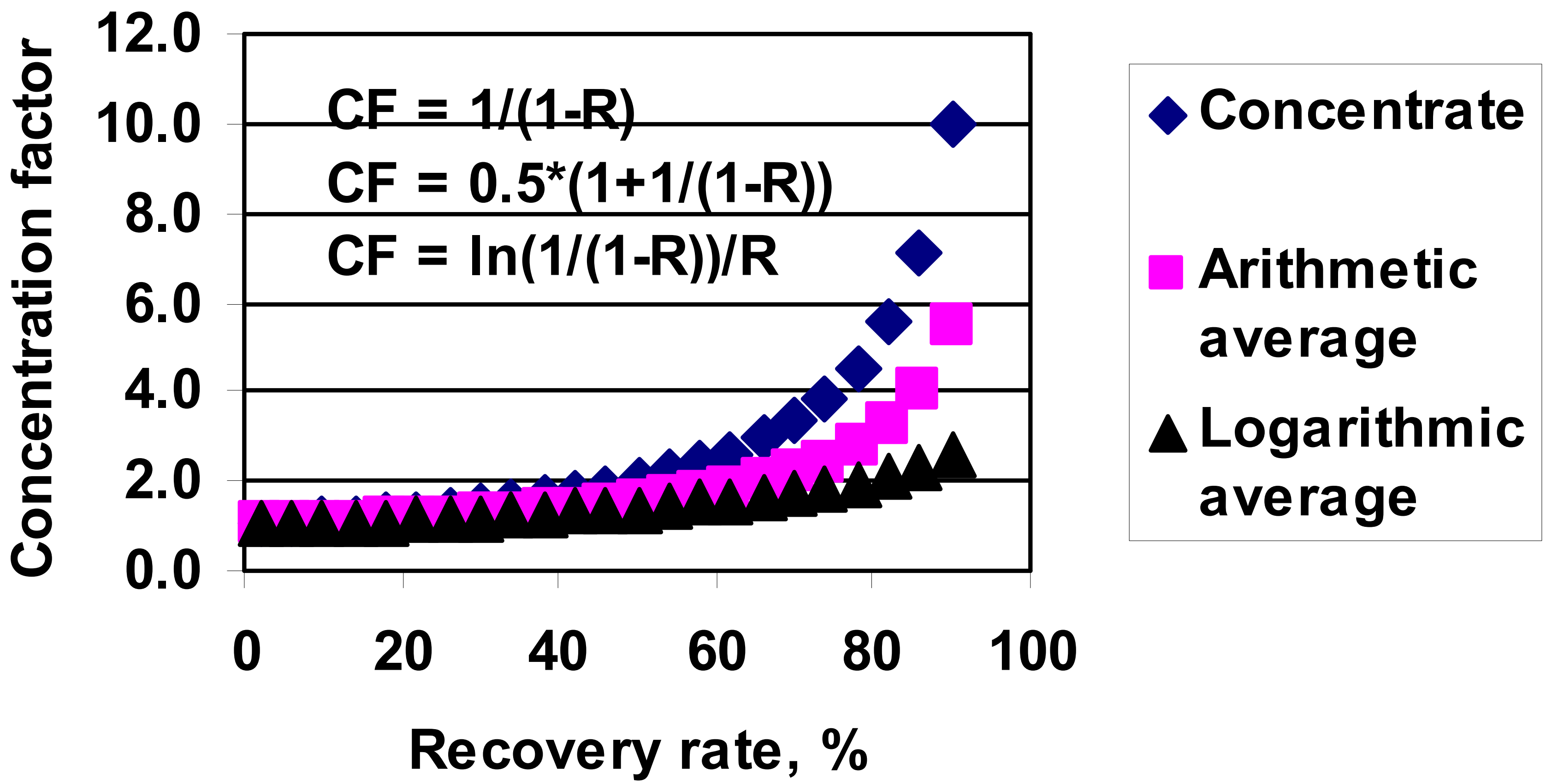
Driving force of the water transport (flux) through the membrane.

$$NDP = P_f - P_{os} - P_p - 0.5 * P_d \ (+ Perm_{os})$$

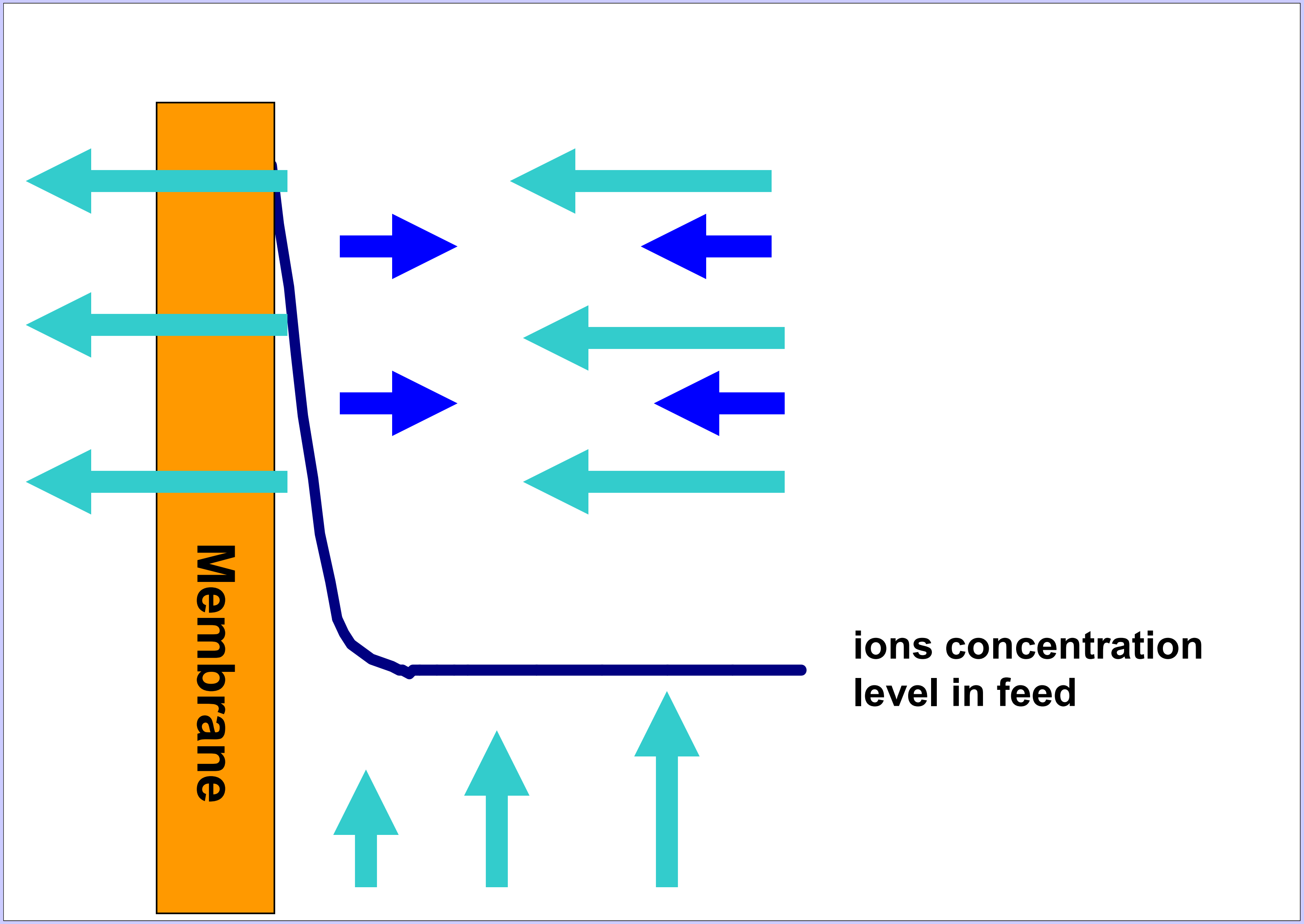
- P_f - feed pressure
- P_{os} – average feed osmotic pressure
- P_p - permeate pressure
- P_d - pressure drop across RO element
- $Perm_{os}$ - permeate osmotic pressure


