



Membrane Desalination Processes



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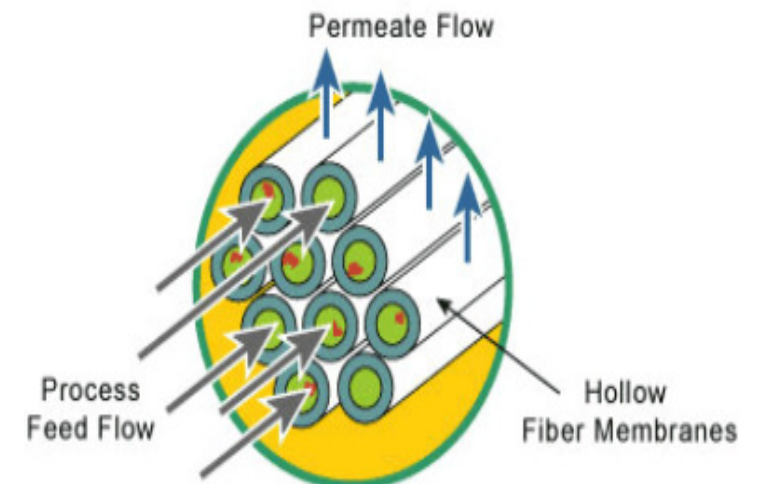
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King Saud University,
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Membrane Desalination Processes



Content:

- ***Desalination: An Overview***
- ***Overview of Membrane Desalination Technologies***
- ***Pretreatment Processes:
microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF)***
- ***Commercial Processes:
Reverse Osmosis (RO), Electrodialysis (ED) and ED Reversal***
- ***Innovative Processes:
Forward Osmosis (FO) and Membrane Distillation (MD)***



Membrane Desalination Processes



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- ***Innovative Processes:
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Membrane Desalination Processes



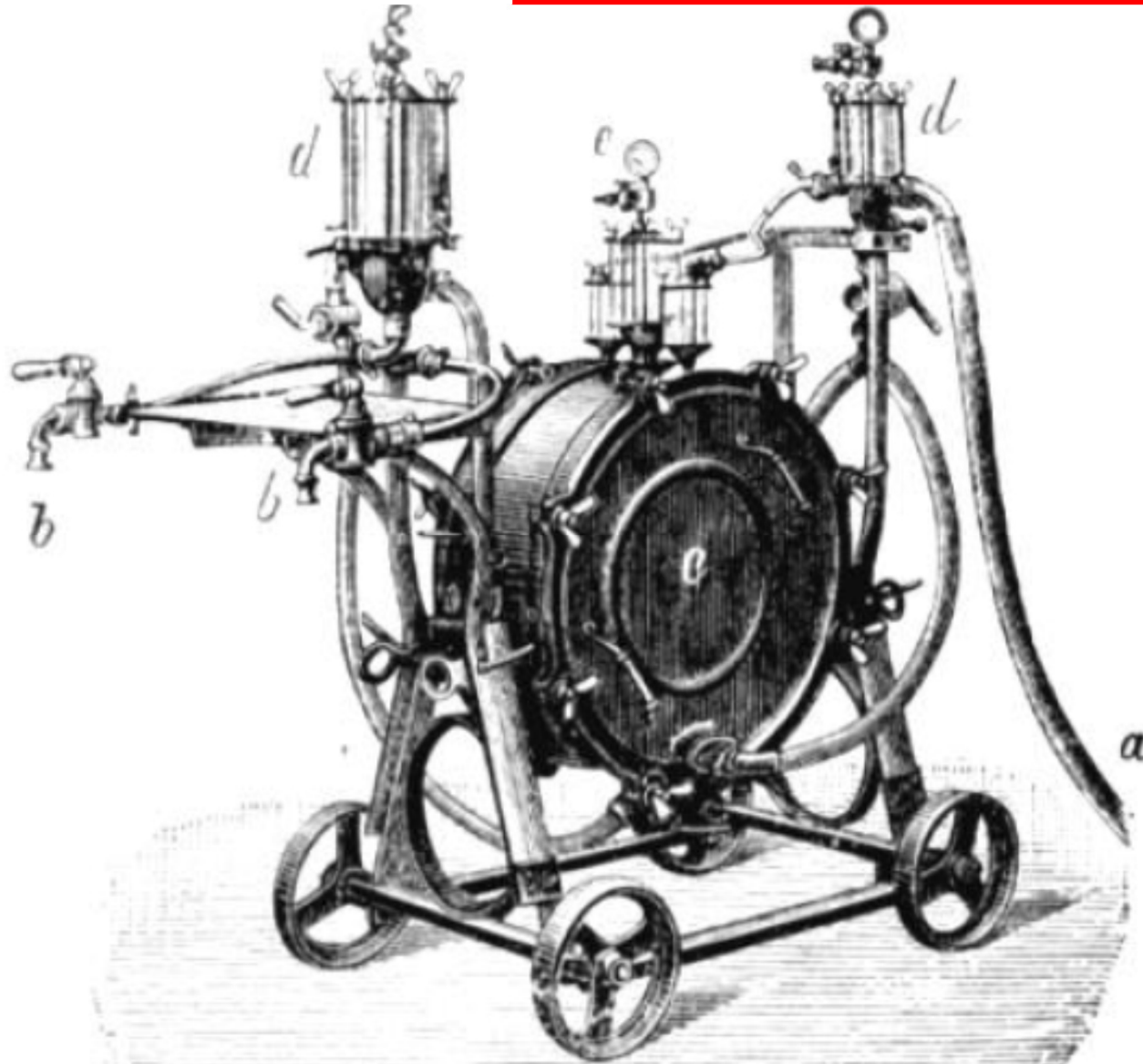
Content:

- *Desalination: An Overview*
 - *Historical Developments*
 - *Market Status*
 - *Growth of the Desalination Industry*
 - *Desalination Technologies: Membrane / Thermal Processes*

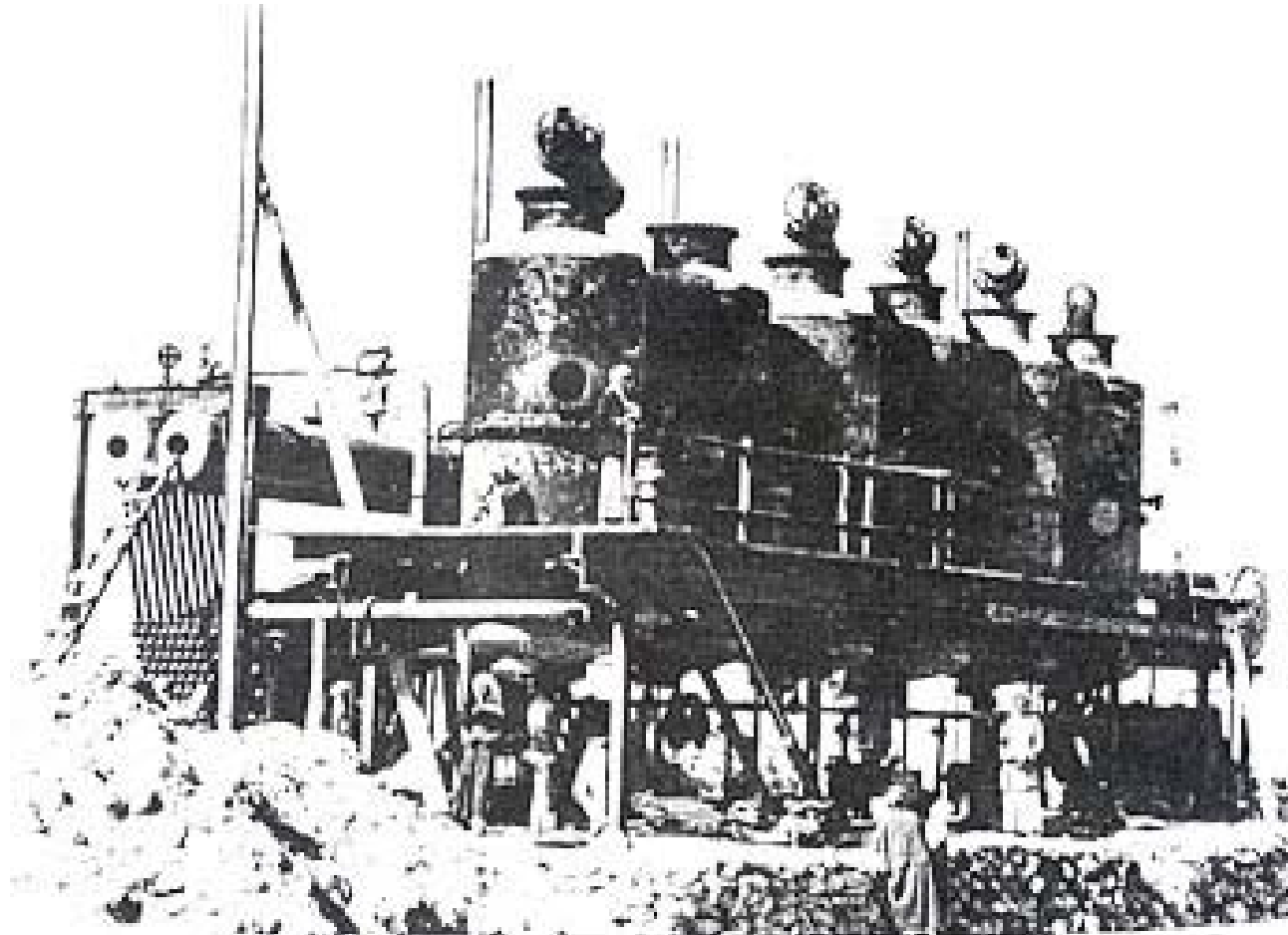


Water Desalination





THE FIRST MEMBRANE PLANT



THE FIRST EVAPORATOR PLANT



Saltwater, when it turns into vapor, becomes sweet and the vapor does not form saltwater again when it condenses.

Aristotle, fourth Century B.C.

حدد جابر بن حيان قواعد التقطير و صنفها في أواخر القرن السابع الميلادي ، كما أن العالم الإسلامي أبو المنصور الموفق بن علي الحروري قال منذ ذلك الزمان ” إن التبخير هو الوسيلة للحصول على ماء عذب“

If we could ever competitively at a cheap rate, get freshwater from saltwater, that would be in the long term interests of humanity and would dwarf any other scientific accomplishments.

John F. Kennedy, 1961



"No water resources program is of greater long-range importance—for relief not only of our shortages, but for arid nations the world over—than our efforts to find an effective and economical way to convert water from the world's greatest, cheapest natural resources—our oceans—into water fit for consumption in the home and by industry. Such a break-through would end bitter struggles between neighbors, States, and nations—and bring new hope for millions who live out their lives in dire shortage of usable water and all its physical and economical blessings, though living on the edge of a great body of water throughout that parched lifetime."

President, United States of America

John F. Kennedy, 1961



Historical Developments

History of Thermal Desalination (Pre-1955)

320 BC - Greek Philosopher Aristotle writes of seawater distillation

70 AD - Rome's Pliny the Elder describes seawater distillation with condensation on fleece

200 AD - Greece's Alexander of Aphrodisias describes seawater distillation with condensation on sponges

975 AD - Persia's Muwaffaq and al-Harawi write that distillation is a suitable method of seawater conversion

1565 - French explorer Jean De Lery reports seawater was successfully distilled during voyage to Brazil

1616 - Spain's Pedro Fernandez de Quiros discovers Australia and makes successful use of a small copper still

1675 - Walcot files seawater distillation patent in England

1683 - Fitzgerald files conflicting seawater distillation patents, leading to protracted patent dispute with Walcot

1739 - Hales recommends limiting recovery in simple stills to 33% to improve quality and suggests aeration to improve taste



Historical Developments

History of Thermal Desalination (Pre-1955)

- 1753** - Watson and Appleby report on pretreating seawater with bone phosphate and quicklime
- 1756** - Lucas publishes article skeptical of many distillation designs and especially critical of recommended additives
- 1759** - Chapman reports on successful use of emergency seawater still on North Sea voyage
- 1761** - Lind experiments with parabolic mirrors for use with solar distillation
- 1772** - James Cook begins successful use of seawater still while circumnavigating the world
- 1791** - Thomas Jefferson publishes Report on the Method of Obtaining Fresh Water from Salt
- 1793** - Spain's Phillip II assembles a crude still producing 40 barrels/day of fresh water while fighting the Turks in Tunisia
- 1828** - Pécelet hints at but does not build successful multi-effect evaporator



Historical Developments

History of Thermal Desalination (Pre-1955)

- 1840** - Swiss firm Escher Wyss installs vapour compression distiller in British Columbia, Canada
- 1843** - Rillieux patents, builds, sells successful multi-effect evaporators
- 1851** - France's Alphonse Normandy patents first of series of vertical tube single stage seawater stills in England
- 1862** - Three 27 m³/d Normandy stills installed at Key West Florida, Fort Pulaski Georgia and Tortugas
- 1879** - Picard and Weibel describe, then patent first mechanical vapour recompression system
- 1881** - Seawater distiller installed on Malta
- 1885** - Wilson designs, installs 19 m³/d solar distiller for mining application in Las Salinas, Chile
- 1886** - Yaryan introduces rising film vertical tube evaporators



Historical Developments

History of Thermal Desalination (Pre-1955)

- 1888** - Lillie introduces spray-film horizontal tube evaporator with provision for removing non-condensable gases
- 1895** - Mirlees-Watson installs two six-effect seawater distillers in Sudan
- 1899** - Kestner patents first of a series of rising and falling-film long tube vertical evaporators
- 1900** - Addison Waterhouse's US patent anticipates multistage flash distillation process
- 1907** - Two small land-based seawater plants known as "The Kindasa" (the condenser), installed in Jeddah, Saudi Arabia
- 1908** - Prache designs, patents thermocompressor nozzle design and establishes TVC business
- 1910** - Frank Normandy publishes 244-page book entitled Sea Water Distillation
- 1912** - Weir installs six-effect evaporators on Red Sea in Safaga Bay, Egypt
- 1928** - UK's Aiton installs a Prache & Broullion TVC evaporator on Curaçao



Historical Developments

History of Thermal Desalination (Pre-1955)

- 1930s** - Weir installs many submerged tube multi-effect evaporators on Curaçao and Aruba
- 1934** - SS Queen Mary launched, with triple effect cupronickel evaporators using ferric chloride as an anti-scalant
- 1940** - MECO manufactures diesel engine driven VC distillers for US military producing 12 lb water for 1 lb fuel
- 1941** - MECO introduces Model K diesel powered vacuum distiller with 260:1 water to fuel ratio
- 1946** - Kuwait Oil Company installs country's first evaporator using a unit from an old World War I destroyer
- 1954** - Cleaver Brooks (later Aqua Chem) provides four 190 m³/d 5-stage MSFs for aircraft carrier Independence



Historical Developments

History of Thermal Desalination (after 1955)

- 1957 First industrial scale flashing unit by Westinghouse in Kuwait. Four stage flashing system a performance ratio of 3.3.
- 1957 Silver patent for the MSF configuration.
- 1959 Shuwaikh mix (poly-phosphate based) allowed for increase in the plant factor to values between 70-90%.
- 1960 First MSF plants commissioned in Shuwaikh, Kuwait and in Guernsey, Channel Island. The MSF unit in Shuwaikh had 19 stages, a 4550 m³/d capacity, and a performance ratio of 5.7. In Guernsey, the unit had 40 stages, a 2775 m³/d capacity, and a performance ratio of 10.
- 1962 Point Loma MSF plant with a capacity of 1 mgd



Historical Developments

History of Thermal Desalination (after 1955)

- 1965 Dearation of feed stream.
- 1966 Reduction in specific volume
- 1966 Sasakura, Japan, exported the first MSF Desalination Plant (2,300 m³/d) for land installation to Arabian Oil Company.
- 1966 Sasakura, Japan, installed MSF Desalination Plant (2,650T/D) at Ikeshima Island, Japan
- 1967 Sasakura, Japan, Obtained an order (world's largest at the time) for 36,400 T/D MSF Desalination Plant from the Kuwait Government
- 1967 First on-line ball cleaning system by Weirwestgarth in the Bahamas.
- 1967 Acid cleaning
- 1969 Co -Generation, energy cost reduction by 50%
- 1969 Increase in load factor to 85%



Historical Developments

History of Thermal Desalination (after 1955)

- 1970 Development of commercial grade RO membranes
- 1972 Sasakura, Japan, obtained an order (world's largest at the time) for 180,000 m³/d MSF Desalination Plant from the Hong Kong Government.
- 1973 Cladding of partition walls.
- 1973 Construction of the standard MSF units, 6 m³/d, 24 stages, and a performance ratio of 6-8.
- 1979 Sasakura, Japan, obtained an order for 470,000 m³/d MSF Desalination Plant from Saudi Arabia(A1 Jobail Phase 2)
- 1980 Design and operation of low temperature mechanical vapor compression units
- 1980 Design and operation of low temperature multiple effect evaporation units combined with thermal vapor compression



Historical Developments

History of Thermal Desalination (after 1955)

- 1983 Sasakura, Japan, obtained an order for the world's largest class Reverse Osmosis Desalination Plant (46,000 m³/d) from the Government of the State of Bahrain
- 1985 Use of polymer antiscalant at top brine temperatures of 110° C.
- 1996 Construction of the largest MSF units known to day with capacity of 57,735 m³/d in UAE.
- 1999 Construction of large scale RO plant in Florida, USA
- 1999 Increase in unit capacity of multiple effect evaporation units
- 2000 Design and construction of high performance of MSF system with 43 stages, 17280, and a performance ratio of 13
- 2001 Construction of an MSF unit with performance ratio of 13 in Italy.



Historical Developments

History of Membrane

Abbe Noilett	1748	Discovering of osmosis phenomenon in natural membranes
Matteucci	1845	Research on anisotropy of natural membranes
Graham	1866	Research on dialysis
Fick	1865	The first synthetic membrane from nitrocellulosis
Graham	1866	Research on gas separation on rubber membranes
Traube	1867	Research on osmosis on synthetic membranes
Pfeffer	1877	Research on osmosis on ceramic membranes
Gibbs i van Hoff	1877	Theory of osmosis phenomena
Donnan	1911	Distribution law
Abel	1926	Research on dialysis
Michaels, Manegold, McBain	1926- 31	Research on reverse osmosis
Elder i in.	1934	Research on electro dialysis
Kammermeyer	1957	Gas separation on silicone rubber
Kammermeyer	1957	Pervaporation of azeotropic mixtures
Lonsdale	1960	Research on composite membranes
Loeb i Surirayan	1962	Preparation of assymetric membranes
Loeb i Surirayan	1962	Pore size controlling in membranes
Mahon	1963	Kapillary membranes
Merten	1963	Concentration polarisation
Porter	1975	Klassification of pressure-driven processes
Goddard	1977	Modells of facilitated transport
Leblanc	1980	Membranes with immobilised carriers
Yoshikawa	1986	Membranes with active centers
Cussler, Aris, Brown	1989	The chain model of facilitated transport
Rautenbach	1990	Membrane hybrid processes



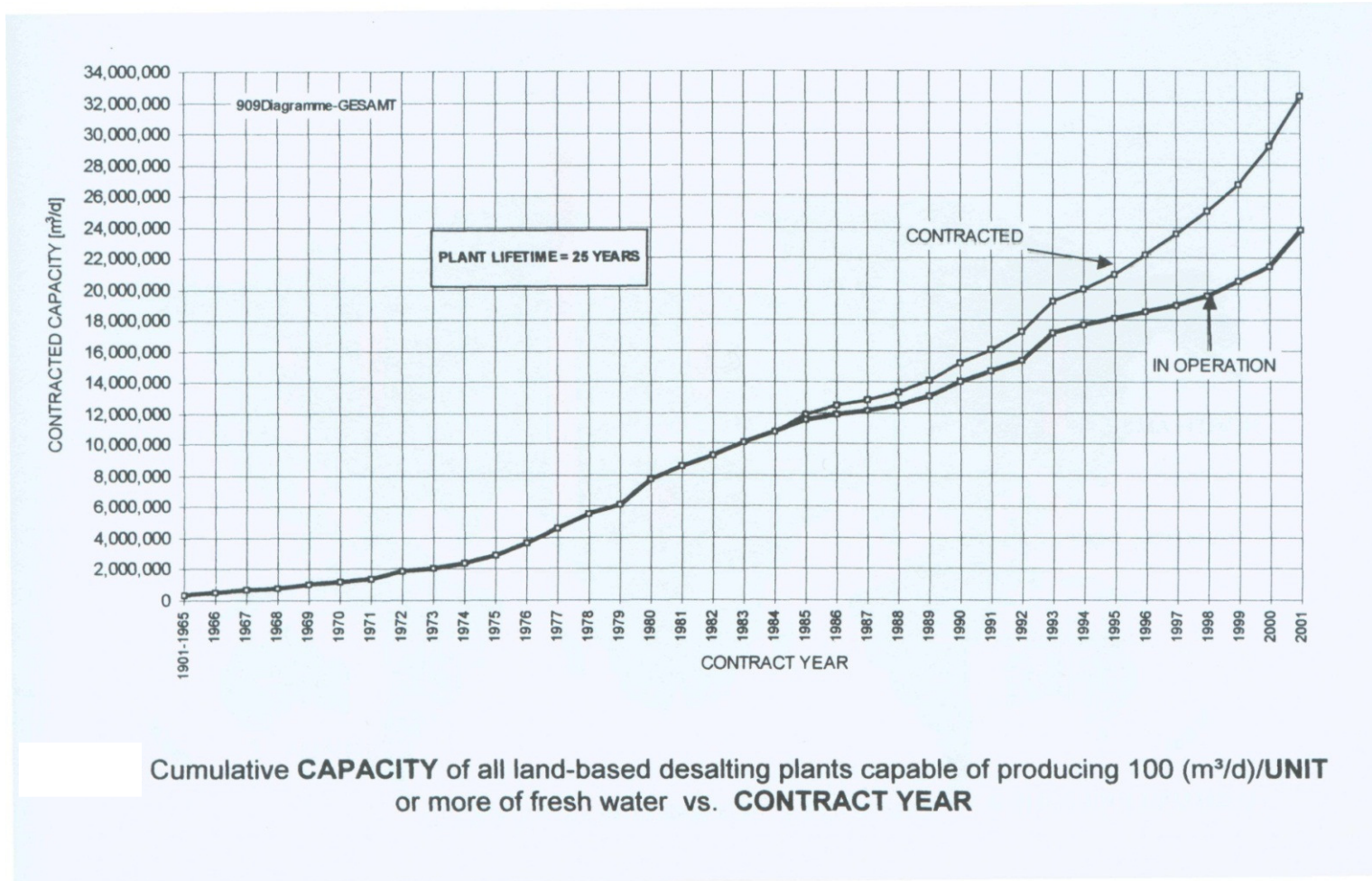
Historical Developments

History of Membrane

- 1748** - Abbe Noilett discovered the phenomenon of osmosis in natural membranes.
- 1855** - Adolph Fick created a cellulose nitrate (nitrocellulose) membrane as the first synthetic membrane.
- 1866** - Thomas Graham a British physical chemist first used the term dialysis.
- 1869** - The first synthetic polymer studied & produced commercially by Schoenbein.
- 1907** - Bechold first introduced the term ultrafiltration.
- 1927** - Sartorius Company first made membranes commercially available.
- 1934** - Research on electrodialysis done by G. R. Elder
- 1950** - Gerald Hassler introduces the first concept of membrane desalination
- 1958** - C. E. Reid and E. J. Breton showed that cellulose acetate was an effective membrane material for water desalination.
- 1960** - Sidney Loeb and Srinivasa Sourirajan developed the first practical membranes for a water desalting process called reverse osmosis.
- 1960** - H. K. Lonsdale develops thin film composite type membranes.
- 1963** - H. I. Mahon developed the first capillary (Hollow Fibre) membranes.
- 1965** - The world's first commercial RO plant was built in Coalinga, CA
- 1977** - John Cadotte patents thin film composite membrane under government gra

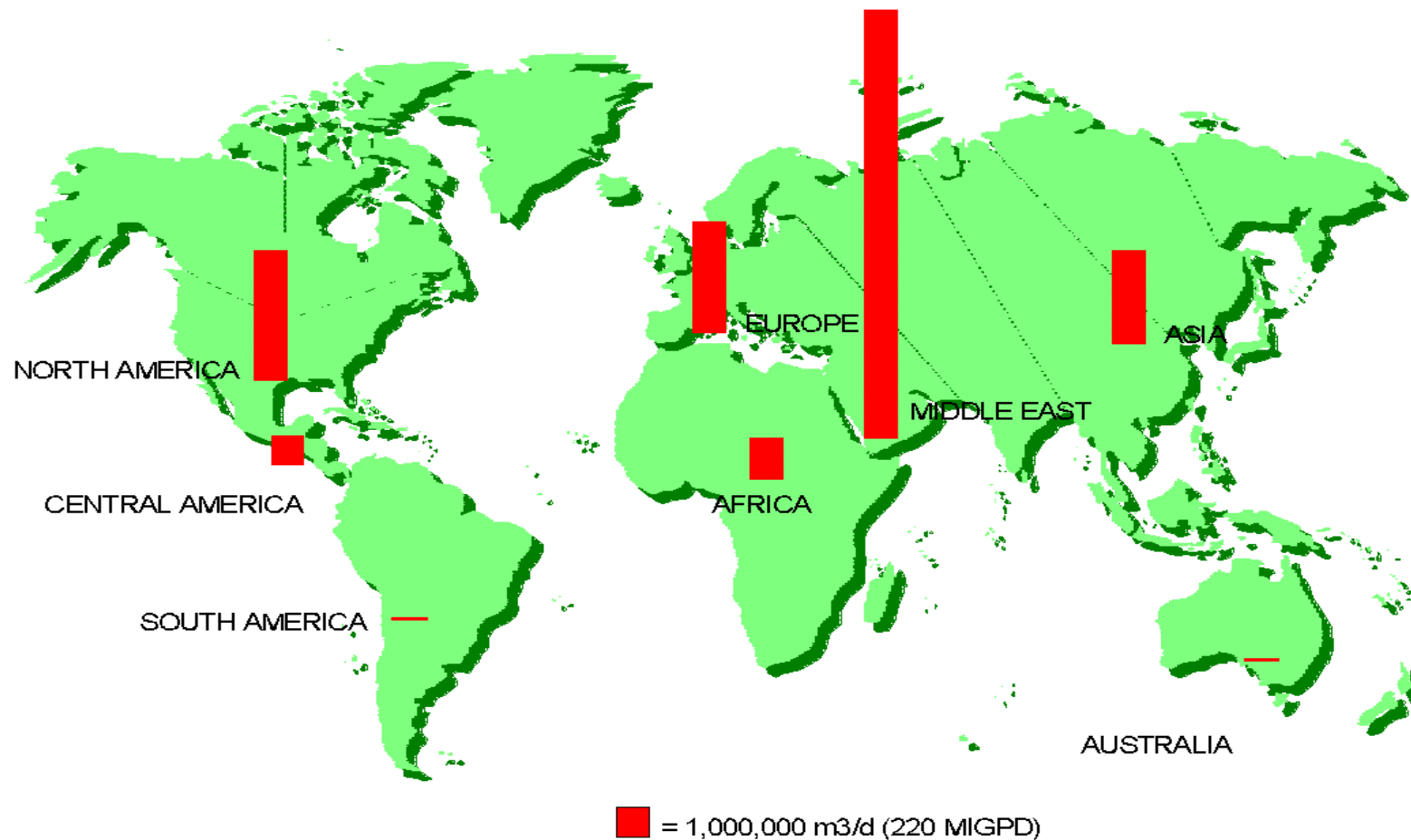


Cumulative Capacity of Desalination Plants





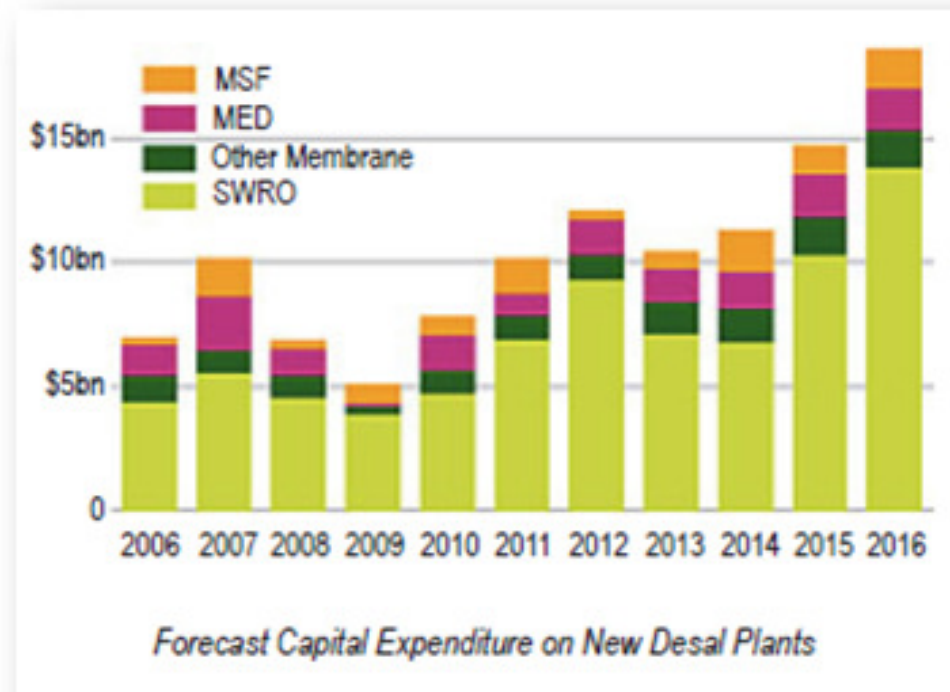
Market Status





Market Status

Desalination Markets 2010



Over the past 40 years different progresses in pre-treatment operations, in pressure recovery systems and in membrane modules performances have contributed to the *exponential* growth of Reverse Osmosis (RO) for brackish and sea water desalination.

Water Desalination Report, Volume 46, Number 27, 19 July 10



Market Status

- Approximately, \$10 billion (5.3×10^6 m³/d) is allocated for the next 5 years.
- In 1996, 65% of the world production is found in the Gulf countries and the US.
- A similar situation is found in 2000; however, other countries such as Japan, Spain, Italy, and Korea have increased their production capacity to higher and similar levels.
- Spain increased its production capacity by a factor of two.



Market Status

- The majority of the MSF operating plants are the brine circulation type.
- The MEE operates in a parallel feed mode, at low temperature, with/without thermal vapor compression (MEE or MEE-TVC).
- The MVC operates in single or multiple effect.
- In 2000, MSF and RO total shares are 42.4% and 41.1 %, respectively.



Market Status

- The MSF and RO seawater market share are 70.2% and 18.1%, respectively.
- The MSF accounts for 93% of all thermal desalination processes.
- RO represents 88% of all membrane desalination processes.
- Desalination in all of the Gulf countries is dominated by the multistage flash desalination (MSF) with shares varying from 60% up to 96%.
- RO dominates the US, Japan, and Spain.
- MSF, RO, and MEE contracts in 2000 are 32, 54, and 14%, respectively.



Market Status

Country	Total Capacity (m ³ /d)	Percentage Relative to total world production	MSF(%)	MEE(%)	MVC(%)	RO(%)	ED(%)
Saudi Arabia	5253208	23.6	65.66	0.31	1.21	30.97	1.85
	5429334	20.96	64.22	0.329	1.39	32.254	1.8
USA	3092533	15.6	1.71	1.78	4.51	78.04	11.37
	4327596	16.7	1.32	4.49	6.35	74.63	13.56
UAE	2164507	9.8	89.80	0.38	2.97	6.49	0.24
	2890689	11.16	86.66	7.7	0.03	5.51	0.09
KUWAIT	1538426	6.8	95.47	0.68	0.00	3.39	0.33
	1614861	6.2	96.52	0.08	0.00	3.25	0.15
JAPAN	745318	3.67	4.72	1.97	0.00	86.41	6.78
	945163	3.65	3.86	2.34	0.00	84.32	7.35
LIBYA	683308	3.37	67.70	0.94	1.84	19.56	9.79
	701303	2.71	65.66	10.7	0	15.91	7.73
QATAR	566904	2.79	94.43	0.64	3.26	0.00	0.00
	572870	2.21	94.34	3.86	0	1.8	0.00
SPAIN	529891	2.61	10.62	0.90	8.65	68.91	10.90
	1233835	4.76	4.51	3.5	2.79	84.25	4.95
ITALY	518711	2.56	43.22	1.88	15.14	20.43	19.16
	581478	2.24	43.76	12.4	6.53	21.67	16.24
BAHRAIN	309158	1.52	52.02	0.00	1.46	41.73	4.50
	473391	1.83	62.74	9.67	0	26.88	0.71
OMAN	192586	0.95	84.06	2.18	0.00	11.73	0.00
	377879	1.21	87.31	1.111	3.7	7.63	0.237

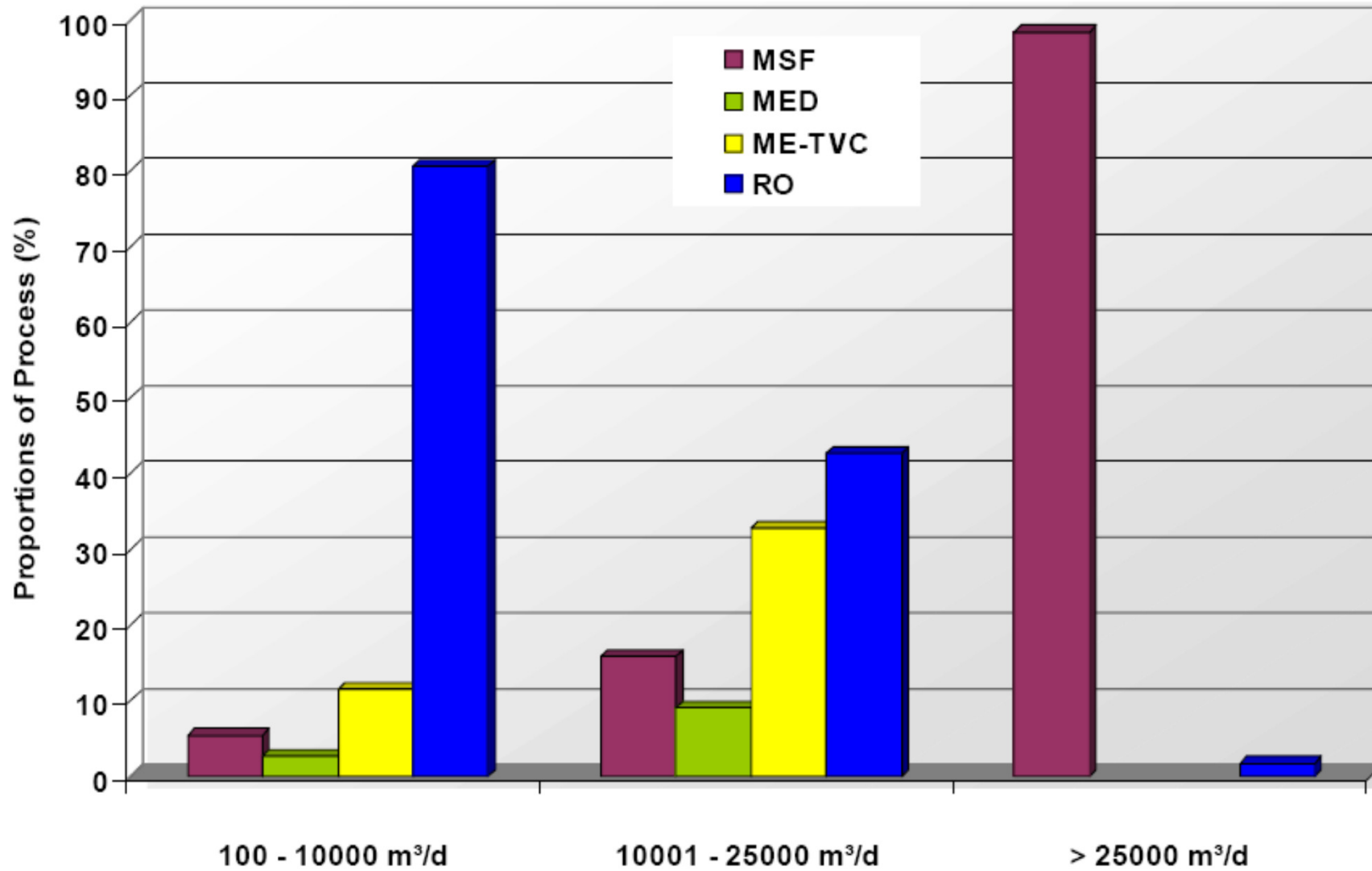


Market Status

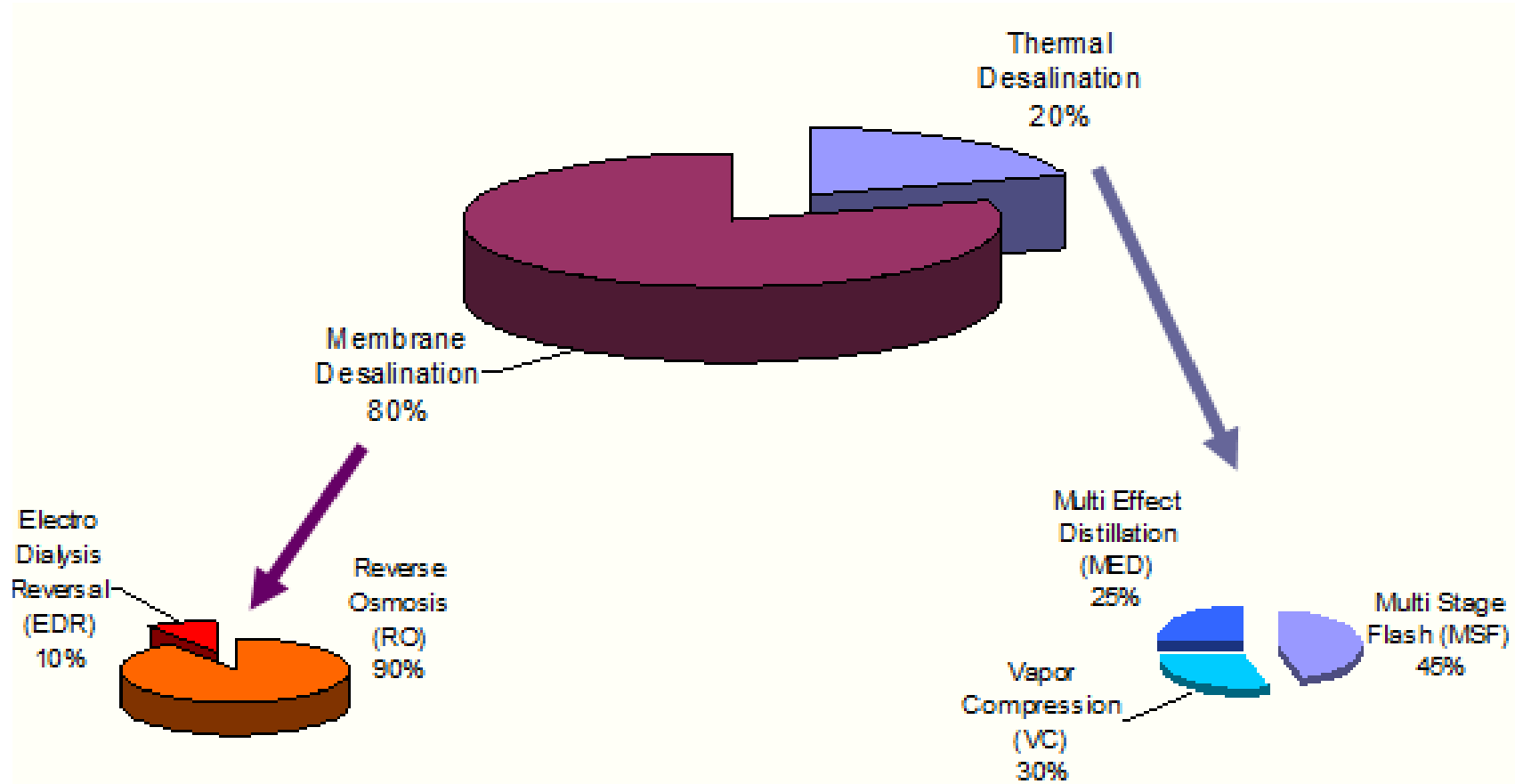
- From this table, the following conclusions can be made:
 - MSF is capable of withstanding the harsh conditions in the Gulf environment.
 - RO dominates the desalination industry in USA, Spain, and Japan.
 - The majority of the RO process operates on brackish and low salinity water.
 - The features of the MSF, gained experience, and conservative nature of the owner, make MSF the workhorse of the seawater desalination.
 - The MEE process looks to be promising for future applications with a rate of increase of 13%.



Market Status



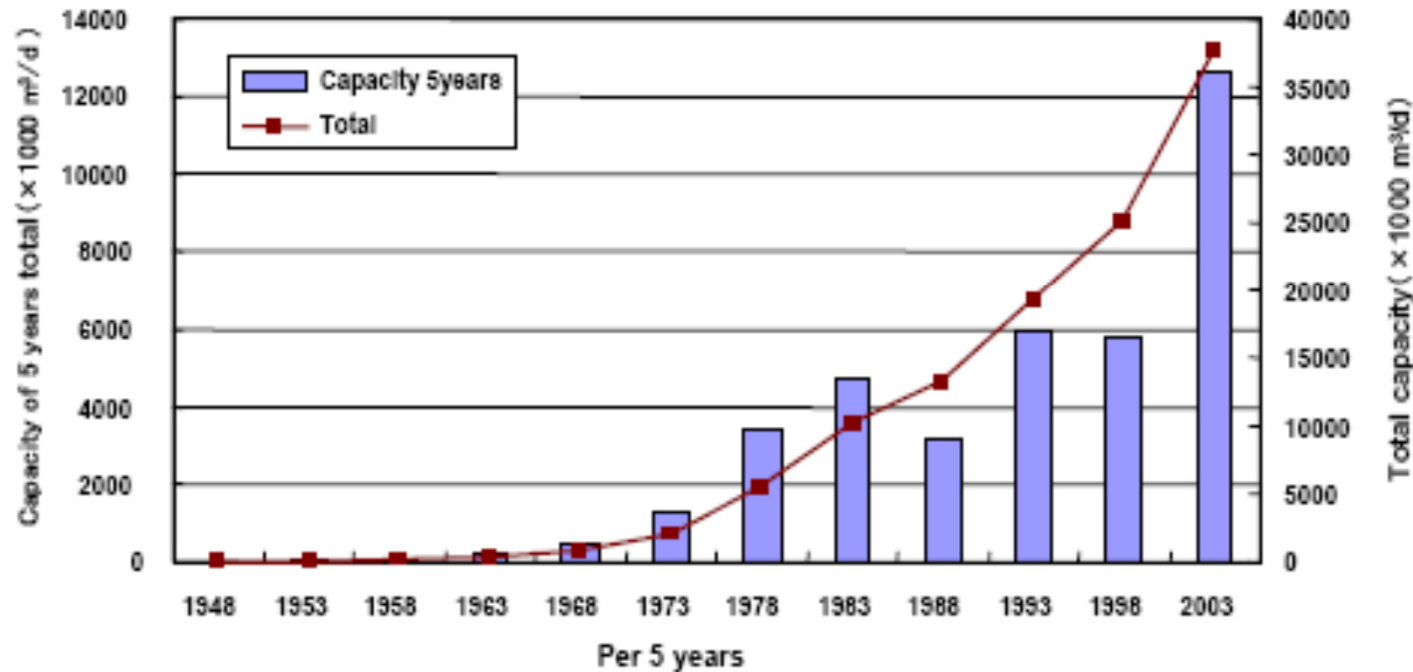
Market Status



V. Frenkel, Desalination & Water Reuse 17 (2008) 47-50

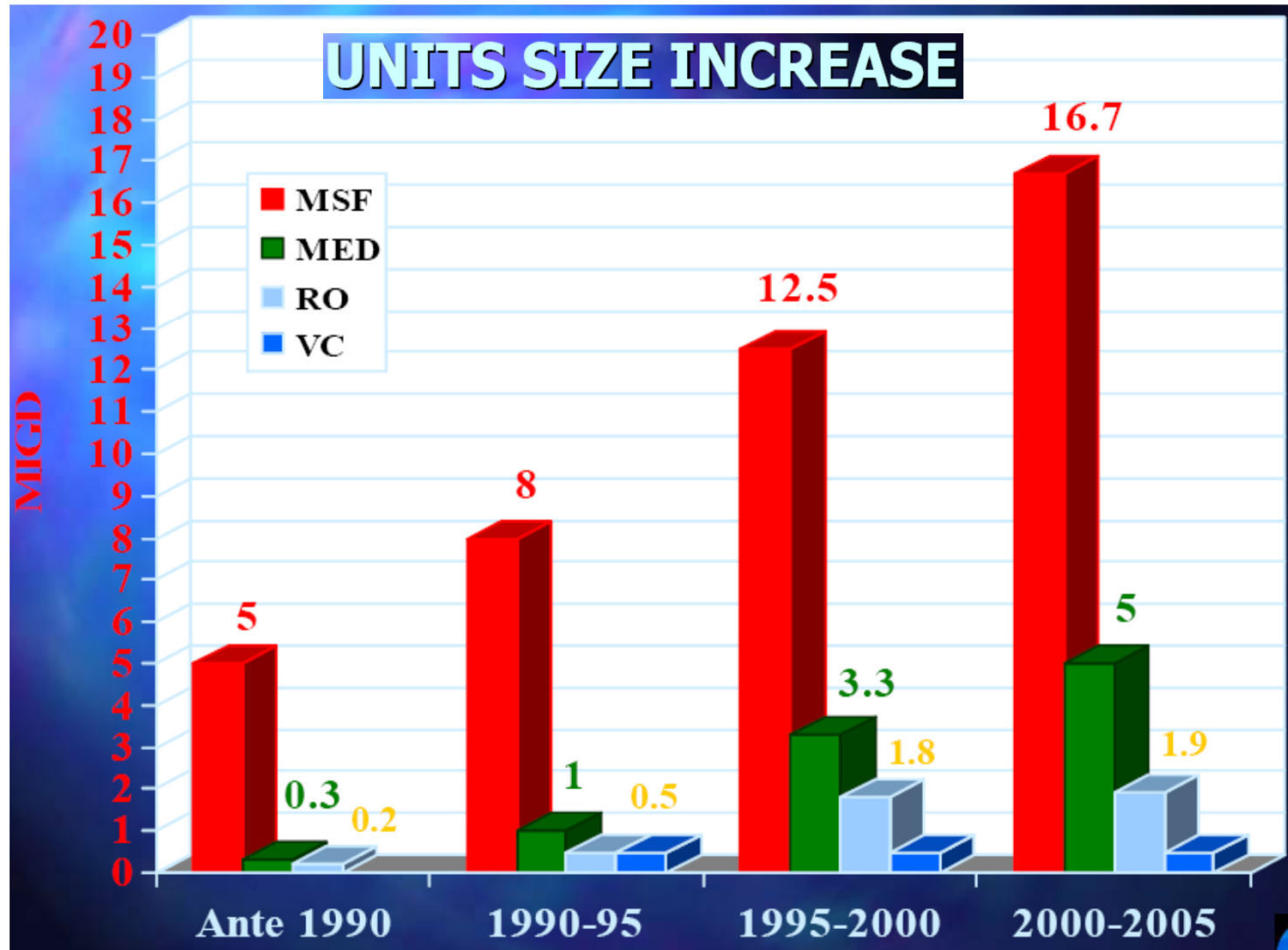
Growth of Desalination Industry

Total capacity of desalination plants in the world

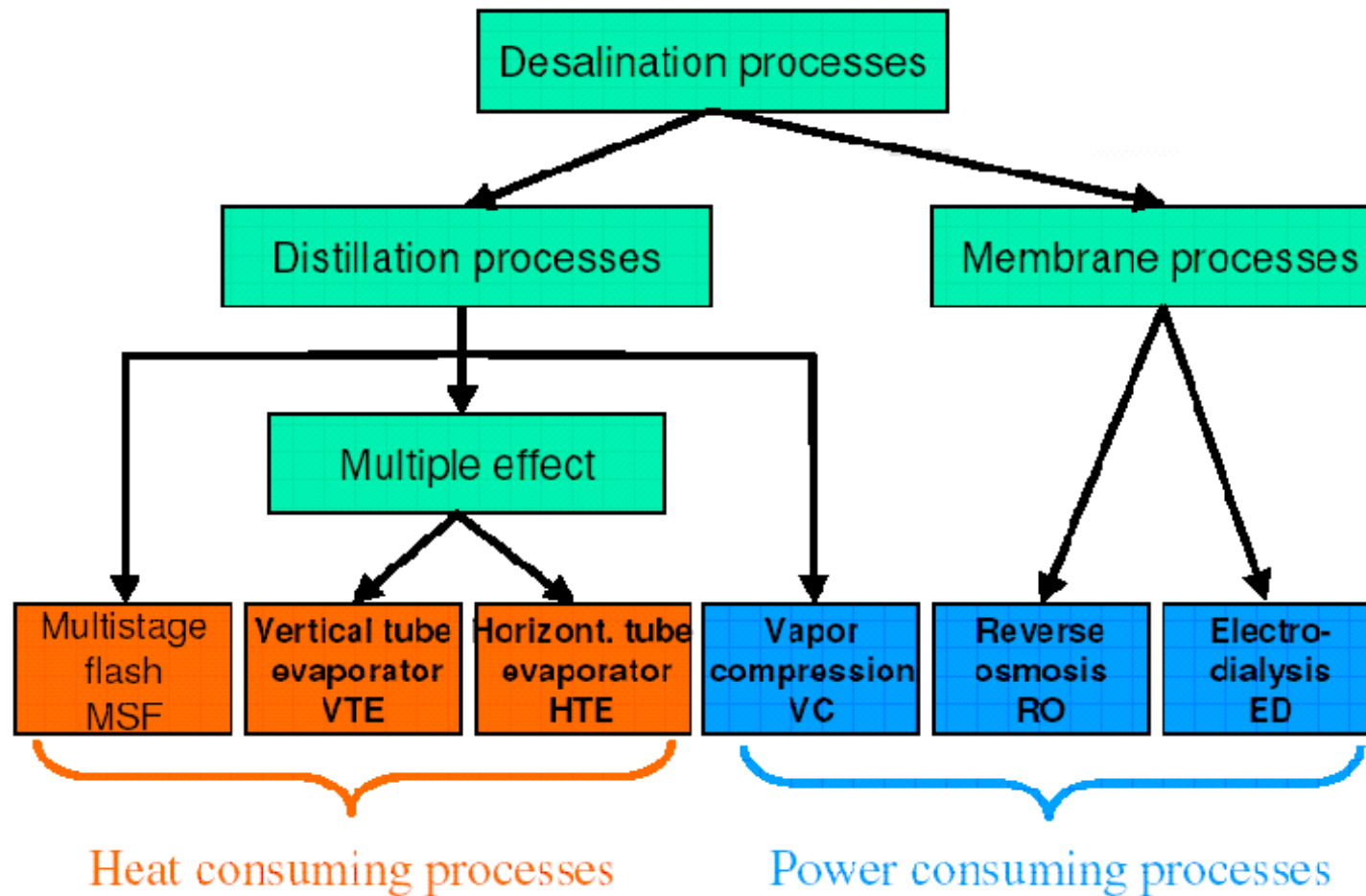


- As of 2005, installed total capacity in worldwide : 40 million ton/day
- Estimated future increase rate of capacity :10-12 %/year until 2020
- Estimated total capacity : 63 million ton/day until 2010 and 94 million ton/day until 2015

Growth of Desalination Industry

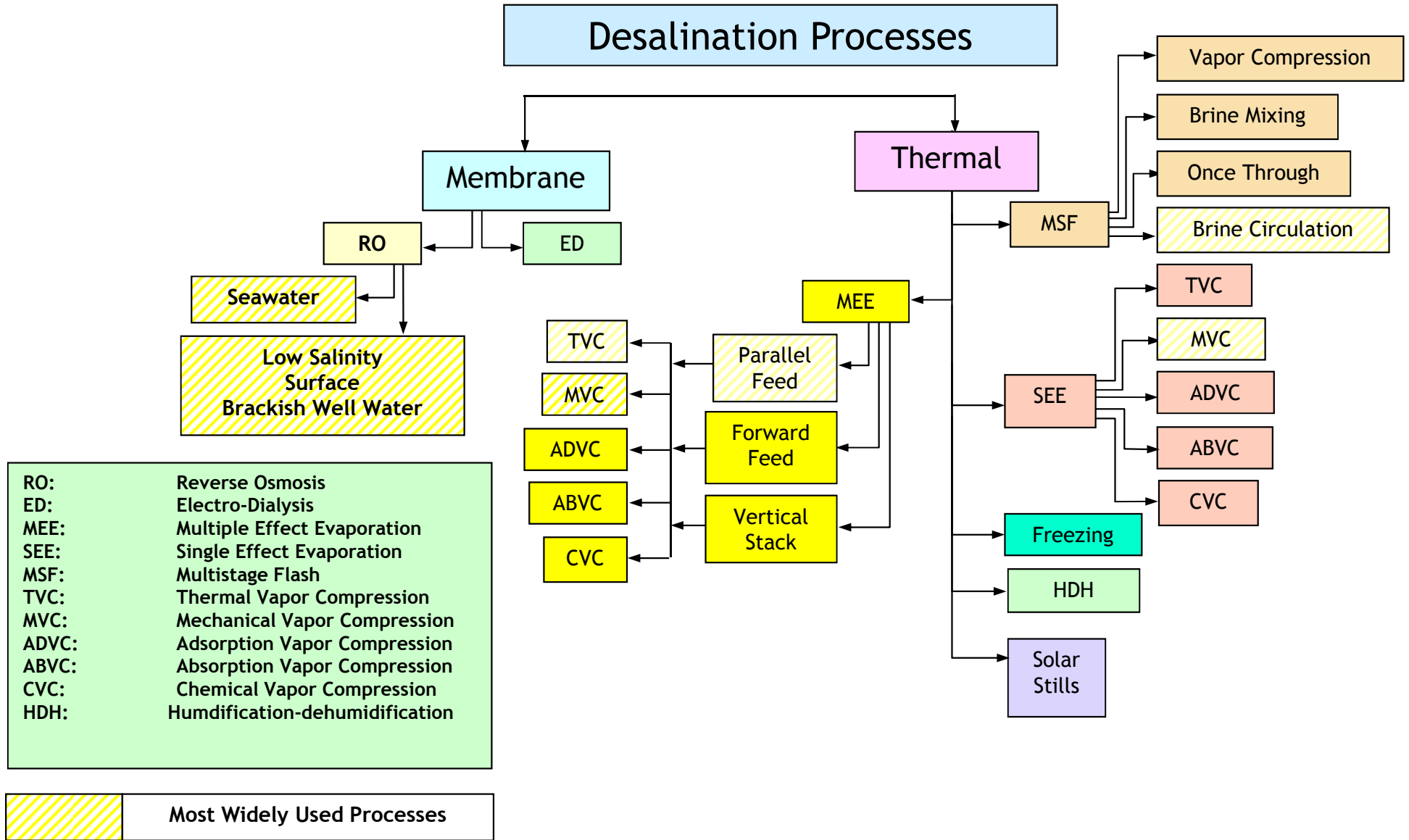


Classification Desalination Processes





Desalination Processes





Classification Desalination Processes

Separation	Energy Use	Process	Desalination Method
Water from Salts	Thermal	Evaporation	Multi-Stage Flash (MSF)
			Multi-Effect Distillation(MED)
			Thermal Vapour Compression (TVC)
			Solar Distillation (SD)*
	Crystallisation		Freezing (FR)
			Gas Hydrate Processes (GH)
			Membrane Distillation (MD)
	Mechanical		Evaporation
Filtration			
Electrical		Selective Filtration	
		Exchange	



Desalination Processes

Classification	Process	Energy Required
<u>Thermal</u> = Distillation (Phase Change, liquid → Vapor)	<ol style="list-style-type: none">1. Multi-Stage Flash Evaporation (MSF)2. Multiple Effect Evaporation (MEE)3. Vapor Compression (MVC)	Electrical + Heat Electrical + Heat Electrical, Heat + Electrical
<u>Membrane</u> (no phase change)	<ol style="list-style-type: none">1. Reverse Osmosis (RO)2. Nanofiltration (NF)3. Electrodialysis, ED4. Electrodialysis Reversal (EDR)	Electrical



Distillation-based Processes

Based on water evaporation

- *Multistage Flash Distillation (MSF)* involves heating saline water to high temperatures and passing it through vessels of decreasing pressures to produce (fresh) water vapour.
- *Multi-Effect Distillation (MED)* operates at lower temperatures but uses the same principles as multistage flash distillation.
- *Vapour Compression Distillation (VC)* where the heat for evaporating water comes from the compression of vapour, rather than the direct exchange of heat.



Membrane-based Processes

Membrane-based Processes

- *Reverse Osmosis is a pressure driven process which forces saline water through a membrane, leaving salts behind.*
- *Electrodialysis: With Electrodialysis, an electric current moves salts selectively through a membrane, leaving fresh water behind.*



Advantages / Disadvantages of Desalination Processes

Advantages and disadvantages of desalination techniques

Desalination type	Usage	Advantages	Disadvantages	Companies
Distillation				
Multi-stage flash distillation (MSF) Desalination process that distills seawater by flashing a portion of the water into steam in multiple stages of what are essentially regenerative heat exchangers.	Accounts for 85% of all desalinated water; used since early 1950s	MSF plants, especially large ones, produce a lot of waste heat and can therefore often be paired with cogeneration	High operating costs when waste heat is not available for distillation. High rates of corrosion	Doosan Heavy Industries (South Korea)
Multiple-effect evaporator (MED ME) Using the heat from steam to evaporate water. In a multiple-effect evaporator, water is boiled in a sequence of vessels, each held at a lower pressure than the last.	Widely used, since 1845	High efficiency, while relatively inexpensive	A large heating area is required	Niro (United States)
Vapor-compression evaporation (VC) Evaporation method by which a blower, compressor or jet ejector is used to compress, and thus, increase the temperature of the vapor produced.	Mainly used for wastewater recovery	Technique copes well with high salt content in water	-	Vacom, Water Desalination International (United States)
Evaporation/condensation Evaporation of seawater or brackish water and consecutive condensation of the generated humid air, mostly at ambient pressure.	Widely used	Easiest method of distillation	Time-consuming and inefficient in comparison to other techniques	-



Advantages / Disadvantages of Desalination Processes

Advantages and disadvantages of desalination techniques

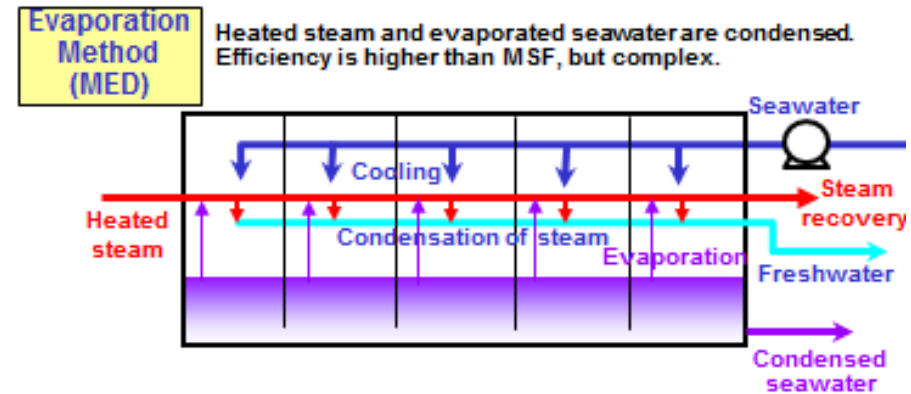
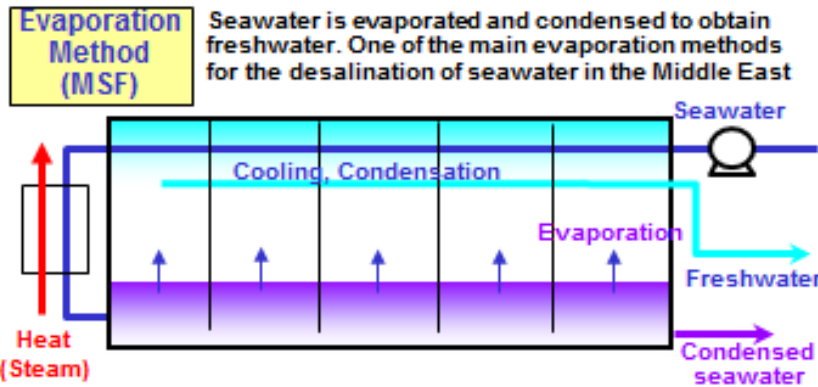
Desalination type	Usage	Advantages	Disadvantages	Companies
Membrane processes				
Electrodialysis reversal (EDR) Electrochemical separation process that removes ions and other charged species from water and other fluids.	Widely used, since early 1960s	Long membrane lifetime and high efficiency (up to 94% water recovery, usually around 80%)	High capital and operational costs	General Electric (GE), Ryan Herco Flow Solutions (United States)
Reverse osmosis (RO) Separation process that uses pressure to force a solvent through a membrane that retains the solute on one side and allows the pure solvent to pass to the other side.	Widely used, first plant installed in Saudi Arabia in 1979	In water purification, effectively removes all types of contaminants to some extent	Requires more pretreatment of the seawater and more maintenance than MSF plants	Multiplex-Degremont Joint Venture (Australia) Consolidation Water (Cayman Islands), GE
Nanofiltration (NF) Nanofiltration membranes have a pore size in the order of nanometers and are increasingly being used for water desalination.	Emerging technology	Very high efficiency	High capital cost, unknown lifetime of membrane, no large-scale plant built yet	Stoneybrook Purification (United States)
Forward osmosis (FO) Osmotic process that, like reverse osmosis, uses a semi-permeable membrane to effect separation of water from dissolved solutes.	Emerging technology	Low or no hydraulic pressures, no energy needed for separation	Cannot produce pure water, only concentrated solutions	Apaclara (United Kingdom)
Membrane distillation (MD) In membrane distillation, the driving force for desalination is the difference in vapor pressure of water across the membrane, rather than total pressure.	Widely used	Low energy consumption, low fouling	-	KeppelSeghers (Belgium)



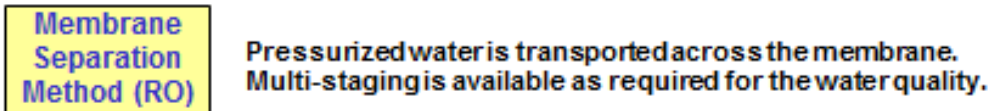
Comparison between Thermal and Membrane Processes

Thermal desalination processes (MSF, MED, VC)	Membrane desalination processes (RO)
Desalted water with low total dissolved solids concentrations (10-20 ppm)	Desalted water with total dissolved solids concentrations between 100 and 550 ppm
Energy consumption (MSF)^A = 17 ÷ 18 kWh/m³	Energy consumption^{B, C, D} = 2.2 ÷ 6.7 kWh/m³
Recovery factor ≈ 10%	Recovery factor^{E, F} ≈ 40 ÷ 60^A %
High capital costs High operating costs	Low capital costs Low operating costs
Desalted water cost^E ≈ 1.0 ÷ 1.4 \$/m³ (MSF) ÷ 2.34 \$/m³ (MED, TVC)	Desalted water cost ≈ 0.50 ÷ 0.70\$/m³ (in the most part of SWRO plants^{C, G}) and 0.36\$/m³ (from brackish water sources^{E, H})

Features of Evaporation Methods and Membrane Method

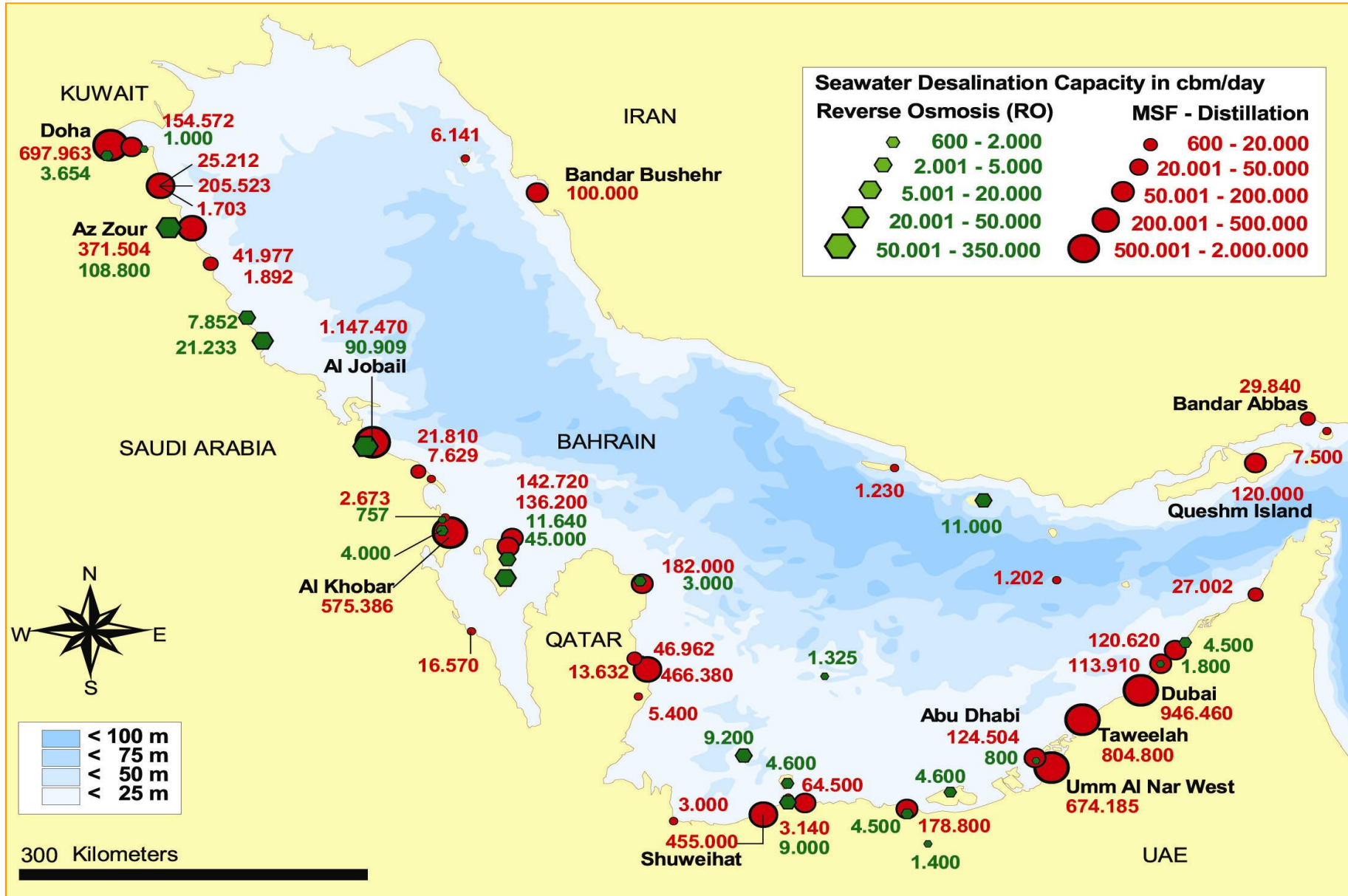


Features: By parallel establishment with an electric power plant, it can utilize the heat sources. (The reason why it is the mainstream in the Middle East.)
 It requires almost no preprocessing and provides simple operation. (MED is rather complex.)



