薄膜相關新技術用於電導度控制技術及處理成本分析

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4. 成本分析
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1. 前言

薄膜工業發展歷史

薄膜程序	年代	先驅者
Microfiltration	1936	Sartorius Millipore
Electrodialysis	1960	Ionics INC
Reverse osmosis	1965	Havens Industry,FilmTech/DOW
Dialysis	1965	Enka(AKZO)
Ultra-filtration	1970	Amicon Corp.
Controlled release	1975	Alza Corp.
Gas separation	1980	Permea(Dow)
Pervaporation	1990	GFT Gmbh,

1. 前言

薄膜種類

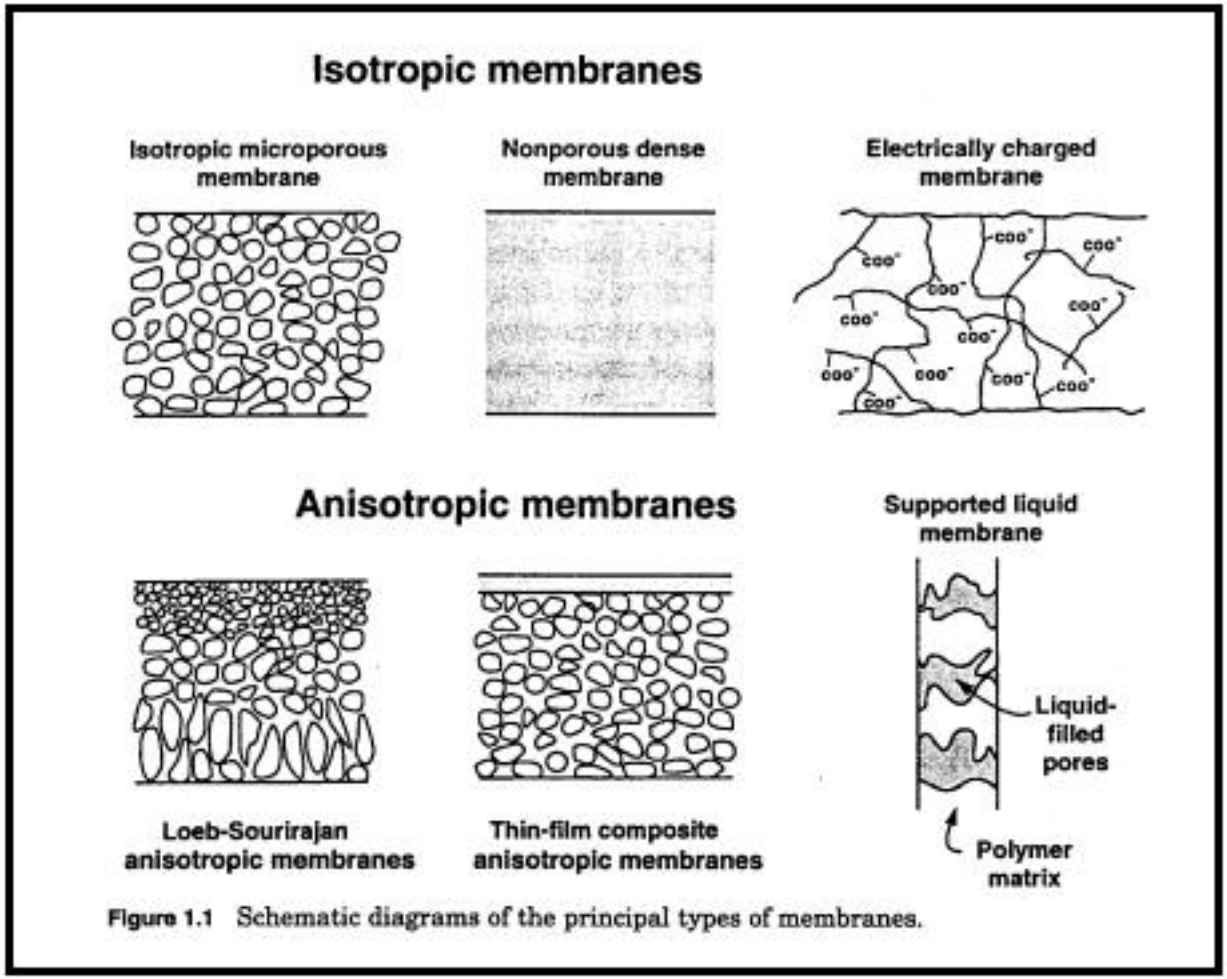
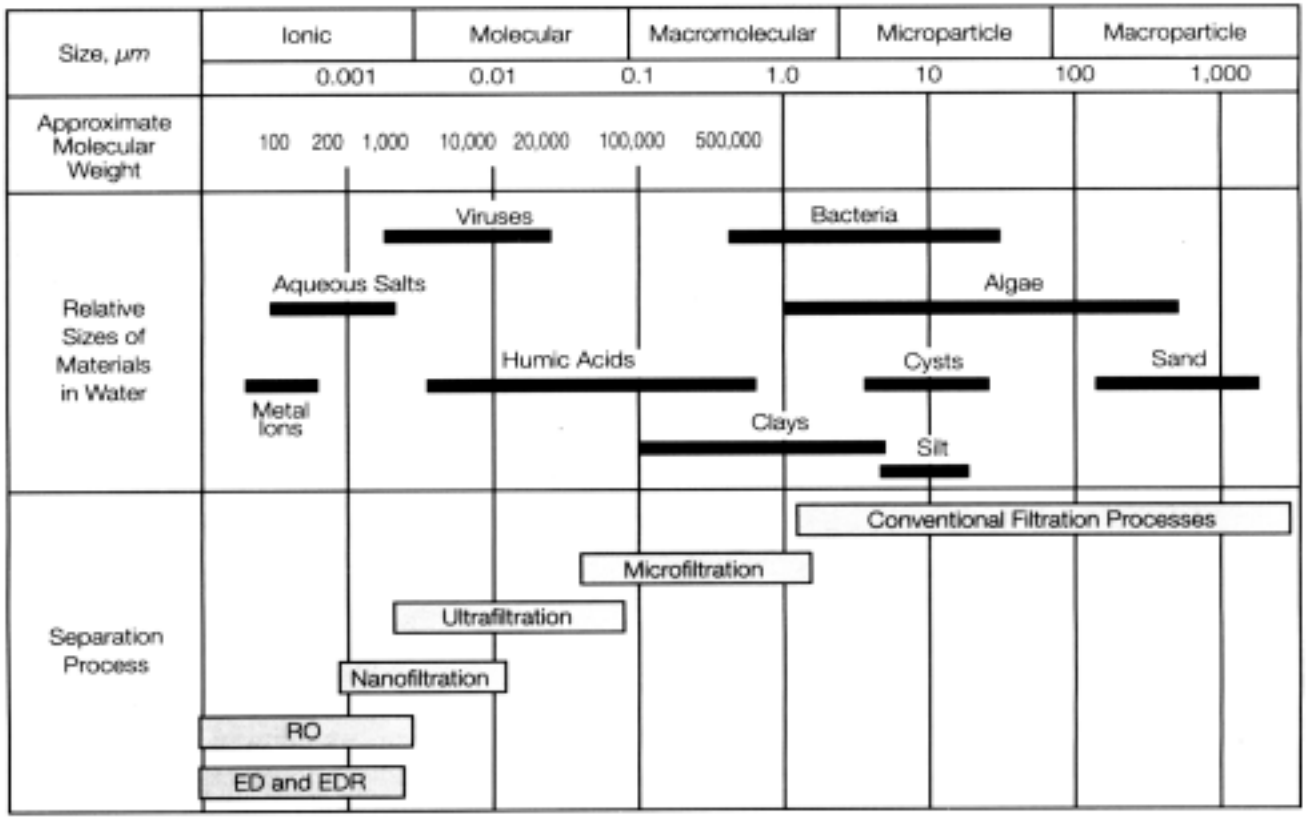


Figure 1.1 Schematic diagrams of the principal types of membranes.

