역삼투막의 제조 및 최근 동향

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RO MEMBRANES : History,Fabrication and Application

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SAEHAN INDUSTRIES INC

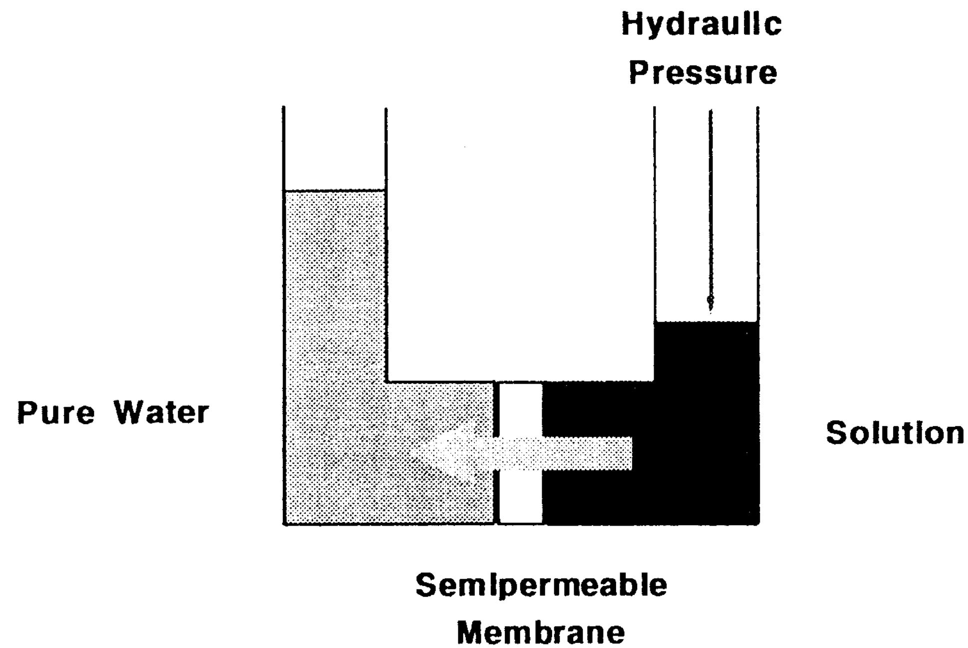
SAEHAN

MEMBRANE SELECTIVITY

Range	Electron Microscopy		Optical Microscopy			Visible to Naked Eye	
	Ionic Range	Molecular Range	Macro Molecular Range		Micro Partile Range	Macro Particle Range	
Micrometer	10^{-3}	10^{-2}	10^{-1}	1	10	100	
Angstrom	10	10^{2}	10^{3}	10^{4}	10^{5}	10^{6}	
Molecular Weight	100	1000	100000				
Particle Type	Sugars, Carbon Black, Pyrogen, Paint Pigment, Soluble Salts, Oil Emulsions, Bacteria, Human Hair, Virus, Colloids, Metal Ions, Proteins / Enzymes, Sand						
Membrane Type	Reverse Osmosis, Microfiltration, Nanofiltration, Ultrafiltration, Particle Filtration						

역삼투 현상

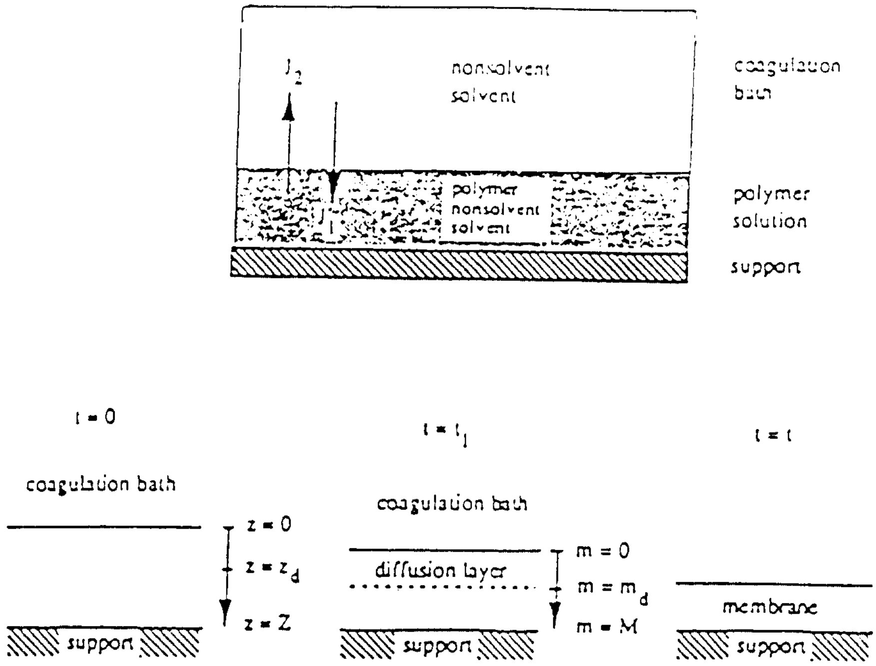
REVERSE OSMOTIC FLOW



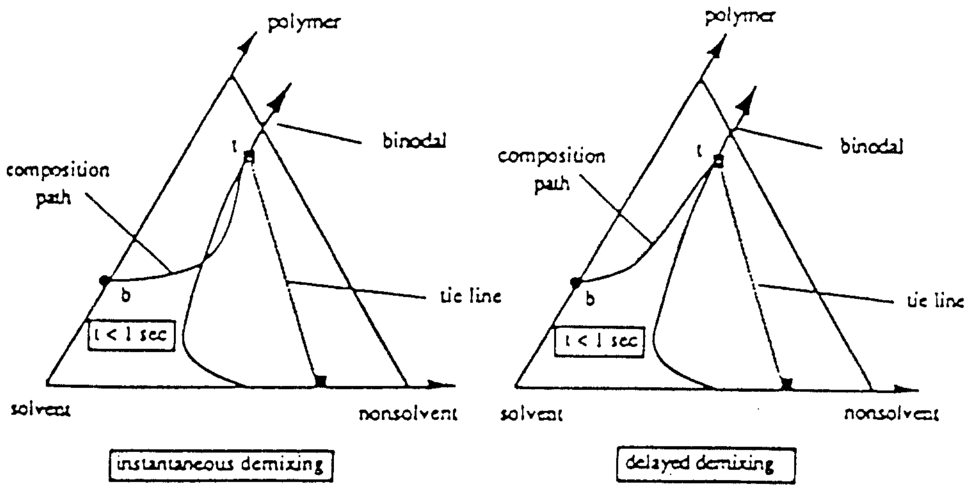
History of RO membrane

Year	Events	
1959	◎Reid & Breton : Demonstration of desalination capability of cellulose acetate film	
1963	◎Loeb & Sourirajan : Development of asymmetric cellulose acetate reverse osmosis membrane	UCLA
1965	◎Riley,Lonsdale : Elucidation of asymmetric CA membrane structure and proposal of solution-diffusion transport model.	
1966	◎Francis : Cellulose acetate thin film composite membrane concept	North Star
1972	◎John Cadotte : Interfacially synthesized thin film composite membrane NS-100 (PEI + TDI)	North Star R&D Institute
1978	◎John Cadotte : Fully aromatic polyamide thin film composite membrane	Filmtec
1982	◎Filmtec (J. Cadotte) Marketed "FT-30"	R : 98% FLUX : 25 GFD
1985	Dow purchase Filmtec	
1992	◎Dow Lost right of US patent 4,277,344 in lawsuit by Hydranauctics and Fluid-systems	
1994	◎SAEHAN: Developed TFC type RO membrane.	R : 99% FLUX : 35 GFD
1995	◎Hydranautics : Marketed High flux membrane "ES-10" ESPA	R : 99% FLUX : 45 GFD
1997	◎SAEHAN: Developed High flux membrane "CSM-BL"	R : 99% FLUX : 50 GFD