Features: Low facility cost
 Low seawater usage (High recovery rate)
 Low energy consumption (Heat + Electric power)

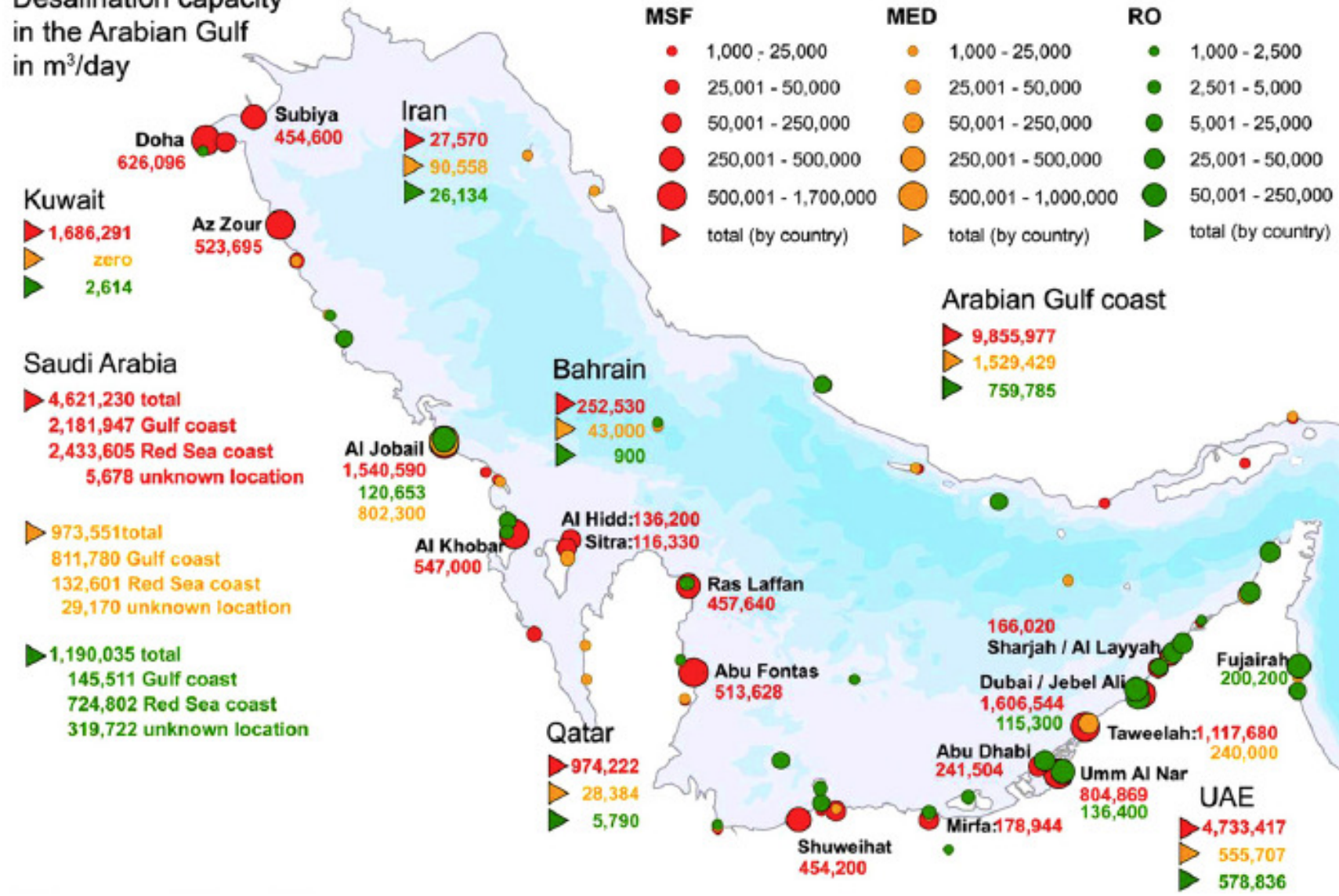
0.5 – 0.9 times compared to evaporation methods
 1/4 or less compared to evaporation methods
 1/5 or less compared to evaporation methods

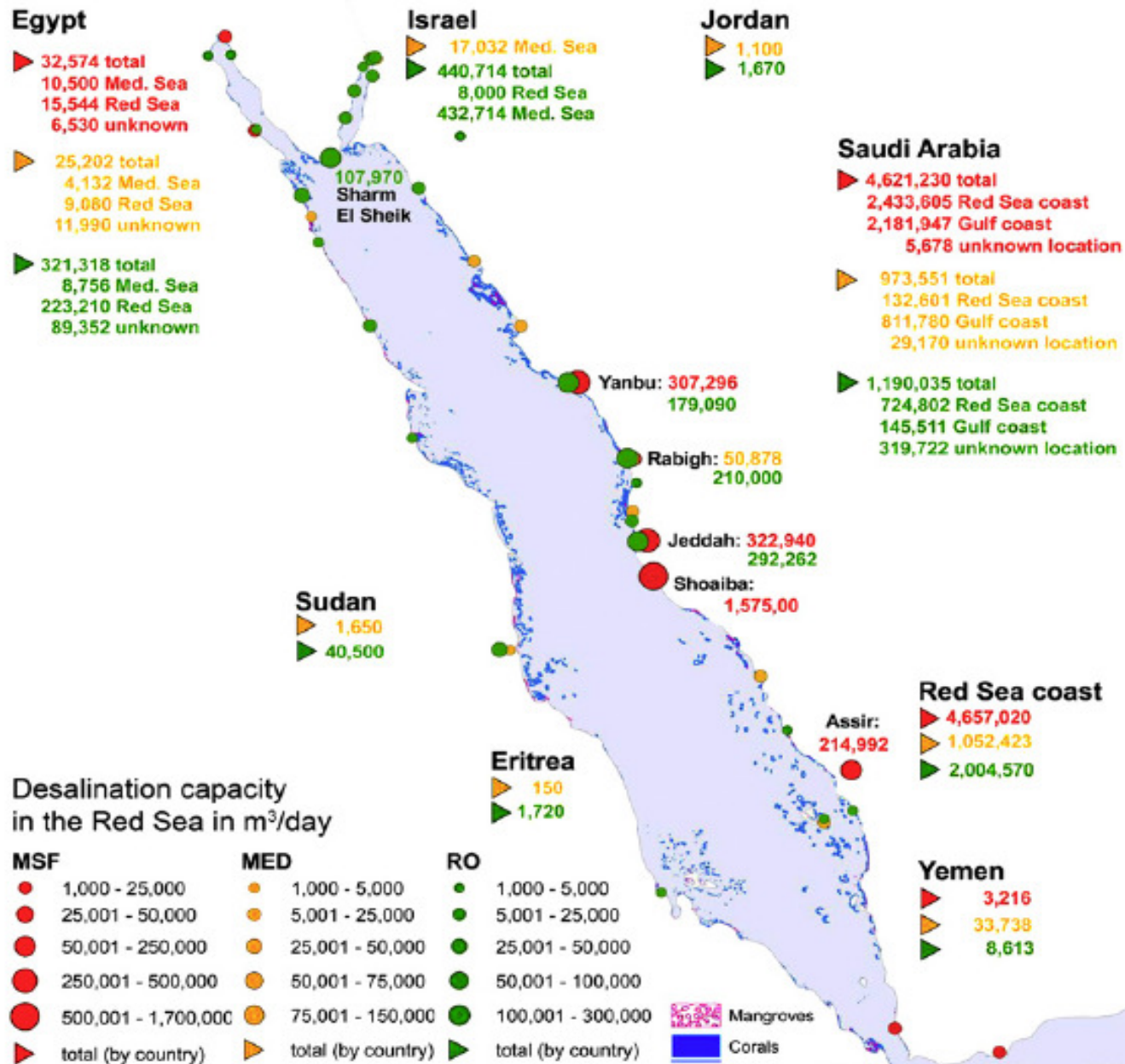


Source: Wagnick 2000



Desalination capacity in the Arabian Gulf in m³/day







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Membrane Desalination Processes



Content:

- *Overview of Membrane Desalination Technologies*
 - *Membrane Characterization*
 - *Membrane Chemistry and Structure:*
(Cellulose Acetate (CA) membrane, Composite Aromatic Polyamide (CAP) Membrane)
 - *Membrane System Concepts*
 - *Classification of Membrane Separation Processes*
 - *Applications of Membrane Processes*

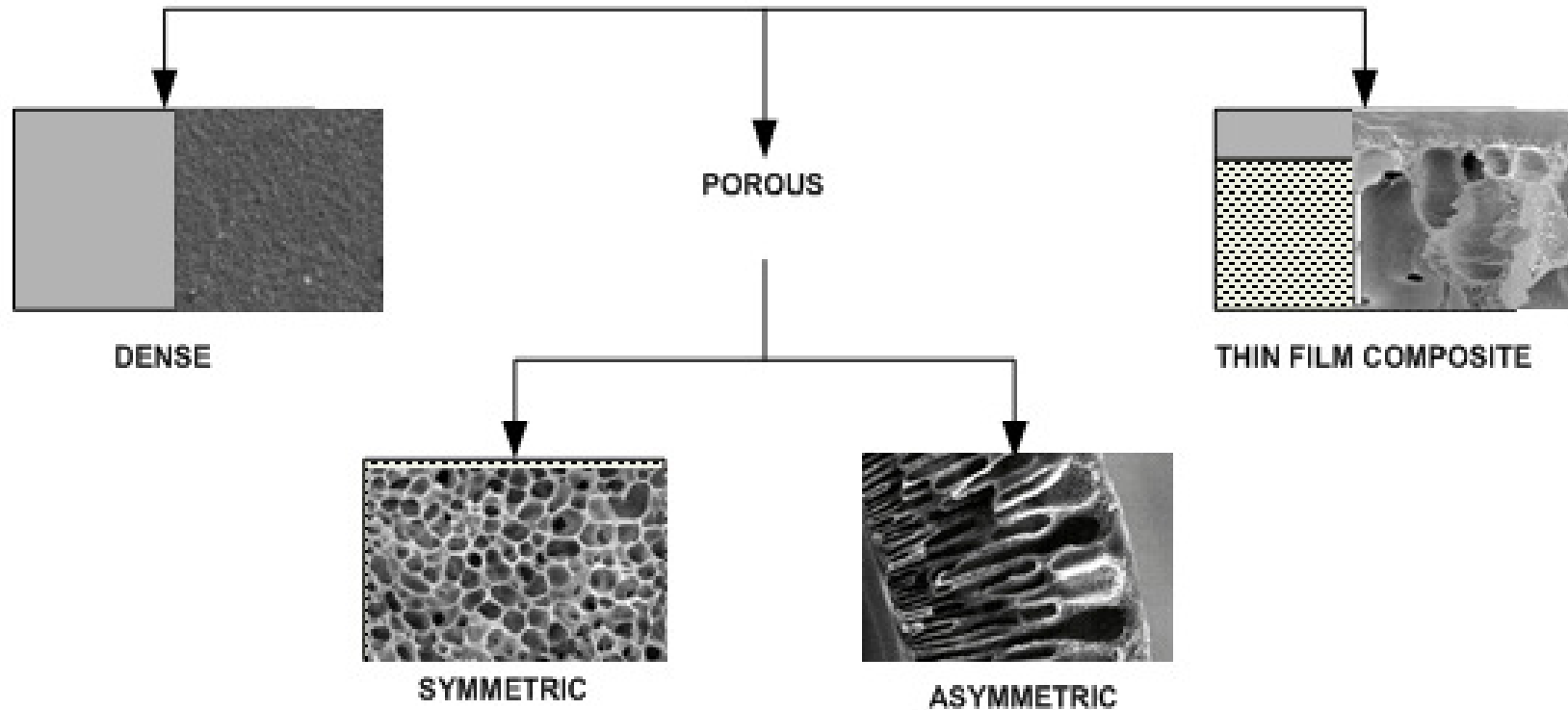


Historical Background

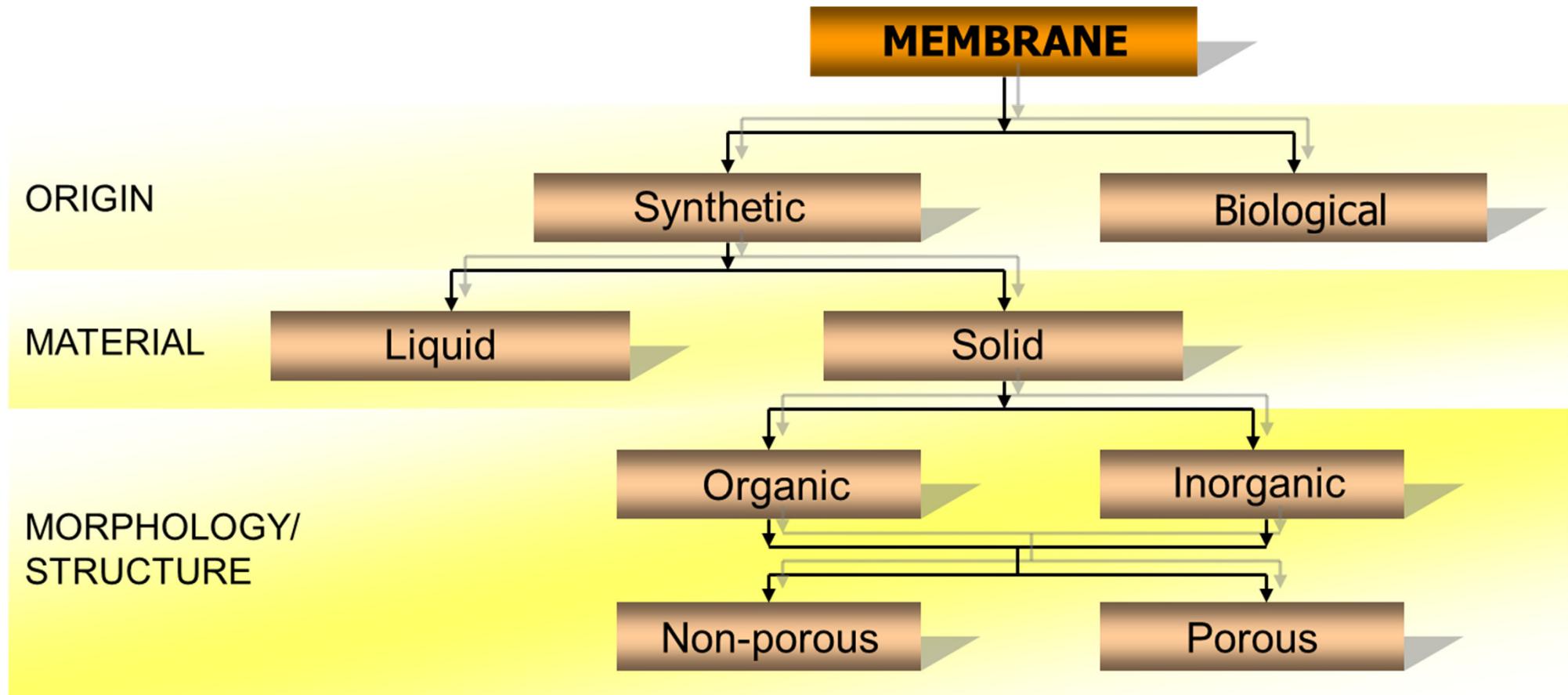
Development of practical membrane processes

Membrane process	Year	Application
Microfiltration (Germany)	1920	Laboratory use (bacteria filter)
Ultrafiltration (Germany)	1930	Laboratory use
Hemodialysis (Netherlands)	1950	Artificial Kidney
Electrodialysis (USA)	1955	Desalination
Reverse Osmosis (USA)	1960	Sea water desalination
Ultrafiltration (USA)	1960	Concentration of macromolecules

Membrane Classifications



Membrane Classifications





Membrane Classifications

✓ Based on Material

- ❑ Biological: Animal or Plant origin
- ❑ Synthetic: Organic (polymeric) and Inorganic (ceramics) membranes are of importance in Env. Eng.

(Example of organic membrane: cellulose acetate, cellulose esters, polypropylene polyamides, polysulfones, etc.); organic- cheaper.

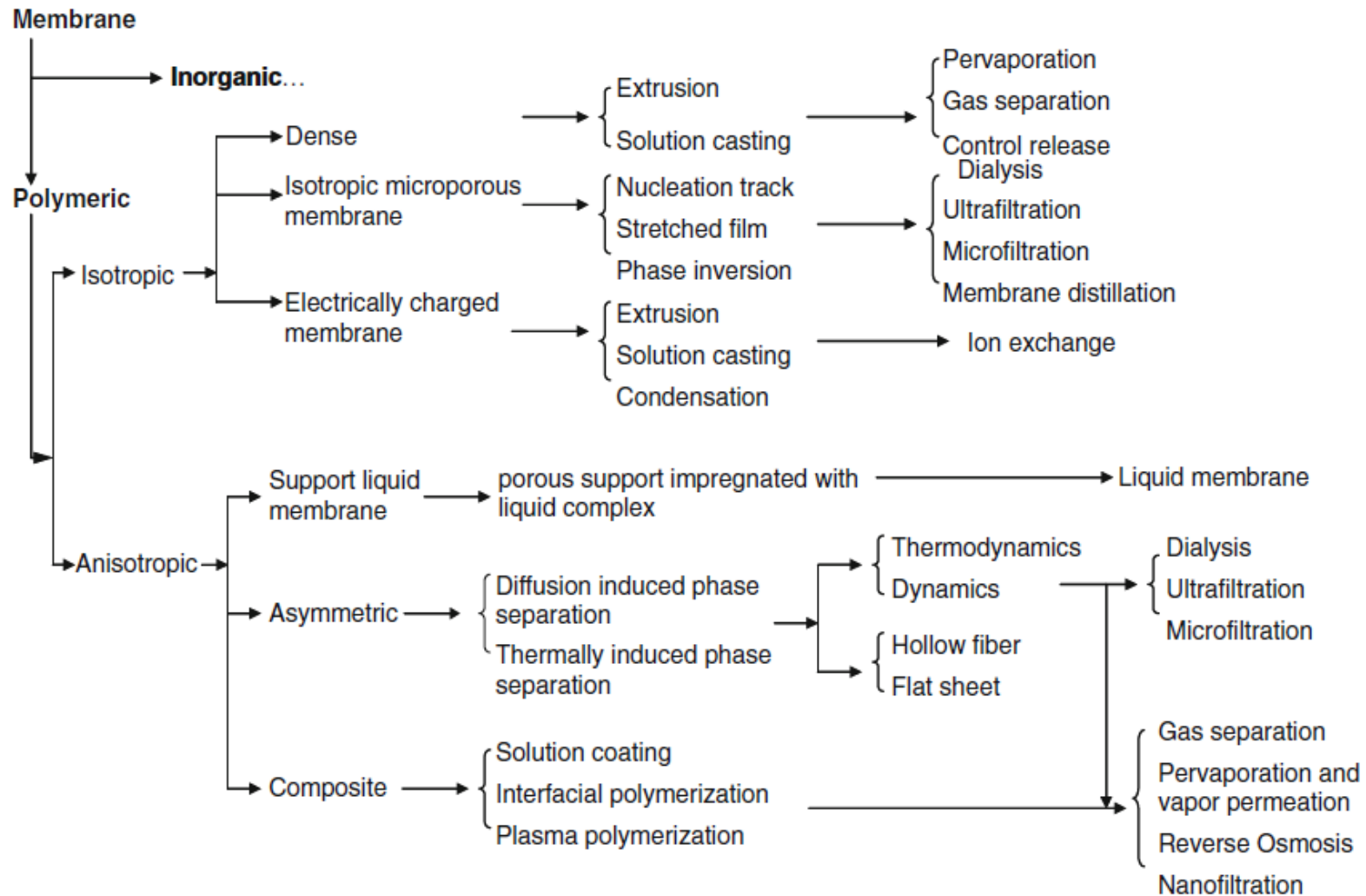
Ceramic: Alumina, Titania, and Zirconia: high thermal/chemical resistant

✓ Based on Morphology or Structure

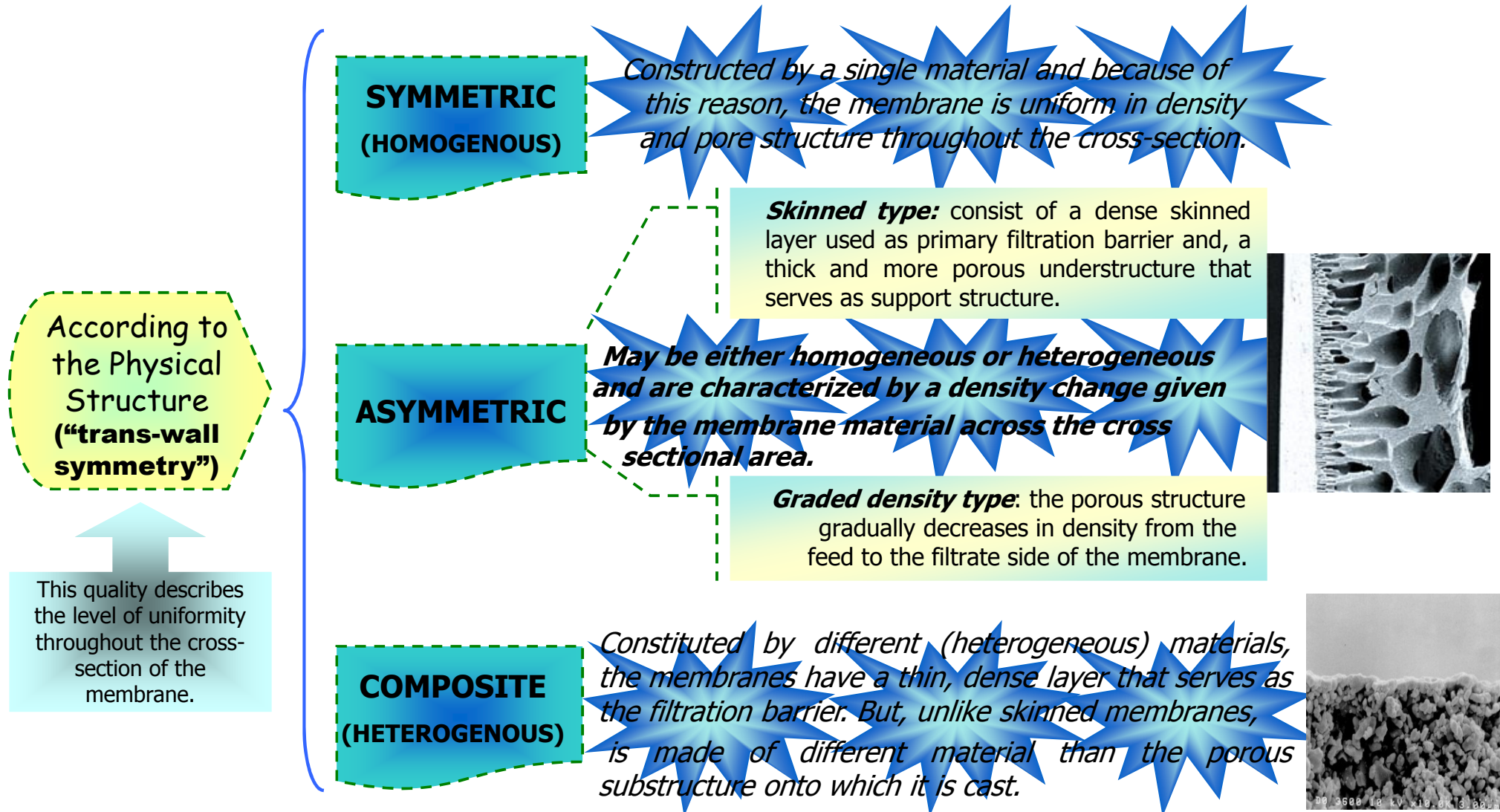
- ❑ Symmetric: All porous or non-porous (10-200 μ m) of identical morphology.
- ❑ Asymmetric: membrane constituted of two or more structural planes of non-identical morphologies A thin dense layer (0.1 -0.5 μ m) or skin supported by a porous sublayer (50 – 150 μ m).



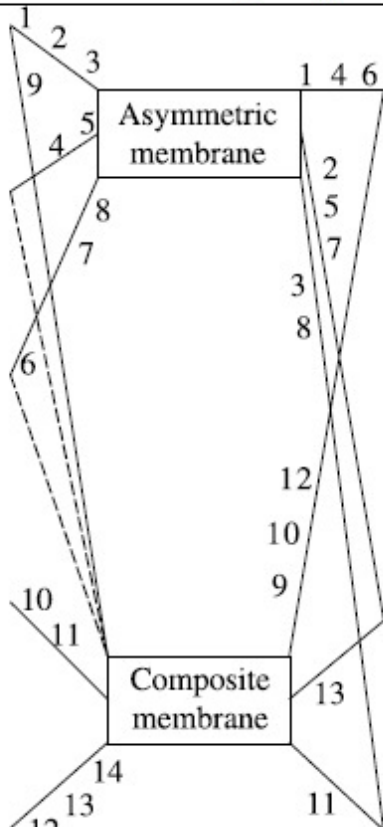
Membrane Classifications



Membrane Classifications



Summary of Membrane Materials for RO

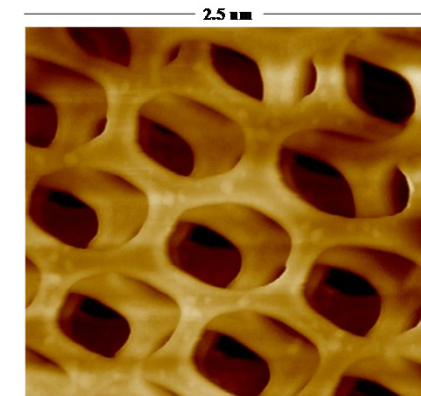
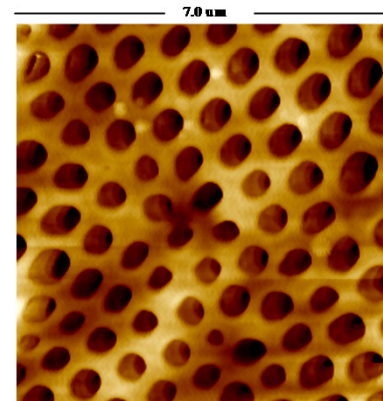
Membrane Material	Membrane Morphology	Module Configuration	Examples of Membrane and Module, Membrane Suppliers
Cellulose acetate Polyamide Heterocyclic polymer		Spiral	1. Toray, UOP, envirogenics, Osmonics, Desalination, Ajax, Hydranautics, Daiseru 4. Toray-Polyamidic acid, Du Pont-DP-1, Monsanto 6. Cellanese-Polybenzimidazole 9. UOP-CTA 10. North Star-NS-100, UOP-PA-300, -100, LP-300, RC-100 12. North Star-NS-200, Osmonics-NS-200 Envirogenics-SPFA (NS-200), Desalination-NS-200(?) 14. North Triangle Inst.-Plasma Polym. Toray-PEC-1000, Film Tec-FT-30 Asahi Glass-MVP, Nihon Syokubai
Cross-linked water-soluble polymer		Hollow fiber	2. Dow, Monsanto, Toyobo 5. Du Pont 7. Cellanese-Polybensimidazole 13. FRL-NS-200, Gulf South Research Inst.-NS-100
Polymerizable monomer (cross-linking)		Tubular	3. UOP, Envirogenics, Universal Water Co. Raypak, Abcor, PCI, Nitto, Daiseru 8. Teijin-PBIL 11. North Star-NS-100, Others Sumitomo-PAN-Composite Membrane

Membrane Base on Nature

Membrane technologies learn from nature to cover all operations, from molecular separations to chemical conversions, energy and mass transfer, energy conversion and in advanced biomedical applications.

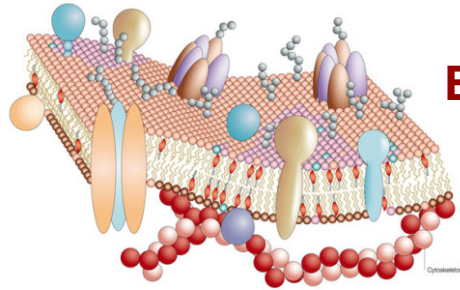


Beehive

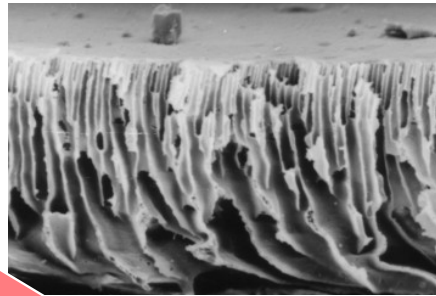


AFM photos of fluoropolymeric membranes with ordered structures

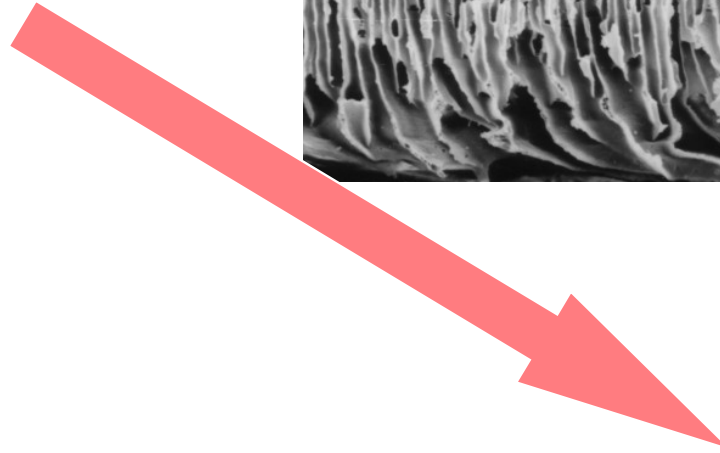
Membrane Base on Nature



Biological Membrane



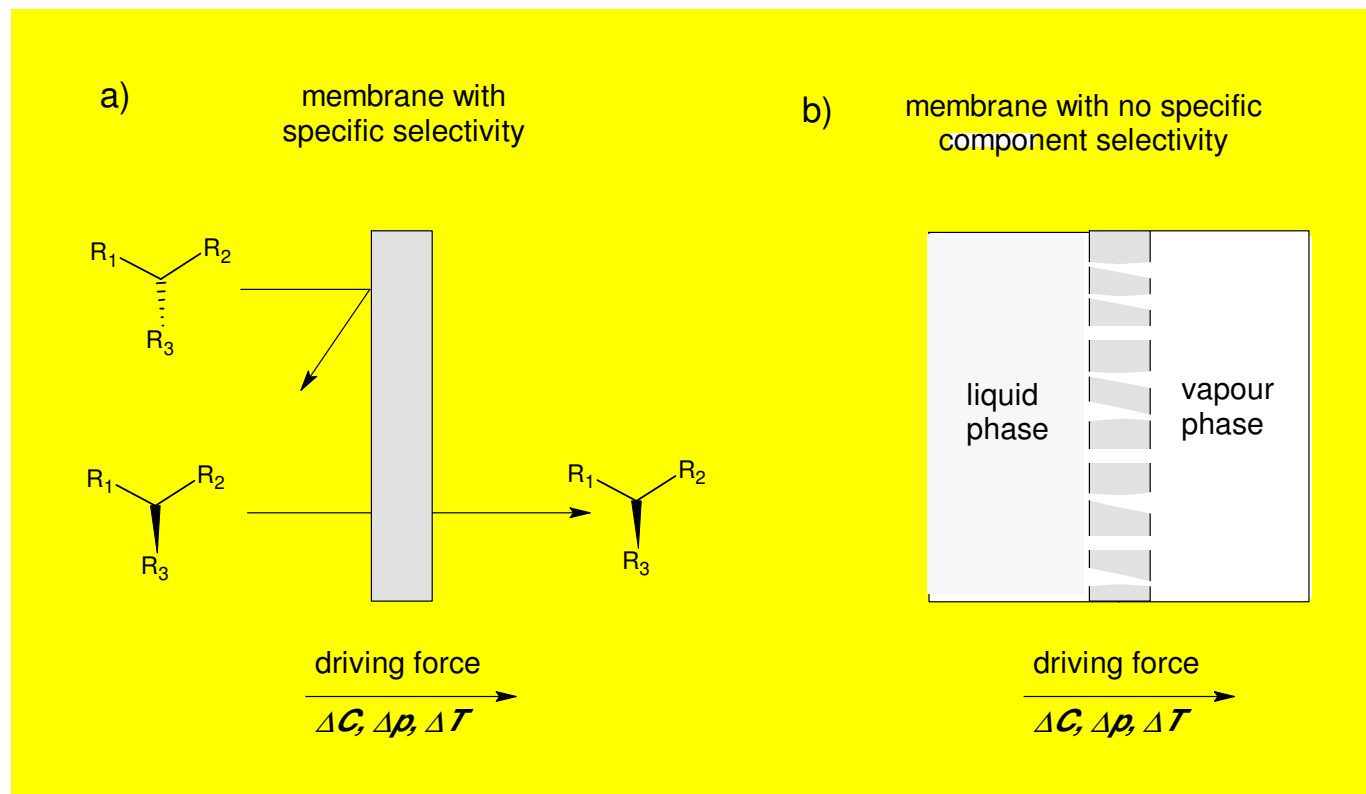
Artificial Membrane



Reverse Osmosis

What is a membrane ?

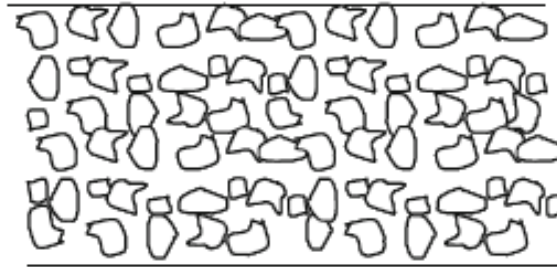
Membrane is a selective or non-selective barrier that separates and/or contacts two adjacent phases and allows or promotes the exchange of matter, energy, and information between the phases in a specific or non-specific manner.



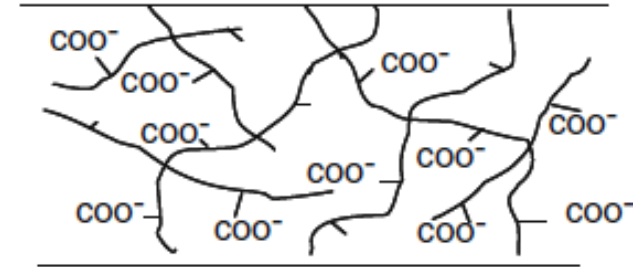
Membrane Morphology



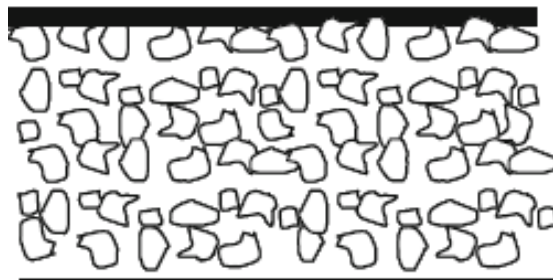
Nonporous dense membrane



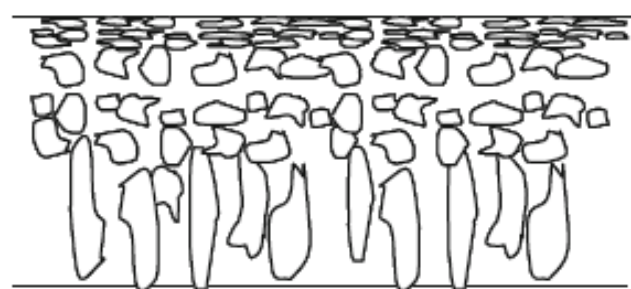
Isotropic microporous membrane



Charged membrane



Composite membranes



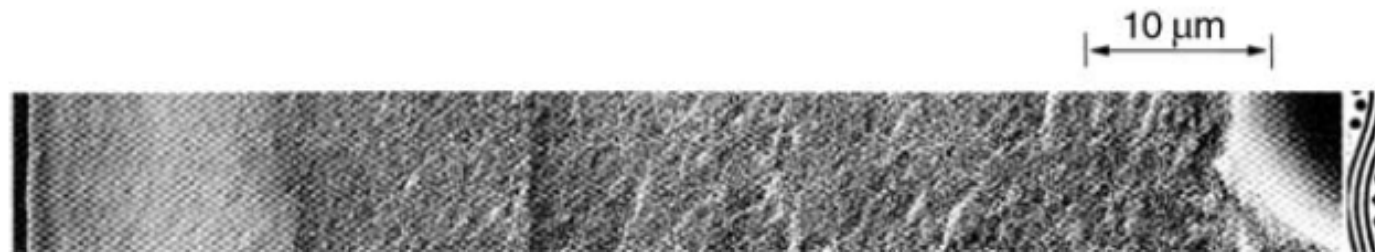
Integrated asymmetric membranes



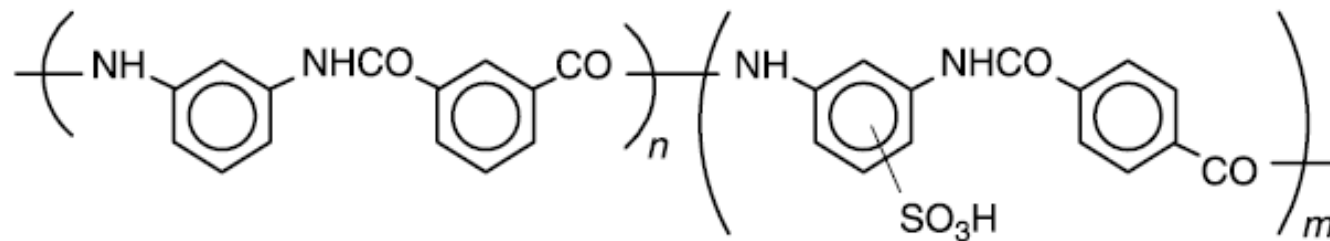
Supported liquid membranes

Schematic diagram of different membrane morphologies

Membrane Morphology



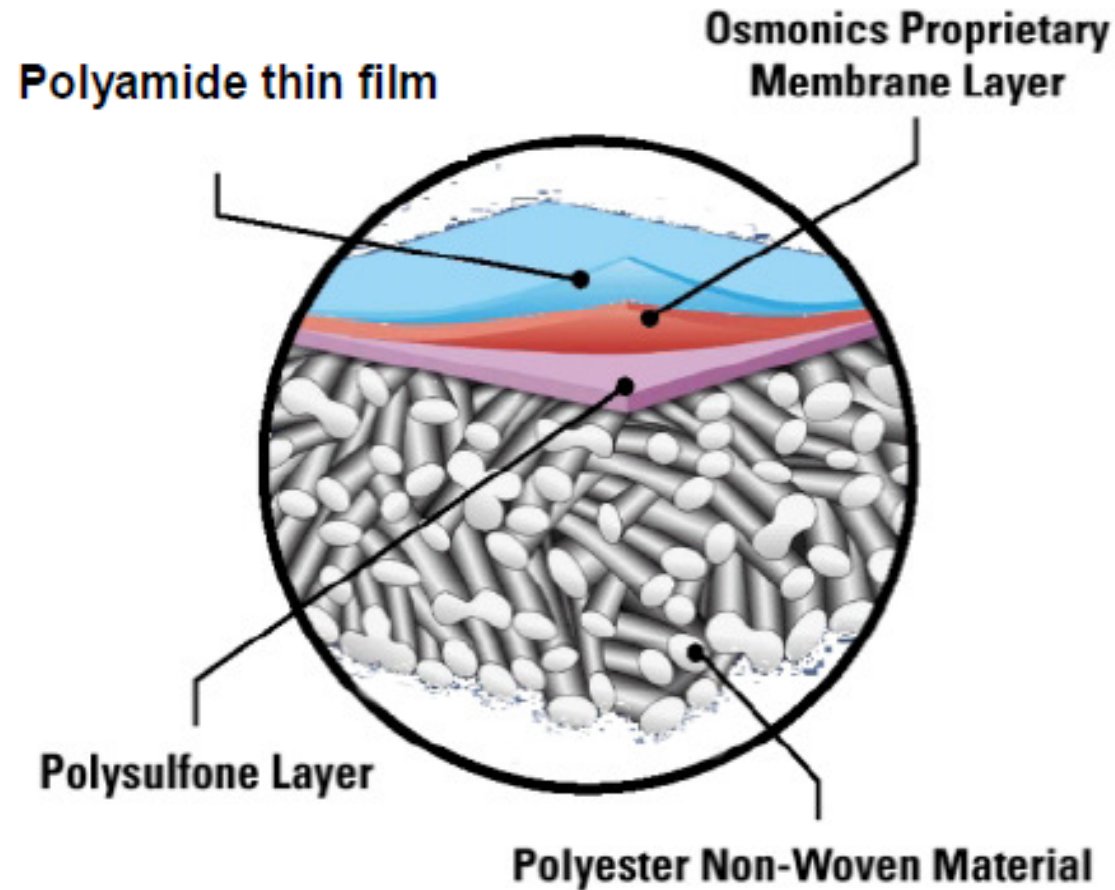
SEM photograph of CA asymmetric membrane



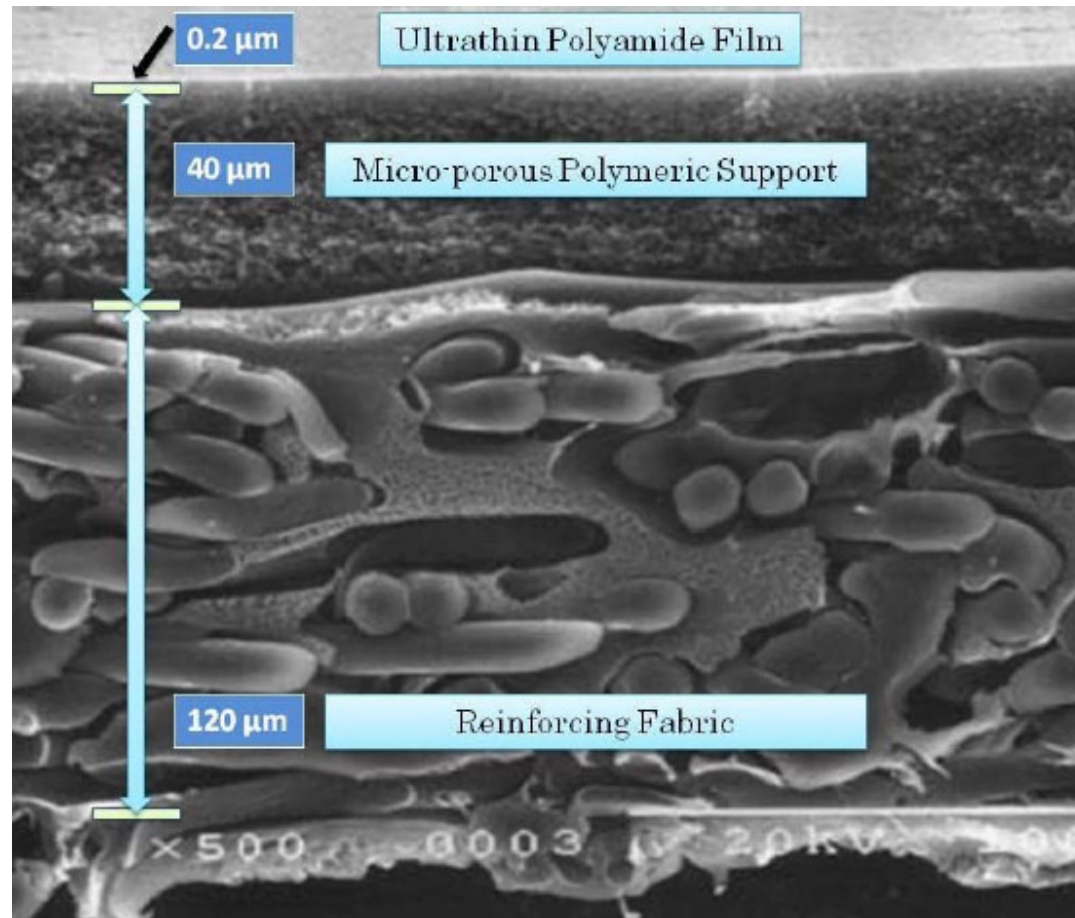
Representative chemical structure of linear polyamide membrane (B-10)



Membrane Morphology

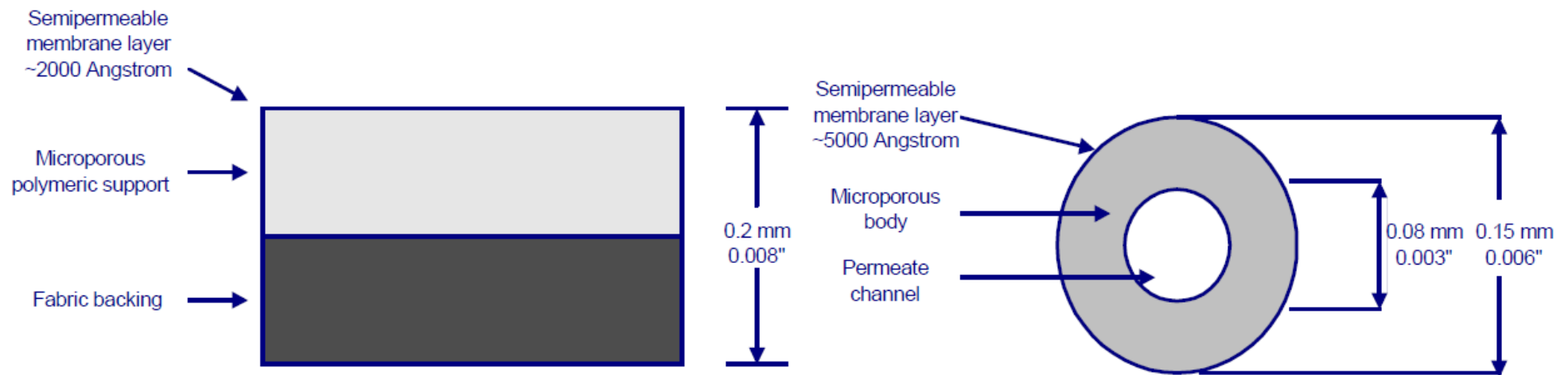


RO Membrane



Structure of Typical RO Membrane

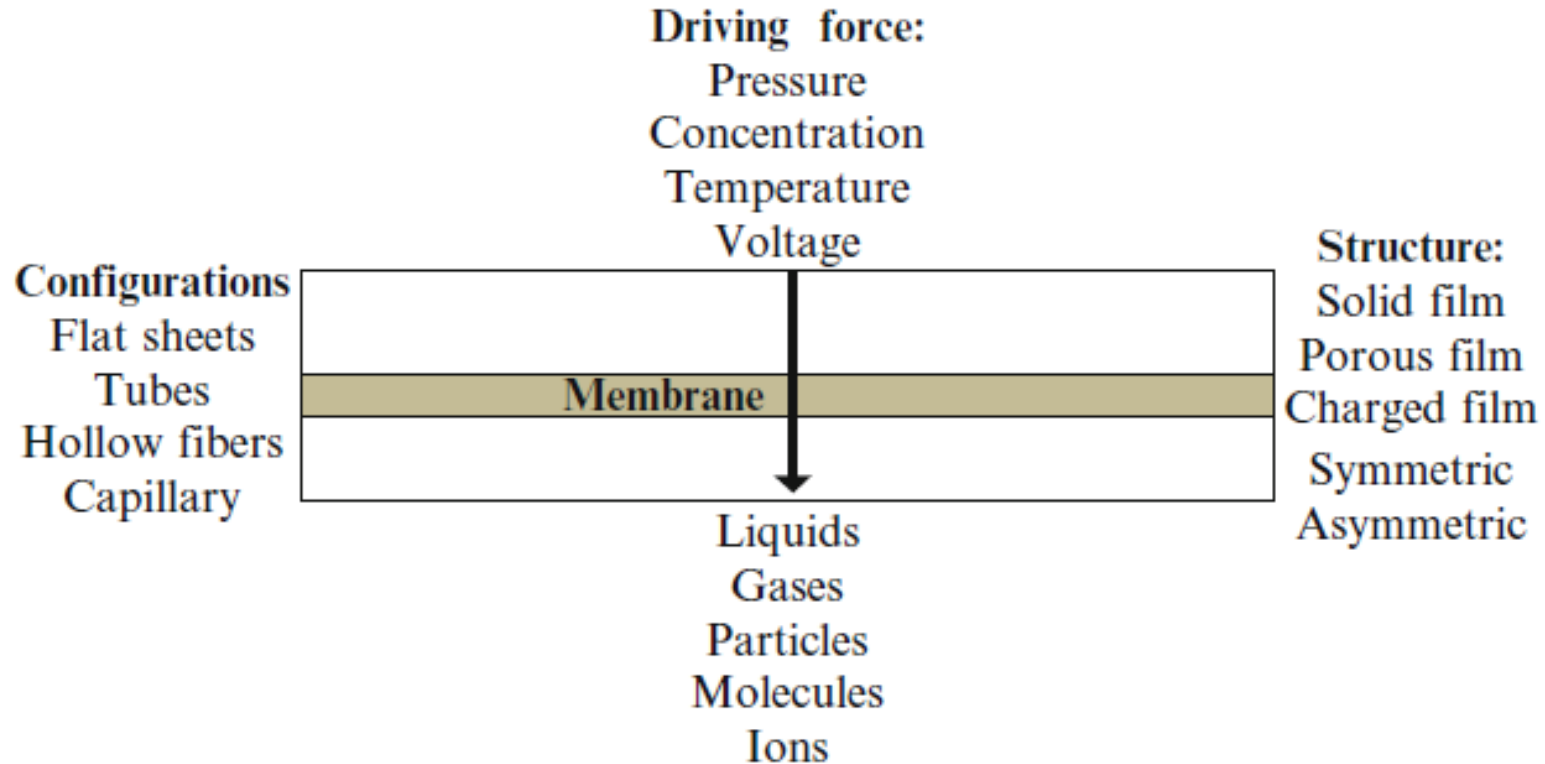
RO Membrane



Cross section of flat and hollow fiber membranes



Membrane Processes



Fundamentals of membrane and membrane processes

Driving Forces for Transport

- In general, four different driving forces are possible in membrane transport:

DRIVING FORCE	PRIMARY EFFECT
Pressure	Flux of solvent
Concentration	Flux of solute
Electrical Potential	Flux of electrical current
Temperature	Flux of thermal energy

- Each of the driving forces have a counter influence on the other fluxes in addition to their primary effect. For example, the pressure gradient can cause a flux of current called the streaming current, besides the flux of solvent.



Membrane Processes - based on Driving Forces

Pressure Gradient (P):

- Reverse osmosis
- Ultrafiltration
- Microfiltration
- Nanofiltration
- Vapor permeation
- Gas permeation
- Pervaporation

Concentration gradient (C):

- Dialysis
- Membrane extraction
- Supported liquid membrane (SLM)
- Emulsion liquid membrane (ELM)
- Non-dispersive solvent extraction with hollow fiber contactors.

Electrical potential Gradient (E):

- Electrodialysis
- Membrane electrolysis
- Electrosorption
- Electrofiltration
- Electrochemical ion exchange

Temperature gradient (T):

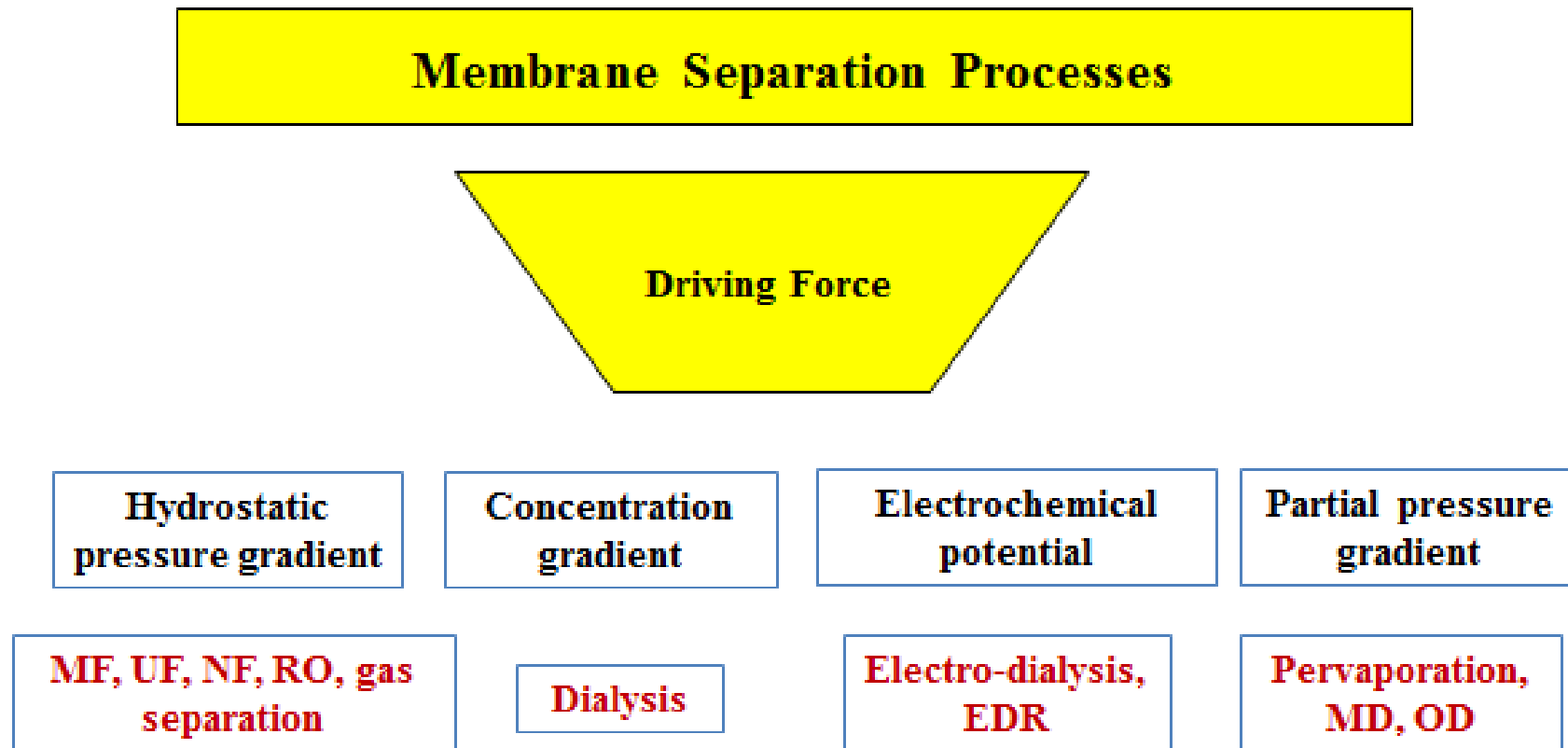
- Membrane distillation
- Thermo-osmosis

Processes with combined driving forces:

- Electro-osmofiltration (P + E)
- Electro-osmotic concentration (E + C)
- Gas separation (P + C)
- Piezodialysis (P + C)



Membrane Processes





Membrane Processes

Process	Applications	Alternative Processes
Microfiltration	Separation of bacteria and cells from solutions	Sedimentation, Centrifugation
Ultrafiltration	Separation of proteins and virus, concentration of oil-in-water emulsions	Centrifugation
Nanofiltration	Separation of dye and sugar, water softening	Distillation, Evaporation
Reverse Osmosis	Desalination of sea and brackish water, process water purification	Distillation, Evaporation, Dialysis
Dialysis	Purification of blood (artificial kidney)	Reverse osmosis
Electrodialysis	Separation of electrolytes from nonelectrolytes	Crystallization, Precipitation
Pervaporation	Dehydration of ethanol and organic solvents	Distillation
Gas Permeation	Hydrogen recovery from process gas streams, dehydration and separation of air	Absorption, Adsorption, Condensation
Membrane Distillation	Water purification and desalination	Distillation

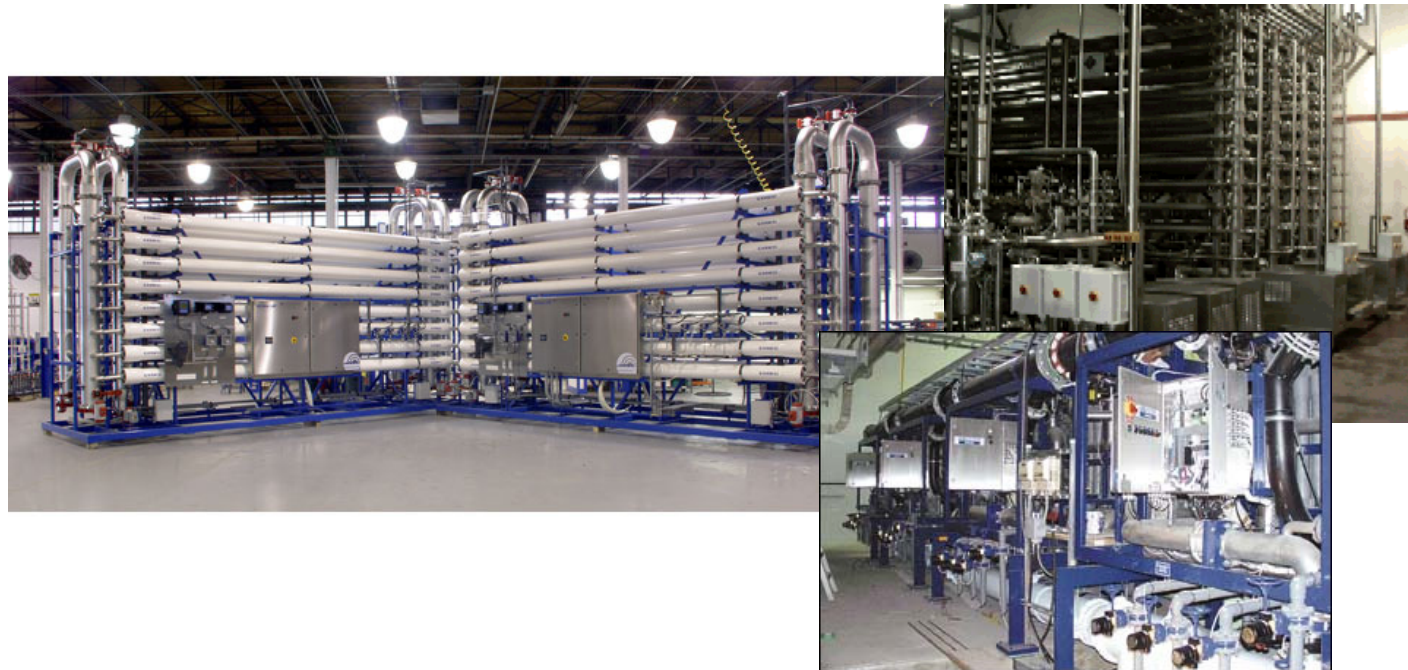


Membrane Processes - Pressure Driven

Separation process	Membrane type used	Applied driving force	Mode of separation	Applications
Microfiltration (MF)	symmetric macroporous, pore radius 0.1-10 μm	hydrostatic pressure 0.05-0.2 MPa	size exclusion, convection	water purification, sterilization
Ultrafiltration (UF)	asymmetric macroporous, pore radius 2-10 nm	hydrostatic pressure 0.1-0.5 MPa	size exclusion, convection	separation of molecular mixtures
Diafiltration (DF)	asymmetric macroporous, pore radius 2-10 nm	hydrostatic pressure 0.1-0.5 MPa	size exclusion and dialysation, diffusion	purification of molecular mixtures artificial kidney
Nanofiltration (NF)	asymmetric mesoporous, pore radius 0.5-2 nm	Hydrostatic pressure 0.3 – 3 MPa	Size exclusion, diffusion, Donnan-exclusion	separation of molecular mixtures and ions
Reverse osmosis (RO)	asymmetric skin-type, dense or microporous	hydrostatic pressure 1-10 MPa	solution-diffusion mechanism	sea & brackish water desalination

Pressure Driven Membrane Processes

- ❖ Pressure driven processes are mature technologies with a large number of successful applications in industrial water and wastewater treatment.
- ❖ Their flexibility in process configurations can optimize performance.
- ❖ They are suitable for system integration with conventional treatment steps.





Pressure Driven Membrane Processes

The following table shows the most used Pressure Driven (PD) Membrane processes and their typical operating values:

PROCESS	PORE SIZE	FLUX (L/m ² h)	PRESSURE (psi)
MF	0.1 to 2 mm	100 – 1000	15 - 60
UF	0.005 to 0.1 mm	30 – 300	10 – 100
NF	0.0005 to 0.005 mm	20 – 150	40 – 200 psig (90 typically)
RO	< 0.5 nm	10 - 35	200 – 300

**PD
membrane
processes
primarily
based on
species size**

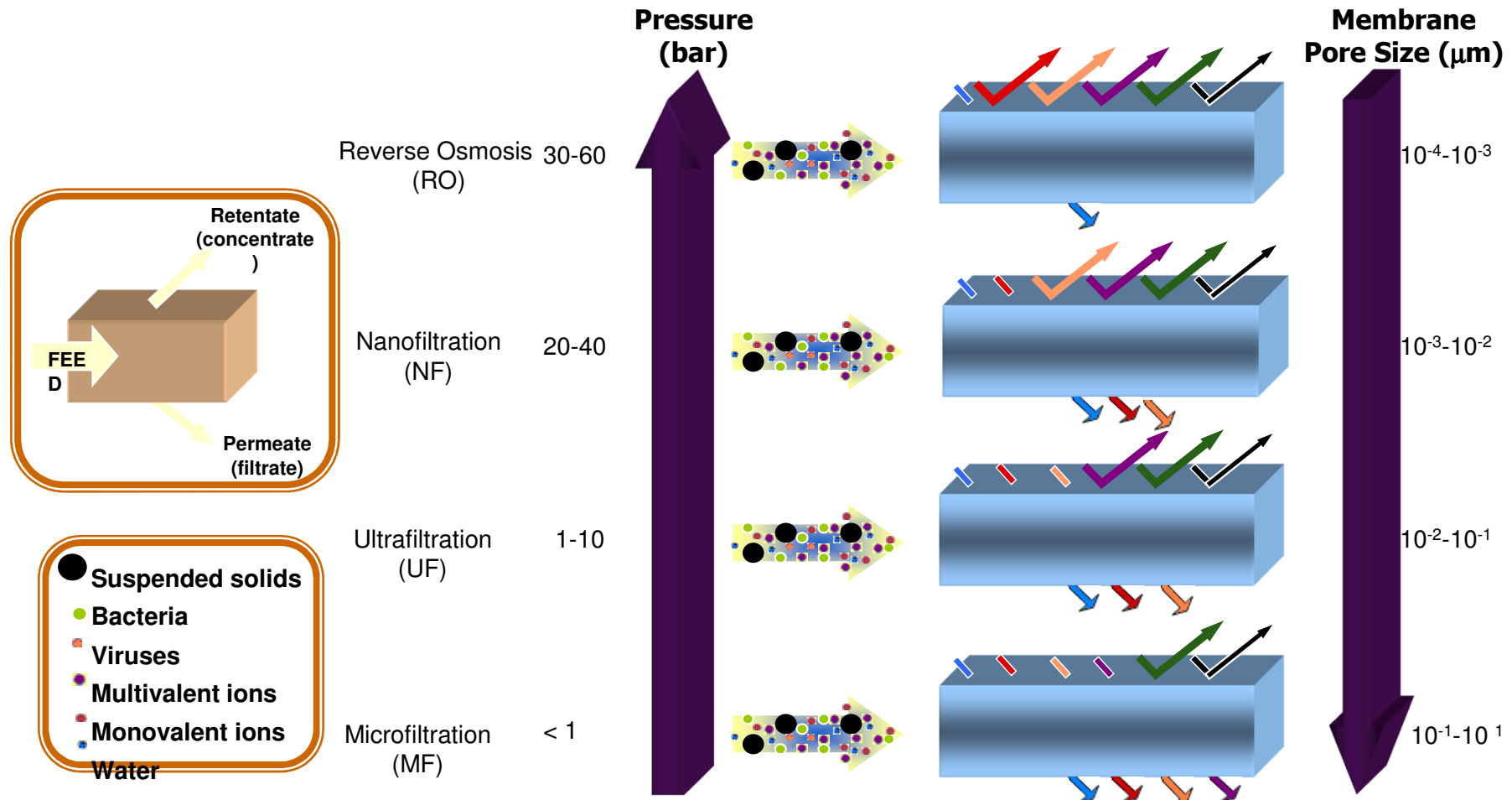


Pressure Driven Membrane Processes

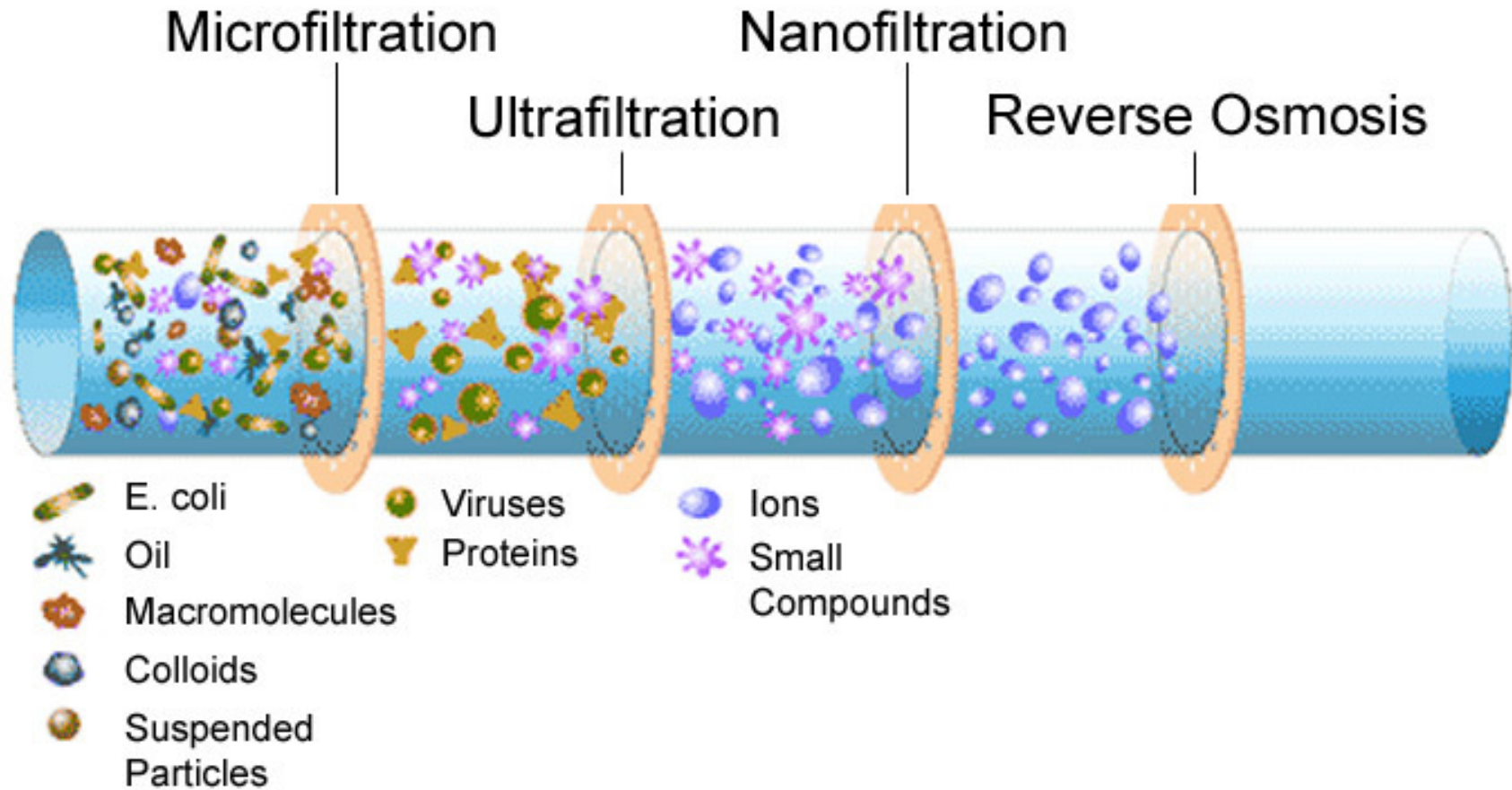
Process	Retentate	Permeate	Common range of feed pressure (atm)	Membrane type	Typical applications/species
Microfiltration	Liquid	Liquid	1.5-7	Porous	Organic and metal suspensions, oil/water emulsions
Ultrafiltration	Liquid	Liquid	2-15	Porous	Oil/water emulsions, pesticides, herbicides, bivalent ions
Reverse osmosis (hyperfiltration or nanofiltration)	Liquid	Liquid	10-70	Porous/nonporous	Desalination, salts, organics, ions, heavy metals
Pervaporation	Liquid	Vapor	1.5-60 (permeate is under vacuum)	Nonporous	Volatile organic compounds
Vapor permeation	Vapor	Vapor	Less than saturation pressure of feed (permeate is under vacuum)	Nonporous	Volatile organic compounds
Gas permeation	Gas	Gas	3.0-55	Nonporous	He, H ₂ , NO _x , CO, CO ₂ , hydrocarbons, chlorinated hydrocarbons

Pressure Driven Membrane Processes

Pressure driven membrane processes are specially useful where a wide range of possible contaminants have to be removed over the entire removal spectrum i.e. macro particles to ionic species.

