

Table 3.5.3 Quality and Quantity of Waste Water

Type of waste-water	Calculation of the quantity of wastewater	Quality of wastewater
Screen cleaning wastewater	Travelling screens: 8 sets Quantity of cleaning water : $100 \text{ m}^3/\text{h} \times 5 \text{ min}/12 \text{ h}$ Quantity of wastewater: $100 \text{ m}^3/\text{h} \times 5/60 \times 24/12 \times 8 = 133 \text{ m}^3/\text{day}$	TDS : 43,300 ppm COD : 1mg/l SS : 3mg/l (equal to seawater)
Dual-media filter cleaning wastewater	Dual-media filter: $60 \text{ m}^2 \times 48$ Quantity of cleaning water : $0.8 \text{ m}^3/\text{m}^2 \cdot \text{m} \times 15 \text{ min}/36$ Quantity of wastewater: $60 \text{ m}^2 \times 0.8 \text{ m}/\text{min} \times 15 \text{ min} \times 24/36 \times 48 = 23,040 \text{ m}^3/\text{day}$	Quantity of seawater $200,000 \text{ m}^3/\text{day} \times 1/0.35 + 23,040 \text{ m}^3/\text{day} = 594,000 \text{ m}^3/\text{day}$ SS concentrate of seawater: 3 mg/l Quantity of solid from seawater: $594,000 \text{ m}^3/\text{day} \times 3 \times 10^{-3} \text{ kg}/\text{m}^3 = 1,782 \text{ kg}/\text{day}$ FeCl <sub>3</sub> dosage : 3mg/l Fe(OH) <sub>3</sub> produced from FeCl <sub>3</sub> $594,000 \text{ m}^3/\text{day} \times 3 \times 10^{-3} \text{ kg}/\text{m}^3 \times 106.8/162.3 = 1,173 \text{ kg}/\text{day}$ total SS $1,782 \text{ kg}/\text{day} + 1,173 \text{ kg}/\text{day} = 2,955 \text{ kg}/\text{day}$ SS concentrate $2,955 \text{ kg}/\text{day} \times 1/23,040 \text{ m}^3/\text{day} = 0.128 \text{ kg}/\text{m}^3 (128 \text{ mg}/\text{l})$ COD : 15mg/l

Table 3.5.3 (continued)

Type of waste-water	Calculation of the quantity of wastewater	Quality of wastewater
Rinsing wastewater	<p>Cleaning time of Dual-media filter:90min</p> <p>Quantity of wastewater</p> $594,000 \text{ m}^3/\text{day} \times 1/24\text{h}/\text{day} \times 1.5\text{h} \times 24/\text{day}/36\text{h} = 24,750\text{m}^3/\text{day}$	<p>SS : neary 0 mg/l</p> <p>COD: 1mg/l</p>
Concentrated brine	<p>Collecting rate: 35 %</p> <p>Quantity of Concentrated brine</p> $200,000 \text{ m}^3/\text{day} \times 0.65/0.35 = 371,000 \text{ m}^3/\text{day}$	<p>TDS of Concentrated brine</p> $43,300 \times 1/0.65 = 66,600\text{ppm}$ <p>SS :nearly 0mg/l, pH :6.5</p> <p>COD : 1mg/l</p>
Chemical-solution cleaning wastewater	<p>Chemical-solution: 2% Cytric acid</p> <p>Frequency of cleaning : 4 per year</p> <p>Quantity of cleaningwater for 1 train:</p> $50\text{m}^3$ <p>Quantity of wastewater per year</p> $50\text{m}^3/\text{train} \times 40\text{train} \times 4 / \text{year} = 8,000 \text{ m}^3/\text{year}$ <p>Average Quantity of wastewater discharge</p> $8,000 \text{ m}^3/\text{year} \times 1/365\text{day}/\text{year} = 21.9\text{m}^3/\text{year}$	<p>COD of cytric acid(2%):10,800mg/l</p> <p>COD of Contminants:10% of cytric acid</p> <p>Total COD of wastewater</p> $10,800\text{mg}/\text{l} \times 1.1 = 11,880 \text{ mg}/\text{l}$ <p>SS: 300 mg/l</p>

Table 3.5.3 (continued)

Type of wastewater	Calculation of the quantity of wastewater	Quality of wastewater
Membrane storage-solution wastewater (construction)	storage-solution:formalin 0.5 % Quantity of storage-solution per train: $7 \text{ m}^3$ Total quantity of storage-solution $7 \text{ m}^3/\text{train} \times 40\text{train} = 280 \text{ m}^3$ In the case of treating this wastewater in a year Average discharge per day $280 \text{ m}^3 \times 1/365\text{day/year} = 0.77 \text{ m}^3/\text{day}$	COD of formalin 0.5% :4,100 mg/l SS : 5 mg/l
Membrane storage-solution wastewater (replacement of membrane)	storage-solution:formalin 0.5 % Quantity of storage-solution per train: $0.7 \text{ m}^3$ Frequency of replacement : 1/5year $0.7 \text{ m}^3/\text{train} \times 40\text{train} \times 1/5\text{year} = 5.6 \text{ m}^3/\text{year}$ Average discharge per day $5.6 \text{ m}^3/\text{year} \times 1/365\text{day/year} = 0.015 \text{ m}^3/\text{day}$	COD of formalin 0.5% :4,100 mg/l SS : 5 mg/l

Table 3.5.3 (continued)

Type of wastewater	Calculation of the quantity of wastewater	Quality of wastewater
Membrane storage-solution wastewater (after long-term storage)	storage-solution: formalin 0.1 % Quantity of storage-solution per train: Number of long-term storage trains: 5 trains per year Quantity of discharge per train $50\text{ m}^3/\text{train} \times 5\text{ train/year} = 250\text{ m}^3/\text{year}$ Average discharge per day $250\text{ m}^3/\text{year} \times 1/365\text{ day/year} = 0.68\text{ m}^3/\text{day}$	COD of formalin 0.1% : 820 mg/l SS : 5 mg/l