1. 前言

薄膜程序應用



Metal Ions
- Antimony
- Arsenic
- Nitrate
- Nitrite
- Cyanide

Aqueous Salts
- Sodium Salts
- Sulfate Salts
- Manganese Salts
- Aluminum Salts

Viruses
- Infectious Hepatitis

Humic Acids
- Trihalomethane Precursors

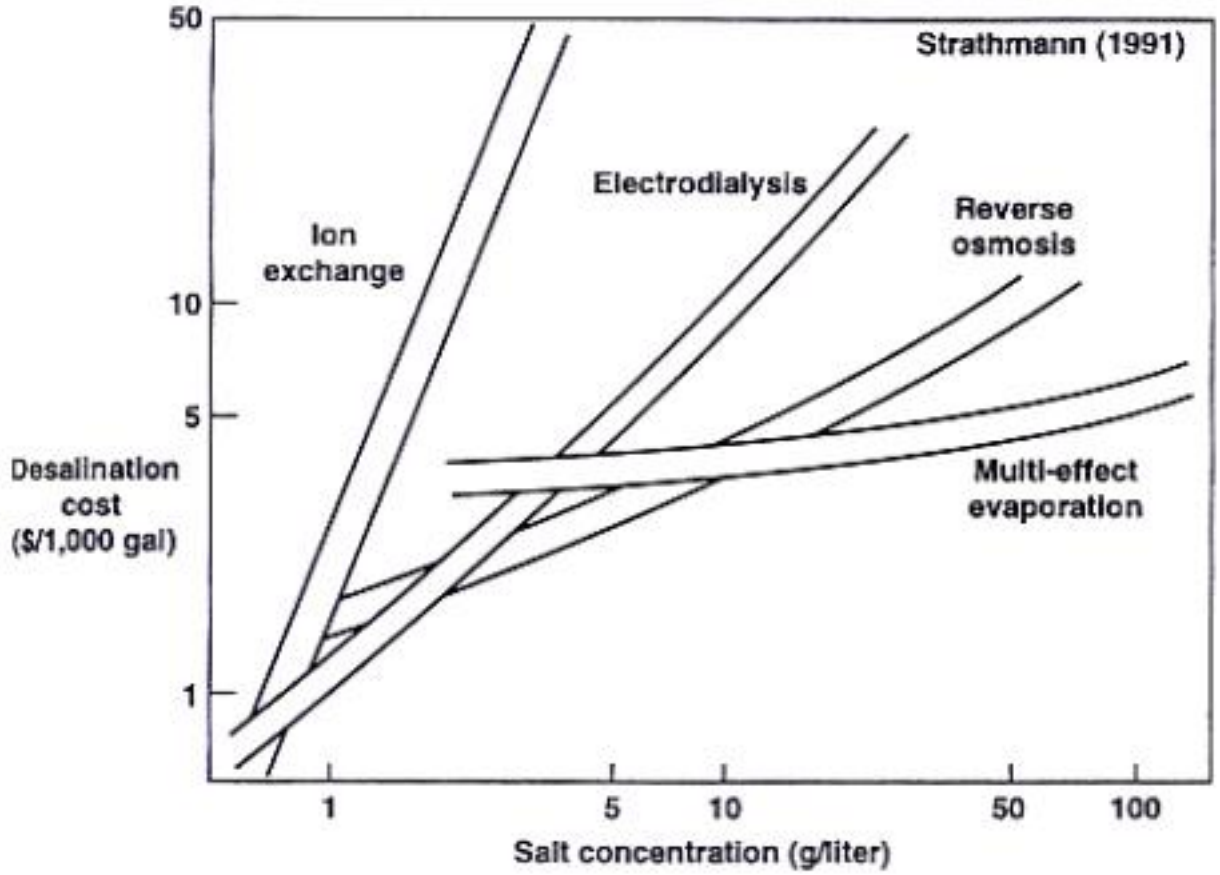
Bacteria
- *Salmonella*
- *Shigella*
- *Vibrio cholerae*

Cysts
- Protozoa
- *Giardia*
- *Cryptosporidium*

(AWWA,1995)

1. 前言

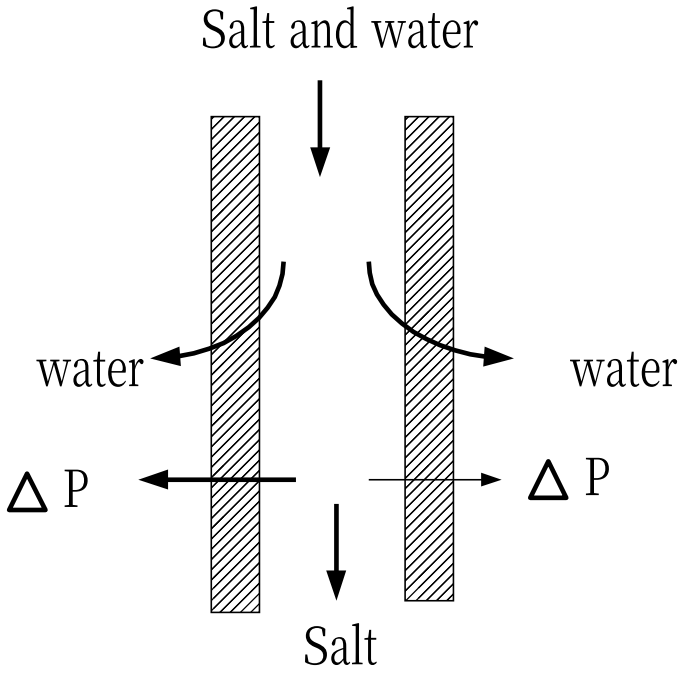
各種商業化脫鹽技術比較



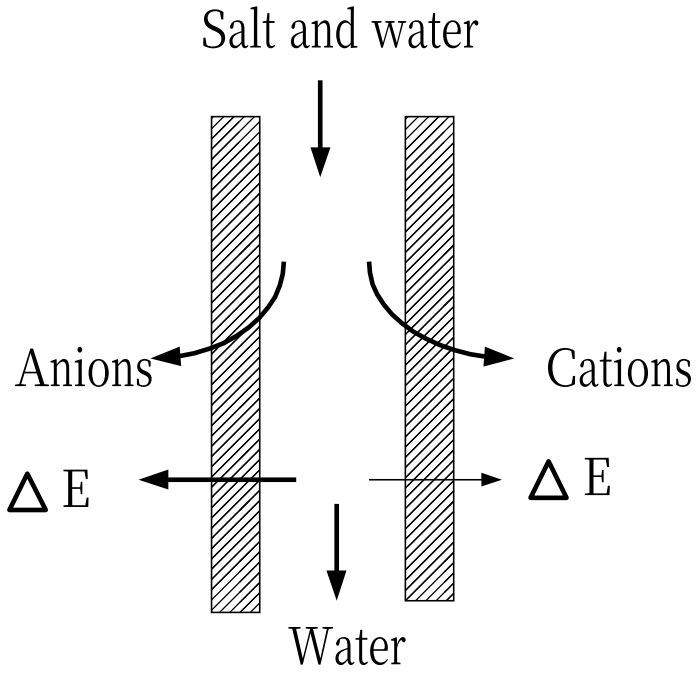
(Richard W. Baker,2000)

1. 前言

逆滲透與電透析法脫鹽



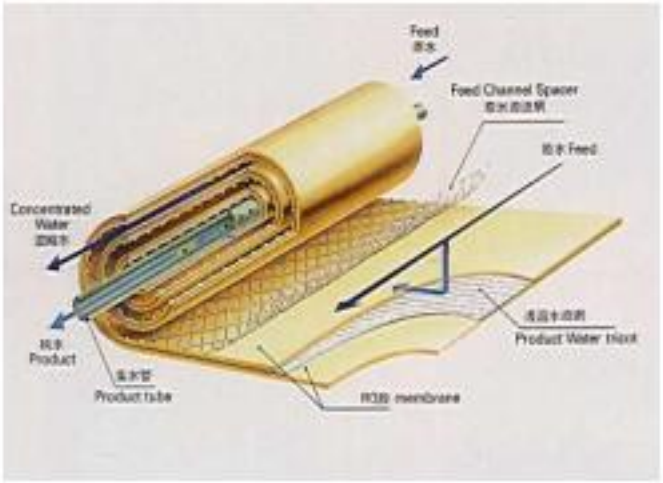
Reverse osmosis

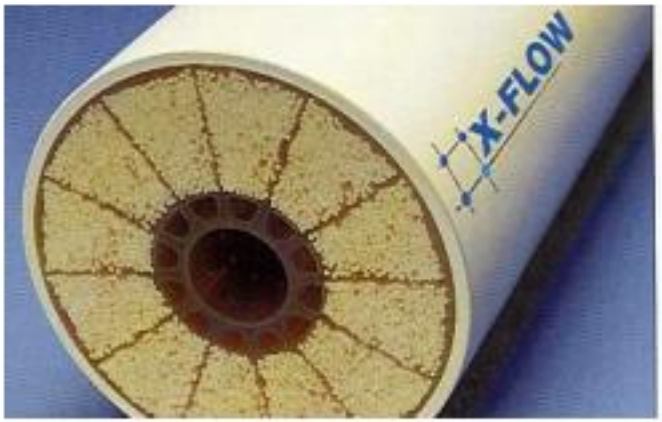


Electrodialysis

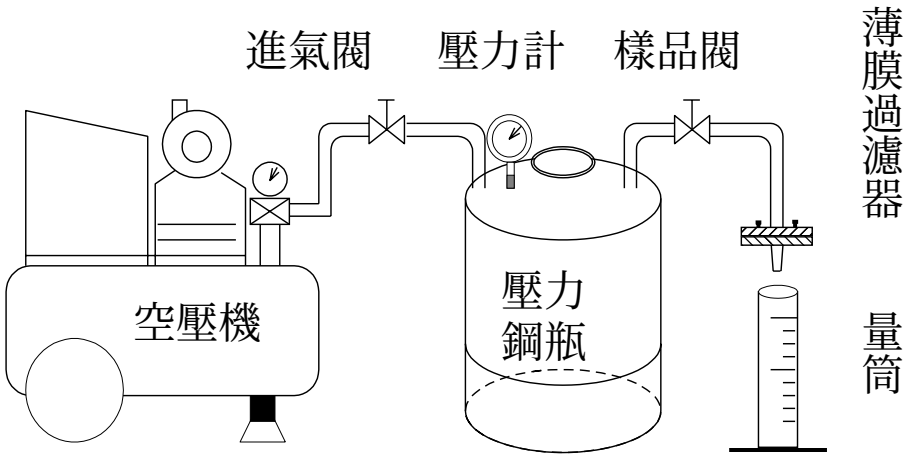
2. RO/NF

薄膜模組


Feed
Feed Channel Spacer
Concentrated Water
Product
Product Water Hoxit
RO membrane


X-FLOW

SDI測定方法



$$SDI_T = \frac{(1 - t_i / t_f) \times 100}{T}$$

$$MSDI = 1/t_E \times 100$$

t_i : 實驗開始，500 ml原液流經濾紙所需之時間
t_f : 實驗經過T分鐘後，500 ml原液流經濾紙所需之時間
t_E :出水流量形成緩慢滴流之時間
max SDI_{15}=6.67
max SDI_5 = 20

