高科技產業純水系統 利用與管理

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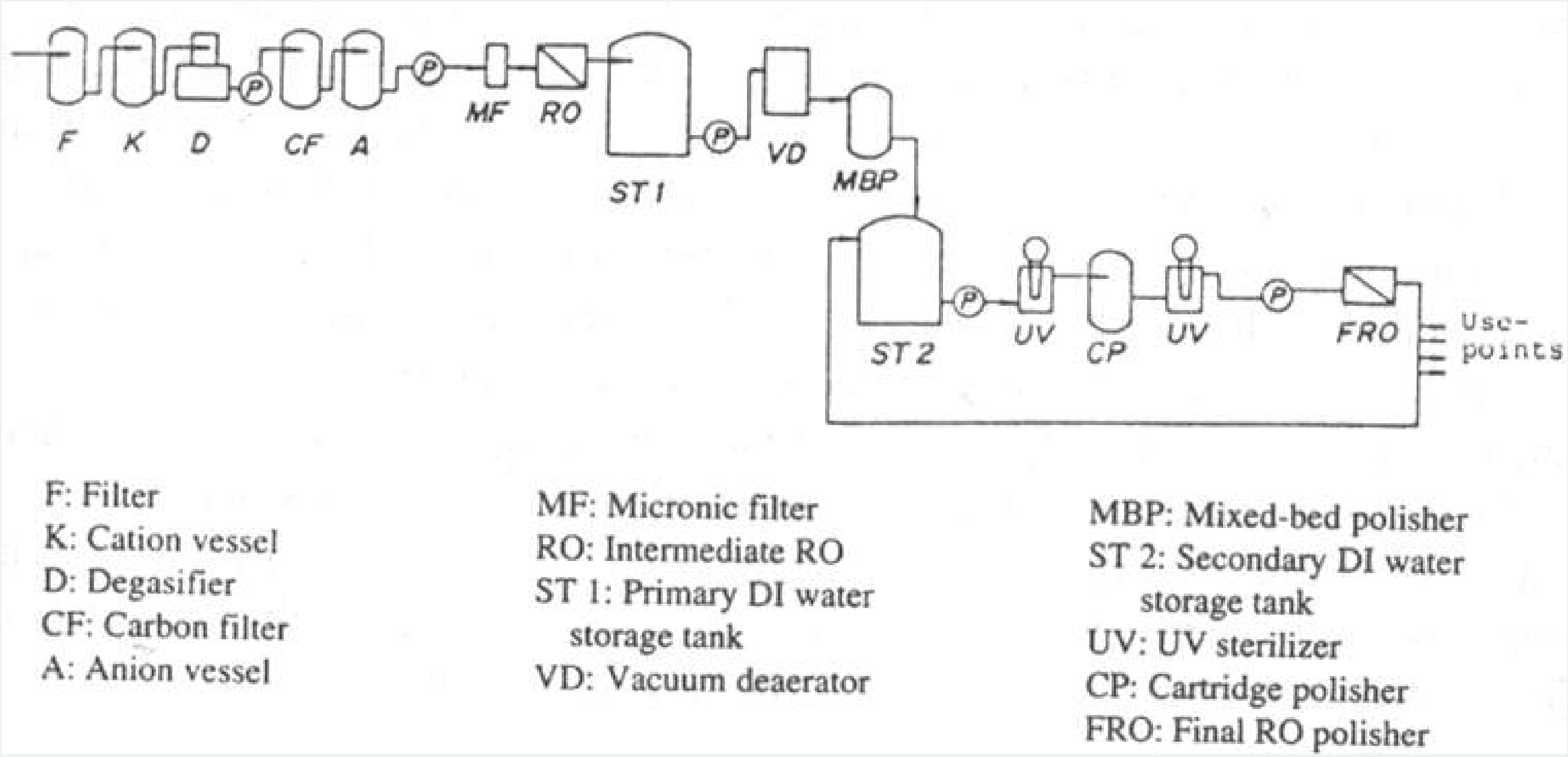
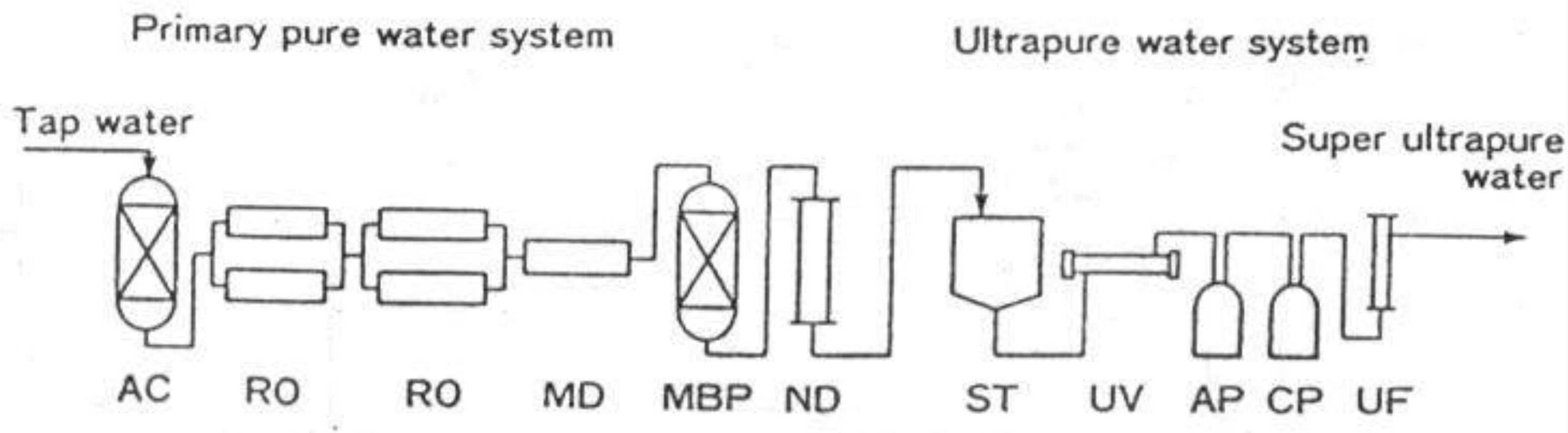
超純水製程

超純水處理流程由各種處理單元組成，包含去除離子、微量有機物與微生物。 所以製程可以有許多不同的組合。



超純水處理參考流程1

超純水製程

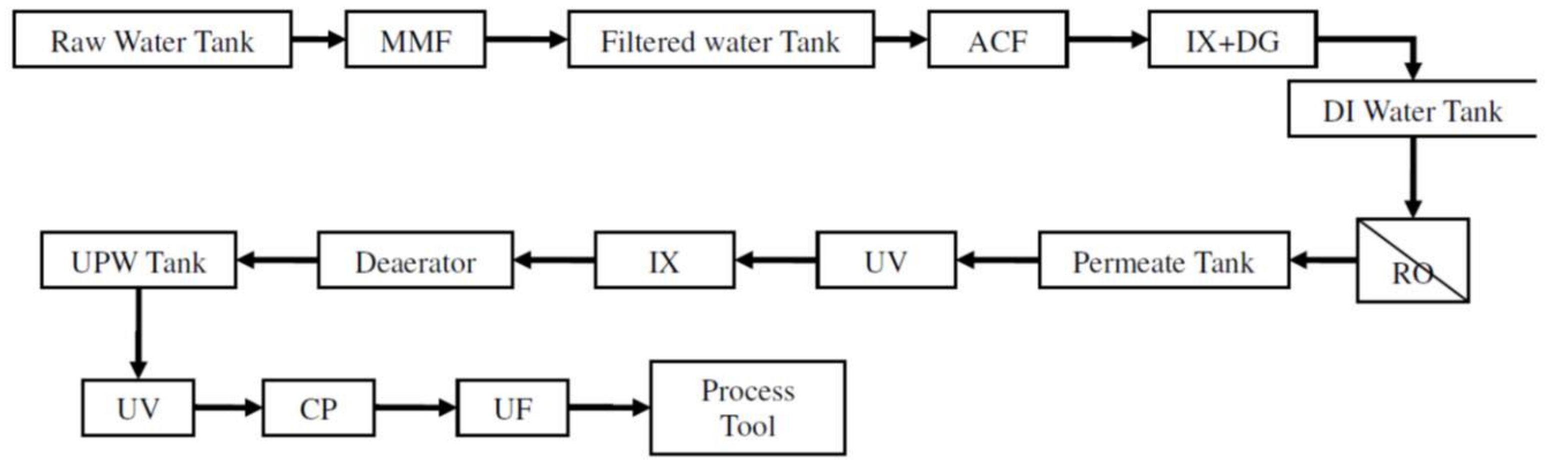


AC : charcoal tower
RO : Low-pressure RO equipment
MD : Membrane deaerator
MBP : Mixed bed column
ND : Nitrogen deaerator

ST : Ultrapure water storage tank
UV : Ultraviolet ray oxidation equipment
AP : Anion polisher
CP : Cartridge polisher
UF : UF equipment

超純水處理參考流程1

超純水製程



超純水處理參考流程1

自來水的主要成分

1. 電解質:
   陽離子有H^+、Na^+、K^+、Mg^{2+}、Ca^{2+}、Fe^{3+}、Mn^{2+}等
   陰離子有F^-、Cl^-、HCO_3^-、SO_4^{2-}、 NO_3^- 、$H2PO_4^-$、SiO_3^-等
2. 有機物：微量
3. 顆粒
4. 微生物
5. 溶解氣體：N_2、O_2、CO_2等

水的純化，就是去除水中雜質

一般製造純水使用的水質指標

污染物	檢測名稱	使用單位
無機鹽類	比電導度 (比阻抗值)	μ S/cm (Megohm.cm)
有機物	總有機碳 (Total Organic Carbon	p.p.b. (ug/L)
懸浮顆粒	1.汙泥密度 Silt Density Index 2 .濁度Turbidity 3.粒子數	1. 無單位 2 .NTU 3. 數量
微生物	生長在 0.45 微米濾 膜上之菌落數 .	CFU/ml (Colony For ming Unit/ml)

超純水水質參考規範

不同規格的產品有不同等級的水質要求

Item		Detection limit**	Specifications 256K DRAM 1985 specs attainable	accept-able	Guidelines 1M DRAM 1988 specs attain-able	accept-able	4M DRAM <1 μm VLSI	ULSI target
Resistivity @ 25°C		18.2 max.	18.2	17.9	18.2	18.0	18.2	18.2
TOC (ppb)		5	<20	<50	<10	<30	<10	5
THM (ppb)		<1	—	—	—		<3	—
Particle/L by SEM	0.1-0.2 μm		—	—	—	—	<1,500	<1,000
	0.2-0.3 μm		—	—		<2,000	<800	<500
	0.3-0.5 μm				<200	<200	<50	<10
	>0.5 μm				<1	<1	<1	<1
Particle/L by on-line laser	0.3-0.5 μm	<1	—	—	—	—	<50	<10
	>0.5 μm	<1	—	—	—	<100	<1	<1

超純水水質參考規範

Item	Detection limit**	Specifications 256K DRAM 1985 specs attain-able	Specifications 256K DRAM 1985 specs accept-able	Guidelines 1M DRAM 1988 specs attain-able	Guidelines 1M DRAM 1988 specs accept-able	Guidelines 4M DRAM <1 μm VLSI	Guidelines 4M DRAM ULSI target
Bacteria/100 mL							
by culture	<1	0	<6	0	<6	0	0
by SEM		—	—	<1	<10	<5	0
by epi		—	—	<5	<50	<10	<1
Silica-dissolved (ppb)	0.25	<3	<5	<0.4	4	3	1
Boron (ppb)	0.05	—	—	<0.05	2.0	0.005	*
Ions (ppb)							
Na^+	0.05	0.05	0.2	<0.05	0.1	0.025	
K^+	0.1	0.1	0.3	<0.1	0.1	0.05	
Cl^-	0.05	0.05	0.2	<0.05	0.1	0.025	
Br^-	0.1	<0.1	0.1	<0.1	0.1	0.05	
NO_3^-	0.1	<0.1	0.1	<0.1	0.1	0.05	
SO_4^{-2}	0.1	0.1	0.3	0.05	0.2	<0.05	
Ions total	0.5	<0.5	1.2	<0.5	<0.7	<0.2	
Residue (ppm)	<0.1	<0.1	<0.3	<0.1	0.1	<0.05	*

超純水水質參考規範

Item	Detection limit**	Specifications 256K DRAM 1985 specs attain-able	accept-able	Guidelines 1M DRAM 1988 specs attain-able	accept-able	4M DRAM <1 μm VLSI	ULSI target
Metals (ppb)***							
Li	0.03	—	—	<0.03	0.05	0.003	
Na	0.05	0.05	2.0	<0.05	0.1	0.005	
K	0.05	0.1	0.3	<0.05	0.1	0.005	
Mg	0.02	—	—	<.02	0.05	0.002	
Ca	2.0	—	—	<2	<2.0	0.002	
Sr	0.01	—	—	<0.01	0.05	0.001	
Ba	0.01	—	—	<0.01	0.05	0.001	
B	0.05	—	—	<0.05	2.0	0.005	
Al	0.05	0.2	2.0	<0.05	0.05	0.005	
Cr	0.02	0.02	0.1	<0.02	0.05	0.002	
Mn	0.02	0.05	0.5	<0.02	0.05	0.002	
Fe	0.1	0.02	0.1	<0.02	0.1	0.002	
Ni	0.02	—	—	<0.02	0.05	0.002	
Cu	0.02	0.02	0.1	<0.02	0.05	0.002	
Zn	0.02	0.02	0.1	<0.02	0.05	0.002	
Pb	0.05	—	—	<0.05	0.05	0.005	

— Not availiable at this time   *Unknown   **With resonable concentration where applicable

***Using ICP-MS, GFAAS, IC where required for lowest level of detection. These elements represent the metals that are usually found in high-purity water.

Balazs Specifications and Guidelines, (1988); Courtesy,Balazs Analytical Laboratory