Table 3.5.4 Summary of Quality and Quantity of Waste Water

Type of wastewater	Quantity ave. m <sup>3</sup> /day	TDS mg/l	SS mg/l	COD mg/l	Remarks	
Screen cleaning wastewater	133	43,300	3	1		
D.M.F. cleaning wastewater	23,040	43,300	128	15		
Rinsing wastewater	24,750	43,300	0	1		
Concentrated brine	371,000	66,600	0	1	pH 6.5	
Chemical-solution cleaning wastewater	21.9		300	11,880	cytric acid 2%	
Storage- solution	construction	0.77		5	4,100	formalin 0.5%
	replacement	0.015		5	4,100	formalin 0.5%
	long-term storage	0.68		5	820	formalin 0.1%
Total	418,946.365	t/d (26,784)	kg/d (2,956)	kg/d (1,005)		
Concentrate(average)		63,930	7.06	2.40	pH about 6.5 cytric acid 0.3ppm formalin 0.01ppm	

waste water standard for any of COD, SS or pH. Therefore, if whole volume is discharged evenly, besides it is sufficiently stirred and mixed, it will be all right to discharge it as untreated. However, realizing it would require a facility, which is capable of storing's and evenly discharging each of the waste water from multiple-layer filter cleaning, waste water from chemical-solution cleaning, and the waste water from preserving solution.

Formalin is a sterilizer, and it should not be discharged at high density. But, according to the existing laws of Japan, COD regulations alone would be applicable to formalin. Therefore, if whole flow is mixed, there would be no problem from legal aspect.

#### (4) Technology for reducing the Volume of Pollutants discharged

As explained above, if whole volume is evenly discharged and sufficiently stirred and mixed, the quality of waste water would sufficiently clear the uniform waste water standard of Japan. However, legal regulations only show a minimum requirement for avoiding negative effects on environment; and, needless to say, it is desirable to apply further advanced treatment.

Besides, for the large-scale seawater desalination system, seawater is taken from and discharged to either the Red Sea or the Arabian Gulf, which form closed water area. When taking this point into account the technology used for not simply diluting the discharge water to lower its density, but also reducing the total volume of discharged pollutants.

So, we should like to explain about the treatment method used for the waste water from multiple layer filter cleaning, waste water from chemical solution cleaning, and formalin.

##### 1) Waste water from multiple layer filter cleaning

The pollutants of this waste water is mainly inorganic SS (suspended substances). Ferric chloride is added as coagulant, thus this waste water features optimum sedimentation. By sedimentation, SS is believed to reach the range of 10 mg/l, thus can be easily treated.

However, it will also be necessary to treat sludge deposited. Sludge may be mechanically dehydrated by means of gravity condensation, or dried to the Sun, into solids, which then could be easily disposed of.

##### 2) Waste water from chemical cleaning solution

This waste water features extremely elevated COD, and cannot be discharged alone. The main ingredients and cannot be discharged alone. The main ingredients of COD are citric acid and other organic acids, and include, depending on the case, surface active agents. For treating this type of waste water, biological treatment method is usually employed.

If the aerobic treatment, which is the most common biological treatment method, is to be used, it should be diluted to nearly 50 times for treatment. It is also possible to treat it by com-

binning with the waste water from various plants. It is also possible to realize anaerobic biological treatment by relying on the fact that this waste water is of high density.

Although the anaerobic treatment method has such shortcomings as the slow treatment speed, or that the quality of the treated water is inferior to that by the aerobic treatment method, it also features such advantages as allowing recycling energy or high-density treatment; thus, the anaerobic method is drawing attention in Japan recently. If the waste water, which was treated by anaerobic method, together with the ordinary waste water from plants by aerobic method, the waste water with optimum quality may be obtained, thus the diluting water may be saved.

By taking into account the weather in the Saudi Arabian Peninsula, natural drying may also be accepted as an economical treatment method. This consists of setting aside a number of shallow treatment ponds; waste water from chemical solution cleaning is put in the pond in order to dry in the sun.

### 3) Waste water of preserving solution

The waste water treatment method varies depending on what is chosen as the preserving solution. If sodium bisulfate is used, it is oxidized by aeration, thus it is possible to turn it harmless. For formalin, the following methods may be applicable:

#### a) Biological treatment

For treating by the activated sludge method, it is necessary to treat after diluting. For the initial density and the treatment time of formalin are shown in Table 3.5.5<sup>29</sup>.

Table 3.5.5 Experiment of Wastewater Treatment Including Formaline by Activated Sludge Progress<sup>9</sup>

Type of activated sludge	MLSS mg/l	Concentrate of formalin mg/l	Decomposition time h	Type of experiment
Non acclimatized	840	75	approx. 12	intermittent
Acclimatized	1000~1300	200	approx. 8	intermittent

By using the conditioned sludge, it is possible to biologically treat formalin of 200 mg/l density. Since the formalin density of preserving solution is 5,000 mg/l, it will be necessary to dilute to 25 times. If the waste water from chemical solution cleaning is treated by aerobic method by diluting it at 50 times, the formalin density may be lowered to the 100 mg/l range by mixing with this waste water; thus, mixed treatment will be possible.

b) Chemical treatment – 1 and 2

For the chemical treatment methods for treating formalin waste water, the following methods are shown in the standard of Poisonous & Toxic Waste Law:

\* Oxidation method by hypochlorite

Plenty of water is added in order to turn it into diluted aqueous solution, then hypochlorite is added for degrading, then is discharged.

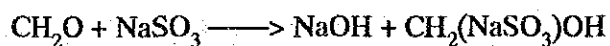
\* Oxidation by hydrogen peroxide

Waste water is turned alkaline by means of the sodium hydroxide aqueous solution, then hydrogen peroxide is added to degrade, and diluted with a plenty of water, then is treated.

c) Chemical treatment – 3

Although not shown in the standard of Poisonous & Toxic Waste Treatment Law, the following chemical treatment method is widely used:

Formalin reacts with sodium sulfite by the following formula:



d) Chemical treatment – 4

Several formalin neutralizers were developed. The product introduced here was made by a Canadian chemical company, and is reputedly capable of producing 36% density formalin with 1.5 l of neutralizer.

e) Combustion method

This is a method shown in the standard of Poisonous & Toxic Waste Method, and is actually used intermediate treatment agents of industrial wastes. For the combustion treatment, since the formalin's boiling point is low, an after burner is always provided in order to burn the exhaust gas. For the first-stage furnace, it is burnt at a temperature range of 600°C so; and, then burnt at 800°C or so by the after burner for treatment. Since the reaction rate is slow, the facility may be compact. However, the waste solution density is lower than the normal ap-



plicable range of combustion method, combustion cost is elevated.