2. RO/NF

防止薄膜形成生物膜的藥劑

藥劑種類	藥劑名稱	薄膜種類	濃度
Biocides oxidizing	Chlorine	CA,PS	0.1-1.0 mg/L
	Monochloramine	All	0.5-5.0 mg/L
	Peracetic	CA,PS	0.1-1.0 mg/L
	Hydrogen peroxide	All	0.1-1.0 mg/L
Biocides Nonoxidizing	Formaldehyde	All	0.5-5.0 %
	Glutaraldehyde	All	0.5-5.0 %
	Bisulfite	All	1.0-100 mg/L
	Quaternary amines	CA,PS	0.01-1.0 %
	Benzoate	All	0.1-1.0 %
	EDTA	All	0.01-1.0 %

2. RO/NF

清洗薄膜的生物膜的藥劑

藥劑種類	藥劑名稱	薄膜種類	濃度
Detergent	SDS SDBS Triton series Quaternary amines	CA,PA,PS CA,PA,PS CA,PS,PE CA,PS,PE	0.01-2.0% 0.01-2.0%0.01-2.0% 0.01-2.0%
Chaotropic agents	Urea Guanidium HCl	CA CA	6-8 molar 1-2 molar
Enzyme(s)	Proteases Esterases Lipases Polysaccharidase	ALL	10-100mg/L 10-100mg/L 10-100mg/L 10-100mg/L
Chelating agents	Citrate EDTA	ALL	0.1-1.0% 0.1-1.0%

RO分離離子的能力

Cation

$Fe^{3+} > Ni^{2+}, Cu^{2+} > Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$

Anion

$PO_4^{3-} > SO_4^{2-} > HCO_3^{-} > Br^{-} > Cl^{-} > NO_3^{-}, F^{-}$

2. RO/NF

各種商業化薄膜的脫鹽率

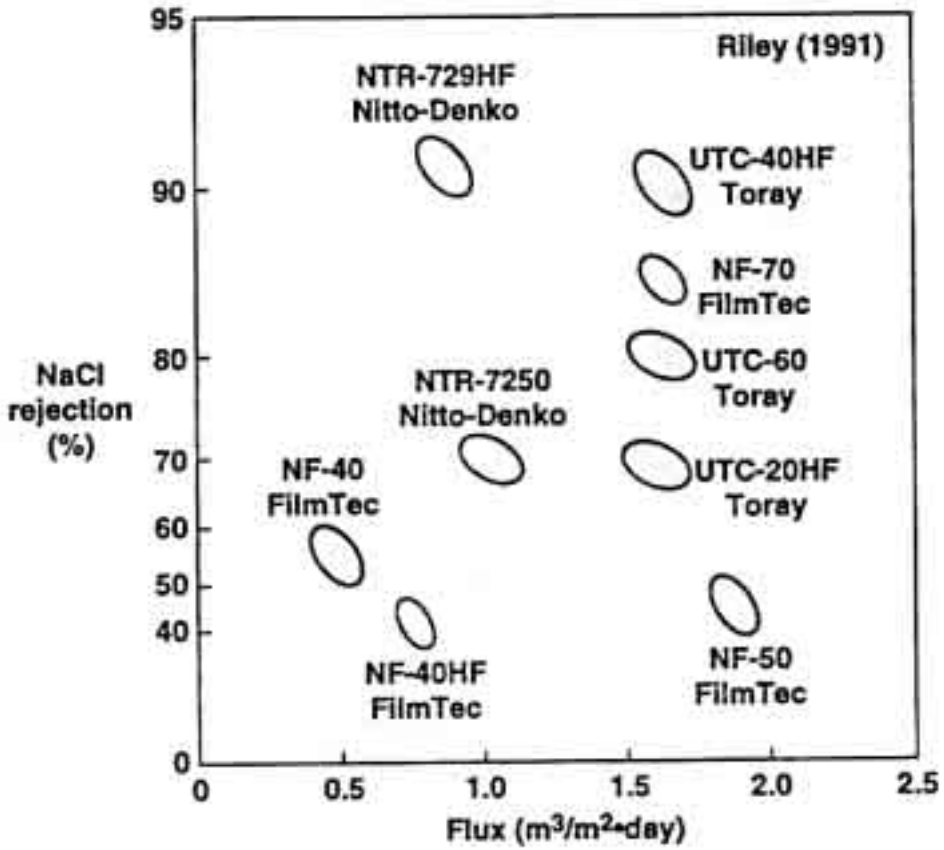
TABLE 5.2 **Properties of Current Good-Quality Commercial Membranes**

Parameter	Seawater membrane (SW-30)	Brackish water membrane (CA)	Nanofiltration membrane (NTR-7250)
Pressure (lb/in^2)	800–1000	300–500	100–150
Solution concentration (%)	1–5	0.2–0.5	0.05
Rejection (%)			
$NaCl_2$	99.5	97	60
$MgCl_2$	99.9	99	89
$MgSO_4$	99.9	99.9	99
Na_2SO_4	99.8	99.1	99
$NaNO_2$	90	90	45
Ethylene glycol	70	—	—
Glycerol	96	—	—
Ethanol	—	20	20
Sucrose	100	99.9	99.0

(Richard W. Baker,2000)

2. RO/NF

各種商業化低壓薄膜的脫鹽率



操作條件:
500 mg/L NaCl
7.5 kg/cm2

(Richard W. Baker,2000)

電透析電透析原理

電透析(electrodialysis，ED)

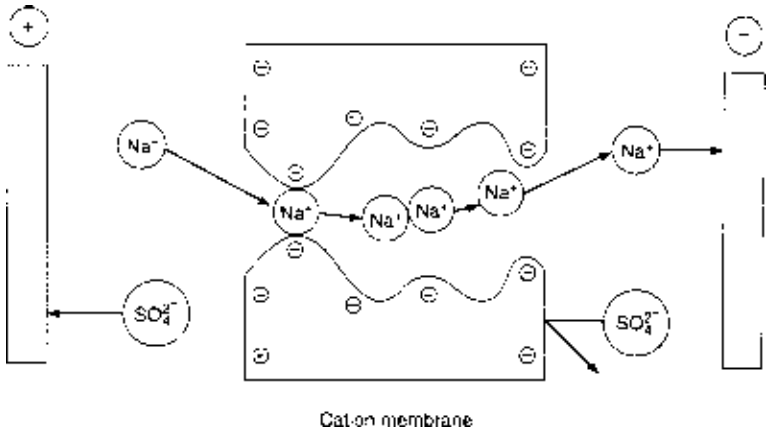
電透析處理技術是利用不同特性的薄膜對水中的離子作分離選擇，水中離子的移動則是靠正負直流電來當吸引的驅動力

倒極式電透析(electrodialysis reversal，EDR)

倒極式電透析是將電透析處理技術作進一步修正，乃利用直流電正負極和內部導流的切換來延長薄膜使用壽命

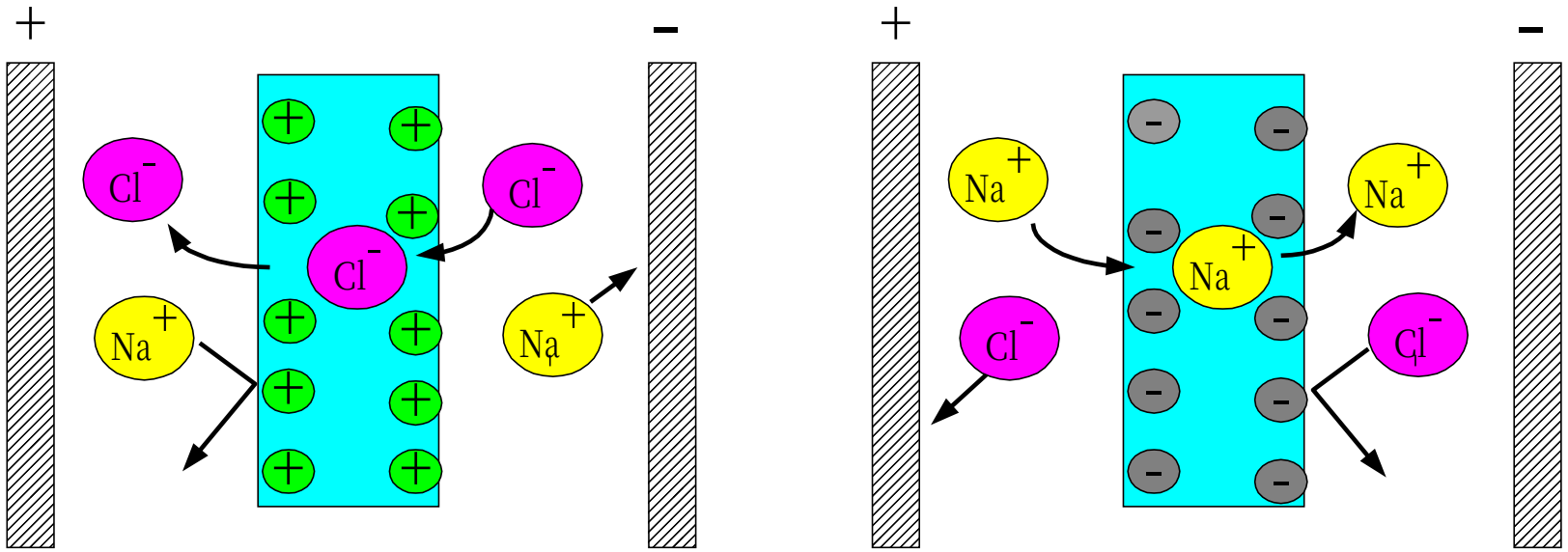
電透析原理

利用陽離子只能穿透陽離子交換膜，而陰離子只穿透陰離子交換膜的特性，在外加直流電場的作用下，水中的陰離子移向陽極、陽離子移向陰極，最後得到淡水及濃水，達到淡化除鹽的目的