水質軟化

-製造純水前處理，避免結垢發生

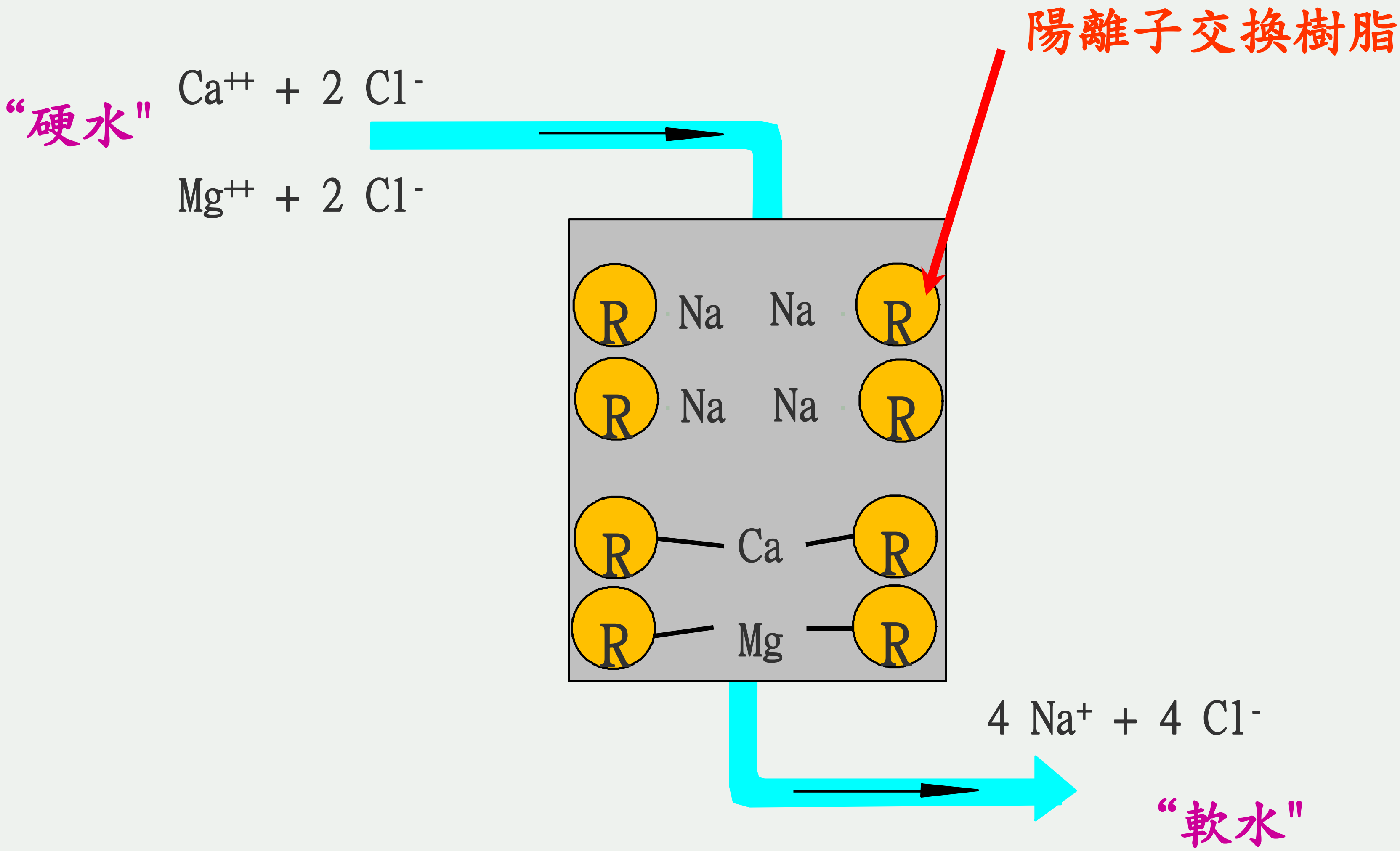
水中碳酸鈣結垢

$$Ca^{++} + CO_3^{=} \longrightarrow CaCO_{3\,(S)}$$

碳酸鈣因過飽會發生沉澱

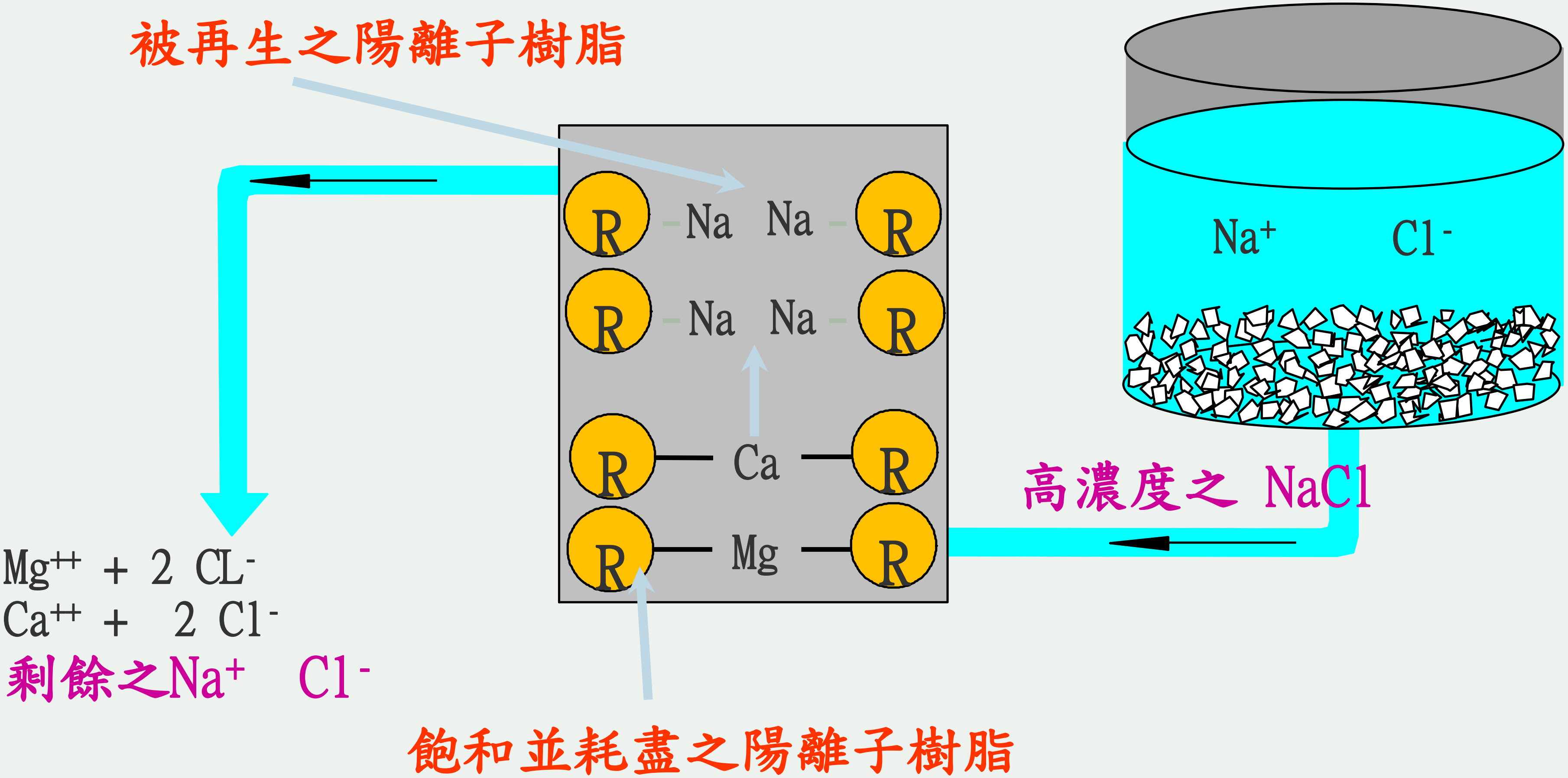
結垢控制

軟水過程



資料來源: Millipore Corporation
Laboratory Water Division

軟水系統再生過程



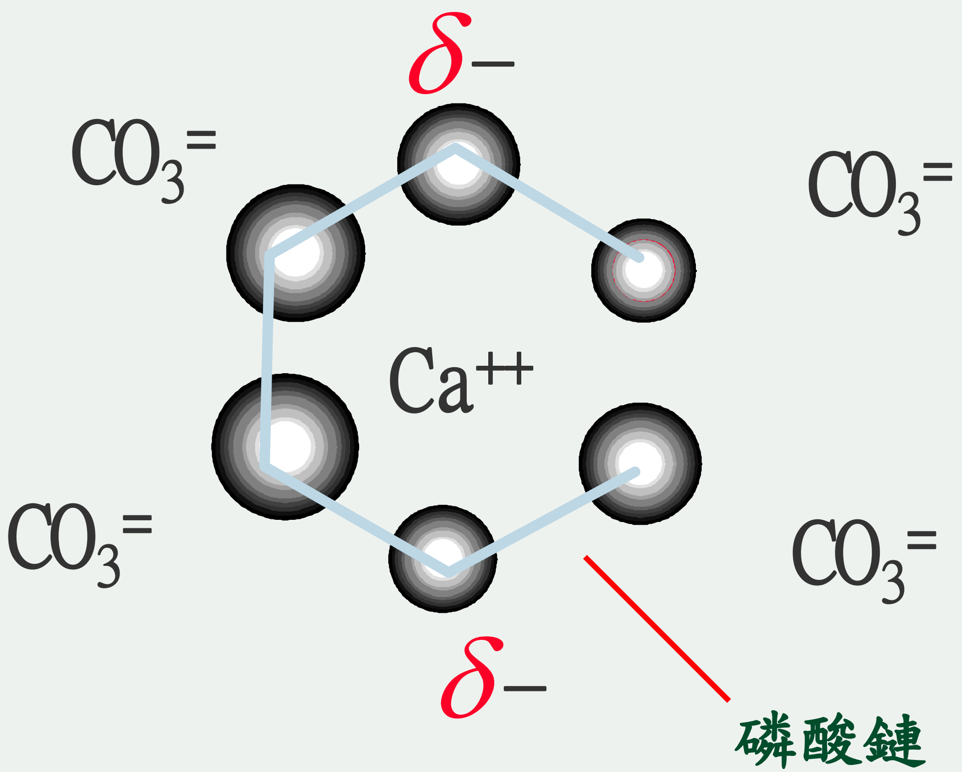
需使用飽和鹽水來再生軟水系統

資料來源: Millipore Corporation
Laboratory Water Division

水中結垢控制

抗結垢劑（分散劑）---聚磷酸

$$Ca^{++} + CO_3^{=} \longrightarrow CaCO_{3(S)}$$



資料來源: Millipore Corporation
Laboratory Water Division

抗結垢劑（分散劑）–聚磷酸 Poly-Phosphate

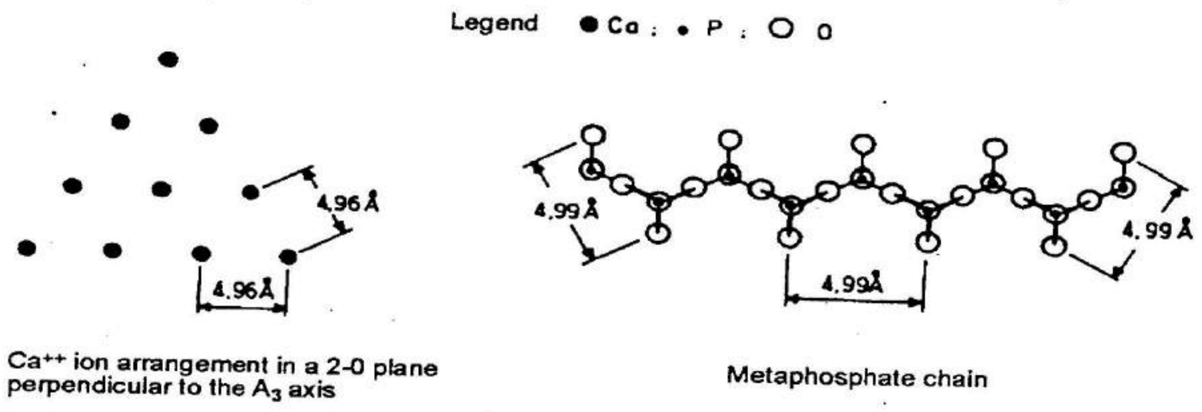


Figure 5.11 Schematic representation of the Ca^{++} ion locations in a reticular calcite plane viewed perpendicular to the A_3 axis. Planar projection of the structure of a metaphosphate.
Source Raistrick (29).

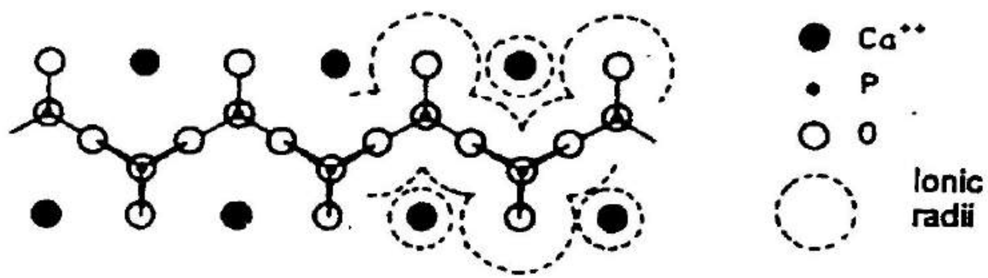


Figure 5.12 Metaphosphate chain positioning on a calcite reticular Ca^{++} plane.
Source Raistrick (29).

螯合劑-EDTA、NTA

If we evaluate the complexation aptitude of a molecule in terms of the number of coordination bonds it is capable of forming, EDTA is seen to offer a maximum number

Table 6.1 Values for log K_S at 20°C

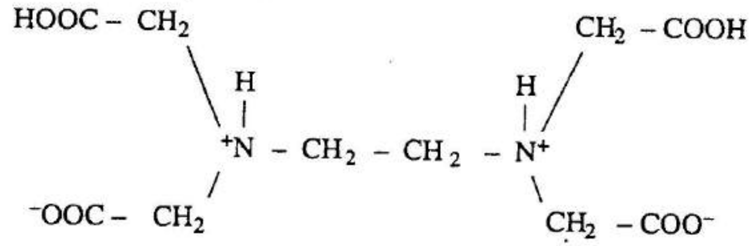
Cation	Ba^{++}	Ca^{++}	Cd^{++}	Co^{++}	Cu^{++}	Fe^{++}	Fe^{3+}	Hg^{++}	Ni^{++}
NTA	4.82	6.41	9.54	10.6	12.68	8.84	15.87	—	11.26
EDTA	7.76	10.70	16.59	16.21	18.79	14.33	25.1	21.8	18.36
DCyTA	7.99	12.50						24.3	

Cation	Mg^{++}	Mn^{++}	Pb^{++}	Sr^{++}	Zn^{++}	Li^{++}	Na^{+}	H^{+}
NTA	5.41	7.44	11.8	4.98	10.45	3.28	2.1	—
EDTA	8.69	13.50	18.3	8.63	16.26	2.79	1.66	10.22
DCyTA	10.32							11.70

Source From data given in Metcalf and Moore (19), Freedman (8), Prakash and Choksi (20), and Schwarzenbach et al. (24).

* Certain acid functional groups of these molecules are very weak acids. A pH above the highest pK_a must therefore be used to ensure near total dissociation.

EDTA 分子結構



They consider that the first well-defined ion that can be obtained in solution (noted H_2C^{2-}) is

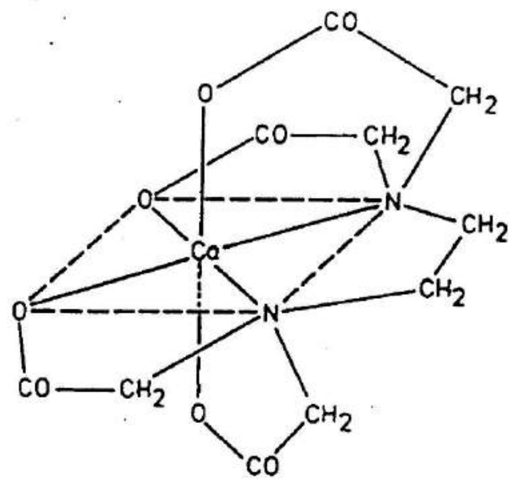
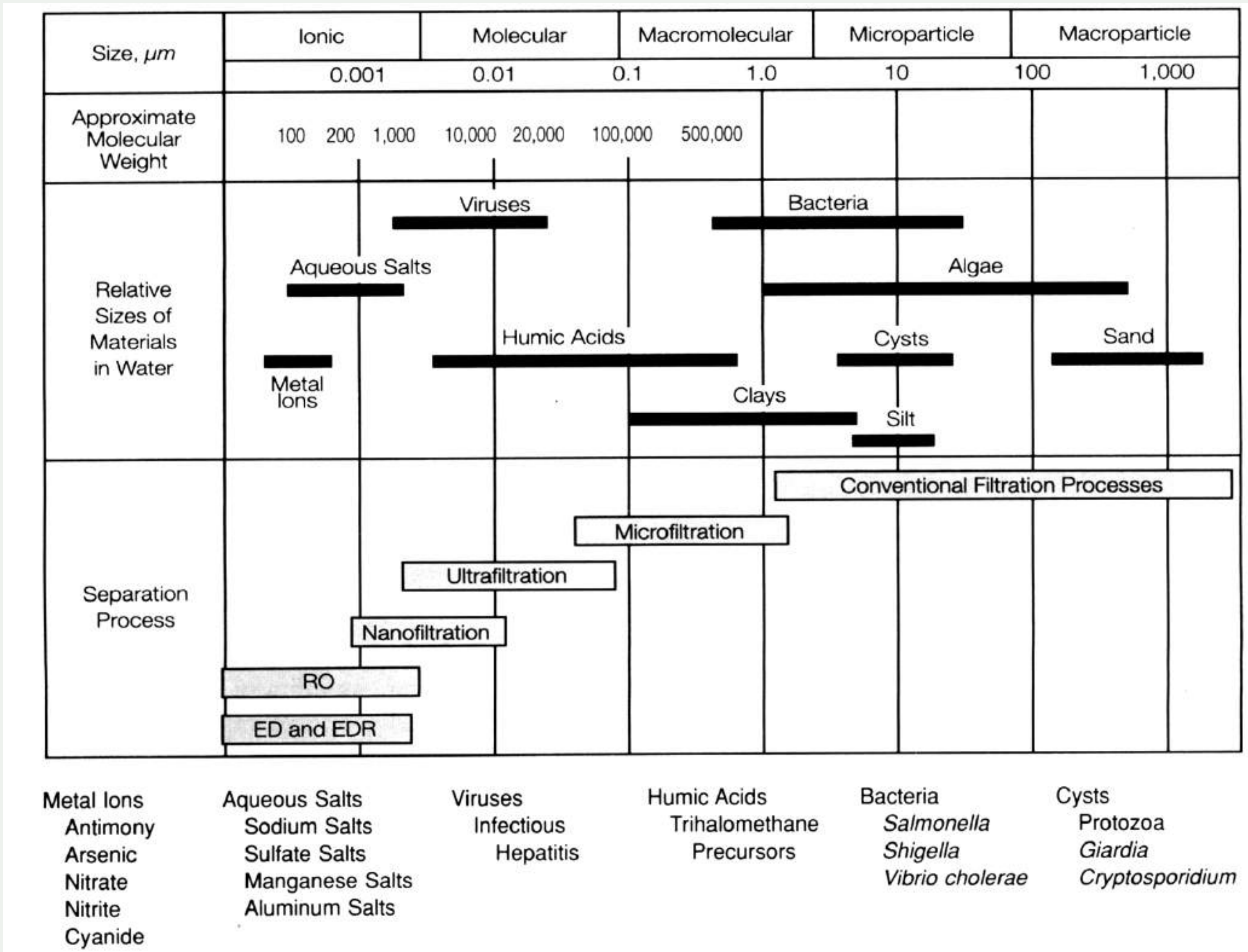


Figure 6.1 Structure of the EDTA–Ca^{++} Complex.
Source Carini and Martell (4).

薄膜處理

- 主要功能分離水中溶解固體（鹽類/分子)
- 產水分為一股淡水與一股濃水

薄膜程序應用



(AWWA,1995)

MF/UF薄膜分離層材料成分

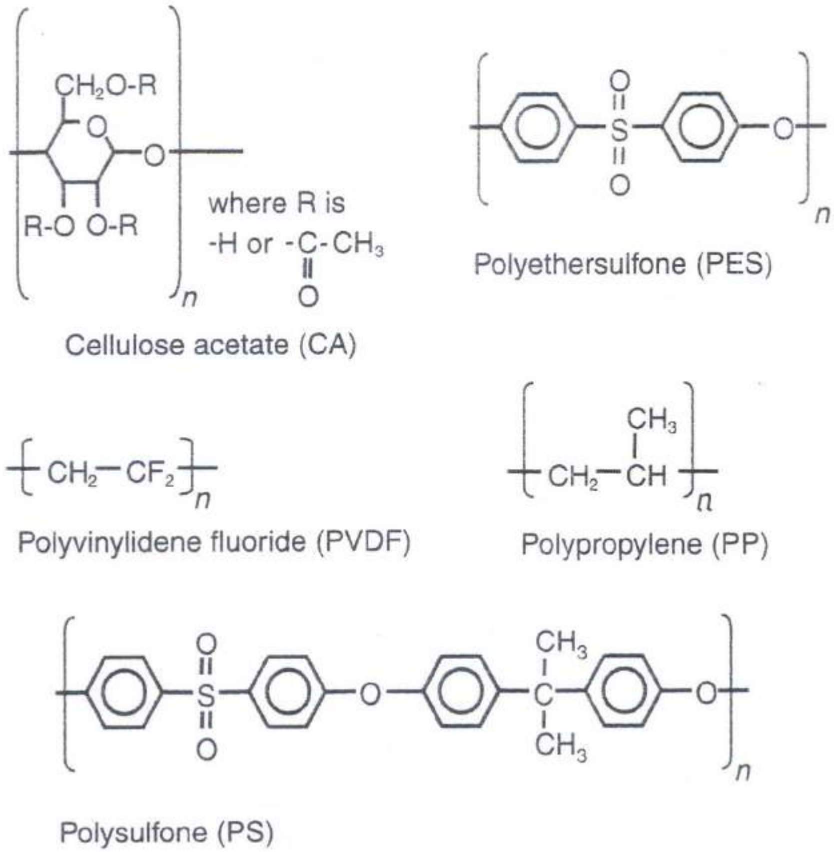


Figure 12-14
Chemical structure of common MF and UF membrane materials.

UF薄膜阻塞的機制說明

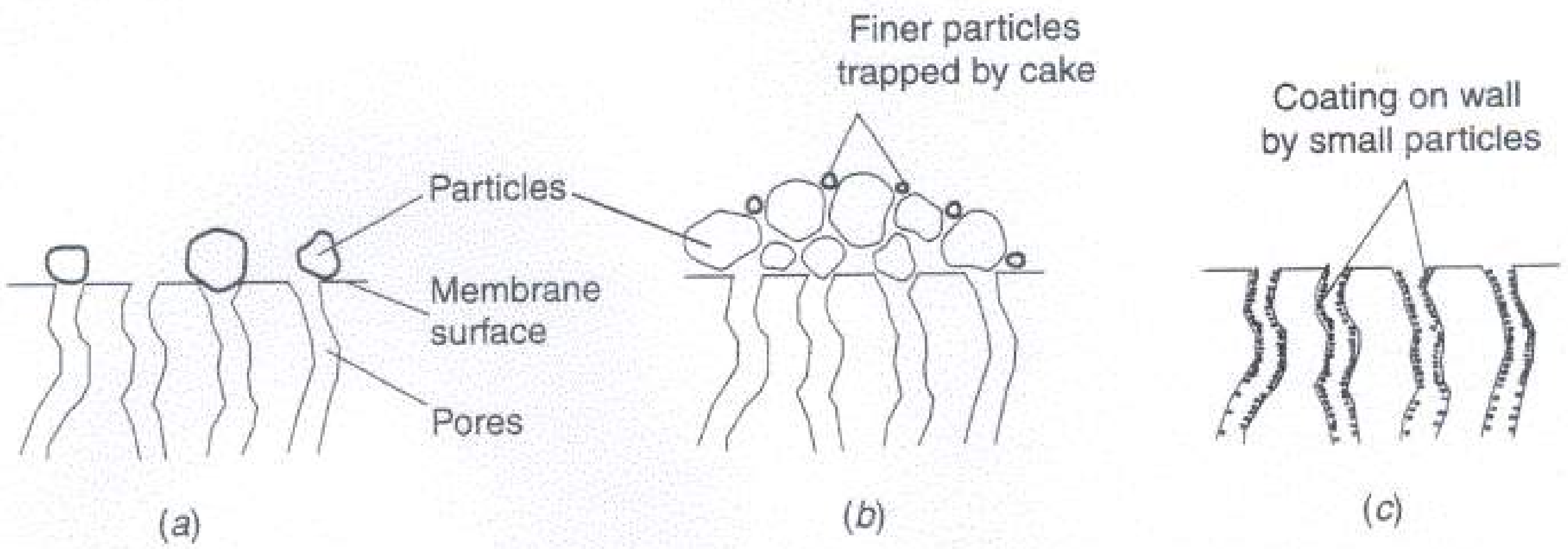


Figure 12-15
Mechanisms for rejection in membrane filtration. (*a*) Straining occurs when particles are physically retained because they are larger than the pores. (*b*) Cake filtration occurs when particles that are small enough to pass through the membrane are retained by a cake of larger material that collects at the membrane surface. (*c*) Adsorption occurs when material small enough to enter pores adsorbs to the walls of the pores.

