R/O막을 이용한 먹는물 처리

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Drinking Water Treatment by RO Membrane Processes

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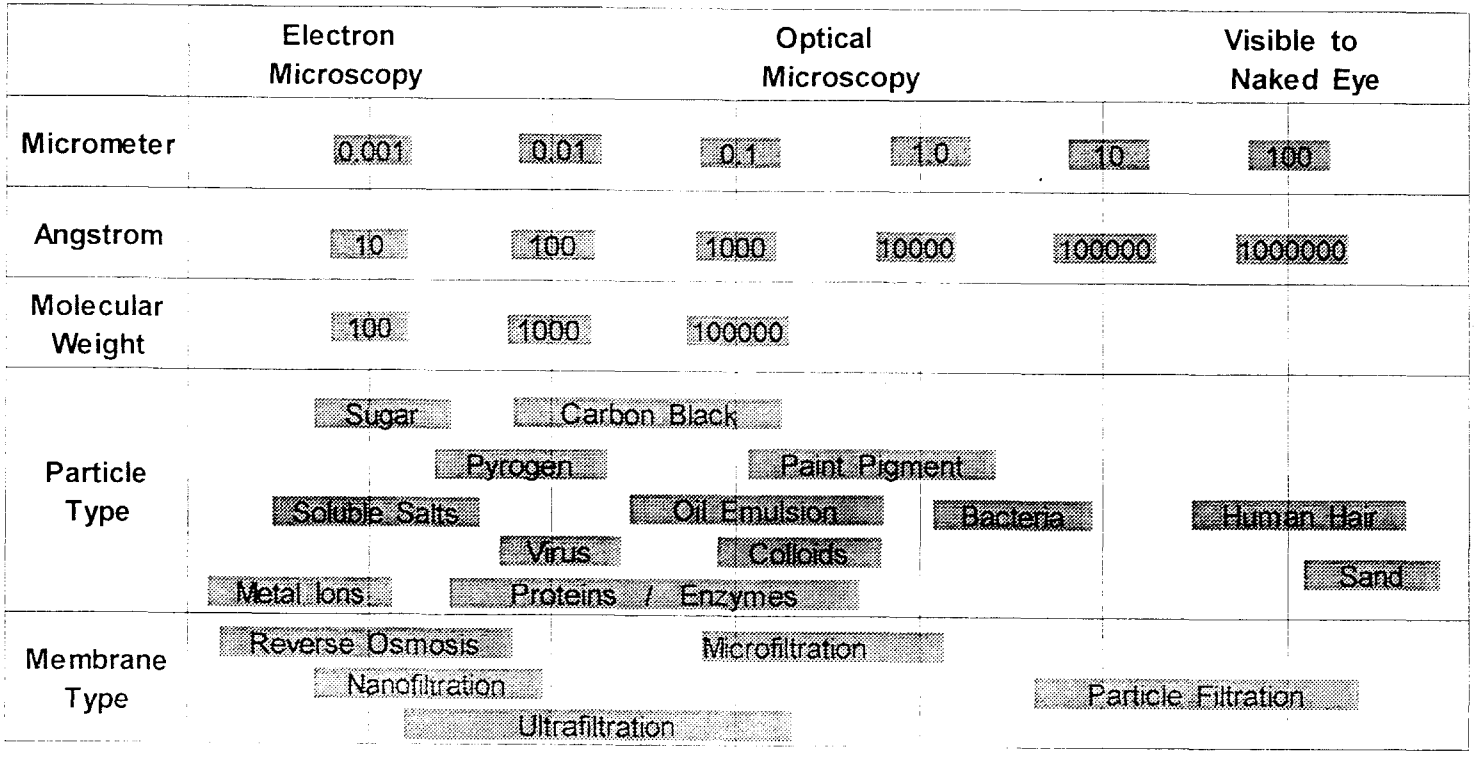
• 서론

산업의 발달과 함께 기존의 상수처리기술로는 제거하기 힘든 질산성 질소, 농약에서 유래한 각종 유기물, 일부 중금속이 지하수 등에 유입될 가능성이 커짐에 따라 이러한 유해물질을 효과적으로 제거하기 위하여 세계적으로 고도 상수처리기술 및 막분리기술이 광범위하게 적용되고 있다.