Ionic permselectivity of ion-exchange membranes

離子交換膜特性


+
-
Cl-
Cl-
Cl-
Na+
Na+
Anion exchange membrane
+
-
Na+
Na+
Na+
Cl-
Cl-
Cation exchange membrane

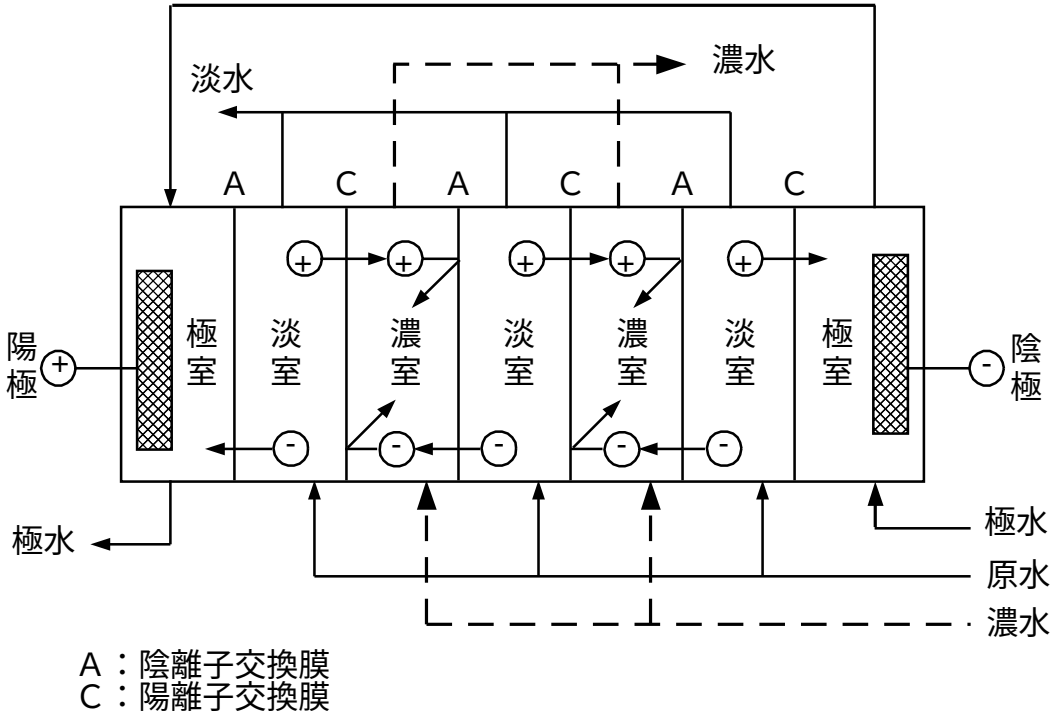
離子交換膜的分類

異相膜：直接用磨細的離子交換樹脂，通過黏合劑混合加工成型的膜。因含有離子交換官能基的部份與形成膜狀結構部份具有不同化學組成，故稱異相膜。

均相膜：是不含黏合劑的離子交換膜，通常是高分子基膜直接接上官能基而得的離子交換膜，或用含官能基的高分子樹脂溶液直接製得的膜。

半均相膜：將離子交換樹脂和黏合劑同溶於溶劑中再成膜。

電透析法脫鹽原理



電透析脫鹽示意圖

多層陰離子交換膜與陽離子交換膜交替排列於兩電極之間形成許多獨立之槽室，運用通壓電極產生之電場將溶液中陰離子及陽離子向正極及負極移動，而得到一股淡水及一股濃水

商業化離子交換膜

Membrane	Type	Structure properties	IEC, meq/g	Backing	Thickness, mm	Gel water, %	Area resistance 0.5 N NaCl, 25°C, Ω·cm²	Permselectivity 1.0/0.5 N KCl, %
Asahi Chemical Industry Company Ltd., Chiyoda-ku, Tokyo, Japan								
K 101	Cation	Styrene/DVB	1.4	Yes	0.24	24	2.1	91
A 111	Anion	Styrene/DVB	1.2	Yes	0.21	31	2–3	45
Asahi Glass Company Ltd., Chiyoda-ku, Tokyo, Japan								
CMV	Cation	Styrene	2.4	PVC	0.15	25	2.9	95
AMV	Anion	Butadiene	1.9	PVC	0.14	19	2–4.5	92
ASV	Anion	Univalent	2.1		0.15	24	2.1	91
DMV	Cation	Dialysis			0.15		—	—
Flemion®	Cation	Perfluorinated						
Ionac Chemical Company, Sybron Corporation, Birmingham, NJ 08011								
MC 3470	Cation		1.5	Tergal	0.6	35	6–10	68
MA 3475	Anion		1.4	Tergal	0.6	31	5–13	70
MC 3142	Cation		1.1		0.8		5–10	—
MA 3148	Anion		0.8	Tergal	0.8	18	12–70	85
Ionics Inc., Watertown, MA 02172								
61AZL386	Cation		2.3	Modacrylic	0.5	46	~6	—
61AZL389	Cation		2.6	Modacrylic	1.2	48	—	—
61CZL386	Cation		2.7	Modacrylic	0.6	40	~9	—
103QZL386	Anion		2.1	Modacrylic	0.63	36	~6	—
103PZL386	Anion		1.6	Modacrylic	1.4	43	~21	—
204PZL386	Anion		1.9	Modacrylic	0.57	46	~8	—
204SXZL386	Anion		2.2	Modacrylic	0.5	46	~7	—
204U386	Anion		2.8	Modacrylic	0.57	36	~4	—

商業化離子交換膜

Du Pont Company, Wilmington, DE 19898								
N 117	Cation	Perfluorinated	0.9	No	0.2	16	1.5	—
N 901	Cation	Perfluorinated	1.1	PTFE	0.4	5	3.8	96
Pall RAI, Inc., Hauppauge, NY 11788								
R-5010-L	Cation	LDPE	1.5	PE	0.24	40	2–4	85
R-5010-H	Cation	LDPE	0.9	PE	0.24	20	8–12	95
R-5030-L	Anion	LDPE	1.0	PE	0.24	30	4–7	83
R-5030-H	Anion	LDPE	0.8	PE	0.24	20	11–16	87
R-1010	Cation	Perfluorinated	1.2	No	0.1	20	0.2–0.4	86
R-1030	Anion	Perfluorinated	1.0	No	0.1	10	0.7–1.5	81
Rhone-Poulenc Chemie GmbH, Frankfurt, Germany								
CRP	Cation		2.6	Tergal	0.6	40	6.3	65
ARP	Anion		1.8	Tergal	0.5	34	6.9	79
Tokuyama Soda Company Ltd., Nishi-Shimbashi, Minato-ku, Tokyo 105, Japan								
CL-25T	Cation		2.0	PVC	0.18	31	2.9	81
ACH-45T	Anion		1.4	PVC	0.15	24	2.4	90
ACM	Anion	Low H^+ transport	1.5	PVC	0.12	15	4–5	—
AMH	Anion	Chemical resistant	1.4	—	0.27	19	11–13	—
CMS	Cation	Univalent	>2.0	PVC	0.15	38	1.5–2.5	—
ACS	Anion	Univalent	>1.4	PVC	0.18	25	2–2.5	—
AFN	Anion	Antifouling	<3.5	PVC	0.15	45	0.4–1.5	—
AFX	Anion	Dialysis	1.5	PVC	0.14	25	1–1.5	—
Neosepta®-F		Perfluorinated						

Source: Strathmann, 1992.