UF/MF 清洗

Table 2.14 Cleaning techniques for UF and MF membranes

Foulant	Cleaning reagent	Process condition	Reagent action
Fats and oils, proteins, polysaccharides, bacteria	0.5N NaOH + 200 ppm chlorine	30–60 min at 25–55°C	Hydrolysis and oxidation
DNA, mineral salts	0.1M–0.5M acid (acetic, citric, nitric)	30–60 min at 25–55°C	Solubilisation
Fats, oils, proteins, biopolymers	0.1% sodium dodecyl sulphate, 0.1% TritonX-100	30 min overnight, 25–55°C	Wetting, emulsifying, suspending, dispersing
Cell fragments, fats, oils, proteins	Enzyme detergents	30 min overnight, 30–40°C	Catalytic breakdown (proteolysis)
DNA	0.5% DNAase	30 min overnight, 30–40°C	Enzyme hydrolysis
Fats, oils, and grease	2–50% ethanol	30–60 min at 25–55°C	Solubilisation

薄膜處理

RO

逆滲透壓力

List of Applied Pressure for Typical Membrane Filtration Processes

Membrane processes	Pressure (atm)
RO – Seawater	54.4–68.0
RO – Waste and process	20.4–40.8
RO – Water purification	13.6–23.8
RO – Undersink (home)	3.4
NF	6.8–13.6
UF	1.7–10.2
MF (crossflow)	0.7–1.7

電導度

Table 9 Limiting Equivalent Conductivities of Ions at 25°C in Water (Data from: Electrolyte solutions, R.A. Robinson and R.H. Stokes, Butterworth Publishers London, 1970)

cations	λ^{o}_{equiv} [$cm^2 \Omega^{-1} equiv^{-1}$]	anions	λ^{o}_{equiv} [$cm^2 \Omega^{-1} equiv^{-1}$]
H^+	349.8	OH^-	199.1
Li^+	38.6	F^-	55.4
Na^+	50.1	Cl^-	76.4
K^+	73.5	Br^-	78.1
Ag^+	61.9	NO_3^-	71.5
NH_4^+	73.5	HCO_3^-	44.5
Mg^{2+}	53.0	CO_3^{2-}	69.3
Ca^{2+}	59.5	ClO_3^-	64.6
Ba^{2+}	63.6	ClO_4-	67.3
Cu^{2+}	53.6	SO_4^{2-}	80.0
Zn^{2+}	52.8	$Fe(CN)_6^{3-}$	100.9
Co^{2+}	55.0	formeate	54.6
Pb^{2+}	69.5	acetate	40.9
La^{3+}	69.7	$P_3O_9^{3-}$	83.6
Ce^{3+}	69.8	$Fe(CN)_6^{4-}$	110.1

電導度

Table 10 Limiting Equivalent Conductivities of Ions in Water at Different Temperatures (Data from: Electrolyte solutions, R.A. Robinson and R.H. Stokes, Butterworth Publishers London, 1970)

ion	0°C	5°C	15°C	18°C	25°C	35°C	45°C	55°C	100°C
H^+	225.0	250.1	300.6	315.0	349.8	397.0	441.4	483.1	630.0
OH^-	105.0		165.9	175.8	199.1	233.0	267.2	301.4	450.0
Li^+	19.4	22.7	30.2	32.8	38.6	48.0	58.0	68.7	115.0
Na^+	26.5	30.3	39.7	42.8	50.1	61.5	73.7	86.8	145.0
K^+	40.7	46.7	59.6	63.9	73.5	88.2	103.4	119.2	195.0

電導度

Table 10 (continued)

ion	0°C	5°C	15°C	18°C	25°C	35°C	45°C	55°C	100°C
Mg^{2+}	28.9			44.9	53.0				165.0
Ca^{2+}	31.2		46.9	50.7	59.5	73.2	88.2		180.0
F^-				47.3	55.4				
Cl^-	41.0	47.5	61.4	66.0	76.35	92.2	108.9	126.4	212.0
Br^-	42.6	49.2	63.1	68.0	78.1	94.0	110.6	127.8	
NO_3^-	40.0			62.3	71.5	85.4			195.0
SO_4^{2-}	41.0			68.4	80.0				260

逆滲透操作型式

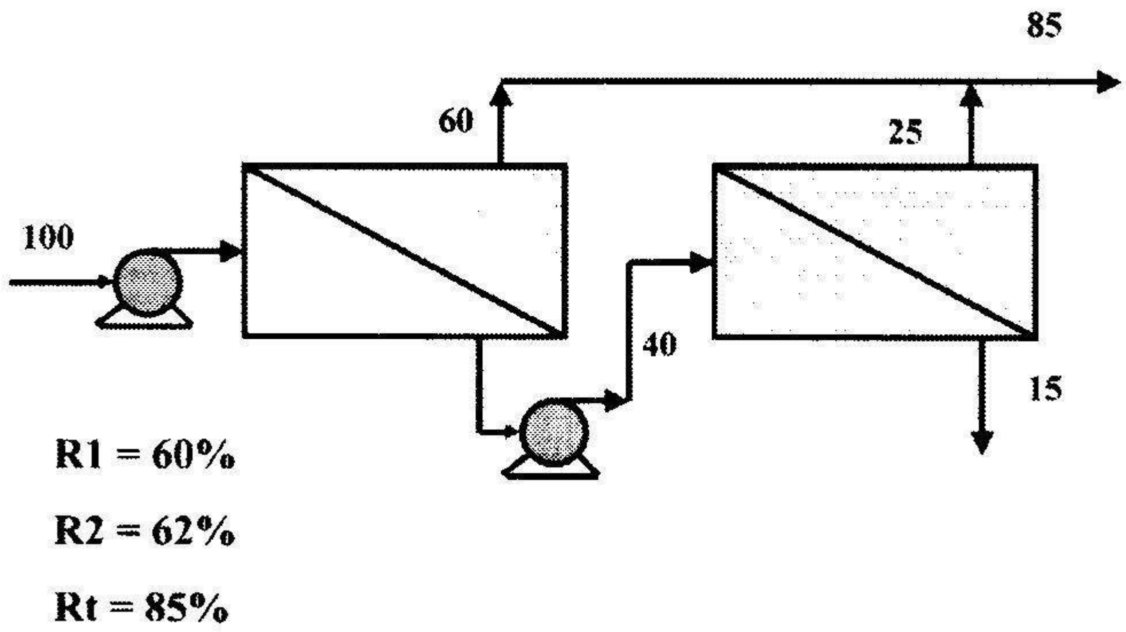
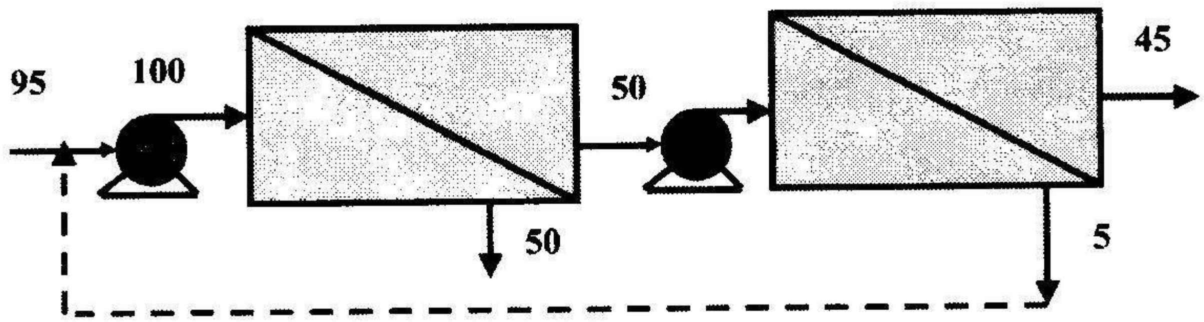


FIG. 5.5 Configuration of two stage RO unit with interstage booster pump.

逆滲透操作型式



R1 = 50.0 %

R2 = 90.0 %

Rt = 45.0% (w/o recirculation)

Rt = 47.3% (w recircirculation)

FIG. 5.7 Recovery rate in a two pass RO unit.

薄膜操作常見的問題

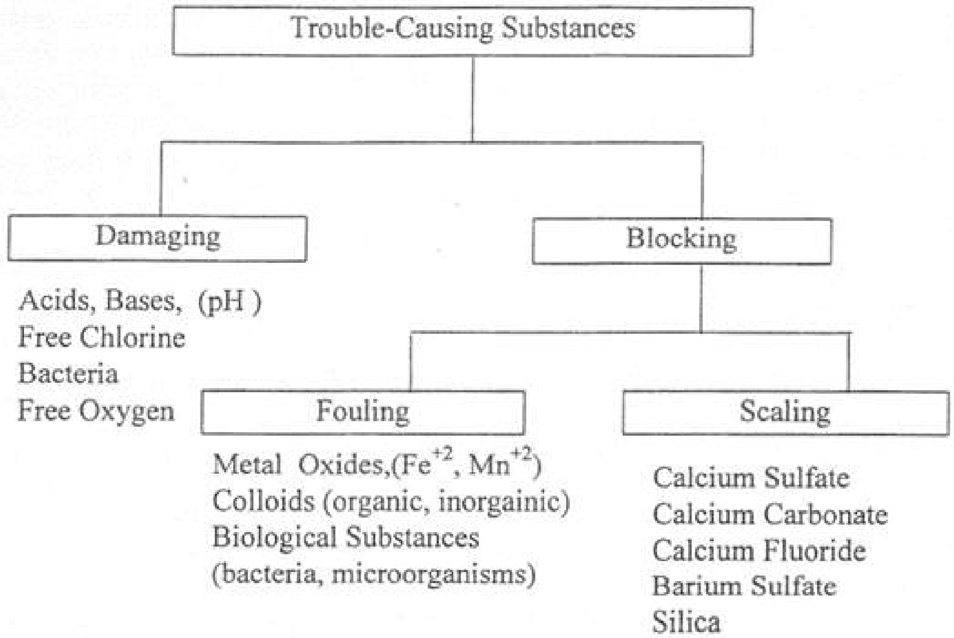


FIGURE 9.9 Substances potentially harmful to membranes. *(Rautenbach and Albrecht, 1989.)*

進水水質要求

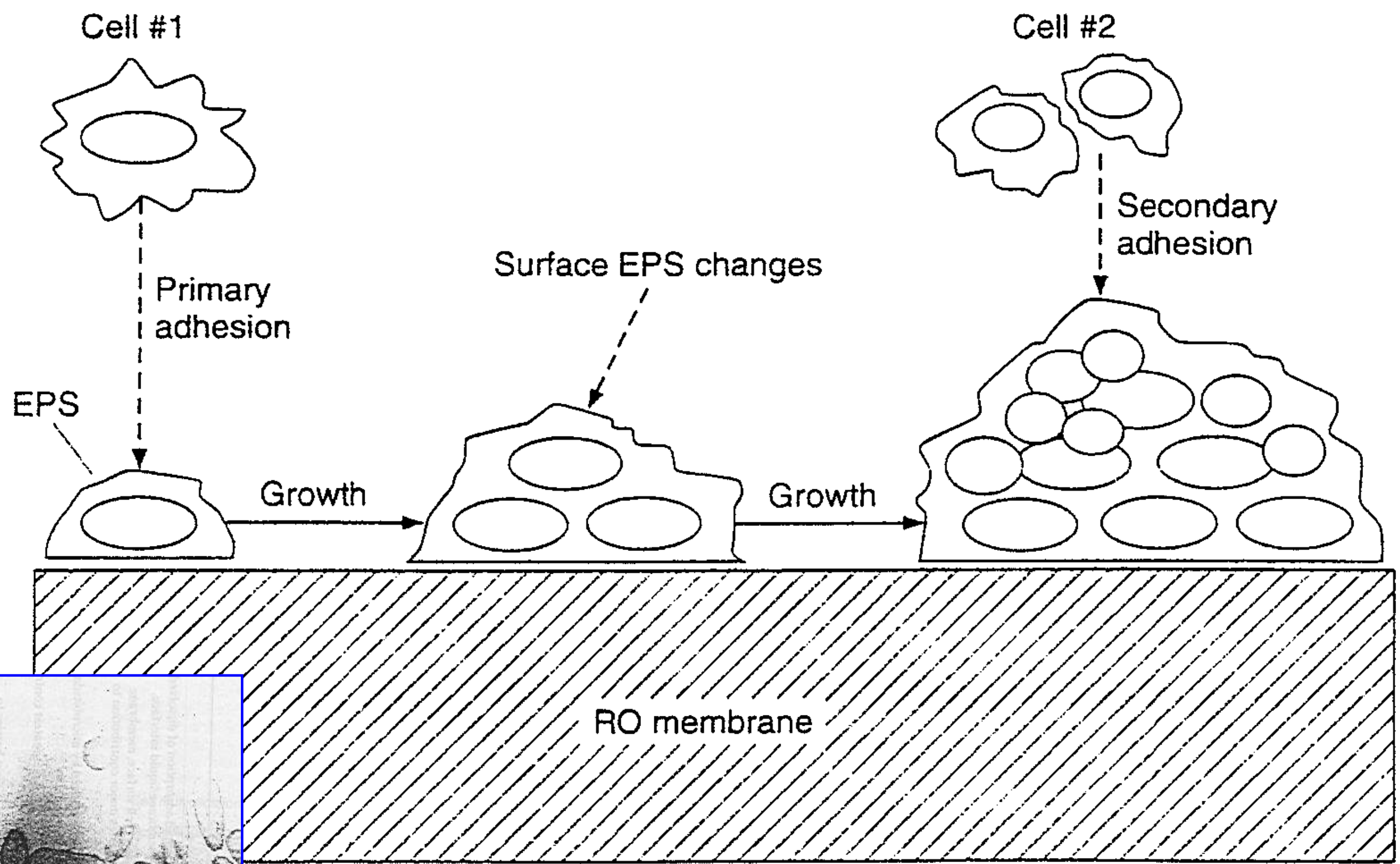
Table 2.7 Feed water requirements to minimise fouling

Parameter	Value
SDI_{15}	≤4
Turbidity	<1*
Iron**	<0.05 mg/l
Manganese	<0.5 mg/l
Hydrogen sulphide	<0.1 mg/l
Organics (TOC)	<10 mg/l

* Some membrane manufacturers recommend that turbidity be <0.2 NTU

** At pH>7.0 and 5–10 mg/l dissolved oxygen; at lower pH and lower oxygen levels, slightly higher iron levels can be tolerated

RO薄膜微生物滋生機制說明



Schematic illustration of major events in membrane biofouling process.

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 %

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%

降低結垢的控制方法

Table 2.8 Treatment methods for controlling fouling

Foulant	Fouling control
General	Hydrodynamics/shear, operation below critical flux, chemical cleaning
Inorganic (scaling)	Operate below solubility limit, pretreatment, reduce pH to 4–6 (acid addition), low recovery, additives (antiscalants).
	Some metals can be oxidised with oxygen
Organics	Pretreatment using biological processes, activated carbon, ion exchange (e.g. MIEX), ozone, enhanced coagulation
Colloids (<0.5 μm)	Pretreatment using coagulation and filtration, MF, UF
Biological solids	Pretreatment using disinfection (e.g. chlorination/dechlorination), filtration, coagulation, MF, UF

Source: Schafer et al.

RO/NF 清洗

Table 2.13 Cleaning methods for RO and NF membrane systems

Foulant	Example	Chemical cleaner
Scale (pH adjustment and/or scale inhibitor)	$CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, SiO_2	Citric acid, 0.2% (wt.) HCl, 0.5% (wt.) phosphoric acid, or EDTA-based solution; Clean silicate-based foulants with ammonium bifluoride-based solutions
Colloidal clays/silt (filtration and/or charge stabilisation)	SiO_2, $Fe(OH)_3$, $Al(OH)_3$, $FeSiO_3$	EDTA- or BIZ-type detergents at high pH; Clean silicate-based foulants with ammonium-bifluoride-based solutions
Biological (sodium bisulphite addition or chlorination)	Iron-reducing bacteria, sulphur-reducing bacteria, mycobacteria, pseudomonas	EDTA- or BIZ-type detergents at high pH; Shock disinfection with hydrogen peroxide, peracetic acid
Organic (filtration)	Polyelectrolytes, oil, grease	Detergents/surfactants, isopropanol

Source: Amjad, Reverse Osmosis, 1993

Silica

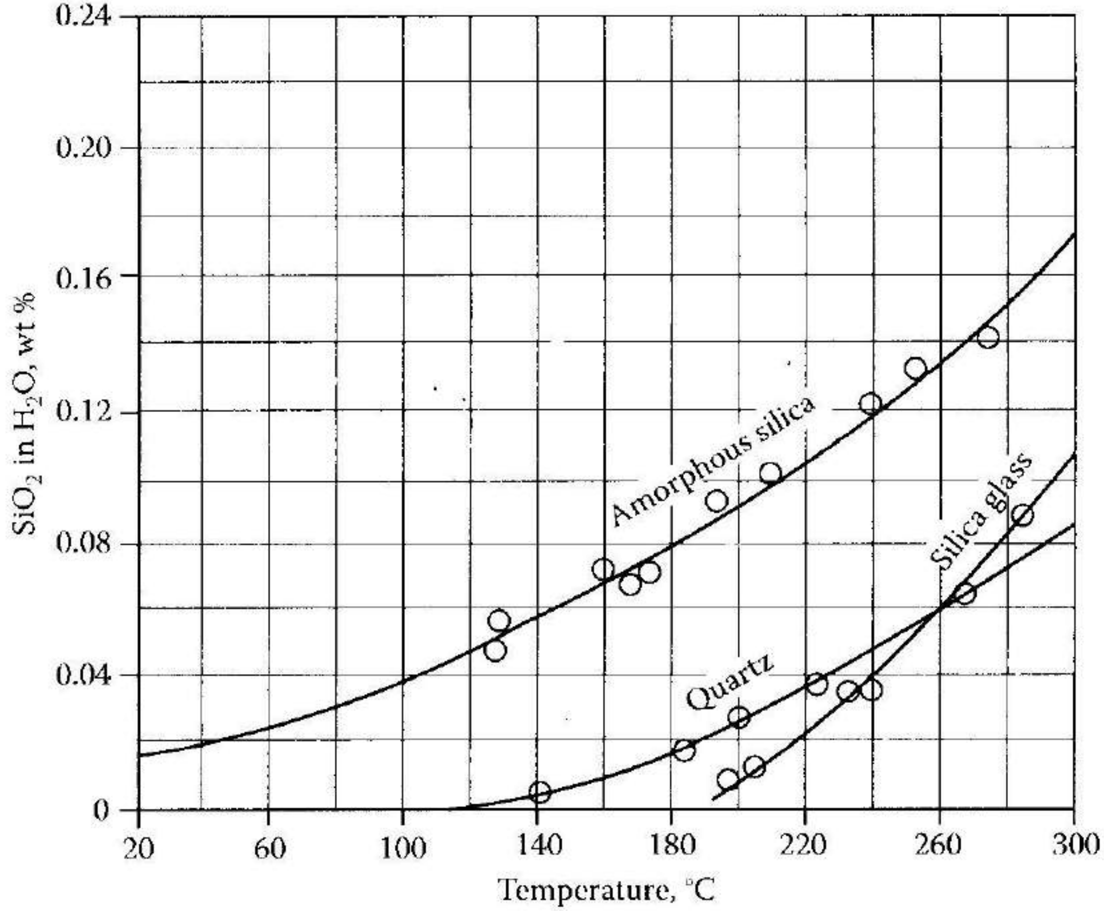
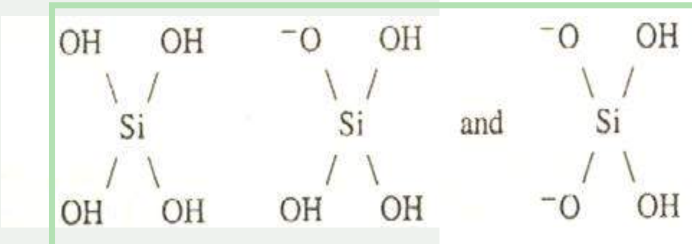
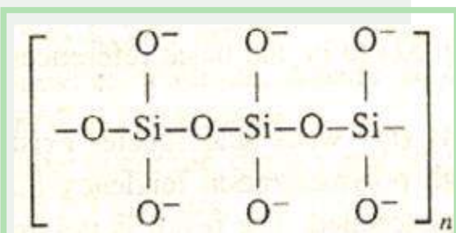
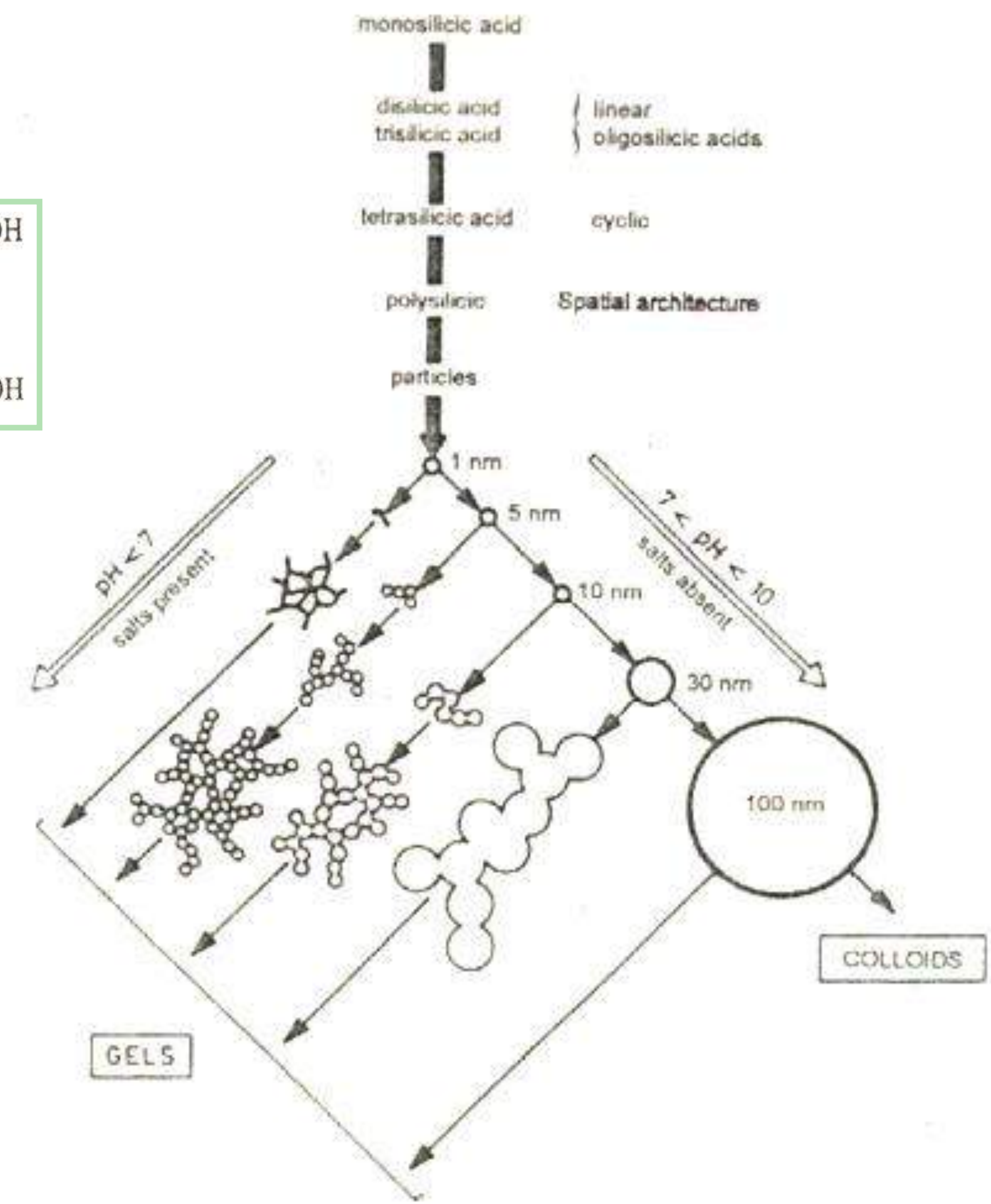