막분리의 용도로 Microfiltration(MF) membrane, Ultrafiltration(UF) membrane, Reverse Osmosis(R/O) membrane들이 단독 혹은 복합적으로 사용되고 있는데 각 membrane들은 원수(Raw water)에 포함된 불순물의 종류 및 양, 원하는 생성수의 순도에 따라 다양한 Grade중에서 선택하여 사용할 수 있다

본 발표에서는 세계적으로 가장 안전한 물처리방법으로 인정받고 있는 R/O막에 대하여 개발역사, 제조공정 및 설비에 대하여 소개하였다. 그리고 국내에서 최초로 개발된 제일합섬의 "CSM" R/O membrane과 전세계적으로 널리 사용되고 있는 R/O막에 대한 각 Grade 및 물성에 대하여 설명하고, 종류에 따라서 NaCl, $MgSO_4$, 질산성 질소, 6가 크롬의 제거능력실험을 통하여 용도에 맞는 R/O막의 선택기준을 제시하였다. 또한, R/O막으로 먹는물 처리 System을 설계할 수 있는 간단한 Procedure 및 R/O system운전의 가장 큰 문제점인 Fouling의 생성과정 및 제거방법에 대하여 소개하고 미국 및 일본의 R/O막을 이용한 먹는물 처리 System실적에 대하여 언급하였다.

Membrane Selectivity



R/O 막의 개발 및 사업 역사

년도	주요사항	비고
1959	· Reid & Breton : CA film에 의한 탈염가능성 확인	
1962	· Loeb & Sourirajan : Asymmetric CA membrane 발명	
1964	· Francis : CA-TFC 개념을 NTIS에서 발표	
1969	· Riley : CA Bilayer로 이루어진 최초의 복합막 개발	
1972	· J. Cadotte : NS-100 개발 (PEI + TDI)	North Star R&D Institute
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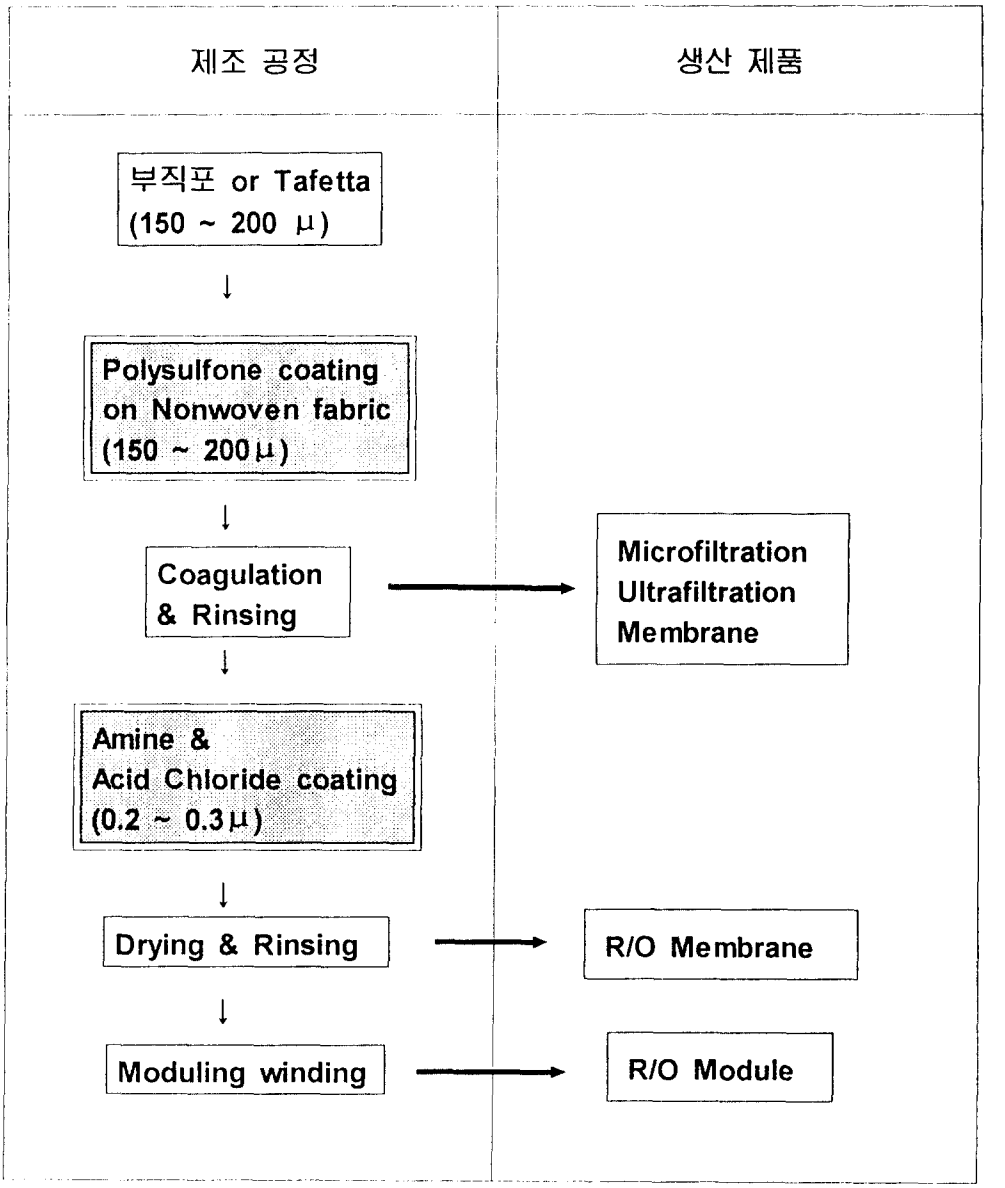
.	.	
1978	· J. Cadotte : "FT-30" 개발	〃
1982	· Filmtec (J. Cadotte) "FT-30" 양산	R : 99.1% FLUX : 25 GFD
1992	· DOW : UOP/Hydranautics와의 특허분쟁서 패소 UOP/Hydranautics/Toray/Desal' → "FT-30" 유사제품 본격 생산	
1995	· Hydranautics : ES-10 생산	R : 99% FLUX : 50 GFD