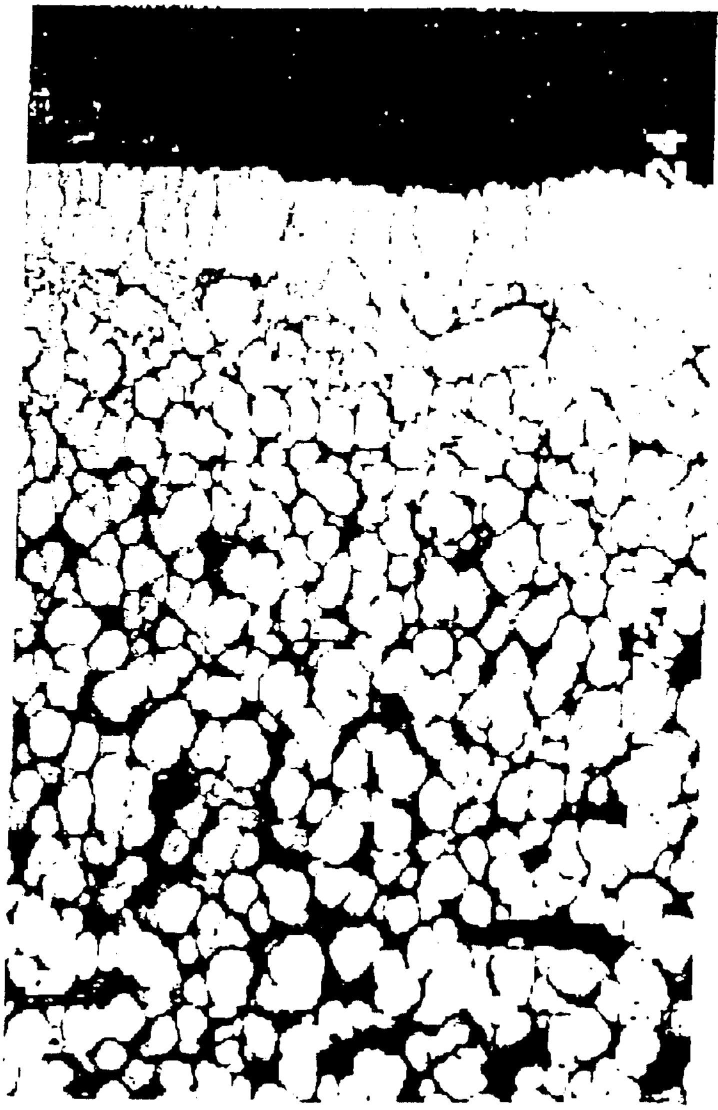
Phase Inversion Process



Schematic representation of the diffusional processes occuring after immersion in a quench medium
[from M.H.V. Mulder, "Basic Principles of Membrane Technology", Kluver Academic Publishers (1991), p.86,91]

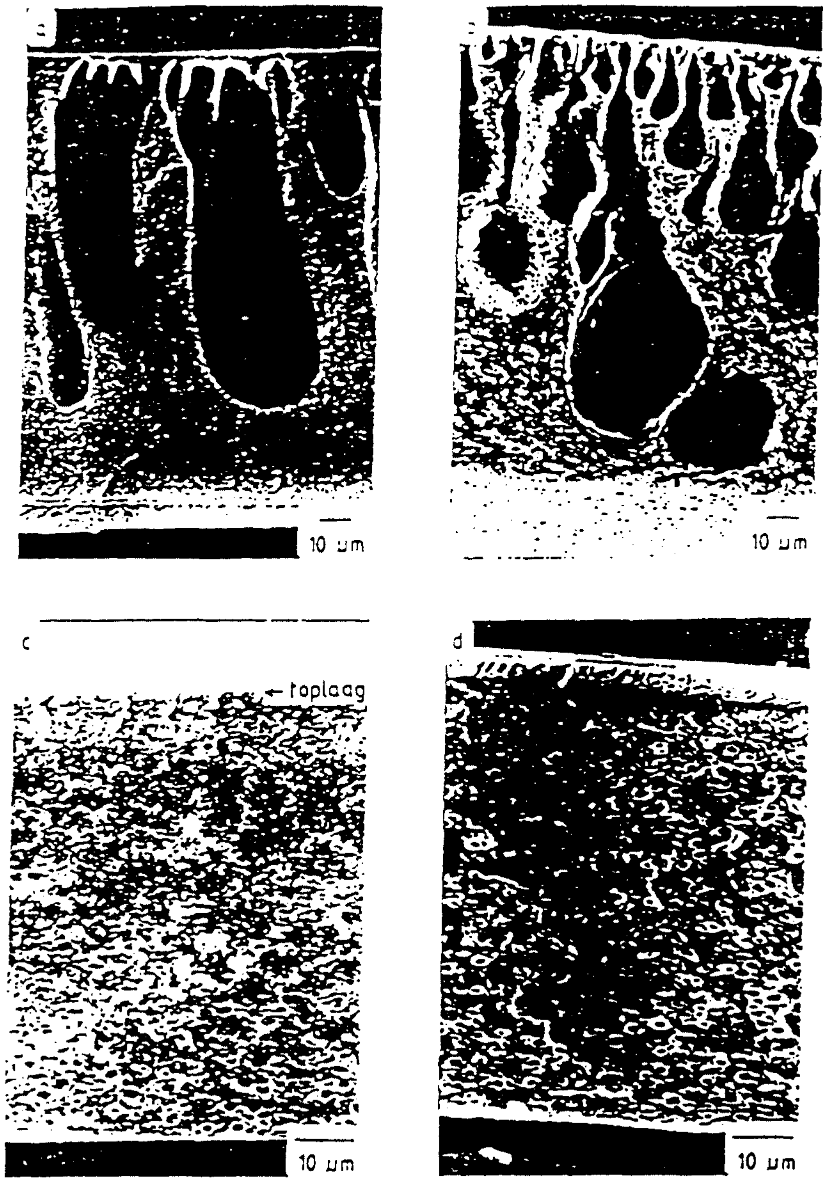


Schematic representation of the compositional change of a cast film at the quench bath-film interface immediately after immersion
[from M.H.V. Mulder, "Basic Principles of Membrane Technology", Kluver Academic Publishers (1991), p.93]


← Ultrathin Barrier Layer
(0.05 – 0.5 μm)
← Microporous Layer
(40 – 100 μm)

RO 단면

III



Cross-sections of cellulose acetate membranes prepared from 15 vol% CA casting solutions in different solvents immersed in pure water.
a) DMF (instantaneous L-L demixing); b) dioxane (instantaneous L-L demixing);
c) acetone (delayed L-L demixing); d) THF (delayed L-L demixing)
[from B. Reuvers, Ph.D. Thesis, University of Twente, The Netherlands (1987)]

Drawbacks of CA Asymmetric membranes

1. Low Flux(2 ~ 5 gfd) and Low Rejection(96 ~ 98%)
2. Narrow operating pH Range : pH 4.5 ~ 7.5
3. Weak to Biological attack
4. Prone to Compaction at High pressure(> 400psi)
5. Prone to Compaction at High temperature(> 35℃)
6. Prone to create defects during phase inversion
7. Once Fouled, No easy means of cleaning
8. Becomes expensive when expensive polymers are used

One advantage of CA membranes

1. Chlorine tolerant up to 1ppm Cl for continuous operation

2. low cost.

Other Asymmetric Membranes

◎ Asymmetric membrane from aromatic polyamide(Nomex, B-9, B-10 DuPont) solved the problems of narrow pH range and microbial attack, but was not chlorine tolerant.

◎ Cellulose Triacetate membrane showed better pH stability and higher salt rejection than CA.