FIGURE 10.3 Dependence of different forms of silica solubility on temperature.

silica


and




monosilicic acid
disilicic acid
trisilicic acid
linear
oligosilicic acids
tetrasilicic acid
cyclic
polysilicic
Spatial architecture
particles
1 nm
5 nm
10 nm
30 nm
100 nm
pH < 7
salts present
7 < pH < 10
salts absent
GELS
COLLOIDS

silica

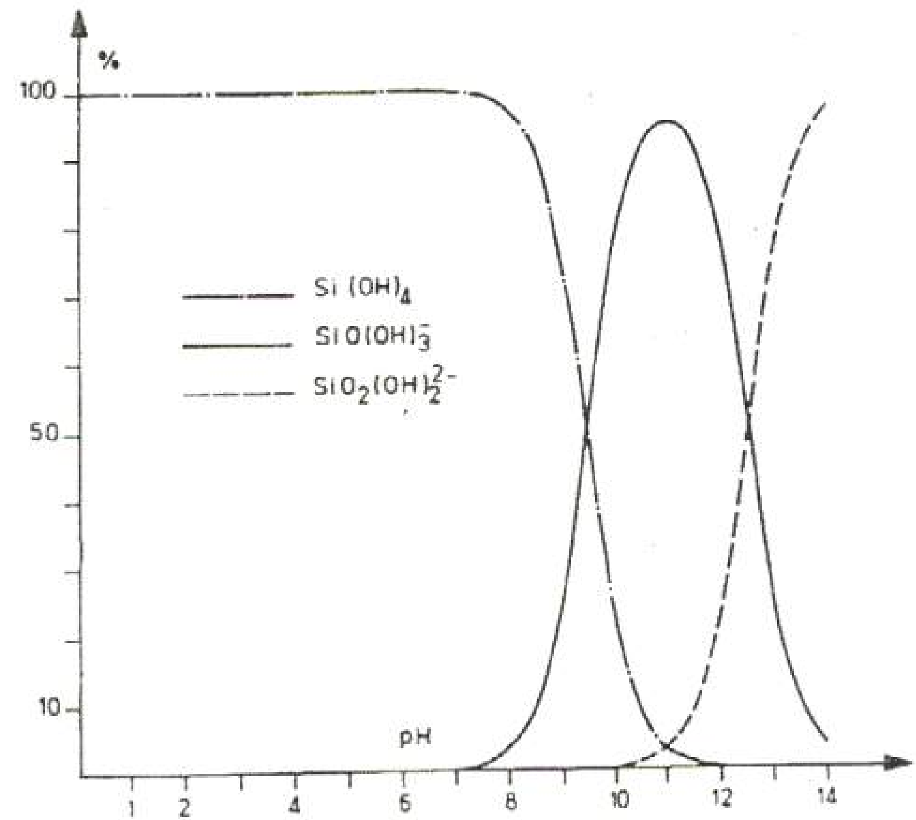


Figure 8.3 Silicon partitioning as a function of pH among orthosilicic acid and its various ionization products.

39

Silica

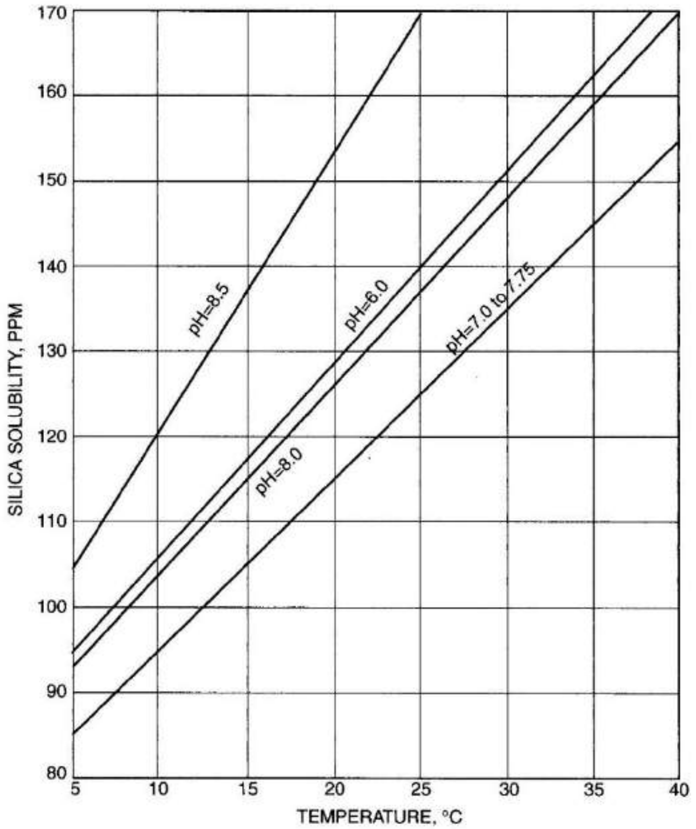


Figure 5.13 Silica solubility plot. Source: Amjad, Reverse Osmosis, 1993

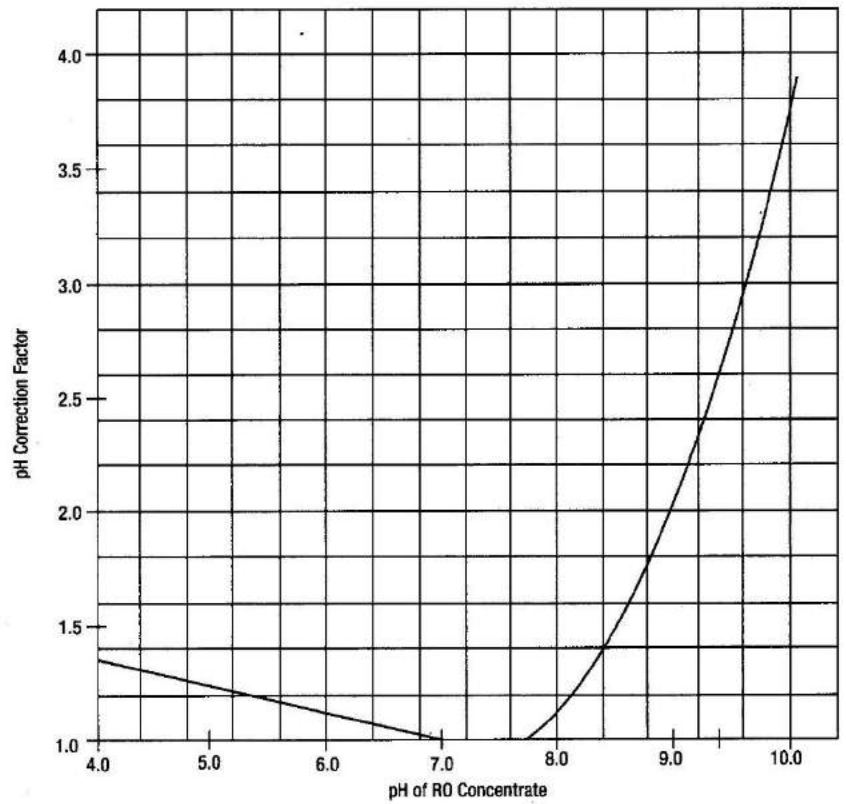


Figure 7.2 Silica solubility as a function of pH. To determine silica solubility at a given pH, multiply the solubility as a function of temperature by the pH correction factor of the given pH of the concentrate solution.

電透析

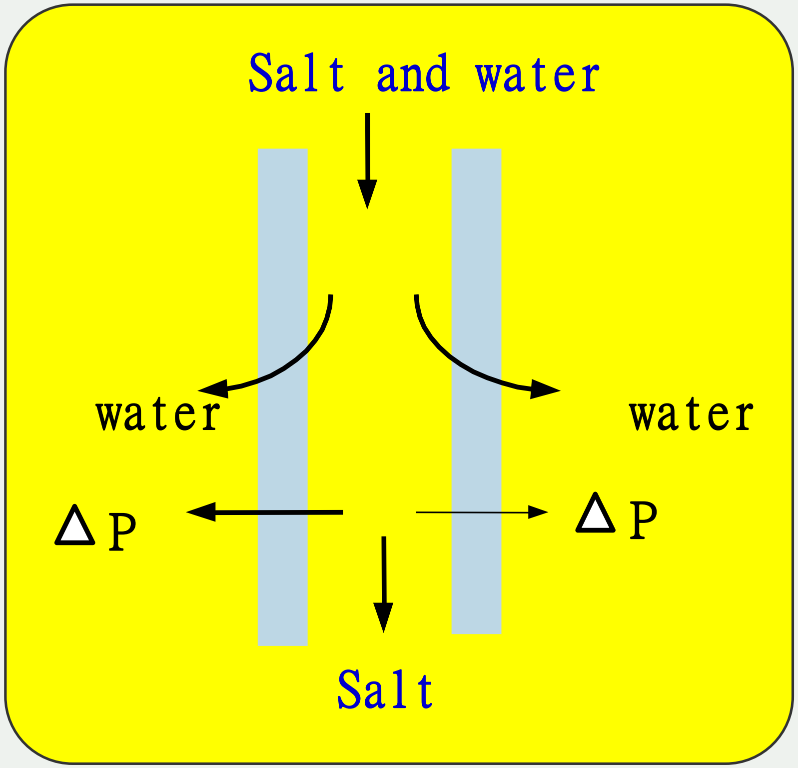
電透析(electrodialysis，ED)

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

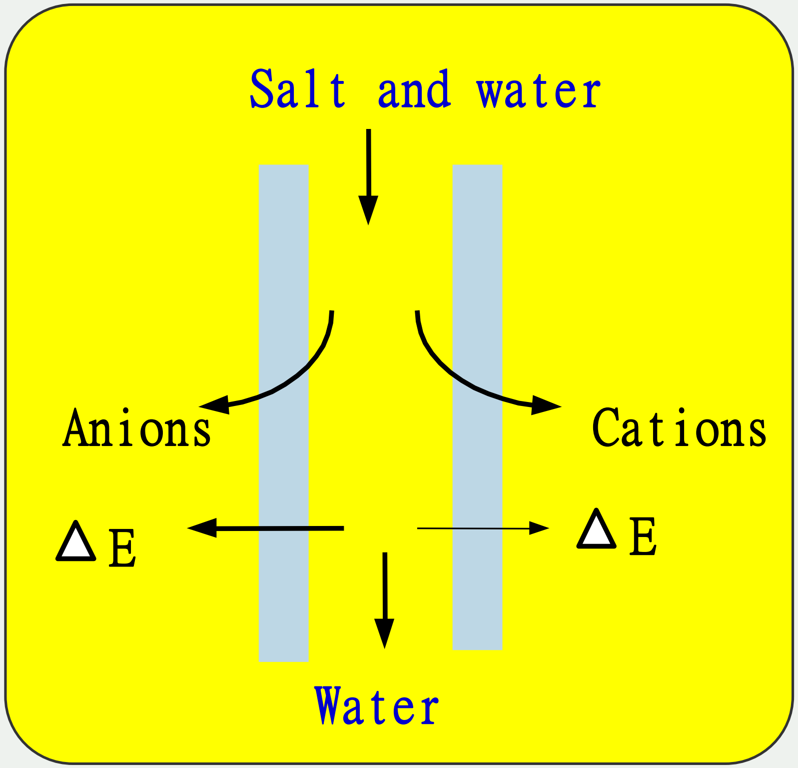
倒極式電透析(electrodialysis reversal，EDR)