Wet-type oxidation method is a kind of combustion method. This method consists of oxidizing organic substances contained in waste water by air under high-temperature and high-pressure ambient; it is also known as submerged combustion method. As organic substances are oxidized under pressure, where no evaporation occurs, it is possible to treat formalin, which has low boiling point, within solution. If operation can be conducted continuously, the treatment facility may be compact and feature superior heat efficiency. Although in Japan it is held economical if COD or is at the density of 20,000 mg/l or more, if the fuel cost is low, it may also prove to be promising for low-density waste water.

#### f) Other methods

##### \* Fenton method

This treatment method consists of oxidizing and degrading organic substances by using hydrogen peroxide and iron catalyzer. Although the oxidizing power of hydrogen peroxide is not very strong; it shows powerful oxidation force in the presence of iron or copper used as catalyzer.

It is used for treating waste water from chemical plants and waste water from plating, as a method for removing hard-to-degrade COD, which is not suitable for biological treatment. It is reported that formalin of 500 mg/l density could almost be completely degraded within the reaction period of 90 minutes<sup>34</sup>.

##### \* Electrolytic oxidation method

For this treatment method, electric energy is given to waste water to cause electrolysis; and, formalin is oxidized and degraded into CO<sub>2</sub> and H<sub>2</sub>O by oxygen that is generated at the anode. It is reported that 3,000 ppm formalin dropped to 1 ppm or less after treatment for several hours in electrolytic solution. And, it is also held possible to degrade formalin in the water<sup>27, 28</sup>.

### ***3.6 Present Condition of and Themes on the Treatment of Waste Water Discharged from RO Seawater Desalination Plants***

A survey of the waste water and the waste water treatment of RO seawater desalination plants was made through a study of reference materials and by gathering information from various manufacturers.

(1) There exist only few cases in which a waste water treatment facility is provided for seawater

desalination plants using the RO (reverse osmotic) membrane method. This is due to the fact that even if the waste water discharged from such facility is likely to cause negative effects, since it is diluted with condensed seawater, which is formed in large quantities, its concentration is lowered, thus according to the current laws of Japan, etc., there is no need to treat it.

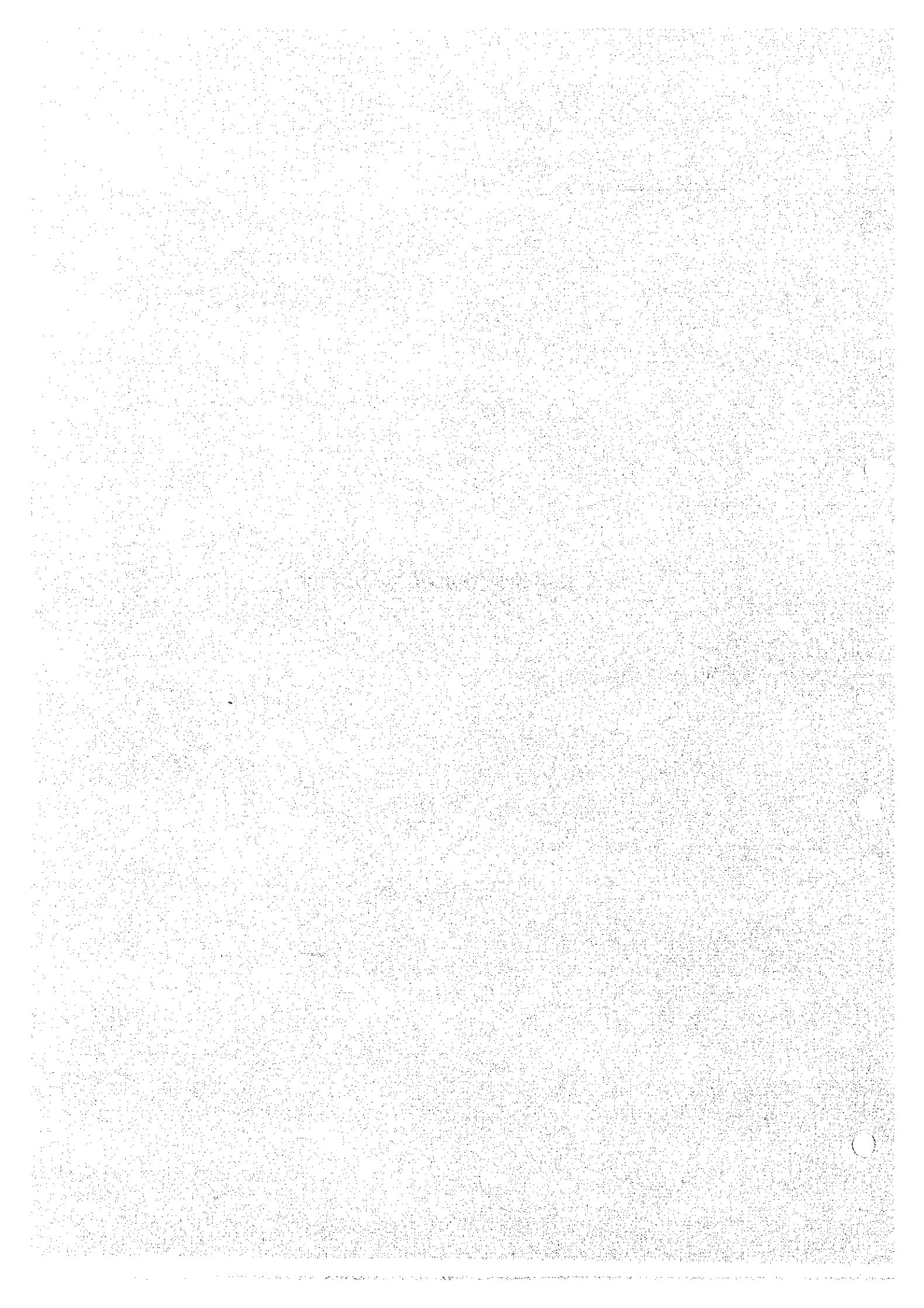
- (2) However, a large-scale facility is liable to generate a large amount of waste water; and, even if its concentration satisfies the legal requirements, the total volume of pollutants discharge may become extremely large. As the RO seawater desalination plants are expected to increase in scale, besides being confined to certain areas. Therefore, to avoid the effects of waste water discharged from RO seawater desalination plants on the environment, it is desirable to start investigating possible remedies, besides implementing relevant domestic laws and regulations.
- (3) As for the waste water treatment technology, the future theme would be the search for a suitable treatment technology matching the characteristics of each area. Among other future themes are the search for cleaning methods designed so as not to discharge noxious chemicals, or developing preserving solutions which enable an easier treatment. And, in view of the possible concentration of industries in the future, establishing a public system for the treatment of wastes generated by industrial activities would also be a desirable direction to follow.