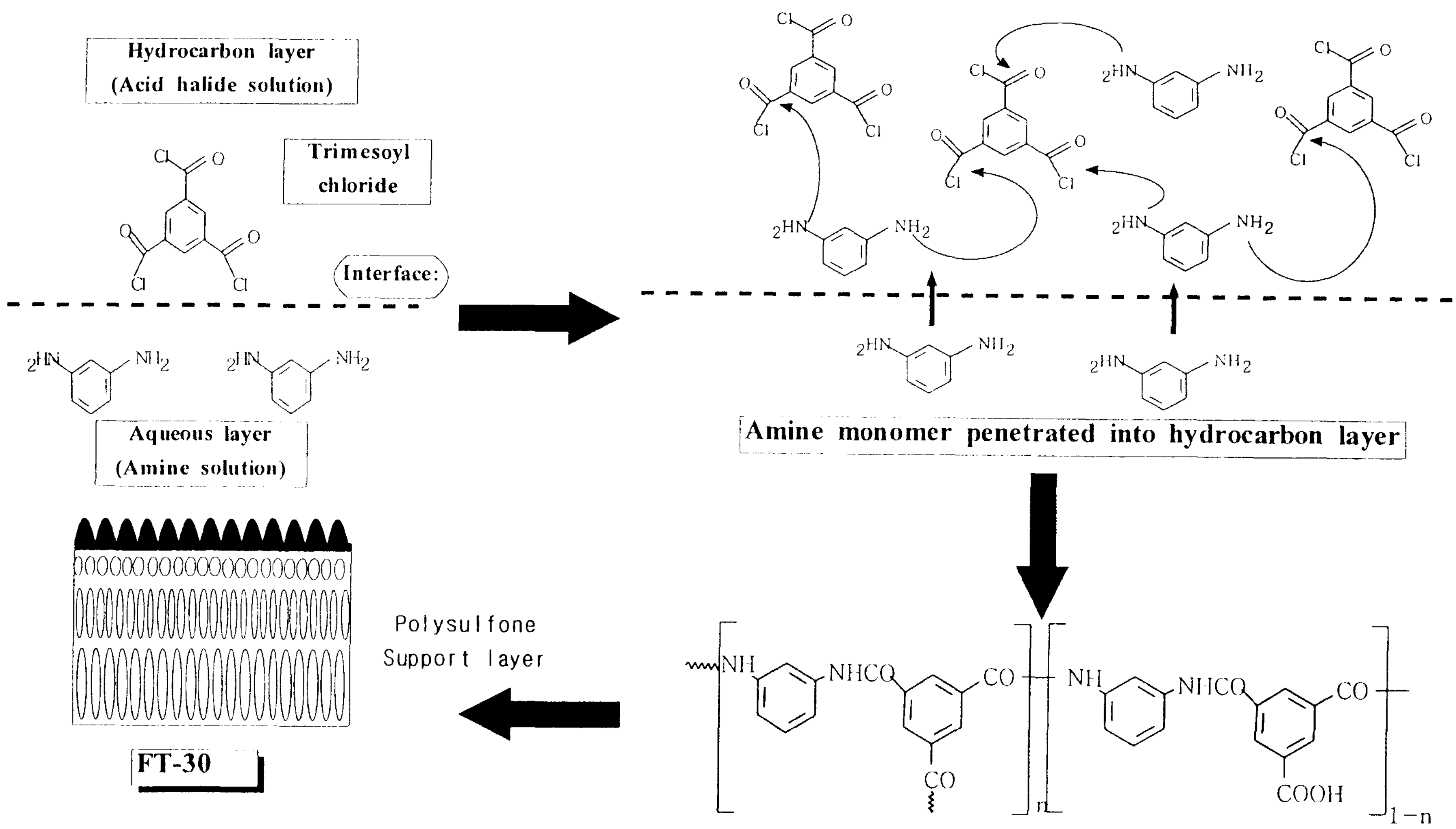
◎ Polybenzimidazole and Polybenzimidazolone.

◎ Solved pH stability, microbial attack and chlorine damage problems, but the polymers were expensive and salt rejection was not as good as CA membrane.

Composite membrane

1. lamination
2. interfacial polym.
3. dip-coating of polymer solution
4. dip-coating of monomers & reaction
5. plasma

Schematic diagram of Interfacial polymerization(FT-30)



% REJECTION COMPARISONS

Substance	Celluosic(%)	Thin-film(%)
Monovalent ions	95 ~ 97	95 ~ 99+
Divalent ions	>99	>99
Dissolved gases	None	None
Dissolved silica	85	90 ~ 99
Colloidal silica	100	100
Nitrates	85	95
Particles & Bacteria	100	100
Large Organics	100	100
Overall	96	98+

Structure and Property Relationship of TFC Membranes from various Diamines

Diamines	Flux(gfd)	Rejection(%)
1,2-Ethylenediamine	1~6	95~97
1,3-Cyclohexane bismethylamine	11~14	85~94
1,4-Cyclohexane diamine	15~36	71~81
1,3-Phenylenediamine (FT-30)	25~30	98~99

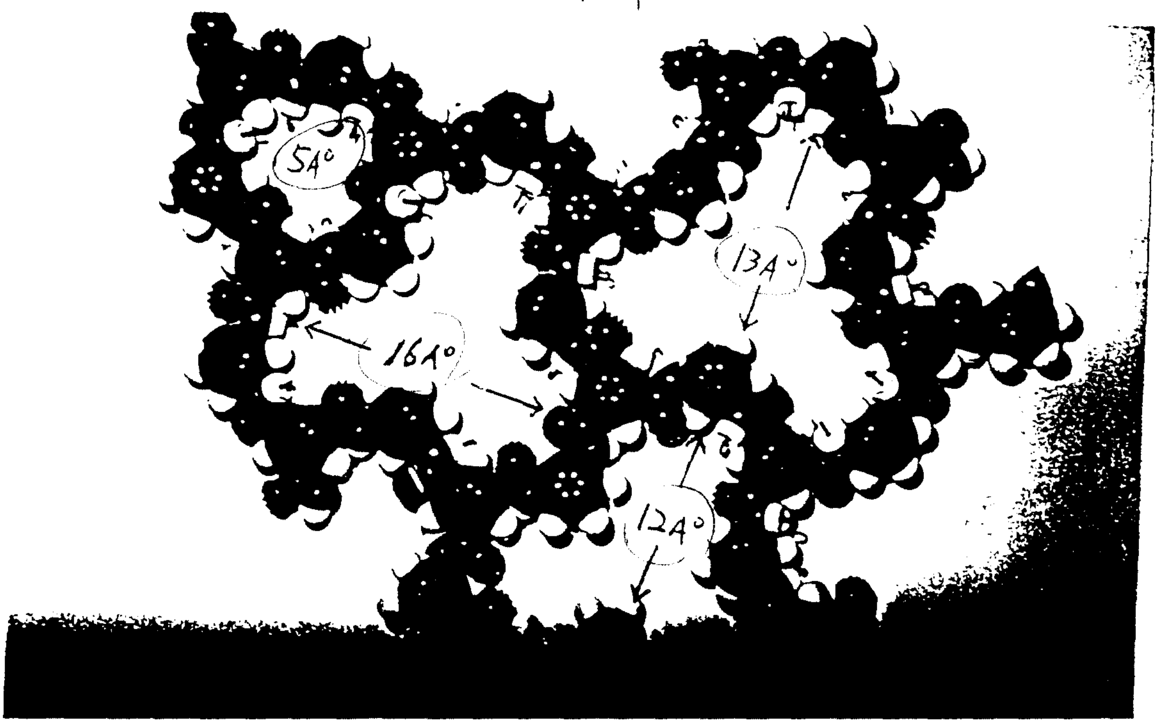
(TEST Condition 225psi 0.2% NaCl solution)

◎Pore size and Flux & porosity

1,2-Ethylenediamine 〈 1,3-Cyclohexanebismethylamine 〈 1,3-Phenylenediamine 〈 1,4-Cyclohexanediamine