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

分離機制



Reverse Osmosis



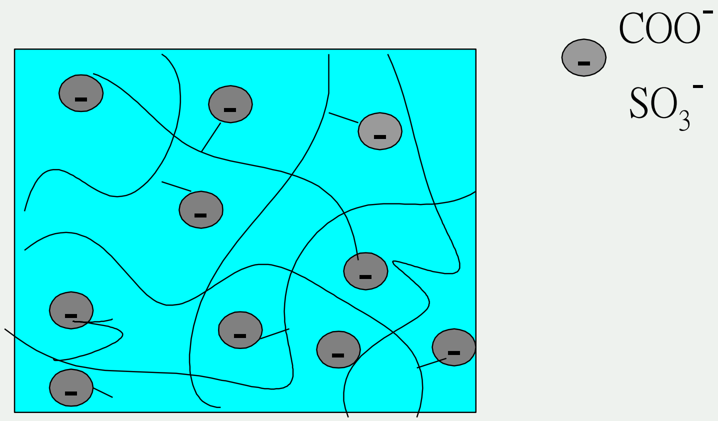
Electrodialysis

離子交換膜的分類

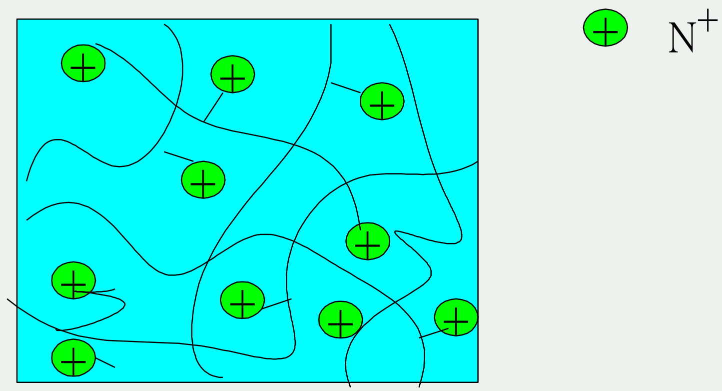
膜中所含官能基的種類

(1)陽離子交換膜：含酸性官能基的膜，如強酸性磺酸型。

(2)陰離子交換膜：含鹼性官能基的膜，如強鹼性季銨型。



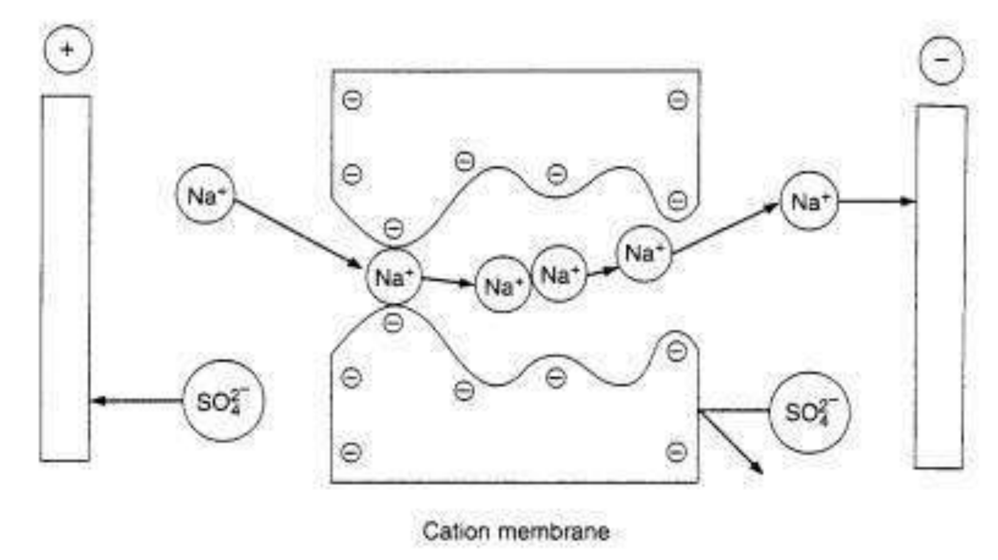
Cation exchange membrane



Anion exchange membrane

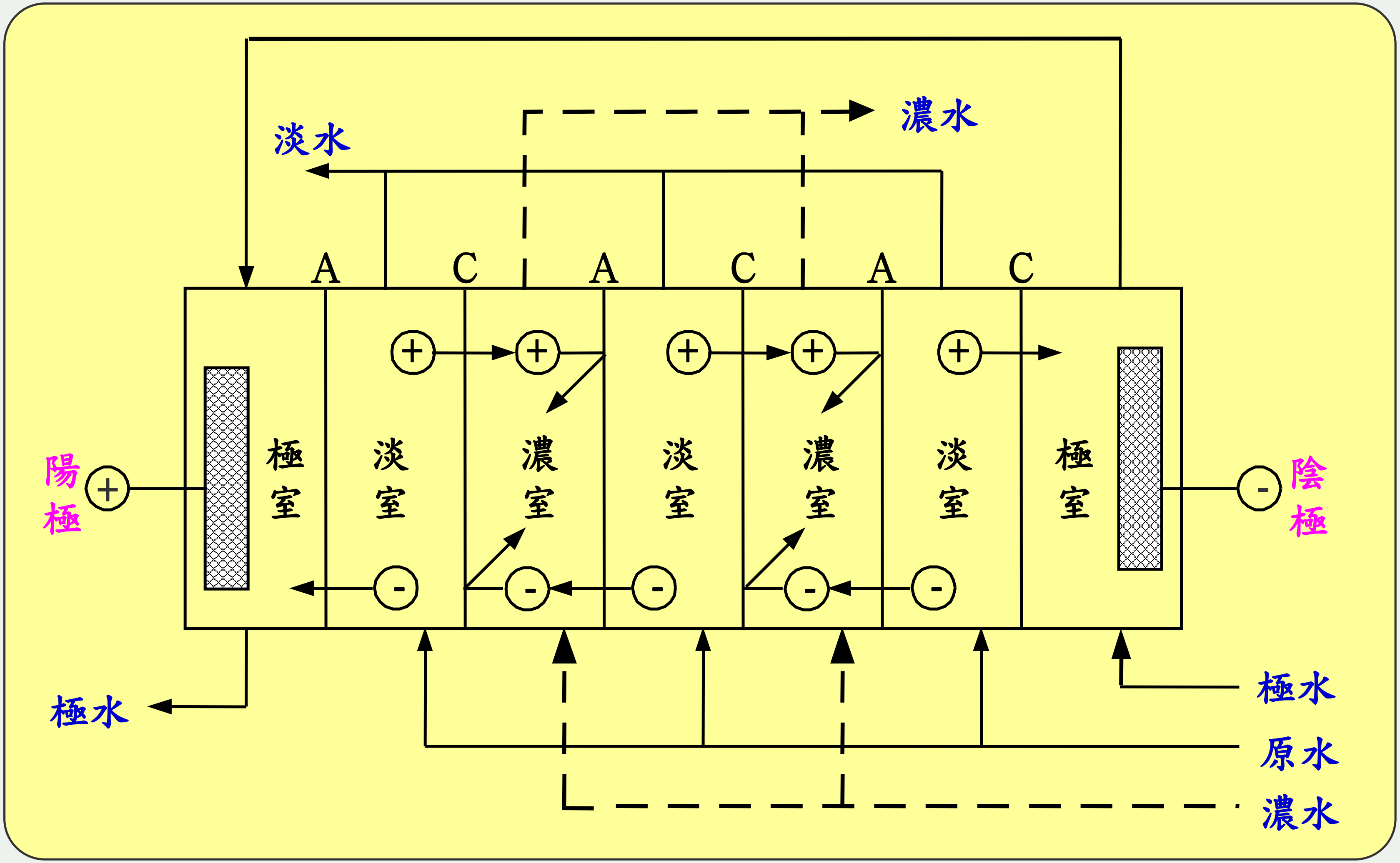
電透析法脫鹽原理

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

電透析模組示意



A：陰離子交換膜　　C：陽離子交換膜

樹脂處理

樹脂結構示意

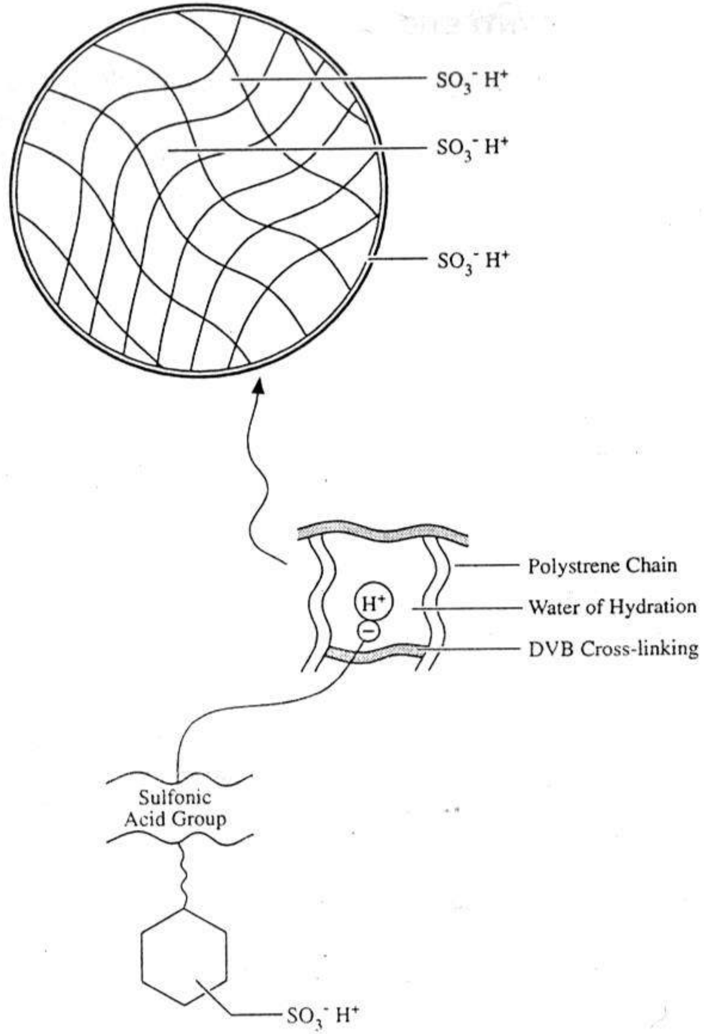
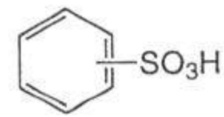
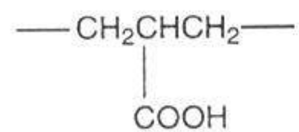
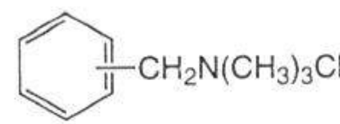
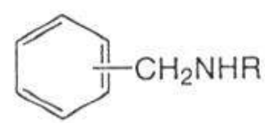
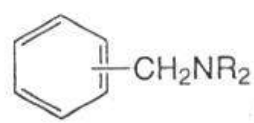


Figure 3-3 Cation exchange resin — strongly acidic (hydrated).

樹脂分類

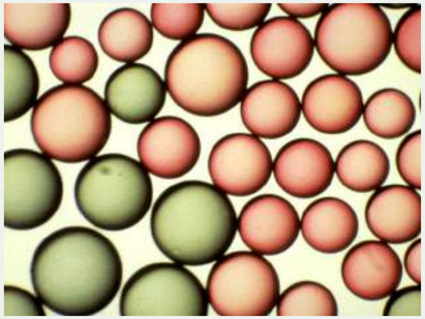
Table 3-1 Classification of the Major Ion Exchange Resins

Type	Active group	Typical configuration
Cation Exchange Resins		
Strong acid	Sulfonic acid	
Weak acid	Carboxylic acid	
Anion Exchange Resins		
Strong base	Quaternary ammonium	
Weak base	Secondary amine	
Weak base	Tertiary amine (aromatic matrix)	

離子交換樹脂之去離子原理

陽離子交換樹脂

$$R\text{-}SO_3^{-}H^{+} + Na^{+} \longrightarrow R - SO_3^{-}Na^{+} + H^{+}$$



$$H_2O$$

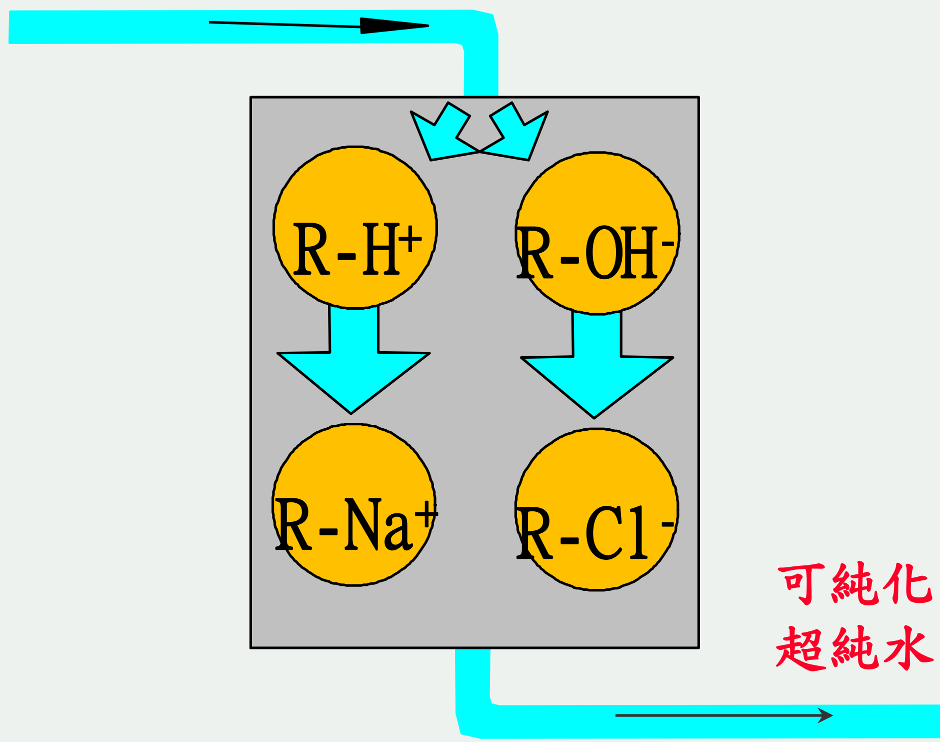
$$R - NH_4^{+}OH^{-} + Cl^{-} \longrightarrow R - NH\ Cl^{-} + OH^{-}$$

陰離子交換樹脂

資料來源: Millipore Corporation
Laboratory Water Division

混床式離子交換方式

$Na^+ + Cl^-$

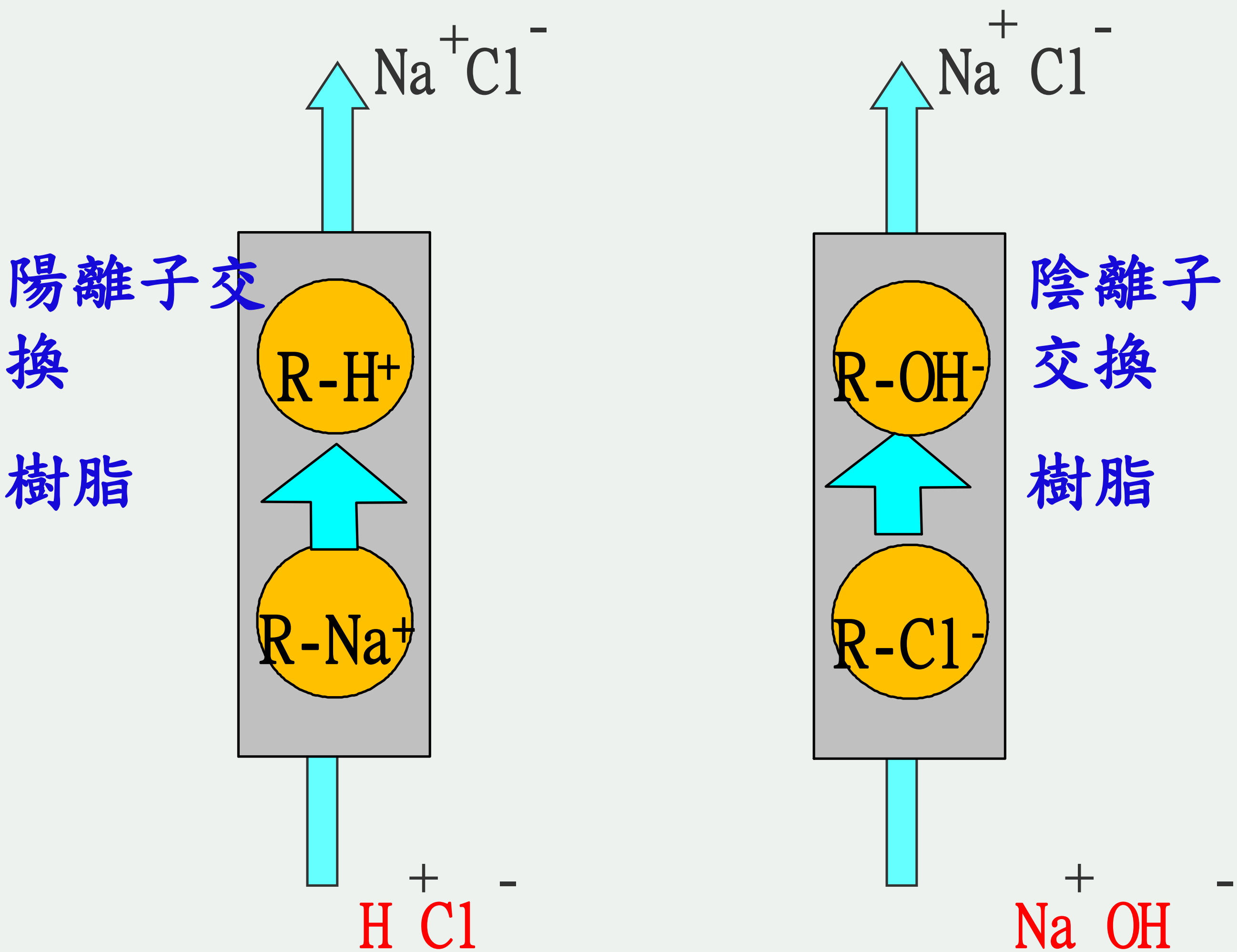


可純化出 18.2 Megohm.cm 之超純水

$$H^+ + OH^- = H_2O$$

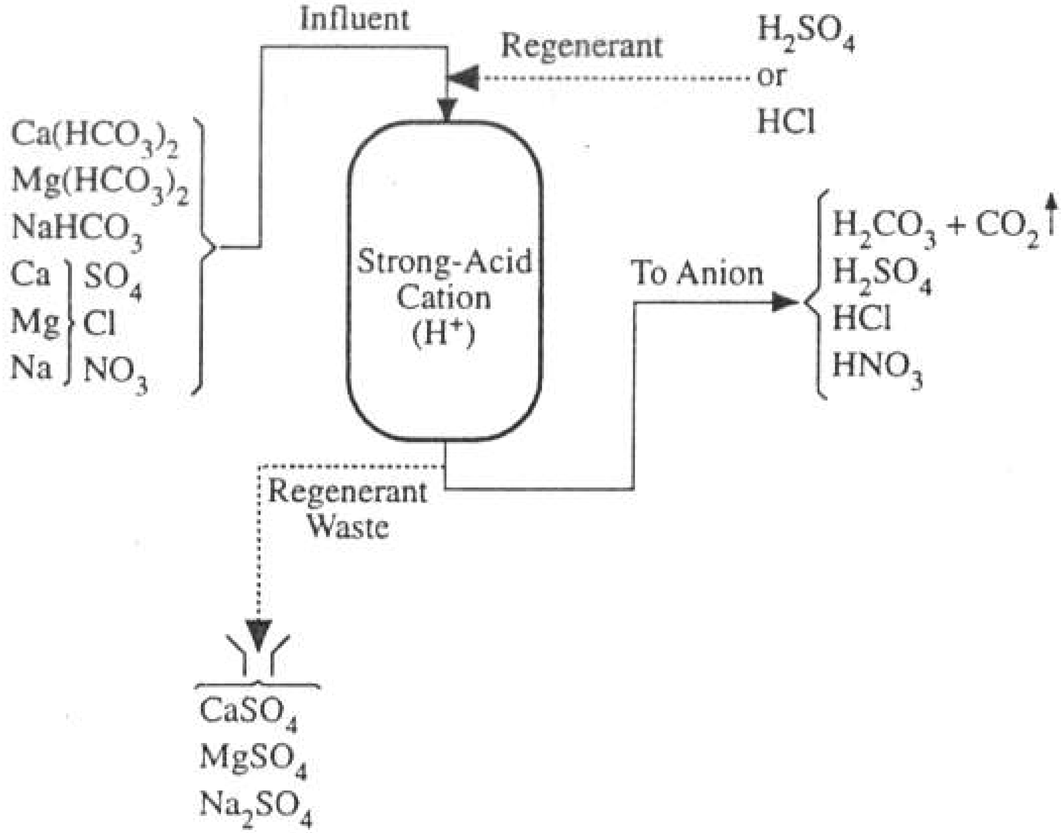
資料來源: Millipore Corporation
Laboratory Water Division

強酸/鹼化學樹脂再生



資料來源: Millipore Corporation
Laboratory Water Division

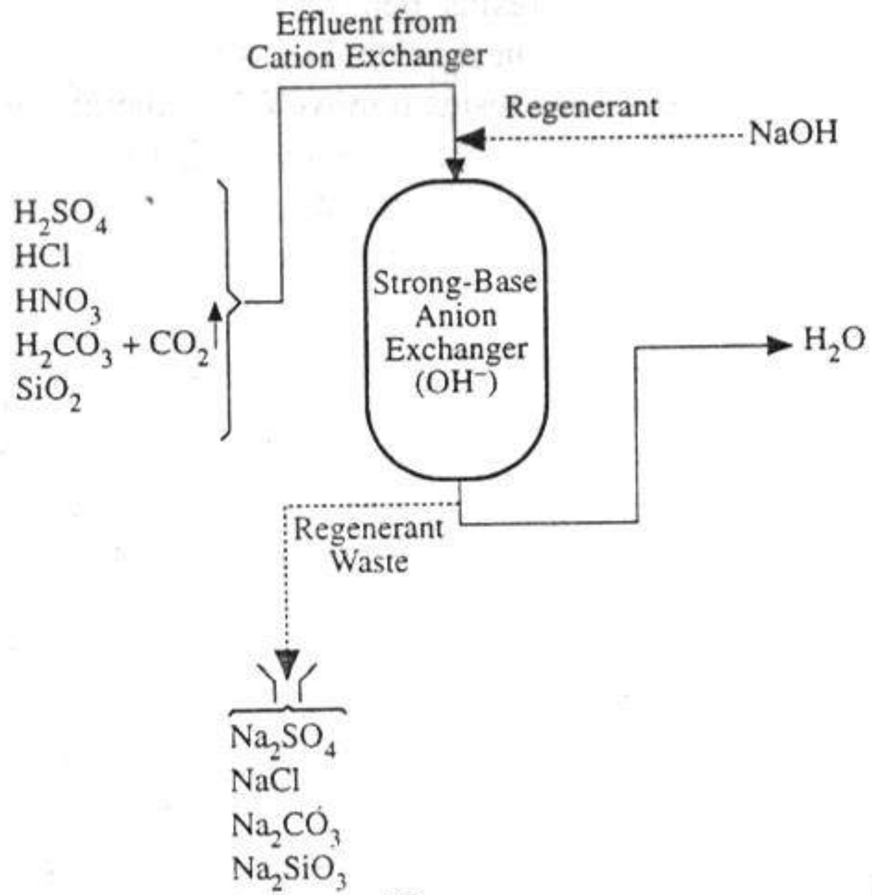
強酸型樹脂反應機制



Regeneration: $$R\left\{\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right. + H_2SO_4 \rightleftharpoons RH_2 + \left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}SO_4$$

Figure 3-4 Hydrogen-cycle strong-acid cation exchange.

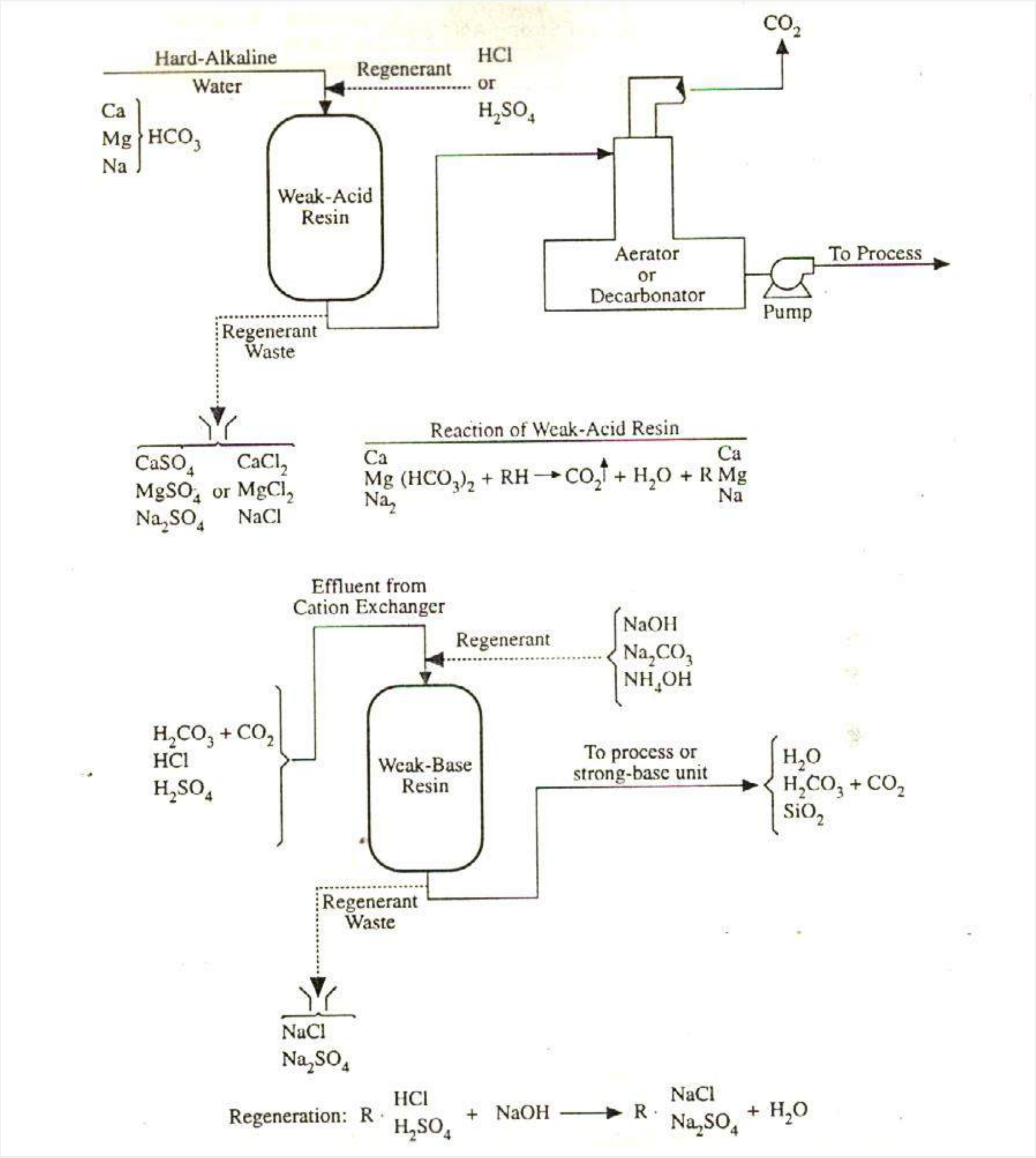
強鹼型樹脂反應機制



$$\text{Regeneration:}\quad R\begin{matrix} SO_4 \\ Cl \\ CO_3 \\ SiO_3 \end{matrix} + NaOH \rightleftharpoons R\cdot OH + \begin{matrix} Na_2SO_4 \\ NaCl \\ Na_2CO_3 \\ Na_2SiO_3 \end{matrix}$$

Figure 3-6 Strong-base ion exchange reactions.