CA막과 PA막의 비교

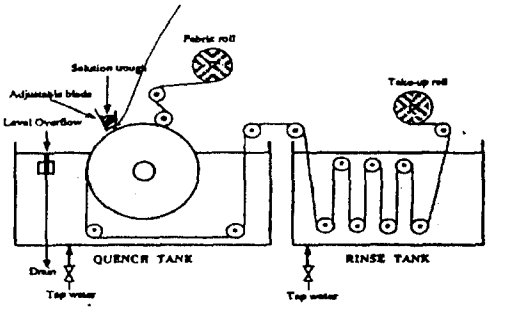
항목		PA	CA	비고
pH Range		2~12	4~6	Acid Addition
Operation Pressure (Kgf/cm^2)		15	30	Energy
Rejection (%)	TDS	99 ↑	98	
	SiO_2	99 ↑	95	
물성 저하		Flux	Rejection	
3년 후	Salt Pssage	30% ↑	100% ↑	
	Rejection	99% → 98.7%	98% → 96%	
OCl^-		제거 (막의 산화)	첨가 (미생물)	
Fouling		More	Less	막의 특성

TFC R/O 막의 제조공정 ("C S M")

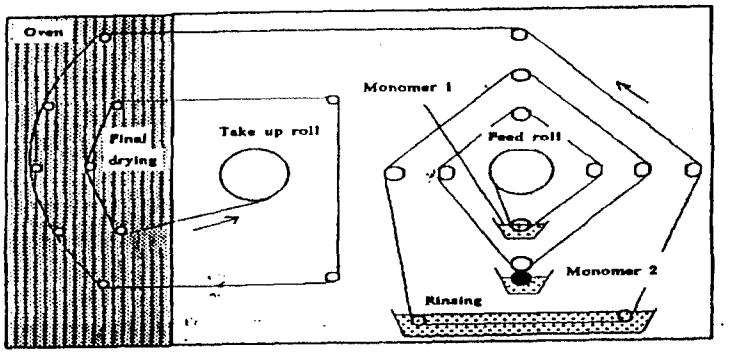


R/O 막의 제조설비 요약도

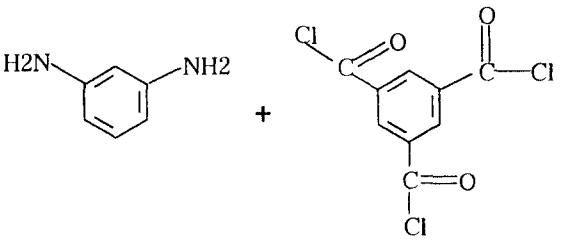
Casting M/C



Thin Film Coater



"C S M" Basic Chemistry & Process Variables



- Properties of porous support membrane
  - · Polymer concentration
  - · Humidity
  - · Surface pore size, distribution and uniformity
  - · Wetting characteristics
  - · Residual surface water and solvent
  - · Substrate tightness

- Amine solution
  - · Solubility in solvent
  - · Concentration
  - · Additive competibility (wetting agent, acid acceptors)
  - · Coating characteristics

- Acid chloride solution
  - · Solubility in solvent
  - · Stability