* effects of acid chlorides on flux & rejection

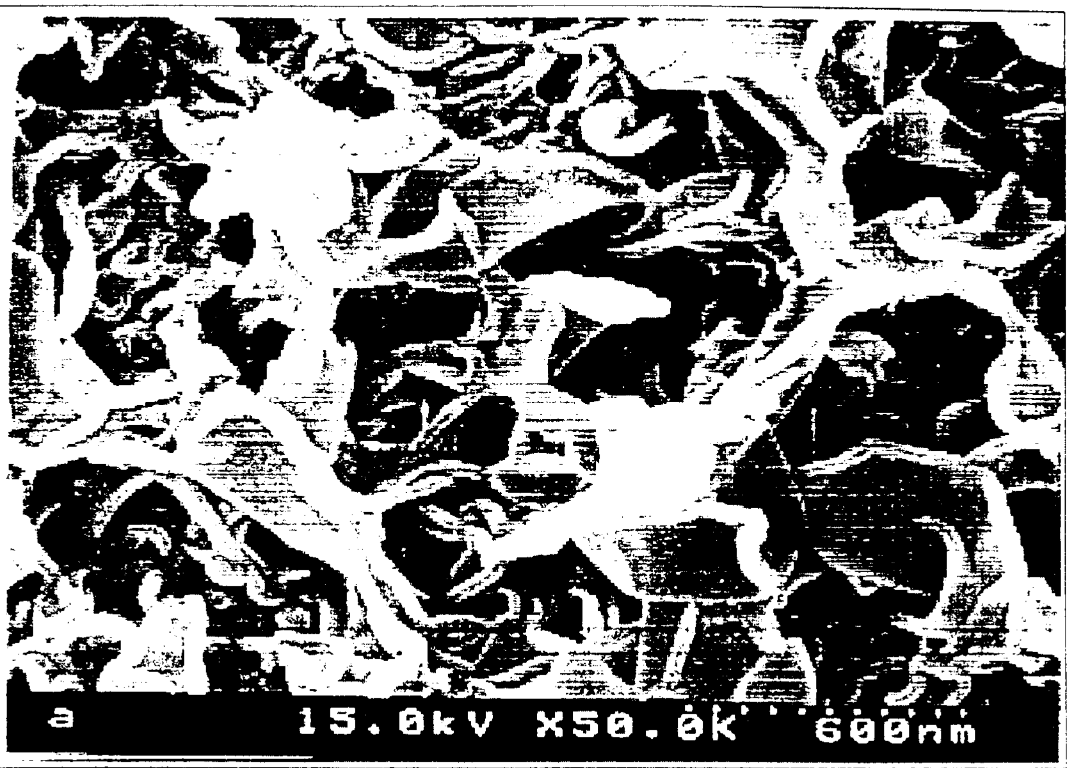
Symmetry of amines → high rejection



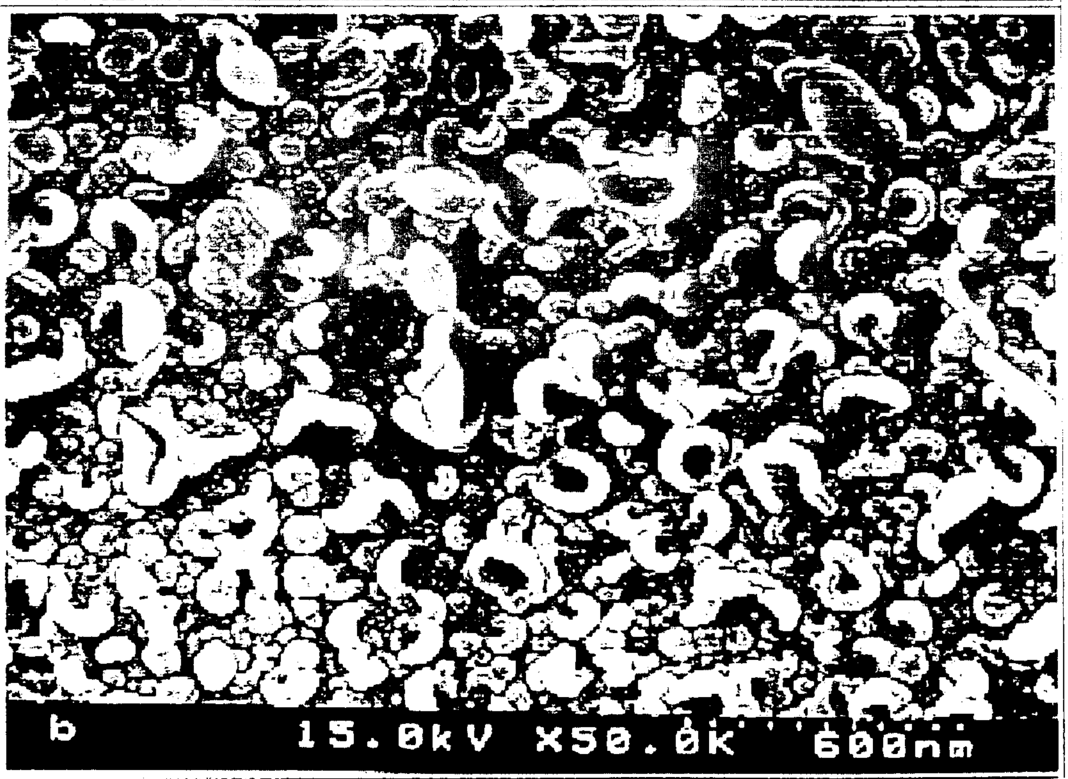
CPK Model of FT - 30 (JMS. 1987, M. Hirose) others

Field Emission SEM

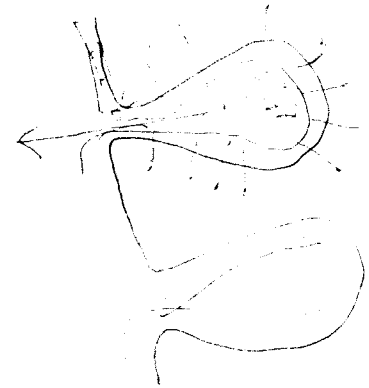
High Flux Membrane



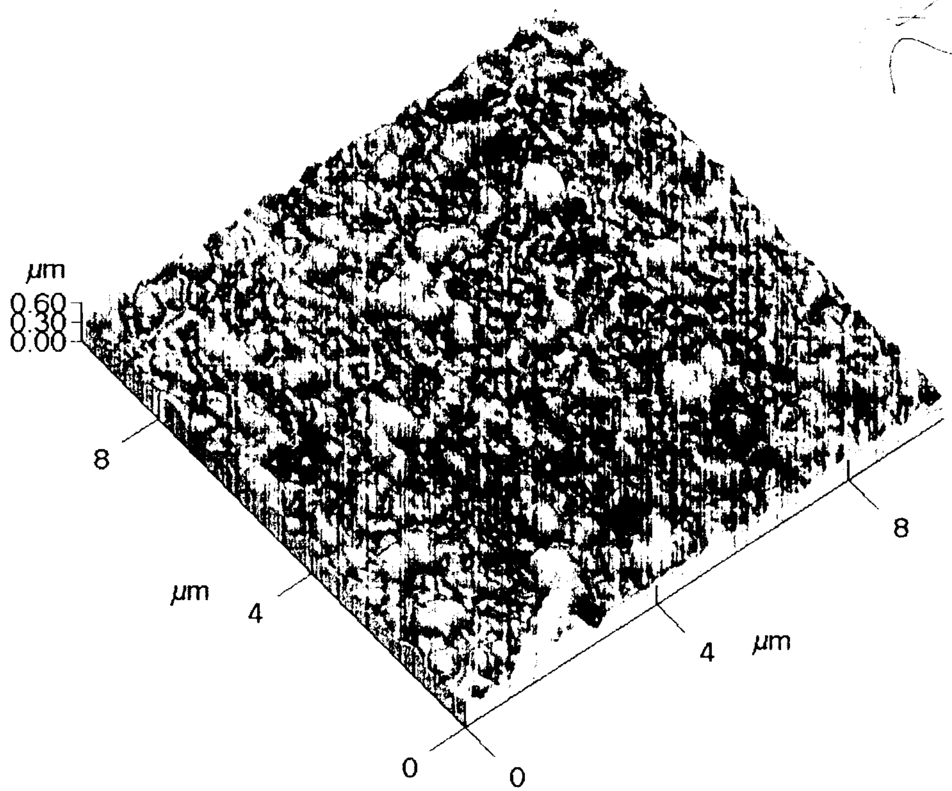
Regular Flux Membrane



AFM



High Flux Membrane



RO Membrane Materials and Manufacturers

- **Cellulose Acetate**
  Desal,Koch Membrane System, Fluid system, Hydranautics/Nitto-Denko, PCI, Stork and Toray
- **Cellulose Triacetate**
  Toyobo
- **Aromatic Polyamide**
  B-9, B-10, B-15(DuPont)
- **Crosslinked Aromatic Polyamide**
  FT-30(FilmTec/Dow), TFCL(Fluid-systems)
  UTC(Toray), CPA and ES-10(Hydranauctics/Nitto-Denko)
- **Polypiperazineamide**
  NF-40(Filmtec/Dow), SU-210(Toray)
  Separem, Desal
- **Polyfuran**
  PEC-1000 (Toray)
- **Sulfonated Polysulfone**
- **Polyvinylalcohol**
  NTR(Nitto-Denko)
- **Aryl-Alkyl polyamide/polyurea**
  RC-100 and PA-300 (Fluid System)
- **Polybenzimidazole**
  Osmonics/Cellulose
- **Polybenzimidazolone**
  Teijin