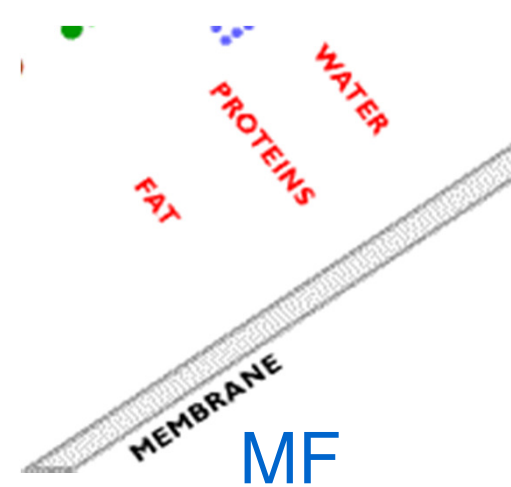
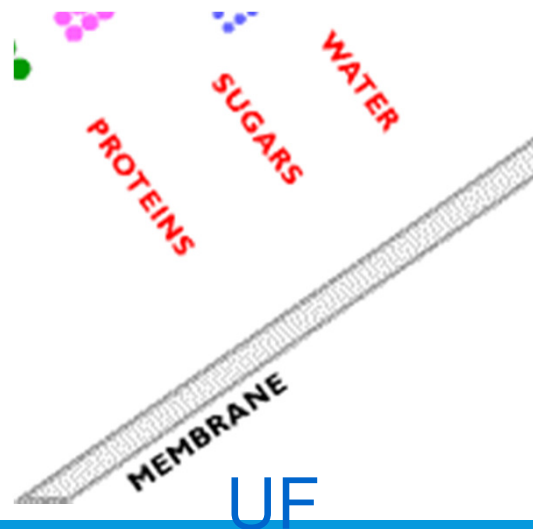
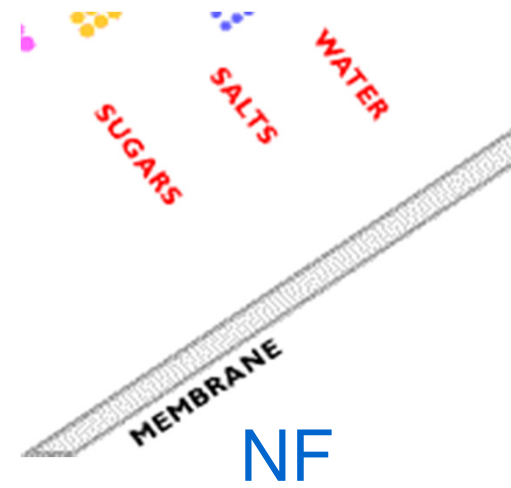
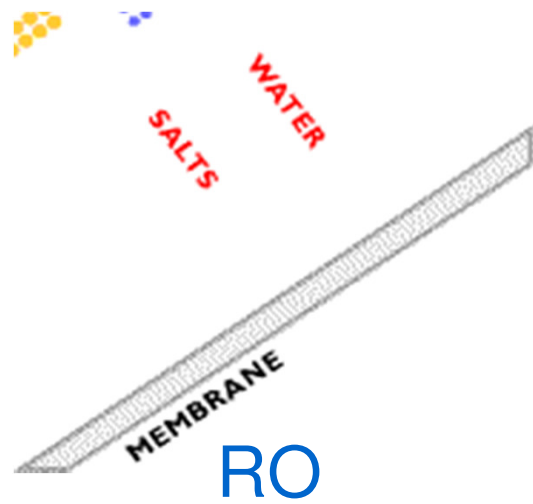


Membrane Processes



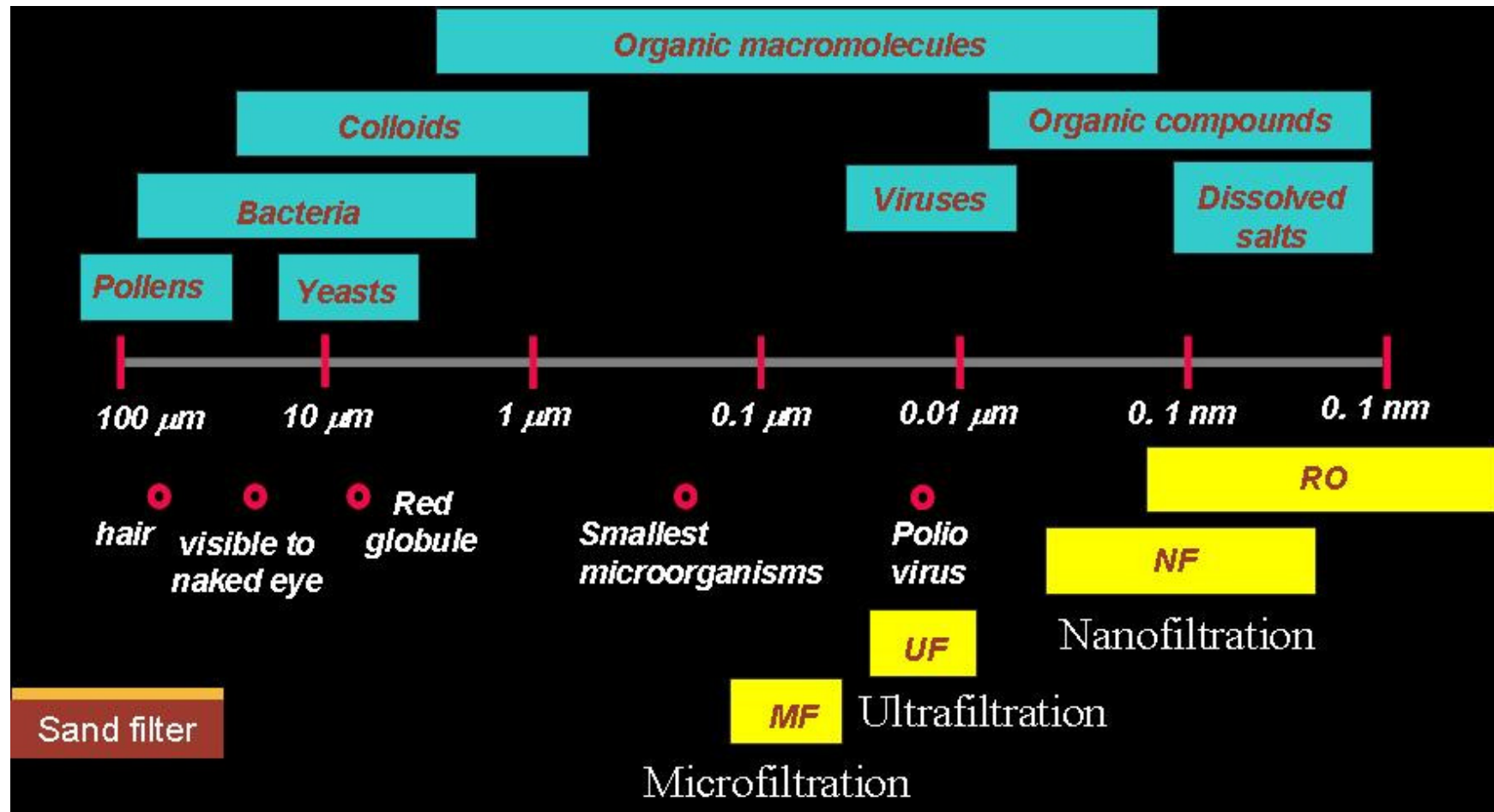


Membrane Processes



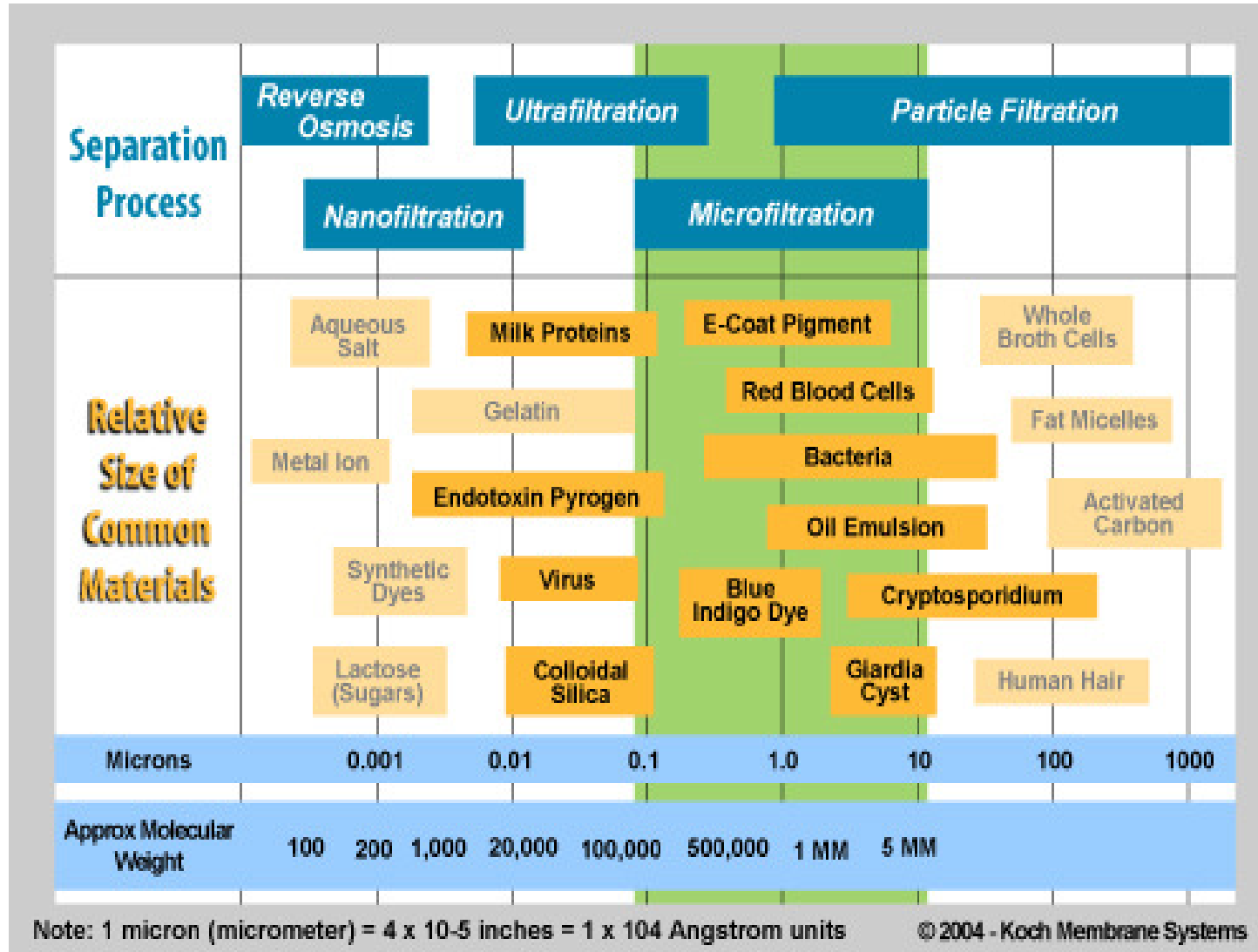


Membrane Processes



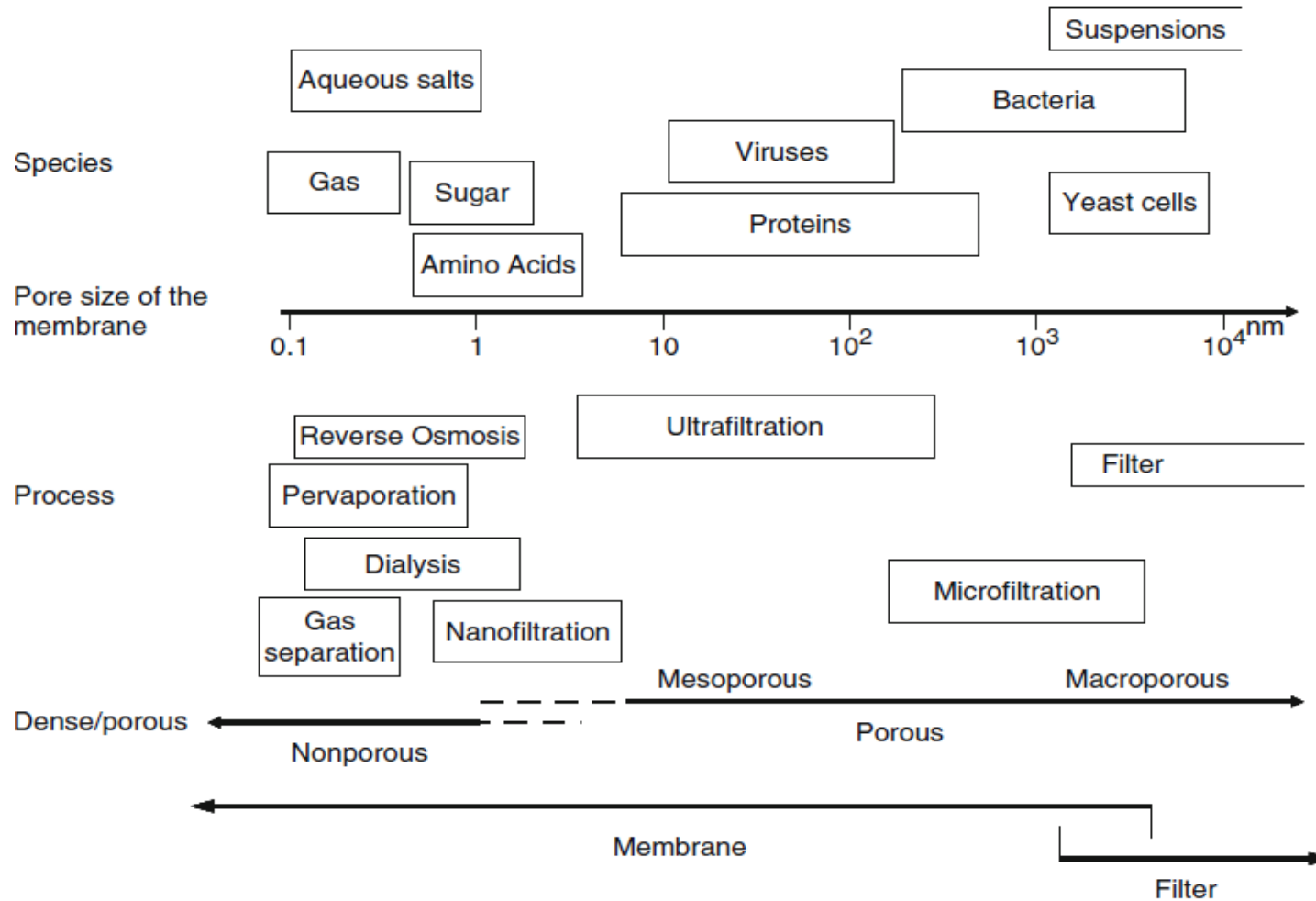


Membrane Processes





Membrane Processes



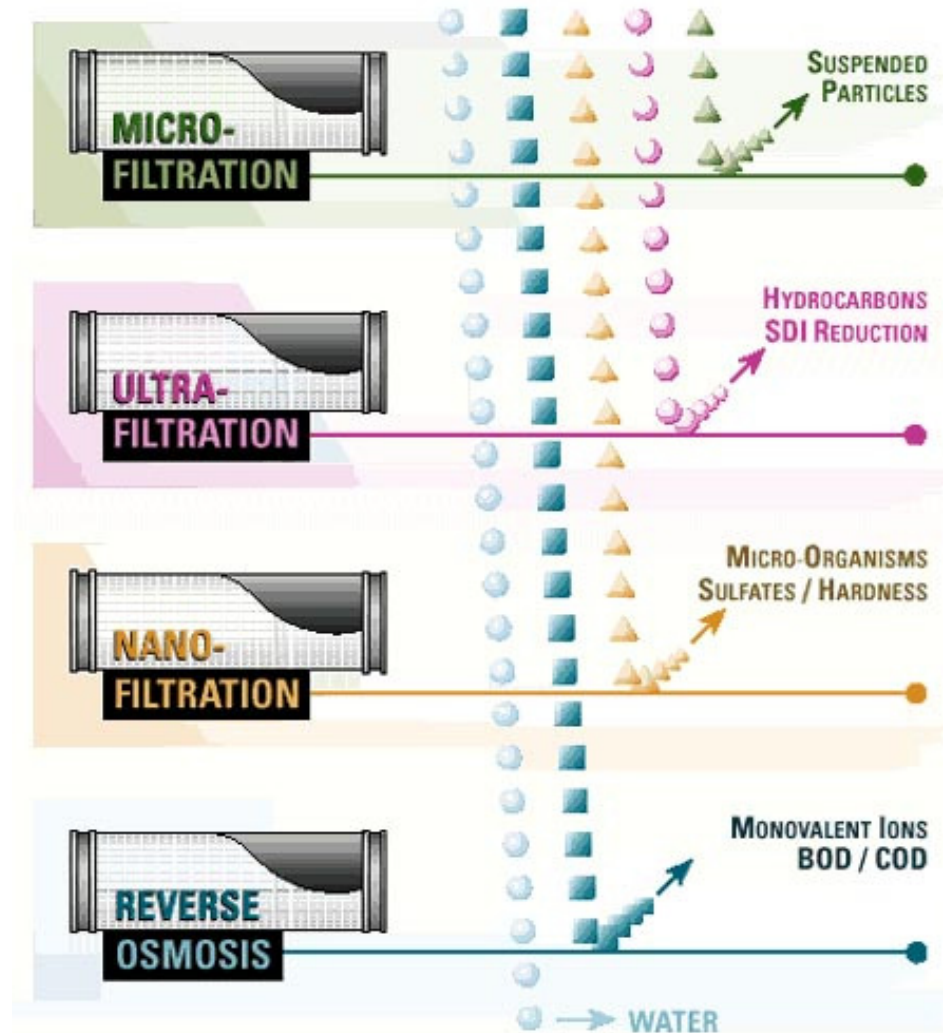
Relationship between membrane pore size and separated species



Membrane Processes

Filter type	Symbol	Pore Size, μm	Operating Pressure, psi	Types of Materials Removed
Microfilter	MF	1.0-0.01	<30	Clay, bacteria, large viruses, suspended solids
Ultrafilter	UF	0.01-0.001	20-100	Viruses, proteins, starches, colloids, silica, organics, dye,
Nanofilter	NF	0.001-0.0001	50-300	Sugar, pesticides, herbicides, divalent anions
Reverse Osmosis	RO	< 0.0001	225-1,000	Monovalent salts

Membrane Separation Spectrum

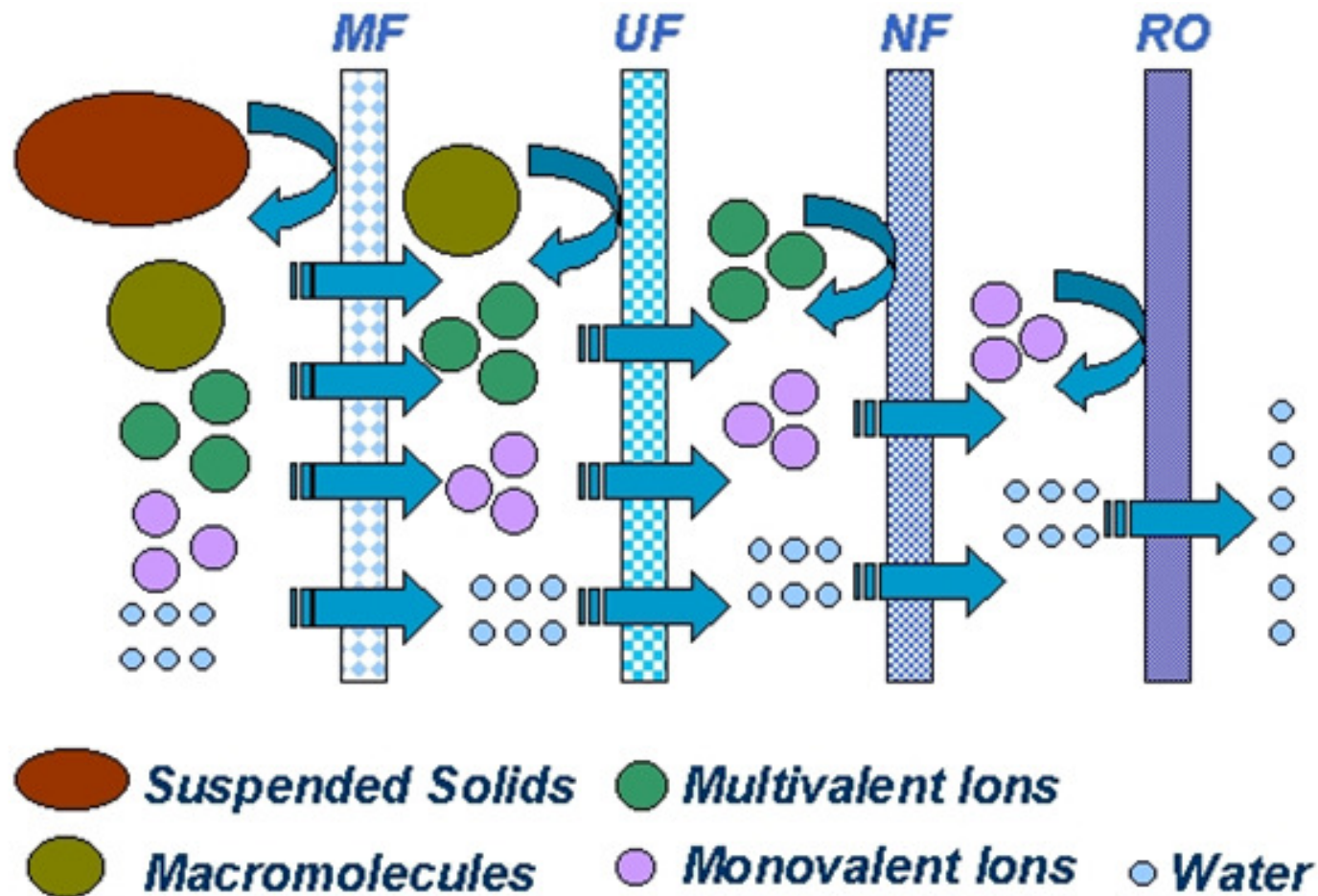


Different layers of the filter

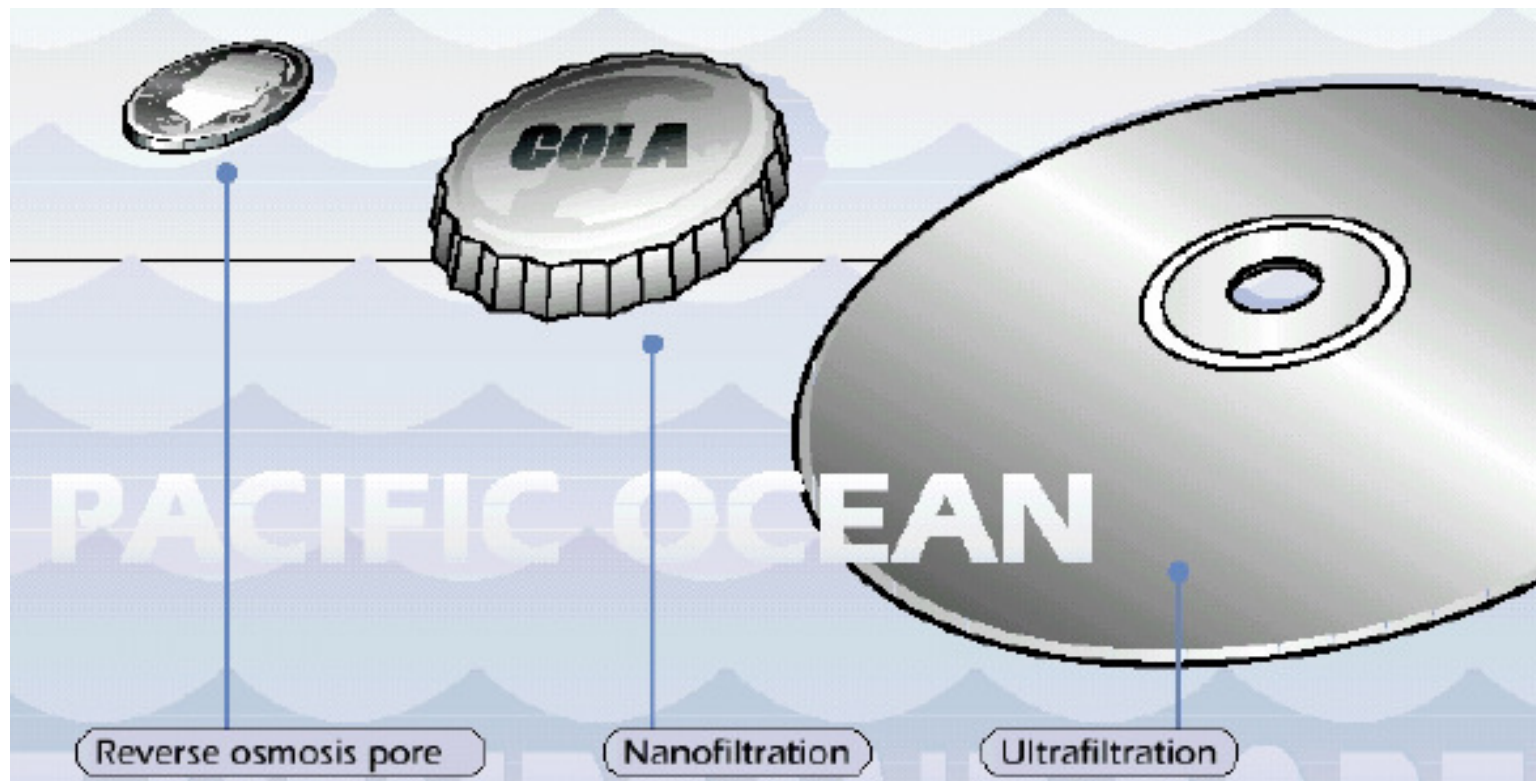
The first filter gets the largest objects out of the water

The last filter layer called the membrane rejects the salt

Membrane Separation Processes



Membrane Separation Processes



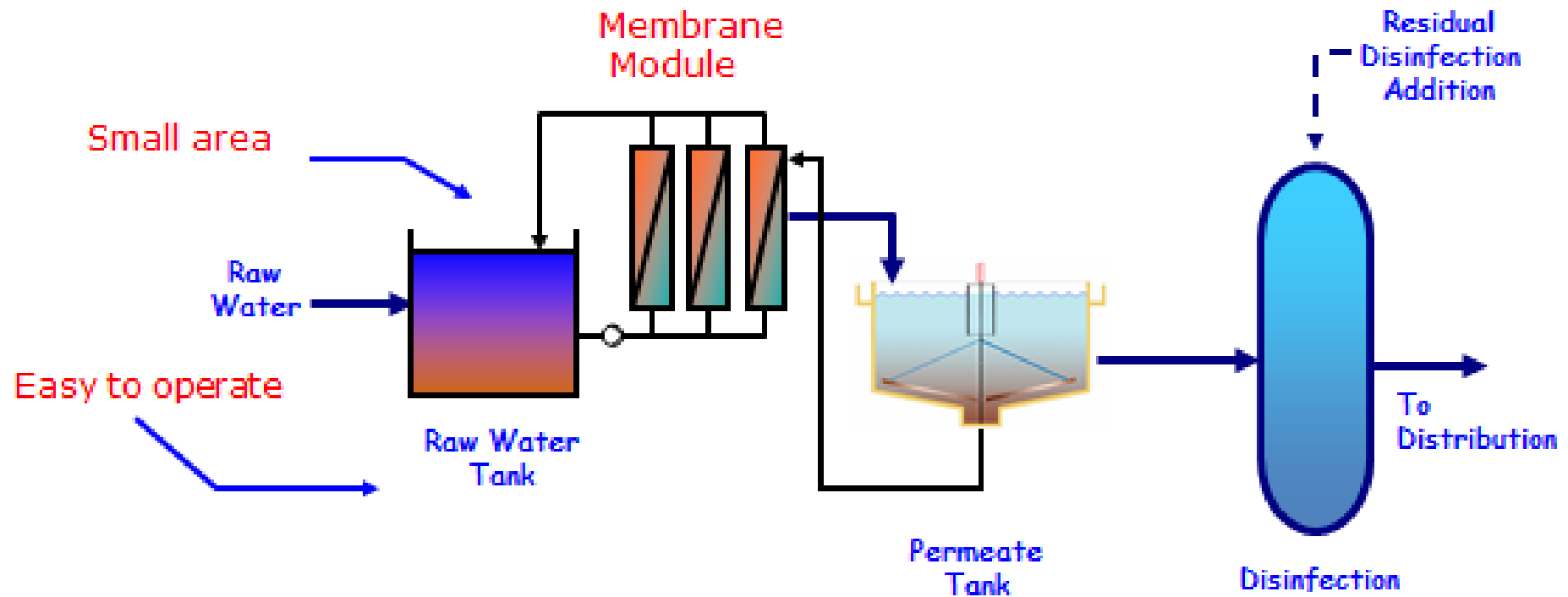
Comparative Size of Membrane Pores



Advantages of Membrane Separation Processes

- Low energy requirement
- Ease of operation
- Continuous separation
- Membrane properties are variable and adjustable
- Portability
- Simplicity
- Compactness
- Environmental friendly
- Direct scale-up

Advantages of Membrane Separation Processes



Comparison between Thermal and Membrane Processes

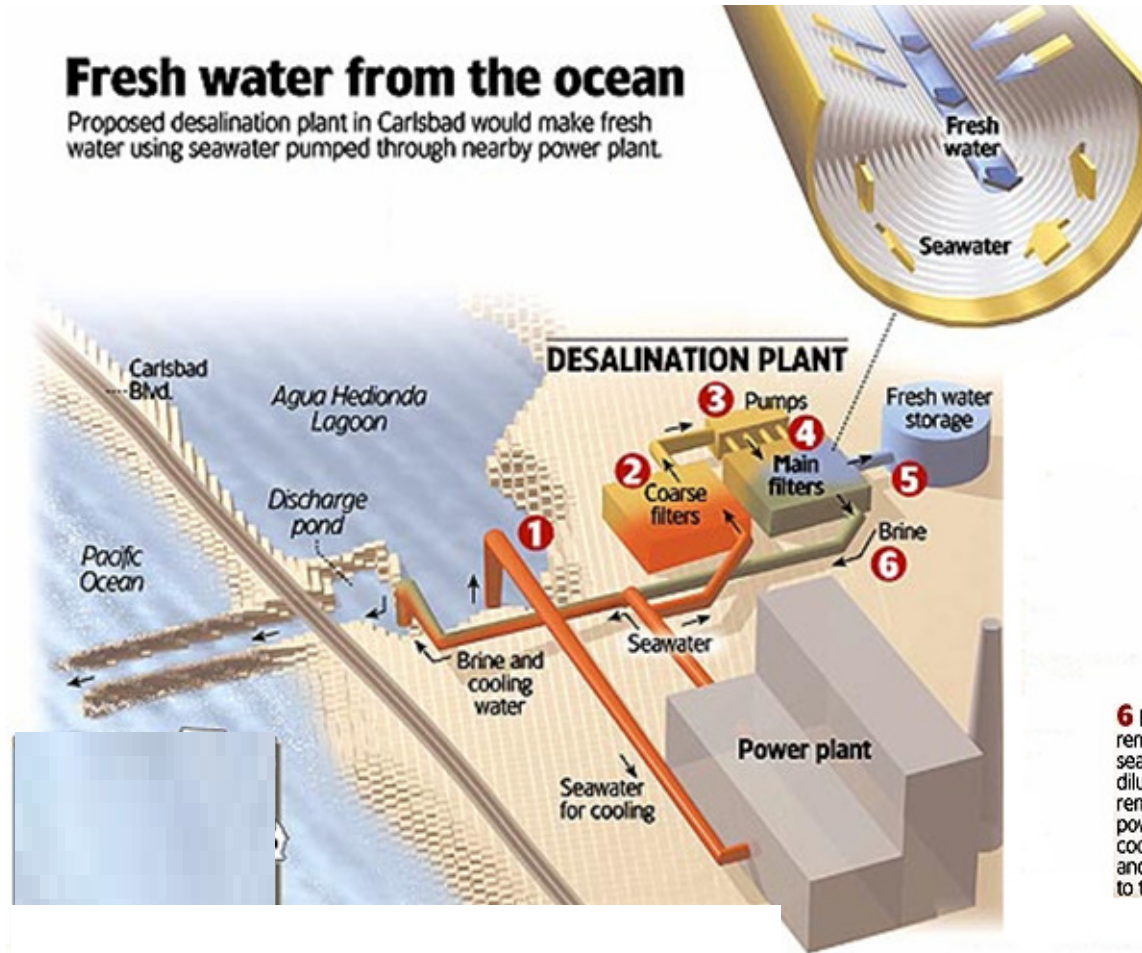
1 Power plant draws cooling water from the ocean. After cooling water runs through the plant, a portion is diverted to the desalination plant.

2 Seawater is pretreated to remove sand and other material that could clog the filtration system.

3 High-pressure pumps force water into reverse osmosis filtration system.

Fresh water from the ocean

Proposed desalination plant in Carlsbad would make fresh water using seawater pumped through nearby power plant.



4 Water squeezes through as many as 19,000 filters to remove salt and other impurities. Clean water migrates to the center of the tubes.

5 The filtered water is treated with lime to adjust the pH before it is ready for distribution.

6 Brine removed from seawater is diluted with remaining power plant cooling water and returned to the ocean.



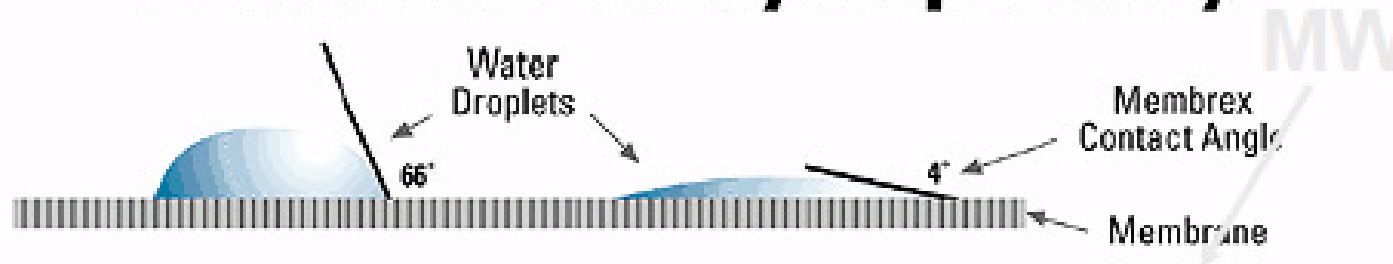
Important Parameters in Membrane Processes

The key properties determining membrane performance are:

- High selectivity,
- High permeability/fluxes,
- Good mechanical, chemical and thermal stability under operating conditions,
- Low fouling tendencies,
- Good compatibility with the operating environment,
- Cost effective,
- Defect-free production

Important Parameters in Membrane Processes

A Measure Of Hydrophilicity



Membrane Material	PTFE	Poly-Propylene	PVDF	Unmodified PAN	Hydrophilic Polysulfone	Ceramic	Membrex UltraChem
Contact Angle	112°	108°	66°	46°	44°	>30°	4°

← Increasing Hydrophilicity →

Oleophilic:

- Repels Water
- Absorbs Oil
- Fouls With Free Oils
- Lower Flux Per Foot
- Diffucult to Clean

Oleophobic:

- Repels Oils
- Absorbs Water
- Not Fouled By Free Oils
- Higher Flux Per Foot
- Easier to Clean



Membrane Processes

Microfiltration and Ultrafiltration are essentially membrane processes that rely on pure straining through porosity in the membranes. Pressure required is lower than RO and due entirely to frictional headloss

Nanofiltration: divalent cations and anions are preferentially rejected over the monovalent cations and anions. Some organics with MW > 100 -500 are removed. There is an osmotic pressure developed but it is less than that of the RO process.

RO: is semi-permeable with thin layer of membrane supported on a porous sub-structure. The thin skin is about 0.25 μ thick and has pore size of 5 - 10 \AA . The pore size of the skin limits transport to certain size molecules. Dissolved ions such as Na and Cl are about the same size as water molecules.



Membrane Processes

Typical recoveries, trans-membrane pressures,
power requirements, consumption

	Recovery (%)	Pressure (kPa)	Consumption (kWh/day)
MF	90–98	100	77.5–70.8
UF	90–98	300	231.5–212.5
NF	75–95	500	463.5–365.5
RO	50–80	1000	1389–868.3



Membrane Manufacturers in the World

		RO	NF	UF	MF	MBR
Overseas	DOW / Filmtec (US)	⊙	⊙		○	○
	Koch (US)	⊙	△	○	○	○
	GE (US)	○	○	⊙		⊙
	Siemens (Germany)				⊙	○
	Norit (Netherlands)			⊙		○
Japanese	Toray	⊙	○	○	○	○
	Nitto Denko /Hydranautics (US)	⊙	⊙	○	○	
	Mitsubishi Rayon				○	○
	Toyobo	○		△	△	
	Daicel Chemical	○		○		
	Asahi Chemical / Pall (US)			○	⊙	○
	Kubota					⊙

⊙:High share product ○:product in the market △:under development



Membrane Processes

Water quality parameters to be measured

Parameter	MF/UF	NF/RO
Cations		
Aluminum		X
Ammonia		X
Barium		X
Calcium	X	X
Iron	X	X
Magnesium	X	X
Manganese	X	X
Potassium		X
Sodium		X
Strontium		X
Anions		
Chloride		X
Fluoride		X
Nitrate		X
Silica	X	X
Sulfate		X
Other chemical/physical parameters		
Algae	X	
Alkalinity		X
pH	X	X
SDI		X
TDS		X
TOC	X	X
TSS	X	
Turbidity	X	X
UV-254	X	X



Membrane Processes

List of commercial membranes: compositions and applications

Membranes	Membrane materials	Applications
Organic membrane	Cellulose regenerated	D, UF, MF
	Cellulose nitrate	MF
	Cellulose acetate	GS, RO, D, UF, MF
	Polyamide	RO, NF, D, UF, MF
	Polysulphone	GS, UF, MF
	Poly(ether sulphone)	UF, MF
	Polycarbonate	GS, D, UF, MF
	Poly(ether imide)	UF, MF
	Poly(2,6-dimethyl-1,4-phenylene oxide)	GS
	Polyimide	GS
	Poly(vinylidene fluoride)	UF, MF
	Polytetrafluoroethylene	MF
	Polypropylene	MF
	Polyacrylonitrile	D, UF, MF
	Poly(methyl methacrylate)	D, UF
Poly(vinyl alcohol)	PV	
Polydimethylsiloxane	PV, GS	
<i>Inorganic membrane</i>		
Ceramic	Metal (Al, Zn, Ti, Si, etc.) oxide	PV, MF
	Metal (Al, Zn, Ti, Si, etc.) nitride	
	Metal (Al, Zn, Ti, Si, etc.) carbide	
Metallic	Metal (Al, Zn, Ti, Si, etc.) oxide	PV, MF
Zeolite	SiO ₂	PV, GS

MF microfiltration, *UF* ultrafiltration, *NF* nanofiltration, *D* dialysis, *PV* pervaporation, *GS* gas separation, *RO* reverse osmosis.

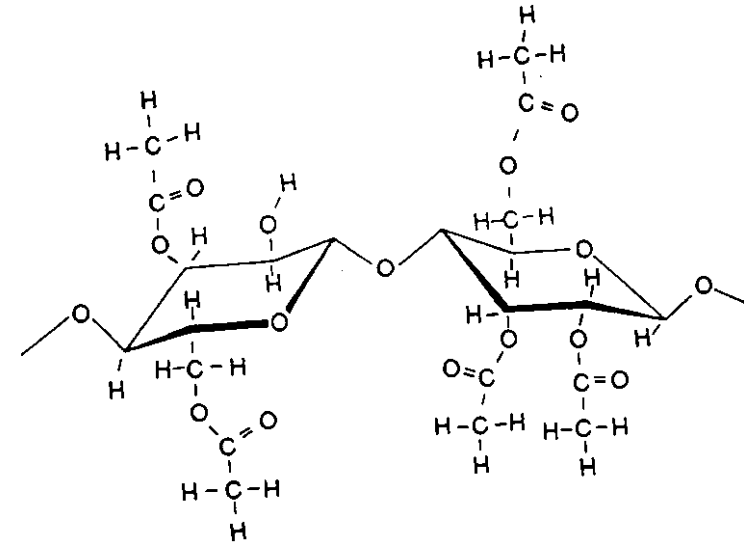


Membrane Materials

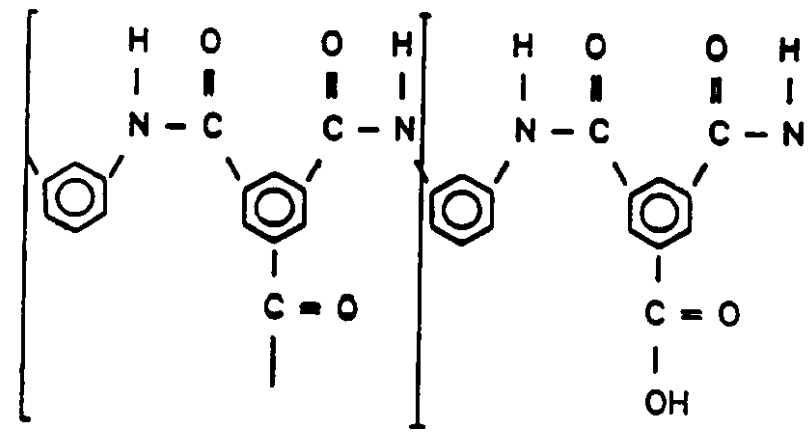
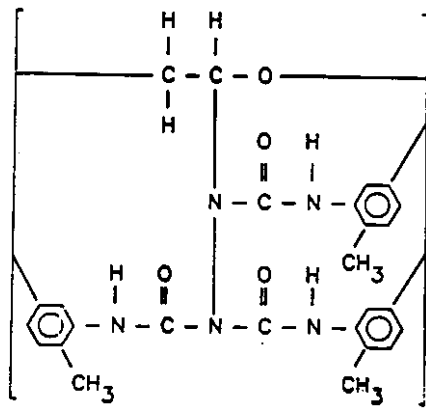
- Made from a thin film of polymeric material (several thousands angstrom) which cast on polymeric porous material
- Commercial membranes have high water permeability; the rate of water permeability must be much higher than salt permeability
- Must be stable over a wide range of pH and T
- Must have good mechanical integrity
- Life of commercial membranes = 3-5 years
- Major types of commercial membranes are cellulose acetate (CA) and polyamides (PA)

Membrane Materials

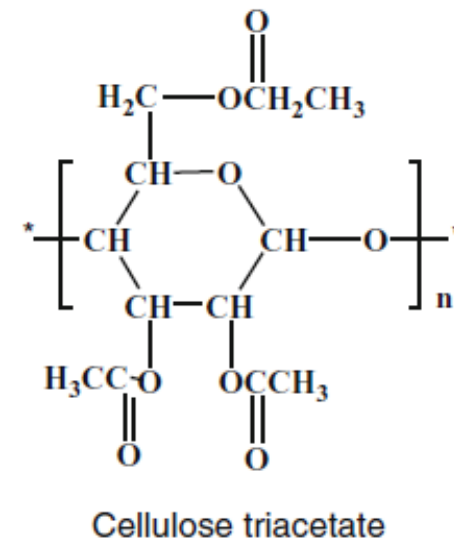
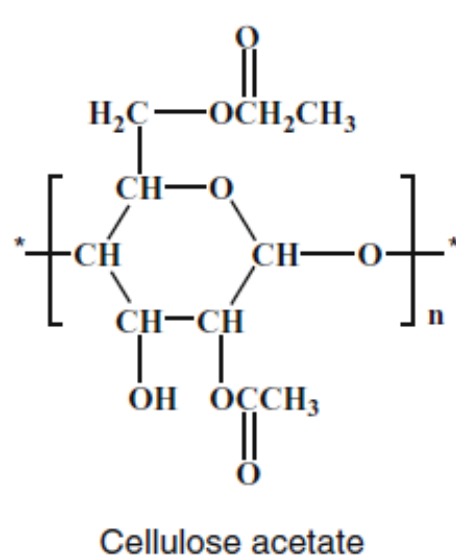
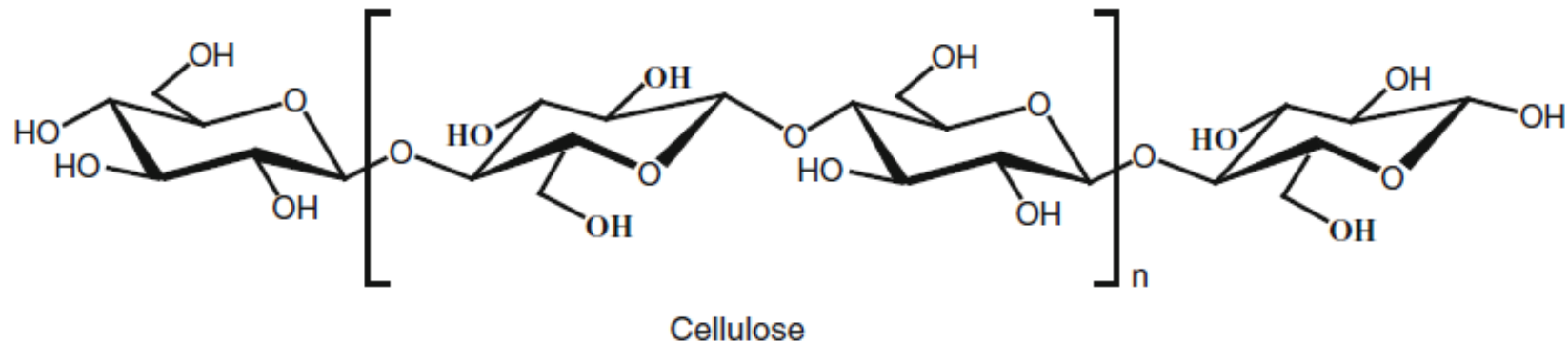
- Cellulose Acetate and Derivatives



- Polyamides

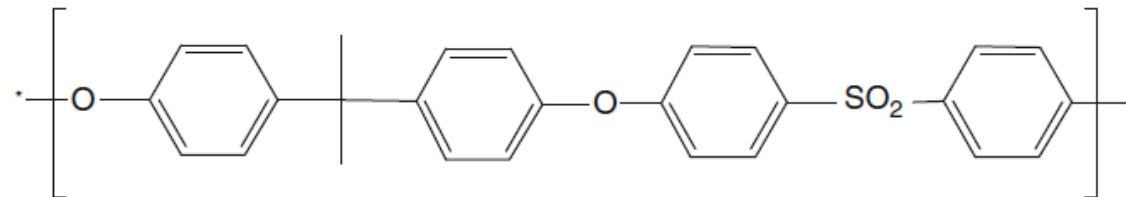


Membrane Materials

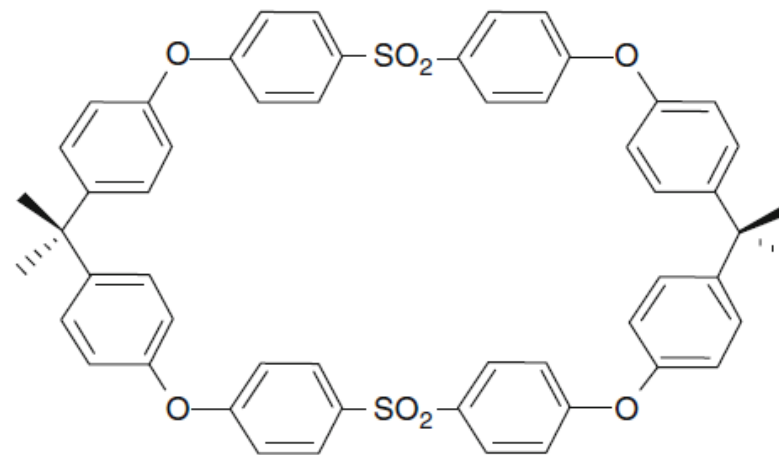


Chemical structures of cellulose, cellulose acetate and triacetate

Membrane Materials



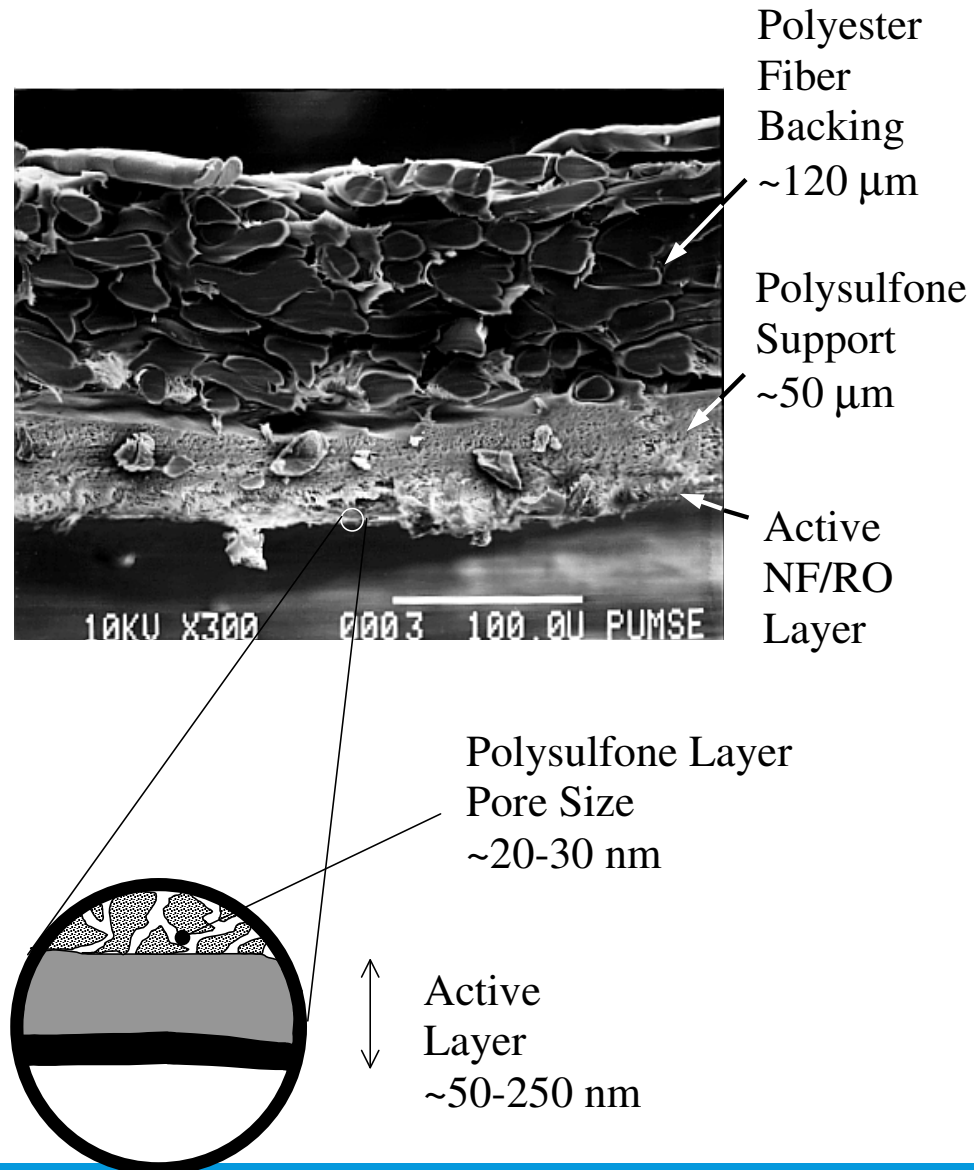
Udel polysulfone



Polysulfone cyclic dimer

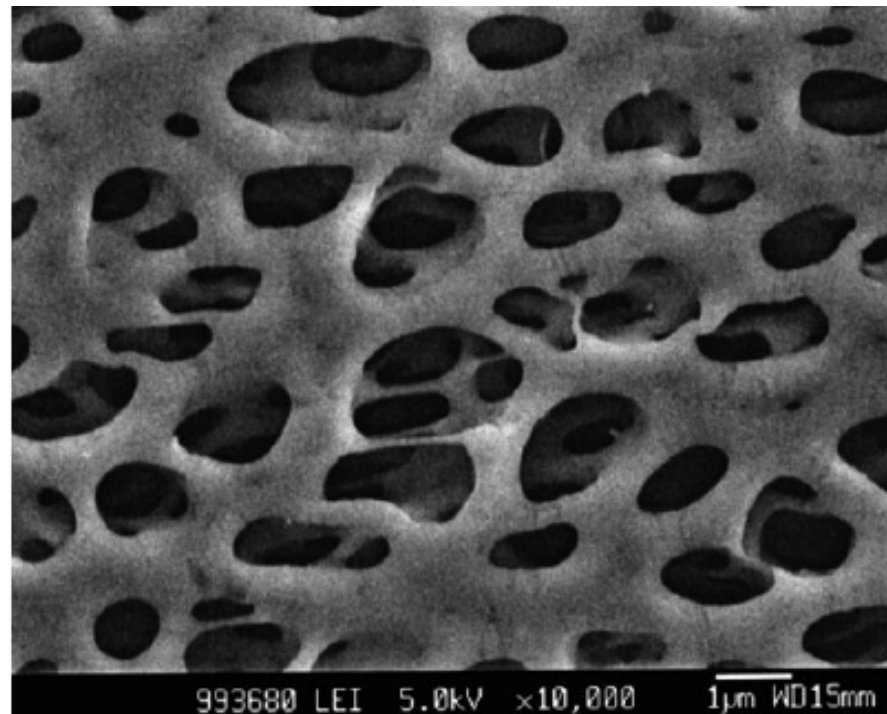
Chemical structure of polysulfone

Thin Film Composite





Porous Polymeric Membrane





Thin Film Composite / Cellulose Acetate

Comparison of Thin-Film Composite and Cellulose Acetate Membranes

Parameter	Thin-Film Composite Membranes	Cellulose Acetate Membranes
Salt rejection, %	Higher (>99.6%)	Lower (Up to 99.5%)
Net driving pressure, bars	Lower (10–15 bars)	Higher (15–30 bars)
Surface charge	Anionic (limits use of cationic pretreatment coagulants)	Neutral (no limitations on pretreatment coagulants)
Chlorine tolerance	Poor (Up to 1000 ppm-h) feed dechlorination needed	Good; continuous feed of 1–2 ppm of chlorine is acceptable
Cleaning frequency	High (weeks to months)	Lower (months to years)
Pretreatment requirements	High (SDI < 4)	Lower (SDI < 5)
Organics removal	High	Relatively lower
Biogrowth on membrane surface	May cause performance problems	Limited—not a cause of performance problems
pH tolerance	High (1–13)	Limited (4–6)



Cellulose Acetate / Polyamide

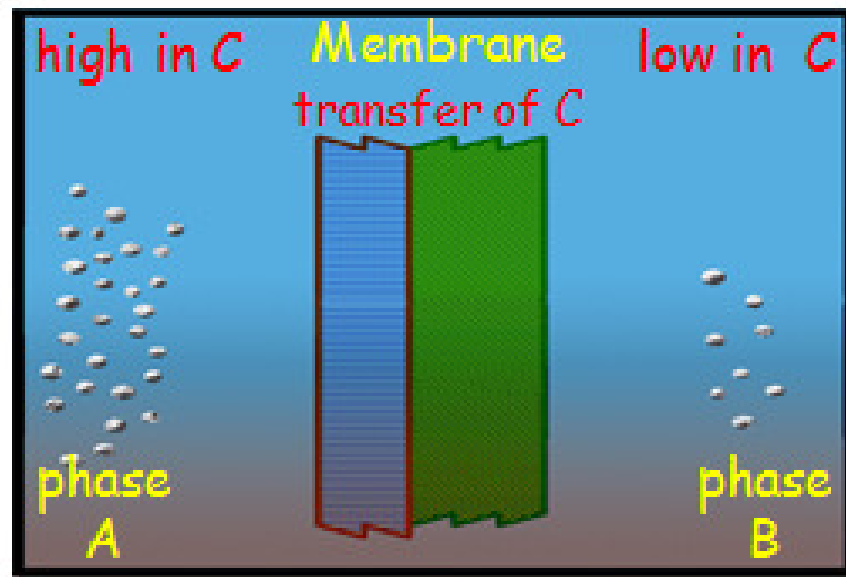
Comparison between symmetric cellulose acetate (CA) membranes and polyamide and polyurea composite membranes

	Asymmetric CA membranes	Polyamide and polyurea composite membranes
Advantages	<ul style="list-style-type: none">• Chlorine-resistant• Tolerant to oxidation• Inexpensive	<ul style="list-style-type: none">• Higher water flux• Higher salt and organic rejections• Higher temperature and pH (4–11)• Immune to biological attack and compaction
Disadvantages	<ul style="list-style-type: none">• Subject to hydrolysis• Susceptible to biological attack• Compaction at high pressures• Narrow pH range (4.5–7.5)• Lower upper temperature limits (~35°C)	<ul style="list-style-type: none">• Less chlorine-resistant• Susceptible to oxidation• More expensive

Semi-Permeable Membrane

Membrane: A selective barrier that allows specific entities to pass through, while retaining the passage of others. The ability of the membrane to differentiate amongst entities is termed its **selectivity**.

It can separate particles and molecules by combination of sieving and diffusion mechanisms over a wide particle size range and molecular weights

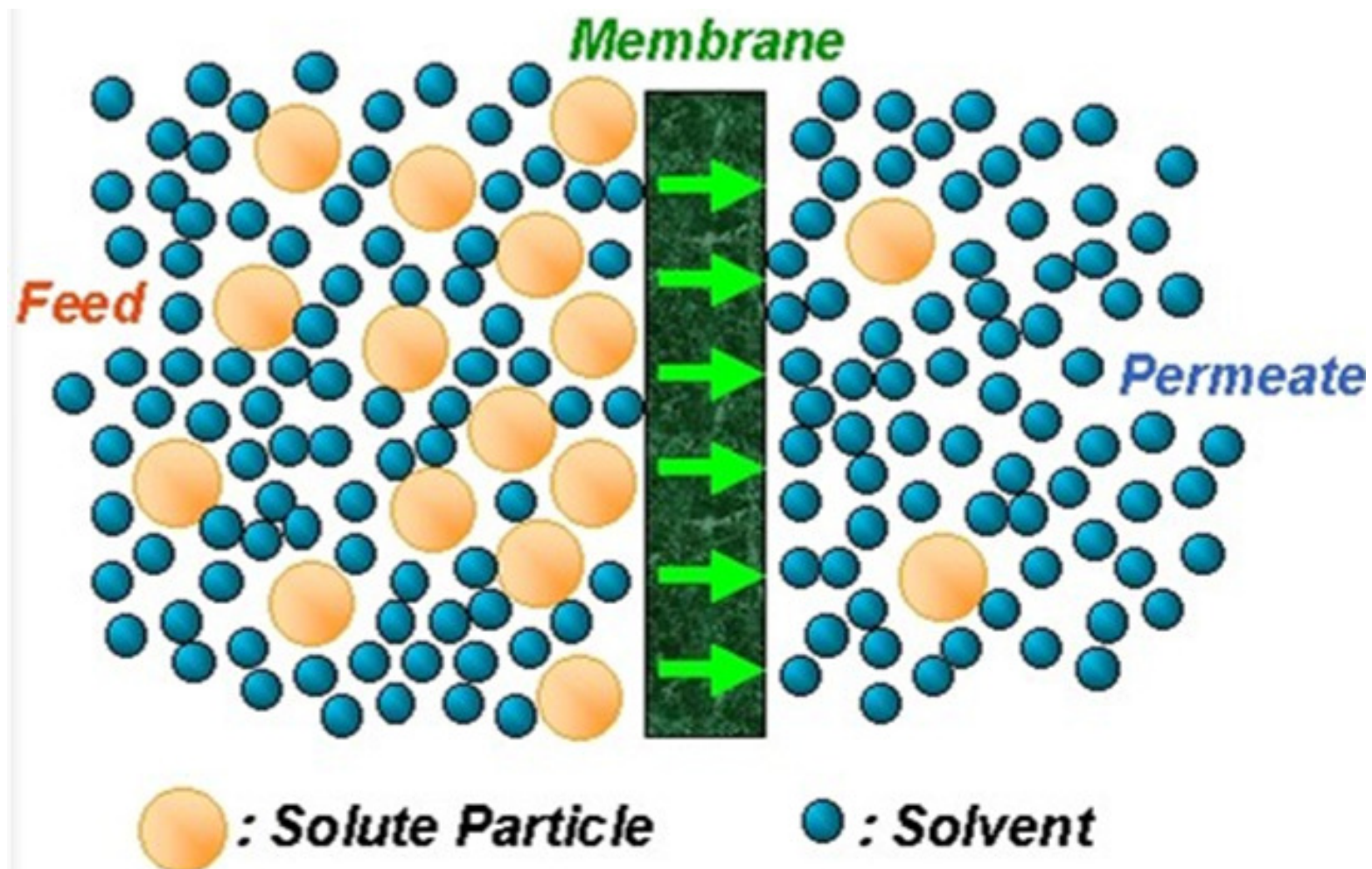




Semi-Permeable Membrane

- Semi-permeable refers to a membrane that selectively allows certain species to pass through it while retaining others.
- In actuality, many species will pass through the membrane, but at significantly different rates.
- In RO, the solvent (water) passes through the membrane at a much faster rate than the dissolved solids (salts). The net effect is that a solute-solvent separation occurs, with pure water being the product.