Seawater system: 40,000 ppm TDS, 50% recovery
Pressure, bar
70
60
50
40
30
20
Feed pressure
Net driving pressure
Concentrate pressure
Osmotic pressure
0
1
2
3
4
5
6
7
8
Element position

Concentration factor in RO system



Concentration polarization



RO TERMS

TCF - temperature correction factor

Temperature affects water and salt transport across the membrane, approximately at the same magnitude. The transport rate changes at about 3% per degree C.

$$TCF = 1/\exp(2700*(1/(273+t)-1/298))$$

t – temperature C

RO TERMS

Water transport, Qw :

$$Qw = Kw * A * NDP * TCF$$

Kw – water transport coefficient

A - membrane area

Salt transport, Qs :

$$Qs = Ks * A * \Delta C * TCF$$

Ks – salt transport coefficient

ΔC - salt concentration gradient

RO TERMS

Permeate salinity

$Cp \propto Qs/Qw$

$= Ks * A * \Delta C * TCF / Kw * A * NDP * TCF$

$= Ks * \Delta C / Kw * NDP$

$\Delta C \propto$ recovery rate

$NDP \propto$ feed pressure

8” and 16” diameter elements

8” element

Membrane area

40m2 (430 ft2)

Nominal flow

45 m3/day
(12,000 gpd)

Avg. field flow

19 m3/day
(5,000 gpd)

16” element

Membrane area

140 m2 (1,500 ft2)

Nominal flow

155 m3/day
(41,000 gpd)