RO Membrane Transport Model

◎ Solution-Diffusion Model

$Jw = A(\triangle P - \triangle \pi)$

A = Water permeability constant

$\triangle P$ = Operatin pressure

$\triangle \pi$ = Osmotic pressure

$Js = B(Cm - Cp)$

B = Solute permeability constant

Cm = Solute concentration on membrane

Cp = Solute concentration in permeate

Salt Rejection(R) = $[\ 1 + B/A(1/(\triangle P - \triangle \pi))]^{-1}$

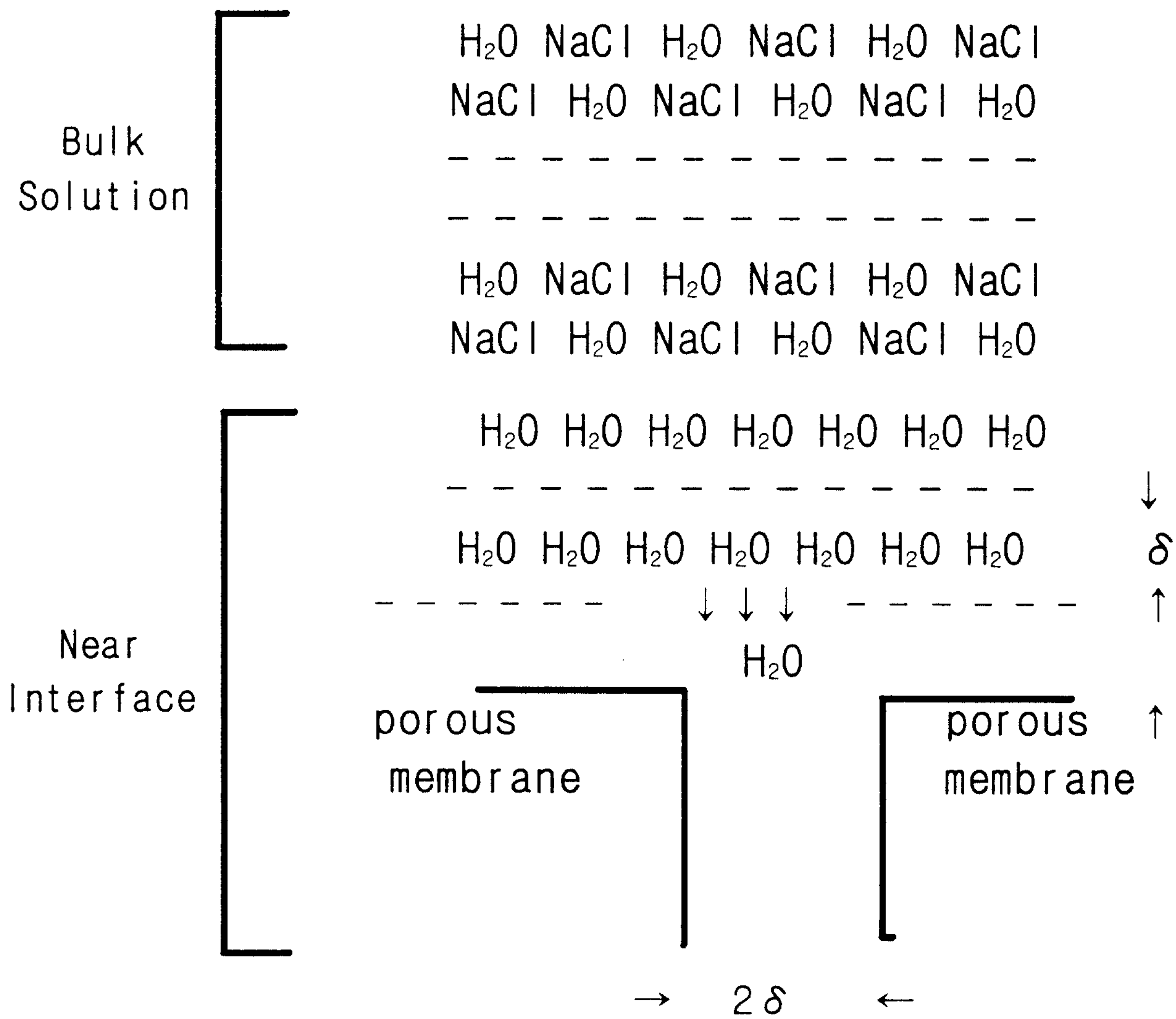
◎ Solution-Diffusion-Imperfection Model

$Jw = A(\triangle P - \triangle \pi) + C\triangle P$

$Js = B(Cm - Cp) + C\triangle PCm$

$R = [1 + B/A(1/(\triangle P - \triangle \pi)) + C/A(\triangle P/(\triangle P - \triangle \pi))]^{-1}$