弱酸/弱鹼型樹脂反應機制



樹脂塔操作貫穿曲線

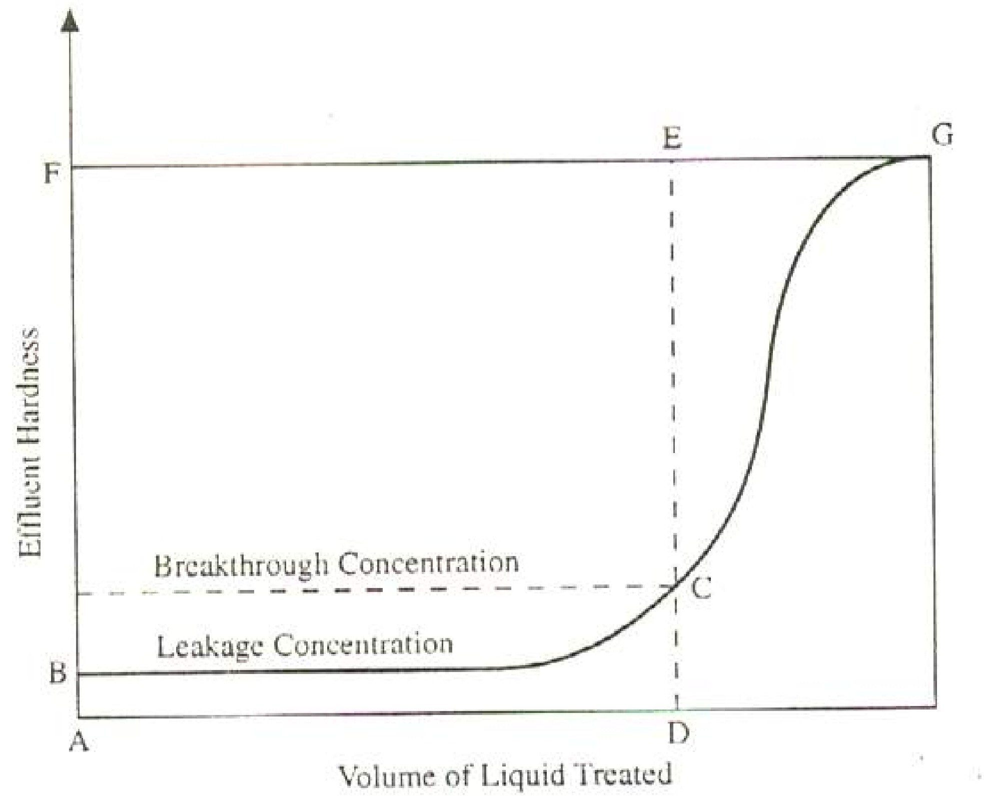


Figure 3-10 Typical breakthrough curve for an ion exchange process.

混床樹脂塔內部示意圖

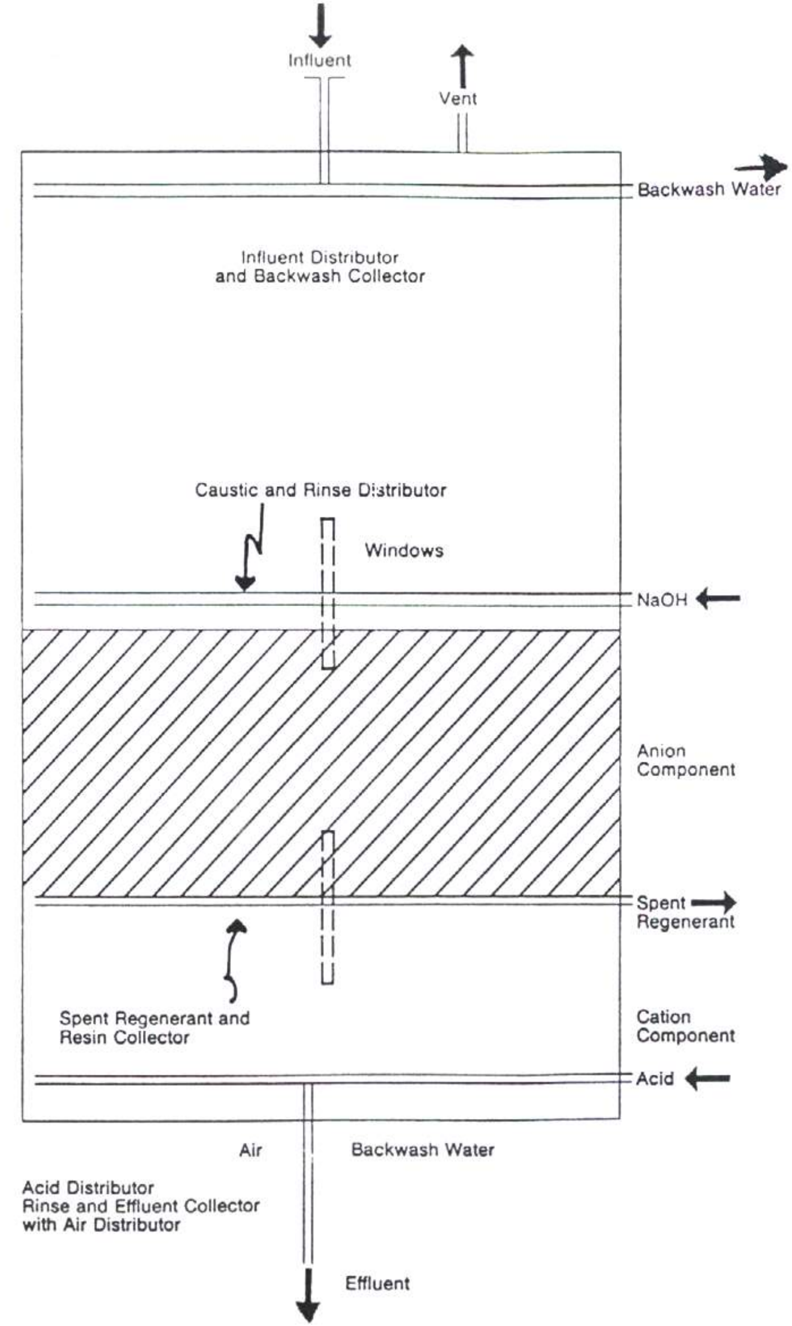


Figure 8-7. Illustrative diagram of a mixed bed.
McGarvey, (1990-A); Courtesy, Semiconductor Pure Water Conference

混床樹脂塔操作示意圖

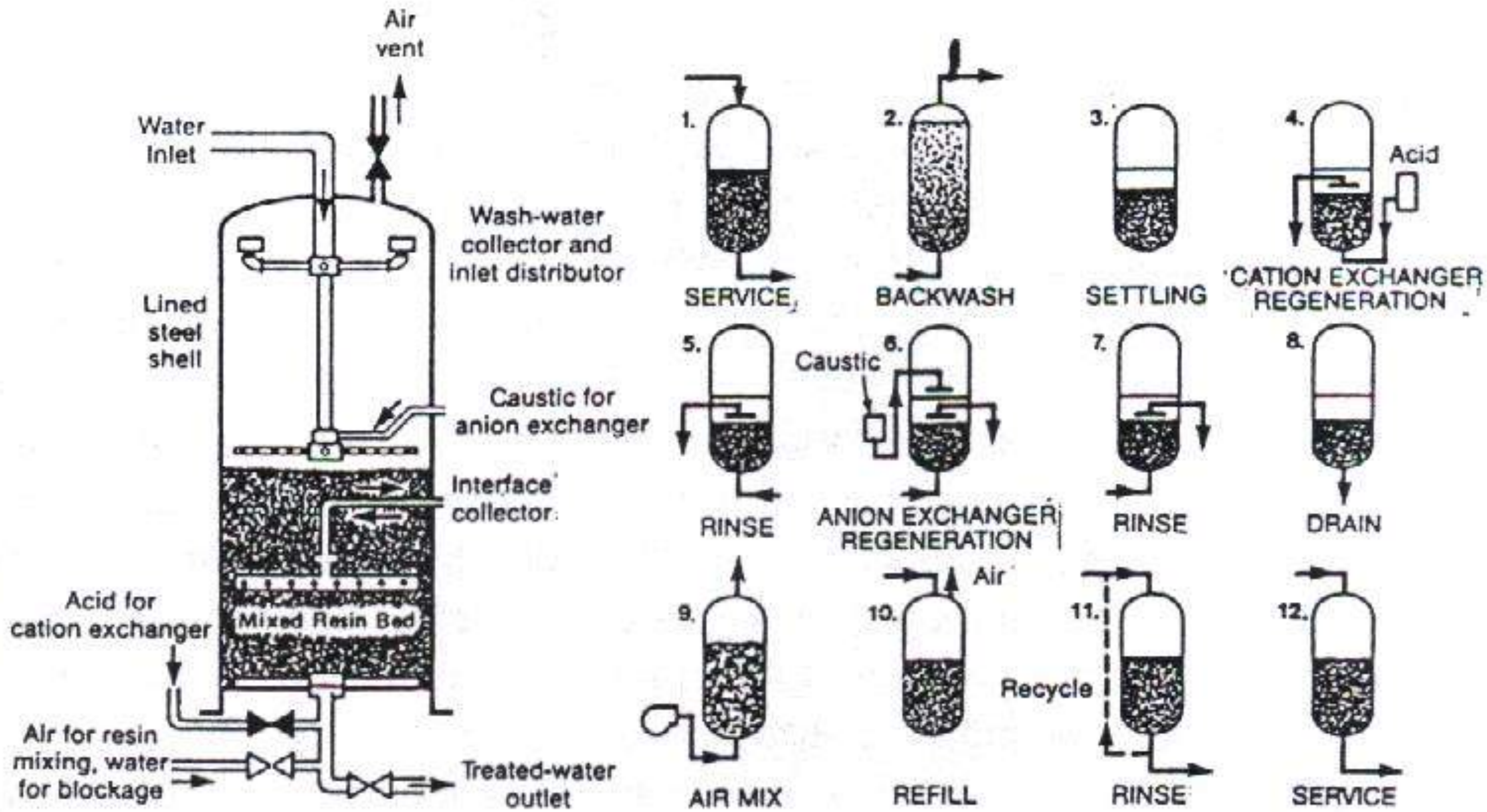


Figure 8-10. Mixed bed regeneration protocol.
Courtesy, Dr. Robert Kunin

EDI

ED與樹脂結合

1. EDI 將離子交換樹脂充夾在陰/陽離子交換膜之間，將一定數量的EDI單元間用格板隔開，形成濃水室和淡水室。又在單元組兩端設置陰/陽電極。EDI純水電阻率可以高達18.2MΩ.cm(25℃)。

2. 進水電導度在4-30us／cm，離子交換樹脂不需酸、鹼化學再生，節約大量酸、鹼和清洗用水。無廢酸、廢鹼液排放。

EDI內部示意圖

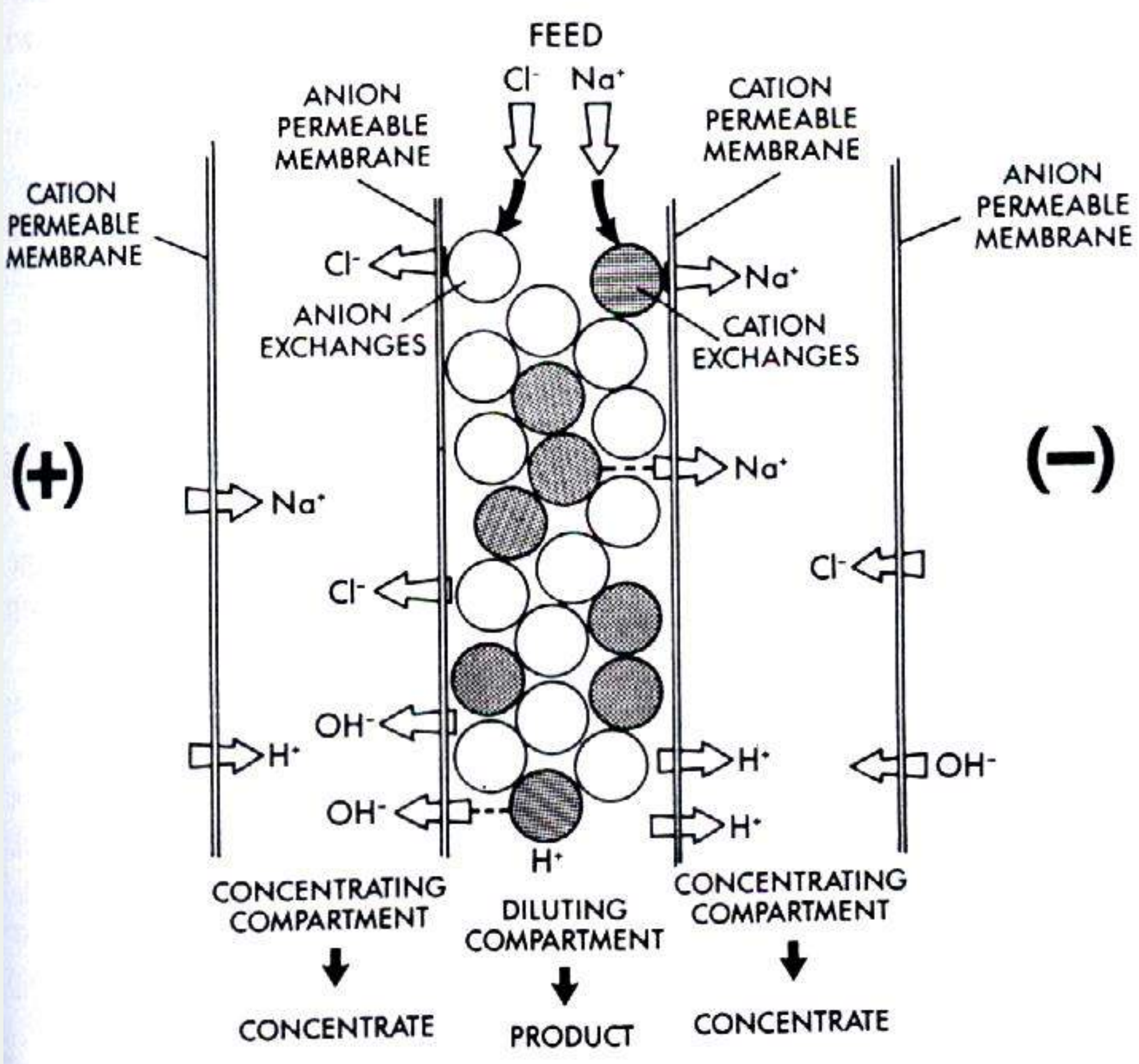


Figure 9-9. Principle of continuous deionization.
Ganzi et al., (1987); Courtesy, *Ultrapure Water* journal

半導體級樹脂

- 此樹脂為做為純水或超純水系統後段之離子交換，內含陰陽樹脂，又稱為不再生樹脂，做為最後超純水之比電阻提升，但此等級較核子級樹脂之等級高，若有TOC要求通常使用此等級

ROHM HAAS

AMBERJET® UP6040

Semi-Conductor Grade Final Polishing Mixed Bed Resin

	Cation H^+	*Anion OH^-*
Moisture holding capacity, %	44.0 - 51.0	54.0 - 60.0
Total exchange capacity, eq/L	≥ 2.00	≥ 1.10
Uniformity coefficient	≤ 1.20	≤ 1.20
H form % of sites	≥ 99	-
OH form % of sites	-	≥ 95.0
Cl form, % of sites	-	≤ 0.5
CO_3 form % of sites	-	≤ 5.0
SO_4 form % of sites	-	≤ 0.1

SUGGESTED OPERATING CONDITIONS FOR BEST RESULTS

(Product may be operated successfully outside these conditions, but results may not be optimum)

Feed water temperature	15 to 25°C (60 to 77° F)
Minimum bed depth	900 mm (3 feet)
Service flow rate	30 to 50 BV*/h
Recommended *influent* water quality	
Inlet Resistivity	> 17 MΩ·cm
Inlet Silica	< 2 ppb
Inlet Total Organic Carbon	< 15 ppb

** 1 BV (Bed Volume) = 1 m^3 solution per m^3 resin (1BV/h = 0.125 gpm/ft^3)*

核子級樹脂

- 此樹脂為做為純水或超純水系統後段之離子交換，內含陰陽樹脂，又稱為不再生樹脂，做為最後超純水之比電阻提升

Specification

Type		Strongly Acidic Cation Gel Type	Strongly Basic Anion Gel Type
Matrix		Polystyrene + DVB (Divinyl Benzene)	
Ionic Form		H^+	OH^-
Shipping Weight (g/L)		695	
Total Capacity		1.9 eq/L ↑	1.0 eq/L ↑
Moisture Contents (%)		52 ± 5	63 ± 5
Uniformity Coefficient		≤ 1.1	≤ 1.1
Particle Size (mm)		630 ± 50	590 ± 50
Ionic Conversion%	H form	99.0 Min	
	OH form		95.0 Min
Mixed Ratio (%)		1:1 (by equivalents) Cation : Anion	
Operating Temperature		60 ℃ Max	

HYDROLUX

We are experts on liquid purification

Suggested Operating Conditions

Feed water temperature	15 to 25°C
Minimum bed depth	900 mm
Service flow rate	30 to 50 BV*/h
Recommended *influent* water quality	
Inlet Resistivity	> 17 MΩ·cm
Inlet Silica	< 2 ppb
Inlet Total Organic Carbon	< 15 ppb

* 1 BV (Bed Volume) = 1 m3 solution per m3 resin

活性碳吸附


Coconut Shell
Coconut Shell Charcoal
Coconut Shell Activated Carbon
Oil Palm Shell
Oil Palm Shell Charcoal
Oil Palm Shell Activated Carbon
PACKING
Our Activated Carbon are mostly packed in 500kg Bulk Bags and 25kg PP Woven Bags with inner PE Liners. However other forms of packing can also be arranged.