Semi-Permeable Membrane



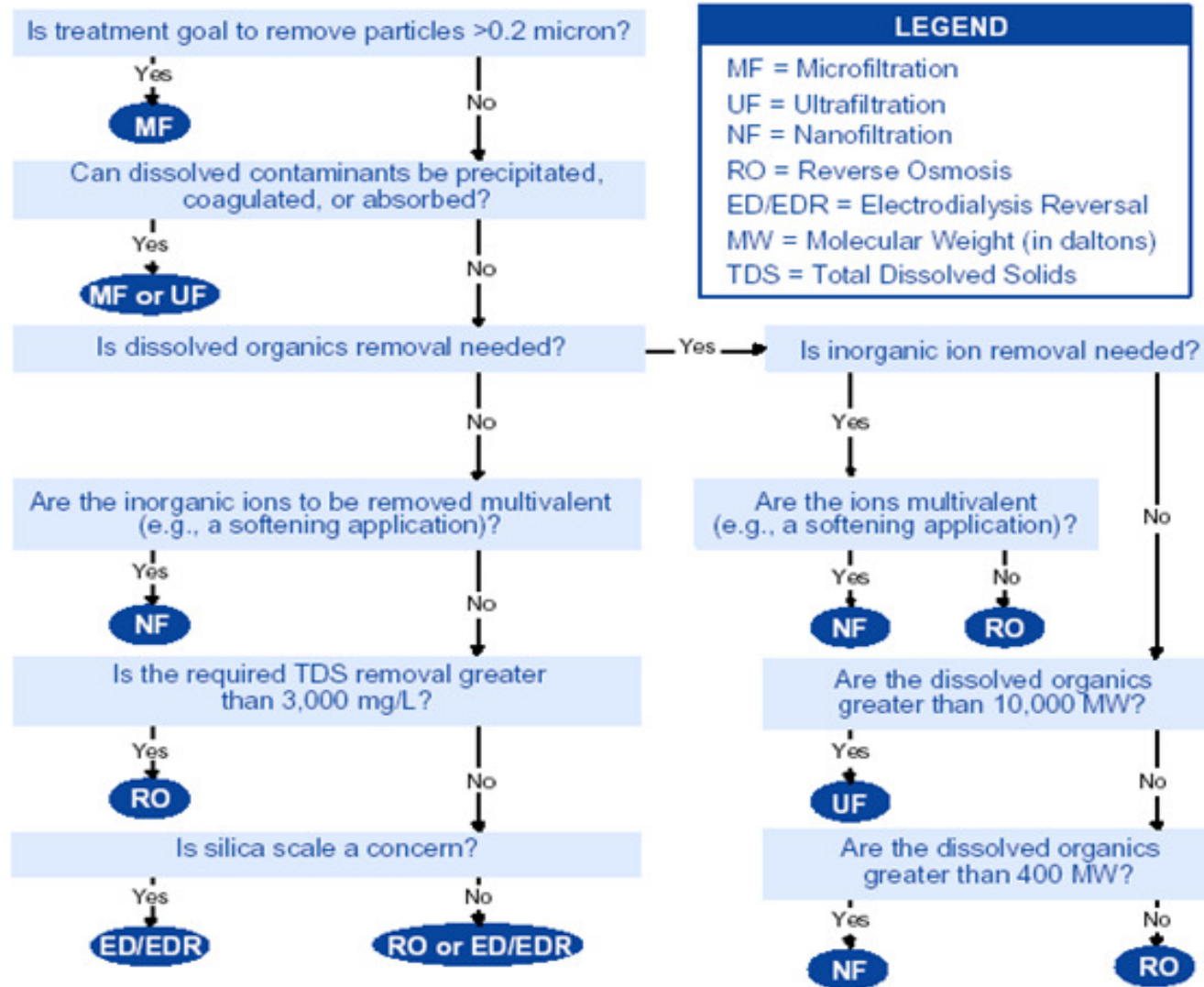


Applications of Membrane Processes

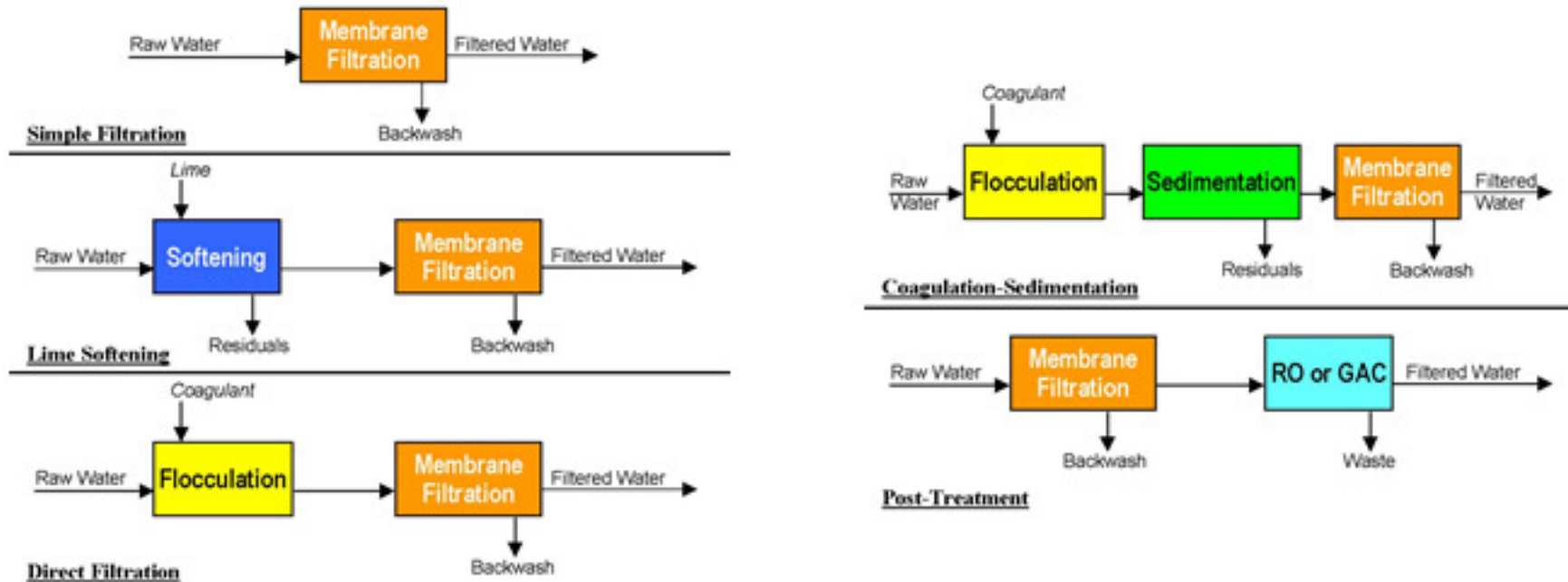
Process	Water Treatment application
MF	Girardia removal, some bacteria partial virus, pretreatment
UF	Microorganisms, viruses, oil, macromolecules, pretreatment
NF	Softening, ion and heavy metal removal, partial desalting, THM, DBP removal
RO	Desalination,
ED	Nitrate removal, desalting of moderate salty soln
PV	Water/organics, volatiles from water
Membrane contactor	Hydrocarbons, metals from water



Applications of Membrane Processes - Processes Selection



Applications of Membrane Processes - Processes Selection





Applications of Membrane Processes - Processes Selection

Type of Target Pollutant	Candidate Processes
Volatile compounds	Pervaporation
Salinity, nitrates	RO, ED/EDR
Hardness, heavy metals	RO, ED, NF
Specific organic compounds, natural organic matter (NOM)	NF, AC-UF, Coagulation-MF, membrane bioreactor (MBR)
microbial contaminants, viruses	UF, coagulation-MF
Microbial contaminants, SS	UF, MF



Membrane Desalination Processes



Content:

- *Desalination: An Overview*
- *Overview of Membrane Desalination Technologies*
- *Pretreatment Processes:
microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF)*
- *Commercial Processes:
Reverse Osmosis (RO), Electrodialysis (ED) and ED Reversal*
- *Innovative Processes:
Forward Osmosis (FO) and Membrane Distillation (MD)*



Membrane Desalination Processes



Content:

- **Pretreatment Processes:**
microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF)
 - *Microfiltration*
 - *Ultrafiltration*
 - *Nanofiltration*



Microfiltration .. Ultrafiltration ... Microfiltration

Microfiltration and Ultrafiltration are essentially membrane processes that rely on pure straining through porosity in the membranes. Pressure required is lower than RO and due entirely to frictional headloss.

Nanofiltration: divalent cations and anions are preferentially rejected over the monovalent cations and anions. Some organics with $MW > 100 - 500$ are removed. There is an osmotic pressure developed but it is less than that of the RO process.

RO: is semi-permeable with thin layer of membrane supported on a porous sub-structure. The thin skin is about 0.25μ thick and has pore size of $5 - 10 \text{ \AA}$. The pore size of the skin limits transport to certain size molecules. Dissolved ions such as Na and Cl are about the same size as water molecules.

Microfiltration

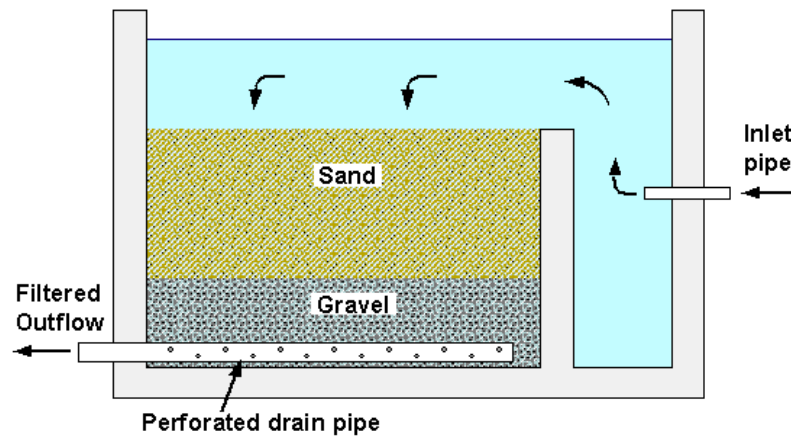
Typical pore size: 0.1 microns ($10^{-7}m$)

Very low pressure

Removes bacteria, some large viruses

Does not filter

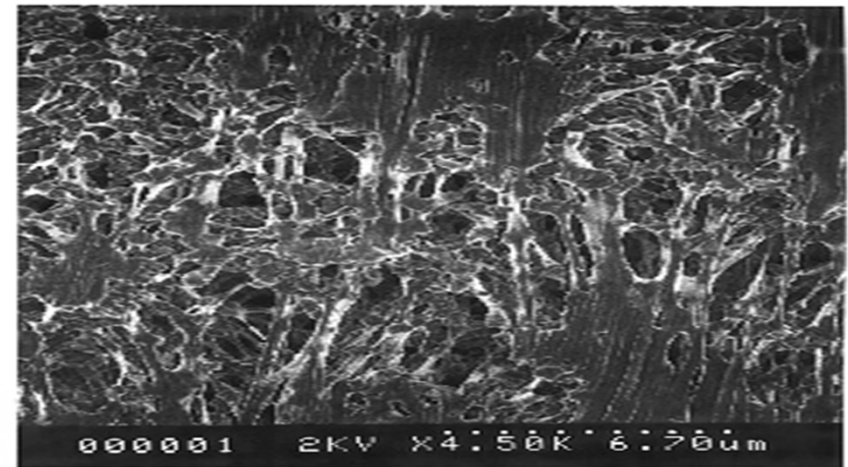
small viruses, protein molecules,
sugar, and salts



Sand and gravel filtration



Microfiltration water plant



A microfilter membrane

Microfiltration

Only large particles with diameters of micron are separated by the membrane, the diffusion of particles and the osmotic pressure difference between the feed and filtrate solution are negligibly low.

$$J_v = \sum_i J_i \bar{V}_i \cong L_v \frac{\Delta p}{\Delta z}$$

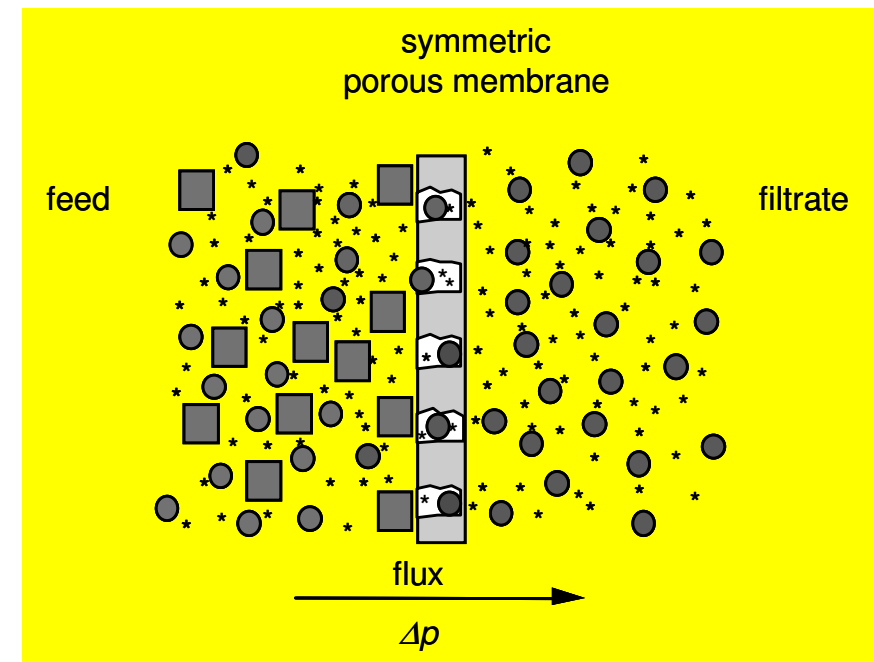
J_v : volumetric flux across the membrane

V : partial molar volume

Δp : pressure

L_v : hydrodynamic permeability of the membrane

Δz is the thickness of the membrane.



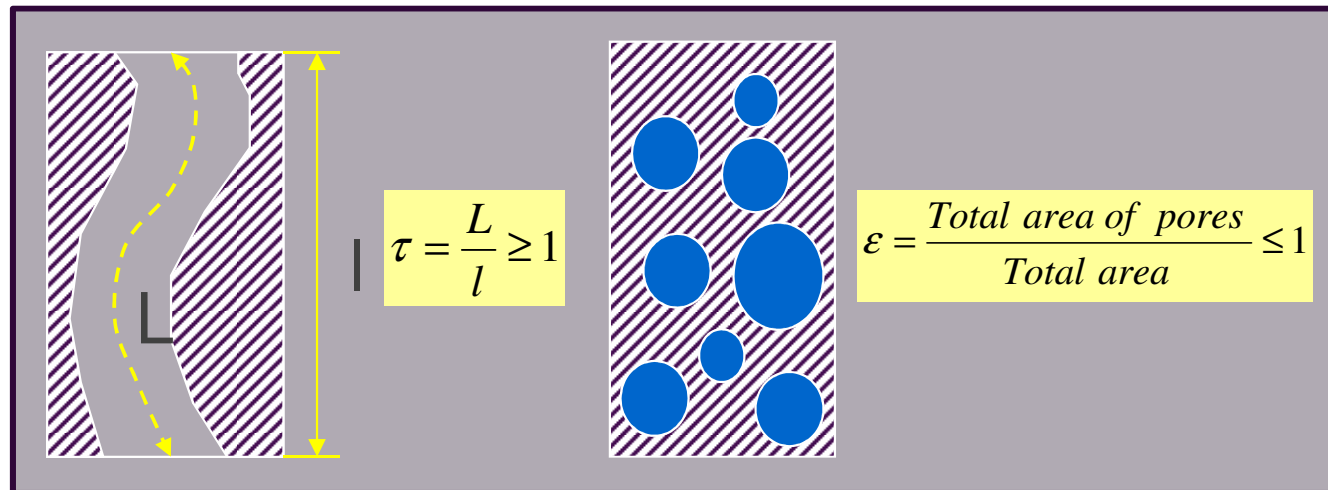
The mass transport in microfiltration membranes takes place by viscous flow through the pores.

Microfiltration

In MF, hydrodynamic permeability is expressed in terms of the membrane pore size and the porosity and the solution viscosity according to **Hagen-Poiseuille's law**:

$$L_p = \frac{\epsilon r^2}{8\eta\tau}$$

ϵ : membrane porosity; r : pore radius;
 η : viscosity; τ : tortuosity.



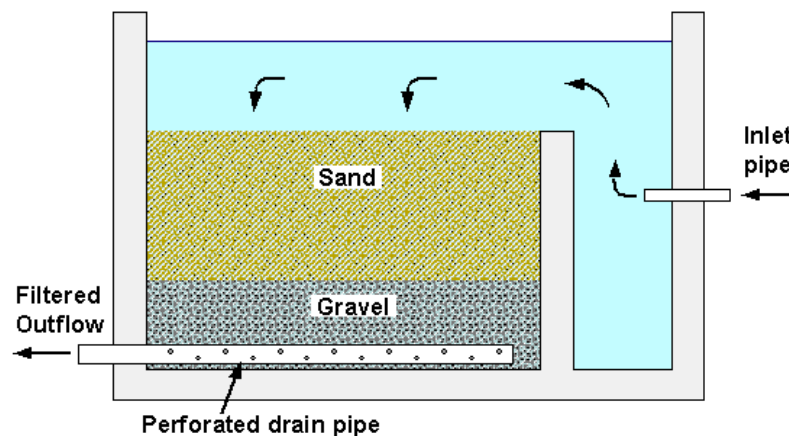
Ultrafiltration

Typical pore size: 0.01 microns (10^{-8}m)

Moderately low pressure

Removes viruses, protein, and other organic molecules

Does not filter ionic particles like lead, iron, chloride ions; nitrates, nitrites; other charged particles



Sand and gravel filtration



An ultrafiltration plant in

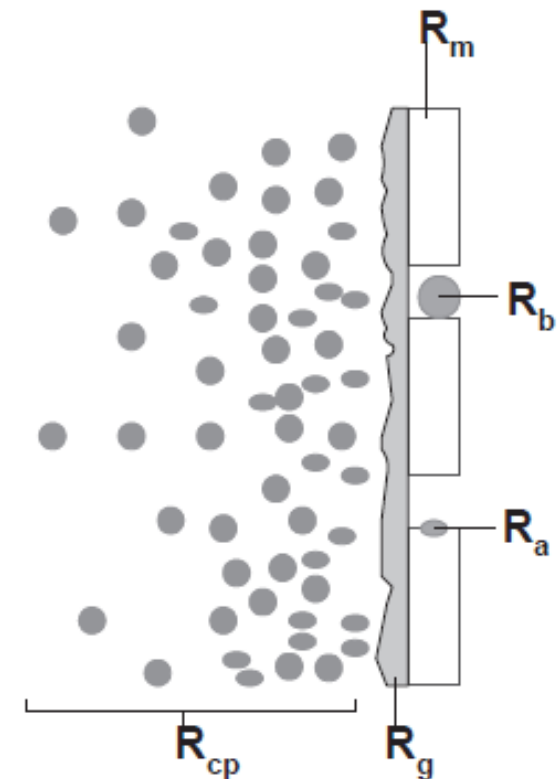
Ultrafiltration

Ultrafiltration is a pressure driven process, the flux J of fluid through the membrane is proportional to the trans-membrane pressure (the pressure drop over the membrane) ΔP applied to the membrane:

$$J = \frac{\Delta P}{\mu R_t} \quad R_t = R_m + R_p + R_a + R_g + R_{cp}$$

Where μ is the viscosity of the fluid and R_t is the total resistance, often the summation of all resistances in series acting on the membrane.

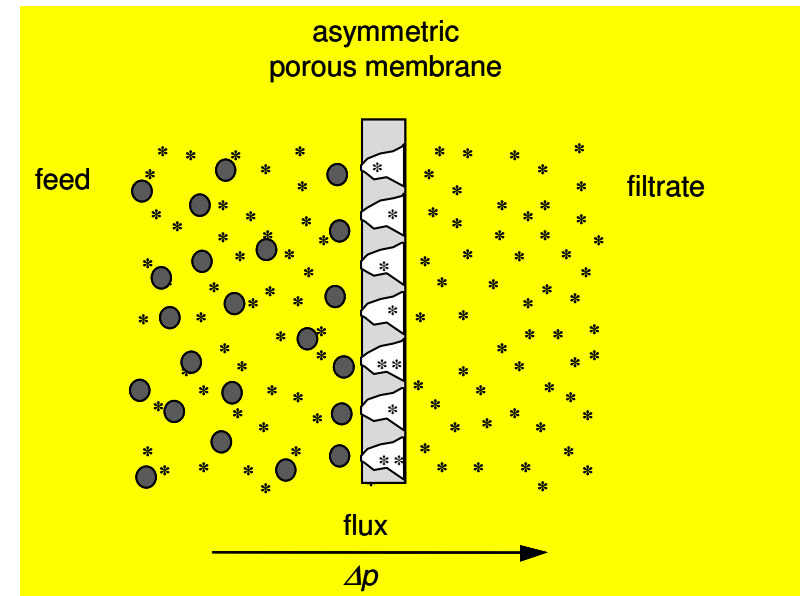
R_m is the membrane resistance, R_p the pore blocking resistance, R_a the resistance as a result of adsorption, R_g the resistance as result of a gel layer and R_{cp} the resistance as an effect of concentration polarization.



Ultrafiltration

In UF, the structure of an ultrafiltration membrane is asymmetric having the smallest pores on the surface facing the feed solution, and its pores are significantly smaller than those of a microfiltration membrane.

Since ultrafiltration membranes retain also some relatively low molecular weight solutes, osmotic pressure differences between the feed and the filtrate can be significant and diffusive fluxes of the solutes across the membrane are no longer negligibly low.



Ultrafiltration

Flux of individual components in ultrafiltration:

$$J_v = \sum_i J_i \bar{V}_i = \sum_i \bar{V}_i L_i \frac{d\mu_i}{dz} + L_v \frac{dp}{dz} = \sum_i \bar{V}_i L_i \frac{d}{dz} (\bar{V}_i p + RT \ln a_i) + L_v \frac{dp}{dz}$$

L : phenomenological coefficients referring to interactions of the permeating components with the membrane matrix;

V : partial molar volume;

μ : chemical potential;

p : hydrostatic pressure;

a : activity

Chemical Potential Gradient

Hydrostatic Pressure Gradient

1) for diluted solutions, the total volume flux can be expressed to a first approximation by the flux of the solvent (water)

$$J_v \cong J_w$$



Ultrafiltration

2) the activity of the solvent in the solution a can be expressed in terms of osmotic pressure gradient ($\Delta\pi$). After arrangements:

$$J_v \cong J_w = \bar{V}_w^2 L_w \frac{\Delta p - \Delta\pi}{\Delta z} + L_v \frac{\Delta p}{\Delta z}$$

L_v is the hydrodynamic permeability

L_w is the diffusive permeability of the solvent

However, in most practical applications of UF, $L_w \ll L_v$:

$$J_v = L_v \frac{\Delta p}{\Delta z}$$



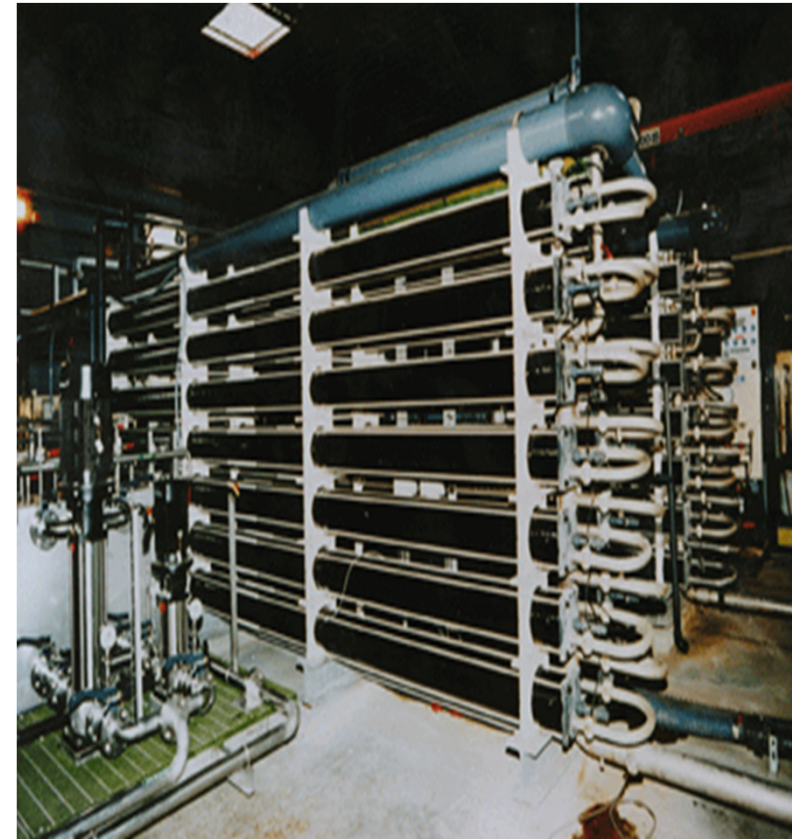
Nanofiltration

Nanofiltration (NF) is a pressure-driven membrane process that falls between reverse osmosis (RO) and ultrafiltration (UF) in its separation characteristics, which permits the separation of certain species in a fluid by a combination of a sieving and sorption diffusion mechanism.

A sieving mechanism is responsible for the retention of uncharged solutes. For charged components an electrostatic interaction takes place between the component and the membrane, as most nanofiltration membranes are charged (mostly negatively). (Donnan exclusion mechanism).

Nanofiltration

- Typical pore size: 0.001 micron (10⁻⁹m)
- Moderate pressure
- Removes toxic or unwanted bivalent ions (ions with 2 or more charges), such as
 - Lead
 - Iron
 - Nickel
 - Mercury (II)

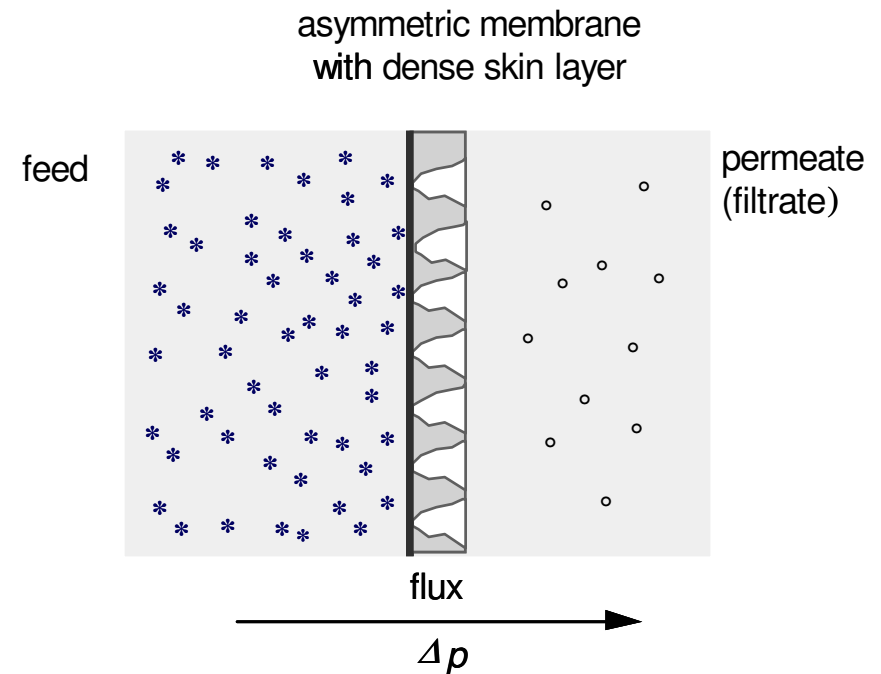


Nanofiltration Plant

Nanofiltration

The separation properties of nanofiltration membrane are determined in general by two distinct properties:

- 1) the pore size of the membranes, which corresponds to a molecular weight cut-off value of about 400 (± 100) Daltons and
- 2) the surface charge which can be positive or negative and affects the permeability of charged components such as salt ions.



Nanofiltration

The transport of individual component i-th (J_i) can be described by:

L_i : phenomenological coefficients referring to diffusion of the permeating components within the membrane matrix;

L_v : hydraulic permeability of the membrane;

V : partial molar volume;

μ : chemical potential;

p : hydrostatic pressure;

a : activity

$$J_i = L_i \frac{d\mu_i}{dz} = L_i \frac{d}{dz} (\bar{V}_i p + RT \ln a_i) + L_v^m C_i \frac{dp}{dz}$$

Chemical Potential Gradient

Hydrostatic Pressure Gradient

The total volumetric flux (J_v) through the membrane is, therefore:

$$J_v = \sum_i J_i \bar{V}_i = \sum_i \bar{V}_i L_i \frac{d}{dz} (\bar{V}_i p + RT \ln^m a_i) + L_v \frac{dp}{dz}$$



Nanofiltration

1: for diluted solutions, the total volume flux can be expressed to a first approximation by the flux of the solvent (water)

$$J_v \cong J_w$$

2: the activity of the solvent in the solution a can be expressed in terms of osmotic pressure gradient ($\Delta\pi$).

After arrangements:

$$J_v \cong J_w = \bar{V}_w^2 L_w \frac{\Delta p - \Delta\pi}{\Delta z} + L_v \frac{\Delta p}{\Delta z}$$

L_v is the hydrodynamic permeability

L_w is the diffusive permeability of the solvent



Nanofiltration

Expressing the phenomenological coefficient L_w by:

$$L_w = \frac{D_w C_w}{RT}$$

follows that:

$$J_v \cong \frac{\bar{V}_w^2 L_w}{\Delta z} (\Delta p + \Delta \pi) + L_v \frac{\Delta p}{\Delta z} = \left(\frac{D_w \bar{V}_w}{RT} + L_v \right) \frac{\Delta p}{\Delta z} + \frac{D_w \bar{V}_w}{RT} \frac{\Delta \pi}{\Delta z}$$

For nanofiltration membranes with pore sizes in the range of ca. 1 nm the term $\frac{D_w \bar{V}_w}{RT}$ is of the same order of magnitude or large than the L_v . Thus, unlike in ultrafiltration the effect of the osmotic pressure on the solvent flux can not be neglected in nanofiltration.



Nanofiltration

3: it is assumed that the solutions treated in NF are relatively dilute and that to a first approximation the activities of the individual components can be replaced by their concentrations.

$$J_i = {}^m D_i \frac{d}{dz} \left(\frac{\bar{V}_i {}^m C_i}{RT} dp + d {}^m C_i \right) + L_v {}^m C_i \frac{dp}{dz}$$

where:

$${}^m D_i = L_i \frac{RT}{{}^m C_i}$$

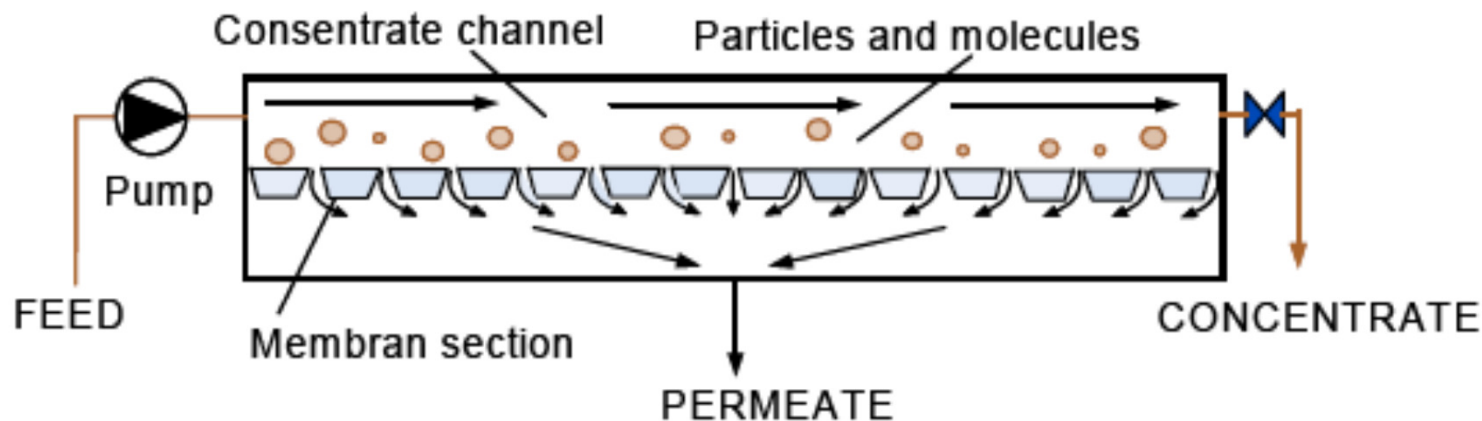
A partition coefficient correlates the concentration at the membrane interface ${}^m C_i$ to the concentration in the solution ${}^s C_i$:

$${}^m C_i = k_i {}^s C_i$$

Nanofiltration

Extended Nernst Planck Equation

Accounts for ionic diffusion, electro migration and convective flow through the membrane



$$j_i = J_v K_{ic} c_i - D_{ip} \frac{dc_i}{dx} - z_i c_i D_{ip} \frac{F}{RT} \frac{d\Psi}{dx}$$

Nanofiltration

Extended Nernst Planck Equation

$$j_i = J_v K_{ic} c_i - D_{ip} \frac{dc_i}{dx} - z_i c_i D_{ip} \frac{F}{RT} \frac{d\Psi}{dx}$$

Flux = Convection diffusion Electric Field Gradient

J_i is the solute flux (mol/m²s)

$D_{i,p}$ is the hindered diffusivity (m²/s)

c_i is the solute concentrations (mol/l)

z_i is the ion valence (-)

F is the Faraday constant (96,489 C/mol)

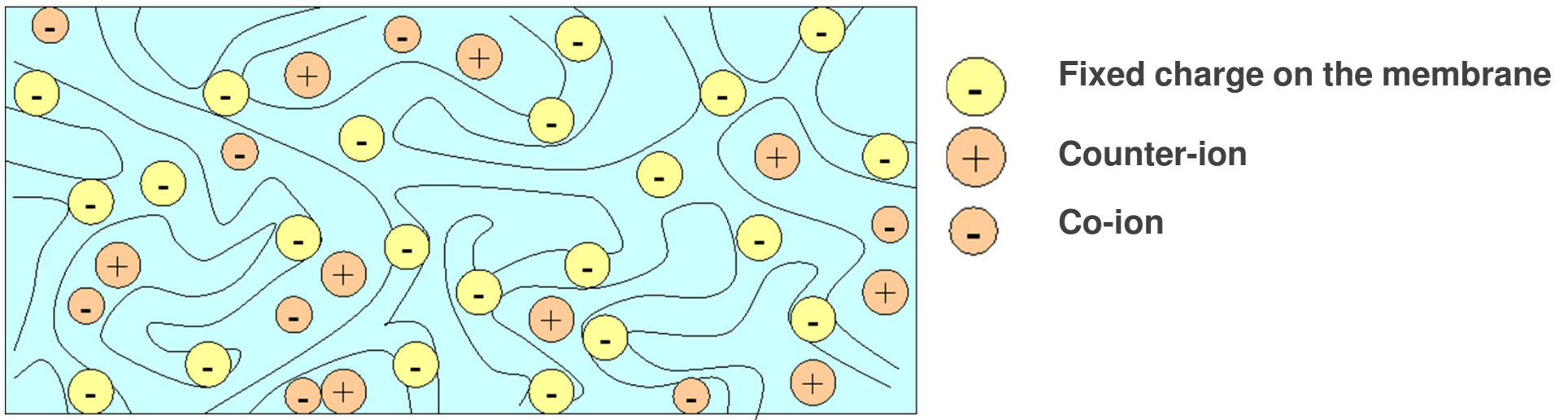
Ψ is the electric potential (V)

$K_{i,c}$ is the hindrance factor for convection (-)

Nanofiltration

Donnan Potential and Donnan Exclusion

If the membrane carries positive or negative electric charges at the surface, the partition coefficient for ionic components such as salt ions is not only determined by size exclusion but also by the so-called Donnan exclusion which postulates that ions carrying the same charge as the membrane, i.e. the so-called co-ions, will be excluded from the membrane.





Nanofiltration

Nanofiltration operated at a 65% conversion

reverse osmosis 56% conversion rate, providing an overall seawater conversion rate of 36.4%.

Compared with the conversion rate of a parallel equipment line of 28%, this represents a 30% increase in overall recovery

nanofiltration and reverse osmosis elements, produced 25% more water per element of a higher quality at a pressure of 54 Bar compared to the 65 Bar in the reference line, which is a pressure reduction of 17%. This translates into the same approximate reduction in energy consumption.

Nanofiltration

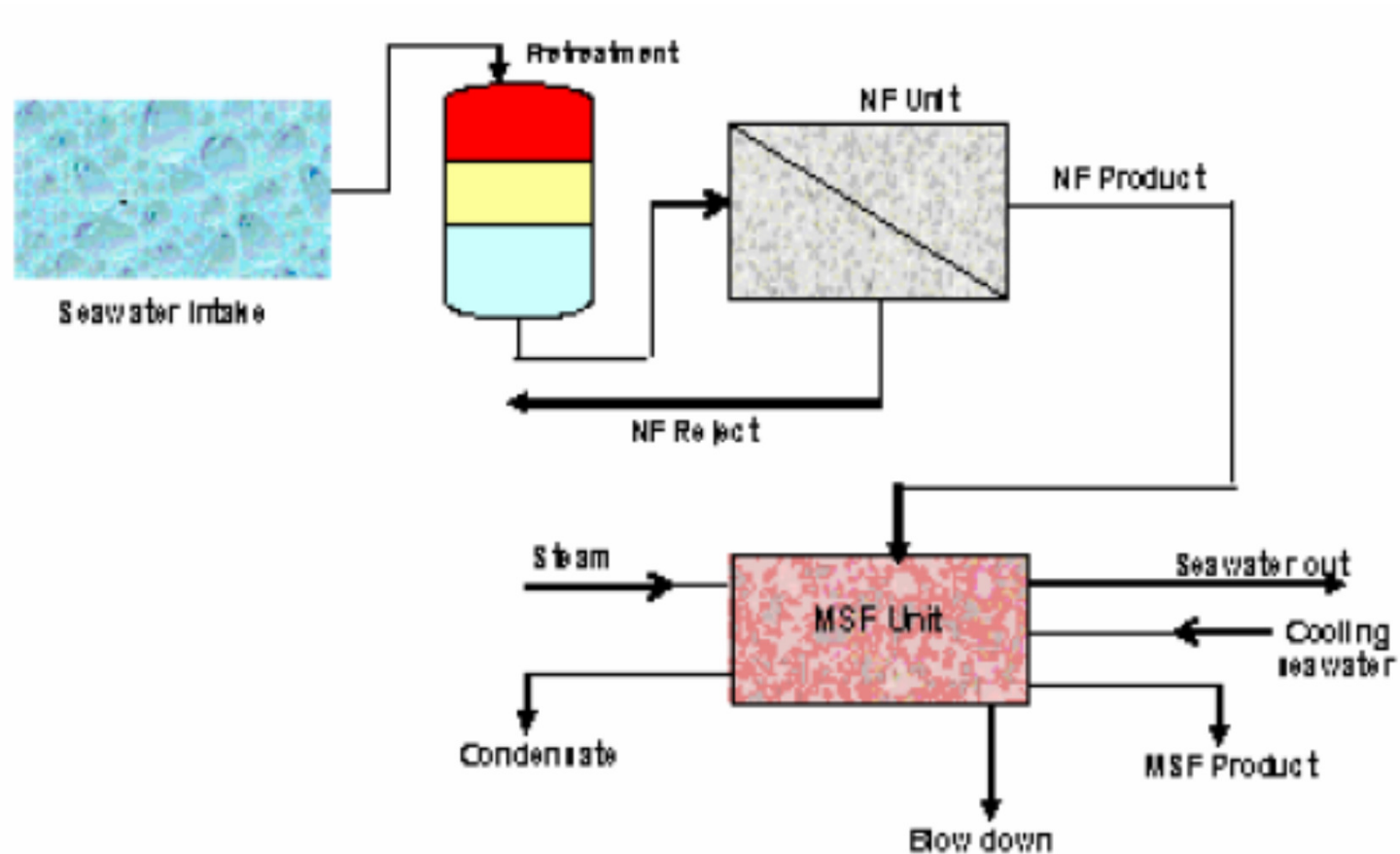
NF pretreatment in the Umm Lujj SWRO NF pretreatment plant reduced:

total hardness from 7500 to 220 ppm, total dissolved solids from 45,460 to 28,260 ppm, and chloride from 21,587 to 16,438 ppm. With the ionic makeup at the Umm Lujj plant, sulfate was rejected at a rate better than 99%, magnesium at 98%, calcium at 92% and bicarbonate at 44%.



The Umm Lujj Nanofiltration Plant for Pretreatment of Seawater Before Reverse Osmosis

Nanofiltration



Schematic flow diagram of dihybrid NF/MSF desalination system



Nanofiltration

The experimental operation of NF at a pressure of 22 bars showed that the NF unit reduced turbidity and microorganisms, removed hardness ions of Ca^{++} , Mg^{++} , SO_4^- , HCO_3^- , and total hardness by 89.6%, 94.0%, 97.8%, 76.6% and 93.3%, respectively. The system also resulted in the reduction of the monovalent ions of Cl^- , Na^+ , K^+ each by 40.3% and the overall seawater TDS by 57.7%.

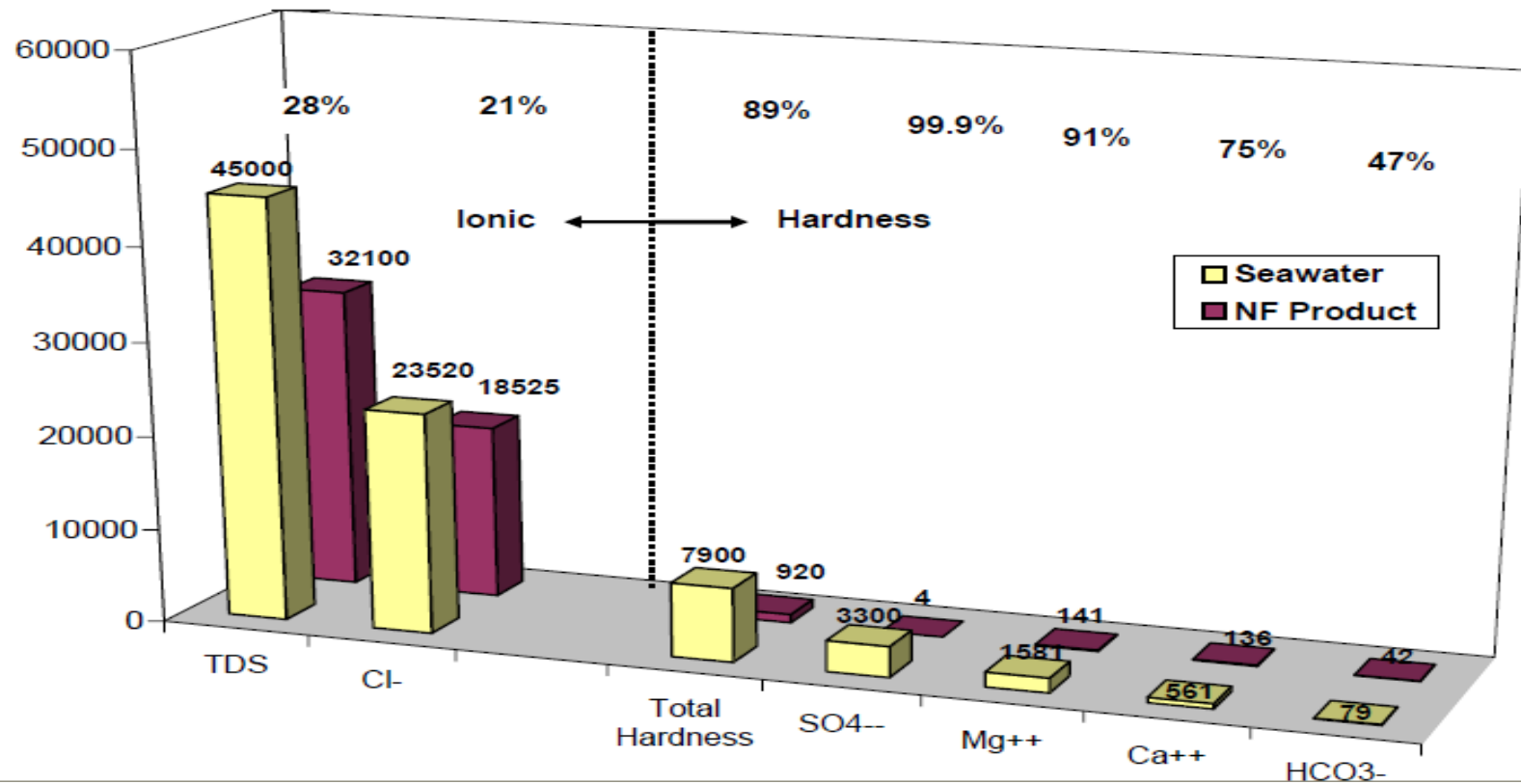
Rejection Characteristics of various ionic pair

Cation	Molecular weight	Anion	
		Cl^-	SO_4^{--}
		35	98
Na^+	23	50%	90%
Mg^{++}	24	20%	35%
Ca^{++}	40	12%	-

Ref: International Desalination & Water Reuse Quarterly, May/June Issue, 1998, Vol. 8/1, p.53-59, and also in August/September Issue 1998, Vol. 8/2 p. 39-45.

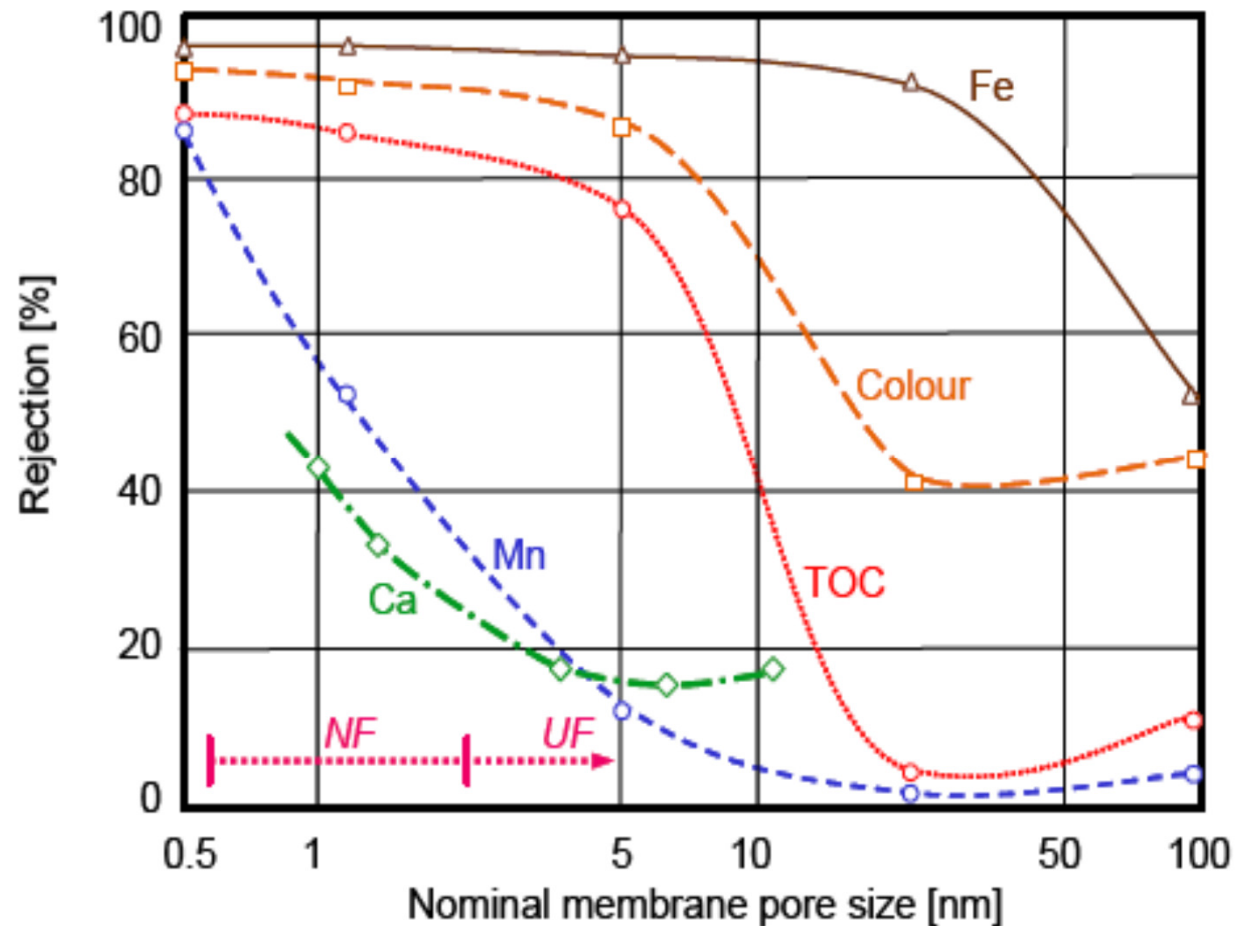


Nanofiltration



Arabian Gulf water Treatment by Nanofiltration

Nanofiltration



Typical rejection of various parameters from various Norwegian sources



Membrane Desalination Processes



Content:

- *Desalination: An Overview*
- *Overview of Membrane Desalination Technologies*
- *Pretreatment Processes:
microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF)*
- *Commercial Processes:
Reverse Osmosis (RO), Electrodialysis (ED) and ED Reversal*
- *Innovative Processes:
Forward Osmosis (FO) and Membrane Distillation (MD)*



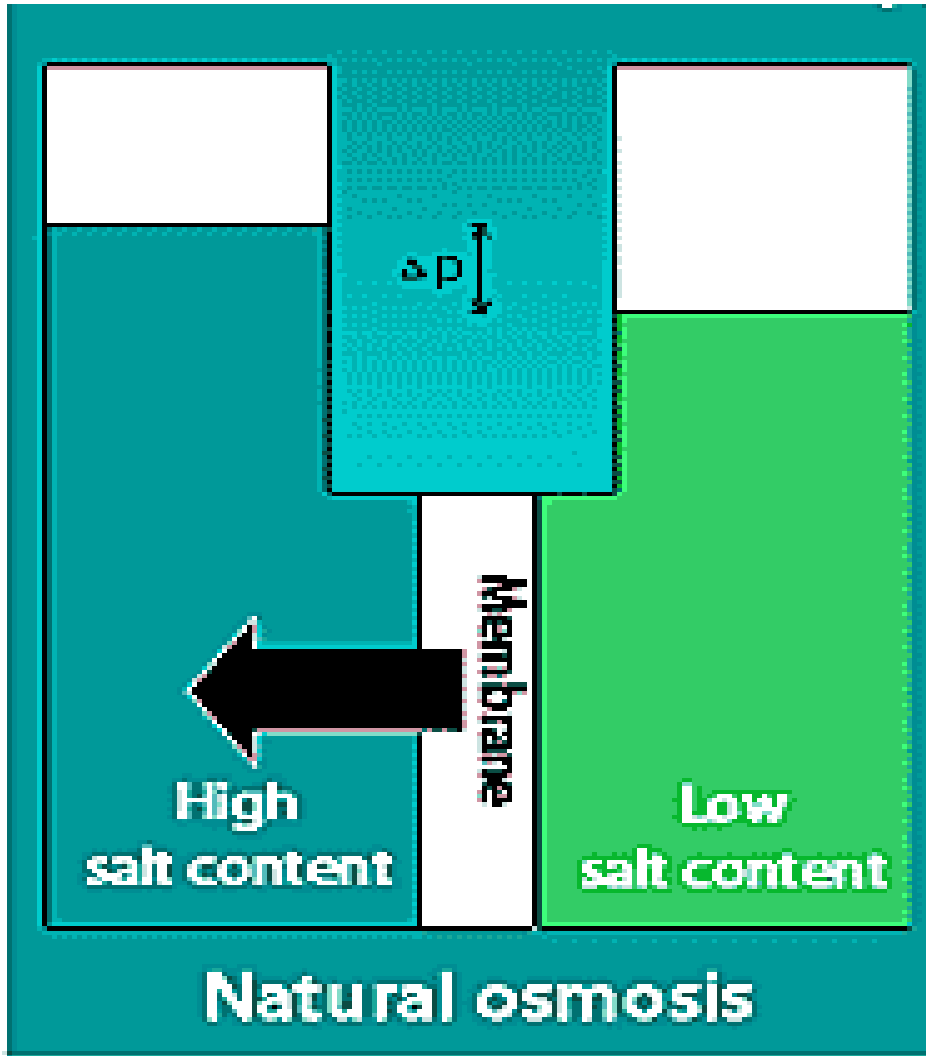
Membrane Desalination Processes



Content:

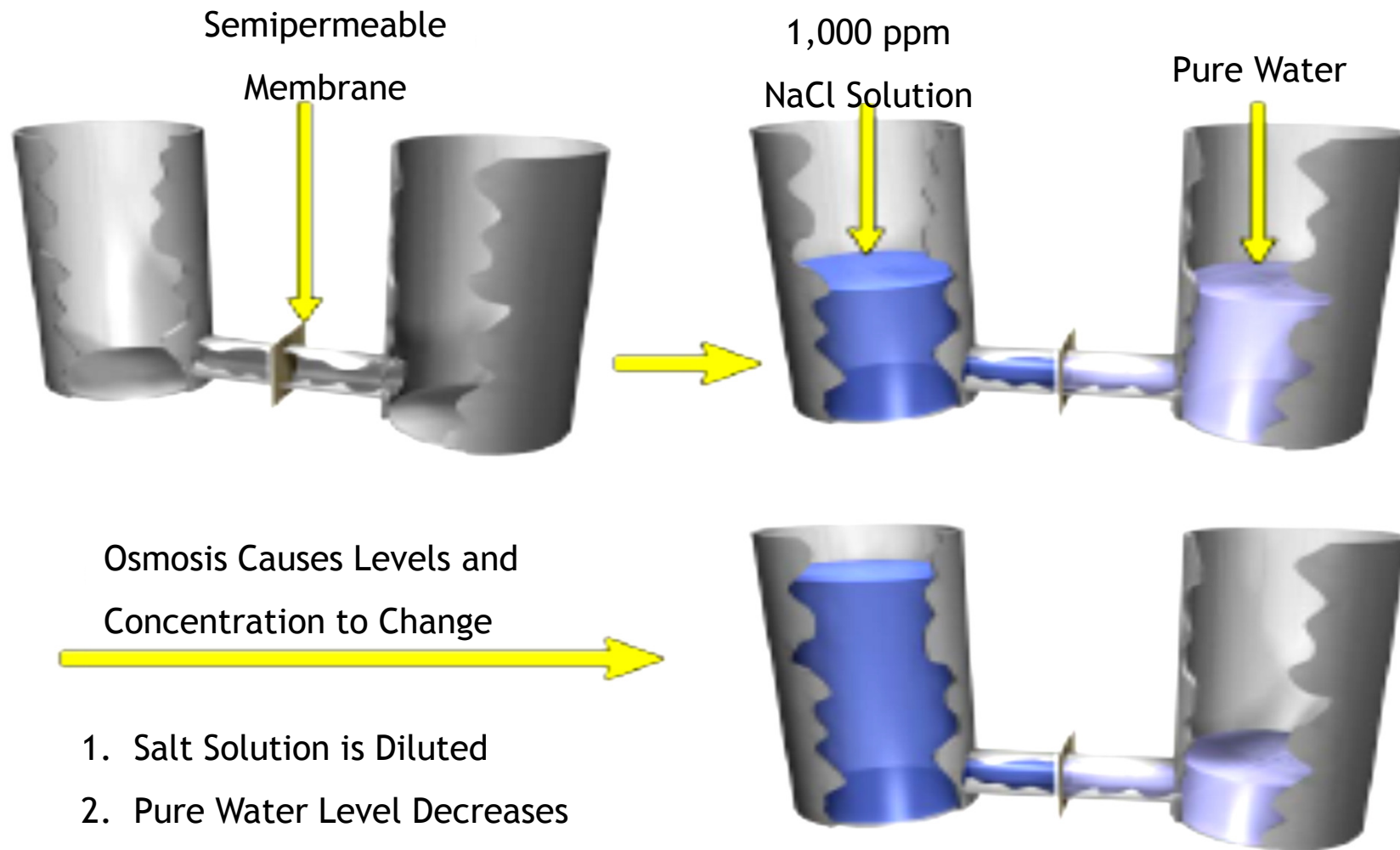
- **Commercial Processes:**
Reverse Osmosis (RO), Electrodialysis (ED) and ED Reversal
 - Principles of Natural Osmosis, Principles of Reverse Osmosis
 - Membrane Module Configurations:
(Flat Sheet, Tube, Hollow Fine Fiber, Spiral Wound)
 - RO System: (Membrane Element, RO Pressure Tube Construction, RO Membrane Pressure Vessel, RO Trains - Alternative Configurations).

Principles of Natural Osmosis

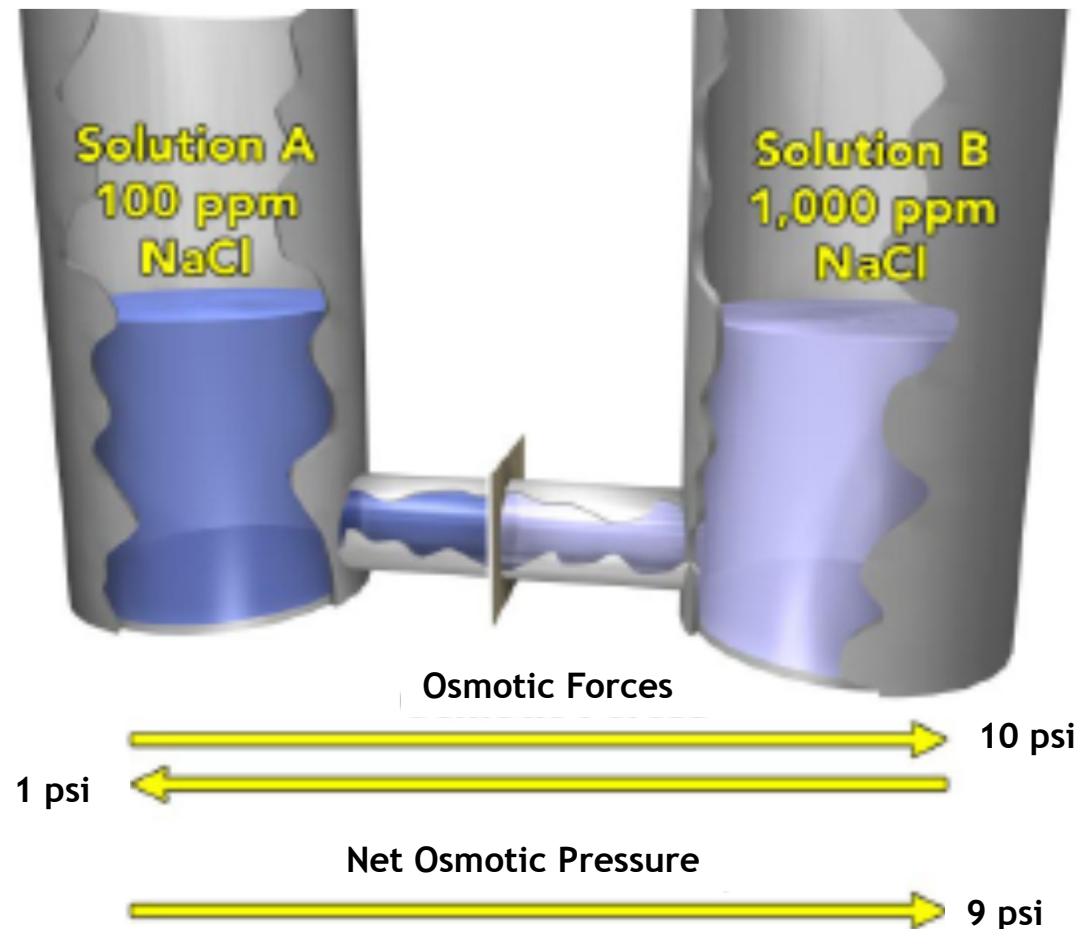


1. Osmosis is a purely natural process.
2. Fluids with a low salt content will always try to mix with fluids with a high salt content until the salt content of the two fluids is the same.
3. If the two fluids are separated by a semi - permeable membrane, the fluid with the low salt content will permeate (go through) the membrane until the salt content is the same at both sides of the membrane.
4. The level difference of the two fluids is called the osmotic pressure.

Principles of Natural Osmosis

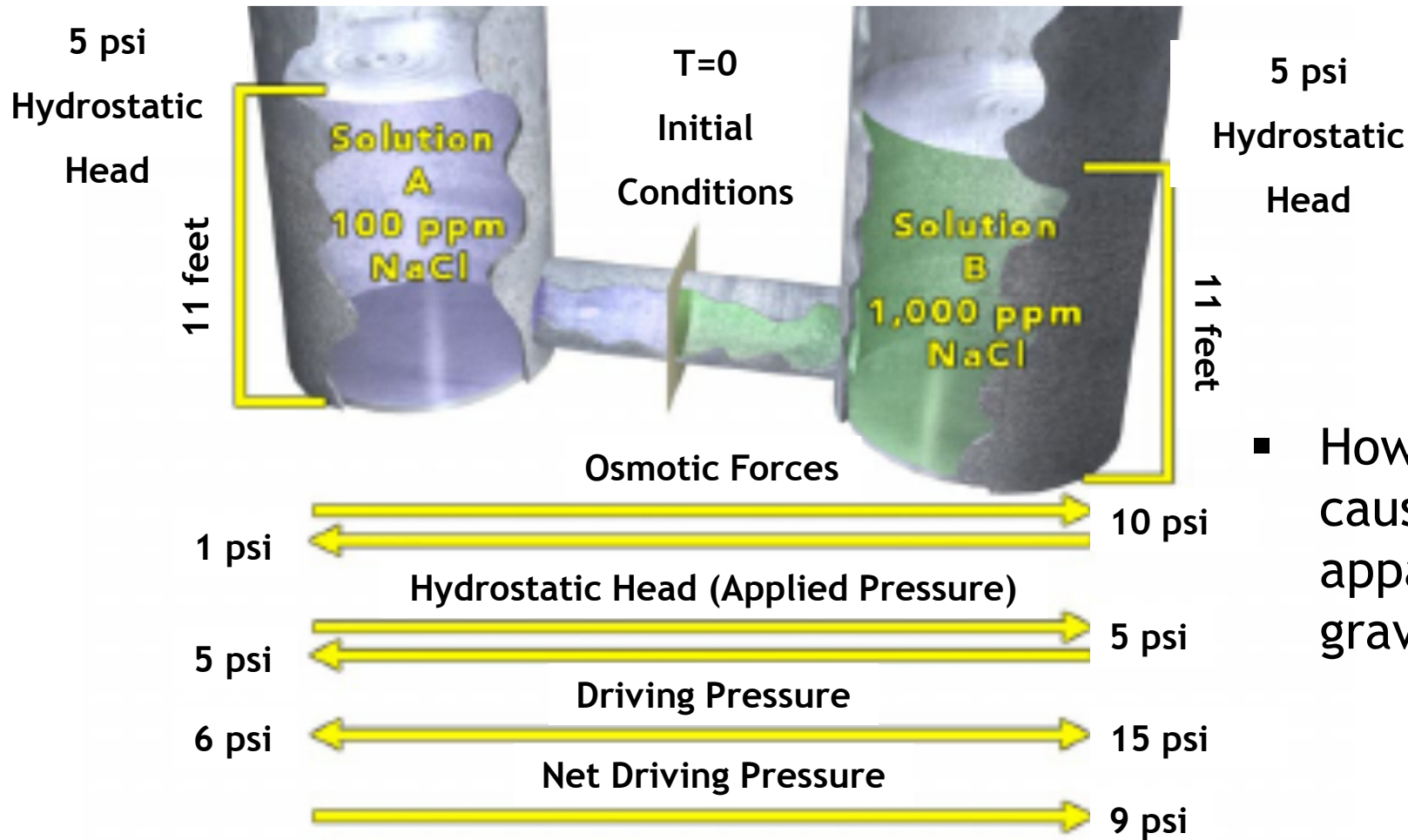


Principles of Natural Osmosis



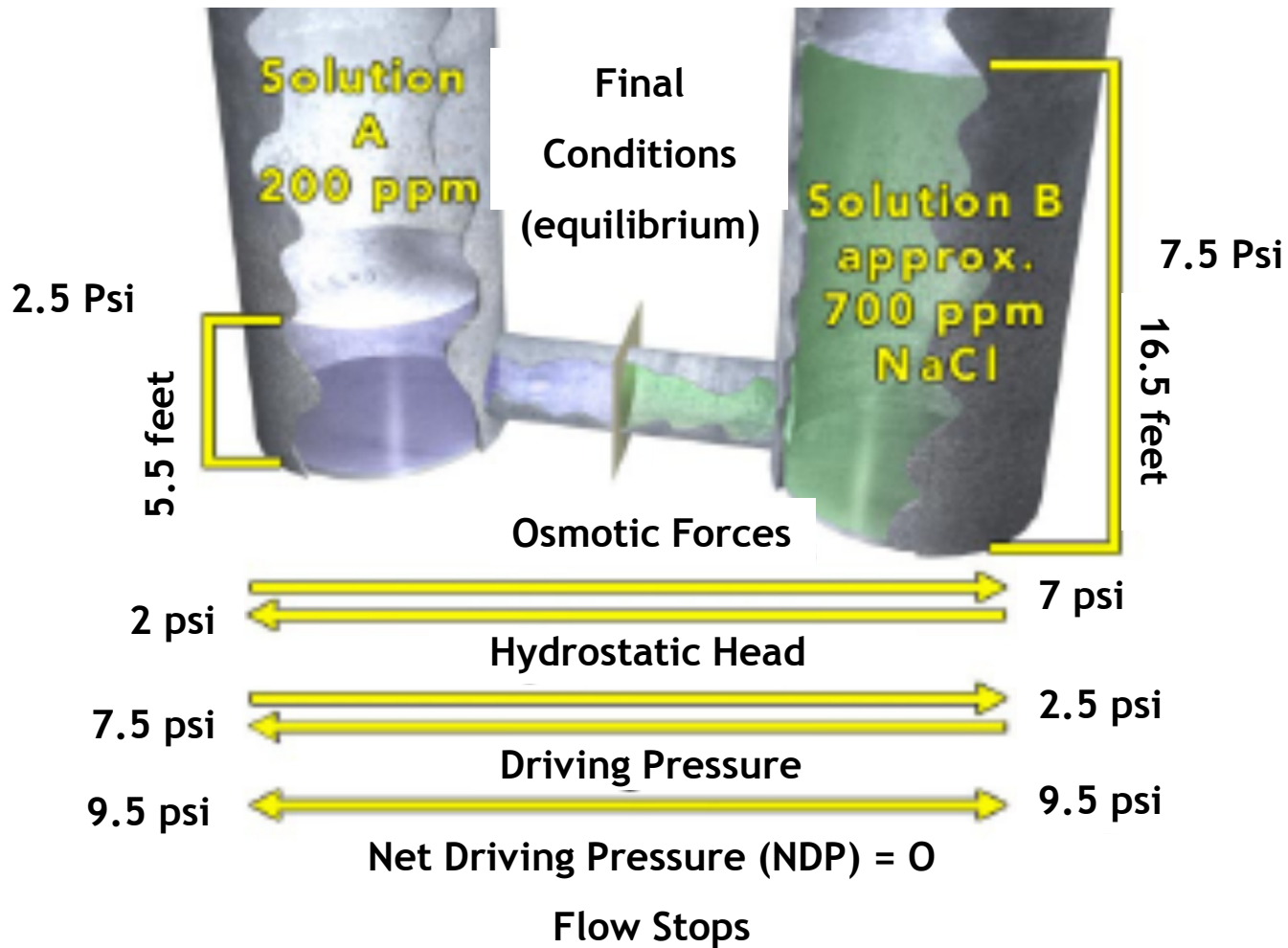
- The force driving the molecules from one side to the other is called the osmotic pressure.
- 1 psi of osmotic pressure is caused by every 100 ppm difference in TDS.