  - · Reactivity
  - · pH
  - · Concentration

R/O 막의 종류

	상품명	회사명	Rejection (NaCl)	용도
NF	· CSM-NE(30)	제일합섬	· 30~40%	· 한국내 먹는물 처리
	· NF-45	DOW	· 45~50%	· 식품, 폐수처리, 먹는물 처리
	· CSM-NE	제일합섬	· 75~80%	
	· PVDF	Hydranautics		· 〃
	· NF-75	DOW		
T/W	· CSM-T/W	제일합섬	· 90~98%	· 먹는물 처리
	· TW-30	DOW		
B/W	· CSM-B	제일합섬	· 98~99.5%	
	· BW-30	DOW		· 보일러 용수
	· CPA-2	Hydranautics		· 순수 처리용
	· SU-720	Toray		
S/W	· CSM-S	제일합섬	· 99~99.75%	· 해수 담수화
	· SW-30	DOW		· 반도체용 초순수
	· SWC	Hydranautics		
	· SU-820	Toray		

R/O 막에 따른 분리능력

모델명(회사명)	항목	원수농도 (ppm)	생산수 (ppm)	배제율 (%)	비고
CSM-NE(30) (제일합섬)	Nacl	423.0	300.8	28.9	
	$MgSO_4$	497.6	6.4	98.7	
	질산성질소	26.2	21.9	16.4	
	6가 크롬	0.143	0.06	58.0	
PDVF (Hydranautics)	Nacl	423.0	75.9	82.1	
	$MgSO_4$	407.6	11.0	97.8	
	질산성질소	26.2	13.9	47.0	
	6가 크롬	0.143	0.03	79.0	
CSM-B (제일합섬)	Nacl	423.0	12.7	97.0	
	$MgSO_4$	407.6	4.1	99.0	
	질산성질소	30.1	9.8	67.4	
	6가 크롬	0.17	0.01	94.1	

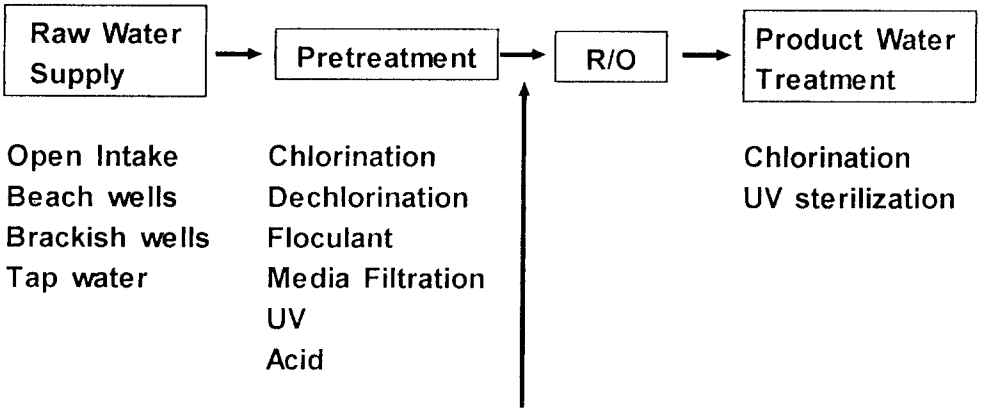
註)

1. 본 실험은 제일합섬 분석실에서 한 실험결과이며 특정회사와 관계없는 일반적인 사항임.