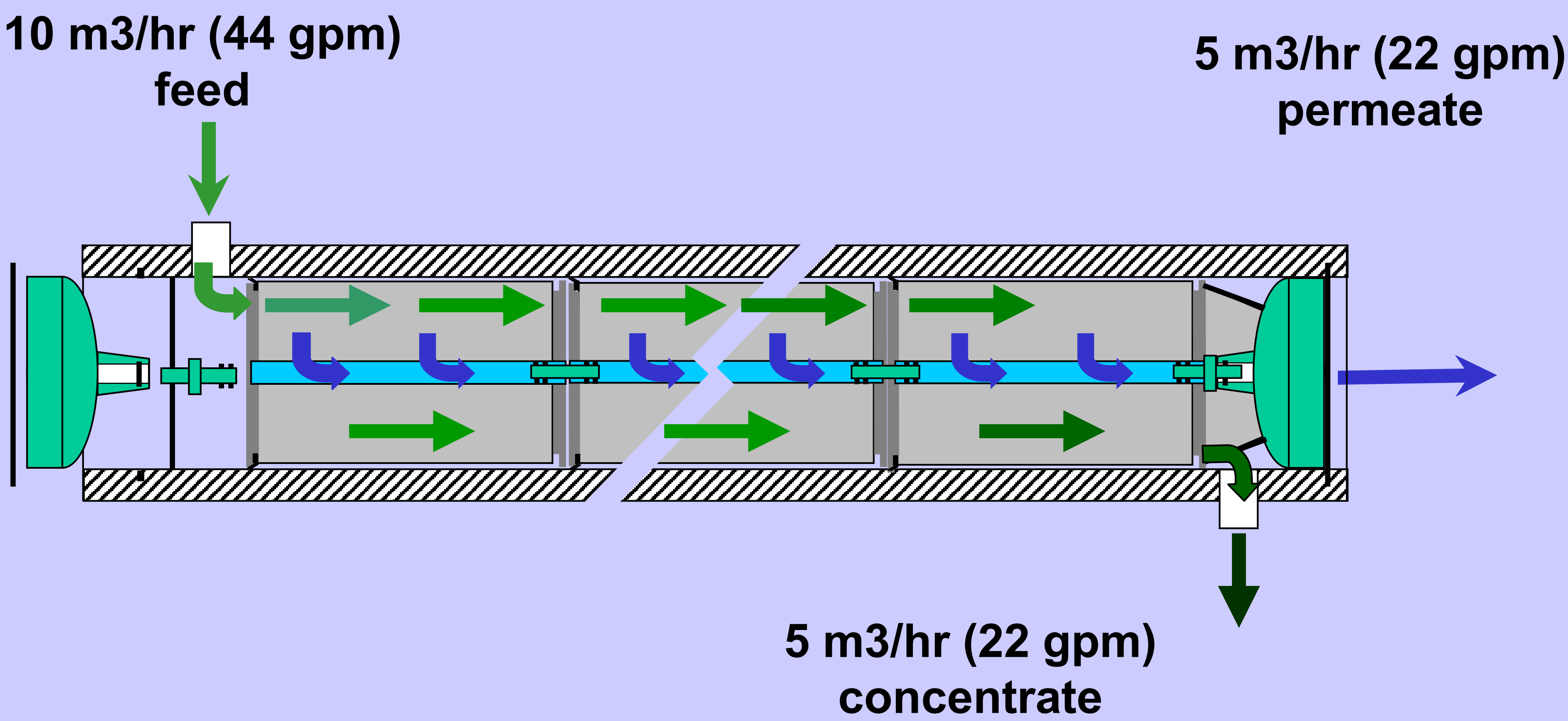
Avg. field flow

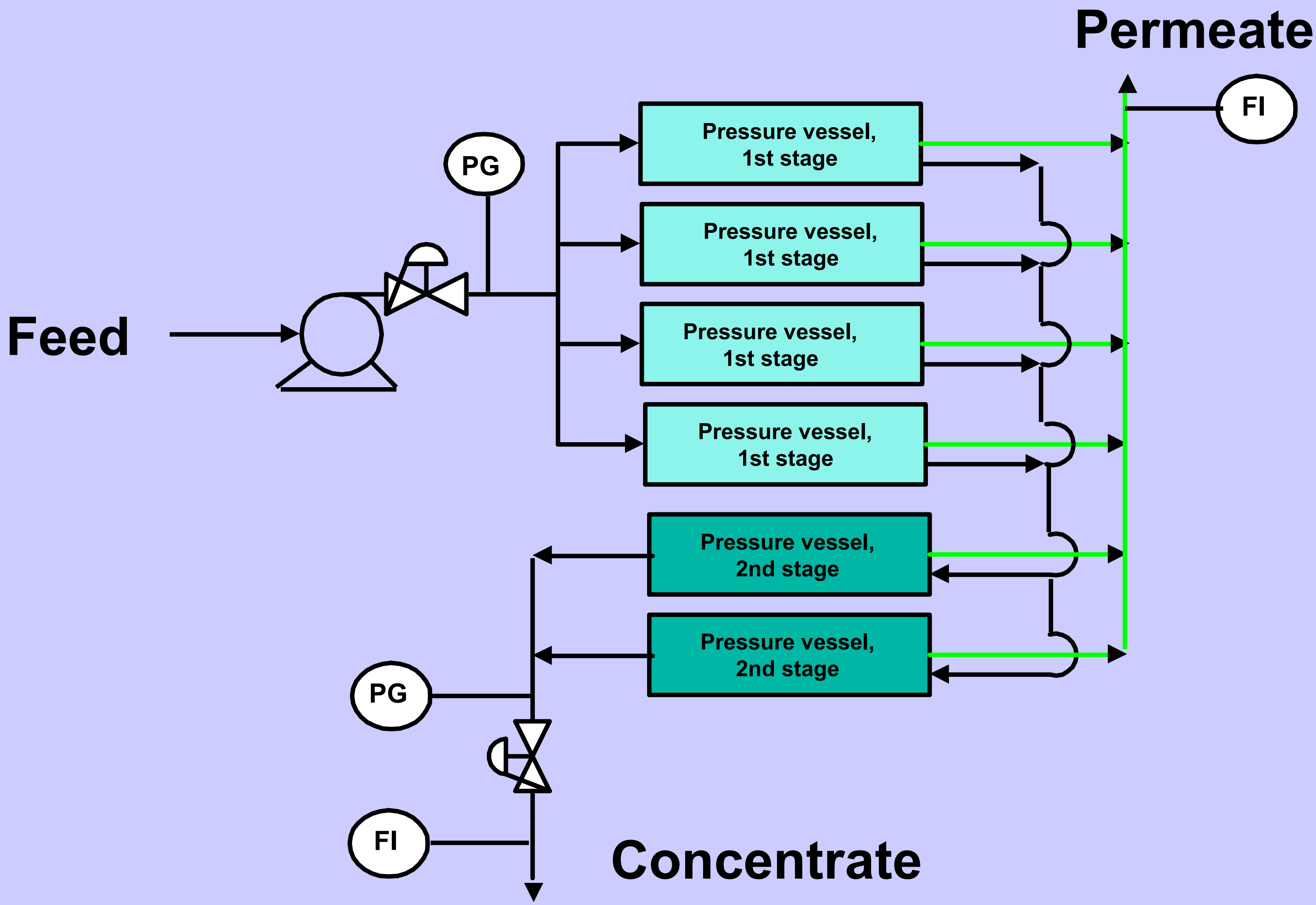
68 m3/day
(18,000 gpd)

Permeate flow per vessel at an average permeate flux rate of 20.4 l/m2-hr (12 GFD)

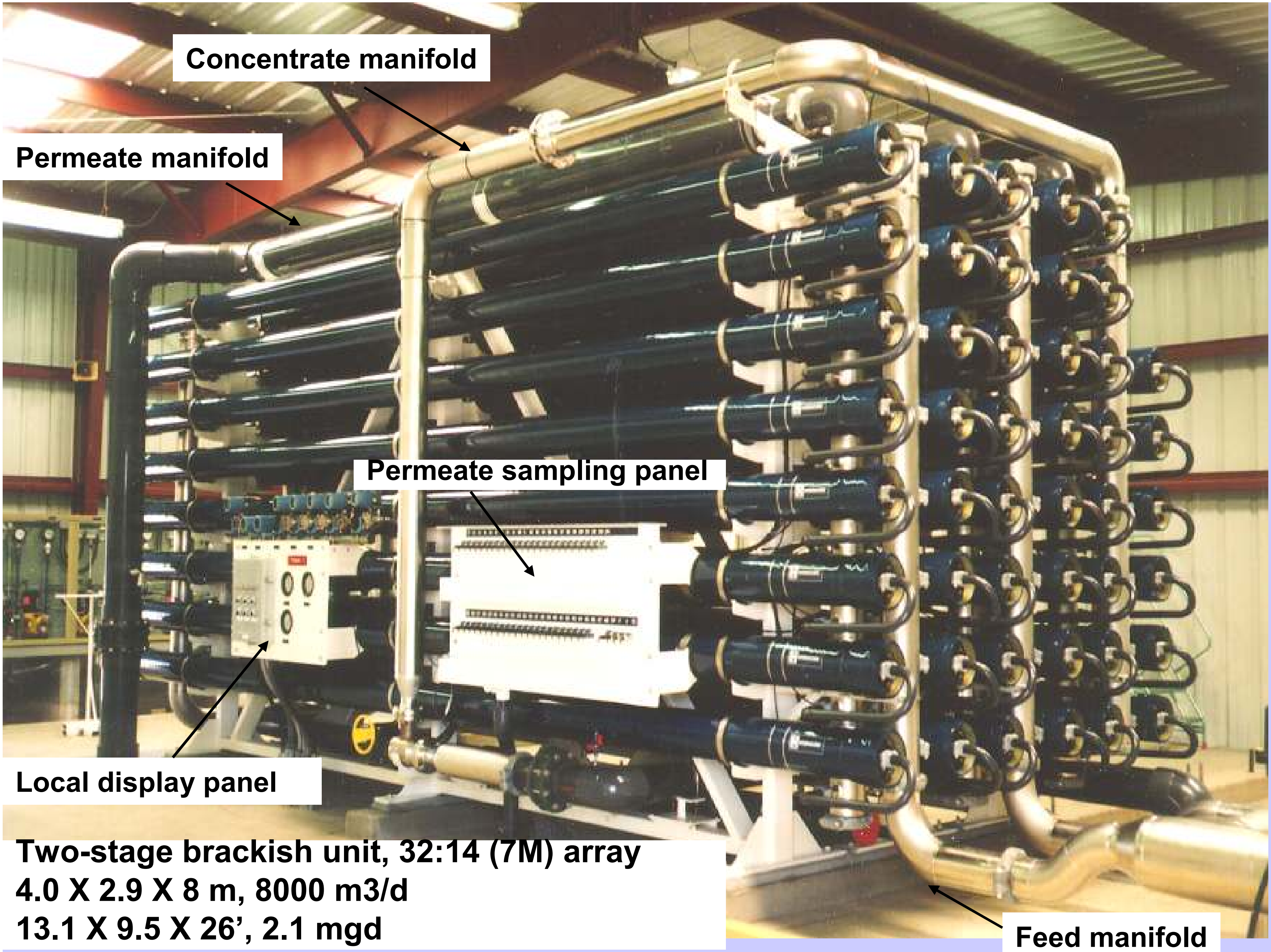
Elements per vessel	8' – 37 m2/el. (400 ft2/el.)	8 – 40 m2/el. (430 ft2/el.)	16" – 140 m2/el. (1,500 ft2/el.)
4			272 m3/day (72,000 GPD)
5			340 m3/day (90,000 GPD)
6	109 m3/day (28,800 GPD)	117 m3/day (31,000 GPD)	408 m3/day (108,000 GPD)
7	127 m3/day (33,600 GPD)	136 m3/day (36,000 GPD)	477 m3/day (126,000 GPD)
8	145 m3/day (38,400 GPD)	156 m3/day (41,300 GPD)	545 m3/day (144,000 GPD)