◎Preferential Sorption- Capillary Model



$$Jw = A(\triangle P - \triangle \pi)$$

$$Js = CtKsDsm(Cb - Cp)/L$$

$$CtKsDsm/L \fallingdotseq B$$

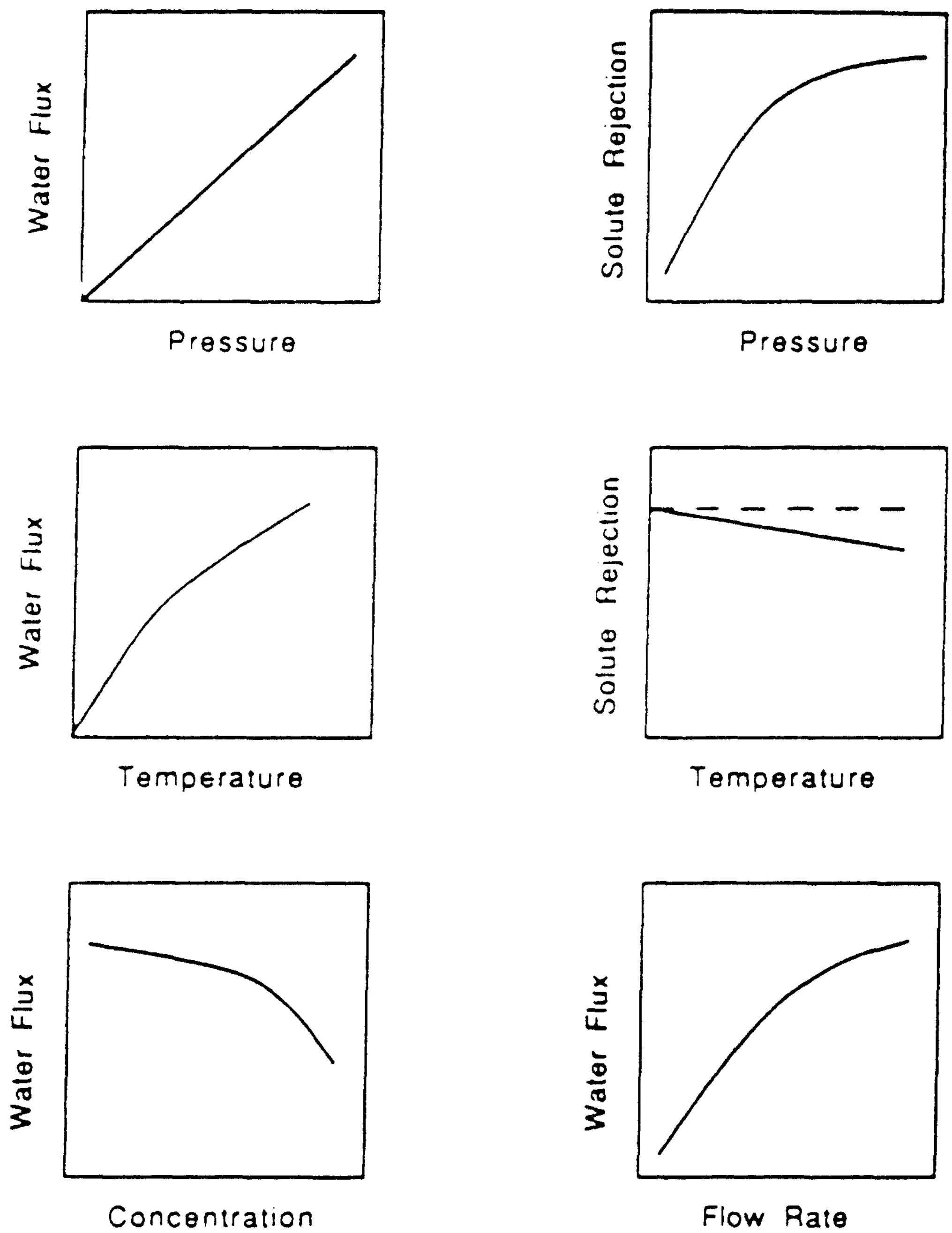
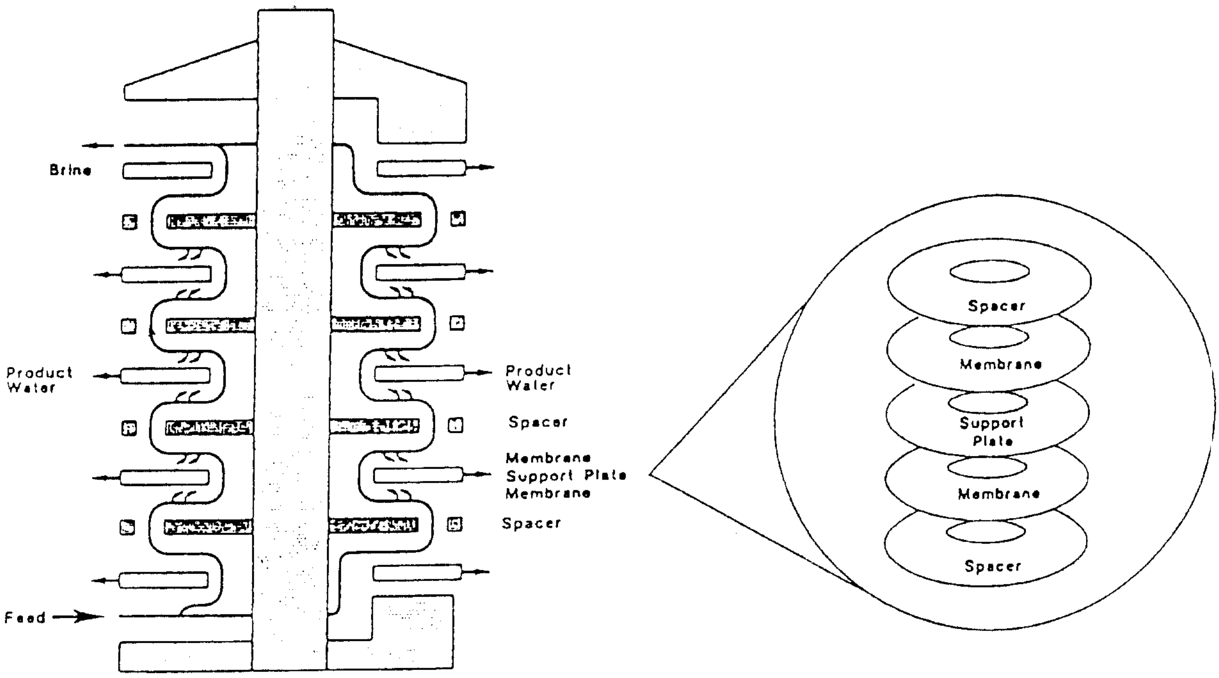


FIGURE Curves showing effect of variables on RO membranes (DOE 1990).

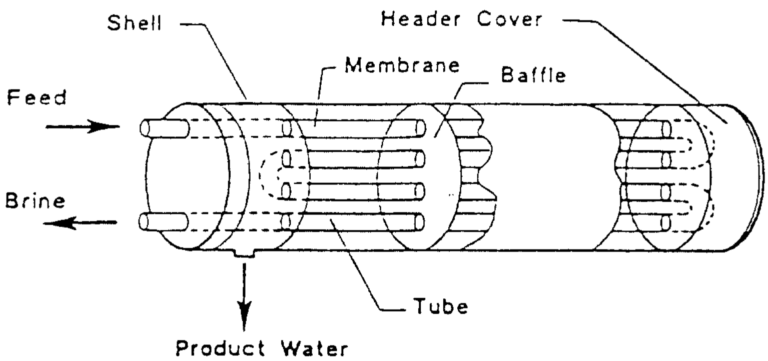
RO Module Configuration

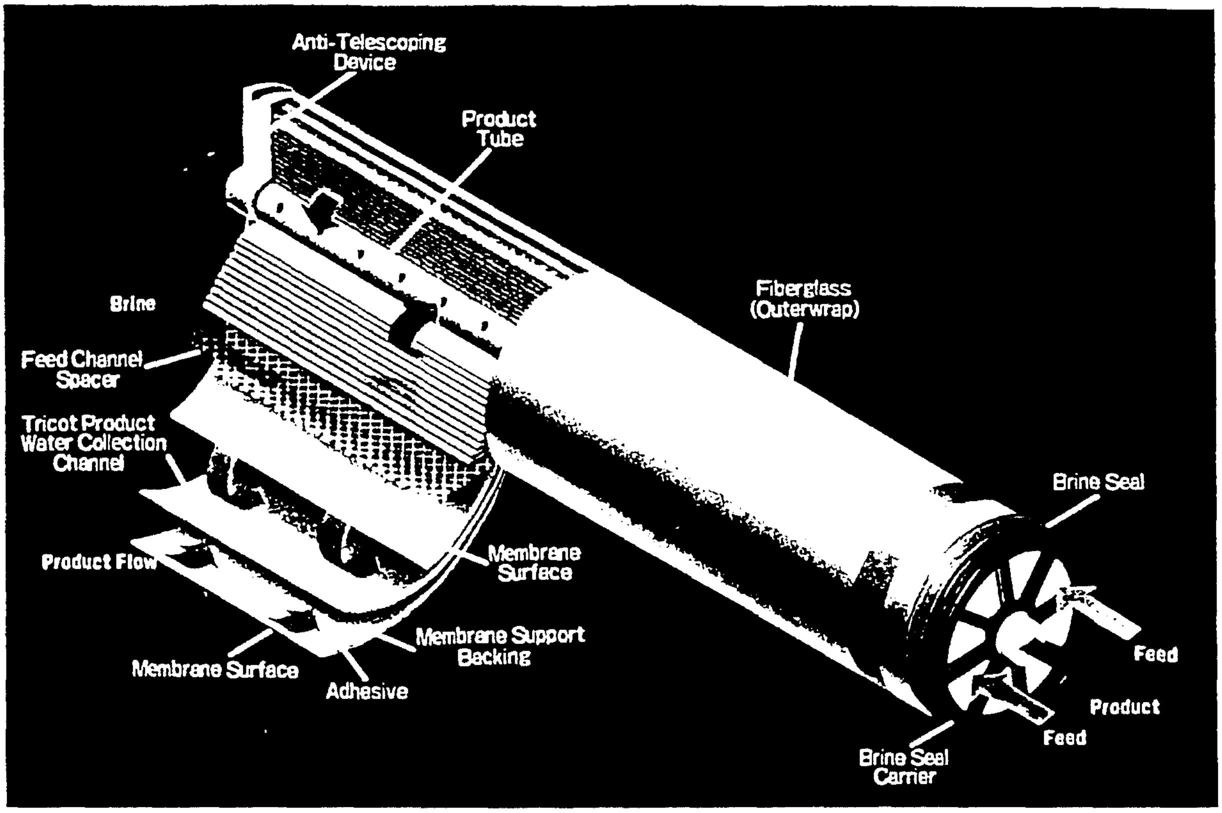
ITEM	Tubular	Plate & Frame	Hollow Fiber	Spiral Wound
Cost	High	High	Low	Low
Cleaning	Easy	Easy	Difficult	Relatively Easy
Space	Large	Medium	Small	Small
Fouling	Low	Low	High	Medium
Energy	High	High	Medium	Low
Flux	Low	Low	High	Medium