## References

1. Quoted from research materials of TOREY, TOYOBO and NITTO DENKO
2. DITTO
3. Quoted from research materials of TOYOBO
4. MITI: The laws and technics of pollution control
5. Tokyo Metropolitan: The plan of industrial wastes disposal
6. DITTO
7. Water Re-Use Promotion Center: Technical papers related to industrial water supply, Industrial waste water treatment, Water analysis and Desalination(1991)
8. DITTO
9. Hosaka: Water purification and liquid wastes treatment, Vol.31, No.4, 205-212



## **4.5 R-4 Selection of Membrane**



**RO DESALINATION  
LITERATURE SURVEY NO. 5, R-4**

**SELECTION OF MEMBRANES**

**JULY 1992**

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## **1. Introduction**

Previously, the dominant desalination system for obtaining drinking water from seawater was the MSF process, but recently the RO process has become important in the desalination of sea water. The reasons for the use of RO desalination are:

- (1) The RO process is simpler than the MSF process and it also consumes less energy.
- (2) The reliability and efficiency of the RO membranes themselves have improved remarkably due to constant technological developments

Originally, the material used for the RO membranes was cellulose acetate but since then many different types of RO membranes have been developed including the so-called thin film composite membranes. However, in the selection of the materials for these membranes, one needs to consider the purpose and condition for which they will be used, the technology and the on-site conditions.

The aim of this research investigation is to establish the most suitable RO membranes for use in Saudi Arabia and also to make comparative investigations of the type of RO membranes that are currently in use, keeping in mind that:

- (1) Concentration of the dissolved solids of raw feed seawater in both the Gulf and Red Sea is high.
- (2) Temperature of raw feed seawater is also relatively high.

## **2. Methods**

Literature survey will be performed using information retrieval by DIALOG, JOIS and also collection of the catalog published by membrane makers.

### **3. Results**

#### **3.1 *Developmental History of the RO Membranes and Future Trends in Technological Development***

Originally RO membranes were developed with the intention of applying them in the desalination field, so that the development of membrane materials was undertaken with taking only separation between inorganic salts and water as its aim. However, while a high level of desalination performance was achieved in the desalination of seawater with the introduction of composite membranes, it was also discovered from this process that membranes of this type are also effective in removing organic compounds with low molecular weight. As a result, the range of their applications is expanding from the traditional desalination of seawater into such diverse areas as the food and semiconductor industries, the recovery of precious resources, and medical treatment.

In the desalination of brackish water, on the other hand, a move towards replacing the traditional medium-pressure membranes with low or ultra low pressure ones is gaining momentum. The principle of osmotic pressure also supports this since raw water is often low in salinity in the desalination of brackish water, thus making it possible to operate it at low pressures as long as the membrane performance permits it. This situation is illustrated in Fig. 3.1.1.

#### **3.2 *Classification of RO Membranes Based on Cross-Sectional Structures***

According to their cross-sectional structures, RO membranes can be classified into three groups – homogeneous, asymmetric and composite – as shown in Figure 3.2.1<sup>2</sup>.

##### **3.2.1 *Homogeneous Membranes***

Homogeneous membranes are regarded as identical with ordinary plastic films and are produced by casting, using polymer solutions with the solvents subsequently removed by heating.

##### **3.2.2 *Asymmetric Membranes***

As distinguished from composite membranes, a typical asymmetric membrane incorporates a surface dense layer as well as porous sublayers, all formed simultaneously from the same material. It is understood that the surface dense layer has a separation function, with porous sublayers merely physically supporting it.

Typical examples of asymmetric membranes are cellulose acetate derivatives (incorporated in a flat sheet or hollow fiber module) and aromatic polyamide (incorporated in a hollow fiber module). As will be discussed in detail later, asymmetric membranes have continuously been