Water flow in a pressure vessel assembly





Two Stage RO System


Concentrate manifold
Permeate manifold
Permeate sampling panel
Local display panel
Feed manifold
Two-stage brackish unit, 32:14 (7M) array
4.0 X 2.9 X 8 m, 8000 m3/d
13.1 X 9.5 X 26’, 2.1 mgd

RO membrane categories

Nanofiltration for color removal
Nanofiltration for sulfate reduction
Nanofiltration for hardness reduction
Low pressure brackish RO
High rejection brackish RO
Low pressure seawater RO
High rejection seawater RO

Commercial offering of nanofiltration RO membrane modules

Element model	Hydracore	ESNA-LF	SU620F	NF-90	NF-270
Membrane area, m2 (ft2)	37.1 (400)	37.1 (400)	37.1 (400)	37.1 (400)	37.1 (400)
Permeate flow, m3/d (gpd)	31.0 (8,200)	29.5 (7,800)	21.9 (5,800)	37.9 (10,000)	47.3 (12,500)
Salt rejection,	50.0	80.0	55.0	97.0	97.0
Test flux rate, l/m2-hr (gfd)	34.8 (20.5)	33.2 (19.5)	24.7 (14.5)	42.5 (25.0)	55.9 (32.9)
Permeability, l/m2-hr-bar (gfd/psi)	7.7 (0.31)	7.2 (0.29)	8.7 (0.35)	11.9 (0.48)	15.7 (0.63)
Relative salt transport: salt passage∗flux rate	17.4 (10.2)	6.6 (3.9)	11.1 (6.5)	1.3 (0.8)	1.7 (1.0)

Commercial offering of brackish RO membrane modules

Element model	ESPA2+	ESPA4+	TMG20-430	BW30-XLE440	BW30 LE-440
Membrane area, m2 (ft2)	40.0 (430)	40.0 (430)	40.0 (430)	40.9 (440)	40.9 (440)
Permeate flow, m3/d (gpd)	41.6 (11,000)	49.2 (13,000)	41.6 (11,000)	48.1 (12,700)	48.1 (12,700)
Salt rejection,	99.60	99.60	99.50	99.0	99.30
Test flux rate, l/m2-hr (gfd)	43.5 (25.6)	51.3 (30.2)	43.5 (25.6)	49.1 (28.9)	49.1 (28.9)
Permeability, l/m2-hr-bar (gfd/psi)	5.0(0.20)	8.2 (0.33)	6.2 (0.25)	7.7 (0.31)	6.0 (0.24)
Relative salt transport: salt passage∗flux rate	0.261 (0.153)	0.308 (0.181)	0.218 (0.128)	0.491 (0.289)	0.344 (0.202)

Commercial offering of seawater RO membrane modules

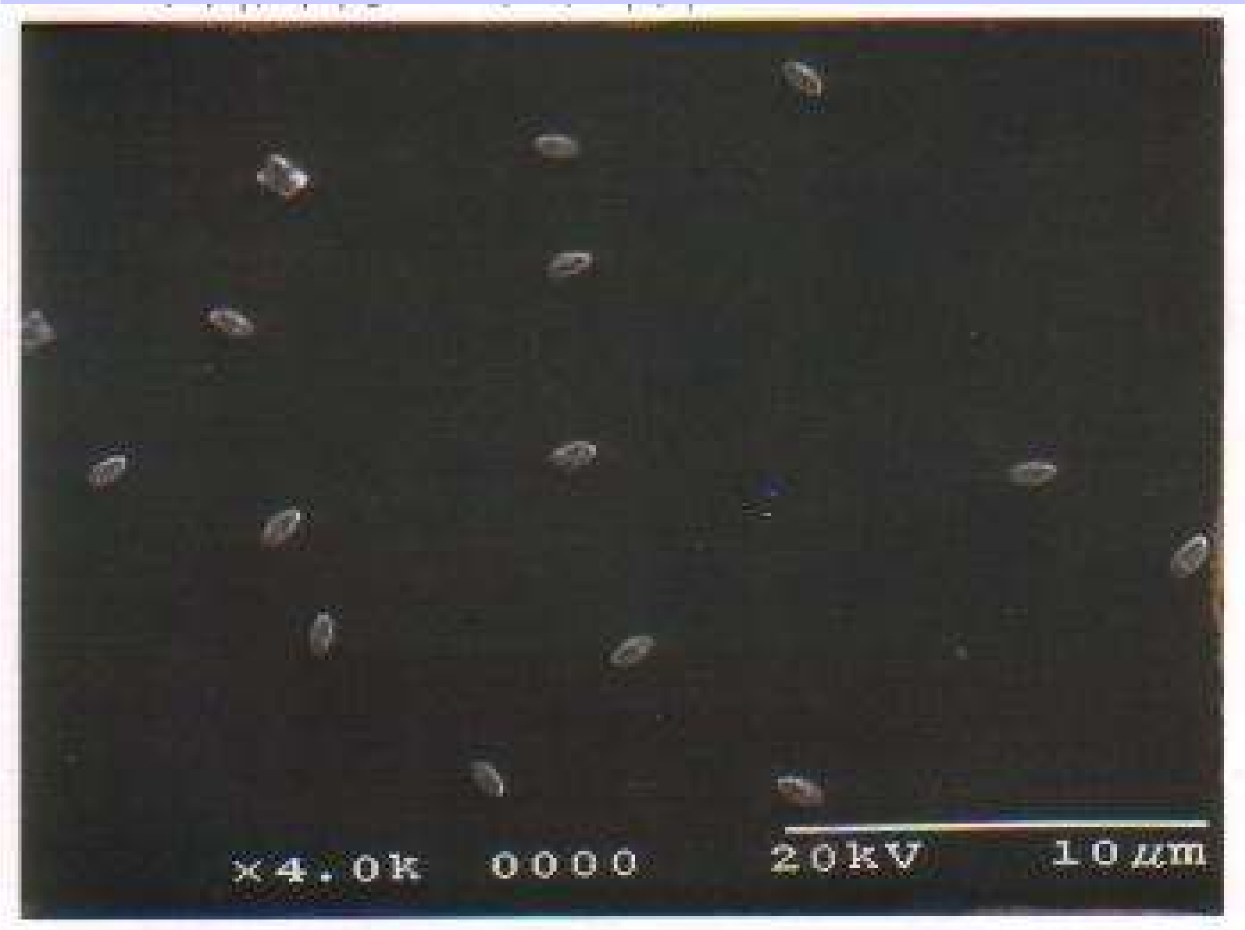
Element model	SWC4+	SWC5	TM820-400	SW30HR-LE	SW30HR-XLE
Membrane area, m2 (ft2)	37.1 (400)	37.1 (400)	37.1 (400)	37.1 (400)	37.1 (400)
Permeate flow, m3/d (gpd)	24.6 (6,500)	34.1 (9,000)	24.6 (6,500)	26.5 (7,000)	34.1(9,000)
Salt rejection,	99.80	99.80	99.75	99.75	99.70
Test flux rate, l/m2-hr (gfd)	27.6 (16.3)	38.2 (22.5)	27.6 (16.3)	31.3 (18.4)	38.2 (22.5)
Permeability, l/m2-hr-bar (gfd/psi)	1.0 (0.04)	1.5 (0.06)	1.0 (0.04)	1.2 (0.05)	1.5 (0.06)
Relative salt transport: salt passage∗flux rate	0.055 (0.032)	0.076 (0.045)	0.069 (0.041)	0.078 (0.046)	0.114 (0.067)