2. 분석조건
   - 온도 : 20 ~ 22 ℃
   - 압력 : 60 psi
   - 회수율 : 33 %

R/O System Design

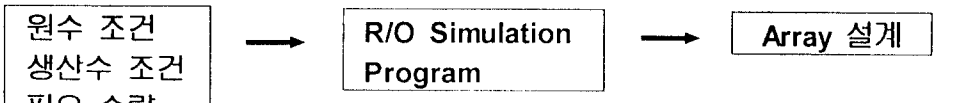
● 기본설비 구성



Required Quality

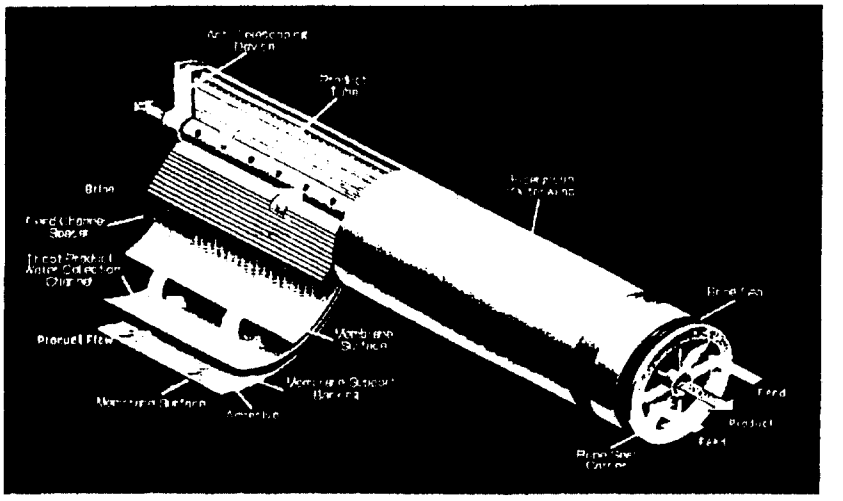
- Temperature : <45℃
- pH range : 2 - 11
- Free chlorine : <0.1ppm
- SDI : <5
- NTU : <1
- Biological Activity : controlled
- LSI : controlled
- Fe, Al, Zn : <0.1ppm

● R/O Array 설계



- Filmtec : "RO System Design"
- Hydranautics : "RODESIGN"
- 제일합섬 : "CSI R/O design"

R/O 막의 Fouling 형성과정



1. Suspended solids are slowly deposited.

2. Micro-organism slowly grow and multiply.

3. Scaling may take place.

4. Oxidizing agents(Chlorine) attack the membrane.

↓ ↓

Increase in Pressure Drop
Loss in Permeate Flow
Increase in Permeate TDS

R/O 막의 Fouling 및 제거

	Foulant	*Salt Passage*	*Permeate Rate*
Membrane Fouling	· Hydrated Oxides (Iron,Nickel,Copper)	Rapid increase (2%)	Rapid increase (20~50%)
	· Cacium Precipitates (Carbonates,Sulfates, and Phosphates)	Significant increase (10~25%)	Slight decrease (10%)
	· Colloids (Alluminum Silicates)	Gradual marked increase (2%)	Gradual marked decrease (50%)
	· Mixed Colloids (Iron,Organic,Silicate)	Rapid increase (2~40%)	Gradual marked decrease (50%)
	· Bacterial Slime	Marked increase (2%)	Marked decrease (50%)
	Deposit	*Removal*	*Method*
Foulant Removal	Phosphates	Easy	Acidification
	Carbonates	Easy	Acidification
	Sulfates	Difficult	Special procedures based on either controll -ed acidification or chelation
	Silicates	Very difficult	Based on Hydroflouric acid
	Hydroxides	Difficult	Special cleaners
	Sulfides	Difficult	Special cleaners

Big R/O plants in Japan for drinking water (as of Mar. 1995)