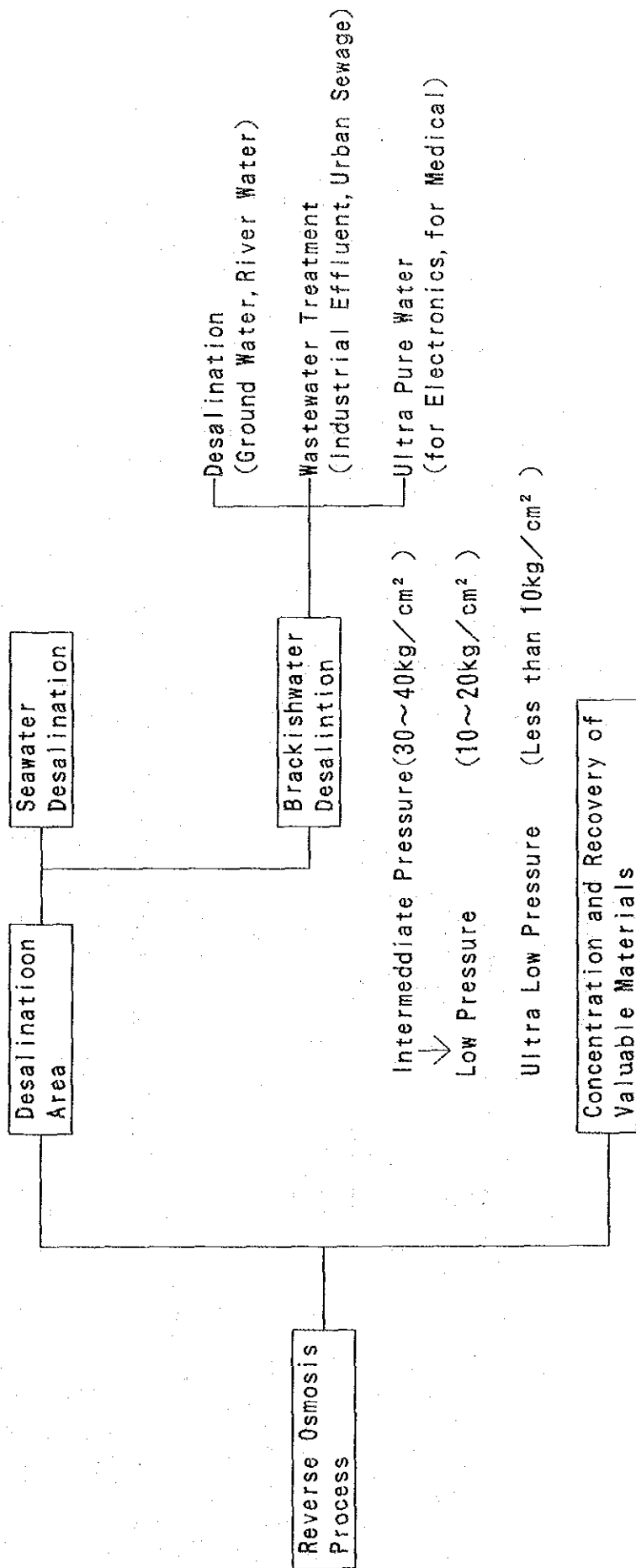


Fig.3.1.1 Spread of Reverse Osmosis Membrane Uses and Technical Direction <sup>5</sup>

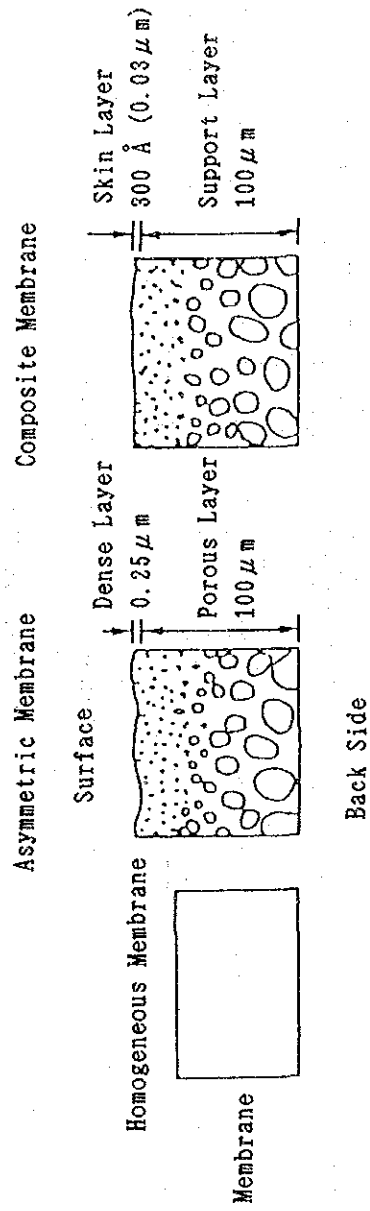


Fig.3.2.1 Cross-sectional structure of RO membranes <sup>2</sup>



used in practical applications.

Asymmetric membranes' disadvantages can be summarized as follows:

- (1) Low salt rejection and permeate
- (2) Low durability (heat resistance, pressure resistance and over-time stability in performance)
- (3) Poor bacteria resistance
- (4) Narrow ranges of applications (operating pH, temperature and pressure ranges)

### **3.2.3 Composite Membranes**

A typical composite membrane is fabricated from a skin layer with a separation function (equivalent to the asymmetric membranes' surface dense layer) plus a support layer, respectively made of different materials. In other words, a thin (100–300Å) macromolecular separation film layer is formed on a microporous support layer (usually made of polysulfonated derivative materials).

Historically, basic research on composite membranes started a few years after the first proposal of asymmetric membranes, when the manufacturing process and structures of the latter, including the function of each surface incorporated in them, became known.

In search of RO membranes with more advanced performance, the trend in the use of membrane structure in recent years is tending increasingly towards composite membranes combined with the skin layer technology, to such an extent it is not an overstatement to say that recently a large segment of commercialized membranes are of the composites-type.

Composite membranes' advantages and disadvantages can be summarized in Table 3.2.1<sup>9</sup>:

### **3.2.4 Classification of Composite Membranes**

Based on cross-sectional structure, composite membranes can be classified into five types, polymer coating (I), monomer polymerization (II), polymer surface cross-linking (III), blocked surface (IV) and interfacial polymerization (V), as shown in Fig. 3.2.2<sup>2</sup>.

#### **(1) Polymer Coating (I)**

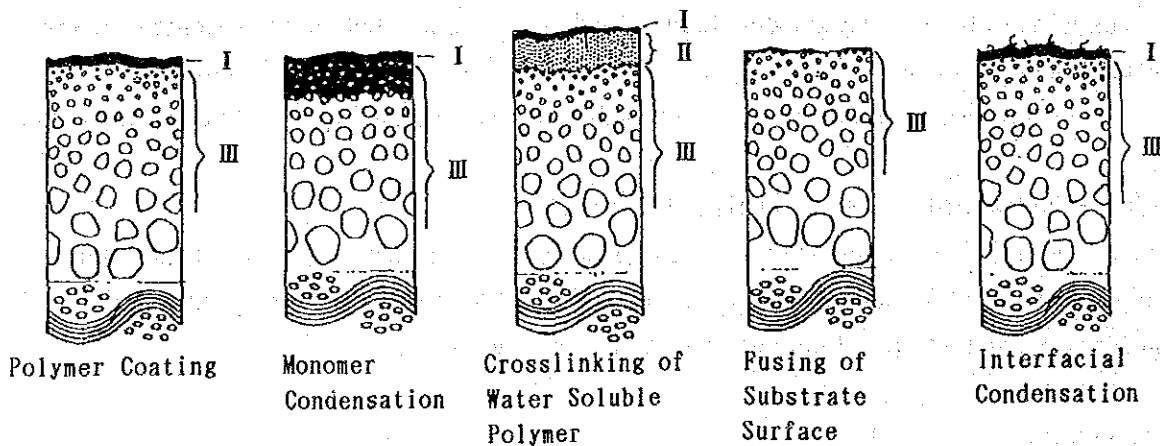
The support layer is coated or laminated with a skin layer, often a linear polymer → UOP's CTA composite membrane.