SPECIAL NANOFILTRATION MEMBRANE (HYDRACORE)

HYDRACoRe

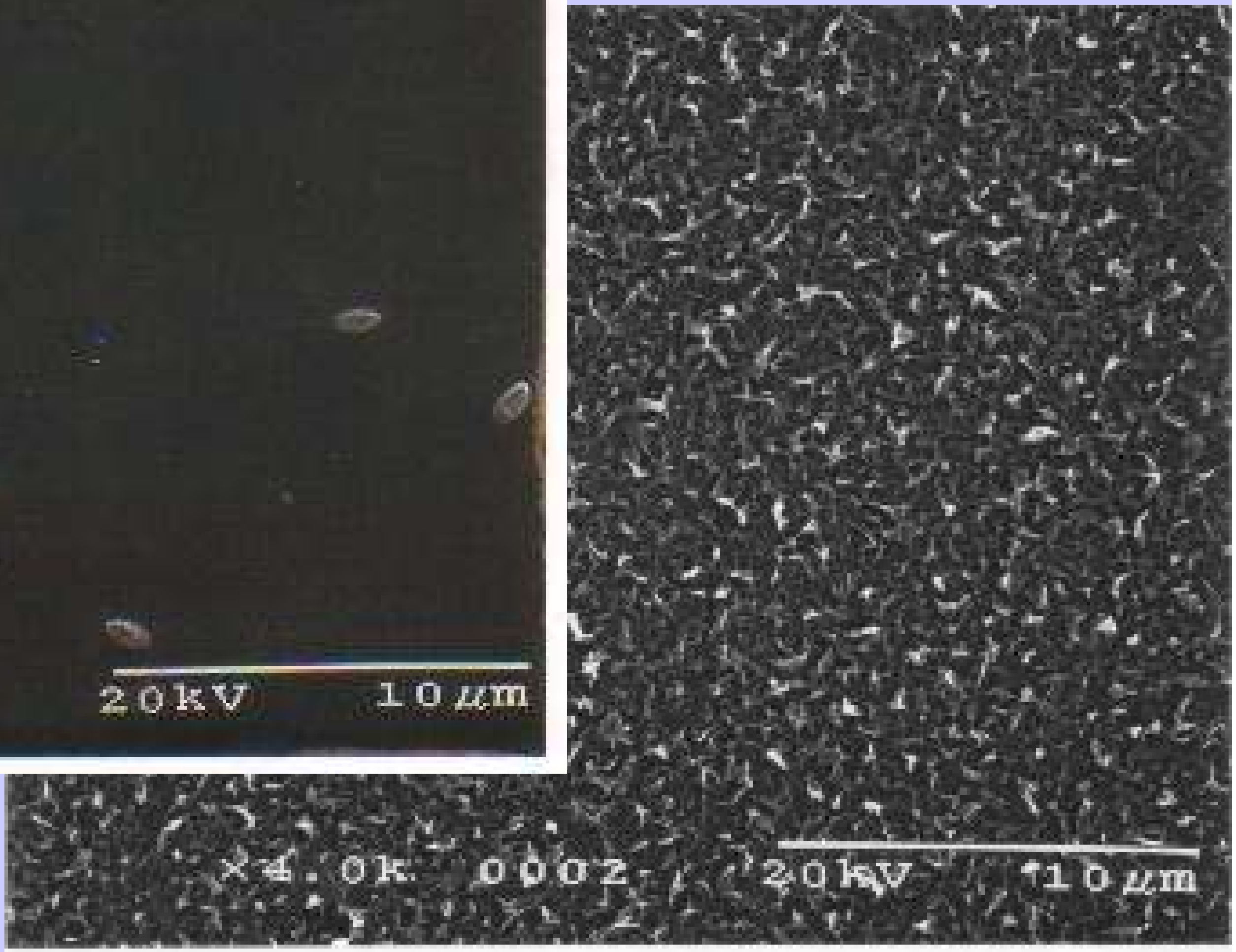
- **Nanofiltration for color removal**
- **1000 MWCO**
- **50% salt rejection, minimizes product water instability and need for post treatment**
- **8,200 gpd for a 365 sq ft element**
- **Chlorine tolerant**