Principles of Natural Osmosis



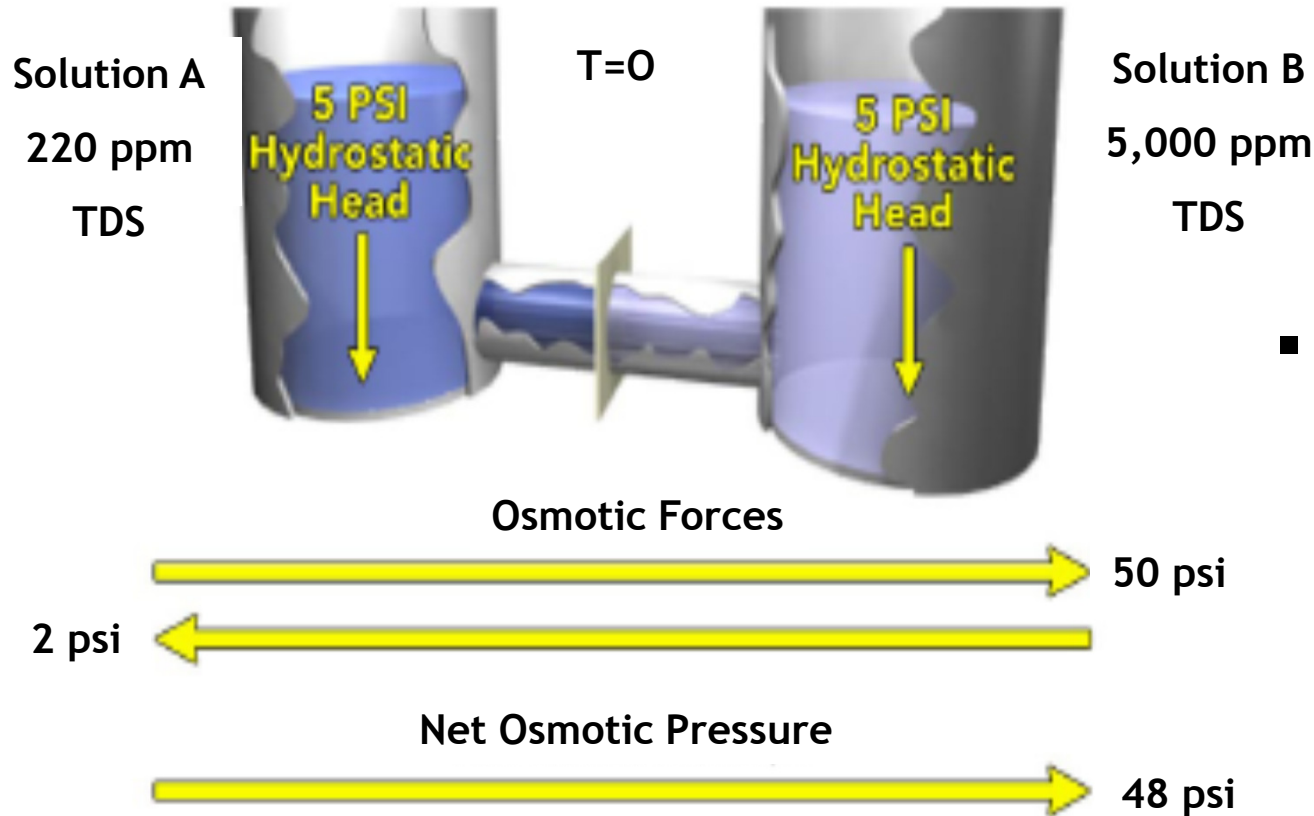
- How can osmoses cause water to apparently defy gravity?

Principles of Natural Osmosis



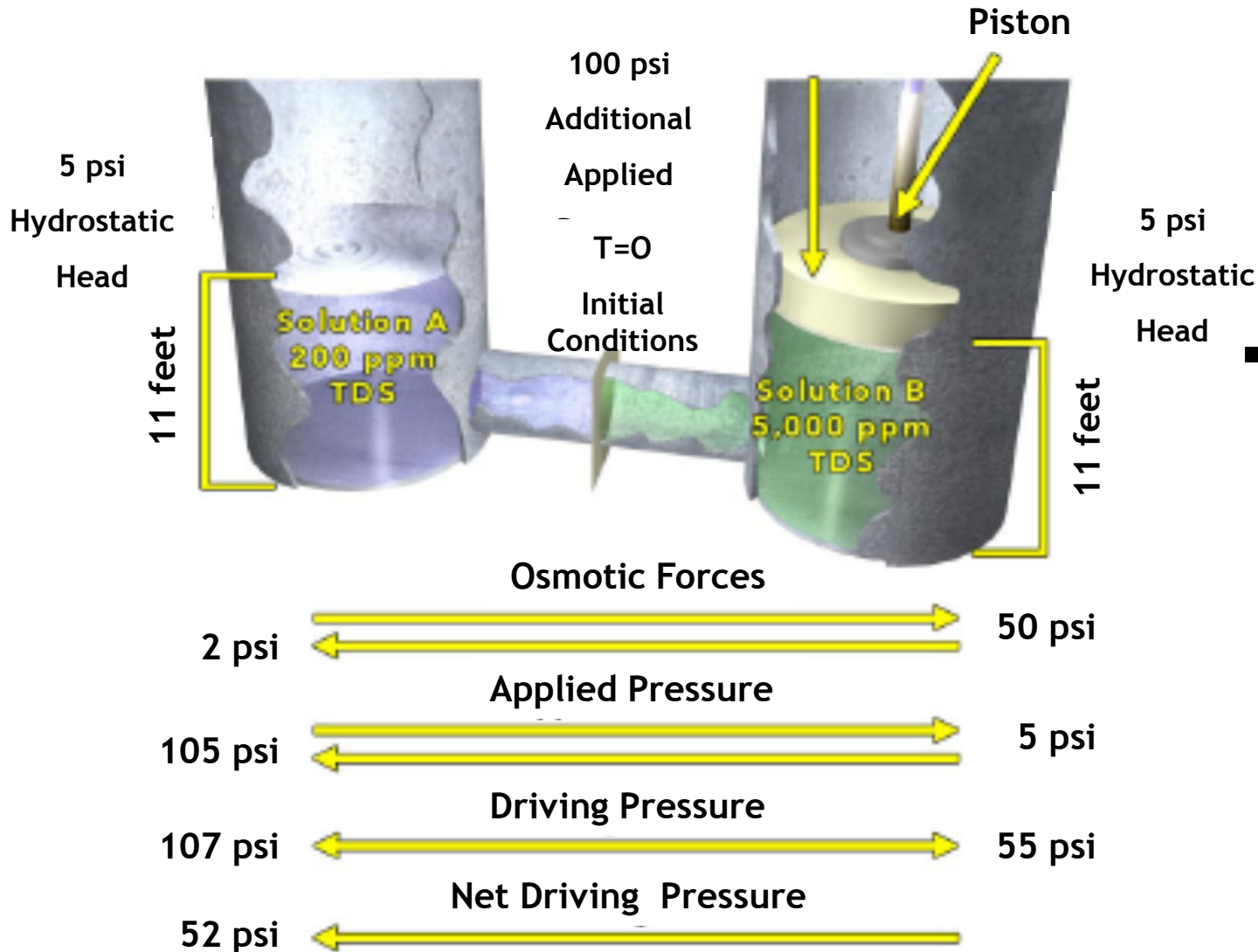
- Final equilibrium condition
- Equilibrium is reached when the NDP goes to zero.

Principles of Reverse Osmosis



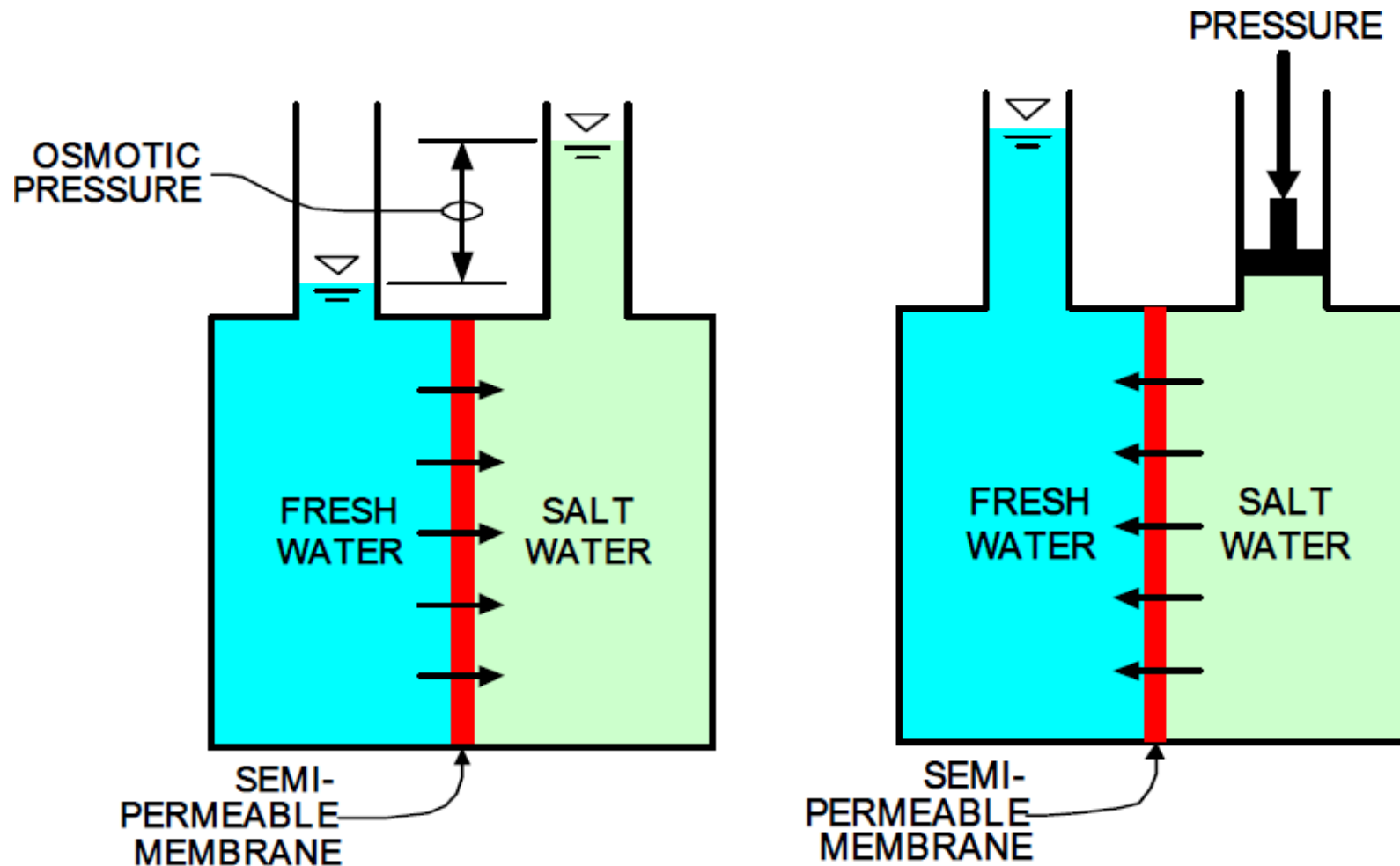
- We can reverse the natural osmosis phenomena by applying a higher pressure on the high salt concentration side.

Principles of Reverse Osmosis



- RO occur when we apply enough pressure to cause +ve net driving pressure against osmoses.

Principles of Reverse Osmosis



Osmosis and Reverse Osmosis

A plate-and-frame module

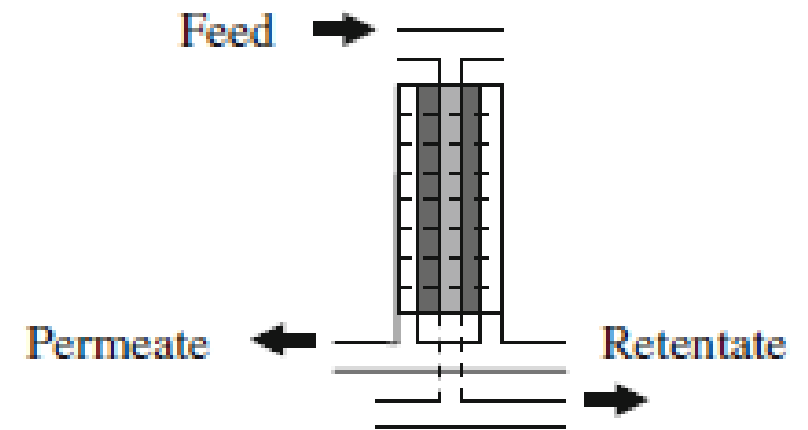
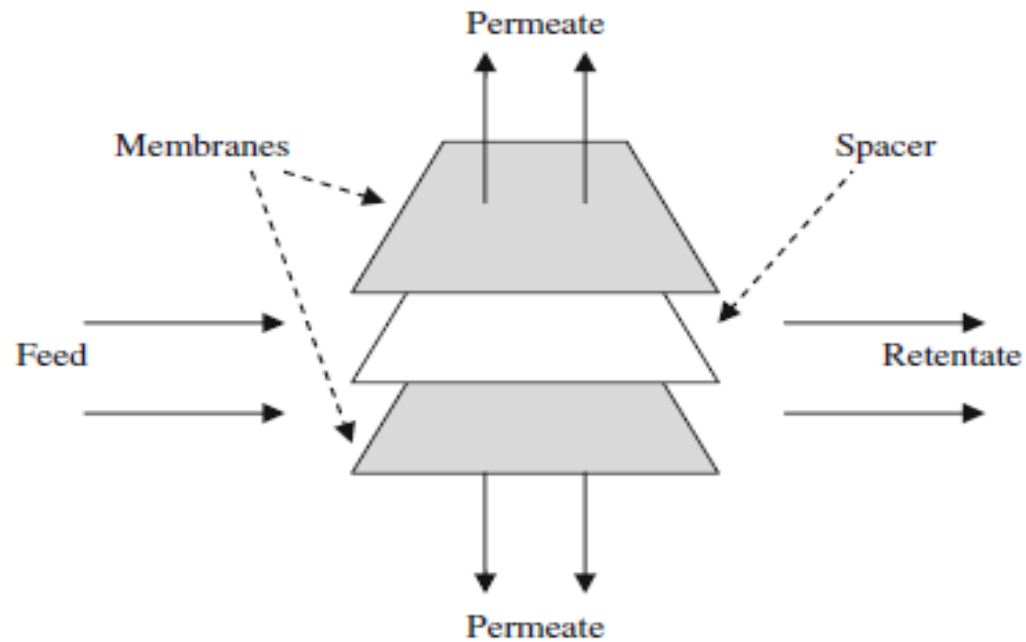


Plate Membrane Module

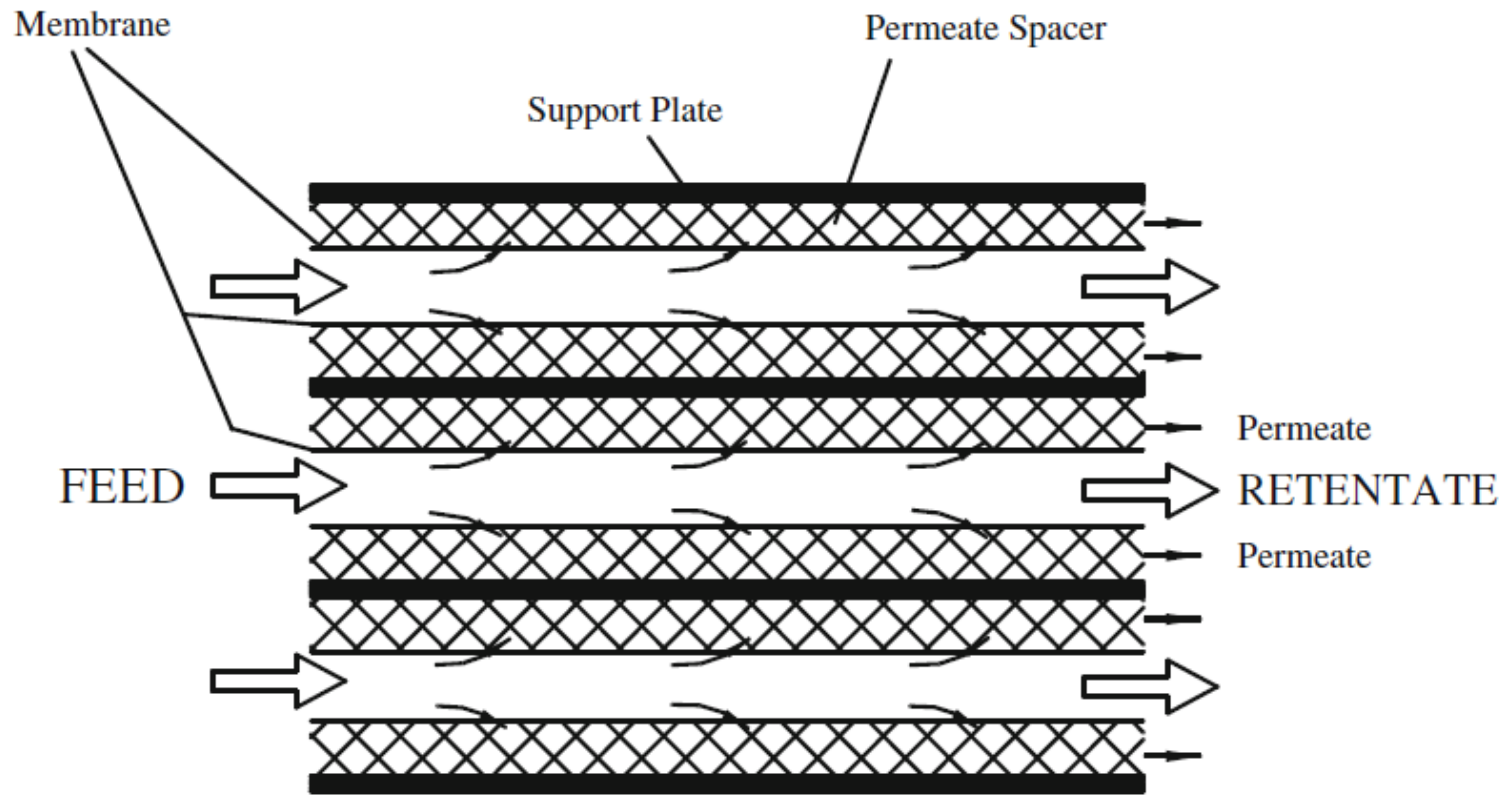
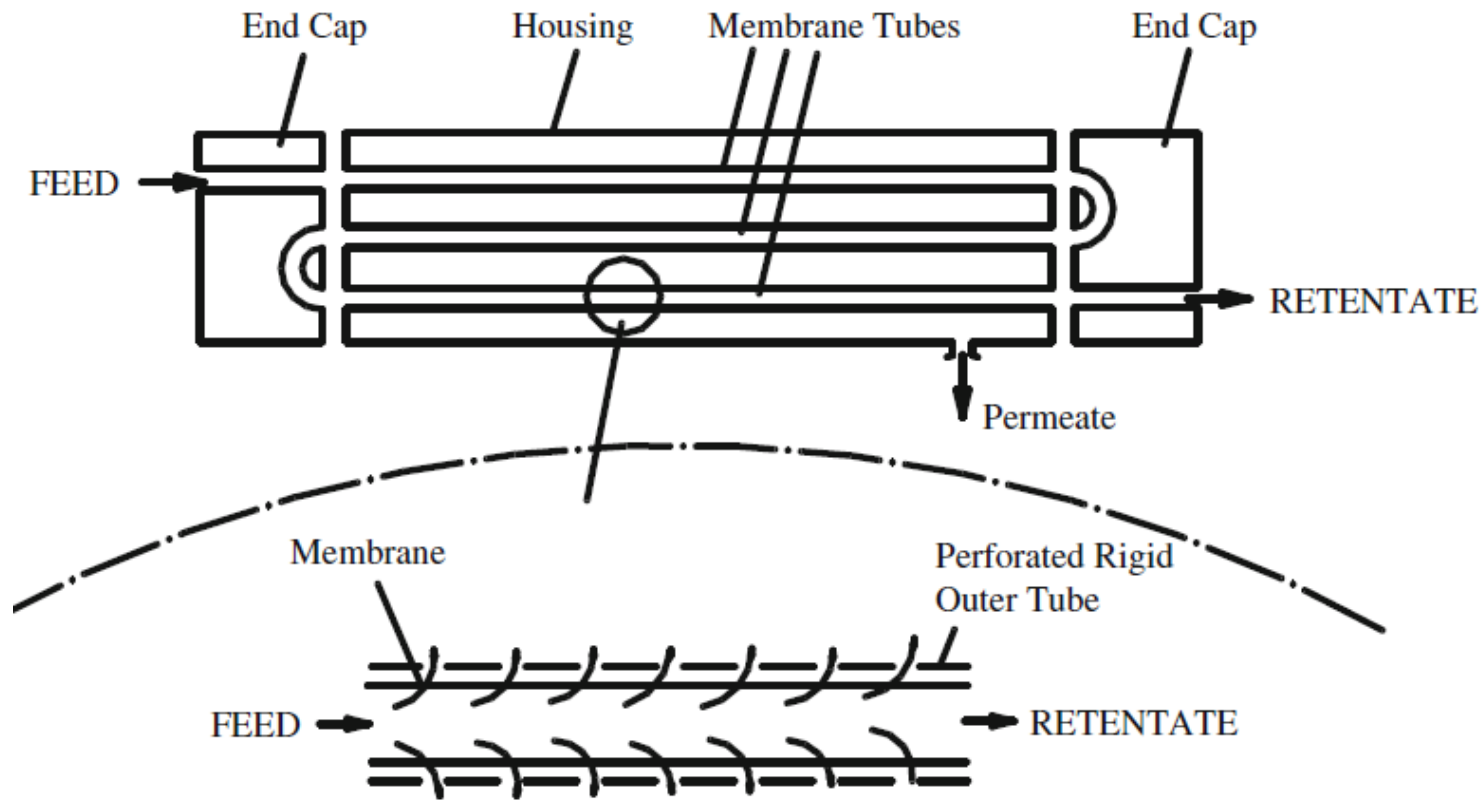




Plate Membrane Module

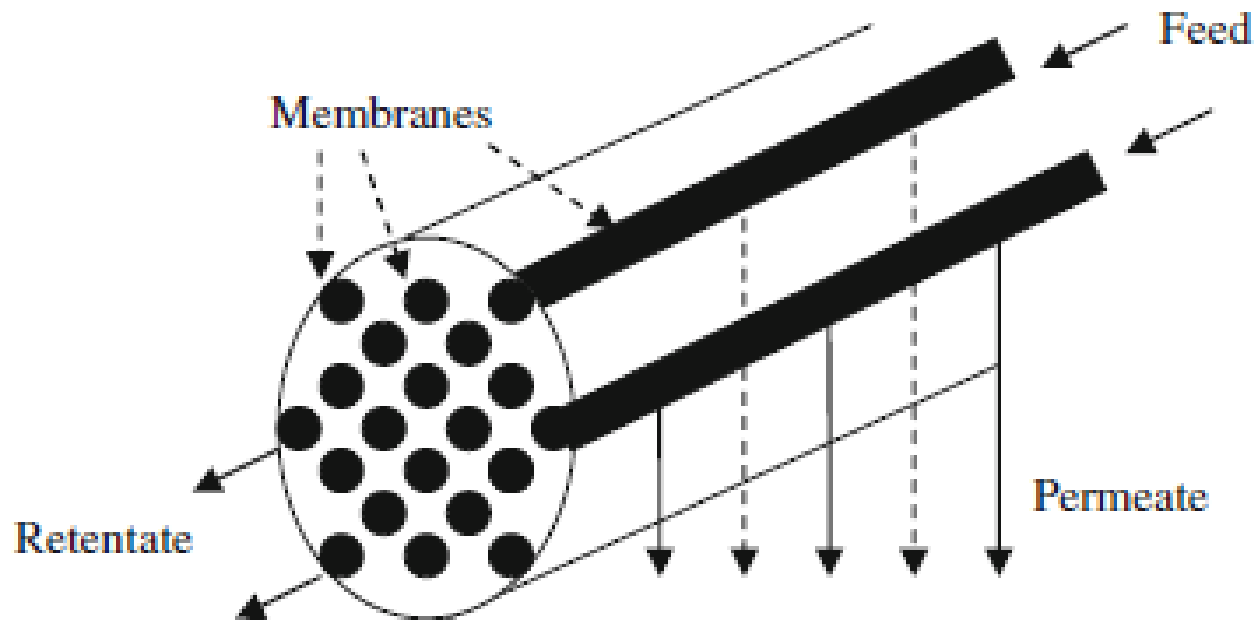


Tubular Membrane Module





Tubular Membrane Module

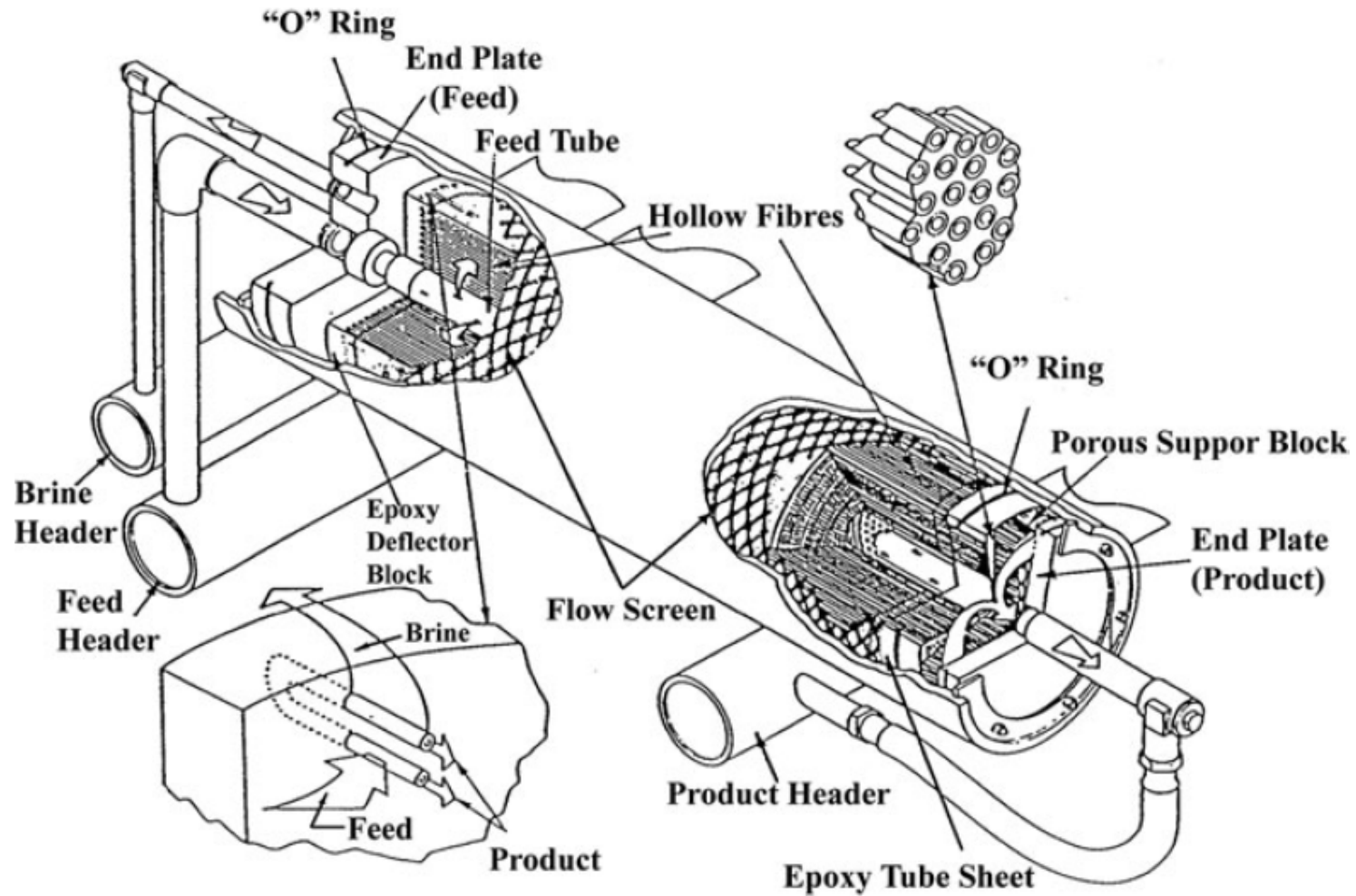




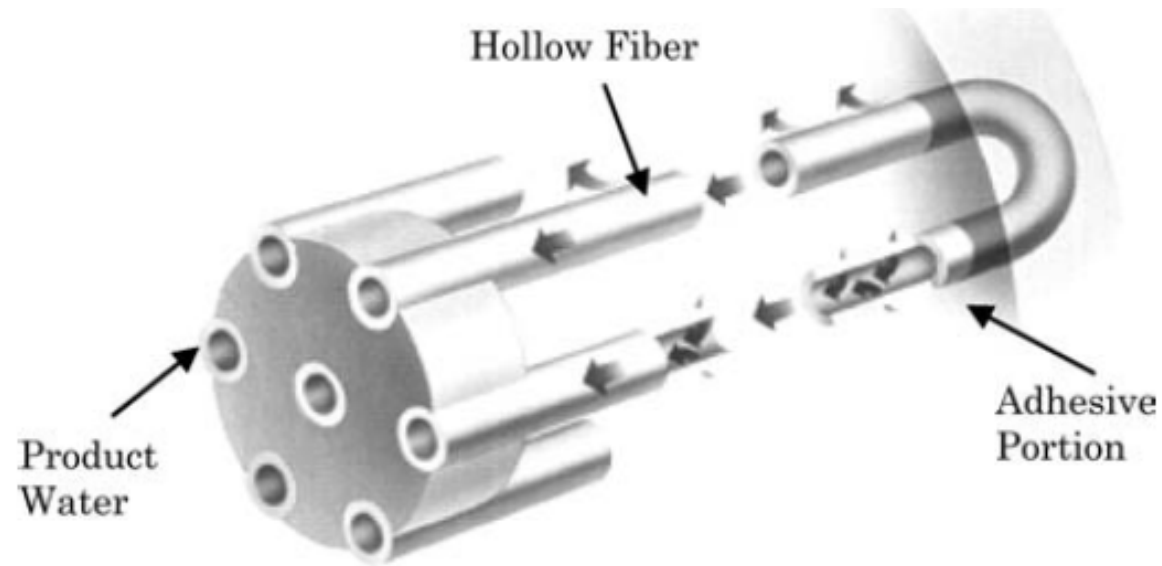
Tubular Membrane Module



Hollow Fine Fiber Membrane Module

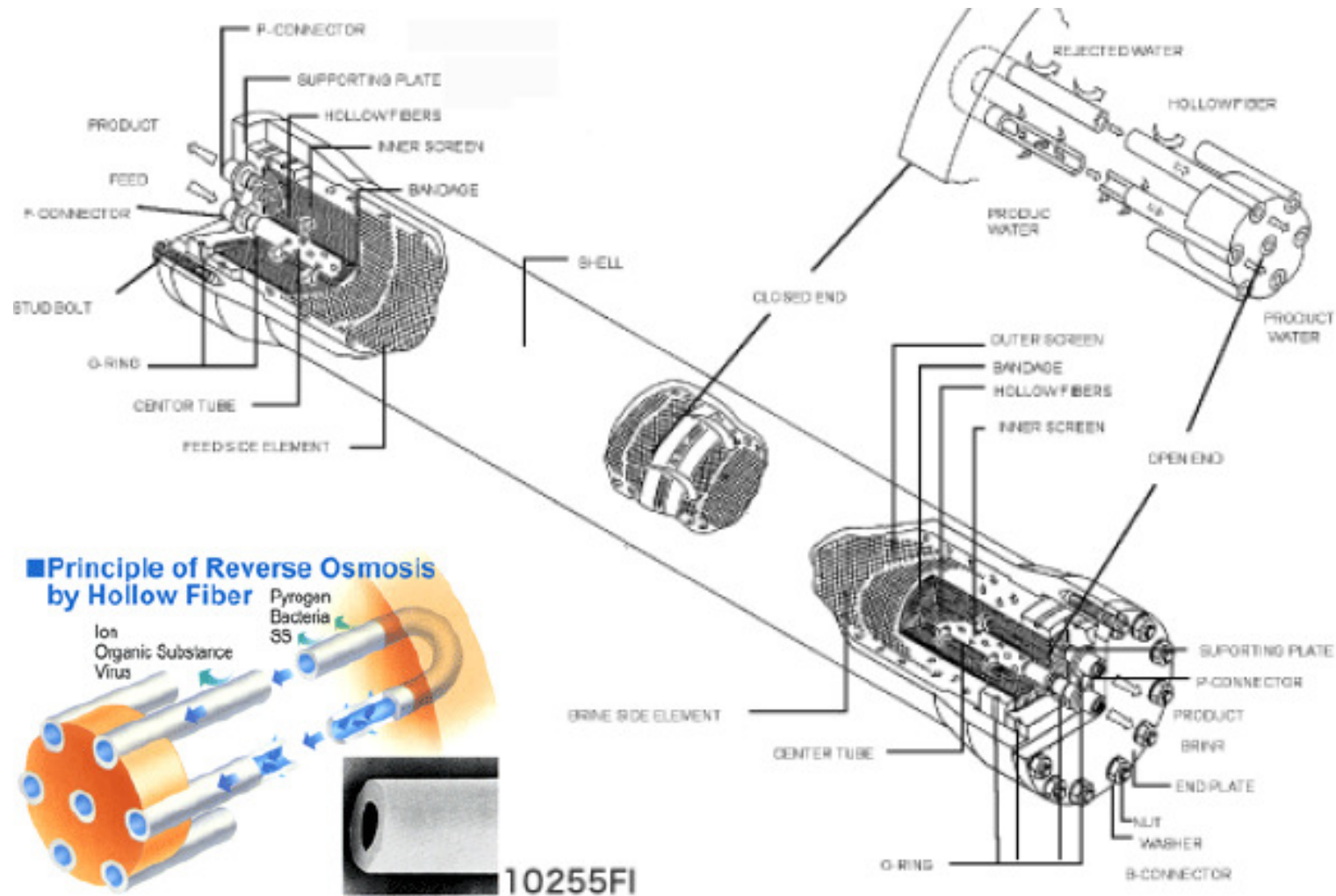


Hollow Fine Fiber Membrane Module



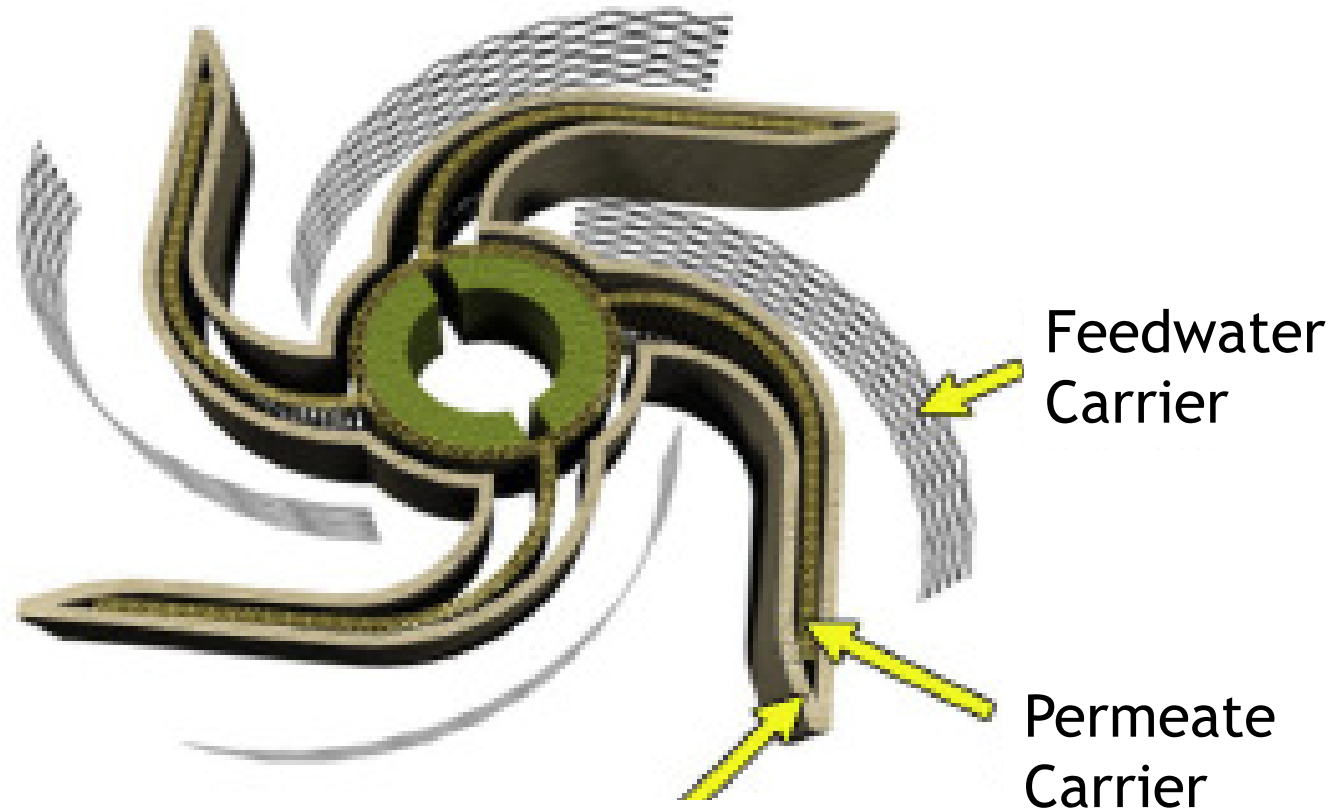
Hollow fibers with epoxy resin.

Hollow Fine Fiber Membrane Module



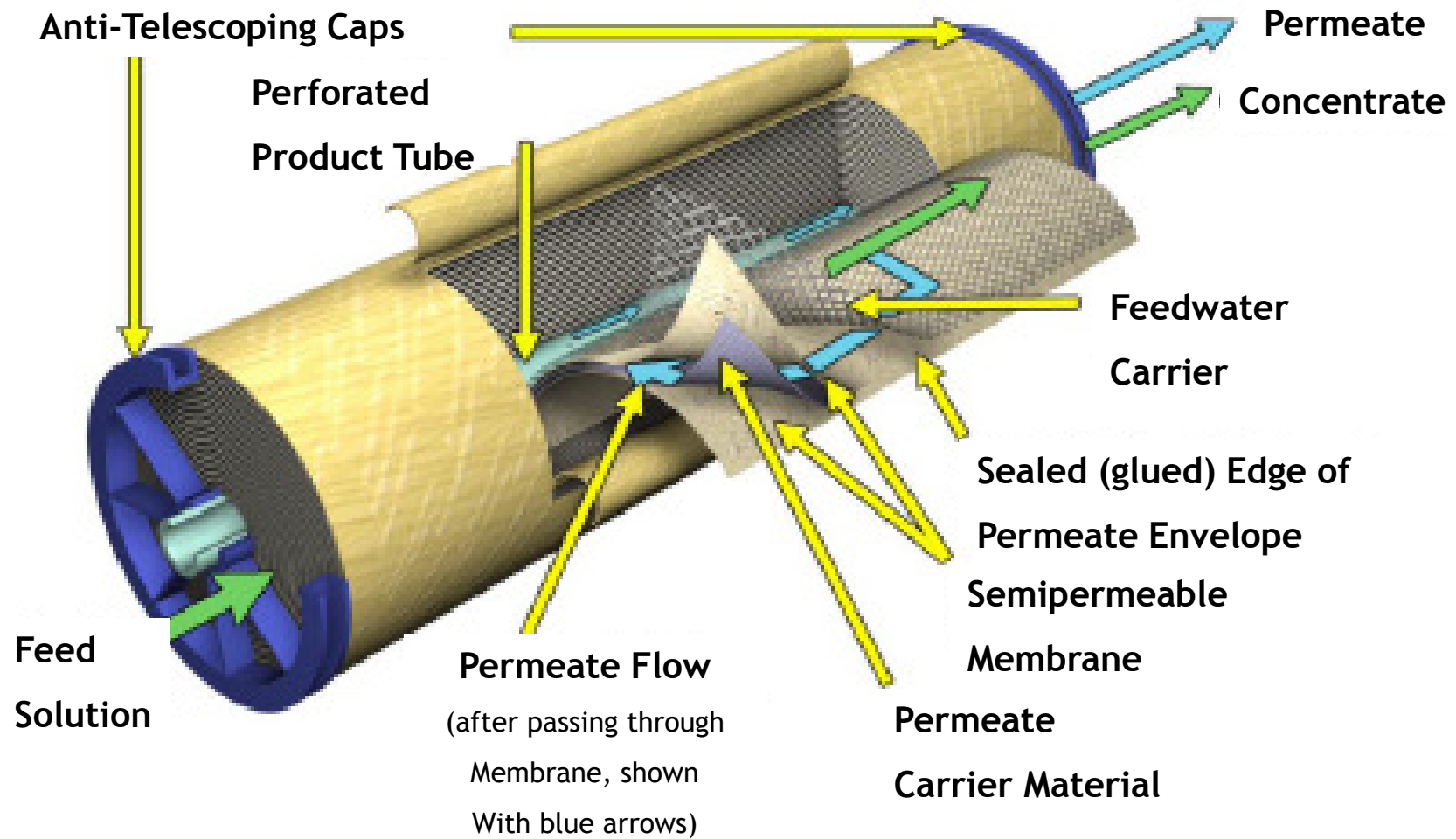


Cut-out view of Spiral Wound Membrane Element

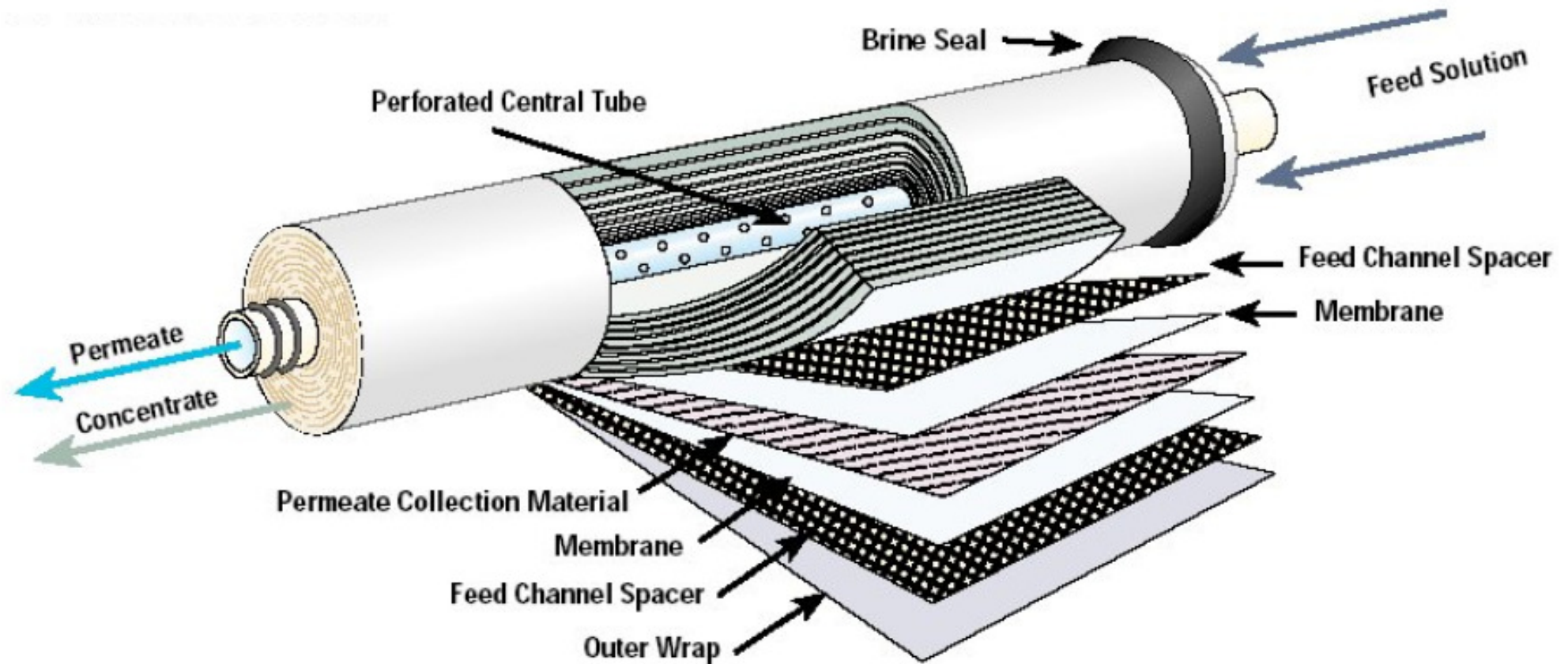


Thin Membrane with Supported Layers

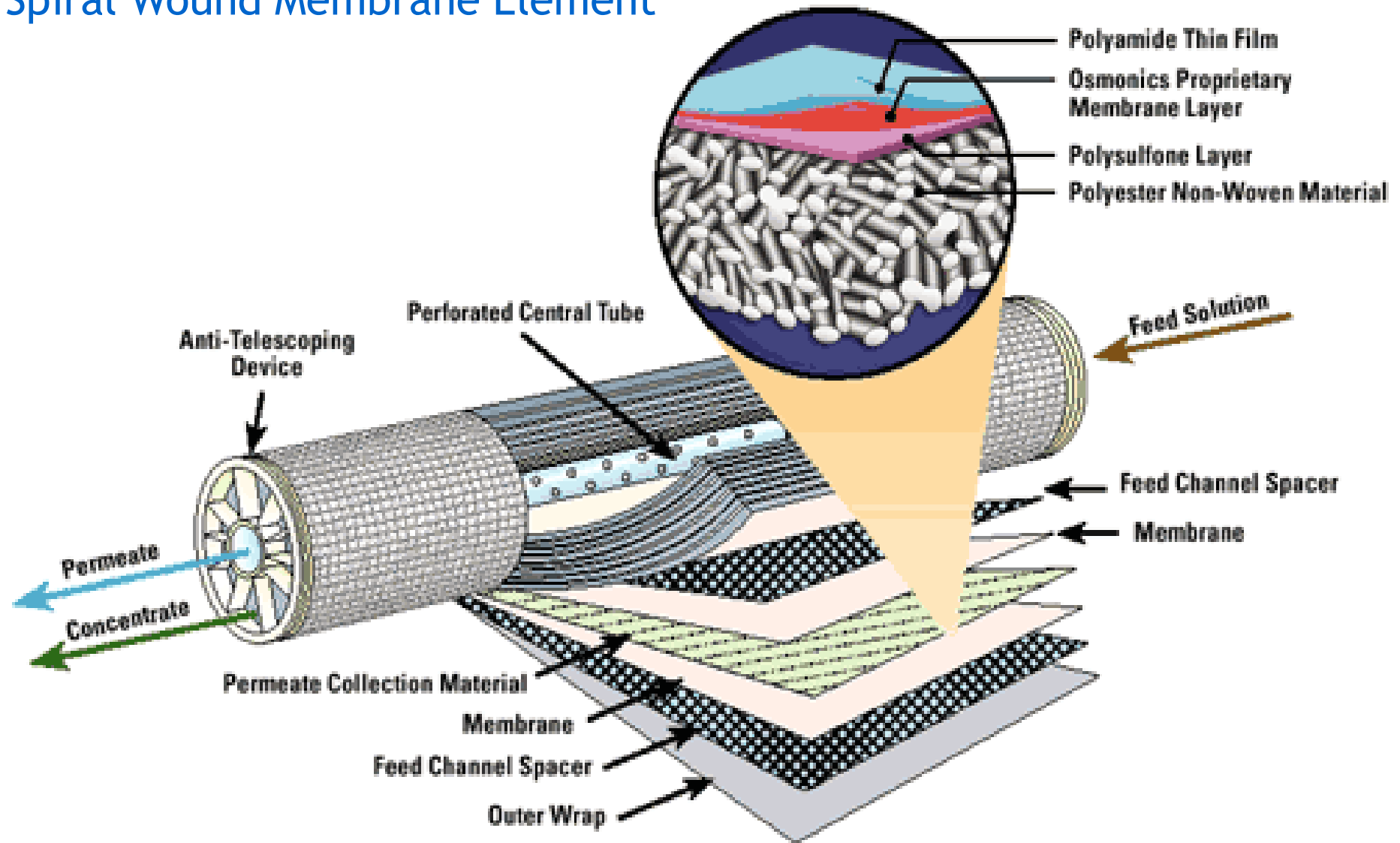
Spiral Wound Membrane Element



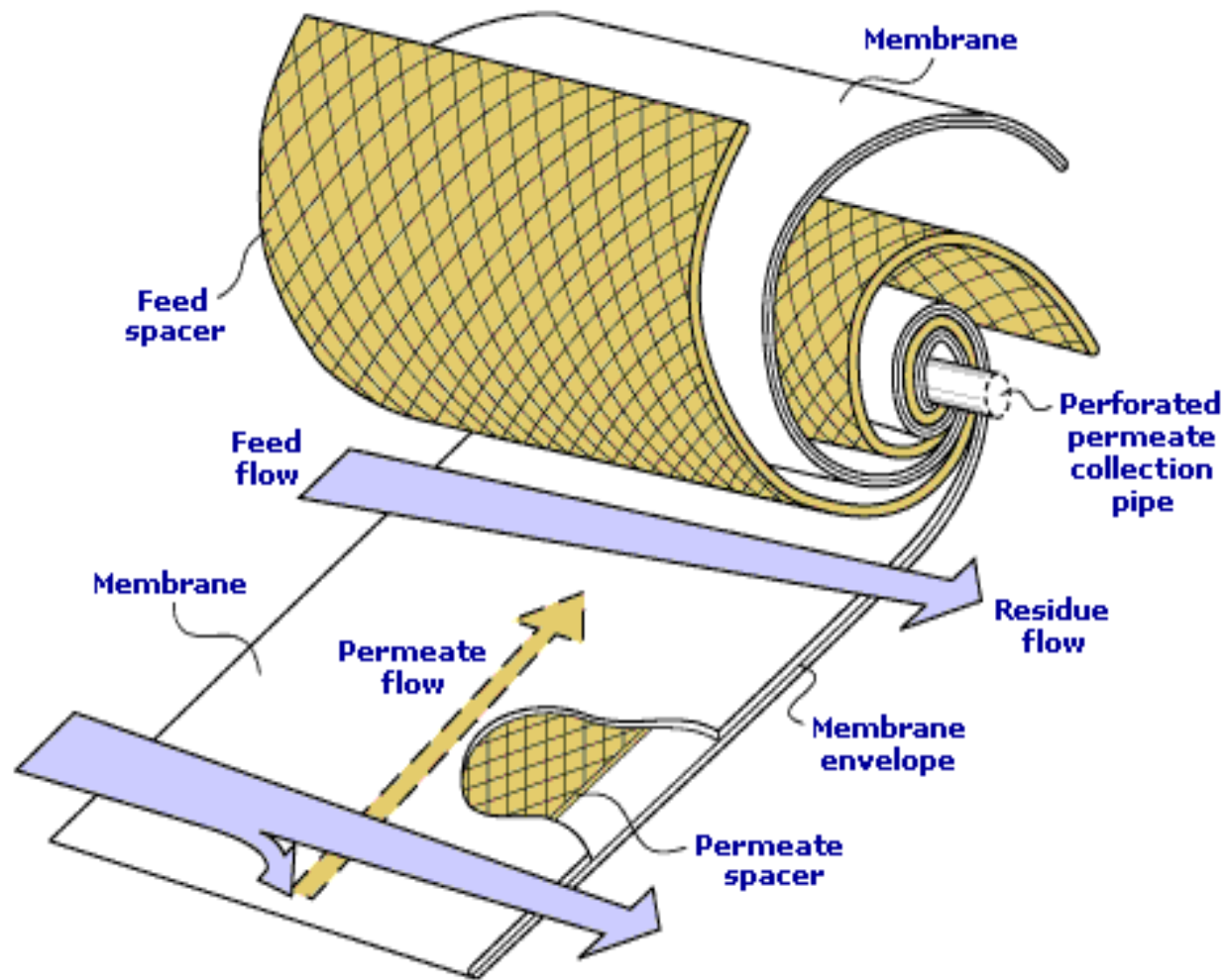
Spiral Wound Membrane Element



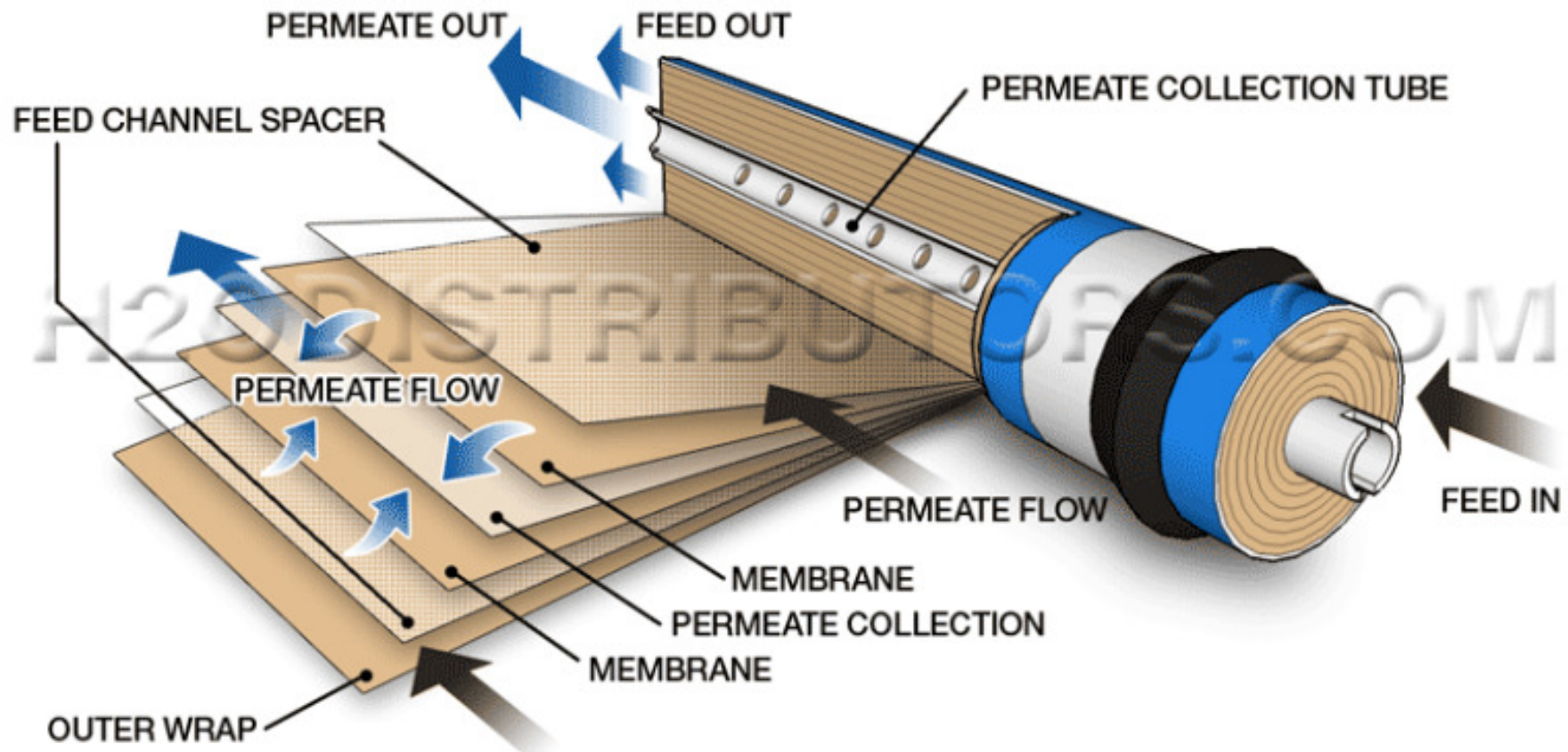
Spiral Wound Membrane Element



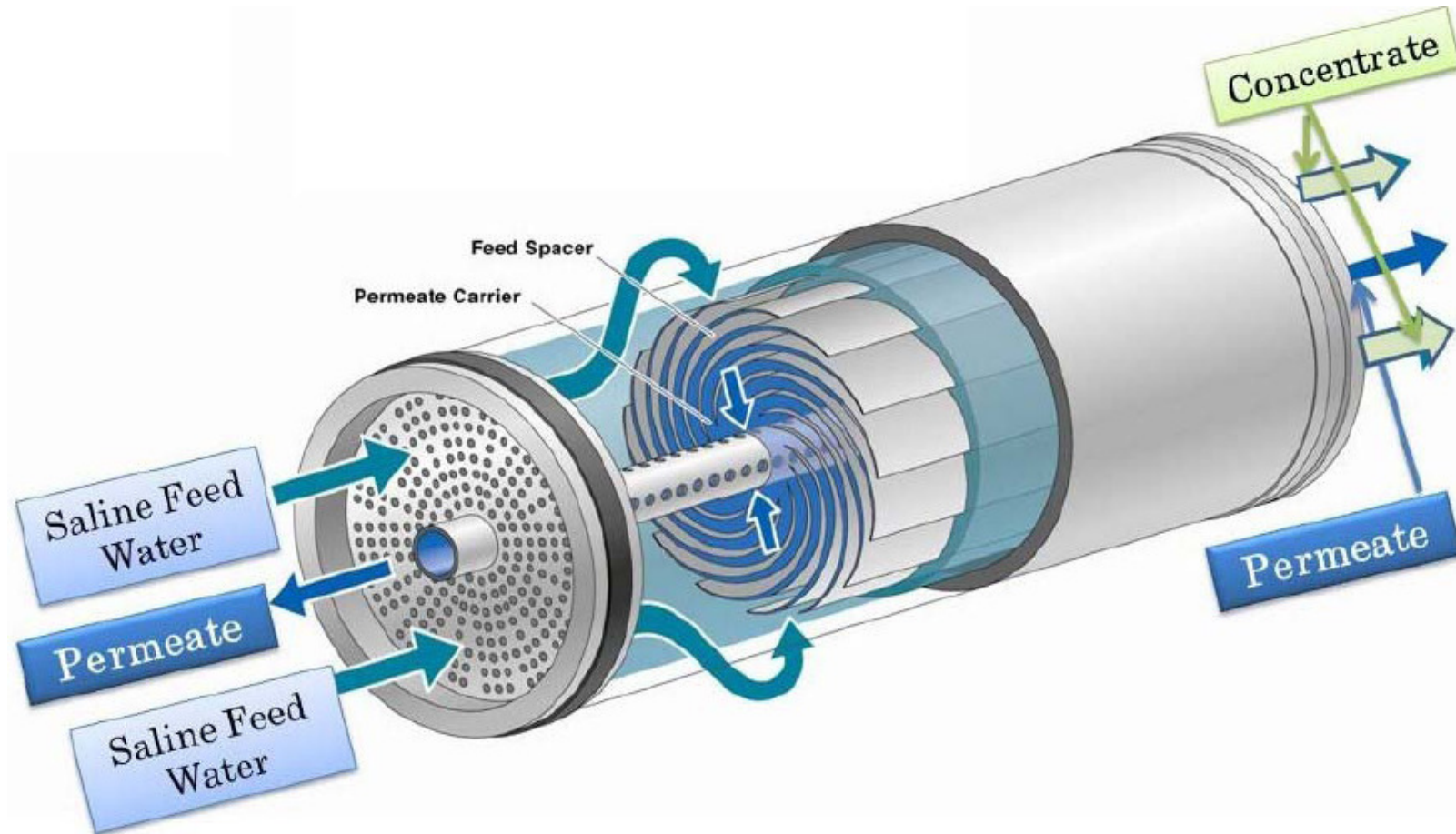
Spiral Wound Membrane Element



Spiral Wound Membrane Element



Spiral Wound Membrane Element



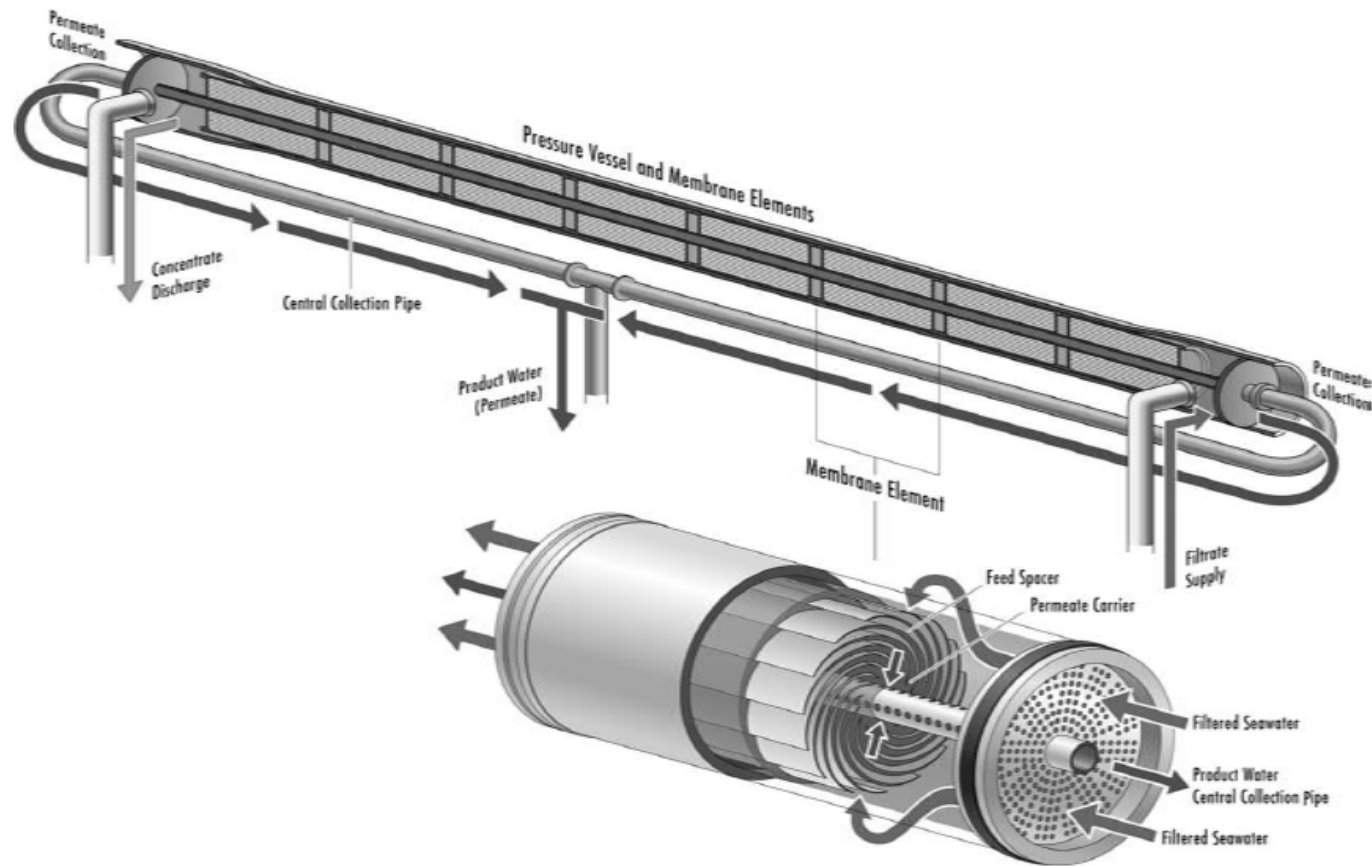


Spiral Wound Membrane Element

The spiral-wound module is featured by:

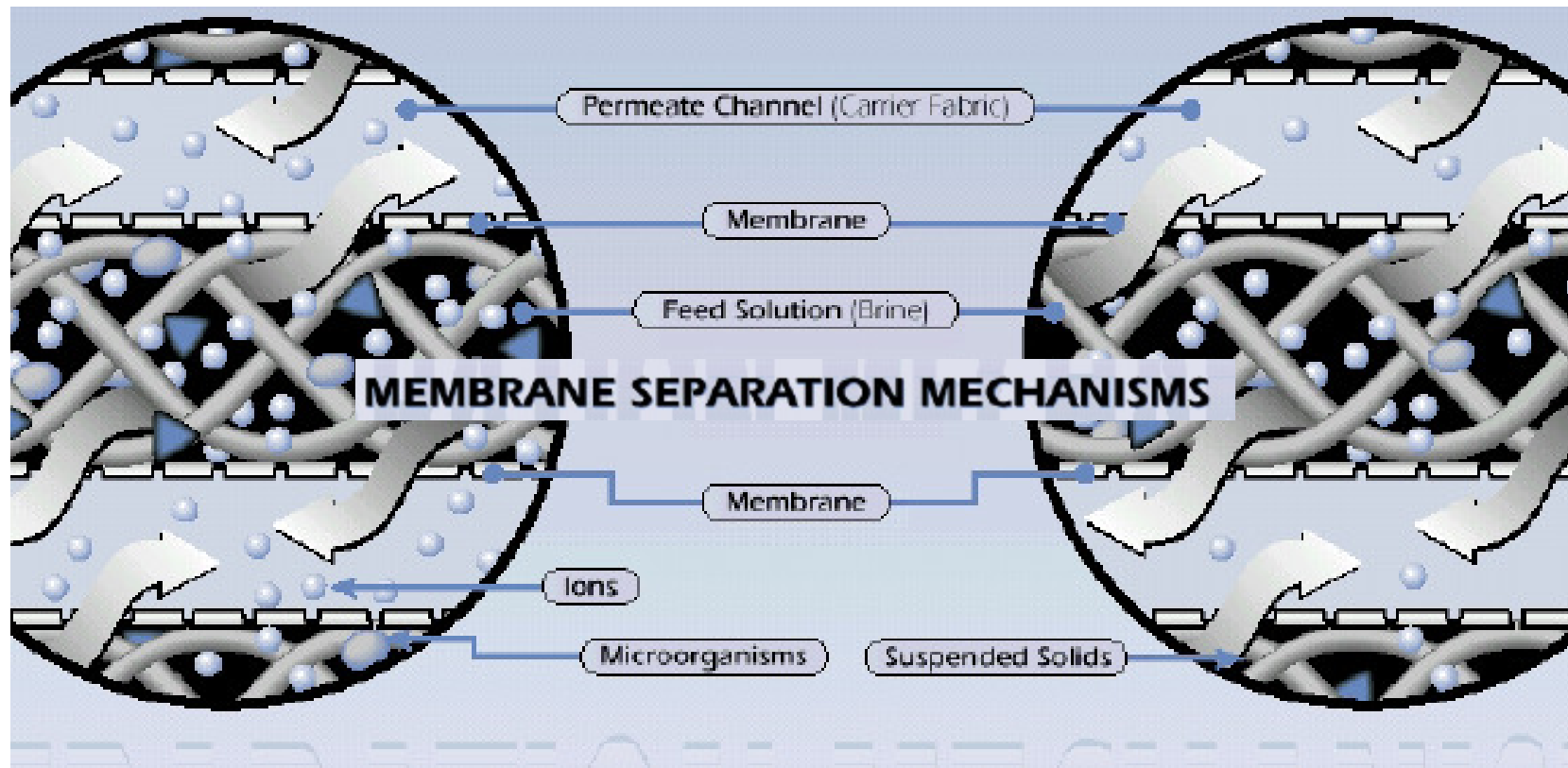
- A compact structure
- High-pressure durability
- Less contamination
- Less pressure drop at the permeate channel
- Minimum concentration polarization

Spiral Wound Membrane Element



Spiral-wound thin-film-composite SWRO membrane element

Spiral Wound Membrane Element



Spiral-wound : Membrane Separation Mechanism



Typical characteristics of membrane modules

	Plate and frame	Spiral wound	Tubular	Hollow fibre
Packing density (m^2/m^3)	30–500	200–800	30–200	500–9,000
Resistance to fouling	Good	Moderate	Very good	Poor
Ease of cleaning	Good	Fair	Excellent	Poor
Membrane material choices	Many	Many	Few	Few
Relative cost	High	Low	High	Low
Applications	D, RO, PV, UF, MF	D, RO, GP, UF, MF	RO, UF	D, RO, GP, UF

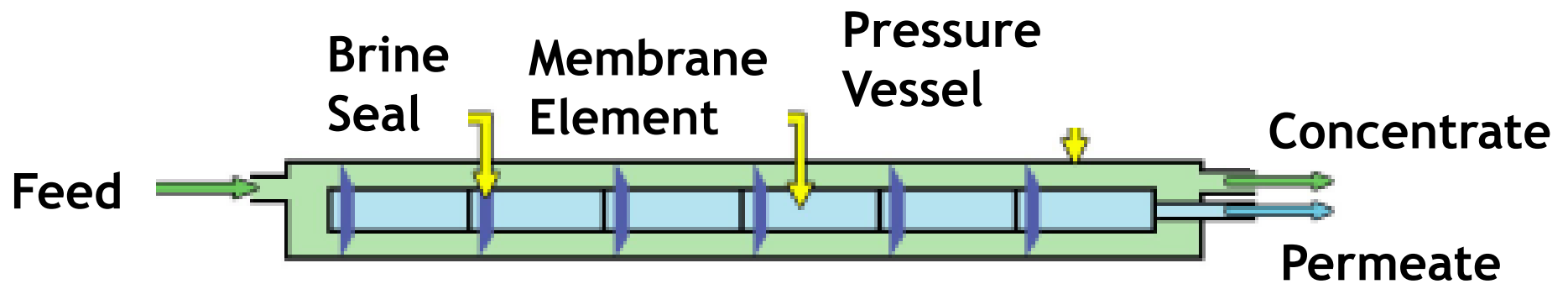
MF microfiltration, *UF* ultrafiltration, *D* dialysis, *PV* pervaporation, *RO* reverse osmosis.