3. 電透析

電透析膜比較

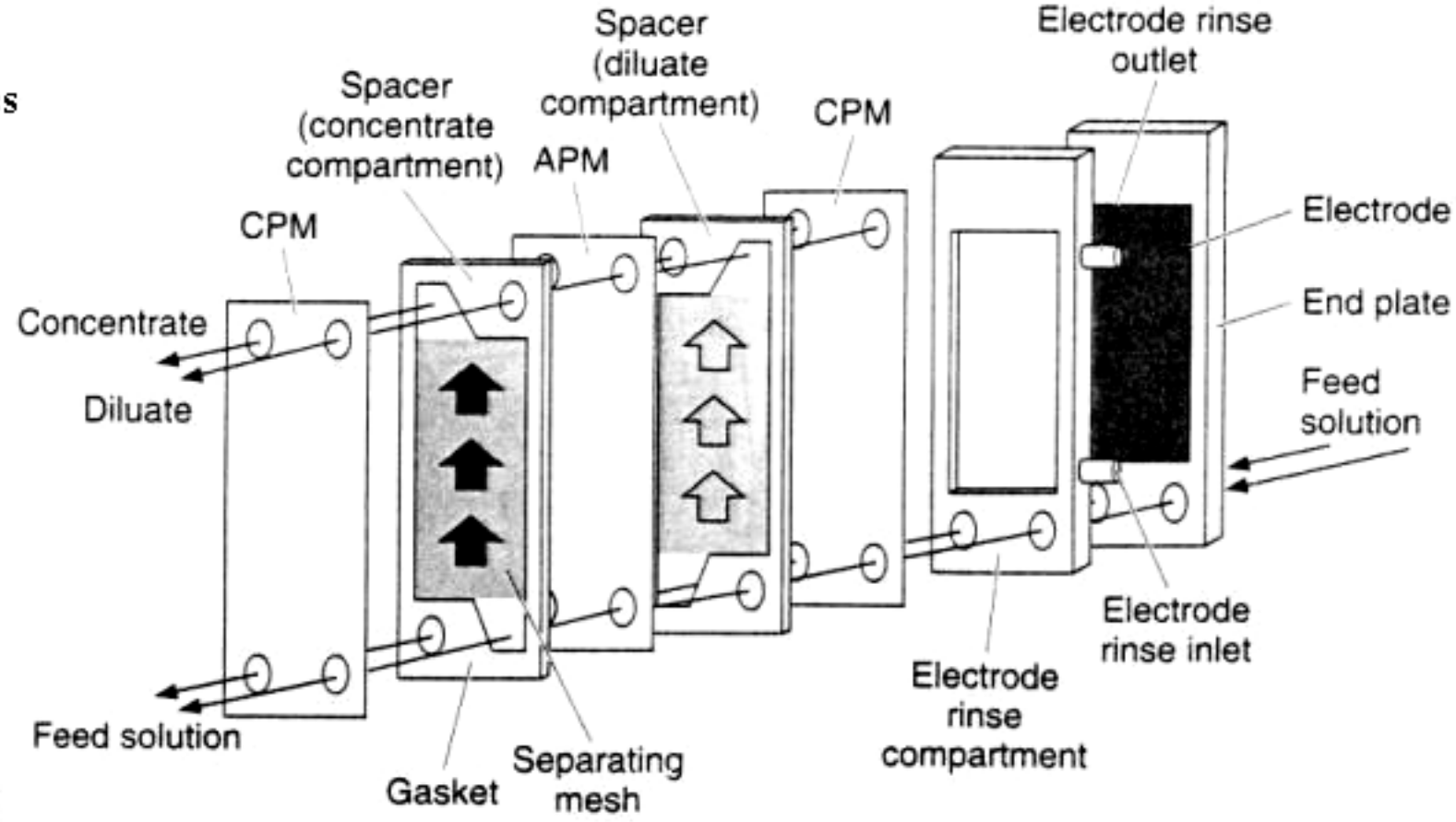
測試條件 / 測試溶液	大陸膜				日本膜			
	脫鹽率* (%)	電流效率 (%)	膜間電壓(V)	操作電流(A)	脫鹽率* (%)	電流效率 (%)	膜間電壓(V)	操作電流(A)
1,000 mg/L NaCl	91.6	76.6	9.4	0.15	92.6	77.7	10.8	0.15
1,000 mg/L $MgSO_4$	85.8	73.4	8.0	0.07	79.1	68.6	8.4	0.07
1,000 mg/L $Al_2(SO_4)_3$	50.7 #	9.4	8.0	0.10	84.7	13.6	9.6	0.16

* 脫鹽率以導電度為指標

\# 大陸膜處理$Al_2(SO_4)_3$溶液之脫鹽率以最低之導電度為計算基準

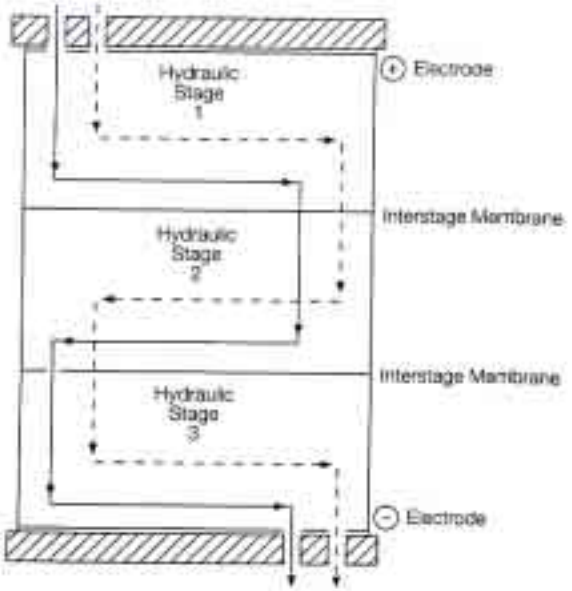
電透析設備

- Membrane stacks
- Electrodes and electrode compartments
- Spacers
- Membranes



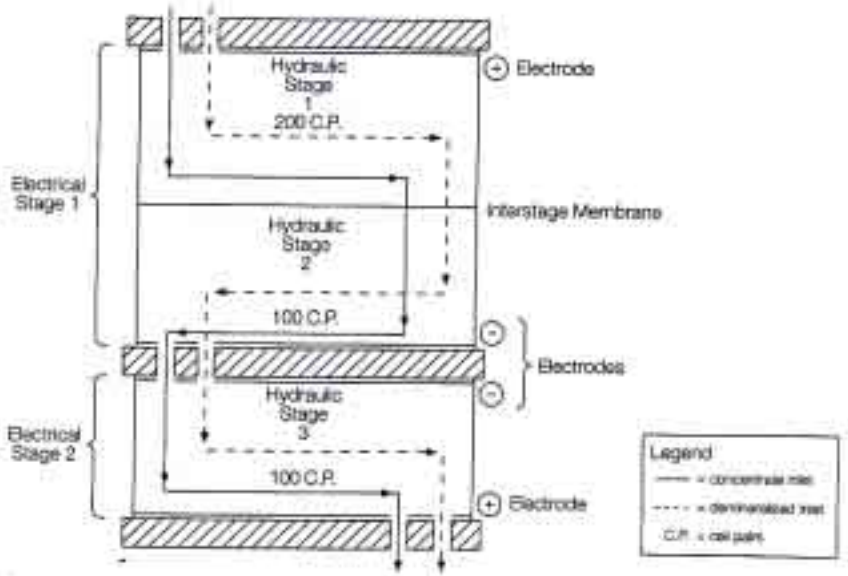
Source: PCA-G

電透析設備



Source: Ionics Inc.

Hydraulic staging within a single membrane stack



Source: Ionics Inc.

Membrane stack with two electrical stages and three hydraulic stages

3. 電透析

倒極式電透析模型設備

電透析操作影響因子

(i) 極限電流密度

(ii)極水導電度對脫鹽率的影響

(iii)原水導電度對脫鹽率的影響

(iv)原水流量對脫鹽率的影響

倒極式電透析

1. 膠質結垢:EDR膜較RO及ED膜厚2-3倍，用彎流式分隔片，線性流速快，配合定期的倒極操作，不易發生膠質結垢
2. 有機物結垢:水中有機物帶負電荷，陰離子交換膜易產生有機物結垢。原水的TOC最好控制在2mg/L以下，EDR的原水TOC為10-20mg/L。
3. 生物結垢: 一般已連續加氯 (自由餘氯= 0.5mg/L)或加H_2O_2即可避免此問題的發生。
4. 淤泥指數(silt density index, SDI)

   RO: $SDI_5<5$

   EDR : $SDI_5<12$

電透析 fouling 與防護

- Fouling
  - Pretreatment
  - Turbulence
  - Optimization of process condition
  - Modification of membrane property
- Cleaning-In-Place (CIP)
  - EDR
  - Pulsed electric field