Surface of HydraCoRe at 4000 X magnification



HydraCoRe Membrane

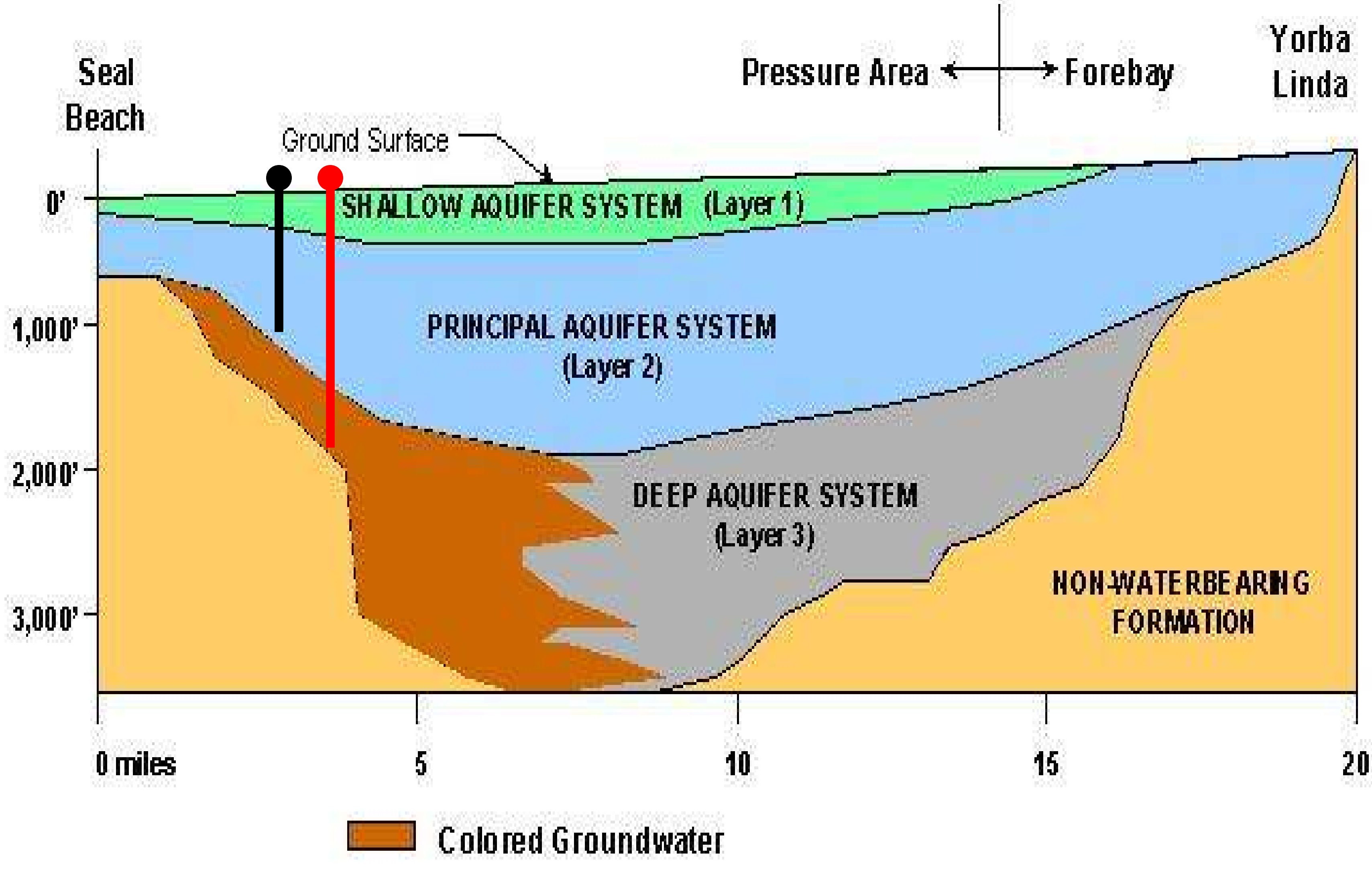
Typical Interfacial Polyamide RO Membrane



HydraCoRe ion rejection

Anion / Cation			A^-	A^{2-}
			Cl	SO_4
		Molecular Weight	35	96
M^+	Na	23	50%	90%
M^{2+}	Mg	24	20%	35%
	Ca	40	12%	-

Orange County Groundwater Basin Cross-Section

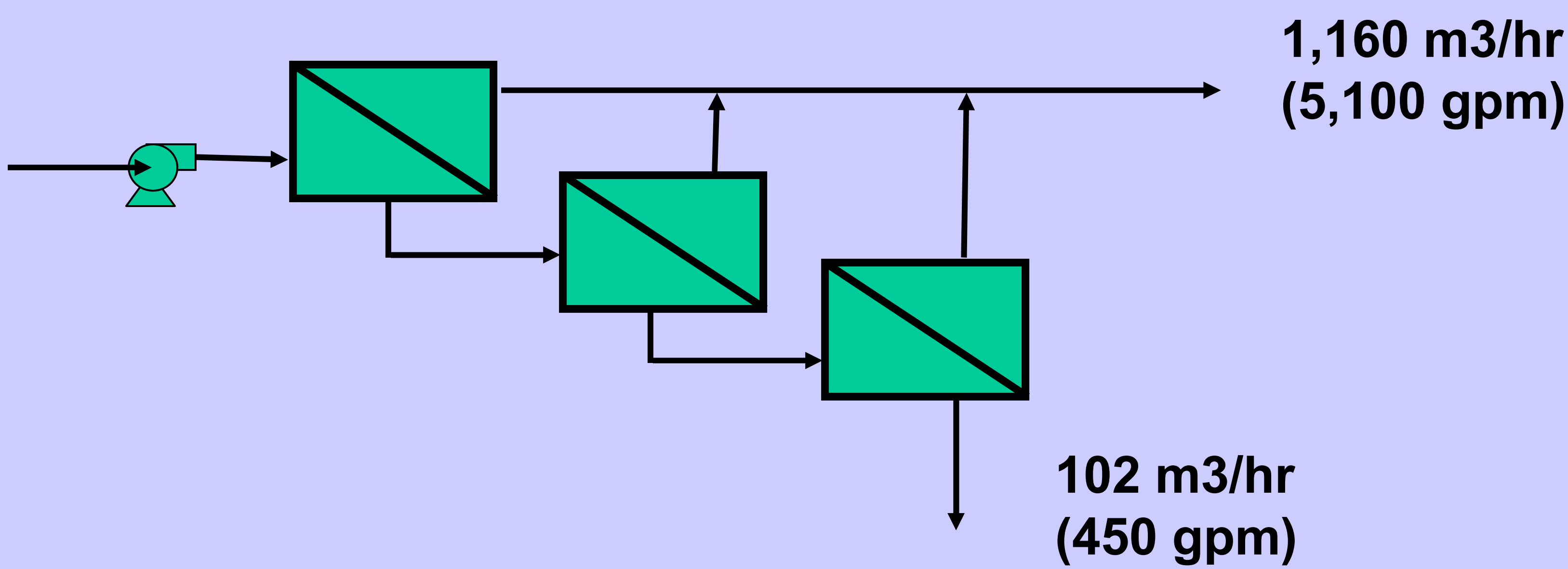


Irvine Ranch Project – membrane elements testing

Parameter	Feed	HydraCoRe permeate	Conventional Nanofiltration permeate
Color , CU	200	<5	<5
Conductivity uS/cm	500	350	48
Calcium mg/L	13	8.5	0.2
Specific flux gfd/psi (l/m3-hr-bar)		0.43 (10.7)	0.48 (11.9)