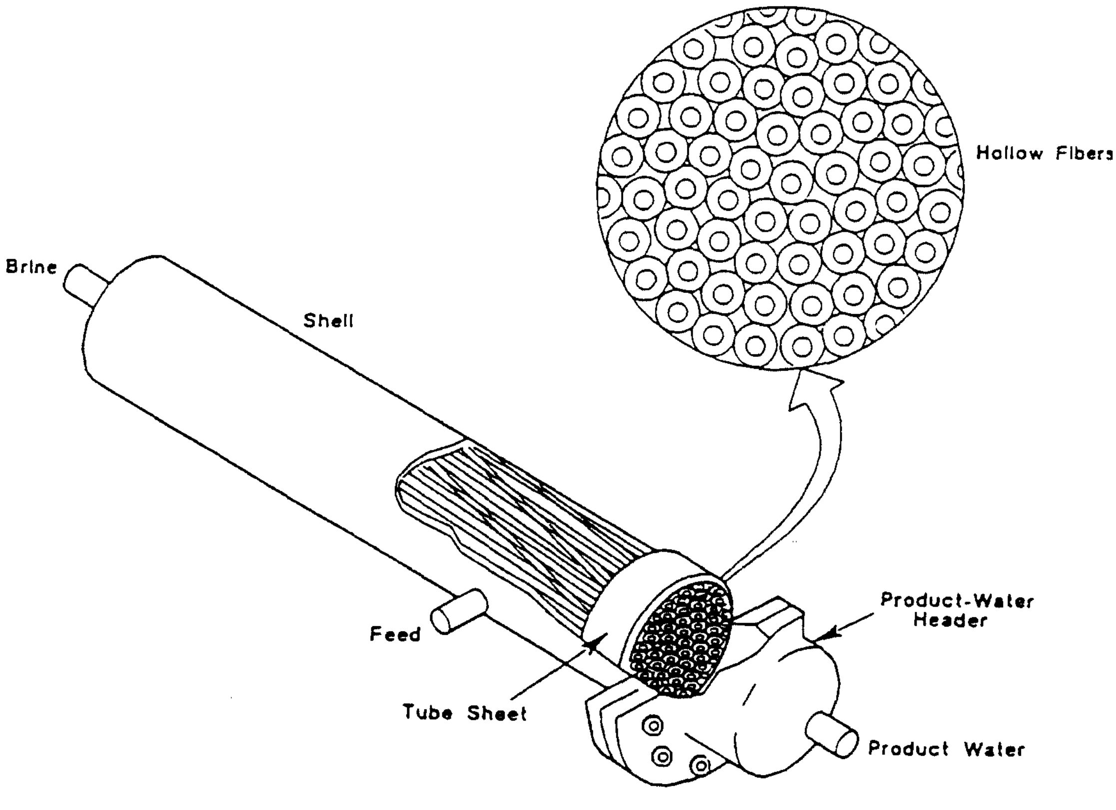
Schematic of a plate-and-frame module.

Tubular membrane



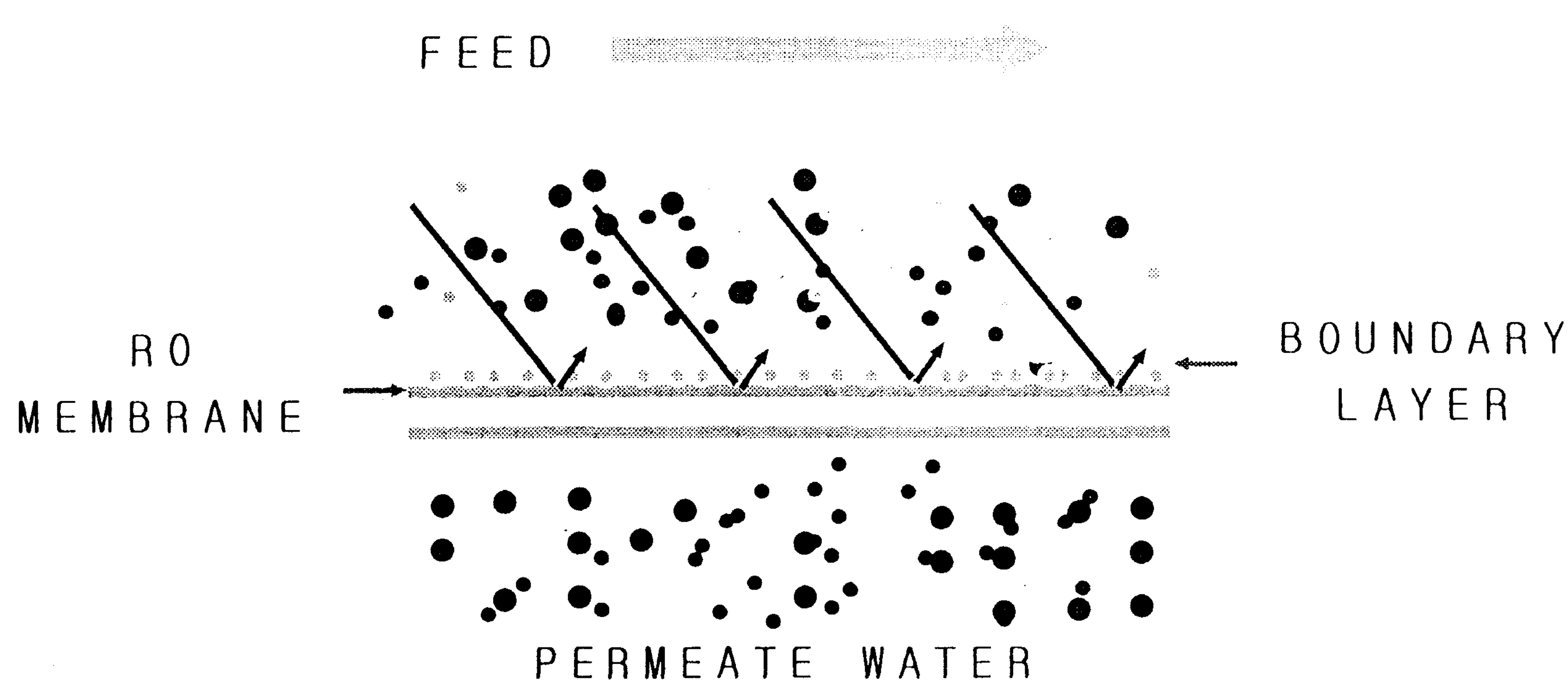


SPIRAL-WOUND TYPE MODULE



Cutaway view of hollow-fiber membrane module.