•脫鹽率下降的情形，使用稀鹽酸循環清洗的方式可達到脫鹽率恢復的效果。

•在此水質下，EDR的操作方式可較傳統ED方式節省60%的酸洗水量 。

電透析操作方法

電透析操作方法分為

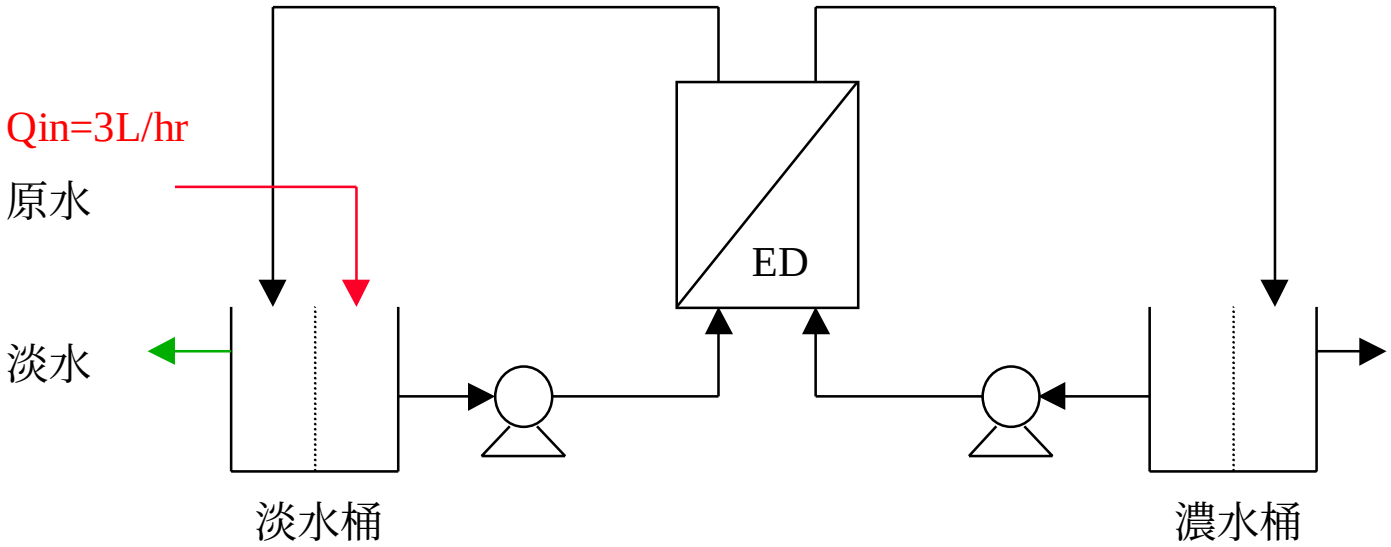
(1)批式

(2)feed-and-bleed（原水進料量≈淡水產量）

(3)連續式三種，連續式又可分為一次流通式(one-pass)及部分循環式

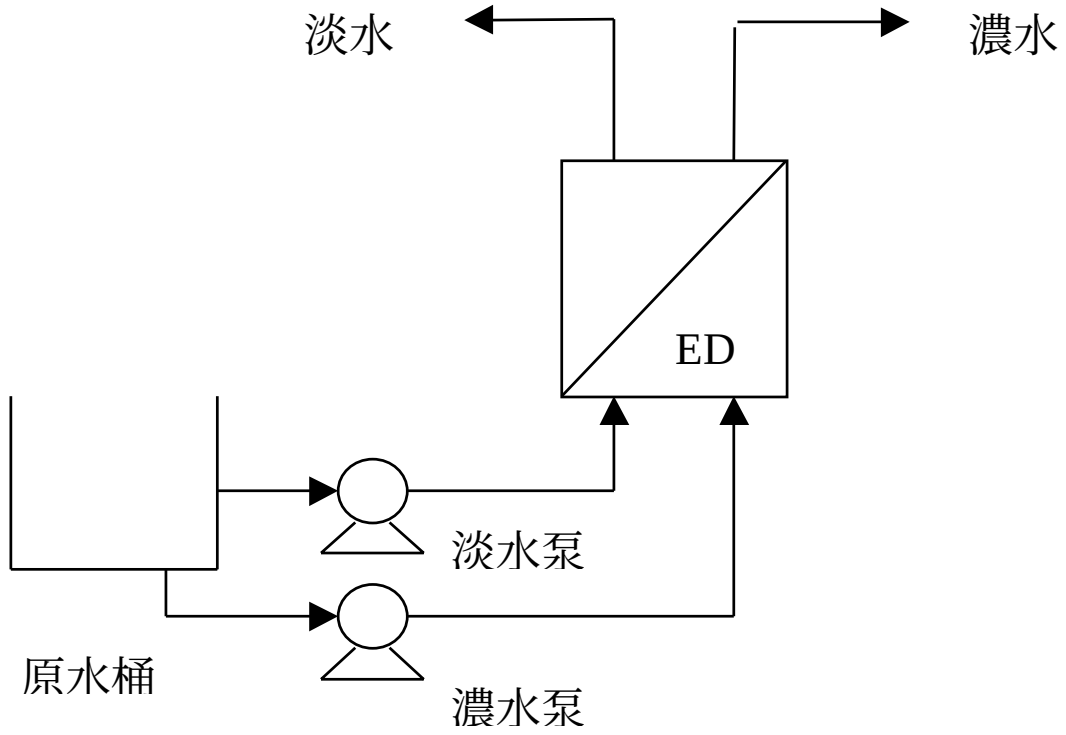
電透析操作方法

feed-and-bleed（原水進料量≈淡水產量）



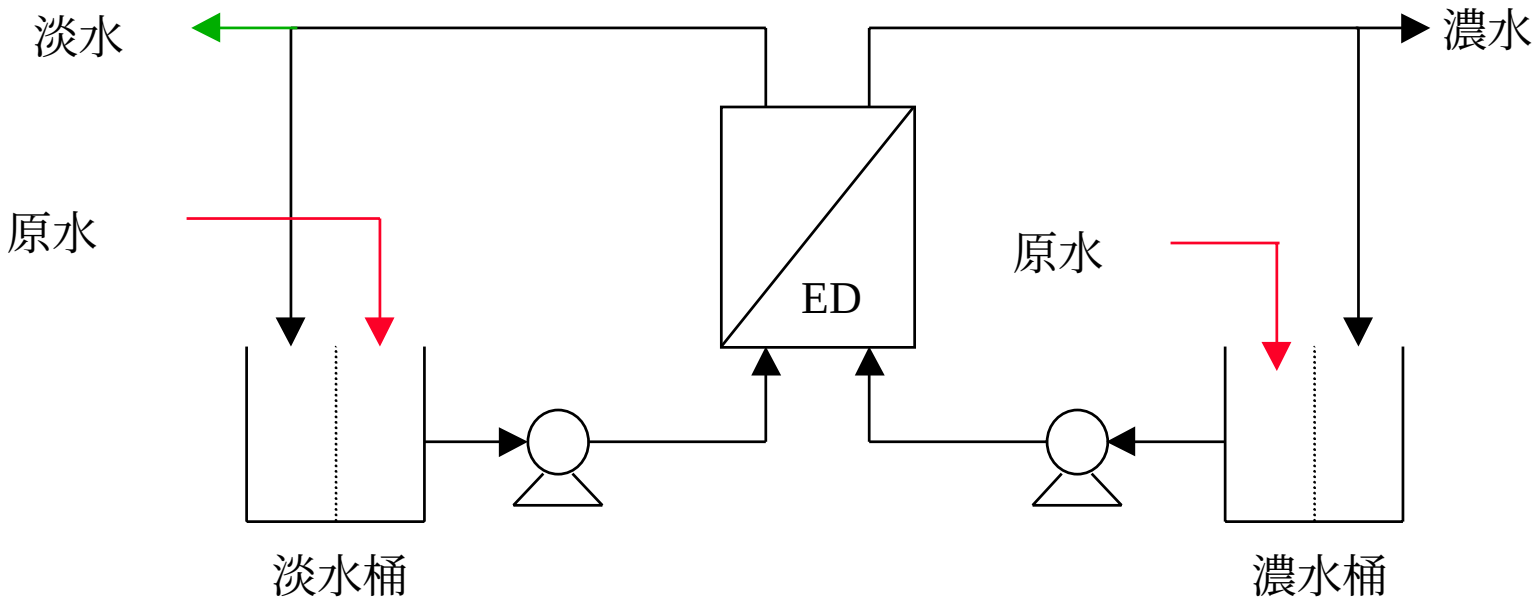
電透析操作方法

一次流通式(one-pass)



電透析操作方法

部分循環式



EDR處理河川水

導電度500 μS/cm

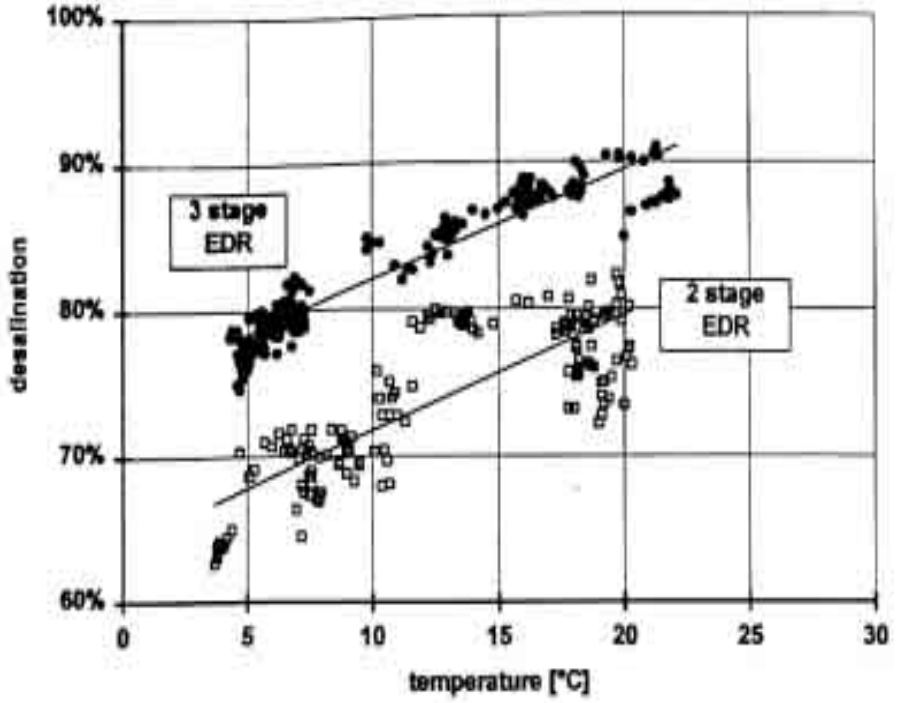


Table 2 *Removal of chloride, sulphate and hardness by the 2 and 3 stage EDR system*

Removal %	2 stage EDR		3 stage EDR	
	4-6 °C	22-24 °C	4-6 °C	22-24 °C
Cl^-	72	83	83	91
SO_4^{2-}	73	89	84	93
hardness	78	89	88	97

Table 4 *Energy and chemicals consumption of a 2 stage and 3 stage EDR system in EDR-IMS 2*

	2 stage EDR	3 stage EDR
Energy consumption ($kWh/m^3_{product}$)	0.4	0.6
Scaling control ($g/m^3_{product}$ 30% HCl)	29	35
Bromate control ($g/m^3_{product}$ 30% HCl)	60	0