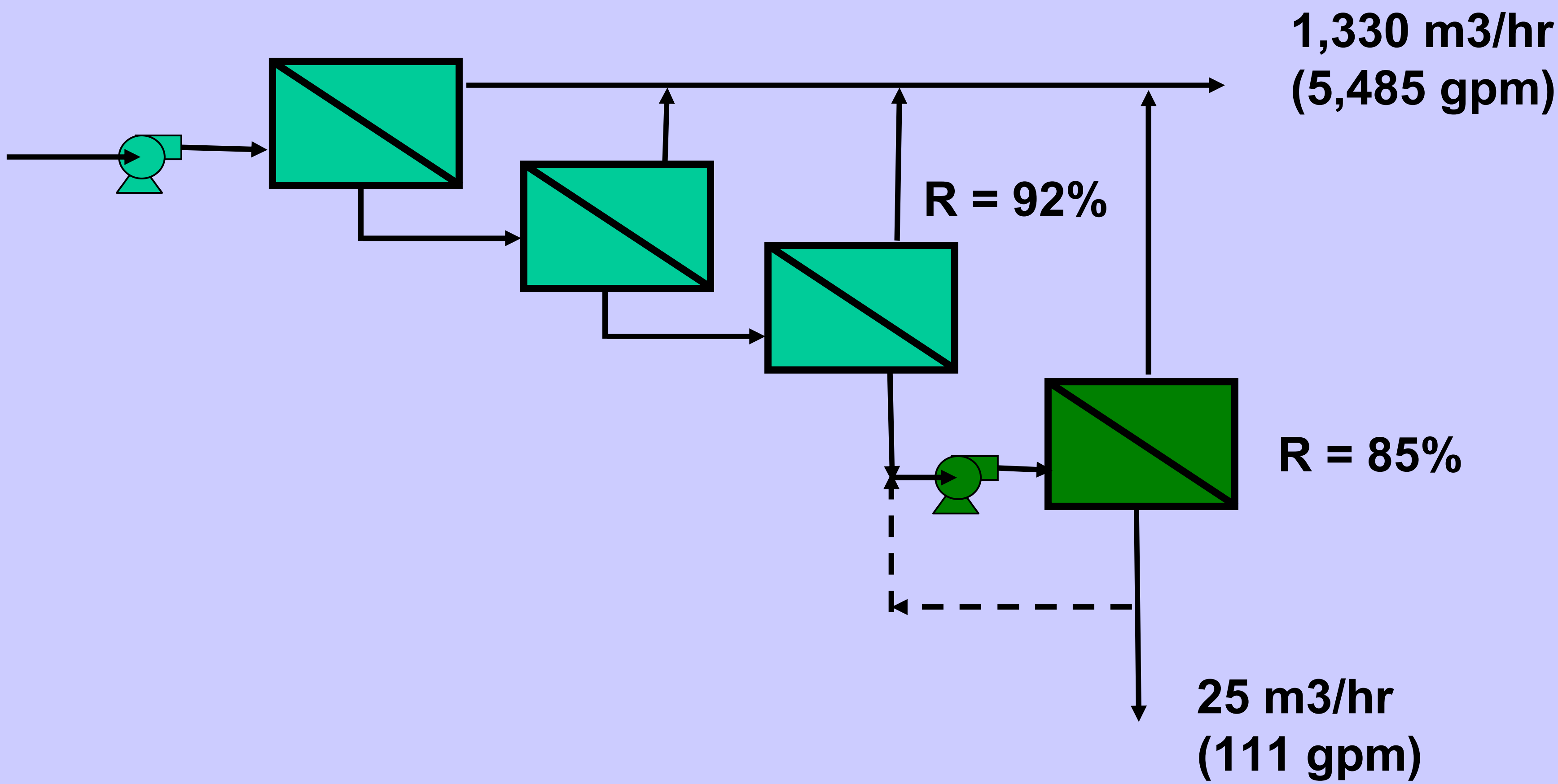
Irvine Ranch Plant hydraulics

Permeate – 28,000 m3/day (7.35 MGD), Concentrate – 2400 m3/day (0.64 MGD), Recovery – 92%

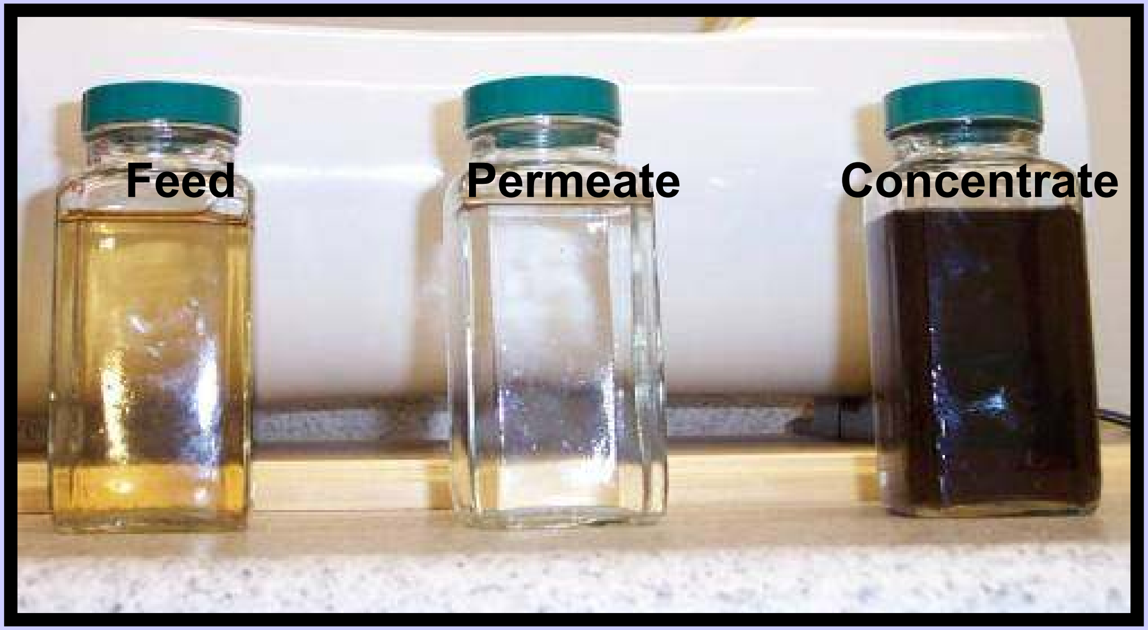


Irvine Ranch Plant concentrate flow reduction

Permeate – 30,000 m3/day (7.90 MGD), Concentrate – 600 m3/day (0.16 MGD), Recovery – 98%