活性碳

活性碳是將碳原料經過特別處理而得，其來源大多取自石油產物、煤礦或木材原料。在製造過程中，先將碳原料進行壓碎處理，再以500～800°F(260～582℃)的高溫加熱(活化處理)，使碳產生大大小小的孔隙，這些大小孔隙稱為大孔及微孔。經過這些過程處理主要有兩個目的：一為增加碳的總表面積；另一目的則為使其產生散佈均勻的大大小小孔隙，以增加活性碳吸附、去除污染物的種類及能力。

活性碳規格指標

- 材料
- 吸附表面積(BET)
- 碘值
- 糖蜜值
- 硬度
- 磨損率
- 尺寸

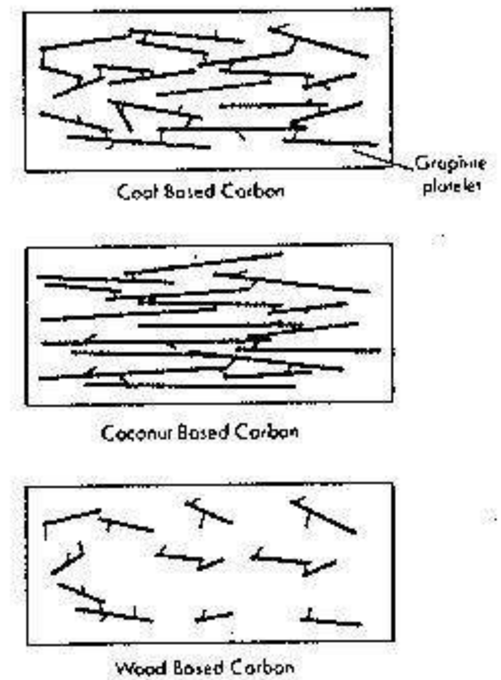


Figure 1 · Molecular structure of activated carbons produced from different raw materials

活性碳尺寸規格

STANDARD MESHOPENING PARTICLE

Tyler	U.S.	mm	inches
4	4	4.75	0.187
6	6	3.35	0.132
8	8	2.36	0.094
10	12	1.70	0.066
12	14	1.40	0.056
14	16	1.18	0.047
16	18	1.00	0.039
20	20	0.85	0.033
24	25	0.71	0.028

活性碳規格

Table 1. Properties of Typical Granular Activated Carbons

	Type A	Type B	Type C	Type D
Physical Properties				
Surface area, m^3/g (BET)	600–630	950–1050	1000	1050
Apparent density, g/cm^3	0.43	0.48	0.48	0.48
Density, backwashed and drained, lb/ft^3	22	26	26	30
Real density, g/cm^3	—	2.1	2.1	2.1
Particle density, g/cm^3	2.0	1.3–1.4	1.4	0.92
Effective size, mm	1.4–1.5	0.8–0.9	0.85–1.05	0.89
Uniformity coefficient	0.8–0.9	1.9	1.8	1.44
Pore volume, cm^3/g	1.7	0.85	0.85	0.60
Mean particle diameter, mm	1.6	1.5–1.7	1.5–1.7	1.2
Specifications				
Sieve size, U.S. std. series				
Larger than No. 8 max. percentage	8	8	8	—
Larger than No. 12 max. percentage	—	—	—	5
Smaller than No. 30 max. percentage	5	5	5	—
Smaller than No. 40 max. percentage	—	—	—	5
Iodine No.	650	900	950	1000
Abrasion No., minimum	—	70	70	85
Ash, percentage	—	8	7.5	0.5
Moisture as packed, max. percentage	—	2	2	1

— = Data not available.

活性碳床操作貫穿曲線

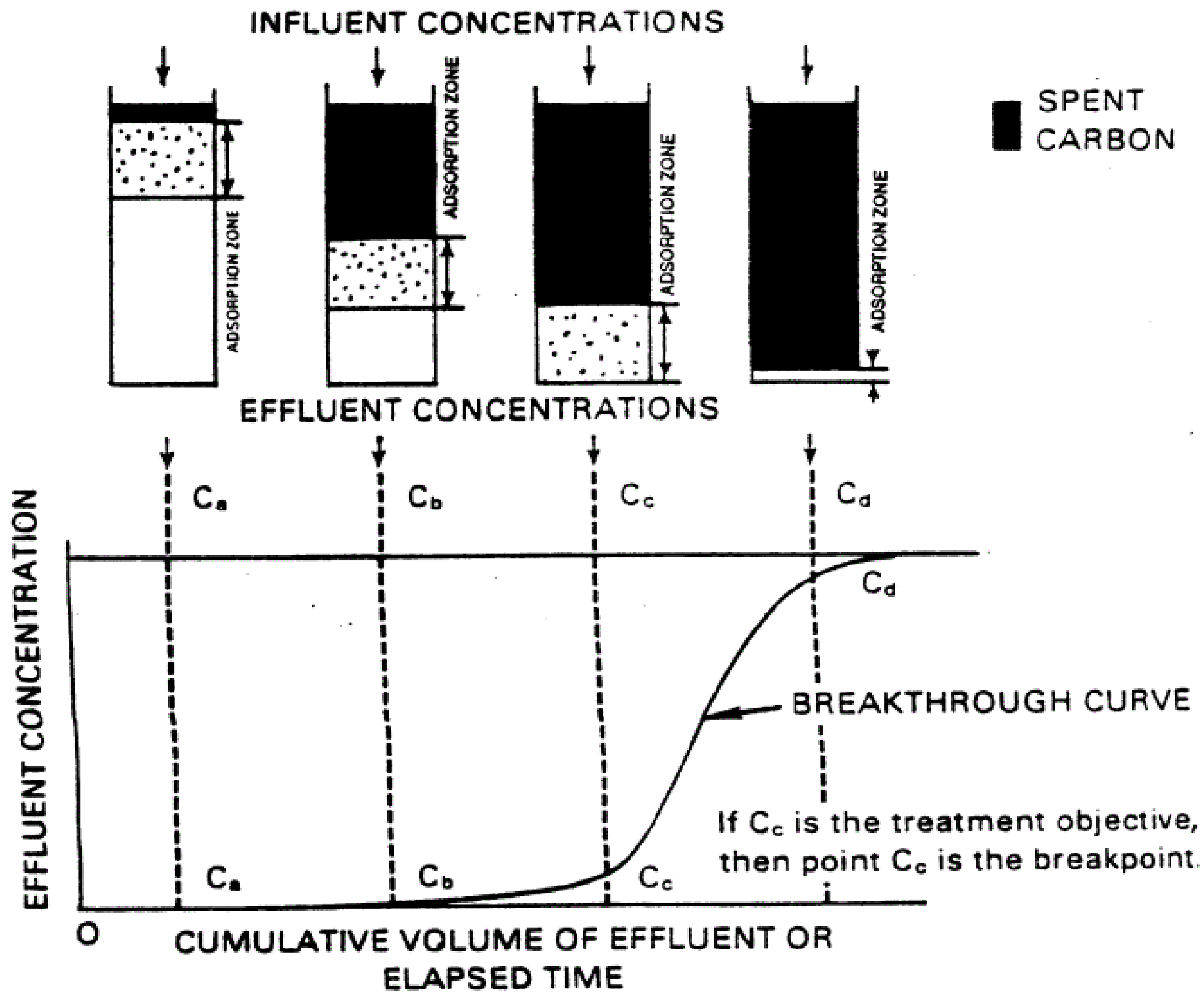


Figure 2. Passage of adsorption wave through a fixed bed and corresponding breakthrough curve.

活性碳床操作水力負荷與水頭損失

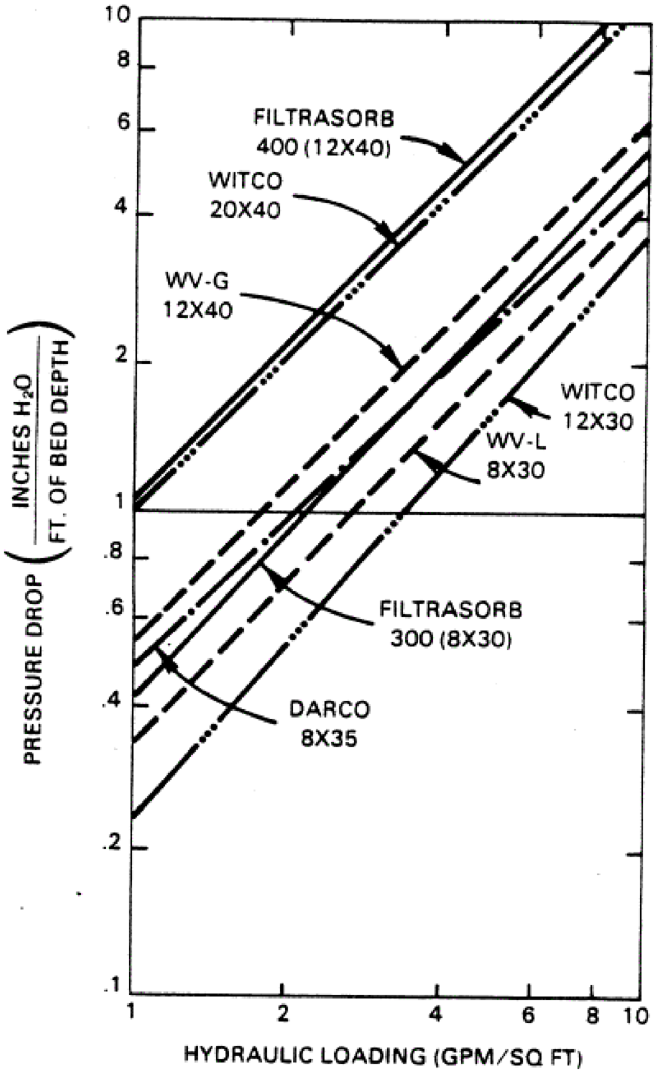


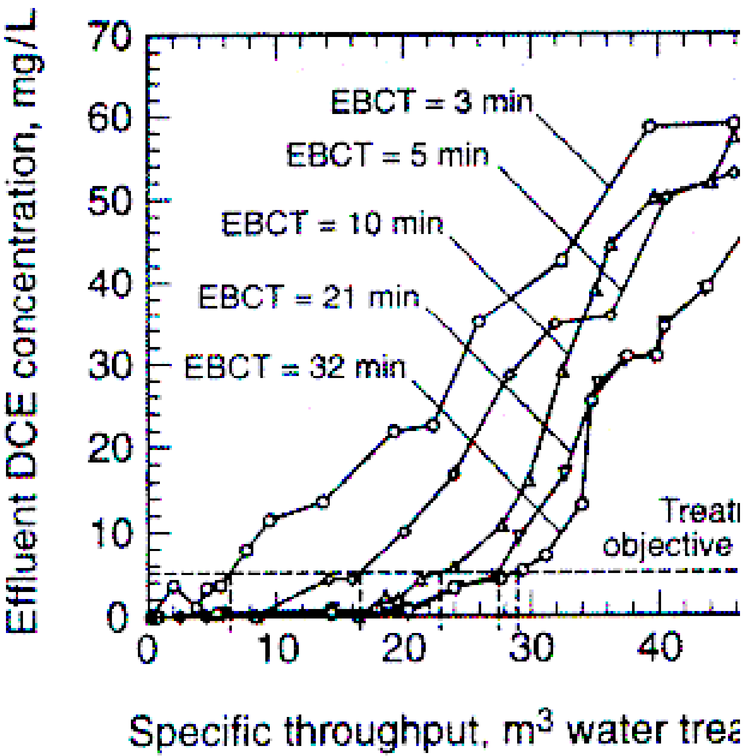
Figure 5. Carbon bed pressure drop vs hydraulic loading.

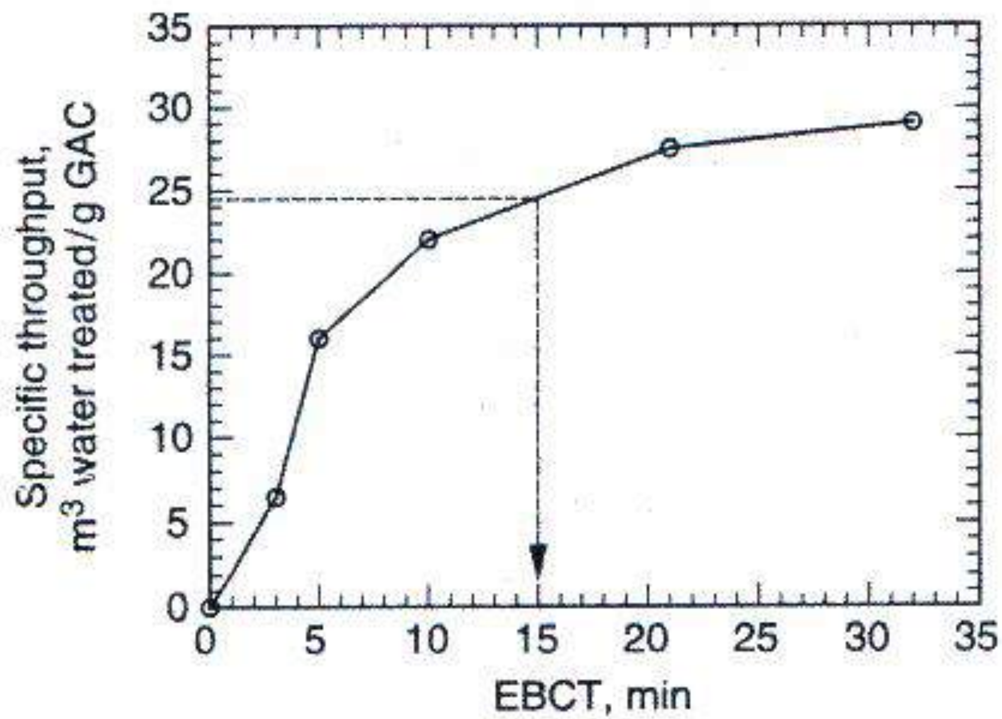
活性碳吸附停留時間與飽和時程

Table 8. GAC Exhaustion for Specific Organic Compounds Detected at Wausau, Wisconsin

Compound	Avg. GAC Influent Concentration (μg/L)	EBCT	Days to Saturation
cis-1,2-Dichloroethene	70.9	1.0	40
		3.1	60
		5.1	100
		10.4	200
		21.2	> 360
		32.2	> 360
Trichloroethene	47.9	1.0	70
		3.1	195
		5.1	> 360
		10.4	> 360
		21.2	> 360
		32.3	> 360
Tetrachloroethene	37.6	1.0	285
		3.1	360
		5.1	> 360
		10.4	> 360
		21.2	> 360
		32.3	> 360
Toluene	19.3	1.0	> 360
		3.1	> 360
		5.1	> 360
		10.4	> 360
		21.2	> 360
		32.3	> 360

活性碳床操作停留時間與處理參數





活性碳床操作貫穿曲線

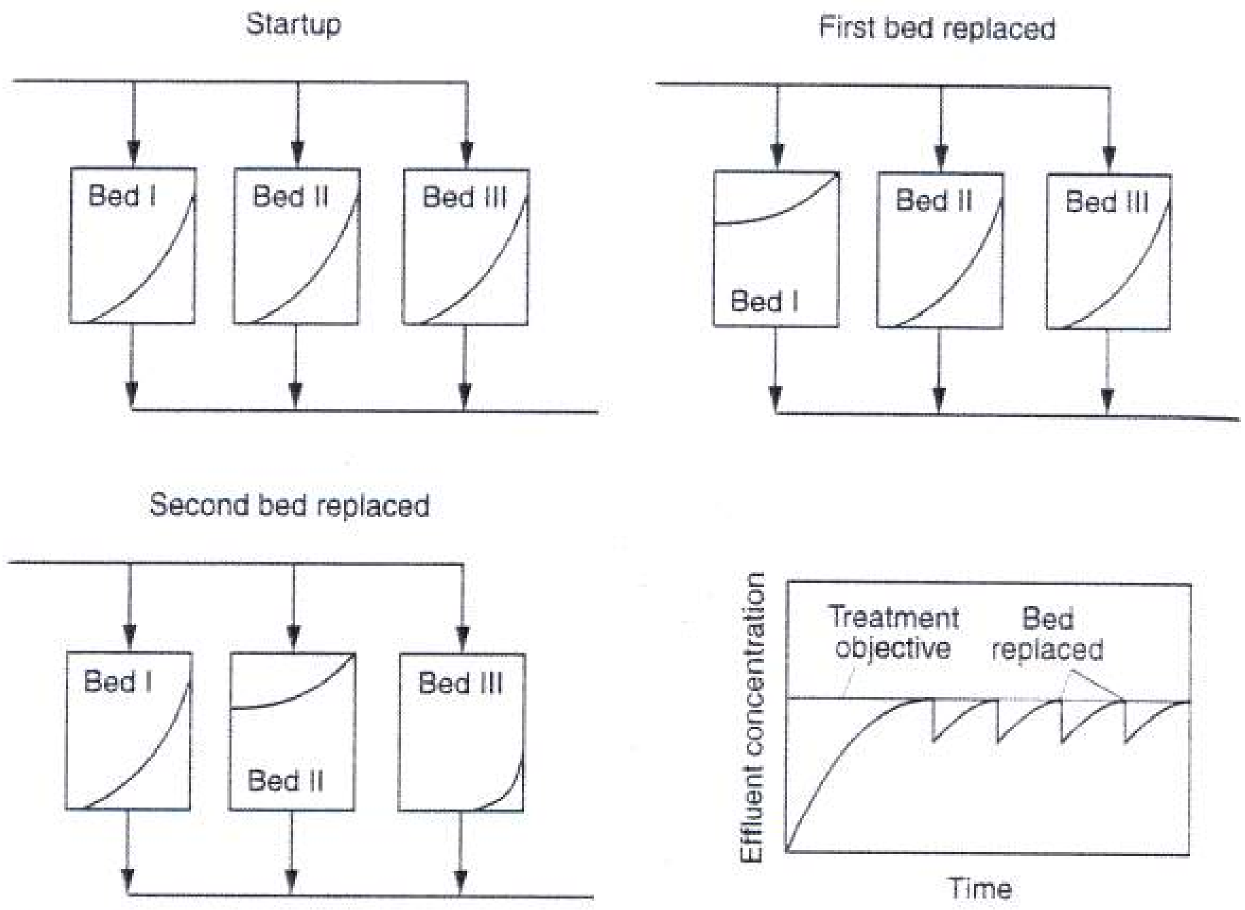
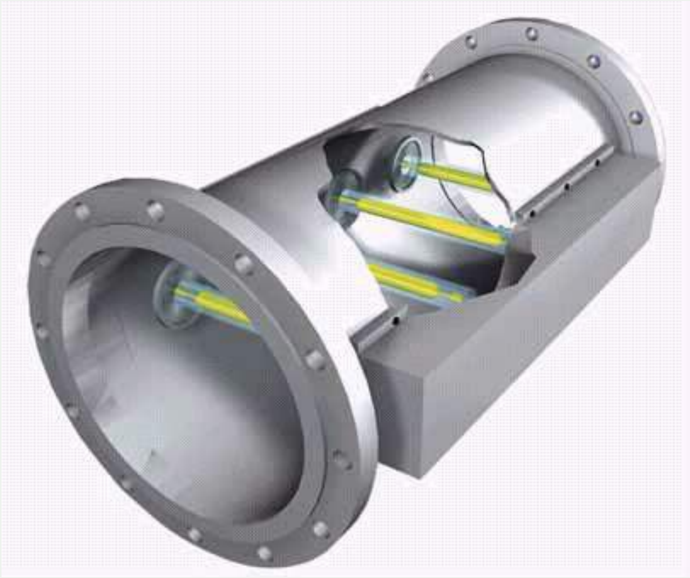
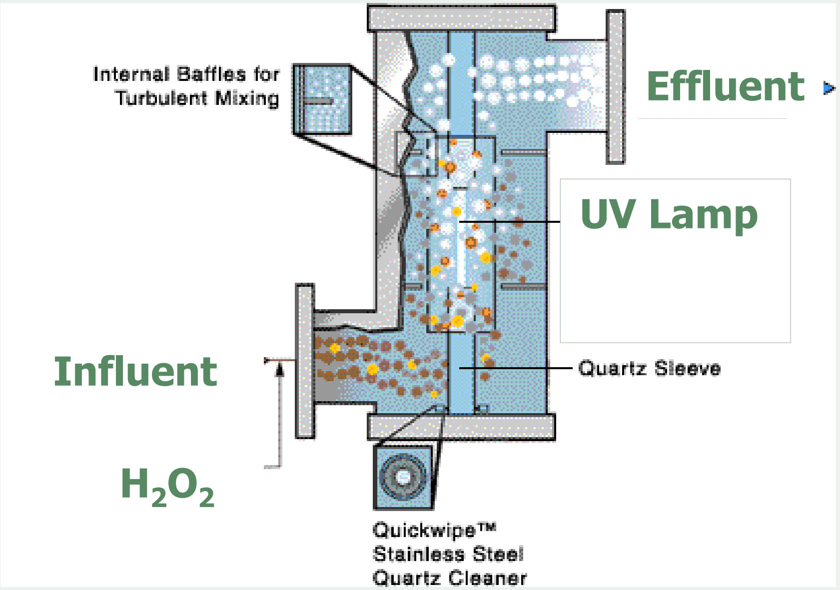


Figure 15-27
Operation of three beds in parallel.