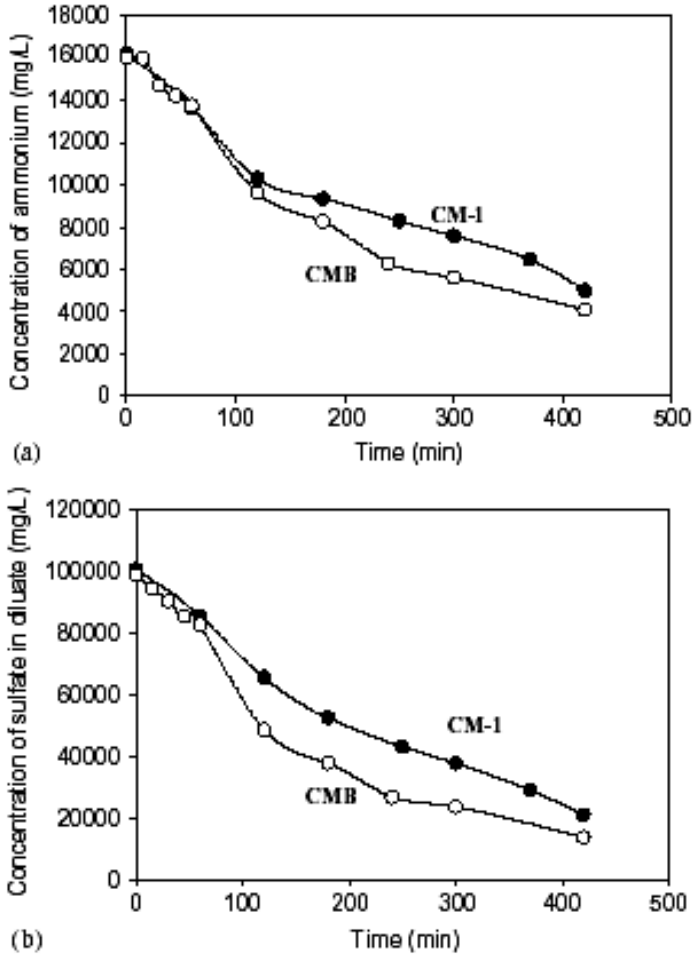
電透析應用於醱酵液脫鹽

用於氨基酸醱酵液中硫酸銨之分離

Comparison between power sources in electrodialysis of lysine fermentation waste

	CMB and AM-1	CM-1 and AM-1
Operating time (min)	420	420
Switching time (min)	58	55
Stack current (A)	10.0	10.0
Conductivity in dilute, final (mS/cm)	24.2	39.7
Removal efficiency of ammonium (%)	73.1	71.9
Removal efficiency of sulfate (%)	83.5	81.4
Power consumption (wh/L)	106	102

Source: Lee et al. / Water Research 37 (2003) 1091–1099



3.電透析

EDR處理高導電度地下水

地下水

pH	導電度 (μs/cm)	TOC (mg/L)	Na^+ (mg/L)	Al^{3+} (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4 (mg/
7.7	1970	6.1	66.2	3.6	22.1	23.2	123	12.4	12(

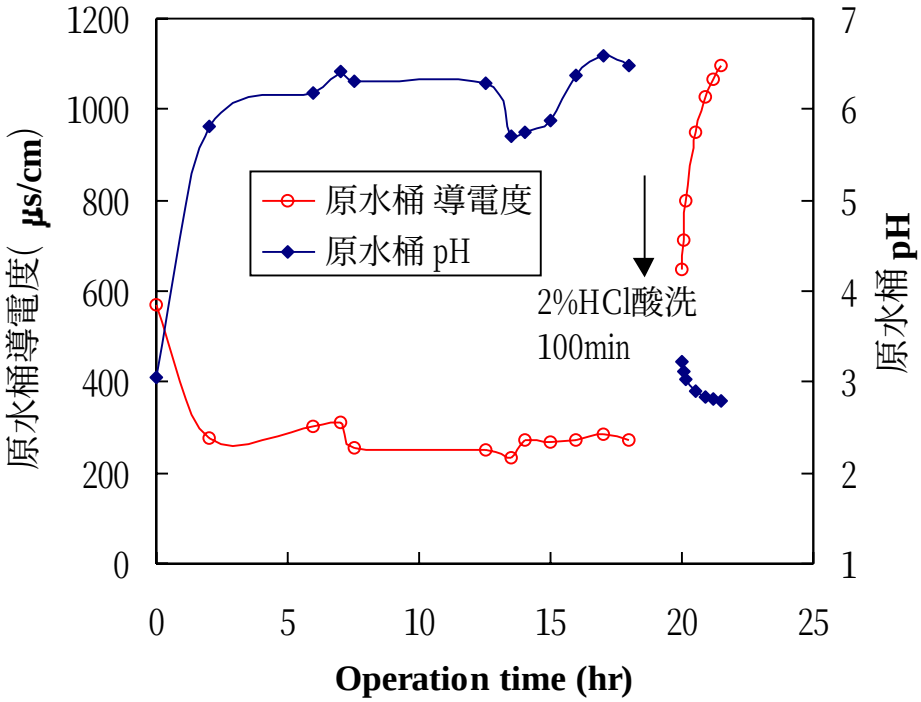
EDR處理

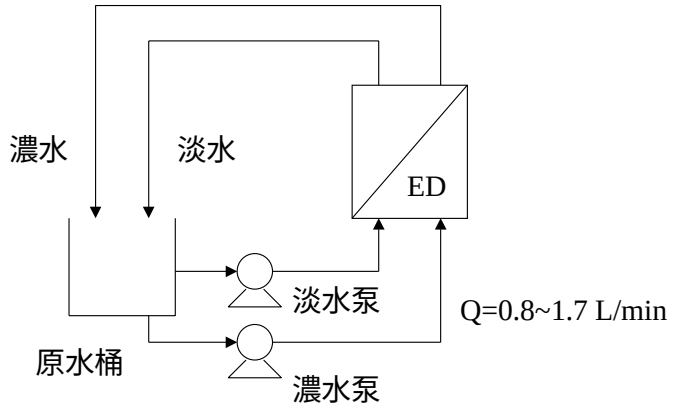
時間 (hr)	Na^+(mg/L)			Ca^{2+}(mg/L)			Mg^{2+}(mg/L)			電壓 (Volt)	電流 (Amp)	導電度（μS/cm）			脫鹽率 (%)
	原水桶	淡水	去除率 (%)	原水桶	淡水	去除率 (%)	原水桶	淡水	去除率 (%)			原水桶	濃水	淡水	
1	69.41	40	42.3	12.15	0.5	95.9	6.54	0.23	96.5	50.0	0.53	2050	3470	429	79.1
2	69.71	42	39.8	11.9	0.9	92.4	4.17	0.29	93.0	50.1	0.53	2120	3270	472	77.7
3	69.22	44.3	35.9	11	0.86	92.2	5.04	0.27	94.6	50.0	0.67	2060	3800	587	71.5
4	71.06	42	40.9	9.35	0.51	94.5	4.14	0.27	93.5	50.1	0.55	2110	3440	496	76.5
6	68.73	43.7	36.4	13.2	0.61	95.4	5.47	0.35	93.6	50.1	0.57	2040	3560	577	71.7
8	61.14	43.9	28.2	11.92	0.73	93.9	4.87	0.34	93.0	50.1	0.62	2020	3450	532	73.7
10	71.26	41.6	41.7	9.36	1.06	88.7	4.66	0.27	94.2	50.1	0.6	2170	3410	474	78.2
12	67.17	40.4	39.8	6.93	0.5	92.8	3.75	0.29	92.3	50.0	0.56	2210	3700	476	78.5

EDR處理清洗水水質變化

清洗水的水質

pH	導電度 (μs/cm)	Na^+ (mg/L)	Al^{3+} (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Fe (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
3.0	570	6.0	15	0.23	0.82	3.1	25	8.6	8	132



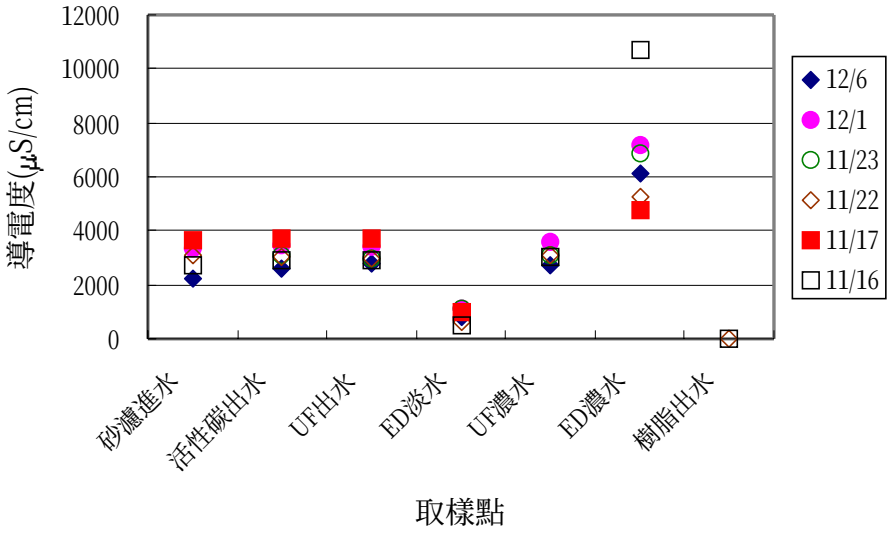


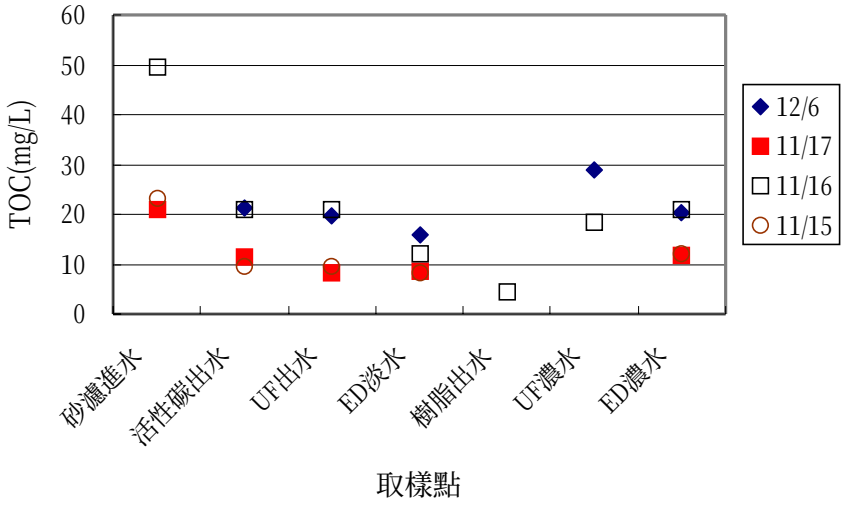
案例A廠地下水處理的操作方式

3.電透析

EDR處理廢水處理場綜合放流水

廢水處理場綜合放流水水質COD 80mg/L
(TOC 25mg/L)及導電度3500 μS/cm預估





電透析法前處理作業

- EDR之前可選擇設置或不設置UF
- 若不設置UF則EDR倒極的頻率須較高(約15分鐘一次)，因此水回收率較低
- 若設置UF則可以延長EDR 薄膜的壽命
- TOC 去除 (活性碳, BAC, BioNET等)
- pH control (concentrate)
- SDI