Standard year	Installed at	Belonging to	Name of Process	Capacity m^3/day	Raw water
1979	Tsuwachijima	Ehime	RO	75	Seawater
1982	Tsushima	Nagasaki	〃	28	Saltwater
1984	Kitadaitojima	Okinawa	〃	240	Seawater
1985	Aijima	Fukuoka	〃	50	〃
1986	Tonakijima	Okinawa	〃	240	〃
1986	Awakunijima	〃	〃	400	Saltwater
1989	Haterumajima	〃	〃	240	〃
1989	Udo city	Kumamoto	〃	3,000	〃
1990	Haterumajima	Okinawa	〃	70	Seawater
1991	Iojima	Tokyo	〃	100	〃
1991	Syoroshima	Fukuoka	〃	20	〃
1992	Saseho city	Kagoshima	〃	1,000	〃
1992	Ishigakijima	Okinawa	〃	600	Saltwater
1992	Ina-machi	Ibaragi	〃	150	〃
1993	Iojima	Tokyo	〃	200	Seawater
1993	Rokujima	Nagasaki	〃	30	〃
1994	Doshima	Nagasaki	〃	200	〃
1994	Kasuga-cho	Hyogo	〃	2,700	Saltwater
1994	Takamatsu city	Kagawa	〃	200	Seawater
1996	Chatan-cho	Okinawa	〃	25,000	〃

NOTES) 1) Surveyed by Japan Water Re-use Promotion Center
2) Only plants which are above 10m^3/day are shown.

Big R/O drinking water system in U.S.A

Plant Name	System -up year	Mem- brane Type	Membrane Manu- facturer	Annual Product mil gal
Alta Municipal	1976	HF	DOW	78.5
Palm beach of Commerce	1988	SW	Filmtec	
St. Lucie west service district	1988	〃	Hydranautics	70
Laurence Water Supply	1990	〃	Filmtec	80
Indian River Country	1991	〃	Hydranautics	1095
City of Dunedin	1992	〃	Hydranautics	1582
Reverse Osmosis desalting	1972			16.4
Marineland Inc.	1972	SW	Filmtec	9.125
Kingstone Shore	1974	HF	Dupont	
Rotunda West	1975	SW		310
Greater Pine Island	1976	〃	Osmonics	2.724
Cape Coral RO plant	1976		UOP,	
		HF	Hydranautics	45.5
Southbay Utilities	1976		Toyobo	25
VA Medical Center	1976	HF		43
Indian River Platation	1977	〃	Dupont	38
Ocracoke Sanitary District	1977		Dupont	
Myakka River State Park	1977	SW		1800
Orange County Water District	1977		Hydranautics	
Kings Gate Club	1978	SW	DOW	
Charlotte Habor	1978	SW	Filmtec	
Island Water	1980	HF	Filmtec	10
Haclendas Del Notre	1981	SW	Dupont	350
Englewood Water District	1981	HF	Hydranautics	1100
City of Sarasots	1982	HF	Dupont	900
Indian River County	1983	HF	Dupont	
Windware Isle MHP	1983		Dupont	15

Plant Name	System -up year	Mem- brane Type	Membrane Manu- facturer	Annual Product mil gal
Tippecanoe	1984	HF	Toyobo	15
City of Nevada	1984		DOW	
Aquarine Service Management System	1984		DOW	5.4
Sarasota County Plantation	1984	SW	UOP	
Bocila Utilities	1985	〃	UOP	
North Beach	1985	〃	UOP	110
Seaside Service System	1986	〃		
Gaviota Chevron	1987	〃	Hydranautics	53
City of Sully	1988	〃	Filmtec	
Olds Water Supply	1988	〃		NA
Holiday Pines Service Corp.	1989	〃	UOP	52
Dare County	1989	〃	UOP	571
Gasparilla Island Water	1990	〃	UOP	1415
Jupiter	〃	HF	Hydranautics	750
Sarasota County Plantation	〃	SW	DOW	
Acme Improvement District	〃	〃	UOP	
Bay Lakes Estates	〃	〃	Toyobo	10.95
Venice	〃	〃	UOP	768
Arilgton Desalter	〃	〃	Hydranautics	1800
City of Tustin	〃	〃	UOP	179.4
North Beach	1991	〃	UOP	1.095
Ewa Beach	〃	〃	UOP	
Mount Pleasant Waterworks	〃	〃	Hydranautics	438
Mount Pleasant Waterworks	〃	〃	Hydranautics	675
Sorrento	〃	〃	Hydranautics	

NA : Not available

Cited from Journal AWWA, Dec. 1994