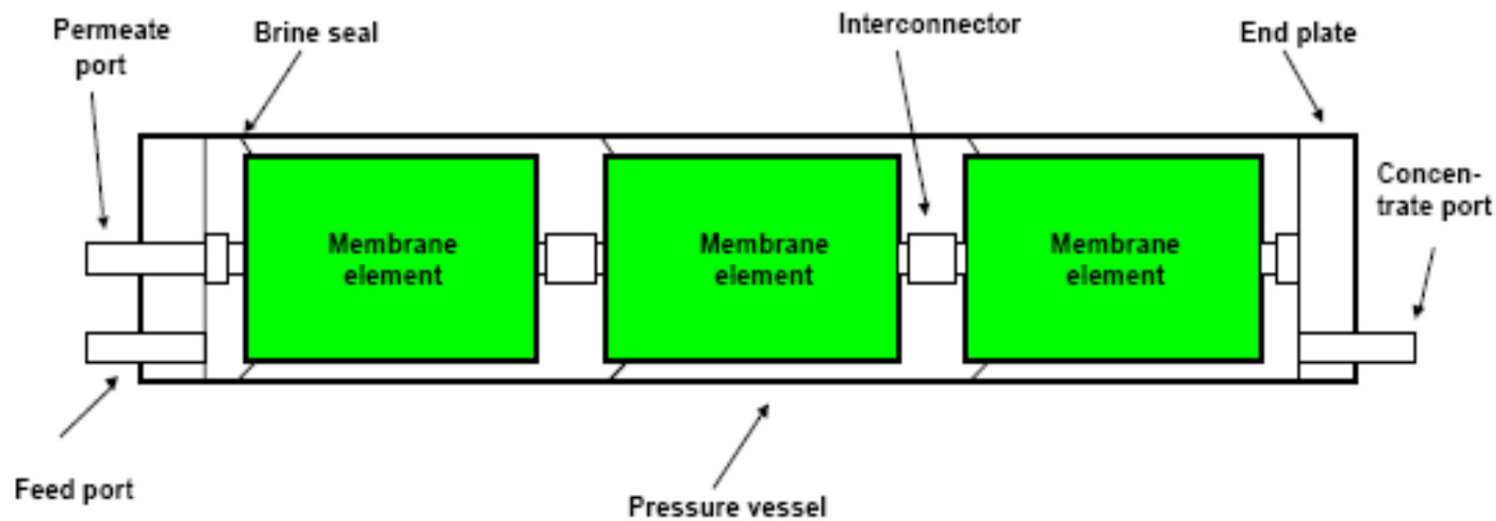
Comparison of membrane module geometries

	Tubular	Capillary	Plate-and-Fram	Spiral Wound
Characteristic flow diameter, mm	4 - 35	0.5-1.5	0.5 - 1	0.5 - 1
Cost/Area	High	Low	High	Low
Membrane replacement	High	Moderate	Low	Moderate/low
Flux, L/M ² h	Good	Good	Low	Low
Packing density, m ² /m ³	poor	excellent	Good/fair	Good
Holdup volume	High	low	medium	medium
Energy consumption	high	low	medium	medium
Fouling Resistance	Excellent	Good/fair	Good/fair	Medium
CIP	Excellent	Good	Fair/poor	Fair/poor

RO Pressure Vessel with a flow Path Identified

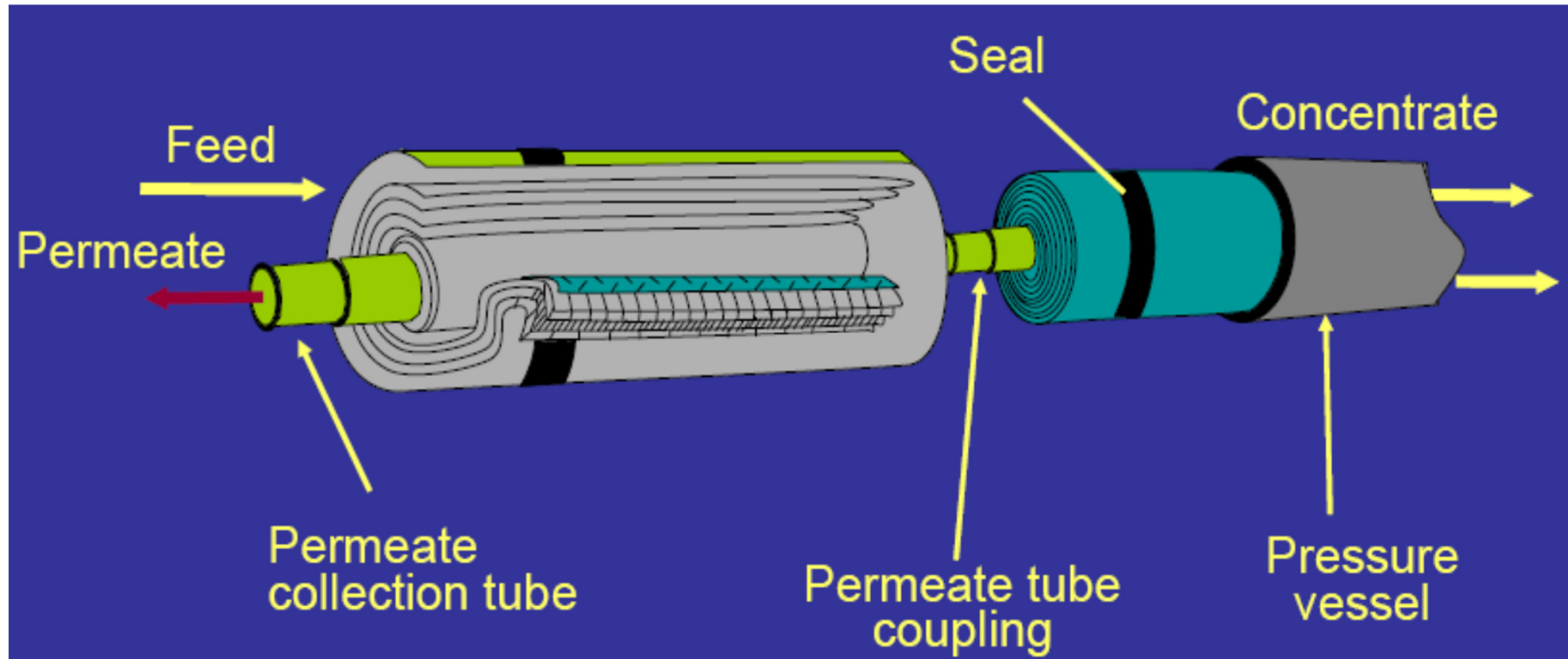


RO Pressure Vessel with a flow Path Identified



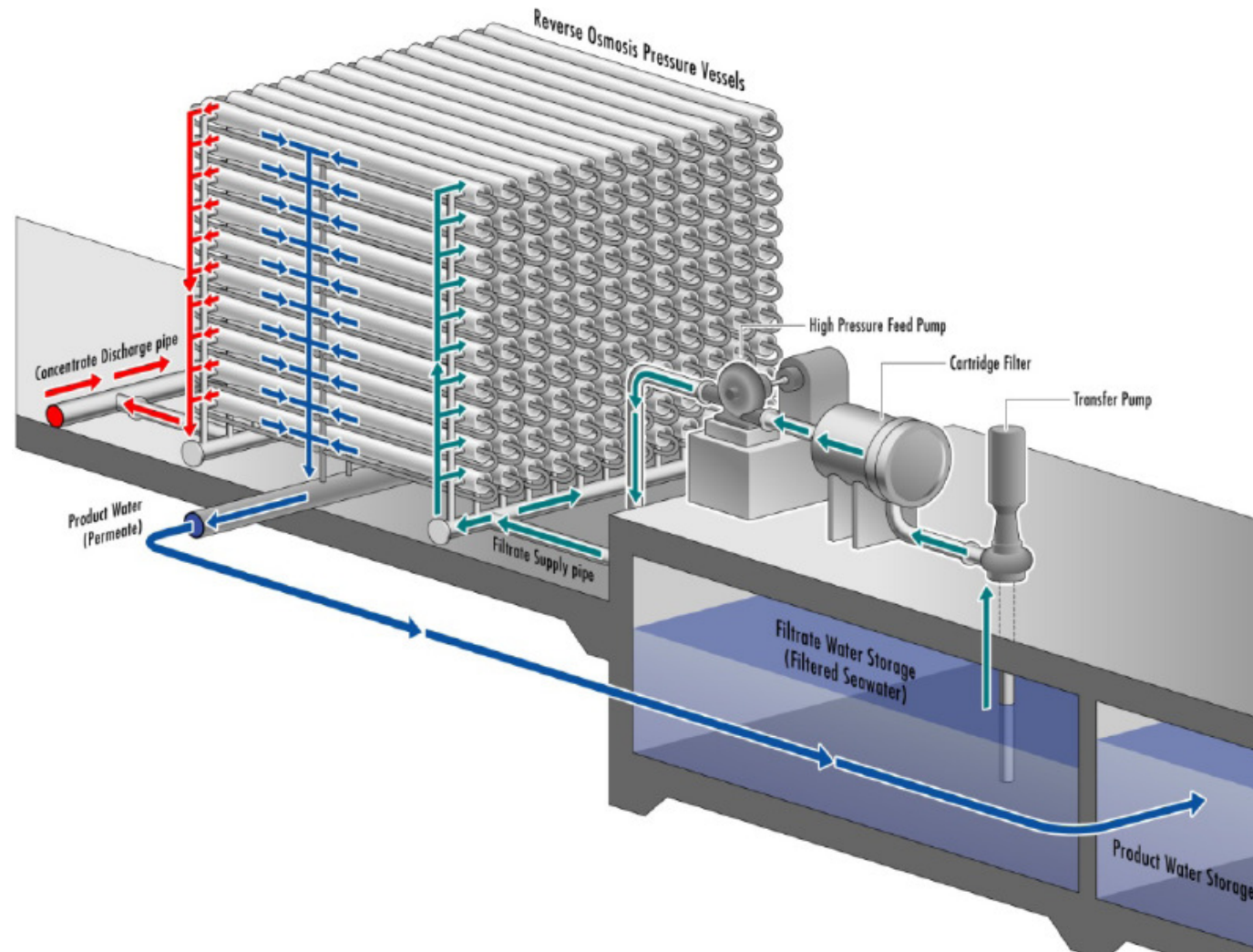
Pressure vessel with three membrane elements

RO Pressure Vessel with a flow Path Identified



RO Pressurized Vessel Structure

RO membrane system configuration

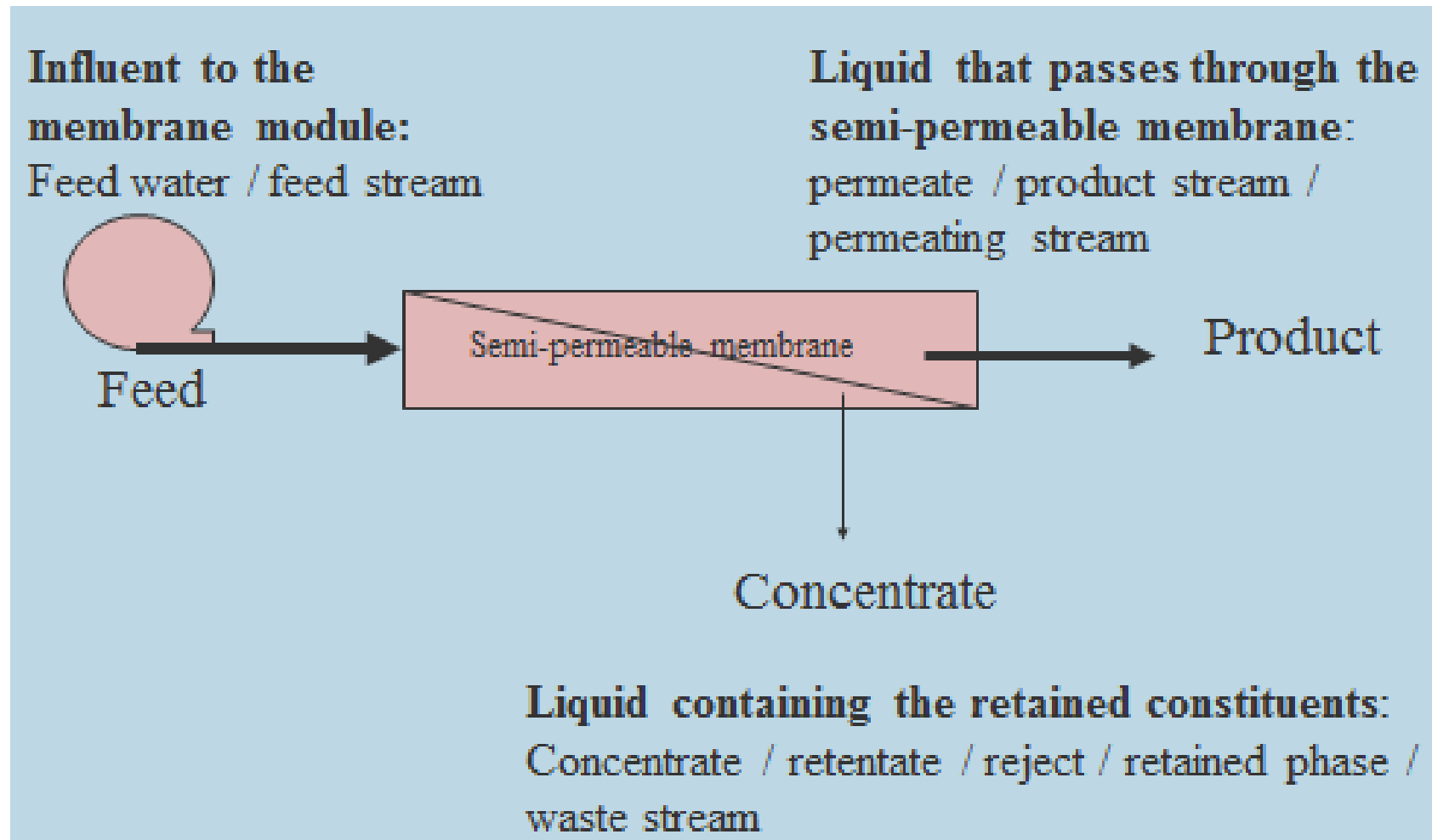




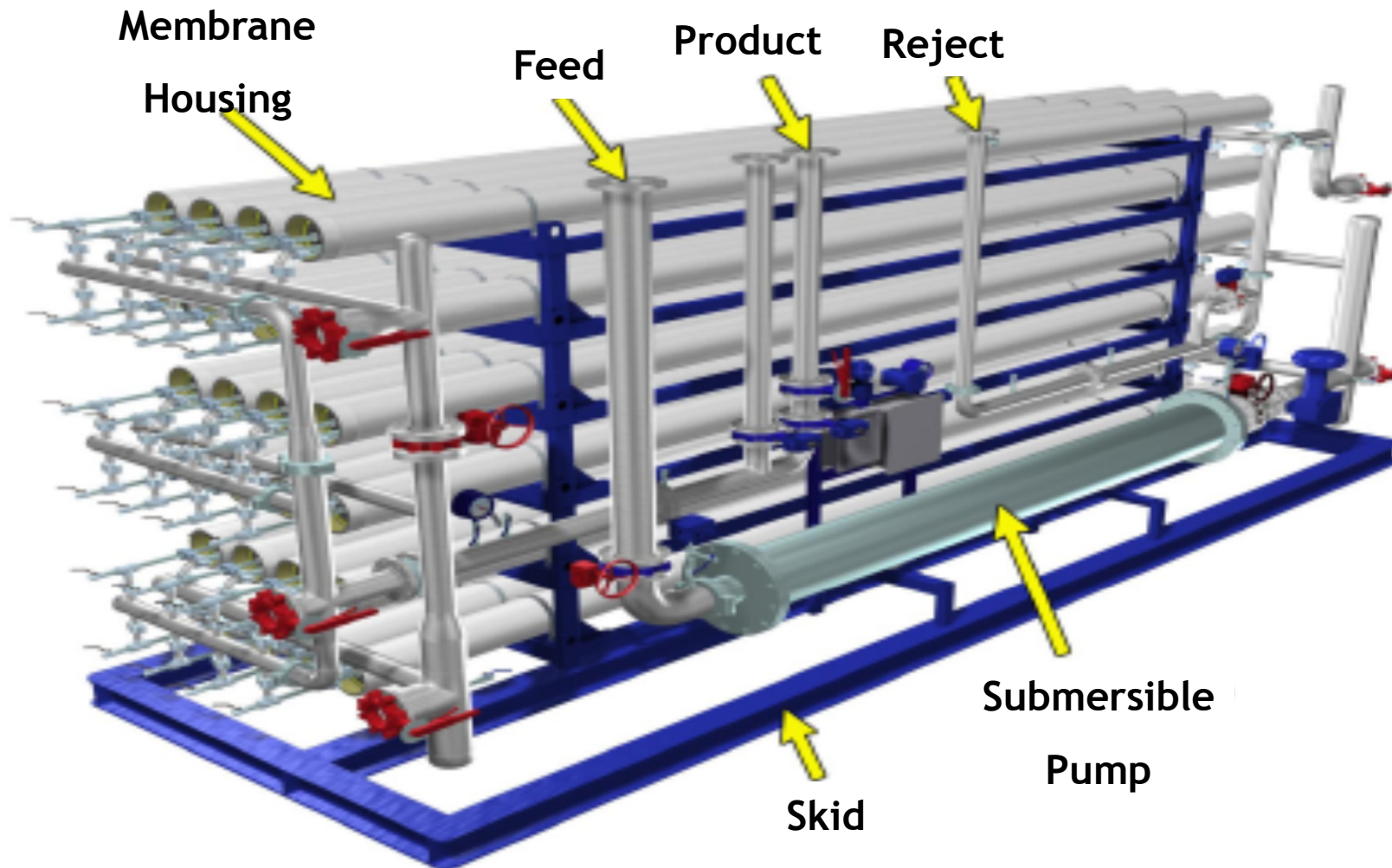
Typical RO Membrane Pressure Vessel



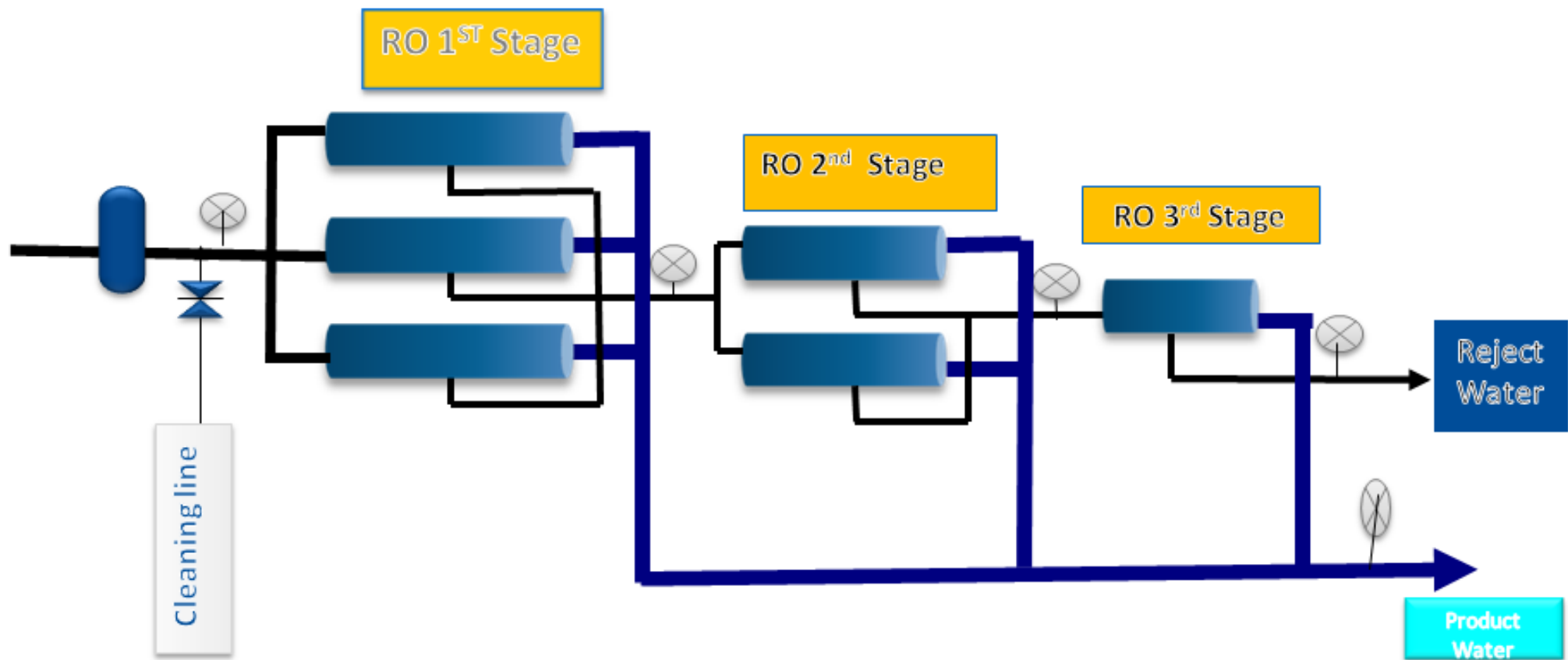
Typical RO system / General Process Configuration



Typical RO system and components

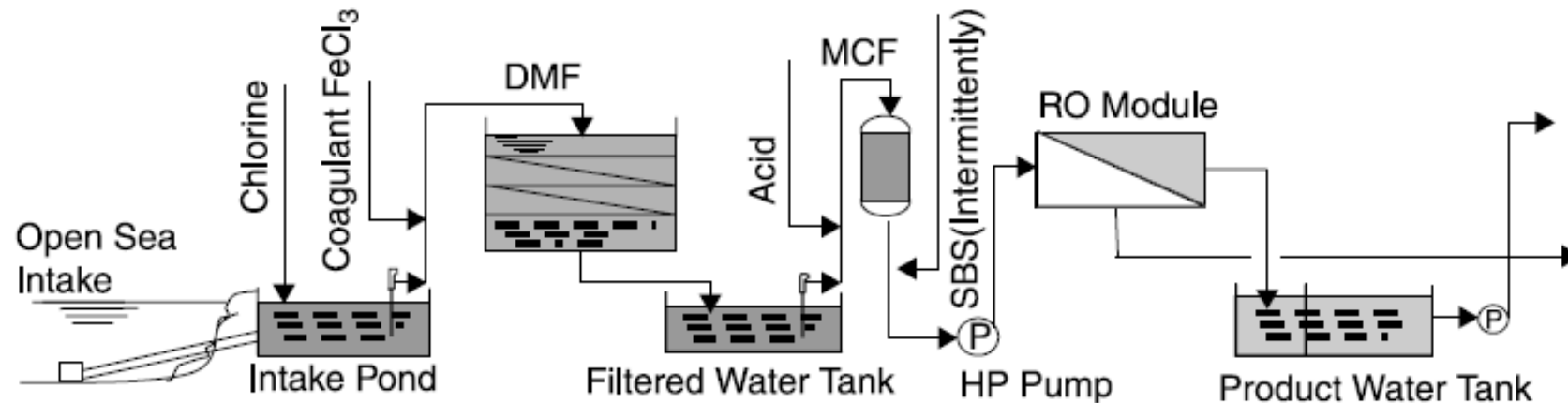


Typical RO system and components



Flow diagram of a three stage RO system

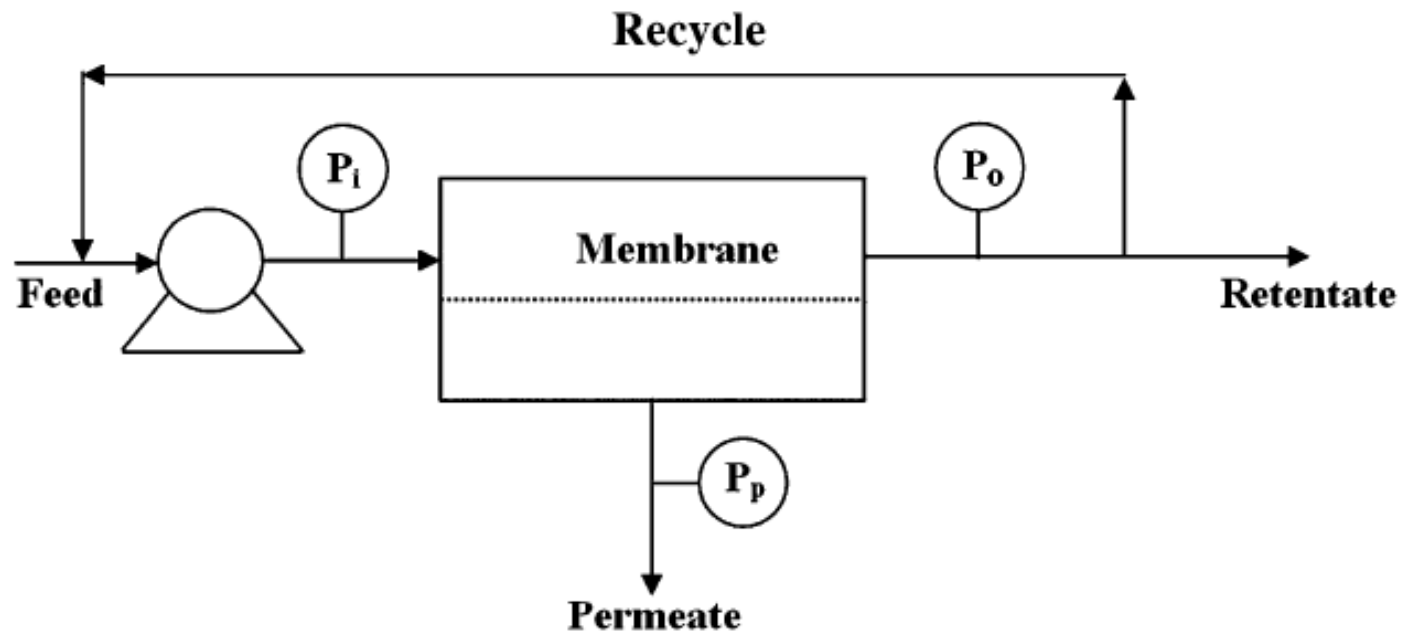
Typical RO system and components



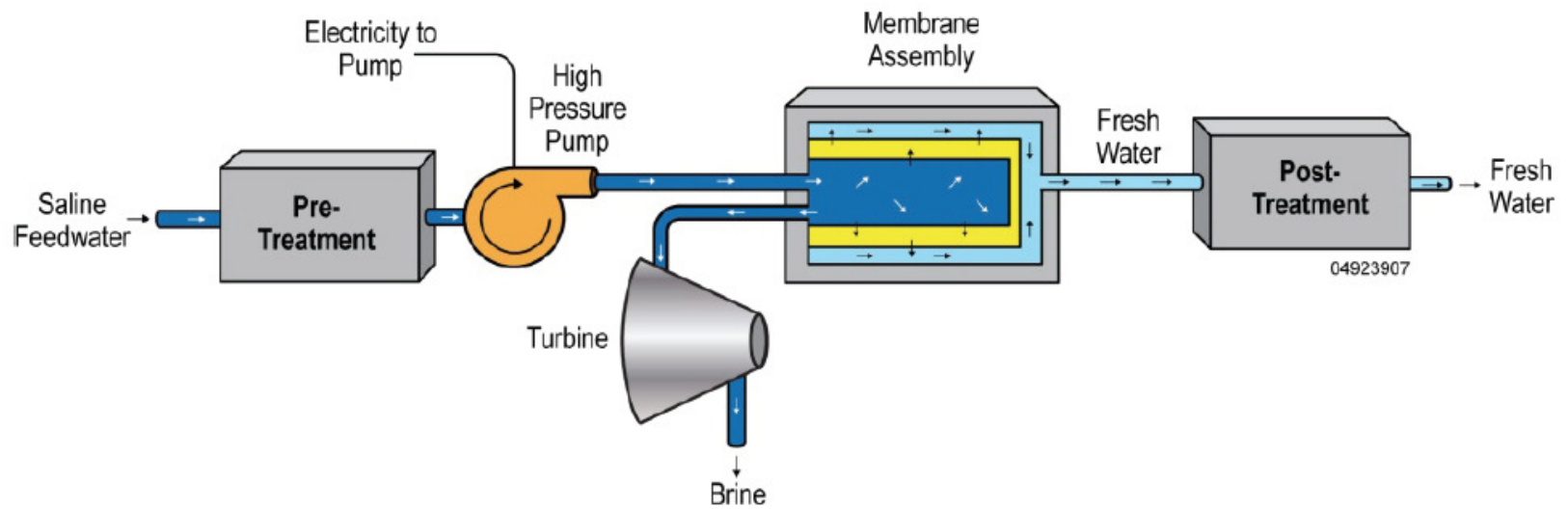
Schematic flow of Jeddah Phase II plant

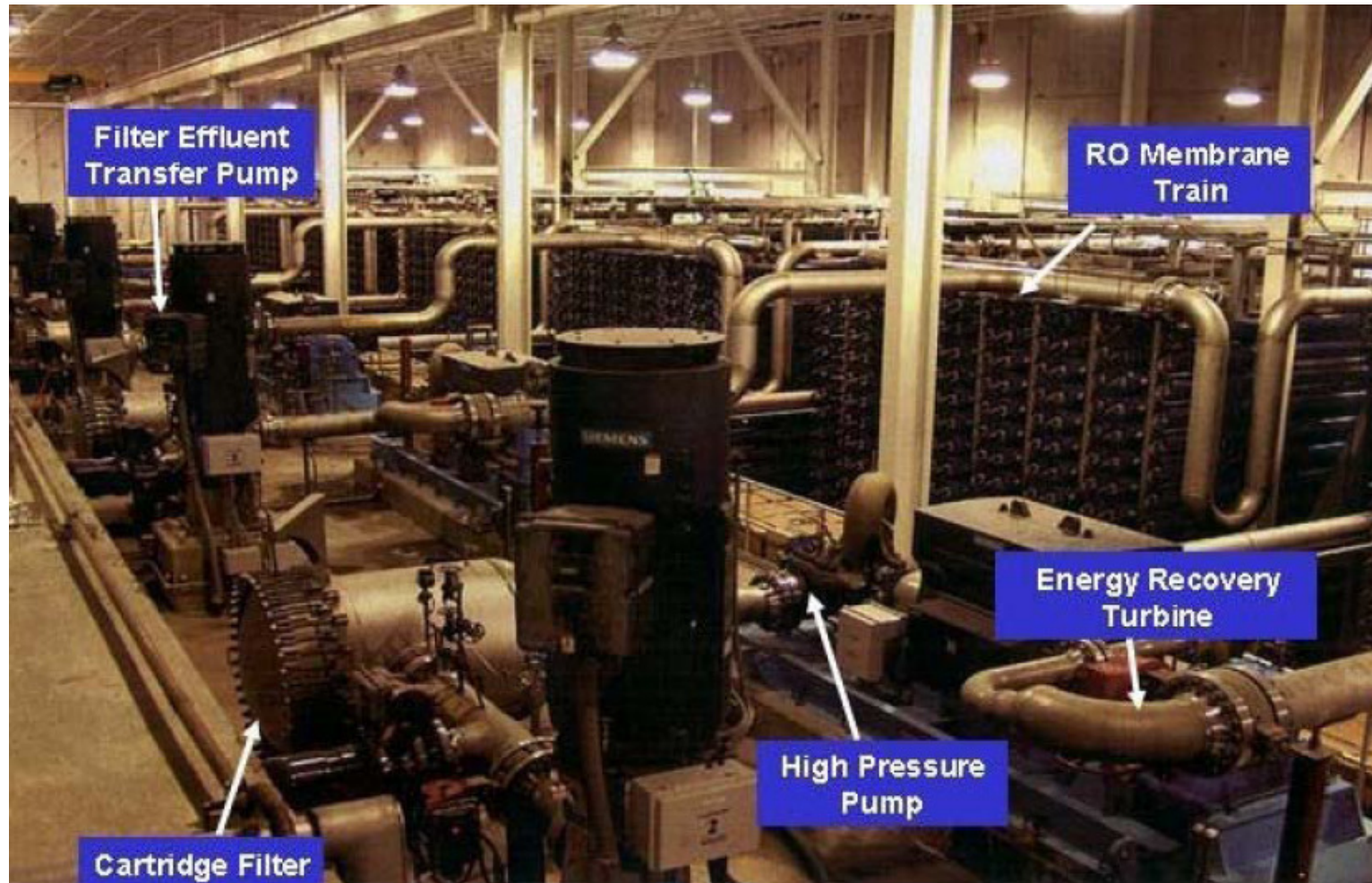


Simplified membrane process system



Major subsystems in a reverse-osmosis system





25 mgd Tampa Bay Seawater Desalination Plant, Florida



Osmotic Pressure Estimation

$$\pi \text{ (atm)} = M R T$$

where

π is the osmotic pressure in atm., M is Molarity, R is the universal gas constant, $R = 0.0821$ liter-atm/mole kelvin, T temperature in degree Kelvin

Example

Calculate the osmotic pressure of a solution that contained 100 grams of NaCl dissolved in enough water to make 1 liter of solution at 25 °C..

1. Convert the grams of NaCl to moles by dividing the grams by the molecular weight of NaCl (58.5). (Na=23, Cl=35.5)

$$100 \text{ grams NaCl} \times 1 \text{ mole} / 58.5 \text{ grams sucrose} = 1.71 \text{ moles NaCl}$$

2. Determine the Molarity concentration.

$$\text{Molarity} = \text{moles NaCl} / \text{volume of solution in liters} = 1.71 / 1 = 1.71 \text{ M}$$

3. Convert the temperature from Celsius to Kelvin, $K = 25 + 273 = 298 \text{ K}$

4. Calculate the osmotic pressure using the formula.

$$\text{Osmotic pressure in atm} = M R T = (1.71) (0.0821) (298) = 41.8 \text{ atm}$$



Osmotic Pressure Correlation

The osmotic pressure, π , in bar is obtained from the data given by Sourirajan (1970) for the NaCl-H₂O system at 25 °C (concentration range: 0-49.95 kgm⁻³) and is correlated as:

$$\pi = 0.7949C - 0.0021C^2 + 7.0 \times 10^{-5}C^3 - 6.0 \times 10^{-7}C^4$$

Reference: Sourirajan, S. (1970). *Reverse osmosis*. New York: Academic.



Osmotic Pressure Correlation

- The osmotic pressure, P_{osm} , of a solution can be determined experimentally by measuring the concentration of dissolved salts in solution :

$$P_{osm} = 1.19 (T + 273) * \Sigma(mi) \quad (1)$$

where

- P_{osm} = osmotic pressure (in psi),
- T is the temperature (in °C), and
- $\Sigma(mi)$ = sum of molal concentration of all constituents in a solution.
- An approximation for P_{osm} may be made by assuming that 1000 ppm of TDS equals about 11 psi (0.76 bar) of osmotic pressure.



Osmotic Pressure Correlation

- The mechanism of water and salt separation by reverse osmosis is not fully understood.
- Two transport models: **porosity** and **diffusion**.
- **Porosity** : transport of water through the membrane may be through physical pores present in the membrane.
- **Diffusion** from one bonding site to another within the membrane.
- The chemical nature of the membrane is such that it will absorb and pass water preferentially to dissolved salts at the solid/liquid interface.
- This may occur by weak chemical bonding of the water to the membrane surface or by dissolution of the water within the membrane structure.
- Either way, a salt concentration gradient is formed across the solid/liquid interface. The chemical and physical nature of the membrane determines its ability to allow for preferential transport of solvent (water) over solute (salt ions).



Pressure Definitions

- Average Operating Pressure

$$P_{AVG} = (P_I + P_O)/2$$

- Effective Pressure (Transmembrane)

$$P_{EFF} = P_{AVG} - P_B - P_{\pi}$$

- The effective pressure is the net pressure after permeate back pressure and osmotic pressure losses - i.e. the pressure difference across the membrane.

P_I : Inlet Pressure - Pressure of the feed stream prior to the membrane elements

P_O : Outlet Pressure - Pressure of the concentrate stream after the membranes

P_B : Permeate Pressure (Back Pressure) - Pressure of the permeate stream after the membranes



Water Transport

The rate of water passage through a semipermeable membrane is:

$$Q_w = (\Delta P - \Delta P_{osm}) * K_w * S/d \quad (2)$$

where

- Q_w is the rate of water flow through the membrane,
- ΔP is the hydraulic pressure differential across the membrane,
- ΔP_{osm} is the osmotic pressure differential across the membrane,
- K_w is the membrane permeability coefficient for water,
- S is the membrane area, and d is the membrane thickness.

This equation is often simplified to:

$$Q_w = A * (NDP) \quad (3)$$

Where

- A represents a unique constant for each membrane material type, and
- NDP is the net driving pressure or net driving force for the mass transfer of water across the membrane.



Salt Passage

The rate of salt flow through the membrane is defined by :

$$Q_s = \Delta C * K_s * S/d \quad (4)$$

where

- Q_s is the flow rate of salt through the membrane,
- ΔC is the salt concentration differential across the membrane,
- K_s is the membrane permeability coefficient for salt,
- S is the membrane area, and d is the membrane thickness.

This equation is often simplified to:

$$Q_s = B*(\Delta C) \quad (5)$$

- Where
- B represents a unique constant for each membrane type, and
- ΔC is the driving force for the mass transfer of salts.



Salt Transport

Equations 4 and 5 show that for a given membrane:

1. Rate of water flow through a membrane is proportional to net driving pressure differential (NDP) across the membrane.
2. Rate of salt flow is proportional to the concentration differential across the membrane and is independent of applied pressure.
 - Salinity of the permeate, C_p , depends on the relative rates of water and salt transport through reverse osmosis membrane:

$$C_p = Q_s / Q_w \quad (6)$$

- The fact that water and salt have different mass transfer rates through a given membrane creates the phenomena of salt rejection. No membrane is ideal in the sense that it absolutely rejects salts; rather the different transport rates create an apparent rejection. The equations 2, 4 and 5 explain important design considerations in RO systems. For example, an increase in operating pressure
 - will increase water flow without changing salt flow, thus resulting in lower
 - permeate salinity.



Salt Passage

- **Salt passage:** is the ratio of concentration of salt on the permeate side of the membrane relative to the average feed concentration. expressed:

$$SP = 100\% * (C_p/C_{fm}) \quad (7)$$

where

- **SP** is the salt passage (in %), C_p is the salt concentration in the permeate,
- **C_{fm}** is the mean salt concentration in feed stream.
- Applying the fundamental equations of water flow and salt flow illustrates some of the basic principles of RO membranes.
- For example, salt passage is an inverse function of pressure; that is, the salt passage increases as applied pressure decreases. This is because reduced pressure decreases permeate flow rate, and hence, dilution of salt (the salt flows at a constant rate through the membrane as its rate of flow is independent of pressure).



Salt Rejection

Salt rejection: is the opposite of salt passage, and is defined by:

$$SR = 100\% - SP \quad (8)$$

where

- **SR** is the salt rejection (in %), and
- **SP** is the salt passage as defined in Equation 7:

$$SP = 100\% * (C_p/C_{fm}) \quad (7)$$



Permeate Recovery Rate (Conversion)

Permeate Recovery: is an important parameter in the design and operation of RO systems.

- Recovery or conversion rate of feed water to permeate is defined by:

$$R = 100\% * (Q_p / Q_f) \quad (9)$$

where

- R** is recovery rate (in %),
- Q_p** is the product water flow rate, and
- Q_f** is the feed water flow rate.
- The recovery rate affects salt passage and product flow. As the recovery rate increases, the salt concentration on the feed-brine side of the membrane increases, which causes an increase in salt flow rate across the membrane as indicated by Equation 5: $Q_s = B * (\Delta C)$.
- Also, a higher salt concentration in the feed-brine solution increases the osmotic pressure, reducing the NDP and consequently reducing the product water flow rate according to Eq. 2: $Q_w = (\Delta P - \Delta P_{osm}) * K_w * S/d$



Membrane Desalination Processes



Content:

- *Desalination: An Overview*
- *Overview of Membrane Desalination Technologies*
- *Pretreatment Processes:*
microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF)
- *Commercial Processes:*
Reverse Osmosis (RO), Electrodialysis (ED) and ED Reversal
- *Innovative Processes:*
Forward Osmosis (FO) and Membrane Distillation (MD)



Membrane Desalination Processes



Content:

- **Commercial Processes:**
Reverse Osmosis (RO), Electrodialysis (ED) and ED Reversal
 - *Introduction*
 - *Basic Equations for ED& RO*
 - *Comparisons between ED and RO*
 - *ED Process Characteristics*
 - *ED Voltage Requirements*
 - *ED Basic Operation*
 - *EDR: Electrodialysis Reversal*



Introduction

- ED membrane was discovered in 1950
- First commercial ED plant was built in 1954
- EDR is developed in 1968
- Developments in the technology are:
 - Better membranes and module designs
 - ED is generally applied for brackish water desalination
 - Capital cost is US\$ 2.42 per installed gallon/day
 - Desalinated water cost is US\$ 0.3 to 1.0 per m³ for brackish water desalination



Introduction

- **History: Ostwald 1890 (membrane potential), Donnan 1911 Elder 1934**
- **Driven force: ELECTRICAL POTENTIAL GRADIENT, electroosmosis.**
- **Transport mechanism: counter ions via ion exchange membranes, coupled transport**
- **Models: Nernst-Planck equation and Donnan equilibrium.**
- **Separation principle: Donnan exclusion mechanism**
- **Size of retained species: coions, macroions**
- **Type of membrane: ION-exchange and bipolar, SEMIPERMEABLE**
- **Membrane materials: crosslinked copolymers based on divinylbenzene (DVB), with polystyrene or polyvinylpyridine copolymers of polytetrafluoroethylene (PTFE) and polysulfonyl fluoride-vinyl ether)**
- **Pore size: nonporous**
- **Type of module: flat sheet**
- **Flux: DEPENDENT ON REQUIRED SEPARATION**
- **Energy consumption: depends on feed concentration (~0.4 kWh/m³)**
- **Costs: operating costs: 0.1\$/m³, total 0.34 \$/m³**
- **Applications: brackish water, table salt, wastewater treatment, desalting of solutions in food,, chemical and pharmaceutical industries, concentrating of brines.**



Introduction

LOCATION	COUNTRY	APPLICATION	Production m ³ /d	YEAR	
EURODIA					
Montefano	Italy	Groundwater	Nitrate removal	1.000	1991
Munchenbuschsee	Switzerland	Groundwater	Nitrate removal	1.200	1996
Kleylehof	Austria	Groundwater	Nitrate removal	3.500	1997
GENERAL ELECTRIC WATER & PROCESS (formerly ionics Inc)					
Abrera, BCN	SPAIN	Surface water	bromide reduction	200.000	2008
Magna, Utah	USA	Groundwater	As, Perchlorate reduction	22.728	2008
Sherman, Texas	USA	Surface water	salinity reduction	27.700	1993-96-98
Suffolk, Virginia	USA	Groundwater	Fluoride reduction	56.000	1990
Sarasota, Or	USA	Groundwater	Hardness & salts reduction	45.420	1995
Maspalomas	SPAIN	Groundwater	salinity reduction	37.000	1986
Barranco Seco, Canary Is.	SPAIN	Waste Water	Reuse	26.000	2002
Bermuda WaterWorks	Bermudas	Groundwater	Hardness & Nitrate reduction	2.300	1989
Falconera, Valencia	SPAIN	Groundwater	Nitrate reduction	16.000	2007
MEGA a.s.					
Sant Boi, BCN	SPAIN	Waste Water	salinity reduction	55.296	2010
Dolni Rozinka	Czech Rep.	Uranium mining	Desalination of sludge	1.752	2007
ZIAR nad HRONOM	Slovakia	Waste water	Desalination of sludge	350	2003
Arak	Iran	Waste water	cooling tower	4.800	2008 -10
Alberta	Canada	Well water	Gas well water desalination	40	2008



Electrodialysis, Electrolysis and Dialysis

Electrodialysis (ED): is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference.

Electrolysis: is a method of using a direct electric current to drive non-spontaneous chemical reaction. For example, electrolysis of water is the decomposition of water (H_2O) into oxygen (O_2) and hydrogen gas (H_2) due to an electric current being passed through the water.

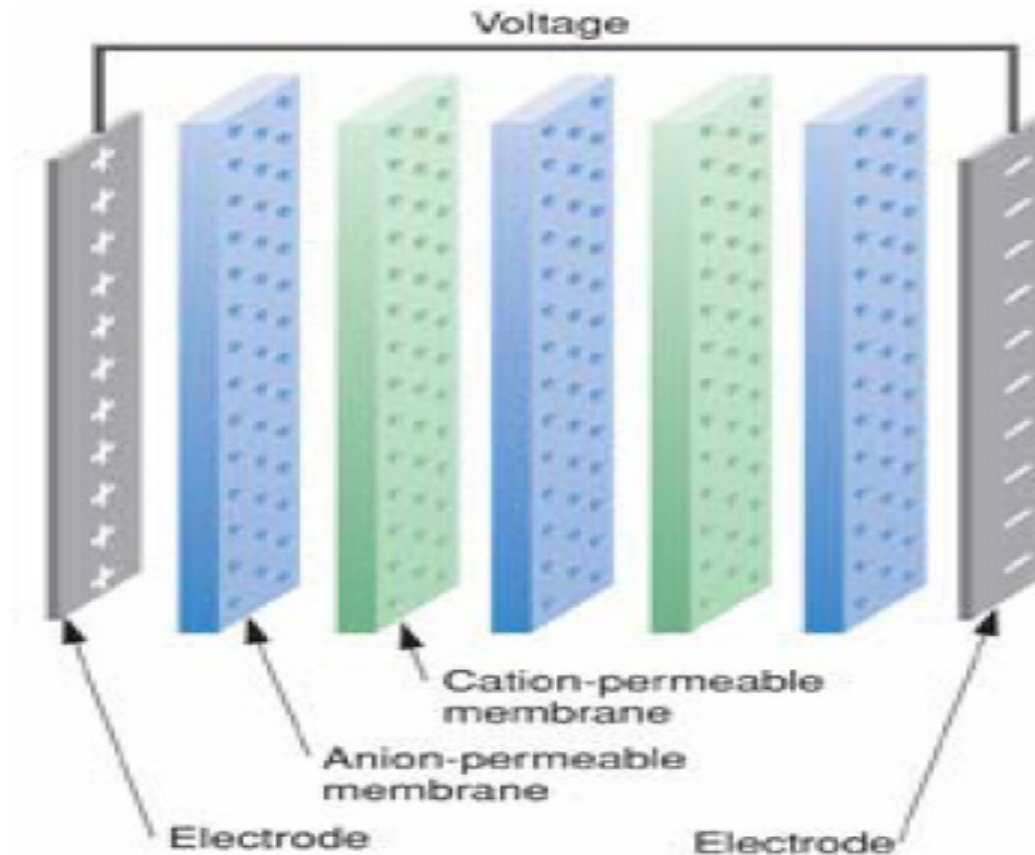
Dialysis: is a membrane process where solutes ($MW \sim < 100$ Da) diffuse from one side of the membrane (feed side) to the other (dialysate or permeate side) according to their concentration gradient.



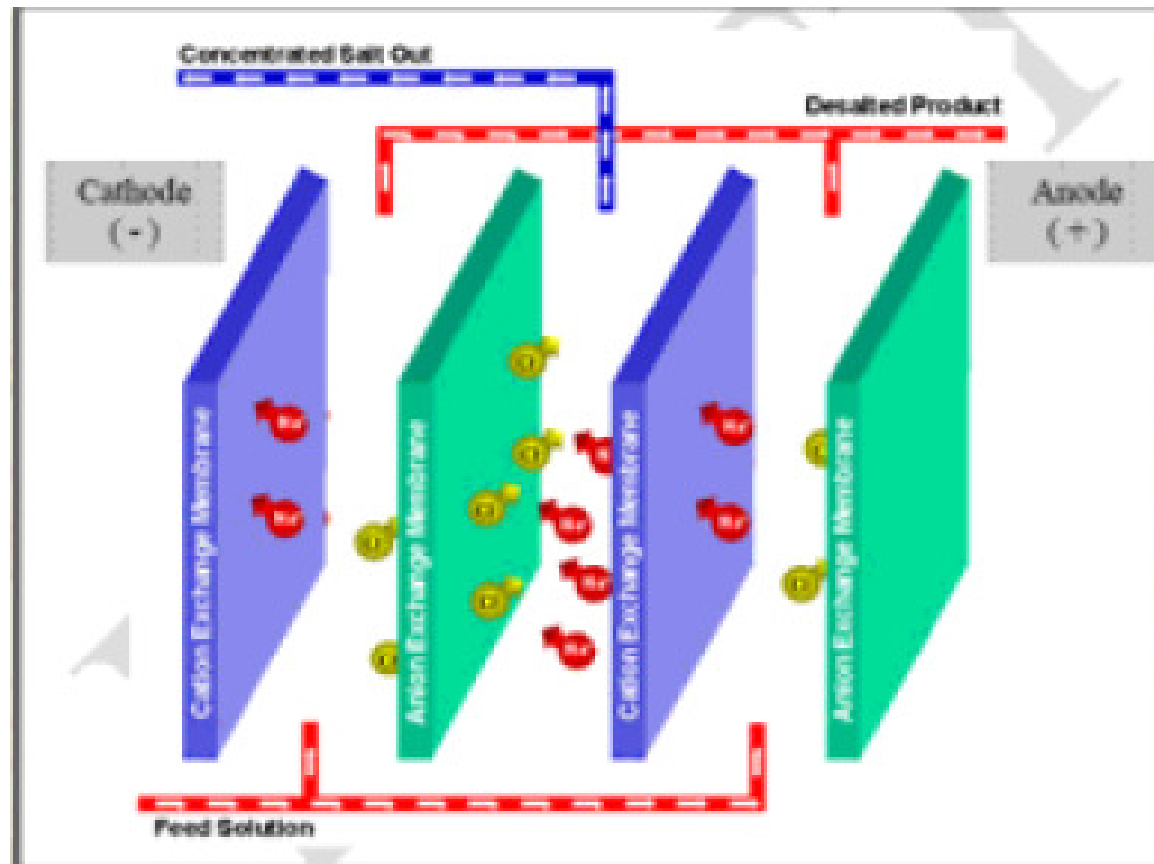
Electrodialysis Basic Operation

Electrodialysis (ED) is an electrochemical separation process in which ions are transferred through **ion exchange membranes** by means of a **direct current (DC) voltage**. The process uses a driving force to transfer ionic species from the source water through cathode (positively charged ions) and anode (negatively charged ions) to a concentrate wastewater stream, creating a more dilute stream.

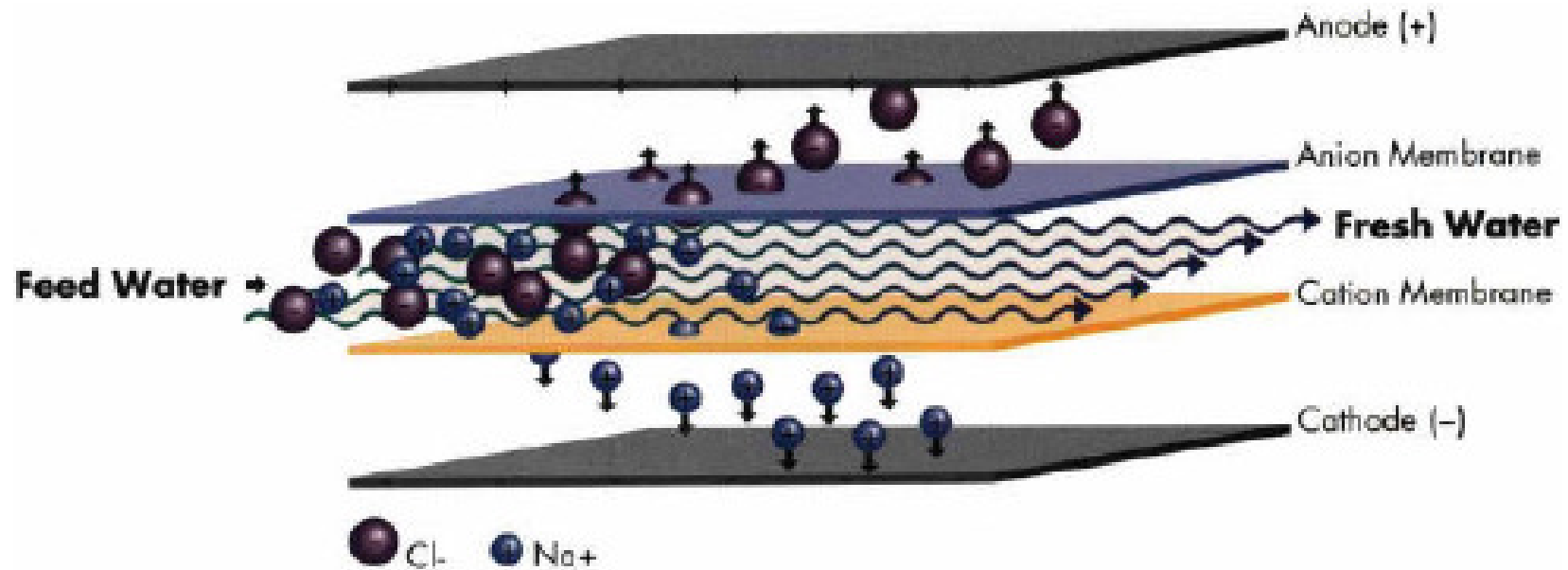
Electrodialysis Basic Operation



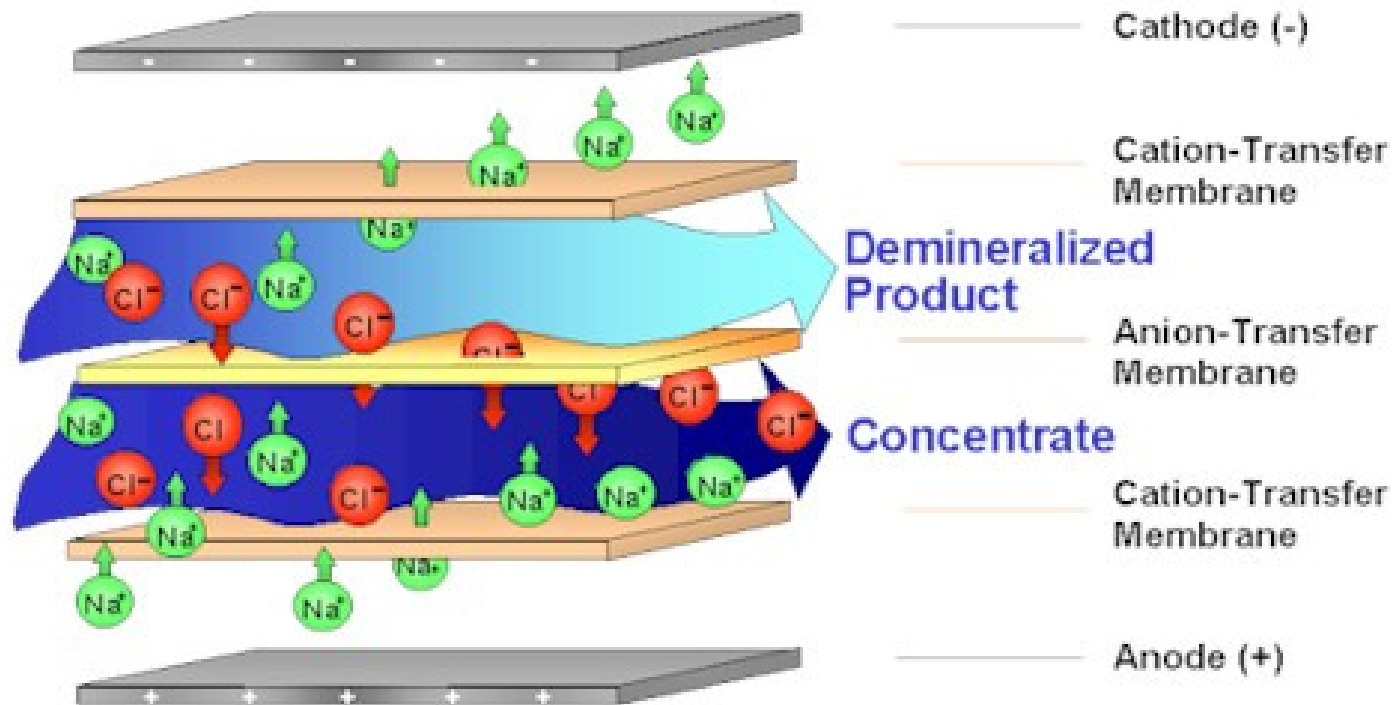
Electrodialysis Basic Operation



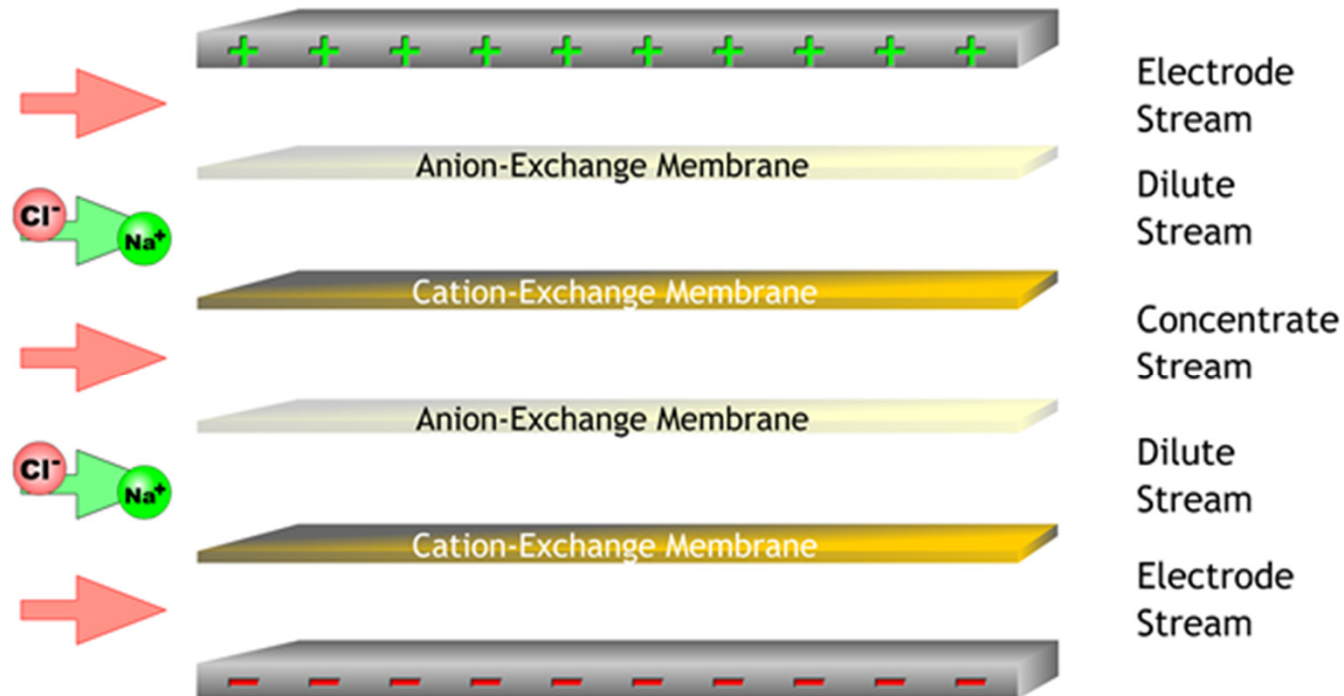
Electrodialysis Basic Operation



Electrodialysis Basic Operation

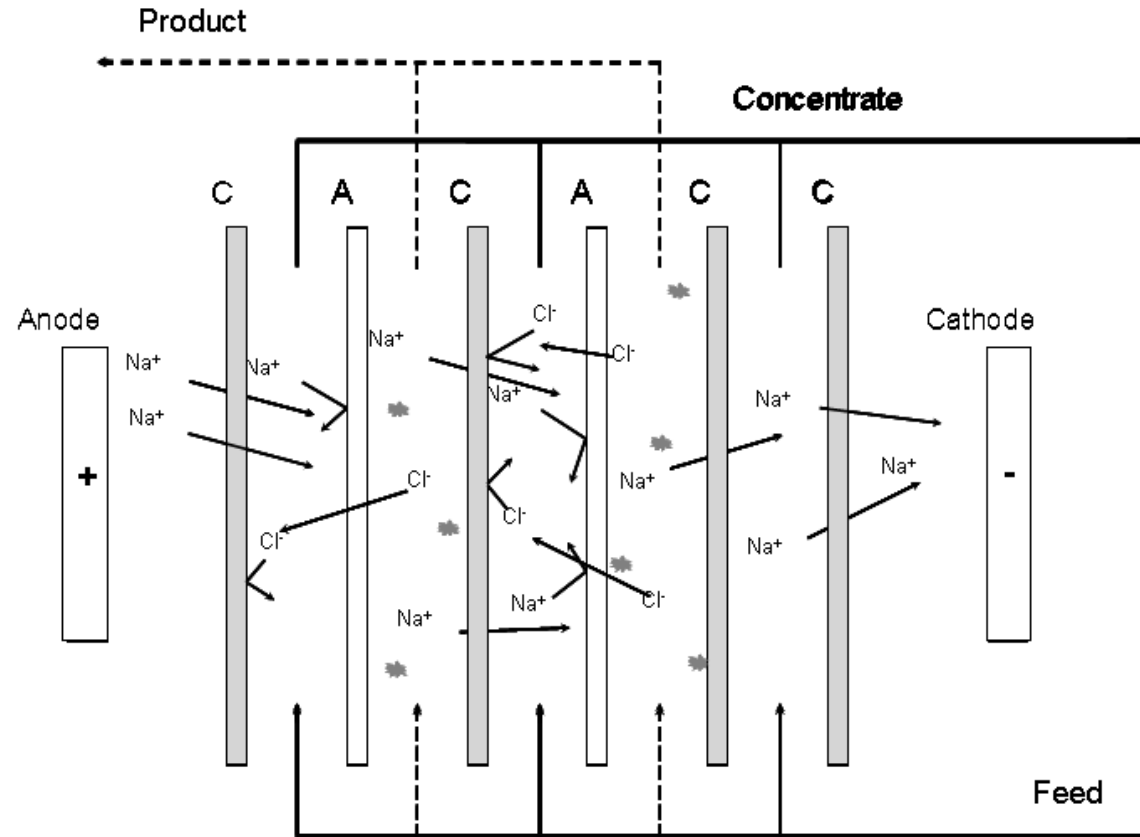


Electrodialysis Basic Operation



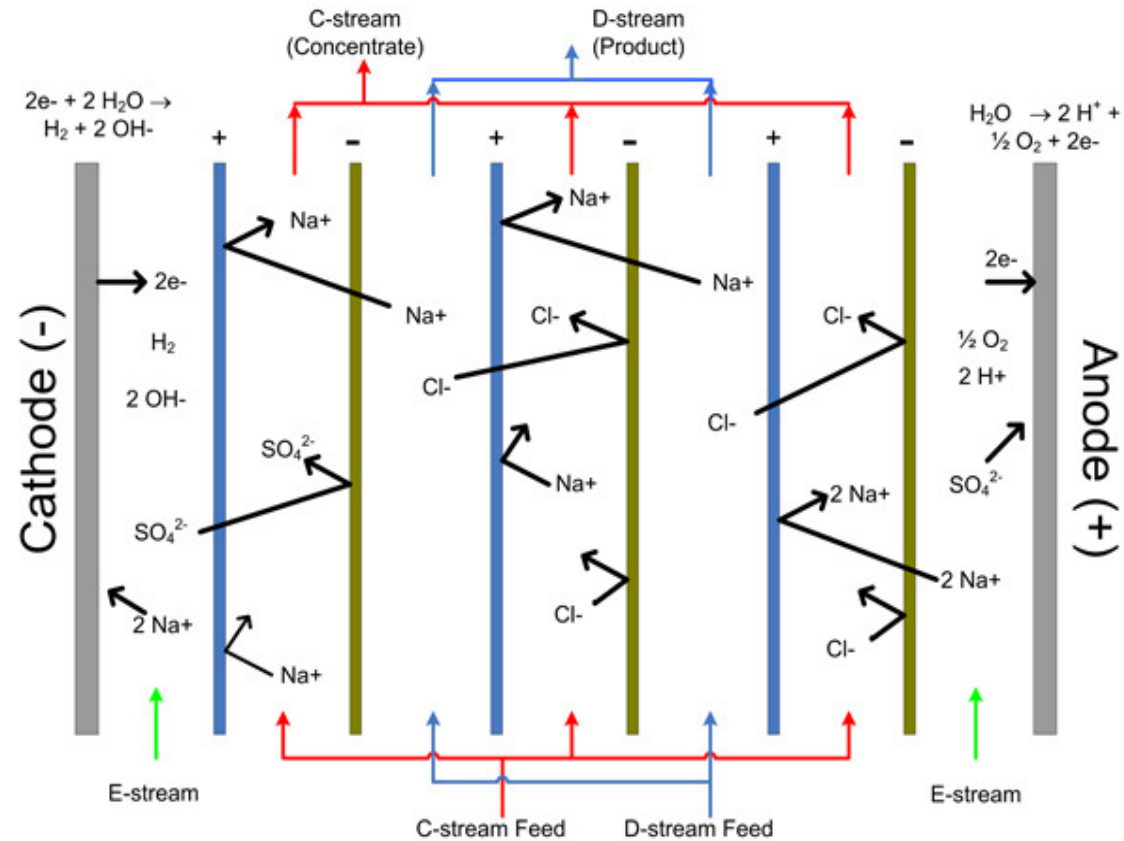
Schematic Cross Section of an Electrodialysis Plant