UV 應用

UV 光應用





1. UV/H_2O_2 $H_2O_2 \xrightarrow{h\nu} 2 \bullet OH$ (λ < 300 nm)

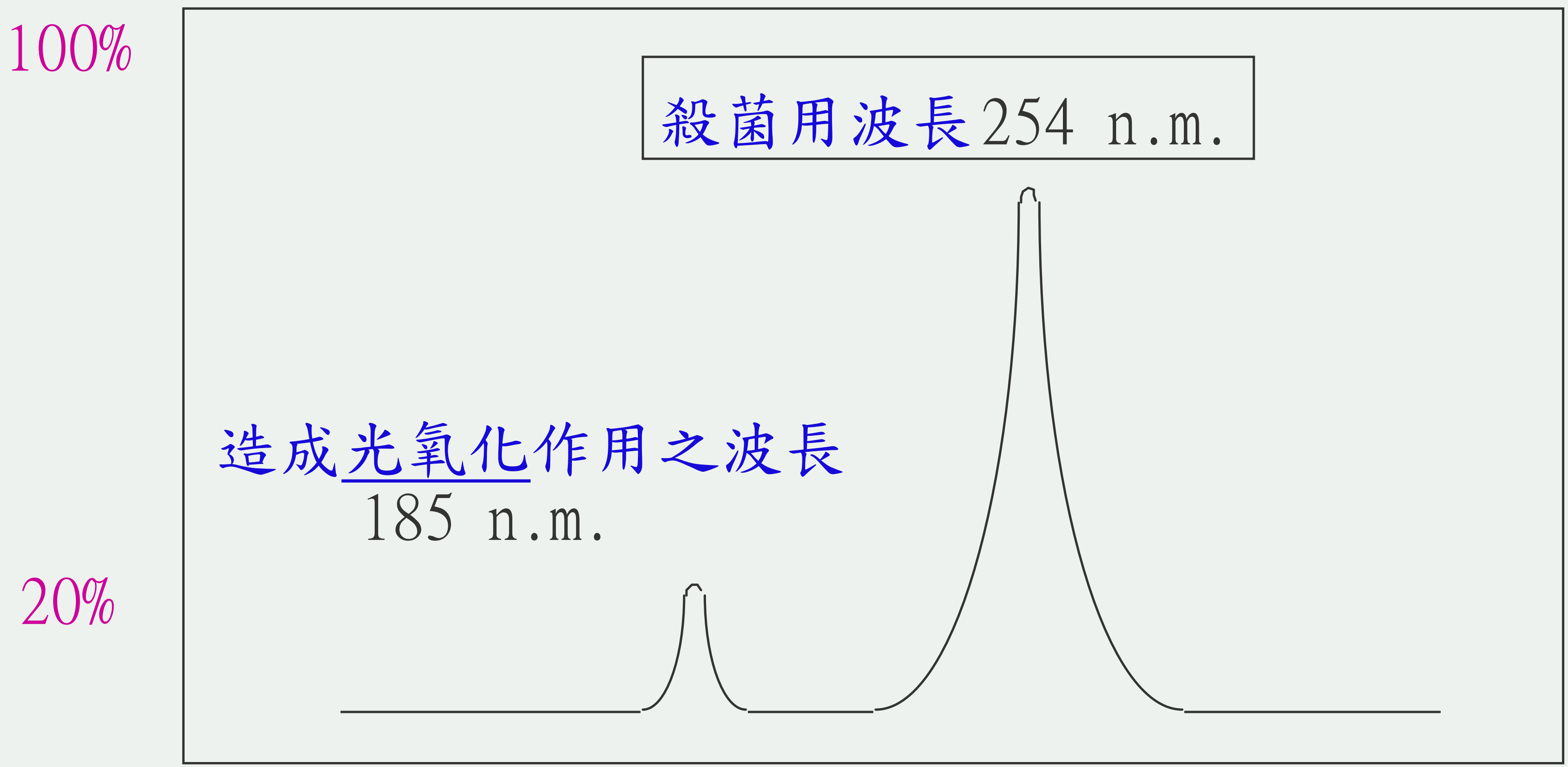
$\bullet OH$ + Pollutants → By-products

2. UV only (Photolysis) Pollutants $\xrightarrow{h\nu}$ By-products

資料來源: Sun Liang, Ph.D., P.E.The Metropolitan Water District of Southern California

紫外線波長

相對輻射強度%



波長 (n.m.)

資料來源: Millipore Corporation
Laboratory Water Division

紫外線波長對化學鍵結破壞能

TABLE 4-8
Dissociation Energies for Interatomic Bonds in Organic Substances

Bond	*Dissociation Energy*	*Maximum Wavelength for Dissociation*	*Possibility of Dissociation with184.9-nm UV(154kcal)*
C-C	82.6	346.1	yes
C=C	145.8	196.1	yes
C≡C	199.6	143.2	no
C-Cl	81.0	353.0	yes
C-F	116.0	246.5	yes
C-H	98.7	289.7	yes
C-N	72.8	392.7	yes
C=N	147.0	194.5	yes
C.N	212.6	134.5	no
C-O	85.5	334.4	yes
C=O(aldehydes)	176.0	162.4	no
C=O(ketones)	179.0	159.7	no
C-S	65.0	439.9	yes
C-S	166.0	172.2	no
H-H	104.2	274.4	yes
N-N	52.0	549.8	yes
N=N	60.0	476.5	yes
N.N	226.0	126.6	no
N-N(NH)	85.0	336.4	yes
N-N (NH3)	102.2	280.3	yes
N-O	48.0	595.6	yes
N-O	162.0	176.5	no
O-O(O2)	119.1	240.1	yes
-O-O-	47.0	608.3	yes
O-H(water)	117.5	243.3	yes
S-H	83.0	344.5	yes
S-N	115.2	248.6	yes
S-O	119.0	240.3	yes

水中有機物光氧化

$$CH_3OH + 2\ OH\cdot \xrightarrow{UV} HCHO + 2\ H_2O$$

$$HCHO + 2\ OH\cdot \xrightarrow{UV} HCOOH + H_2O$$

$$HCOOH + 2\ OH\cdot \xrightarrow{UV} CO_{2(aq)} + 2\ H_2O$$

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow HCO_3^- + H^+$$

資料來源: Millipore Corporation
Laboratory Water Division

UV 光應用

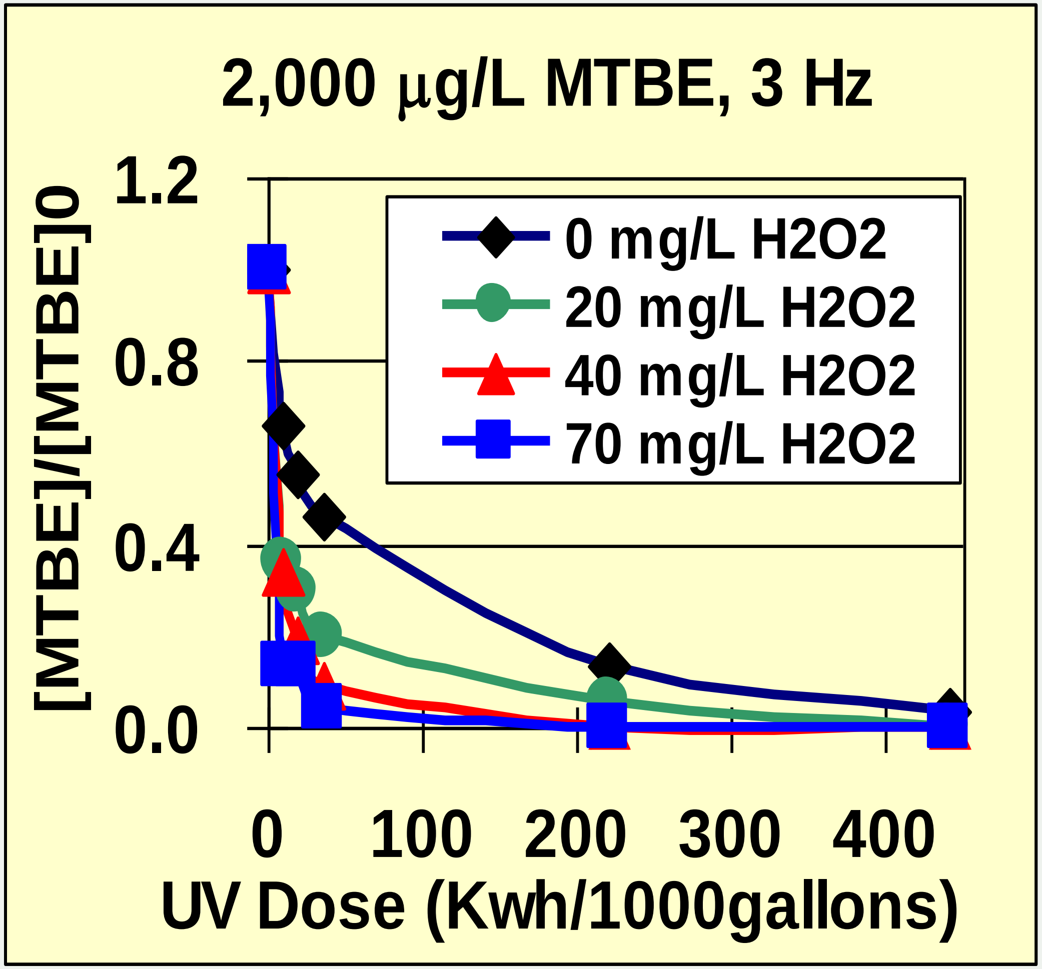
TABLE 4-7
UV Dose* Required for Microbial Kill

Organism	*90%*	*99.99%*
Gram-negative fermenters *Coliforms, Salmonella, Serratia marcescens*	2-8	8-32
Gram-negative nonfermenters *Pseudomonas*	6	24
Gram-positive rods (spores) *Bacillus, Clostridium*	4-7(9-12)	16-28(36-48)
Gram-positive cocci *Micrococcus*	6-23	24-92
Fungi Mildew, pigmented water molds	30-300	120-1200

*µW sec/cm² at 254 nm

Courtesy, J.M. Martin, Pall Corp.

Effect of H_2O_2 and UV Dose on By-product Formation (High MTBE)



資料來源: Sun Liang, Ph.D., P.E.The Metropolitan Water District of Southern California

重要觀念-1

➢ 空氣中二氧化碳溶於超純水造成水質劣化

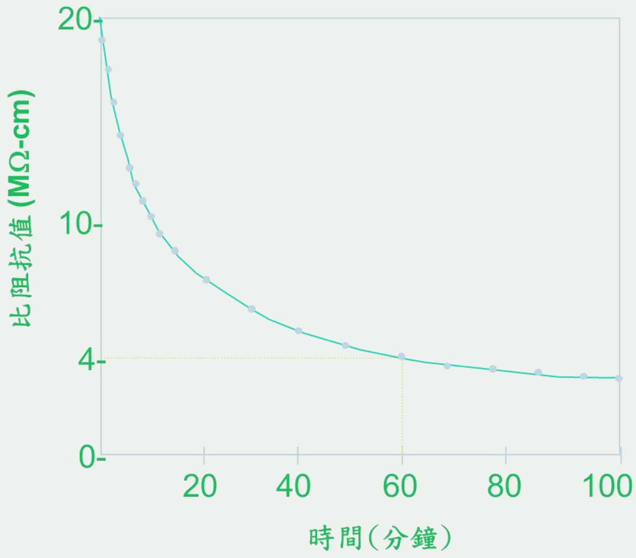
- 18.2 Megohm.cm 超純水, 放置一小時之後, 阻抗會下降至4 Mohm.cm, pH 則降至5.7左右。
- 氮封純水箱：氮氣是惰性氣體能防止CO2等其它物質溶入水中影響水質，避免水箱內的水不受二次污染而導致水質下降。

- 空氣中二氧化碳與純水反應

$$CO_2 + H_2O \longleftrightarrow H_2CO_3$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^-$$



1.從碳酸中解離出之氫離子濃度 $[H^+] = 2 \times 10^{-6}$ 或 pH= 5.7
2.因氫離子及碳酸根離子增加,造成比阻抗值下降至 4 左右.

資料來源: Millipore Corporation
Laboratory Water Division

重要觀念-2

- <u>比阻抗值</u>僅能用來表示水中離子濃度高低, 無法直接連結各污染物之濃度.
- 18.2 Megohm.cm超純水之僅能代表水中總離子濃度在1 ppb 以下, 其它污染物需另以不同的方法檢測.
- 存在於自來水中又很難去除之矽酸鹽,美國 <u>N</u>ational <u>C</u>ommittee of <u>C</u>linics and <u>L</u>aboratory <u>S</u>tandards 建議之矽酸鹽濃度需低於 10 ppb。

水中NaCl濃度的比電導度與阻抗值之關係 (25°C 之下)

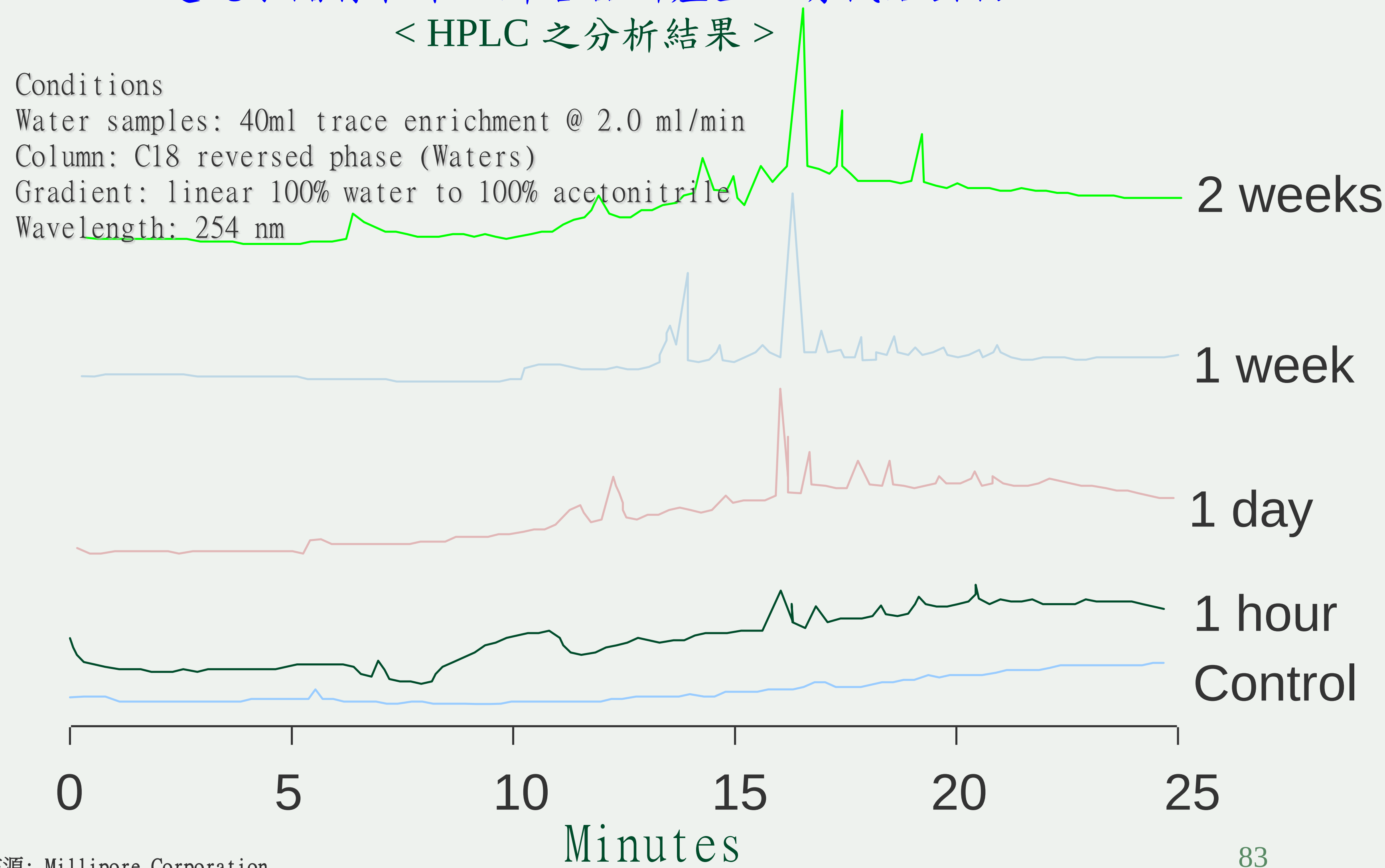
NaCl (μg/l)	比電導度 (μS/cm)	比阻抗值 MΩ-cm
0	0.055	18.18
1	0.057	17.60
5	0.066	15.20
10	0.076	13.10
20	0.098	10.20
50	0.16	6.15
100	0.27	3.70
300	0.70	1.43
500	1.13	0.88
1 000	2.21	0.45
5 000	10.80	0.093
20 000	42.70	0.023

重要觀念-3

容器材質不當，易有溶出物問題

超純水儲存在聚乙烯容器所產生之有機溶出物

< HPLC 之分析結果 >



資料來源: Millipore Corporation
Laboratory Water Division

重要觀念-4

微生物汙染，會產生什麼樣的問題?

- 生物膜(Biofilm)的形成會使超純水無法達到微生物數(<1cfu/ml)標準。

- 微生物膜的污染會造成逆滲透膜操作背壓上升，導致對水中雜質的去除能力降低，影響產出水質，也有可能損害薄膜分離層材質，致使出水水質變差。
- 生物膜包覆的離子交換樹脂將損失很高以上的交換表面積，不只耗材壽命變短，也會變成微生物的孳生溫床，影響甚巨!

常見微生物滋生原因

- **水溫過高:** 環境溫度導致純水系統的水溫過高(>30°C)，會使微生物繁殖速度加快。
- **水質變差:** 當水質變差，主要是RO或離子交換樹脂出問題時，會因為水中的成分升高，也會導致微生物快速繁殖。
- **用水量不足:** 純水系統的每日製水能力通常很大，如每天實際用水量卻很少，這樣會導致系統在大部分的時間是在停機狀態。
- **純水槽**呈現死水狀態
- **純水槽沒有氣密設計:** 容易被環境汙染，滋生細菌。
- **管線水不流動:** 單向水系統基本上是一個「死水管線」，供水管線非<動態循環設計>或流速不足，或存在嚴重的盲管(dead leg)問題，微生物的汙染是必然的宿命。
- **沒有定期更換耗材:** 活性碳及離子交換樹脂，使用越久，微生物繁殖越嚴重。
- **紫外燈的功能失效:** 每周檢查紫外燈的功能需定期更換。
- **沒有定期進行系統消毒(化學藥劑):** 特別是針對純水槽及配水管線，因為單靠紫外燈是無法去除菌膜的。

化學殺菌

- 系統之化學藥劑消毒法，包括：
- 次氯酸鈉、過氧化氫、臭氧或過醋酸等。
- 次氯酸鈉是有效的消毒劑，會有殘留問題，但成本最低，安全性最高，但破壞菌膜的能力較差。
- 過氧化氫、臭氧和過醋酸等化合物藉由形成活性過氧化物和自由基（以氫氧基最顯著），來氧化細菌和菌膜。
- 臭氧的半衰期很短，因此在消毒過程中，需要持續添加。
- 過氧化氫和臭氧會迅速分解成水和氧；過醋酸在紫外燈下則分解成醋酸。

紫外線殺菌有效嗎?

- 在純水系統中，長期使用可能誘發能夠抵抗紫外線的微生物，所以必須配合其它的手段來控制微生物濃度。
- 紫外燈無法去除已存在的菌膜。

如何有效控制純水系統的微生物呢?

- **耗材要在合理的時間之後更換**
- **系統每天的運作時間要足夠,** 最好能在4小時/天以上，
- 並且最好具備內部清洗（Flush）、消毒，循環等功能。
- **水質檢測功能要正常並準確**，
- **紫外線燈管一定要定期更換**
- **機台運作環境要儘量保持低溫**(<30°C)，
- **建立維修保養記錄簿**，建立責任制及緊急聯絡人，定期記錄所有水質狀況。
- **建立定期化學殺菌機制及週期**，由專業的人員來執行。
- **改善配水管線的流路設計**，到無死水，無盲管。

結語

- 技術面
  - 各單元技術原理、功能特性與限制條件
  - 單元整合與系統功能目標
  - 原水水質的成分與變異
- 操作維護面
  - 系統線上與離線清洗
  - 更換系統耗材
  - 儀表校正與維護
  - 量測儀器與技術
  - 設備與零件保養與維護
  - 操作SOP