#### **(2) Monomer Polymerization (II)**

This is similar to polymer coating in that the membrane is composed of two kinds of layers, a skin layer and support layer, but there is a difference in that its skin layer is a cross-linked polymer, which penetrates into the adjoining support layer (pores), such that both layers merge and become inseparable – Toray's PEC-1000.

Table 3.2.1 Features and Weak Points of Composite Membrane (General)

Features	<ol style="list-style-type: none"> <li>1. Materials of membrane and supporting layer can be selected based on functional viewpoints and composition to be the most suitable feature.</li> <li>2. Membranes can be made extremely thin.</li> <li>3. Thin membrane can be interfacially polymerized at the surface of supporting layer.</li> <li>4. High performance (high rejection, high flux) and good tolerance to high temperature feed solution.</li> <li>5. Treatable under dried condition.</li> <li>6. Applicable for recovery of valuable materials.</li> </ol>
Weak Points	<ol style="list-style-type: none"> <li>1. Ultra thin membrane technology — requires rigid control of the thin film.</li> <li>2. 2 stage process (supporting layer process and thin membrane process) are required.</li> </ol>



I : Barrier Layer II : Intermediate Transport Layer III : Microporous Substrate

Fig. 3.2.2 Membrane Types Classified by Fabrication Methods<sup>2</sup>

(3) Polymer Surface Cross-Linking Type (III)

The membrane has a buffer (gel) layer between its skin layer and support layers – UOP's PA-300 and RC-100.

(4) Blocked Surface (IV)

This is the type in which the membrane's support layer surface is blocked either physically or chemically (eg. blocking by plasma treatment). The chemical structure of the skin layer is more or less the same as that of the support layer.

(5) Interfacial Polymerization (V)

The membrane's skin layer is formed by means of interfacial polymerization on the support layer surface.

**3.2.5 The Chemical Structure of Skin Layers Incorporated in Composite Membranes**

Examples of the chemical structures of skin layers incorporated in composite membranes are shown in Table 3.2.2<sup>11</sup>.

**3.3 Classification of RO Membranes Based on Separation Performance**

(1) High Rejection Membranes

These are the membranes with rejections (solute removal rates) of more than 99%, typically used for single stage desalination of seawater.

(2) Medium Rejection Membranes

These are the membranes with rejections of around 90%, typically used for desalination of brackish water or industrial water.

(3) Low Rejection Membranes

These are the membranes with rejections of 30–70%, typically used for separation of organic compounds with middle molecular weights and inorganic ions.

**3.4 Classification of RO Membranes Based on Operating Pressure**

Table 3.4.1 shows classification of RO membrane according to operating pressure

**3.5 Classification of RO Membranes Based on Operating Pressure**

The desalination of seawater is carried out by applying high pressures of 20–70Kg/cm<sup>2</sup> to the above RO membranes, which are extremely thin and fragile, with 100 microns or so thick–

Table 3.2.2 Typical Skin Layer for Composite Membrane <sup>11</sup>

NS-100	$\begin{array}{c} \text{OCN} \quad \text{NCO} \\   \quad   \\ \text{C}_6\text{H}_3(\text{CH}_3) \\   \\ \text{CH}_2\text{CH}_2\text{N} \\   \\ \text{H}_2\text{NCH}_2\text{CH}_2 \end{array} + \begin{array}{c} \text{OCN} \quad \text{NCO} \\   \quad   \\ \text{C}_6\text{H}_3(\text{CH}_3) \end{array}$	$\begin{array}{c} \text{---} \text{CH}_2\text{CH}_2\text{N} \text{---} \\   \\ \text{OCHN} \text{---} \text{C}_6\text{H}_3(\text{CH}_3) \text{---} \\   \\ \text{NHCONHCH}_2\text{CH}_2 \end{array}$
PA-100	$\begin{array}{c} \text{ClCO} \quad \text{COCl} \\   \quad   \\ \text{C}_6\text{H}_4 \end{array} + \begin{array}{c} \text{ClCO} \quad \text{COCl} \\   \quad   \\ \text{C}_6\text{H}_4 \end{array}$	$\begin{array}{c} \text{---} \text{CH}_2\text{CH}_2\text{N} \text{---} \\   \\ \text{---OC---} \text{C}_6\text{H}_4 \text{---} \text{OCHNCH}_2\text{CH}_2 \end{array}$
PA-300 LP-300	$\begin{array}{c} \text{ClCO} \quad \text{COCl} \\   \quad   \\ \text{C}_6\text{H}_4 \end{array} + \begin{array}{c} \text{ClCO} \quad \text{COCl} \\   \quad   \\ \text{C}_6\text{H}_4 \end{array}$	$\begin{array}{c} \text{---} \text{CHCH}_2\text{O} \text{---} \\   \\ \text{CH}_2 \\   \\ \text{NHCH}_2\text{CH}_2\text{NHCO---} \text{C}_6\text{H}_4 \text{---} \text{CO---} \end{array}$
RC-100	$\begin{array}{c} \text{ClCO} \quad \text{COCl} \\   \quad   \\ \text{C}_6\text{H}_4 \end{array} + \begin{array}{c} \text{OCN} \quad \text{NCO} \\   \quad   \\ \text{C}_6\text{H}_3(\text{CH}_3) \end{array}$	$\begin{array}{c} \text{---} \text{CHCH}_2\text{O} \text{---} \\   \\ \text{CH}_2 \\   \\ \text{CHCH}_2\text{CH}_2\text{NHCONH---} \text{C}_6\text{H}_3(\text{CH}_3) \text{---} \text{NHCO---} \end{array}$
NS-200	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}_4\text{H}_5\text{O} \end{array} \xrightarrow{(\text{H}_2\text{SO}_4)}$	$\left( \begin{array}{c} \text{---} \text{CH}_2 \\   \\ \text{C}_4\text{H}_5\text{O} \end{array} \right)_m \left( \begin{array}{c} \text{SO}_3\text{H} \\   \\ \text{---} \text{CH}_2 \\   \\ \text{C}_4\text{H}_5\text{O} \end{array} \right)_n$
NS-300	$\begin{array}{c} \text{H} \\   \\ \text{N} \\   \\ \text{C}_6\text{H}_4 \text{---} \text{CO---} \end{array} + \begin{array}{c} \text{ClOC} \quad \text{COCl} \\   \quad   \\ \text{C}_6\text{H}_4 \end{array} + \begin{array}{c} \text{H} \\   \\ \text{N} \\   \\ \text{C}_6\text{H}_4 \text{---} \text{CO---} \end{array}$	$\begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CO---} \text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CO---} \text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CO---} \end{array}$
FT-30	$\begin{array}{c} \text{H}_2\text{N} \quad \text{NH}_2 \\   \quad   \\ \text{C}_6\text{H}_4 \end{array} + \begin{array}{c} \text{ClOC} \quad \text{COCl} \\   \quad   \\ \text{C}_6\text{H}_4 \end{array}$	$\begin{array}{c} \text{---} \text{HN---} \text{C}_6\text{H}_4 \text{---} \text{NHCO---} \text{C}_6\text{H}_4 \text{---} \text{CO---} \end{array}$