Electrodialysis Basic Operation



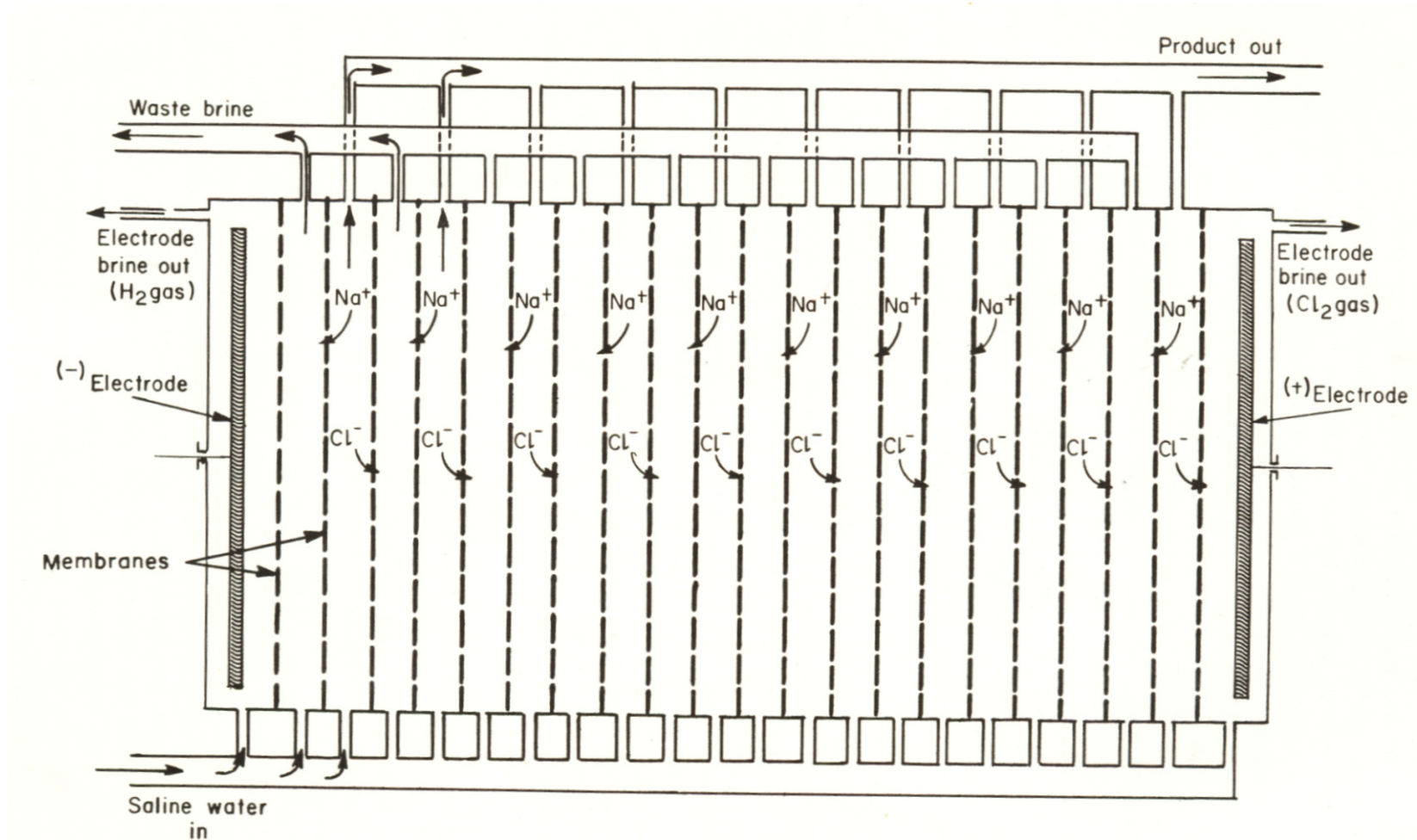
Schematic Cross Section of an Electrodialysis Plant

Electrodialysis Basic Operation



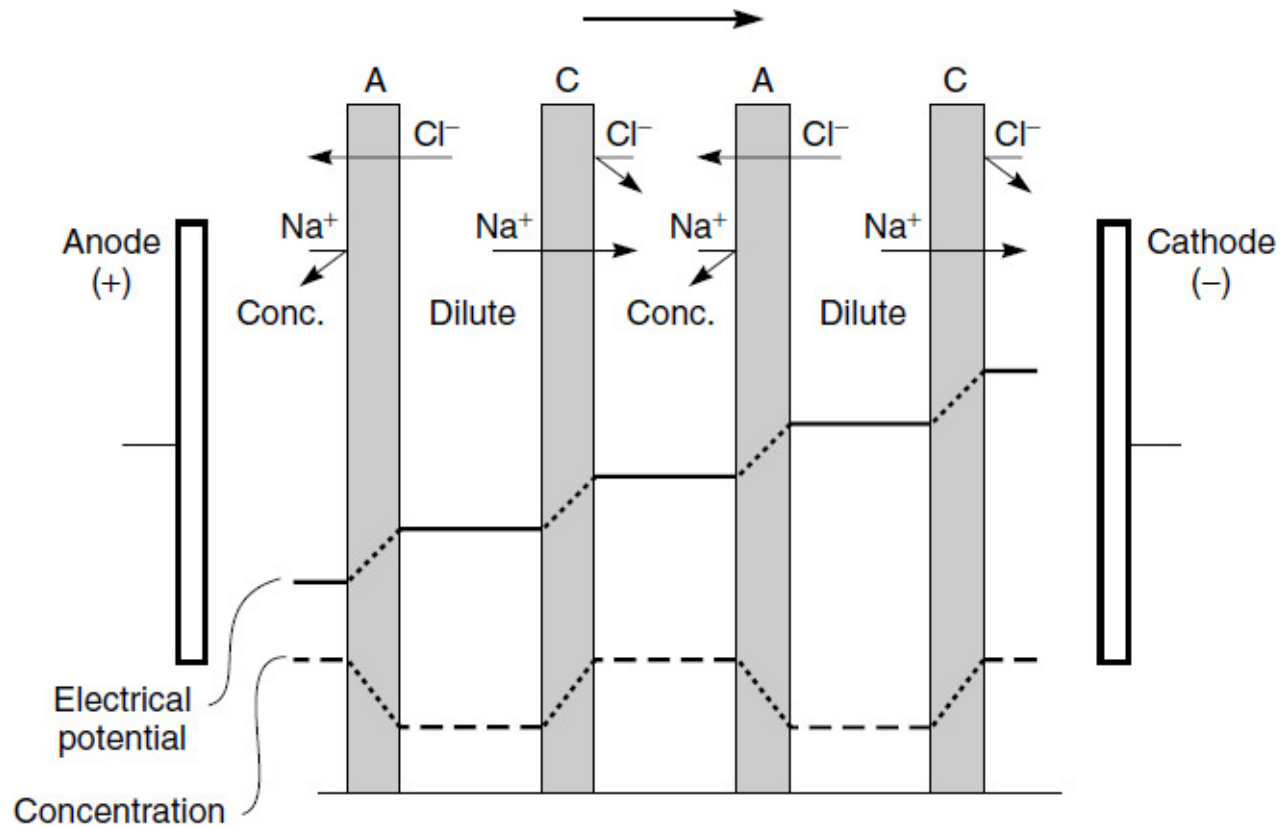
Schematic Cross Section of an Electrodesalination Plant

Electrodialysis Basic Operation



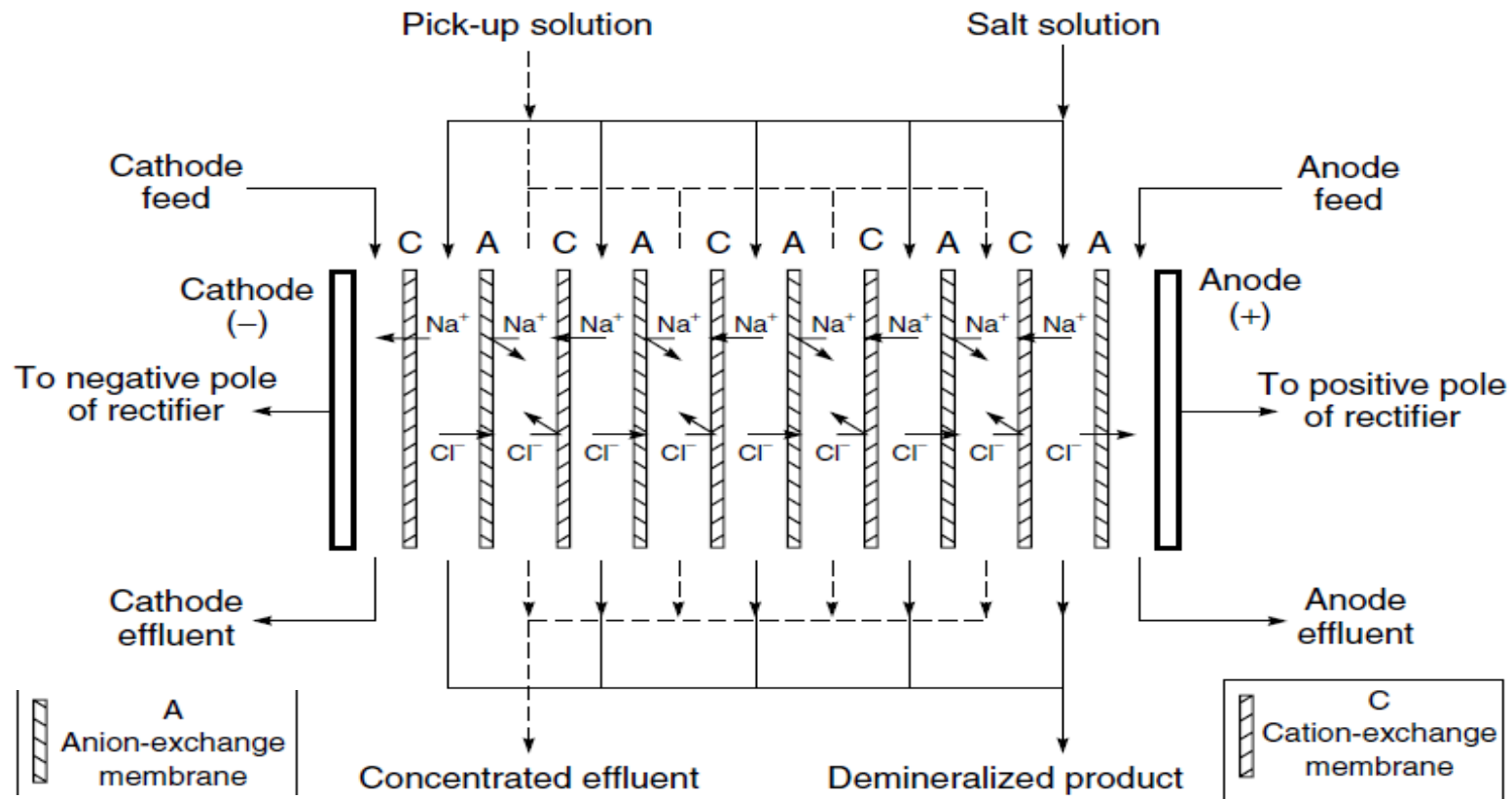
Schematic Cross Section of an Electrodialysis Plant

Electrodialysis Basic Operation



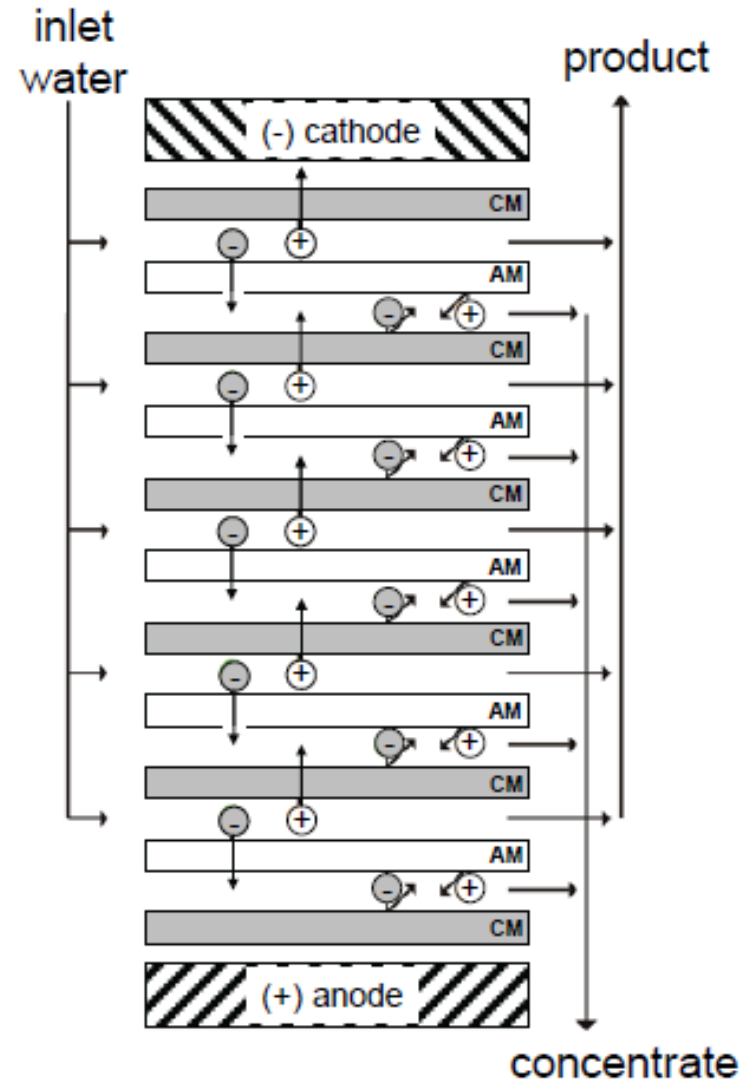
Schematic of Concentration and Potential Gradients

Electrodialysis Basic Operation

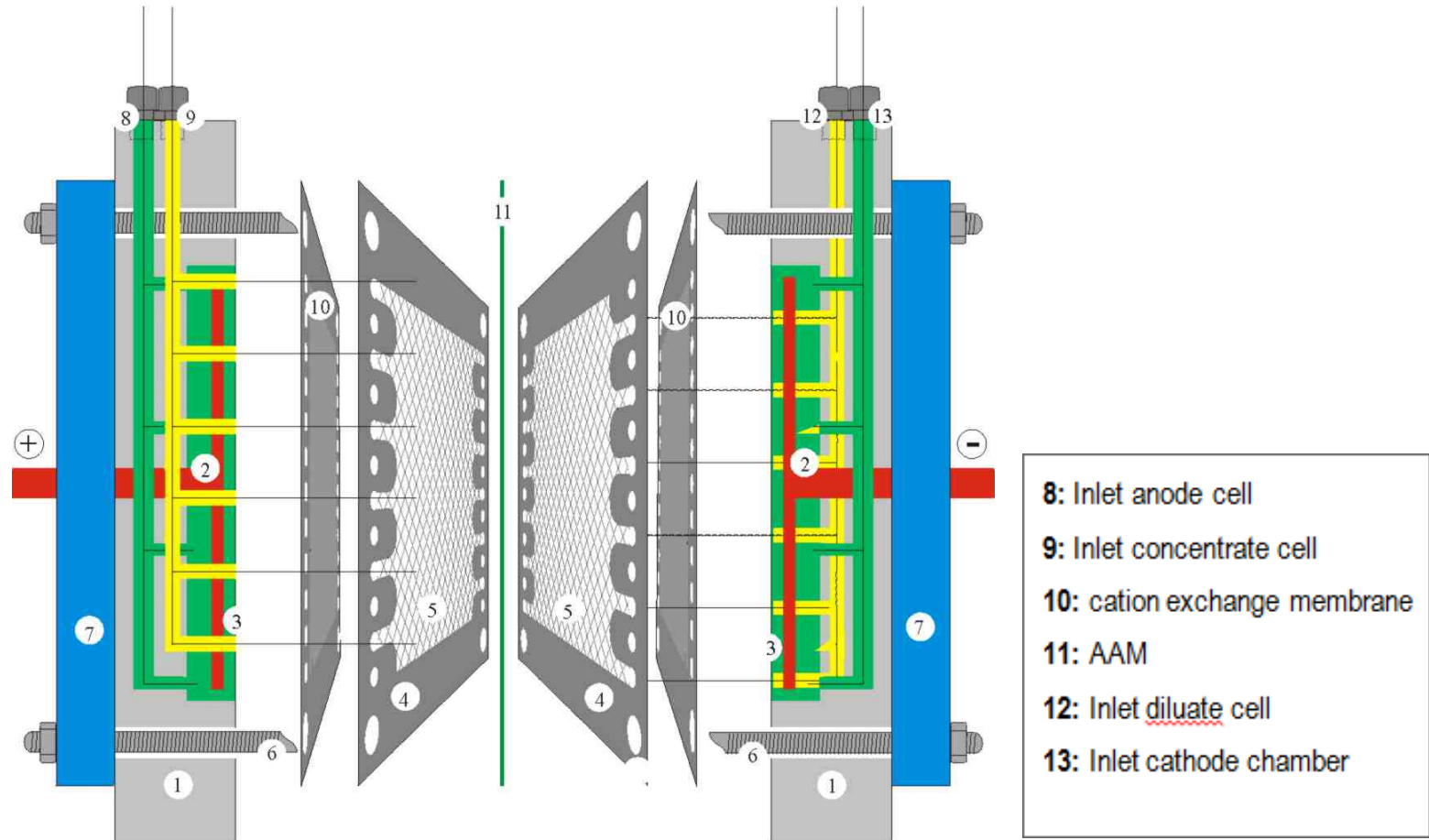


Schematic Cross Section of an Electrodialysis Plant

Electrodialysis Basic Operation

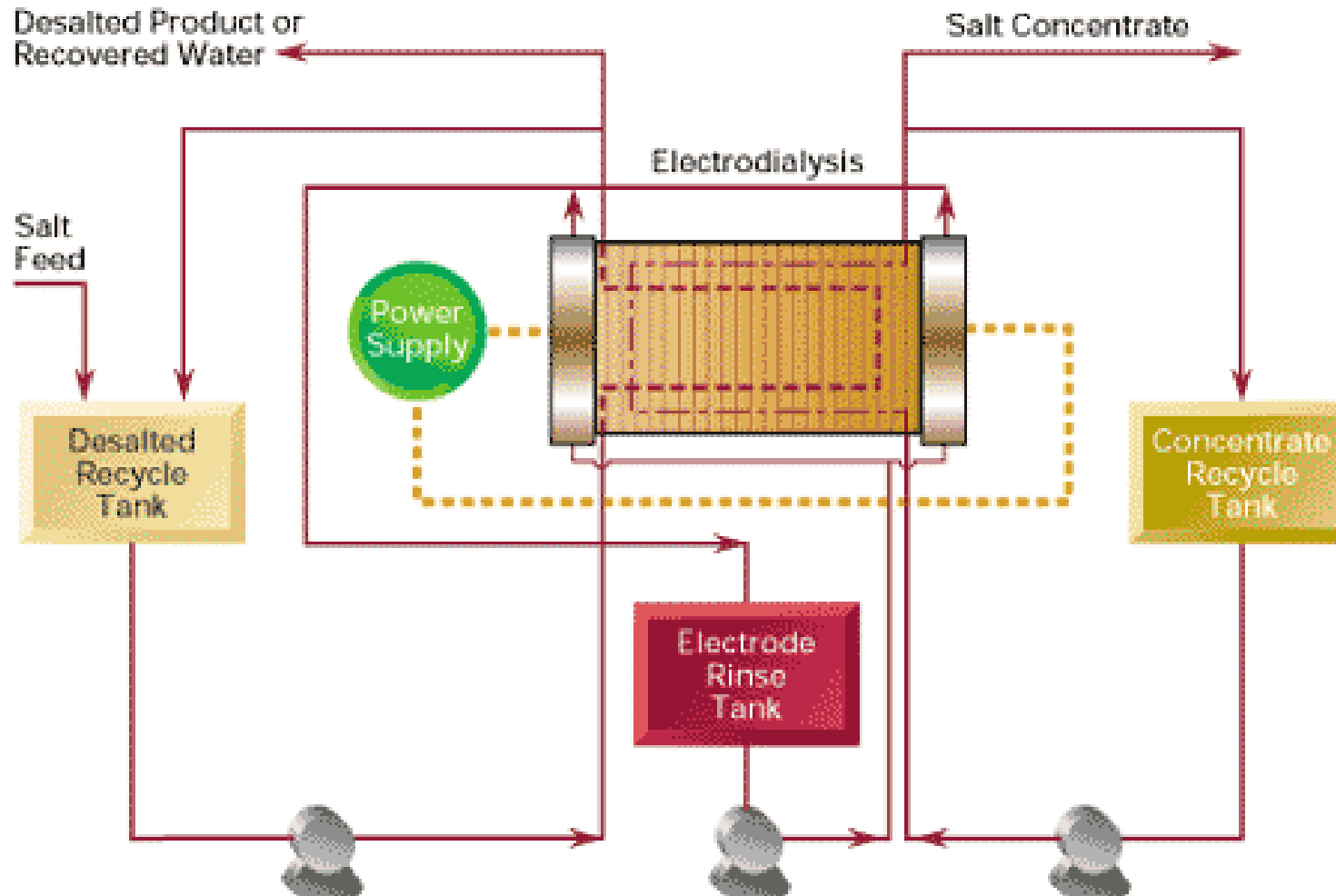


Electrodialysis Basic Operation

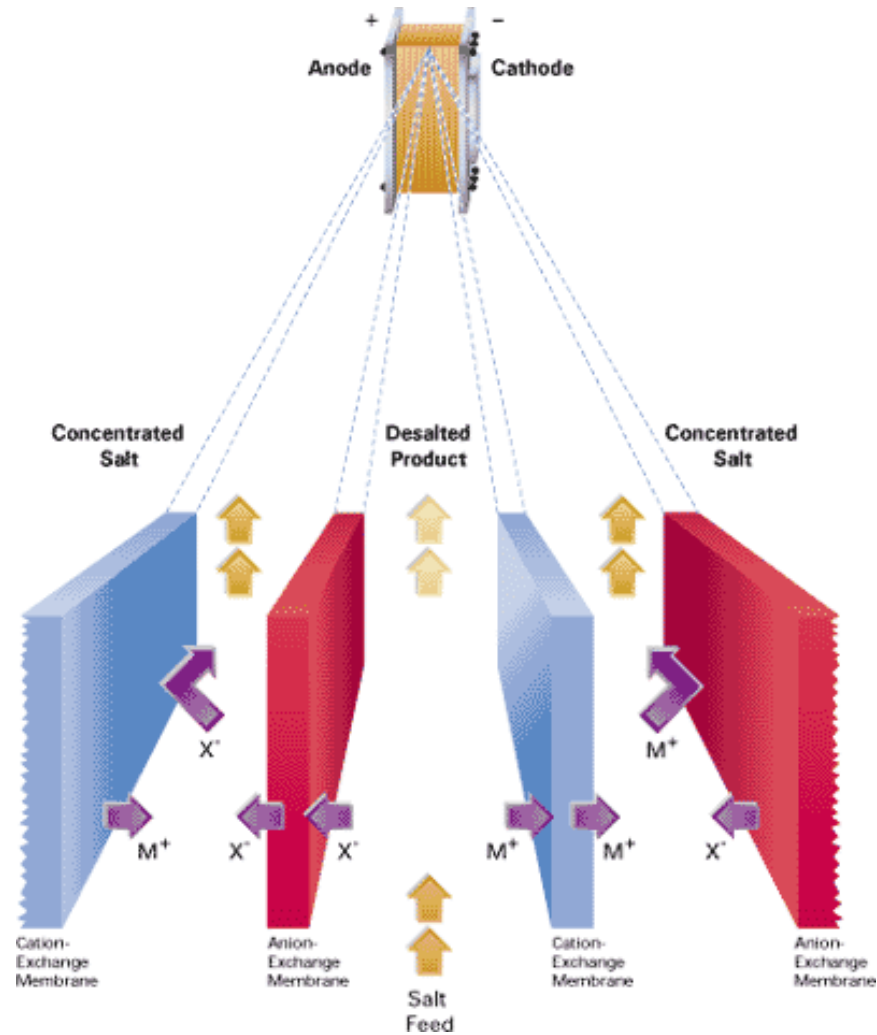


Detailed of Electrodialysis Cell

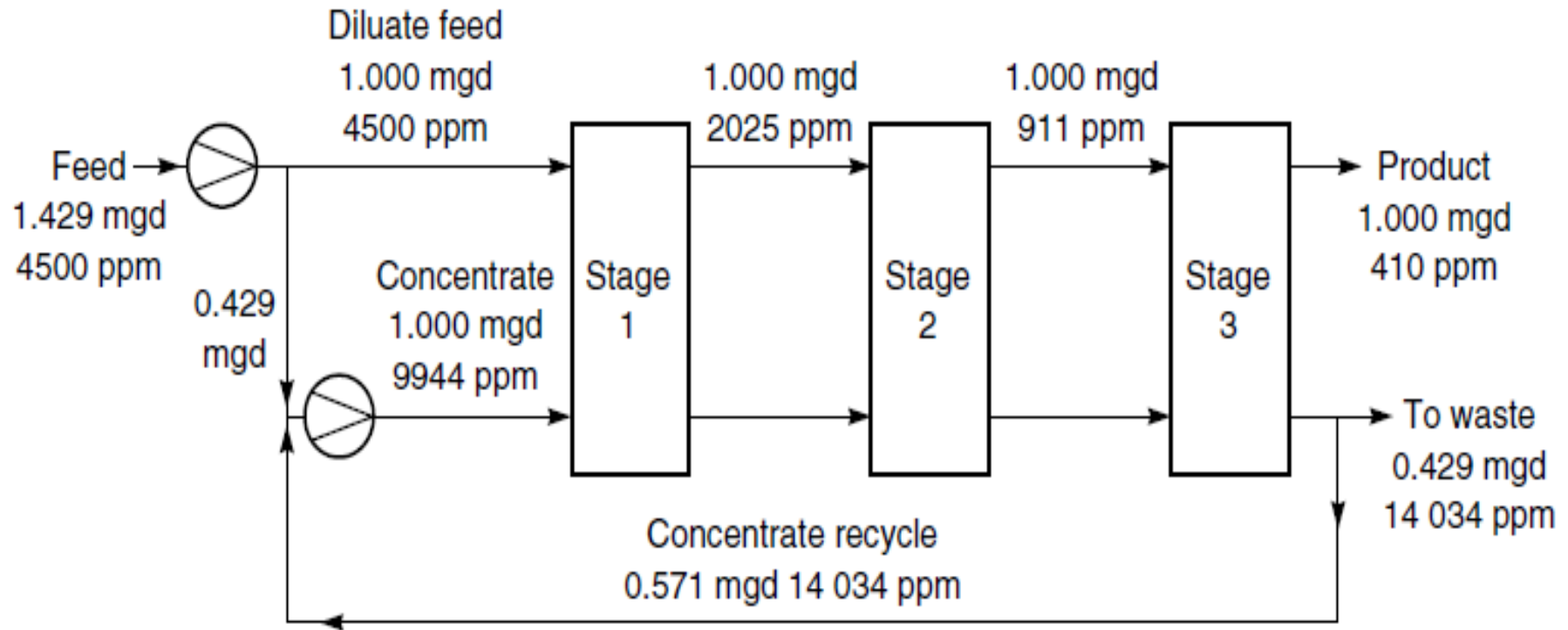
Electrodialysis System



Electrodialysis System



Electrodialysis System



Flow Scheme of 3-stages Electrodialysis Plant



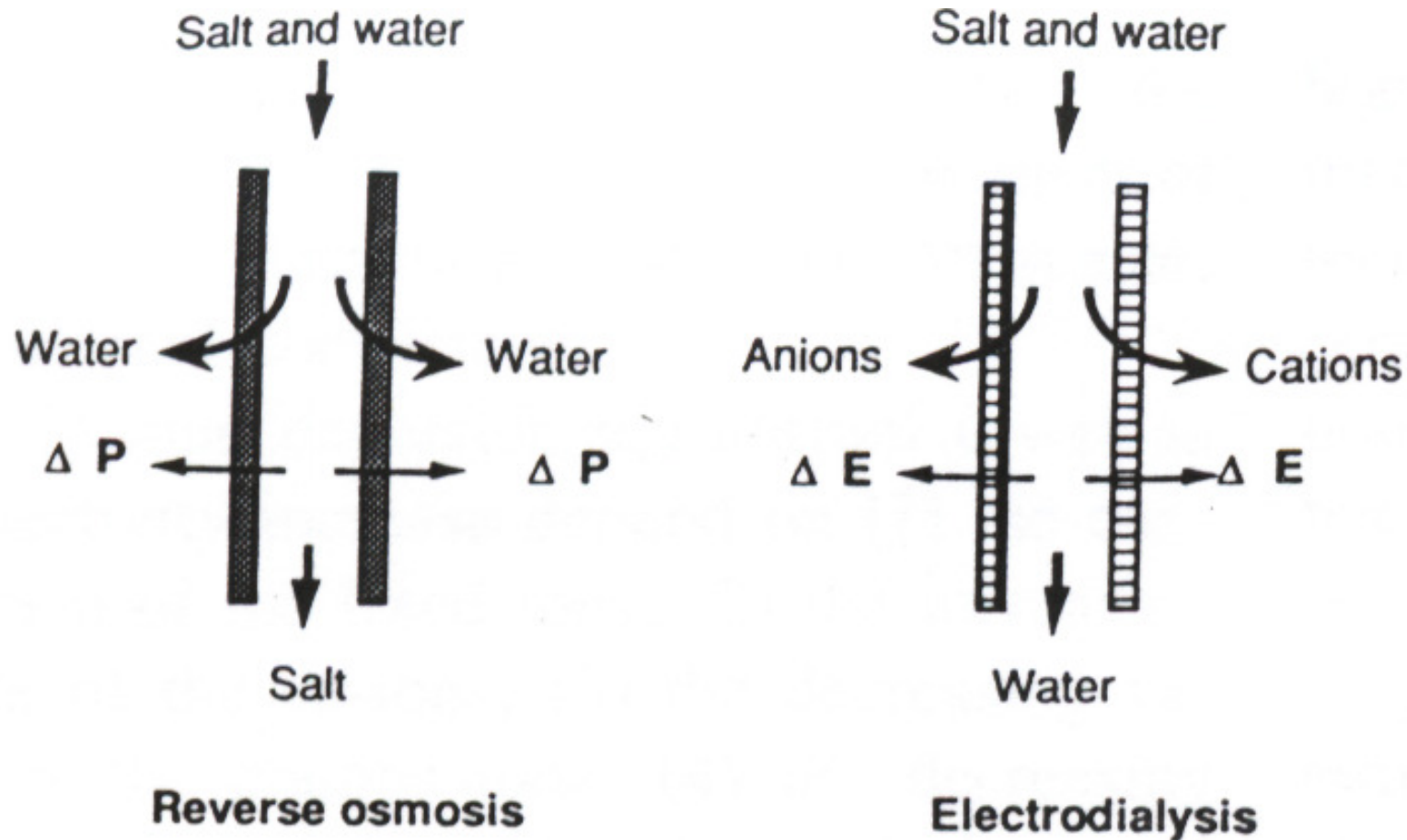
ED Process Characteristics

	RO	EDR	MSF/MED
Preferred Water Source	Any	Brackish	Seawater - Brine
Susceptibility to scaling	high	low	low
Bacterial Contamination	Possible	Post-treatment always needed	Unlikely
Final Product Salinity	On demand (<500 mg/L TDS)	On demand (<500 mg/L TDS)	Can be <10 mg/l TDS
Energy Cost	Moderate, increases with salinity	High, increases fast with salinity	High, independent of salinity
Recovery	Typically 50% for seawater, >80% for brackish water	>80% for brackish water	Poor= 10-25%
Plant Size	Modular, easy to operate, small footprint	Modular, easy to operate, small footprint	Large complex plants



Notes on Cost

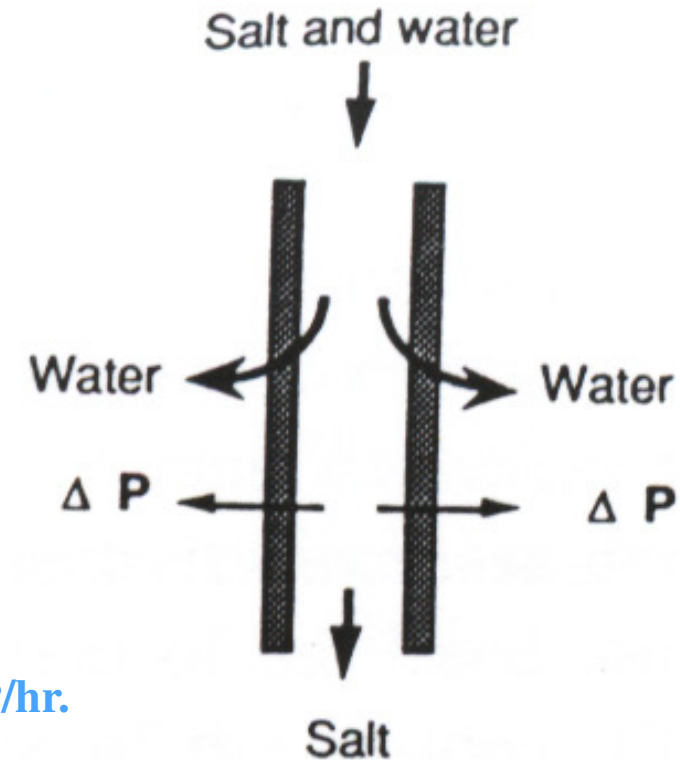
- RO process requirement for brackish water is much less than for seawater, desalination of brackish water is less expensive than desalination of seawater.
- EDR is currently cost-effective only for low salinity sources.
- Distillation based technology cost is not function of salinity, they make sense only for higher salinity sources (seawater).



Operating Principles of Reverse Osmosis and Electrodialysis

RO Basic Equations

$$F_f = A_w (\Delta P - \Delta \Pi) S/t$$



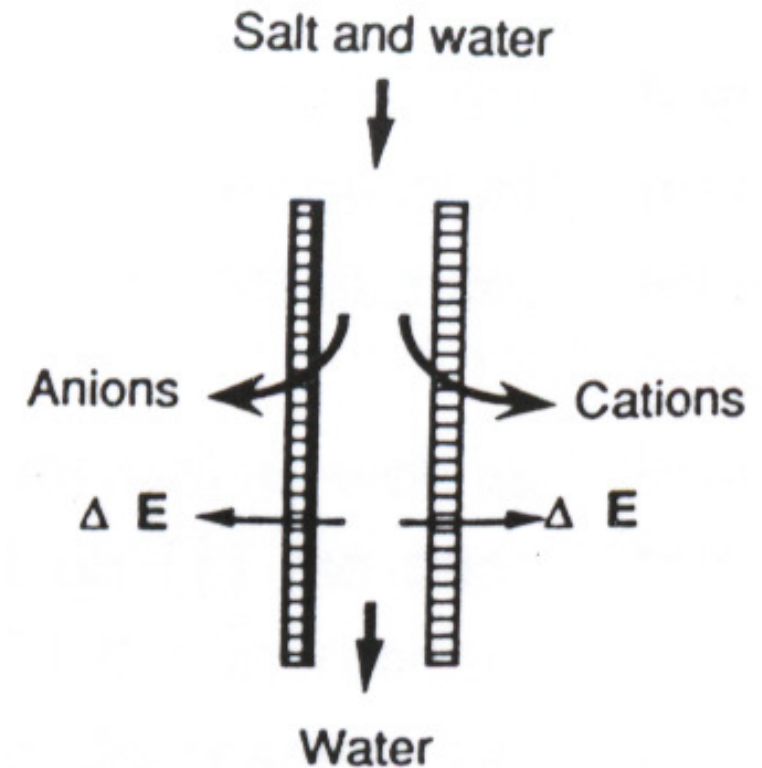
- F_f = flow rate of water through the membrane in m^3/hr .
- A_w = membrane permeability coefficient for water in $cm^2 \text{ sec/gm}$.
- ΔP = hydraulic pressure differential across membrane in $gm / cm \text{ sec}^2$.
- $\Delta \Pi$ = osmotic pressure differential across membrane in $gm/cm \text{ sec}^2$.
- S = membrane surface area in cm^2 .
- t = membrane thickness in cm .

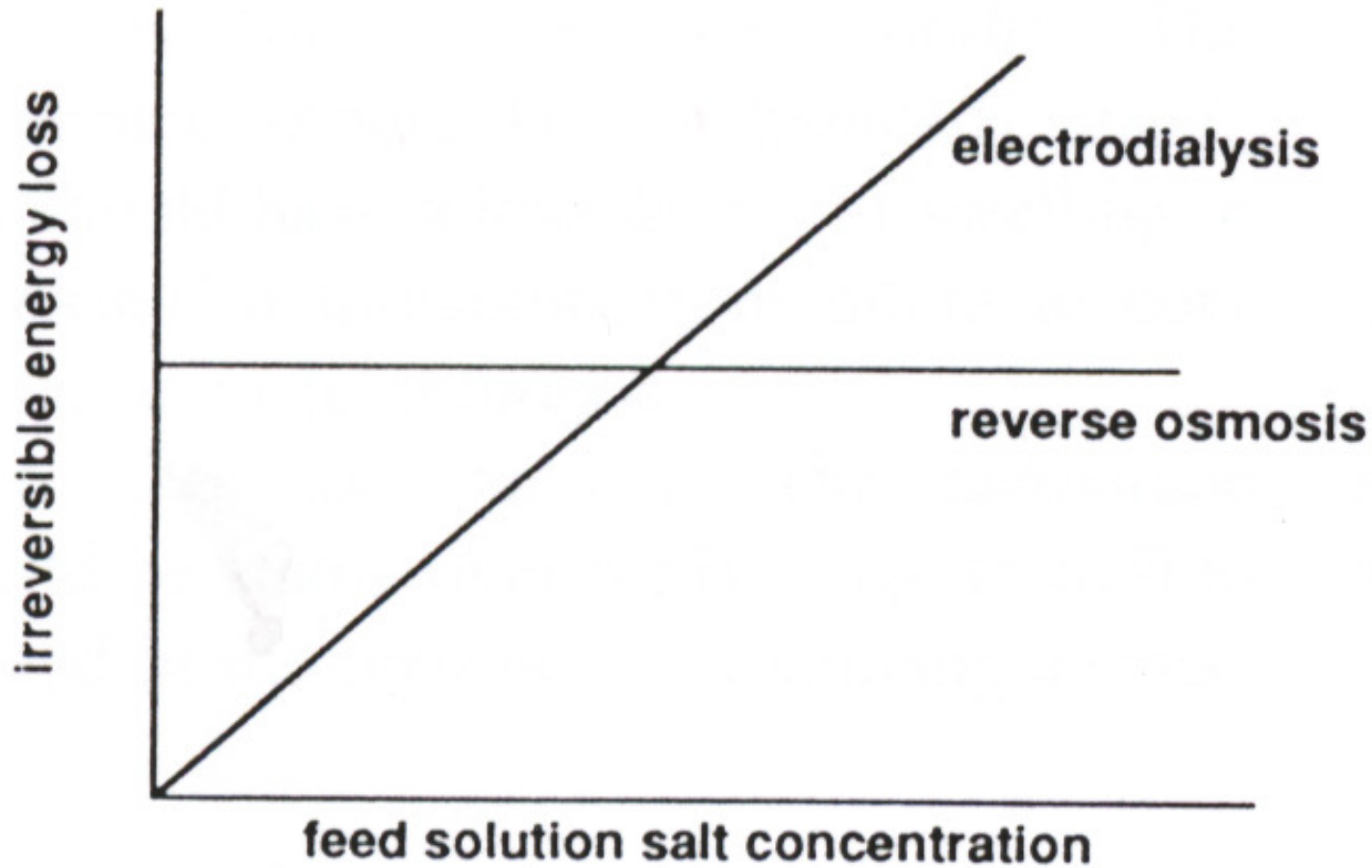
Electrodialysis basic Equations

$$\Delta E = I^2 n R t$$

$$I = z F Q_f \Delta C / \eta$$

- E** = energy consumption
I = electric current through membrane stack
n = number of cell pairs in a stack
R = resistance of the cell pair
t = time
z = valence of the ion species
F = Faraday's constant, 96500 C/q-eqv
 ΔC = concentration difference between the feed and product
 η = current utilization (efficiency).





The irreversible energy losses in ED and RO as a function of feed salt concentration.

Voltage Requirements

The required voltage is sum of :

- the ohmic voltage drop, $I R_c$
- the membrane voltage, V_m
- the polarization potential, V_p

$$V_c = I R_c + V_m + V_p$$

For operating in non-polarization conditions, $V_p=0$

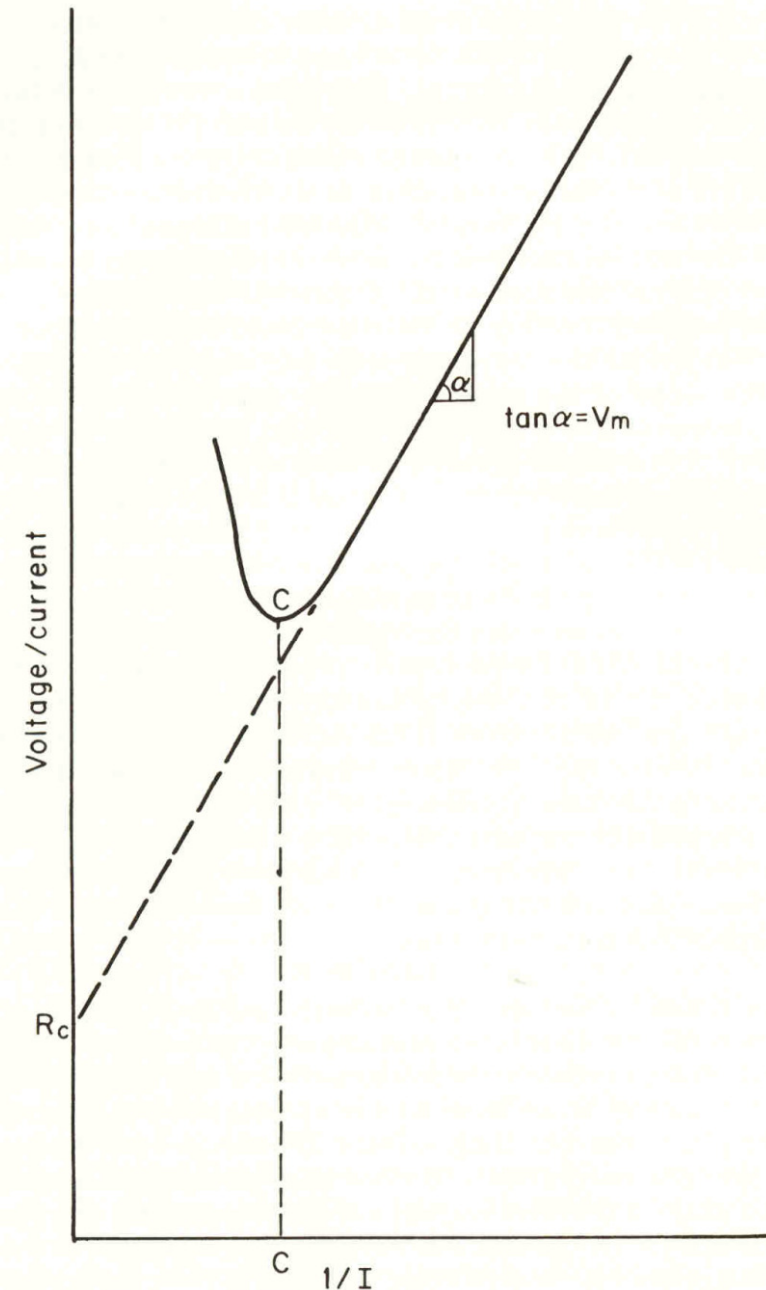
$$V_c = I R_c + V_m, \text{ re-written as}$$

$$V_c/I = R_c + V_m/I$$

In the form of $y = a + bx$;

$y: V_c/I$ and $x=1/I$

Slope = R_c and Intercept = V_m





Ion Exchange Membranes Used in Electrodialysis Applications

<i>Manufacturer</i>	<i>Tradename</i>	<i>Material</i>	<i>Special Features</i>	<i>Location</i>
Solvay		Perfluorinated film with fixed pyridine (anion-permeable) or sulfonic acid (cation-permeable)		France
FuMA-Tech		Polyetherketones, polysulfone, polyphenylene oxide		Germany
Tokuyama Soda	Neosepta®	Styrene-divinyl benzene	Robust high mechanical strength; Moderate electrical resistance	Japan
Asahi Glass	Selmiom®	Polystyrene-based	Very low electrical resistance	Japan
Asahi Chemical	Aciplex®	Styrene-divinyl benzene/PVC backing		Japan
Ionics, Inc.		Heterogeneous polystyrene-based/acrylic fabric, with fixed sulfonate (cation-permeable) and quarternary ammonium cations (anion-permeable)	Rugged, low resistance, high selectivity, chemically stable, low fouling	MA, USA
Dupont Co.	Nafion®	Perfluorinated sulfuric acid polymer	Cation permeable	NC, USA
Sybron	Ionac®	Heterogeneous resin-PVDF/fabric	High mechanical strength	NJ, USA



Ion Permeable Membranes

- Non porous
- Sheets of ion-exchange resins and other polymers
- Thickness 100 - 500 μm

Are divided in

Anion - exchange

Positively charged groups

E.g. Quarternary ammonium salts
 $-\text{NR}_3$ or $-\text{C}_5\text{H}_5\text{N-R}$

Cation - exchange

Negatively charged groups

E.g. Sulfonic or carboxylic acid groups
 $-\text{SO}_3^-$

Chemically attached to the polymer chains
(e.g. styrene/divinylbenzene copolymers)



Requirements for Ion-Exchange Membranes

- High electrical conductivity
- High ionic permeability
- Moderate degree of swelling
- High mechanical strength

Charge density 1 - 2 mequiv / g dry polymer

Electrical Resistance 2 - 10 $\Omega \cdot \text{cm}^2$

Diffusion coefficient 10^{-6} - 10^{-10} cm^2/s



Design of ED Plant

Parameters:

- Stack Construction
- Feed and product concentration
- Membrane permselectivity
- Flow velocities
- Current density
- Recovery Rates

- Width of the cell
- Length of the stack
- Thickness of the cell chamber

- Volume factor
- Shadow effect

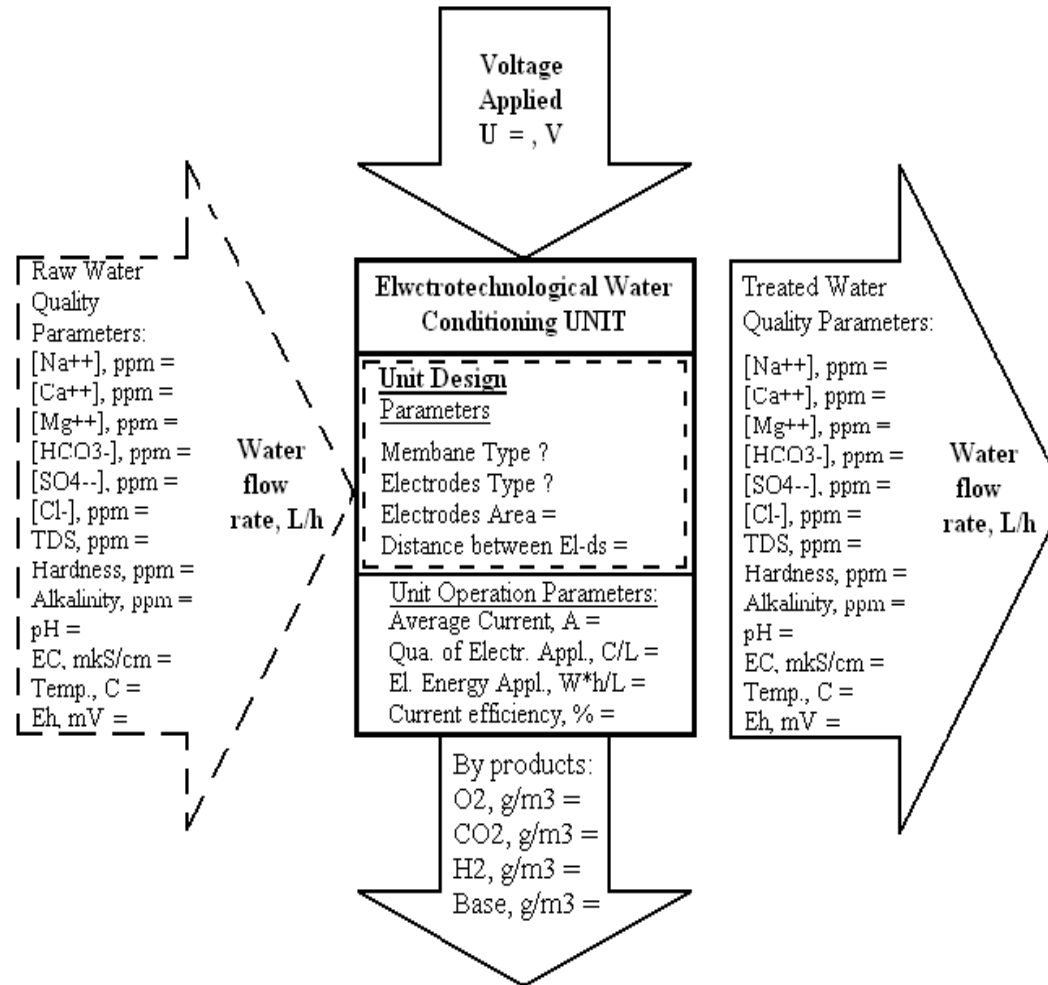
Safety factor

Optimized in terms of

- Component design and properties
- Operating Parameters



Design of ED Plant

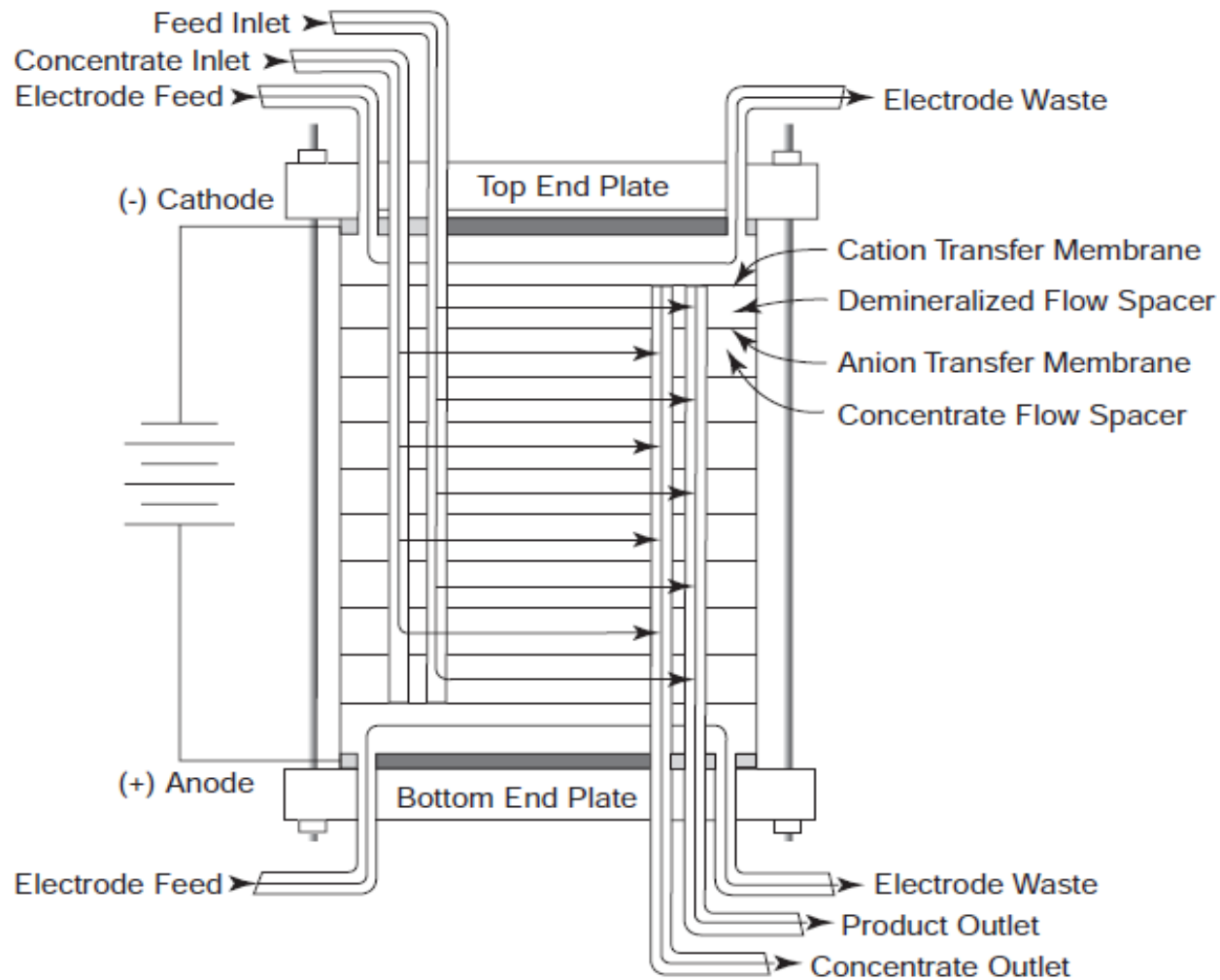




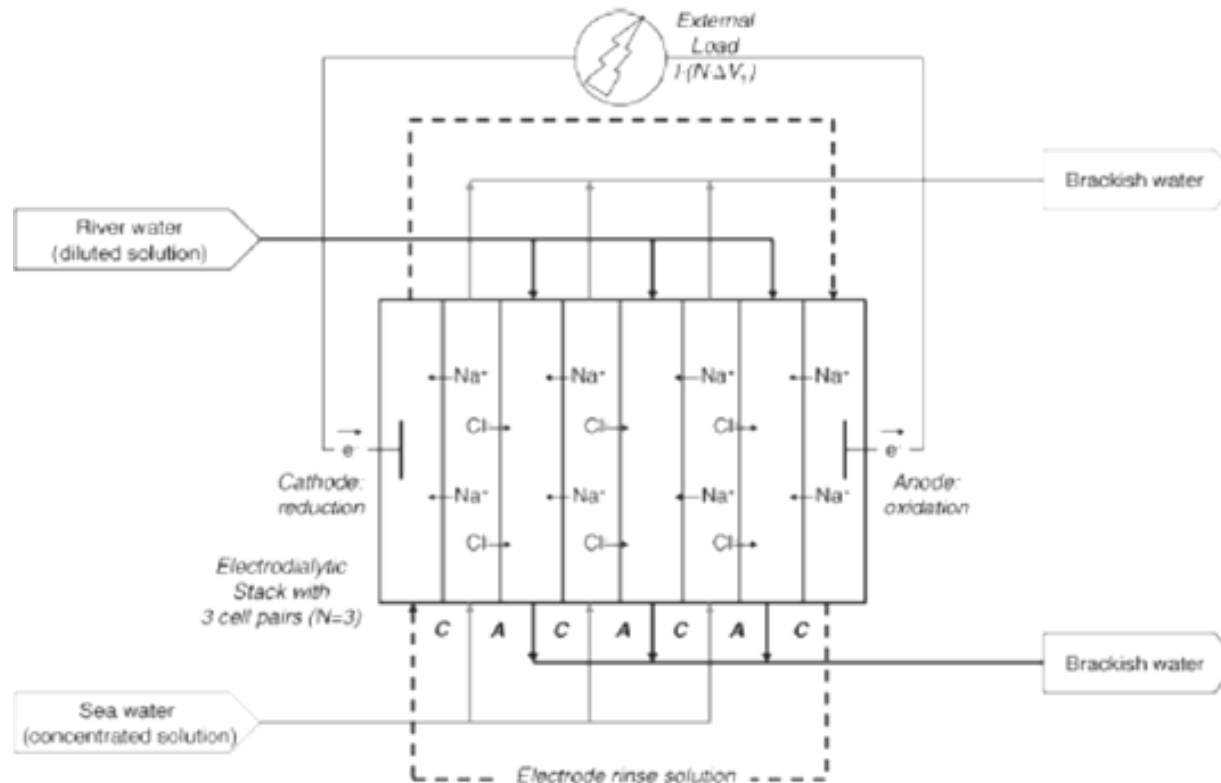
Electrodialysis Reversal (EDR)

EDR is a variation on the ED process, which uses electrode polarity reversal to automatically clean membrane surfaces. EDR works the same way as ED, except that **the polarity of the DC power is reversed** two to four times per hour. When the polarity is reversed, the source water dilute and concentrate compartments are also reversed. This polarity reversal helps prevent the formation of scale on the membranes. The setup is very similar to an ED system except for the presence of reversal valves.

Electrodialysis Reversal (EDR)

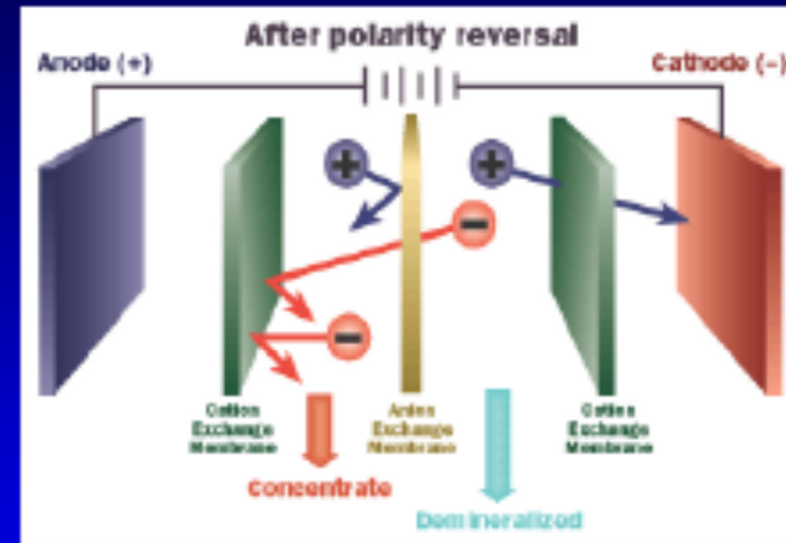
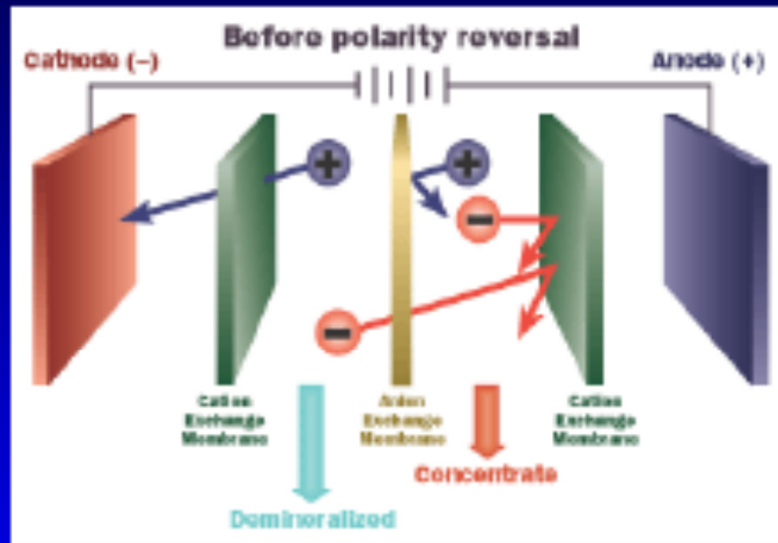


Electrodialysis Reversal (EDR)



Energy conversion scheme using reverse electrodialysis; A is an anion exchange membrane, C a cation exchange membrane, I the electrical current or transported charge(A), N the number of cell pairs (in this case $N=3$), $N\Delta V_1$ the potential difference over the applied external load(V), where as the power generated is $I(N\Delta V)(W)$.