4.成本分析

EDR 操作成本

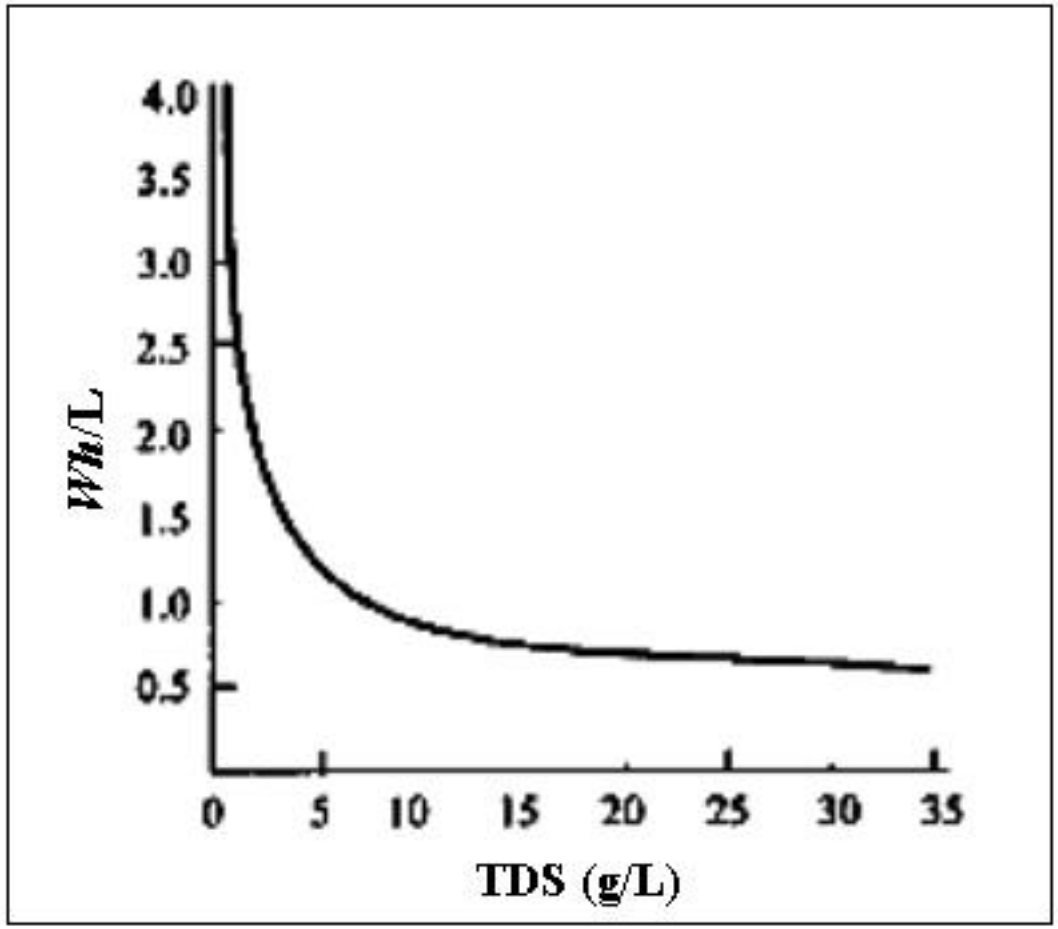
Engineering summary for EDR system used in Buckeye, Ariz.

	A	B	System
Number of plants	1	1	2
Number of lines per plant	2	3	5
Number of stages per line	3	3	3
Source water TDS, *mg/L*	1,587	1,587	1,587
Product water TDS, *mg/L*	246	328	287
Concentrate TDS, *mg/L*	6,951	6,623	6,787
Percent salt removal	84.5	79.3	81.9
Product water capacity, *gpd*	300,000	600,000	900,000
Source water capacity, *gpd*	375,000	750,000	1,125,000
Concentrate capacity, *gpd*	75,000	150,000	225,000
Percent water recovery	80.0	80.0	80.0
Source water temperature, *°F*	80	80	80
Concentrate Langelier Saturation index	+1.79	+1.73	+1.76
Concentrate percent calcium fluoride (CaF_2) saturation	214.3	218.4	216.4
Total electrical consumption, *kW·h/1,000 gal*	4.0	3.9	3.95
DC power consumption, *kW·h/1,000 gal*	1.8	1.9	1.85
Pump power consumption, *kW·h/1,000 gal*	2.2	2.0	2.10
Source water	Well water	Well water	Well water
Pretreatment	Not required	Not required	Not required
Permeate use	Drinking water	Drinking water	Drinking water

Source: Ionics Inc.

4.成本分析

EDR 操作成本

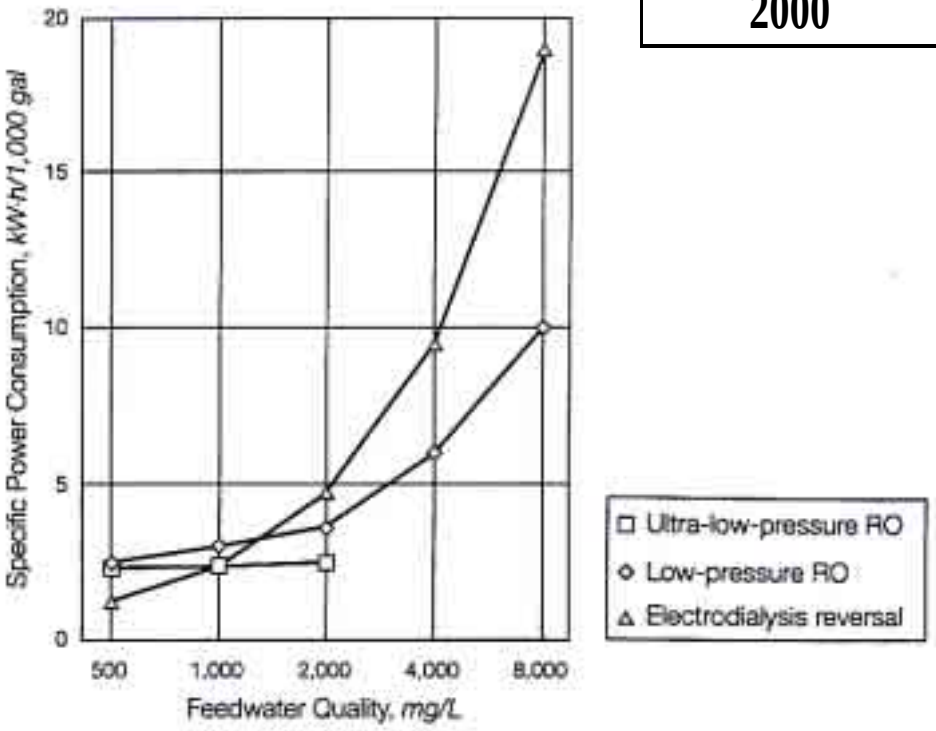


去除1g TDS
消耗的動力
與TDS濃度
有關

B. Pilat / Desalination 139 (2001) 385-392

EDR與RO 動力消耗

TDS, mg/L	EDR, KWh/m^3	RO, KWh/m^3	NF, KWh/m^3
500	0.3	0.6	0.6
1000	0.6	0.75	0.6
2000	1.25	1	0.6



EDR與低壓RO與超低壓RO(NF)的操作成本 (AWWA, 1995)

EDR與RO 操作成本(藥劑)

表 12. EDR 與 RO 的藥劑費用

設備	EDR	RO
使用藥劑	酸鹼 抑垢劑	抑垢劑 酸鹼 清洗劑
來源	中國大陸	一般
初設成本	0.2~0.5 元/m^3	0.5~1 元/m^3

EDR與RO 初設成本

表 13. EDR 與 RO 的初設費用

設備	EDR	RO
規格	TDS: 1,000 mg/L 水量: 1,000 CMD 脫鹽率 60%	TDS: 1,000 mg/L 水量: 1,000 CMD 脫鹽率 90%
來源	中國大陸	一般
初設成本 (不含前處理設備)	0.3~0.5 萬/m^3	0.8~1.2 萬/m^3

大陸製的EDR離子交換膜為異相膜

結語

EDR 、RO與NF處理技術均有適用的範圍，考慮不同程序的組合也是作為脫鹽與控制電導度的方法。

原水水質的特性與產水的用途決定使用前處理與處理技術的種類與操作成本，可以依據不同需求選擇。

TDS< 1000 mg/L，使用EDR是最節省操作成本。

TDS> 1000 以NF是最節省操作成本。

超過2000 mg/L以上之TDS濃度是以RO較為經濟。

結語

EDR(倒極式電透析) 應用方向為下列三項

(1)水質軟化

(2)非自來水來源(如地下水)之用水處理

(3)廢水回收

水質軟化廢水回收需注意濃水中是否會產生$CaSO_4$及$CaCO_3$結垢。