Table 3.4.1 Classification of RO Membrane according to Operating Pressure

Type of RO Membrane	Operating Pressure(M Pa)	Application
High Pressure Type	>4	Seawater Desalination
Intermediate Pressure Type	3	Brackish Desalination
Low Pressure Type	1	Polishing of Pure Water
Ultra Low Pressure Type	<1	Reject of TOC

nesses, thus necessitating some kind of protective measure. The packaged configurations in which membranes are placed in such a manner that they can readily be utilized in industrial applications are called modules.

#### (1) Plate-and-Frame Type Module

For this module type, flat sheet RO membranes in circular or rectangular shapes are used, with two variations in configuration. In the first configuration, membranes and porous support layers are laid on top of each other with intervening spacers acting as passage for filtrate. The filter structure is then fitted to filter press, thereby enabling the alternate sealing of the high-pressure raw water and low-pressure permeate sides; after this, it is placed in a pressure vessel to give it a pressure resistant structure, with the permeate taken out via the permeate collecting pipe which runs through the center of the filter. In the second configuration, membranes, spacers and porous support plates are alternately laid on and then the entire structure is clamped together with a filter press, so that the permeate is taken out of each compartment.

#### (2) Spiral-Wound Type Module

Two rectangular-shaped flat sheet RO membranes are laid on top of each other with a sheet of permeate collection material inserted between them. Three sides of each layer of this sandwich structure are then fused with those of adjoining layers so that the sandwich now looks a little like an envelope. (This envelope-like membrane element is called a leaf.) The permeate is collected via the permeate collection material, whose fourth side is left open. This side, in turn, is connected to the permeate collection tube (with permeate collecting holes provided on its cylindrical surface) which is placed at the center of the spiral into which the above leaf has been wound. The leaf is usually more than one and in that case all the leaves are connected to the

central permeate collecting tube in the same manner. In addition to the leaves, feed channel spacers are also wound into the same spiral, providing passage to the raw water. Fig. 3.5.1 shows the structure of the spiral-wound module.

### (3) Hollow Fiber Type Module

A hollow fiber module incorporates 100,000 to 1 million fine hollow fiber RO membranes, with a typical outer and inner diameter of 85 microns and 42 microns respectively and these hollow fibers are bundled together and placed in a pressure vessel. There the raw water is pressurized as it flows along the exteriors of the hollow fiber membranes, in such a way that only water permeates through the membranes into the interiors of the hollow fibers. After this, the permeate is then collected and extracted from the module at one end.

The advantages of this module are that the total membrane area can be enlarged by reducing the hollow fiber size, capitalizing on the fact that membrane supports are not required, and that the module can be made quite compact by increasing the packaging density of hollow fibers. However, there is a limitation on the reduction of the hollow fiber size since pressure losses arising from the flow of the permeate increase with a decrease in the hollow fiber size.

Also, problems of susceptibility to fouling and difficulty in removing the contaminants are created by the high packaging density, thus necessitating thorough pretreatment of the raw water.

Fig. 3.5.2 shows the structure of the hollow fiber type module<sup>9</sup>.

### (4) Tubular Type Module

This type of module has two variations, internal-pressure and external-pressure types, depending on the way the pressure is applied. The internal-pressure type has its RO membranes stuck onto the inside walls of the porous pipes so that the high pressure raw water is made to flow along the interiors of the porous pipes, with the permeate collected outside the porous pipes after going through the membranes and pipe walls. These pipes, numbering around 18, are inter-connected at one of their ends via a U-shaped pipe, thus making up a module.

The advantages of this module are that the membrane surface can be cleaned with sponge balls and that the use of turbulence inducing agents is allowed.

The external-pressure type has its RO membranes stuck on to the outside walls of the porous pipes so that the high pressure raw water is made to flow along the exteriors of the porous pipes, with the permeate collected inside the porous pipes after going through the membranes and the pipe walls. The advantages of this module are low pressure losses, the ease of membrane cleaning and the possibility of repeated use of the pipes.