Electrodialysis Reversal (EDR)

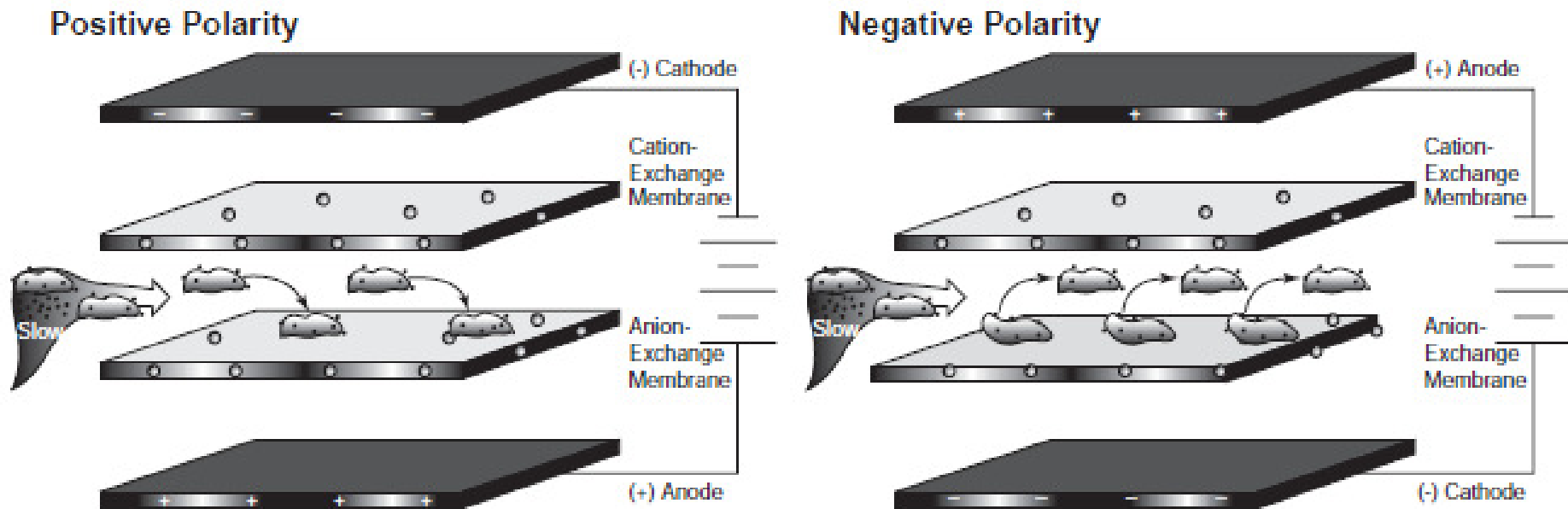


Source: AWWA



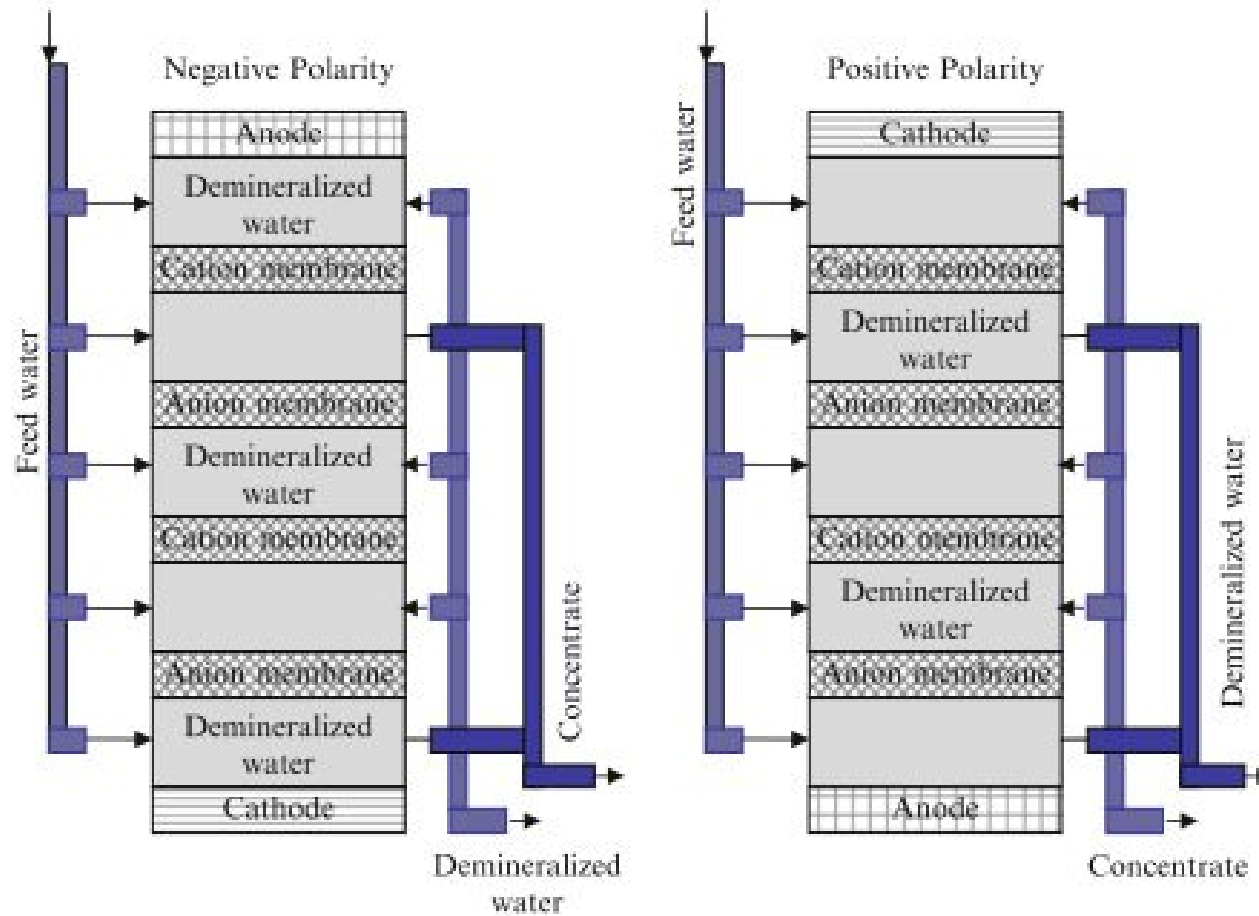
12 MGD Sarasota, FL EDR plant

Electrodialysis Reversal (EDR)



deposition and removal forces in EDR

Electrodialysis Reversal (EDR)





Typical EDR Installation





EDR Design Parameters

Recovery	85 - 94%
Rejection	50% per Stack (3 stacks for 87.5%)
Feed Pressure	35-40 psi
Product Flow Rate	125 - 150 gpm per stack
Energy Required for Desalting	2 kilowatthours (kWh) per 1000 gals per 1,000 mg/l reduction in salinity



EDR Operation and Maintenance

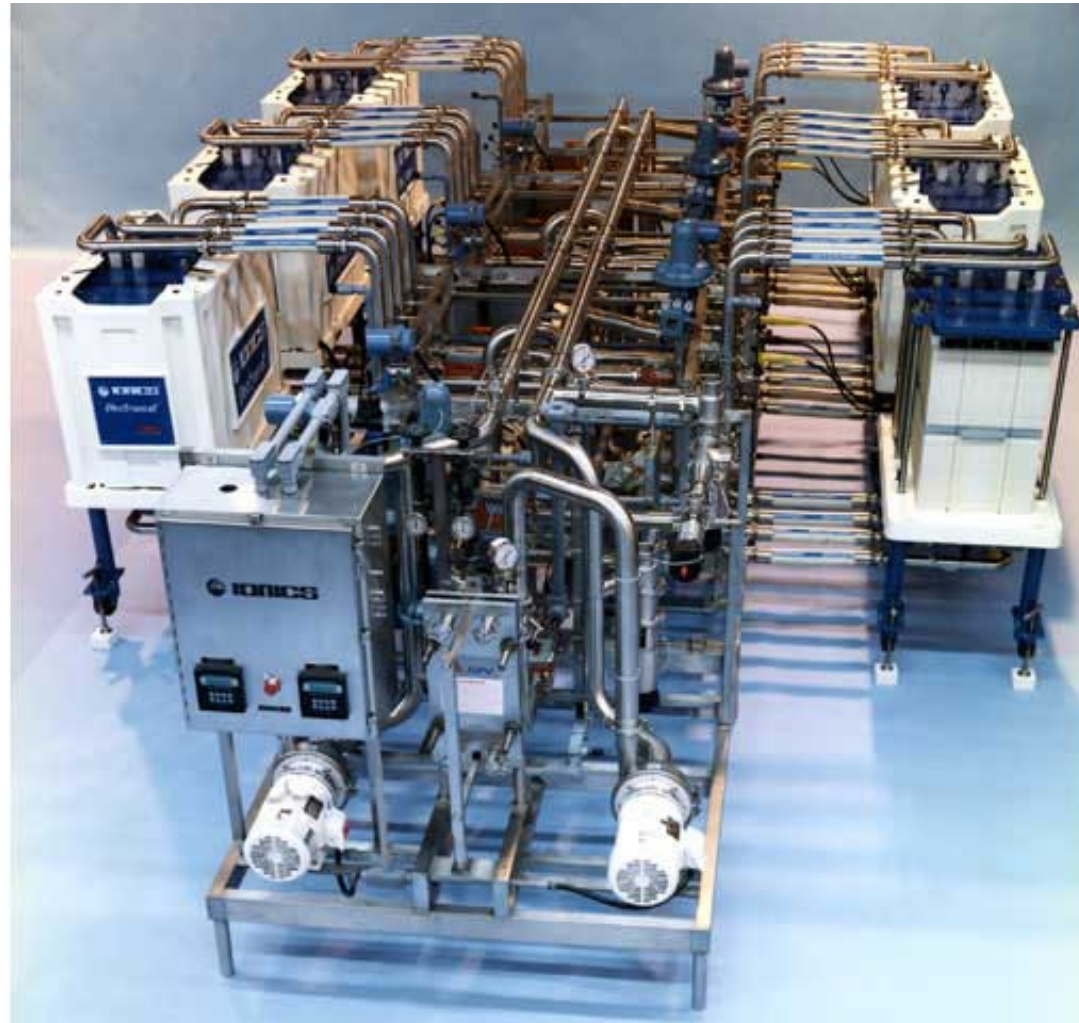
- Daily data collection and daily analysis
- Weekly stack inspection and rinsing
- Stack and electrode probing
- Periodic re-tightening of tie rods
- Stack Clean in Place
- Electrode Clean in Place



















Membrane Desalination Processes



Content:

- *Desalination: An Overview*
- *Overview of Membrane Desalination Technologies*
- *Pretreatment Processes:
microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF)*
- *Commercial Processes:
Reverse Osmosis (RO), Electrodialysis (ED) and ED Reversal*
- *Innovative Processes:
Forward Osmosis (FO) and Membrane Distillation (MD)*



Membrane Desalination Processes



Content:

- **Innovative Processes:**
 - *Forward Osmosis (FO) and Membrane Distillation (MD)*
 - Forward Osmosis (FO) and Membrane Distillation (MD)
 - Classification of Osmotic Processes
 - Forward Osmosis
 - Comparison between RO and FO
 - Concentration Polarization (CP)
 - Forward Osmosis Pretreatment for Reverse Osmosis
 - Forward Osmosis for Re-use of Wastewater



Forward Osmosis (FO) and Membrane Distillation (MD)

- ♦ The driving force is temperature or concentration gradients across the membrane
- ♦ Combination with each other and with pressure-driven membrane processes

Process	Mass Transport	Driving Force
Forward Osmosis (FO)	Diffusion	Osmotic Pressure
Membrane Distillation (MD)	Evaporation	Partial Vapor Pressure



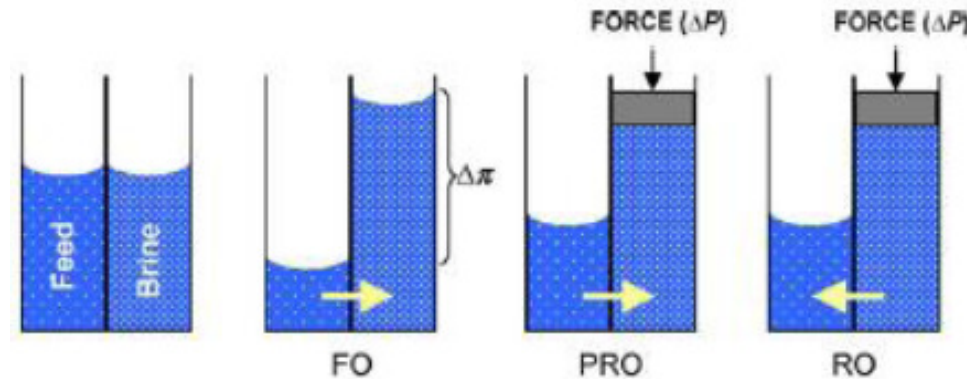
Classification of Osmotic Processes

Osmosis is the transport of water across a selectively permeable membrane from a region of higher water chemical potential to a region of lower water chemical potential.

It is driven by a difference in solute concentrations across the membrane that allows passage of water, but rejects most solute molecules or ions.

Osmotic pressure (π) is the pressure which, if applied to the more concentrated solution, would prevent transport of water across the membrane.

Classification of Osmotic Processes

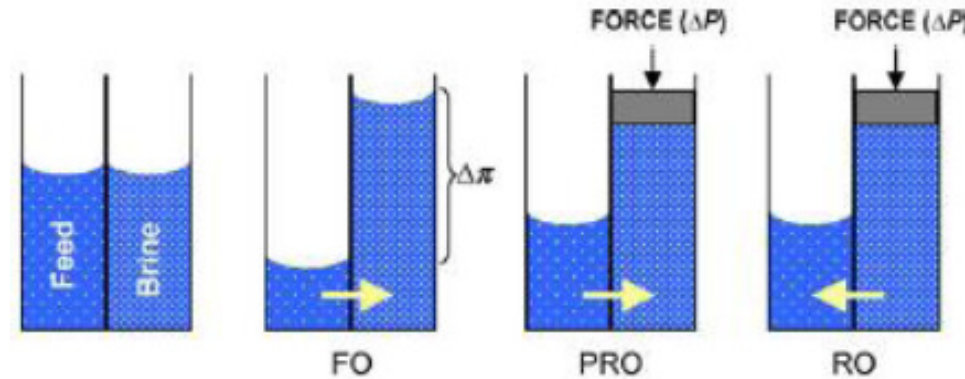


RO uses hydraulic pressure differential as the driving force for transport of water through the membrane.

FO uses π as the driving force resulting in concentration of a feed stream and dilution of a highly concentrated stream (referred to as the draw solution).

PRO (pressure-retarded osmosis) can be viewed as an intermediate process between FO and RO, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient (similar to RO). However, the net water flux is still in the direction of the concentrated draw solution (similar to FO).

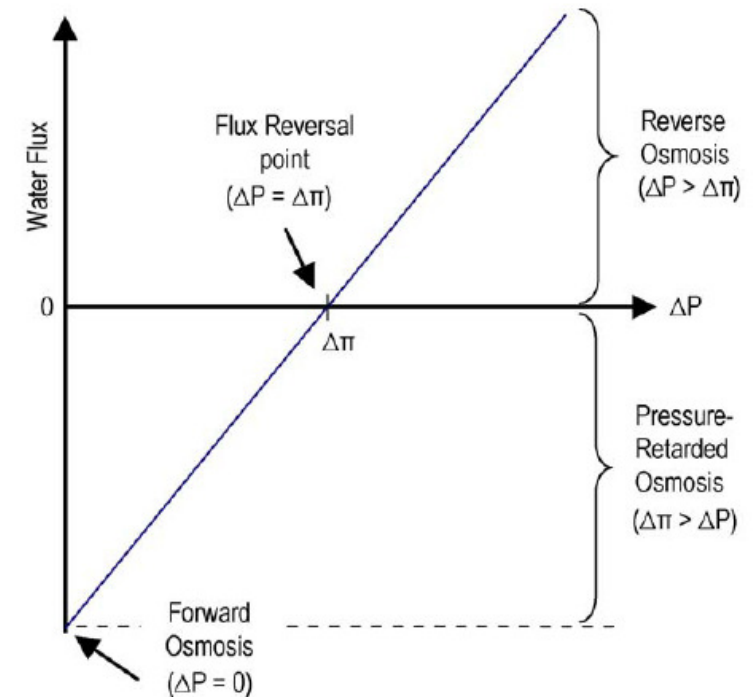
Classification of Osmotic Processes



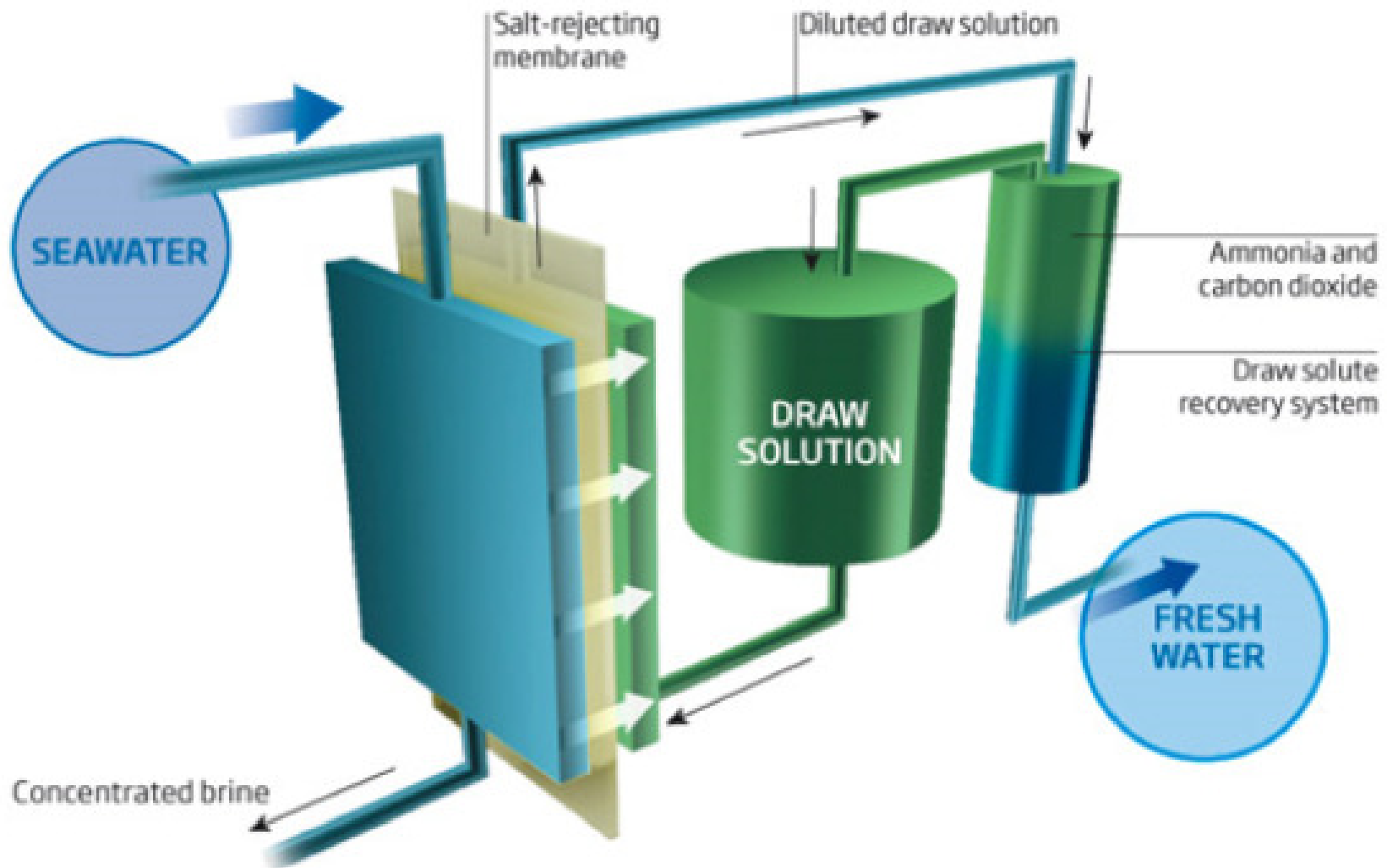
The general equation describing water transport in FO, RO and PRO is

$$J_w = A(\sigma \Delta\pi - \Delta P)$$

where J_w is the water flux, A the water permeability constant of the membrane, σ the reflection coefficient, and ΔP is the applied pressure. For FO, ΔP is zero; for RO, $\Delta P > \Delta\pi$; and for PRO, $\Delta\pi > \Delta P$.



Forward Osmosis





Forward Osmosis

The draw solution is the concentrated solution on the permeate side of the membrane, source of the driving force in the FO process. It has to be a higher osmotic pressure than the feed solution.

Tested draw solutions in FO desalination of seawater:

- Sulfur dioxide solution;
- Mixtures of water and an other gas (e.g., sulfur dioxide) or liquid (e.g., aliphatic alcohols);
- Aluminum sulfate solution;
- Glucose solution;
- A mixed solution of glucose and fructose;
- Solutions of potassium nitrate (KNO_3) and sulfur dioxide (SO_2);
- Ammonia and carbon dioxide gases



Forward Osmosis

FO has been used in the following fields:

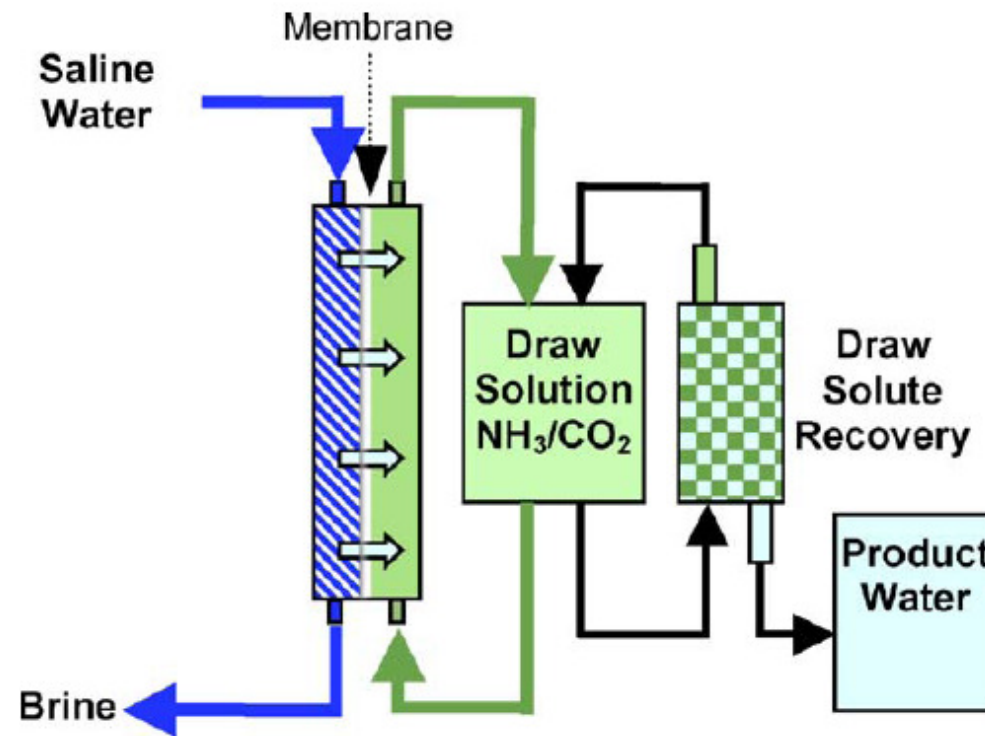
- To desalinate seawater;
- To treat industrial waste waters (at bench-scale);
- To concentrate land fill leachate (at pilot-and full-scale);
- To treat liquid foods in the food industry (at bench-scale).

FO was evaluated:

- For reclaiming waste water for potable reuse in life support systems (at demonstration-scale);
- For purifying water in emergency relief situations;
- For controlling drug release in the body.

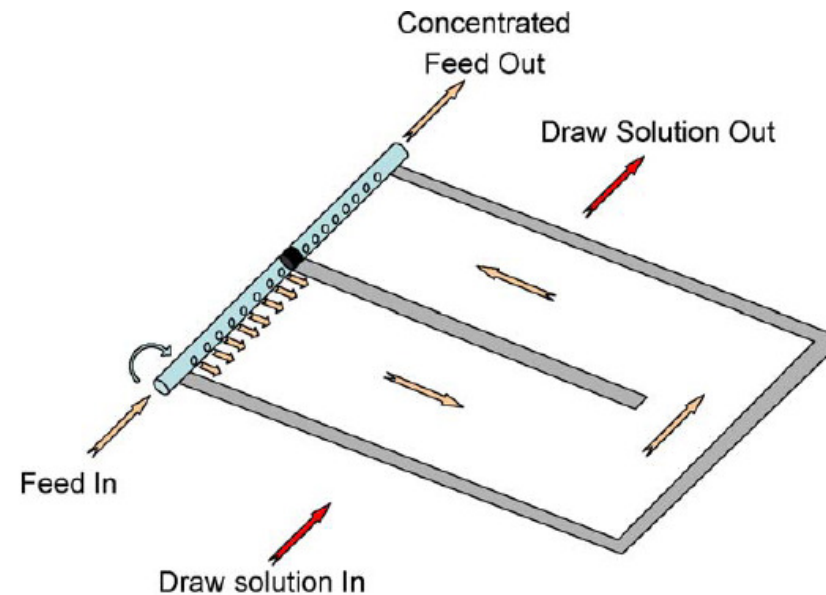
Forward Osmosis

Forward Osmosis desalination pilot plant developed at Yale Univ., USA.



NH_3 and CO_2 gases are dissolved in water forming of ammonium salts. This solution can have a very high osmotic pressure. They have the ability to decompose from solution, when heated, into ammonia and carbon dioxide gases again, so allowing for their efficient and complete removal and reuse

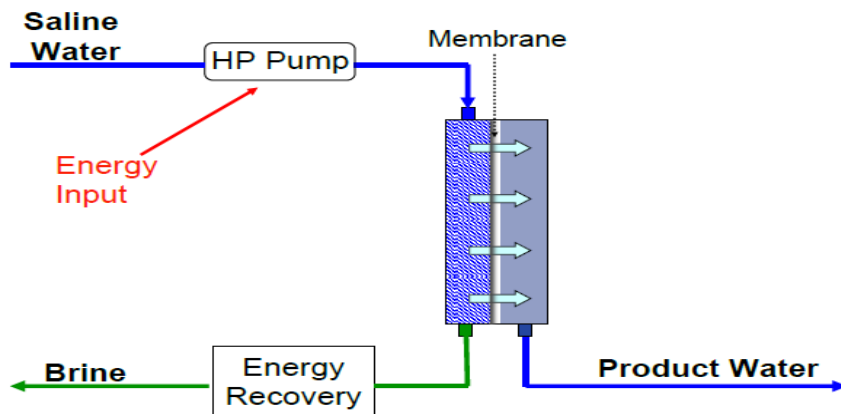
Forward Osmosis



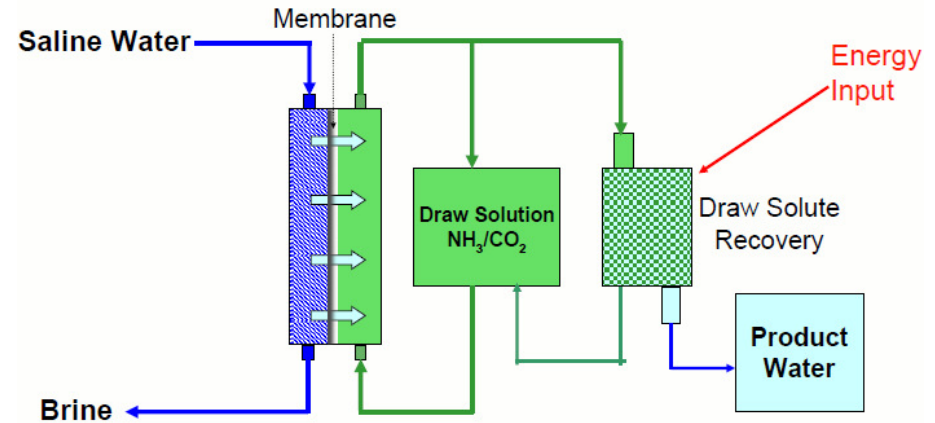
Flow patterns in a spiral-wound module modified for FO. The feed solution flows through the central tube into the inner side of the membrane envelope and the draw solution flows in the space between the rolled envelopes.

Comparison between RO and FO

Reverse Osmosis



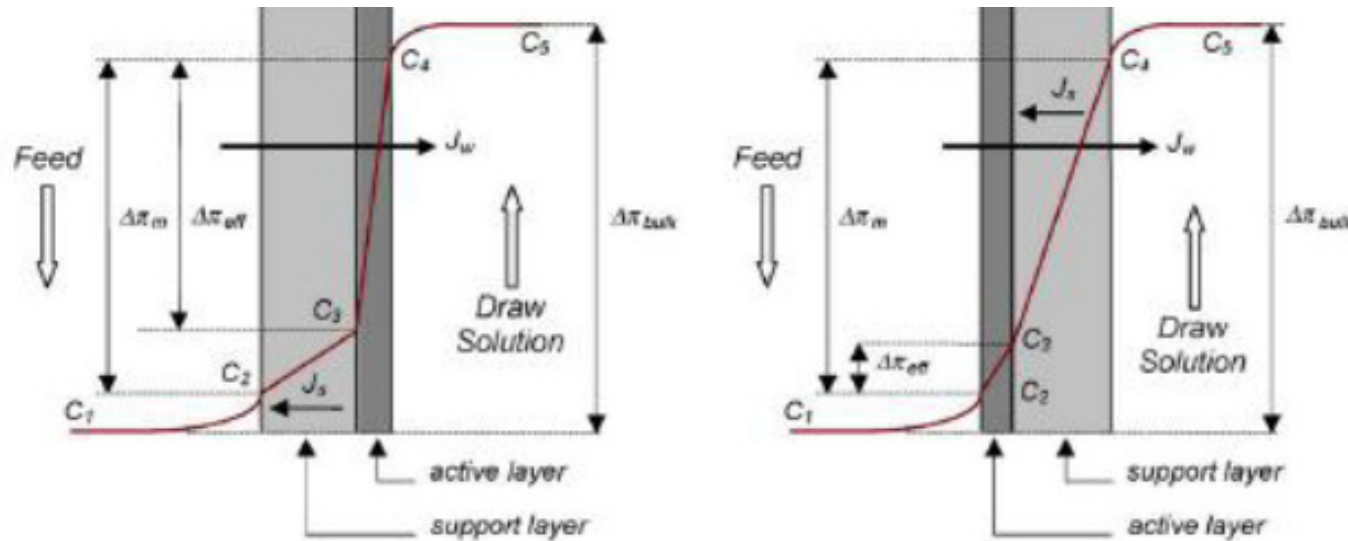
$$J_w = A(\Delta P - \sigma \Delta \pi)$$



$$J_w = A(\sigma \Delta \pi - \Delta P)$$

Forward Osmosis

Concentration Polarization (CP)

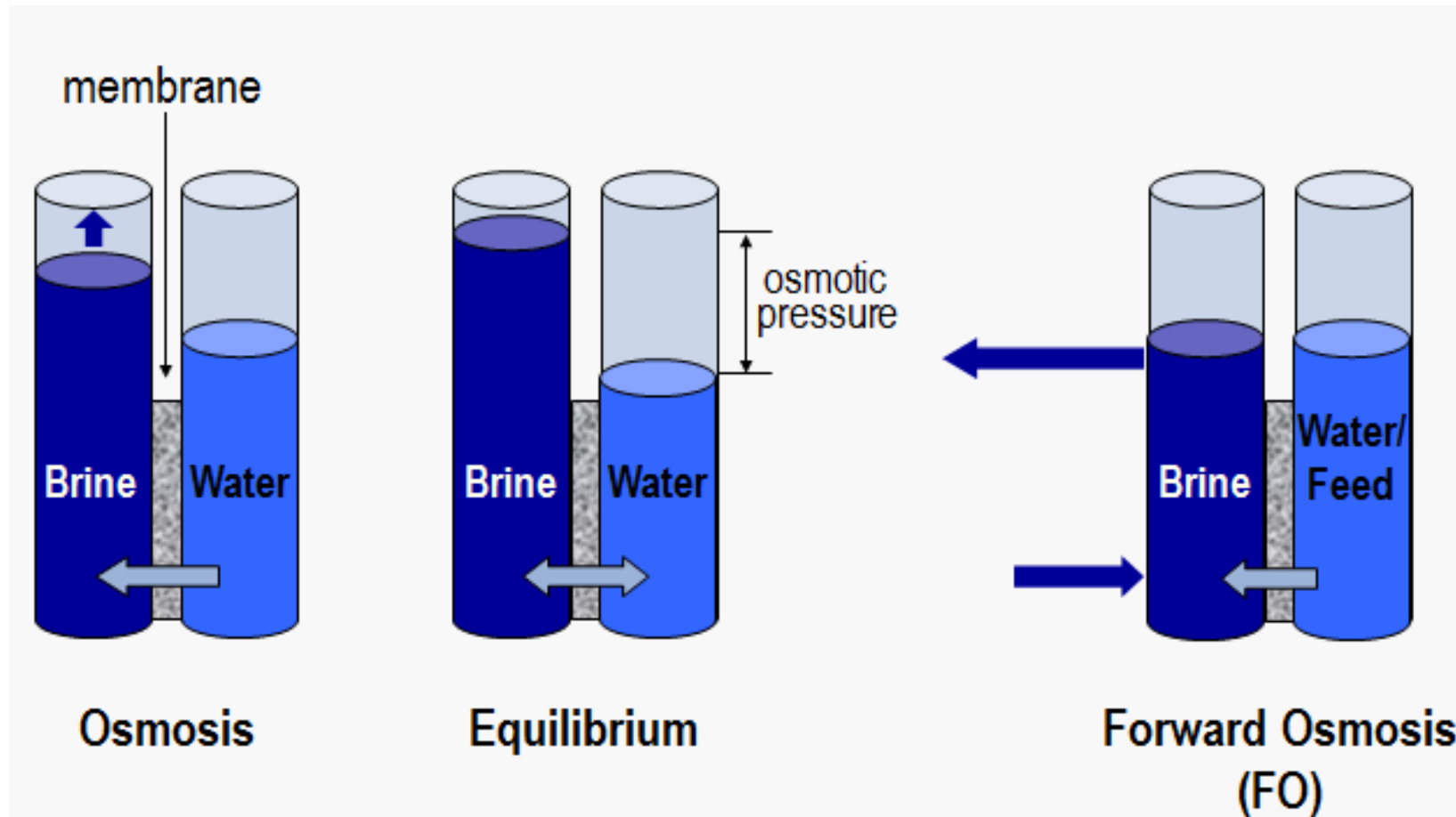


Concentrative internal CP

Dilutive internal CP

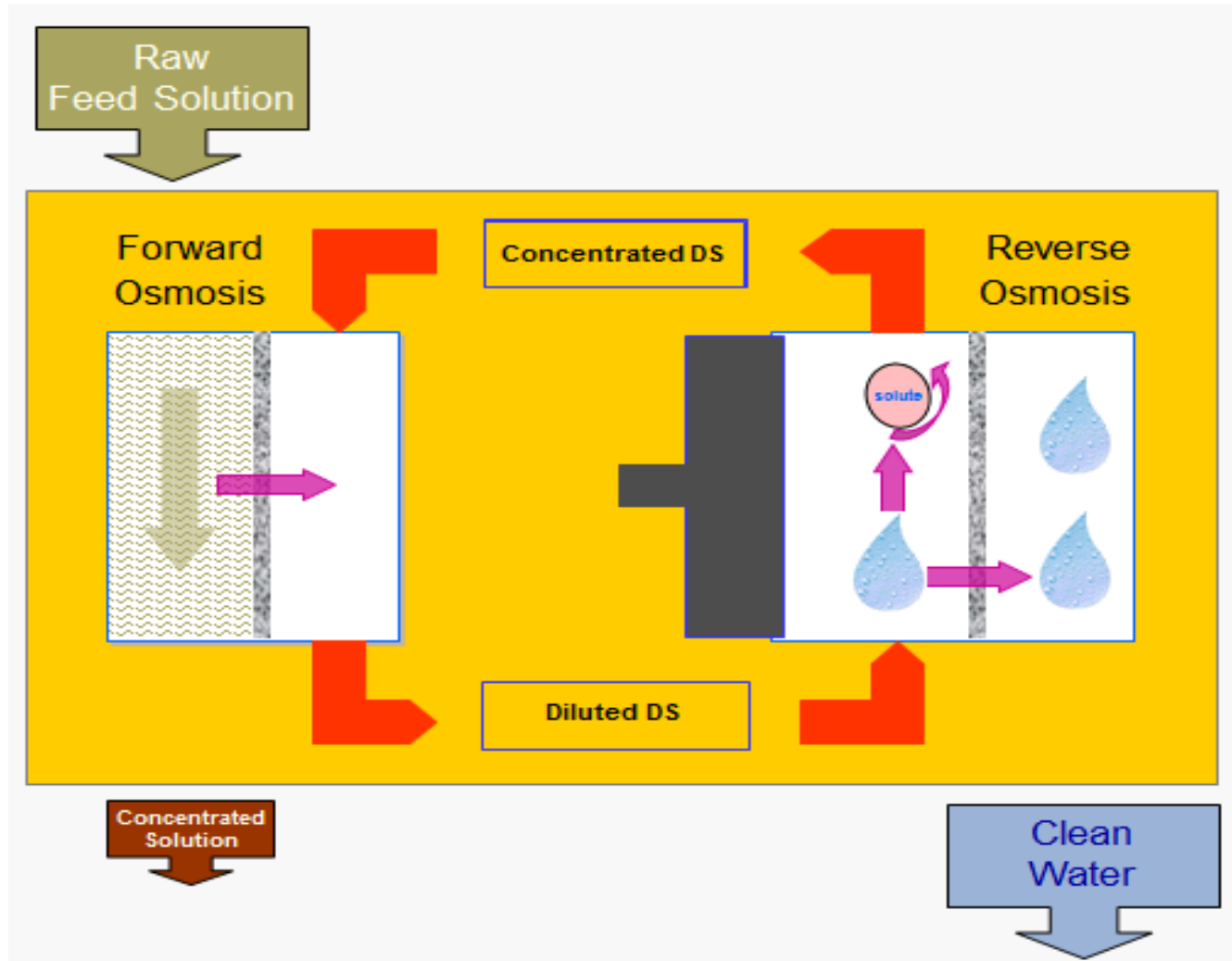
The osmotic pressure difference between the bulk feed and bulk draw solution ($\Delta\pi_{\text{bulk}}$) is higher than the osmotic pressure difference across the membrane ($\Delta\pi_m$) due to external CP. The effective osmotic pressure driving force ($\Delta\pi_{\text{eff}}$) is even lower due to internal CP. Operation of FO in a counter-current flow configuration (feed and draw solution flowing tangential to the membrane but in opposite directions) provides constant $\Delta\pi$ along the membrane module and makes the process more efficient.

Forward Osmosis Pretreatment for Reverse Osmosis

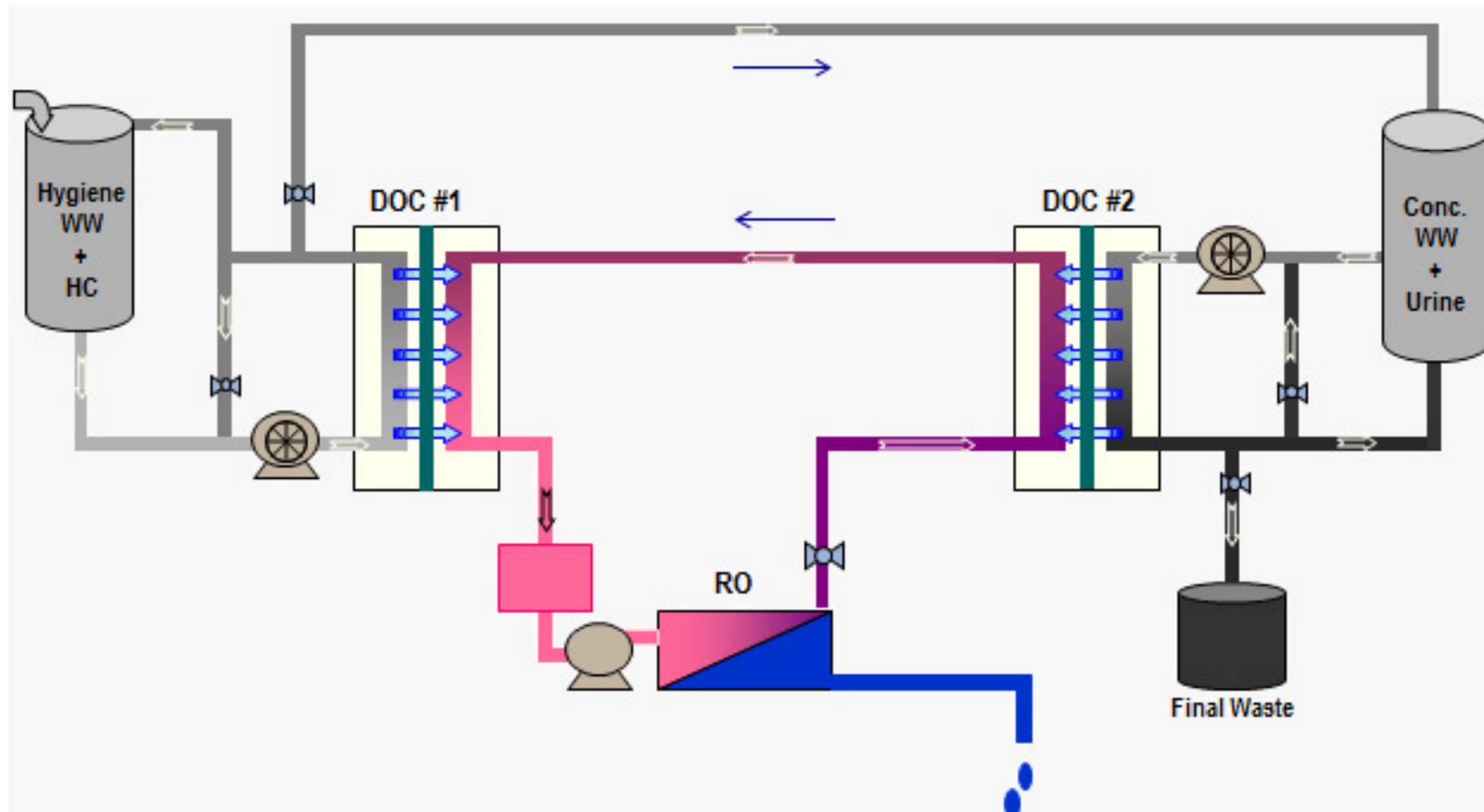


Brine \equiv Draw Solution (DS)

Forward Osmosis Pretreatment for Reverse Osmosis



Forward (Direct) Osmosis for Reuse of Wastewater





Membrane Desalination Processes



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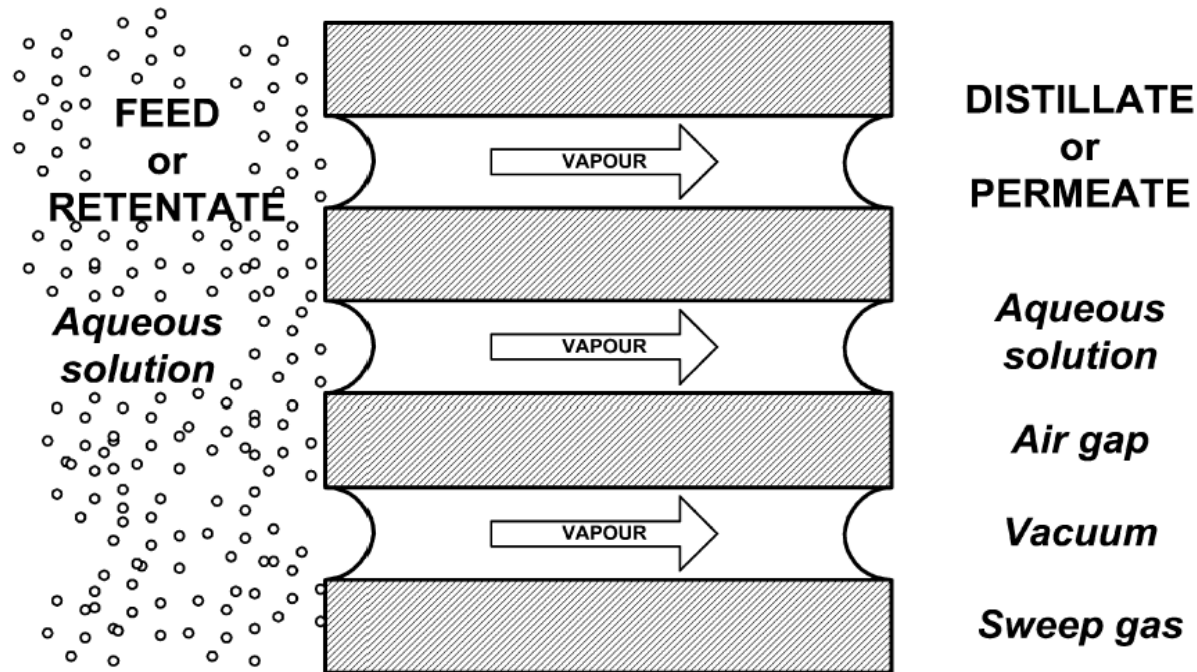
Membrane Desalination Processes



Content:

- **Innovative Processes:**
 - *Forward Osmosis (FO) and Membrane Distillation (MD)*
 - Membrane Distillation (MD) Principle
 - Membrane Distillation Configurations
 - Membrane Distillation Flow Diagram
 - FO (DO) and MD for Reuse of Wastewater
 - Solar MD Compact Systems

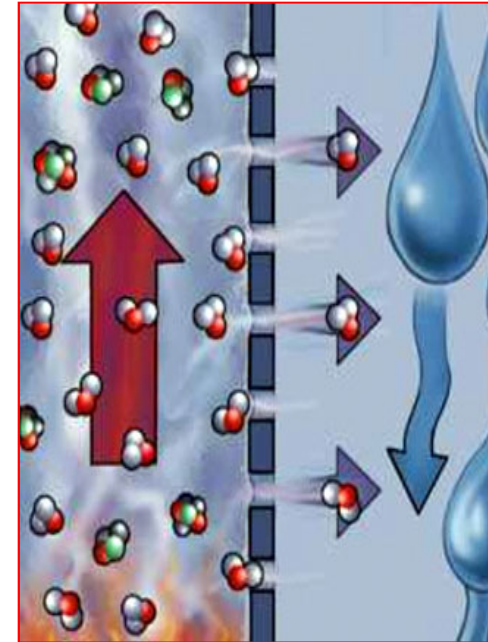
Membrane Distillation (MD) Principle



Volatile compounds evaporate at the interface of a *microporous hydrophobic membrane*, diffuse and/or convect across the membrane, and are condensed and/or removed on the opposite side (permeate or distillate) of the system.

Membrane Distillation (MD) Principle

- heated aqueous feed solution is brought into contact with feed side of hydrophobic, microporous membrane.
- hydrophobic nature of membrane prevents penetration of aqueous solution into pores.
- cold pure water is in contact with permeate side of membrane.
- vapors diffuse through pores and directly condense into cold stream.



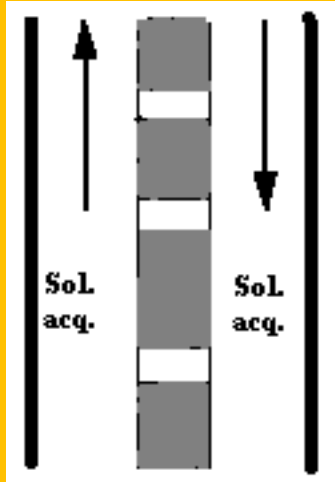
$$J = A_m (P_f^* - P_p^*)$$



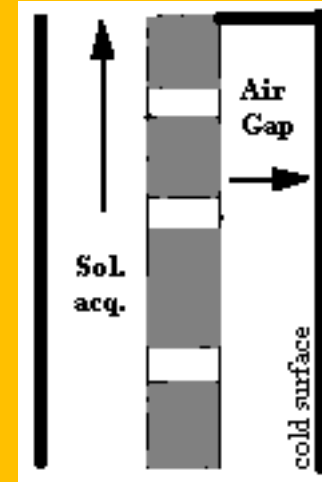
Membrane Distillation (MD) Principle

- Separation of two liquids or solutions at different temperatures by a porous membrane
- Liquids do not wet the membrane
- Non-wettable porous hydrophobic membrane
- Liquids differ in temperature => vapour pressure difference => vapour molecules transport through the pores of the membrane from the high vapour pressure side to the low
 - evaporation on the high-temperature side
 - transport of vapour molecules through the pores of membrane
 - condensation on the low-temperature side
- Pore size: 0.2-1.0 μm
- Driving force: vapour pressure difference
- Only process where membrane is not directly involved in separation

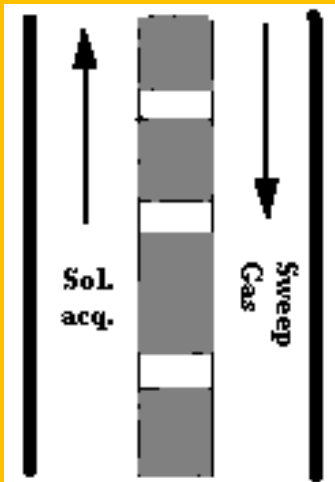
Membrane Distillation Configurations



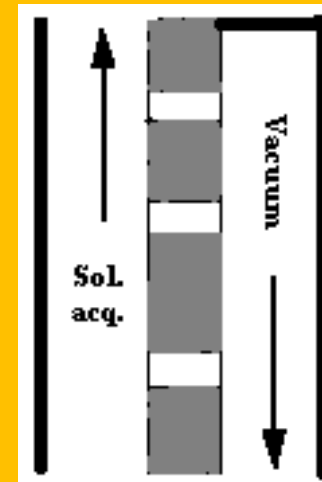
Direct Contact Membrane Distillation (DCMD). The permeate side of the membrane consists of a condensing fluid (often pure water) that is directly in contact with the membrane.



Air Gap Membrane Distillation (AGMD). The permeate side of the membrane consists of a condensing surface separated from the membrane by an air gap.

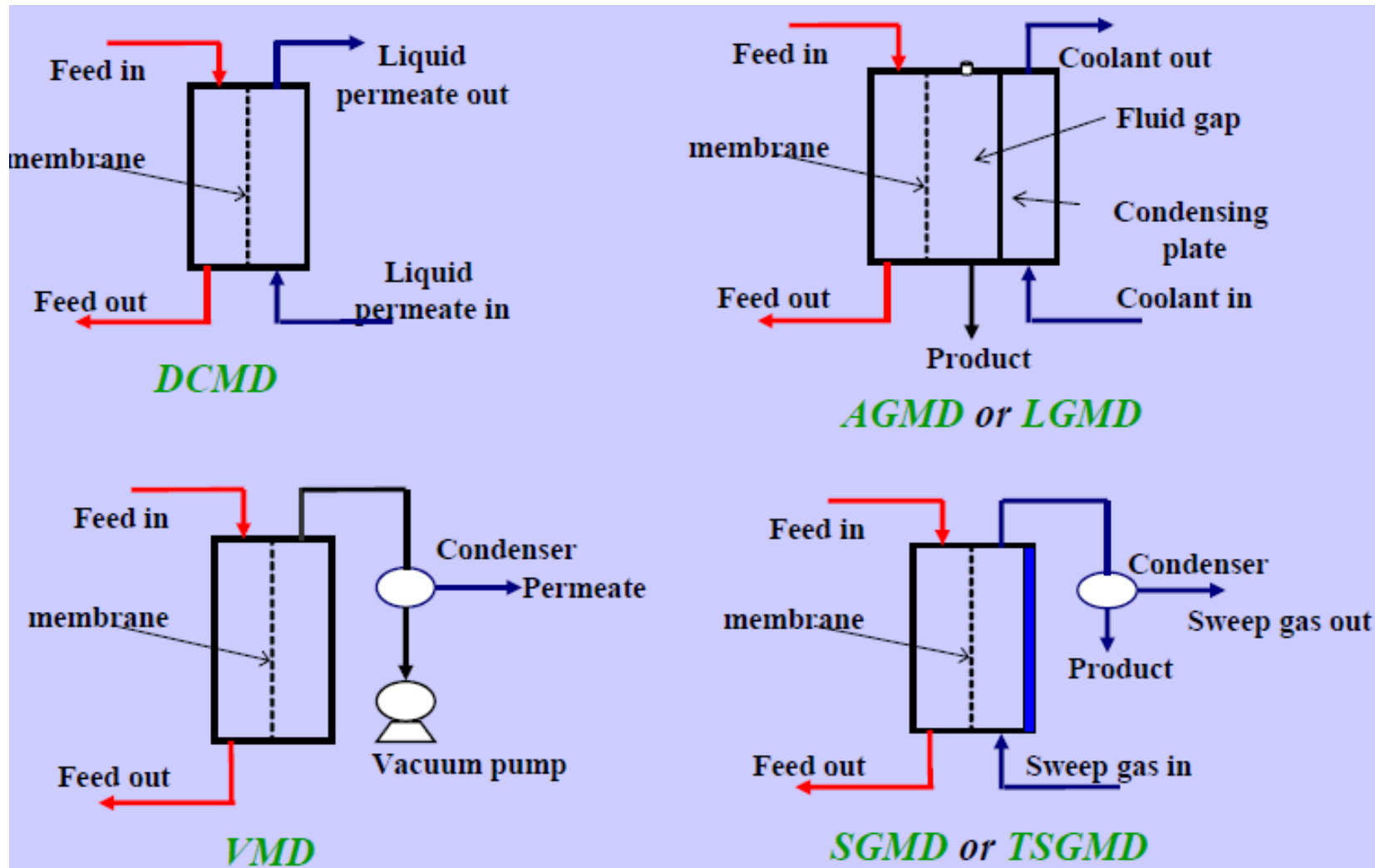


Sweeping Gas Membrane Distillation (SGMD). The vaporized solvent is removed by a sweep gas.

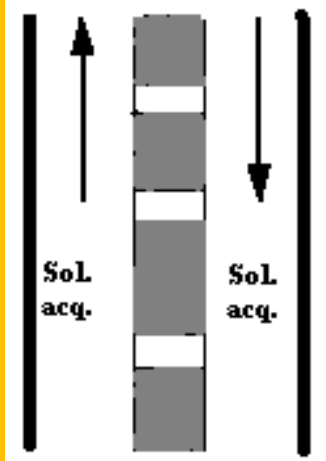


Vacuum Membrane Distillation (VMD). The vaporized solvent is recovered by vacuum.

Membrane Distillation Configurations

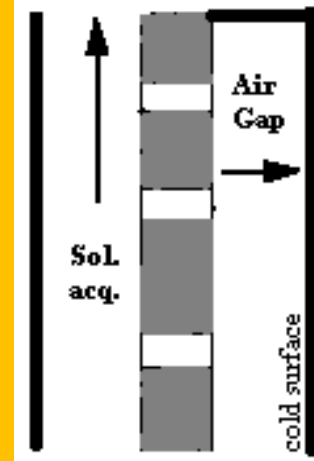


MD Configurations - Advantages and Drawbacks



DCMD:

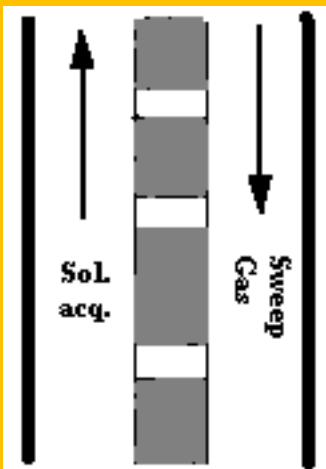
- Low efficiency of heat utilization due to the high heat lost by conduction through the membrane.



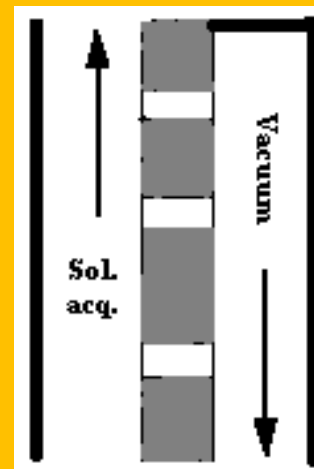
AGMD:

-Low conductive heat loss with respect to DCMD

-- Higher mass transfer resistance than DCMD



SGMD combines the low conductive heat loss of AGMD with the reduced mass transfer resistance of DCMD. The problem is that the permeate is condensed in an external surface.



VMD:

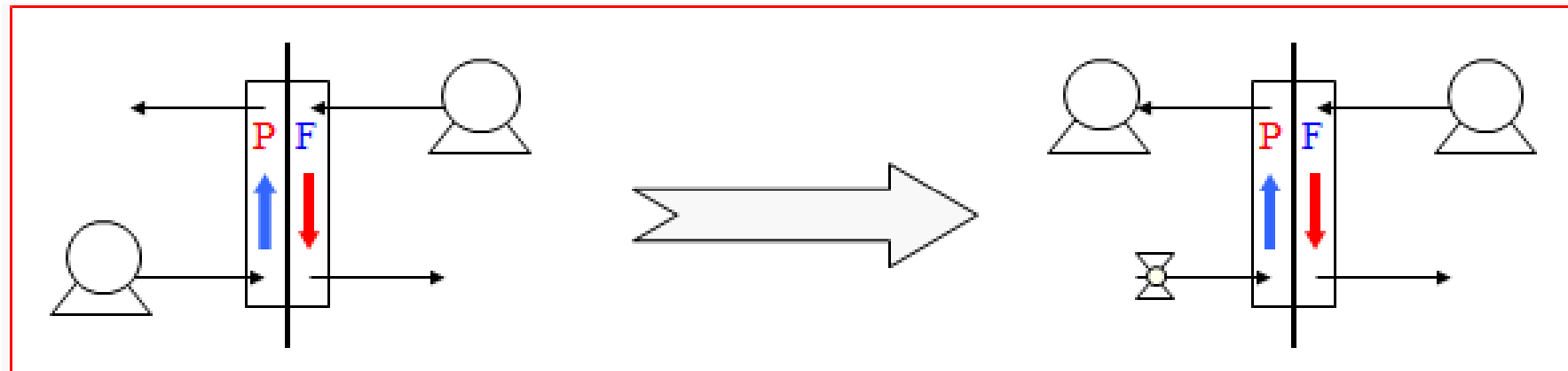
-Negligible conductive heat loss through the membrane

-High sensibility to membrane wetting

Membrane Distillation (MD)

Types of MD:

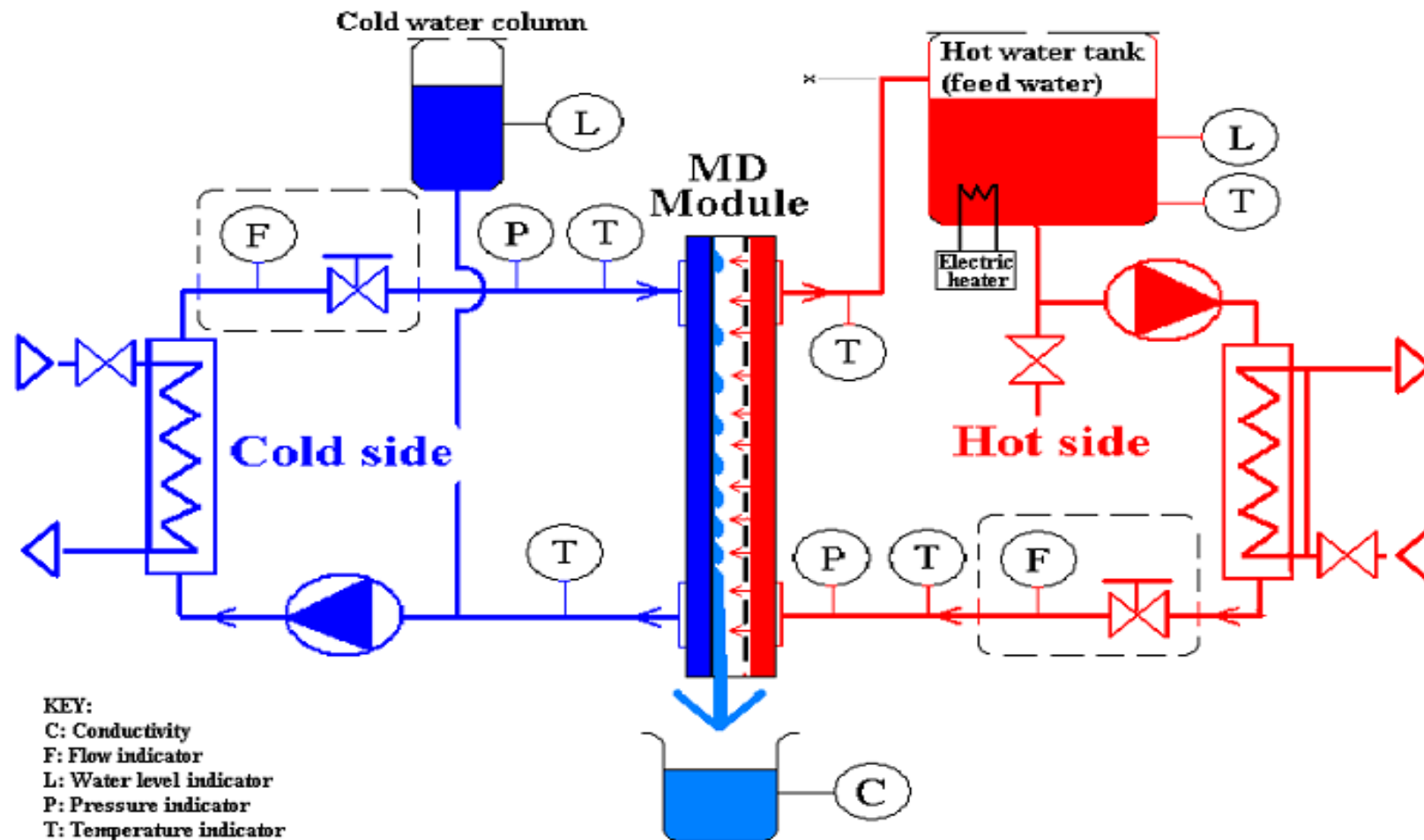
- Direct Contact Membrane Distillation (DCMD)
- Vacuum Enhanced Direct Contact Membrane Distillation (VEDCMD)



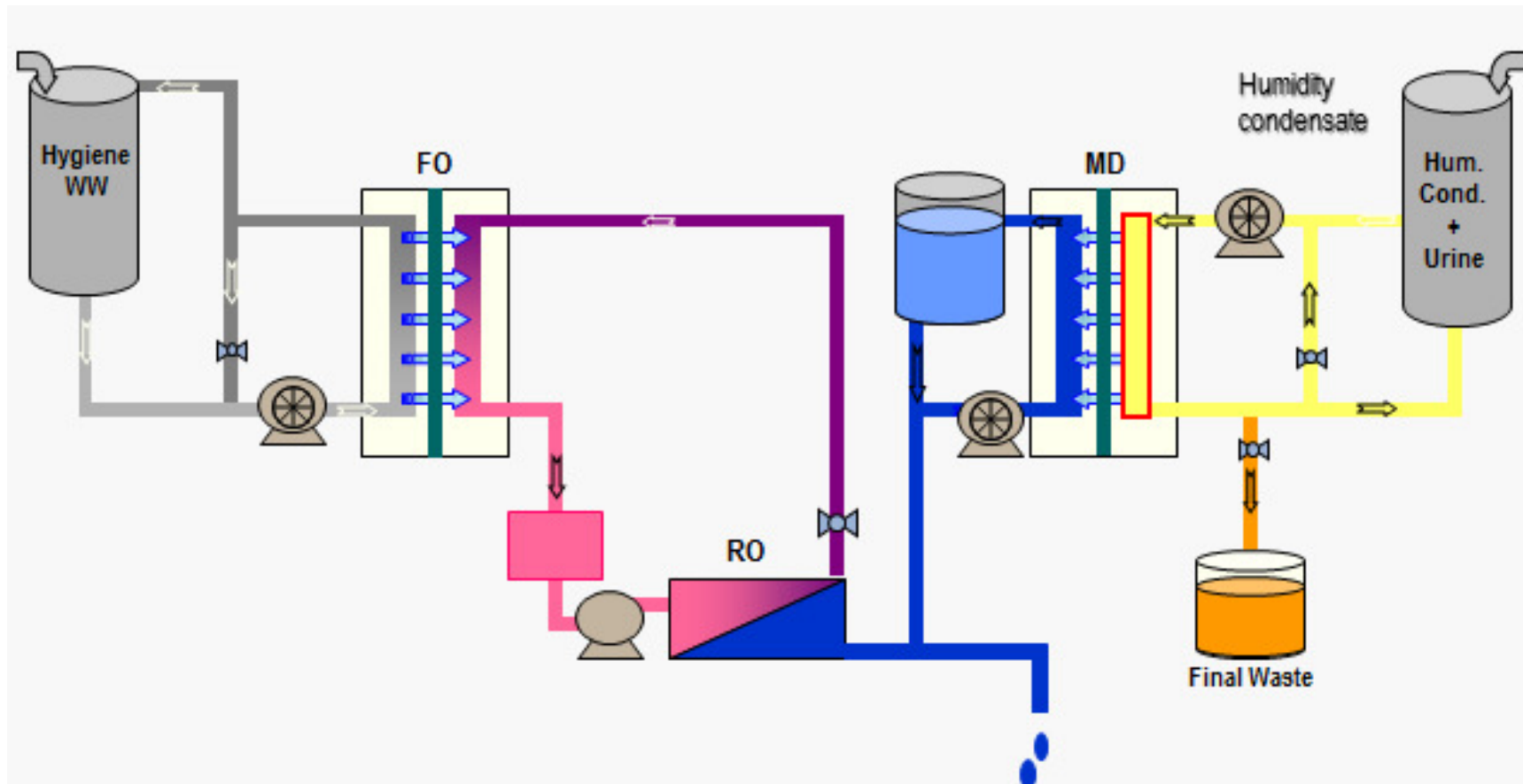
Traditional DCMD

VEDCMD

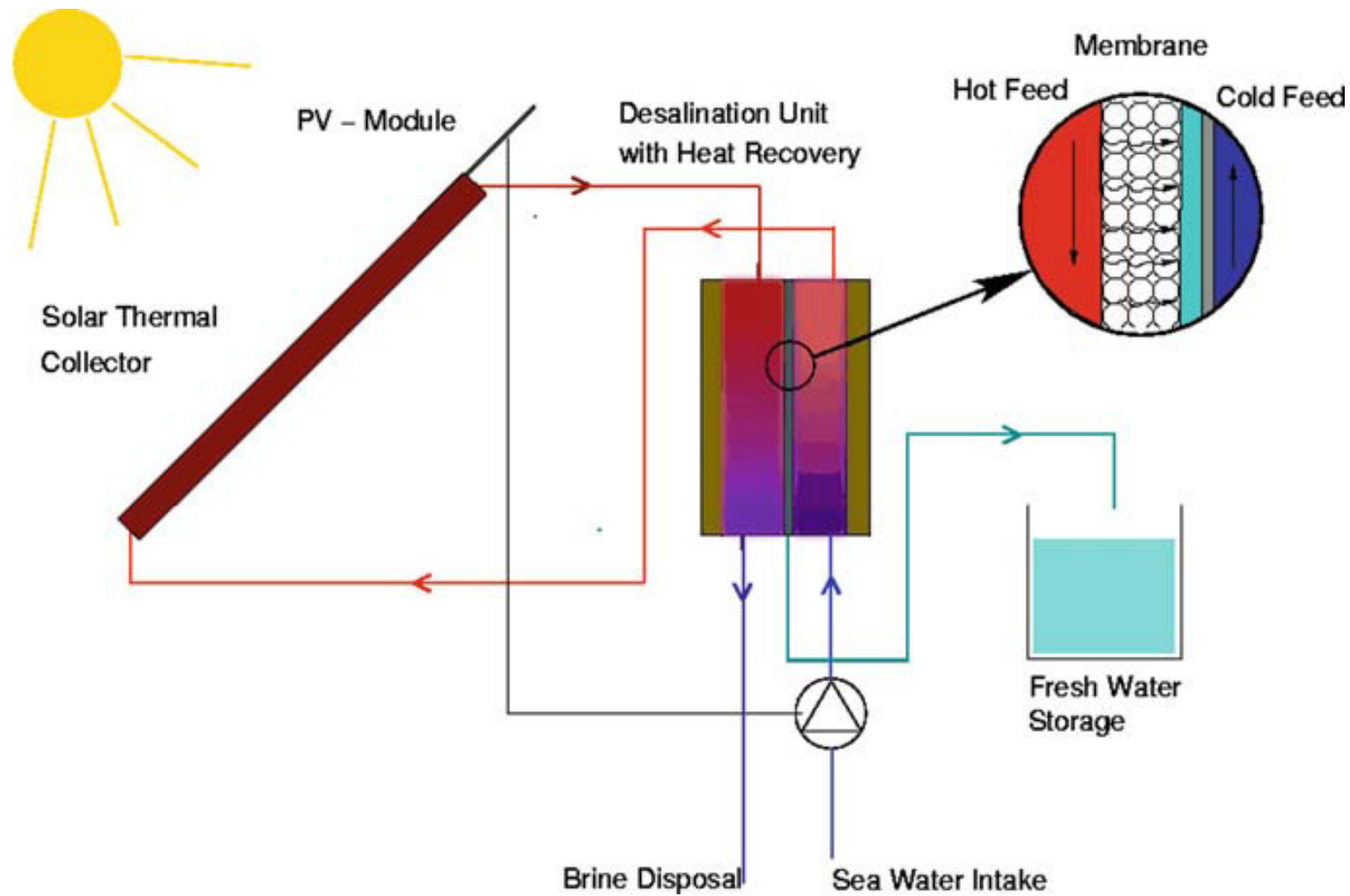
Membrane Distillation Flow Diagram



FO (DO) and MD for Reuse of Wastewater



Solar MD Compact Systems





Promising Future

With more research and development (R&D) efforts into promising approach, new and more cost effective desalination processes will be made available in commercial scale, such as

- Forward osmosis, membrane distillation, capacitive deionization, aquaporin membrane etc.
- Carbon-nanotube-enhanced (CNT) membrane distillation.
- Innovative operational technique such as vibratory shear enhanced processing (VSEP) technology was proved to increase the RO recovery up to 95%.
- The use of a variable frequency drive (VFD) which optimizes flow through the membranes.

Promising Future

1,600 units fabricated on an 8-inch-diameter -
produce about 15 liters of water per hour



A single unit of the new desalination device, fabricated on a layer of silicone. In the Y-shaped channel (in red), seawater enters from the right, and fresh water leaves through the lower channel at left, while concentrated brine leaves through the upper channel