BOUNDARY LAYER



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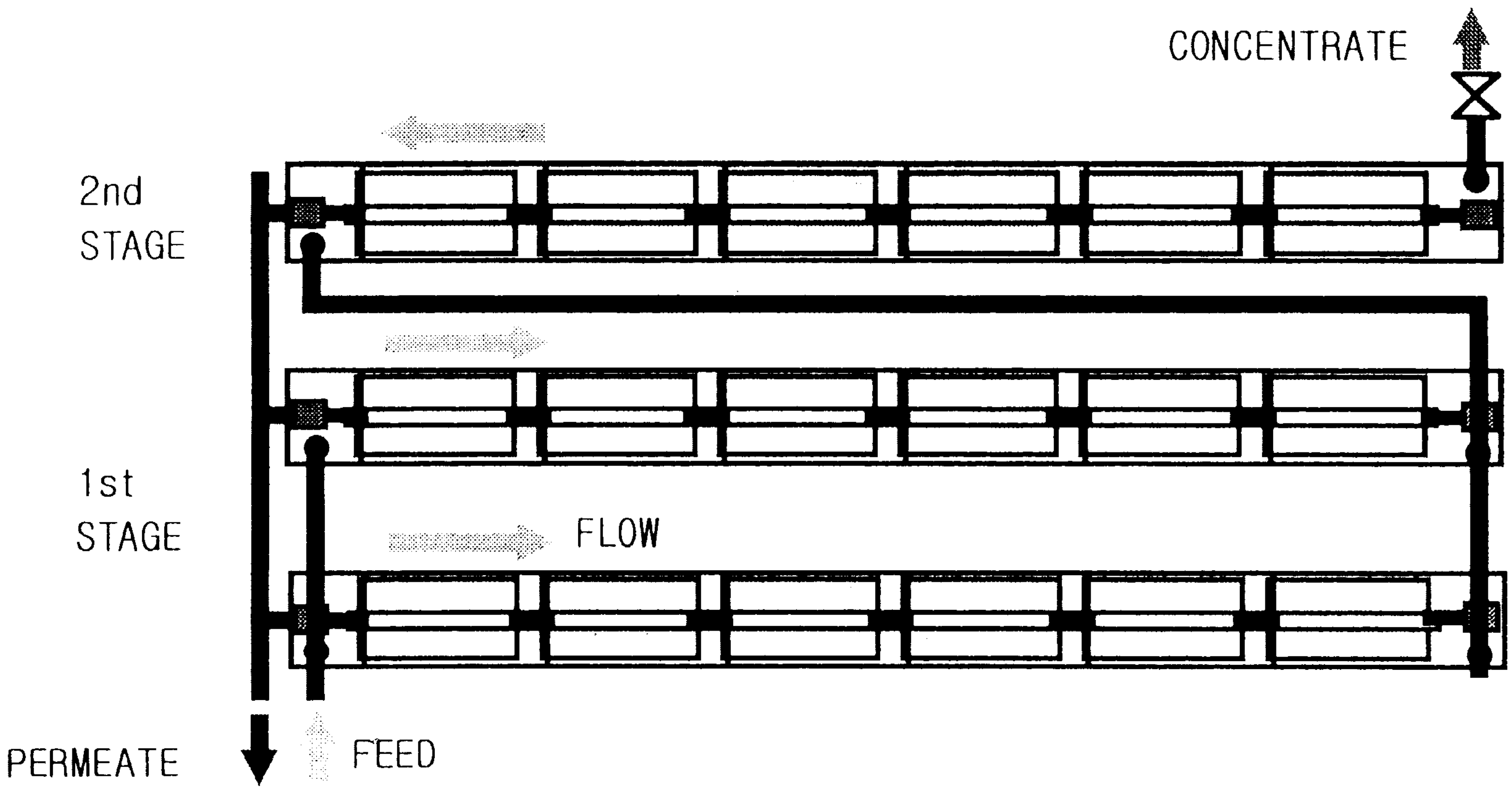
2:1 ARRAY SPIRAL WOUND ELEMENTS



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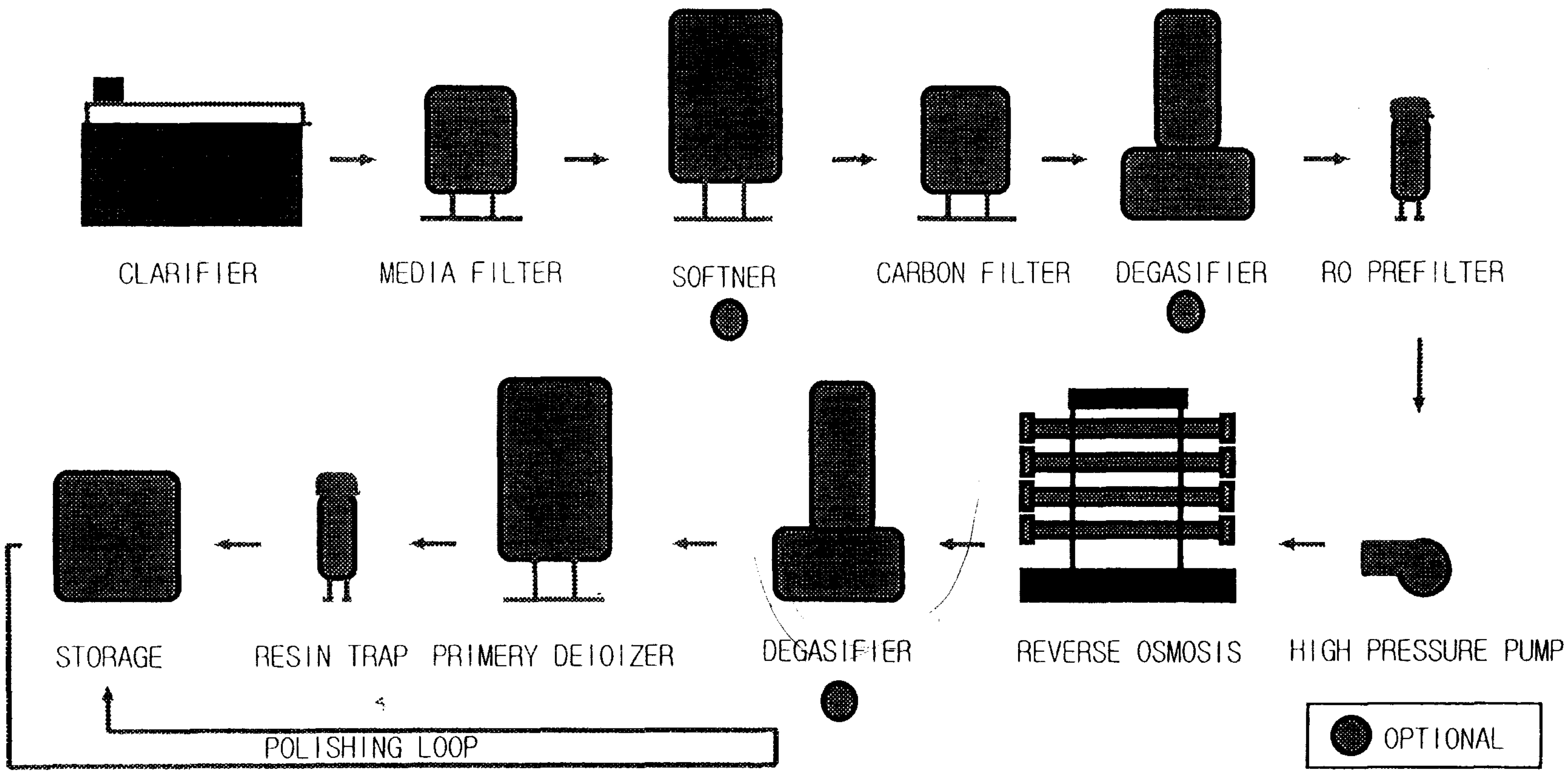
RO PRETREATMENT EQUIPMENT



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TYPICAL WATER ANALYSIS CONCERNS

Major Cations	Major Anions	Other Metals	Other Tests
Calcium (Ca)	Carbonate (CO_3)	Barium (Ba)	SDI
Magnesium (Mg)	Bicarbonate (HCO_3)	Strontium (Sr)	Turbidity
Potassium (K)	Chloride (Cl)	Iron (Fe)	TOC
Sodium (Na)	Nitrate (NO_3)	Aluminum (Al)	Fluoride (F)
	Sulfate (SO_4)	Copper (Cu)	Silica (SiO_2)
		Zinc (Zn)	Carbon Dioxide
			pH
			TDS

* scale inhibitors ; SHMP, phosphate

CONTROL OF FOULING

- CLARIFICATION (CARRY-OVER CAN CAUSE PROBLEMS)
- SAND & MULTIMEDIA FILTRATION
- RO PREFILTERS
- ADDITION OF BIOCIDES
- ADDITION OF DISPERSANTS
- MICROFILTRATION AND ULTRAFILTRATION

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Future Trend in RO Industry

1.High Rejection : 99.5%

2.High Flux : 40~50gfd (225psi)
20~25gfd (150psi)

3.Fouling Resistant Membrane

4.Chlorine Resistant Membrane

5.Temperature Resistant Membrane

6.Organic Resistant Membrane