Irvine Ranch NF Plant: Feed, Permeate and Concentrate Samples



High water pH shifts equilibrium to the right

$$B(OH)_3\ (aq) + H_2O \rightleftharpoons H^+(aq) + B(OH)_4^-\ (aq)$$

Low water pH shifts equilibrium to the left

Seawater RO system. Recovery rate 50%. Boron concentration in feed 5.0 ppm

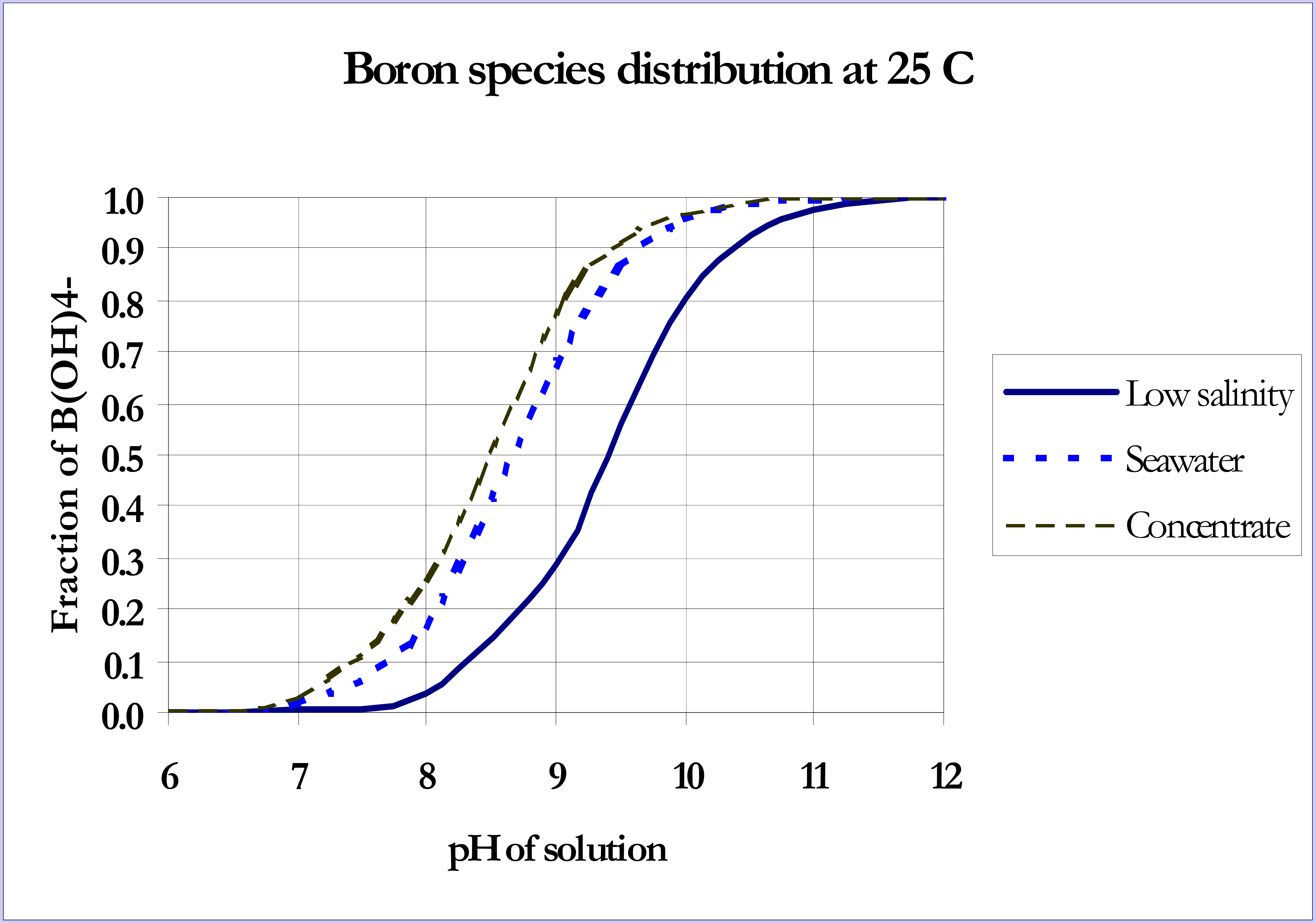
Feed pH	Boron rejection, %	Boron passage, %	Boron in permeate, ppm
6.5	**70**	**30**	**1.5**
7.0	**70**	**30**	**1.5**
7.5	**74**	**26**	**1.3**
8.0	**78**	**22**	**1.1**

Brackish RO system. Recovery rate 85%. Boron concentration in feed 2.0 ppm

Feed pH	Boron passage, %	Boron in permeate, ppm	Boron in passage, %	Boron in permeate, ppm
6.5	**95**	**1.9**	**55**	**1.1**
7.0	**95**	**1.9**	**55**	**1.1**
7.5	**95**	**1.9**	**55**	**1.1**
8.0	**95**	**1.9**	**55**	**1.1**

Brackish membranes

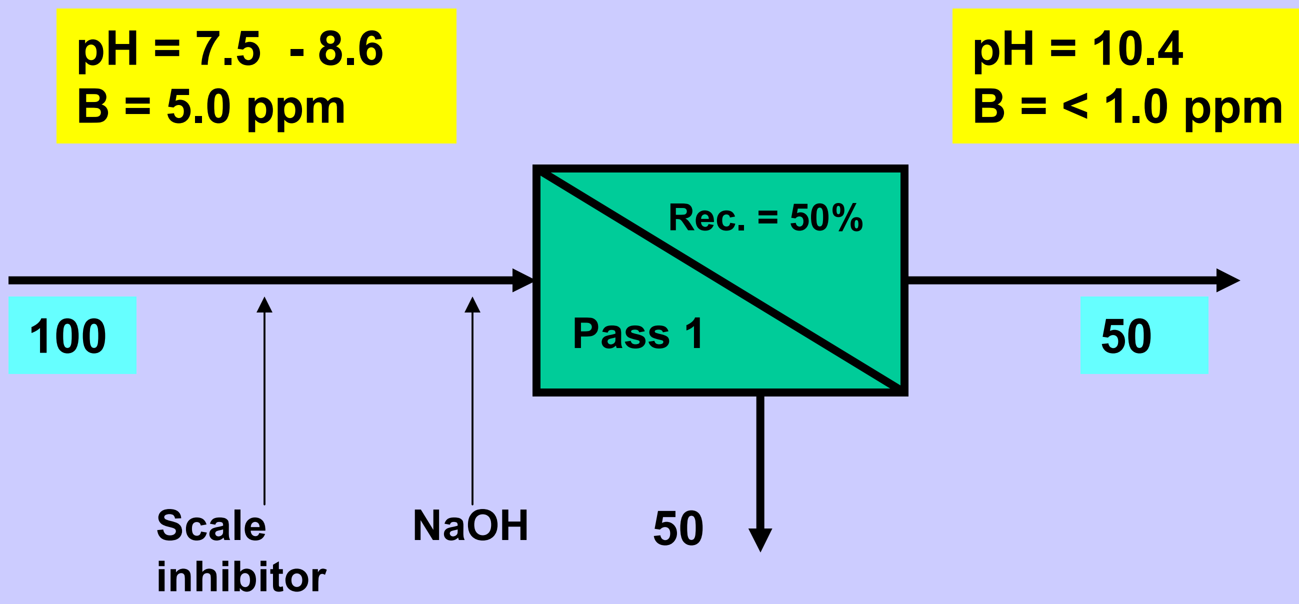
Seawater membranes


Boron species distribution at 25 C
Fraction of B(OH)4-
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
6
7
8
9
10
11
12
pH of solution
Low salinity
Seawater
Concentrate

Second pass RO system. Recovery rate 90%. Boron concentration in feed 1.4 ppm

Feed pH	Boron rejection, %	Boron passage, %	Boron in permeate, ppm
9.0	**30**	**70**	**1.0**
9.5	**48**	**52**	**0.7**
10.0	**72**	**28**	**0.4**
10.4	**83**	**13**	**0.2**

Seawater RO. Combined recovery rate 50%



Single pass system with pH adjustment of the 1st pass feed

R&D directions – reverse osmosis

- Selective rejection of dissolved species
- Higher boron rejection
- Increased water permeability without increasing solute transport
- Reduction of fouling tendency
- Control of biofouling in seawater systems
- Replacement of chemical membrane cleaning with biological processes
- Reduction of scaling tendency in brackish RO processes