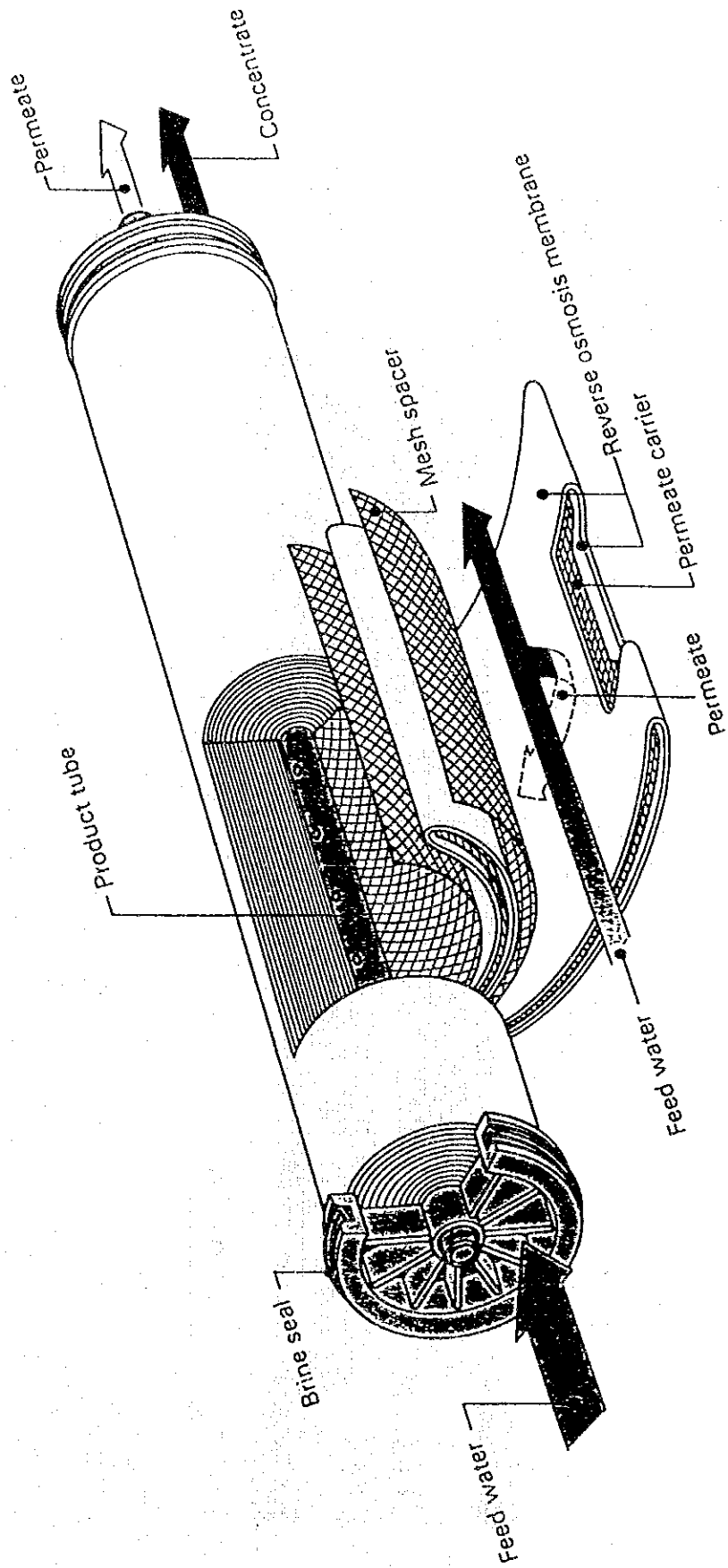
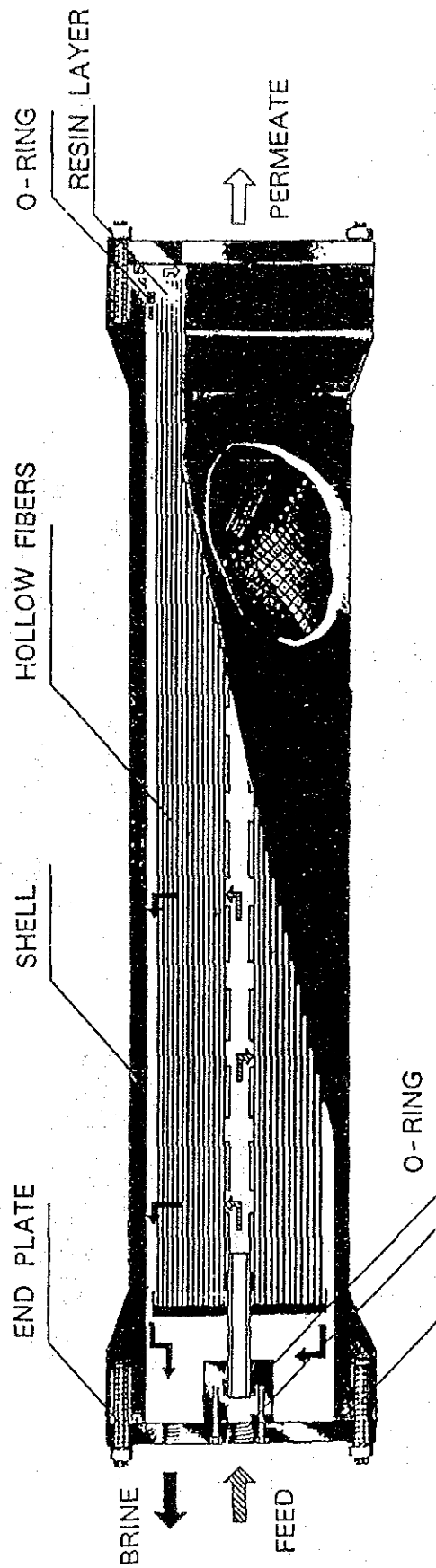


Fig. 3.5.1 Structure of spiral-wound module



4.5.12

Fig. 3.5.2 Configuration of hollow fiber type RO module<sup>9</sup>



### 3.6 Classification of RO Membranes Based on Membrane Material (Chemical Structure), and Characteristics

The characteristics of an RO membrane include a rejection, more widely-defined separation function; permeate volume; durability (heat, chlorine and pressure resistance); bacteria resistance; and the operating range of pH. These characteristics are decided by the membrane material alone. Namely, most of these RO membrane characteristics depend mainly on the kind of chemical structure that the membrane material has. In other words, once a membrane material is selected, the range of its applications is automatically fixed, thus making membrane material a very important factor in selecting an RO membrane. Here, various RO membranes are classified according to their materials, i.e. chemical structures, and membrane characteristics are summarized for each RO membrane.

#### 3.6.1 Cellulose Acetate Membranes (Asymmetric Membranes)

These are classic membranes, existing from the days of Loeb and Sourirajan and are so-called asymmetric membranes. Today they are still widely used in practical applications and are considered to be excellent membranes. The structure of the membrane's cross section is shown in Fig.3.6.1<sup>9</sup>.

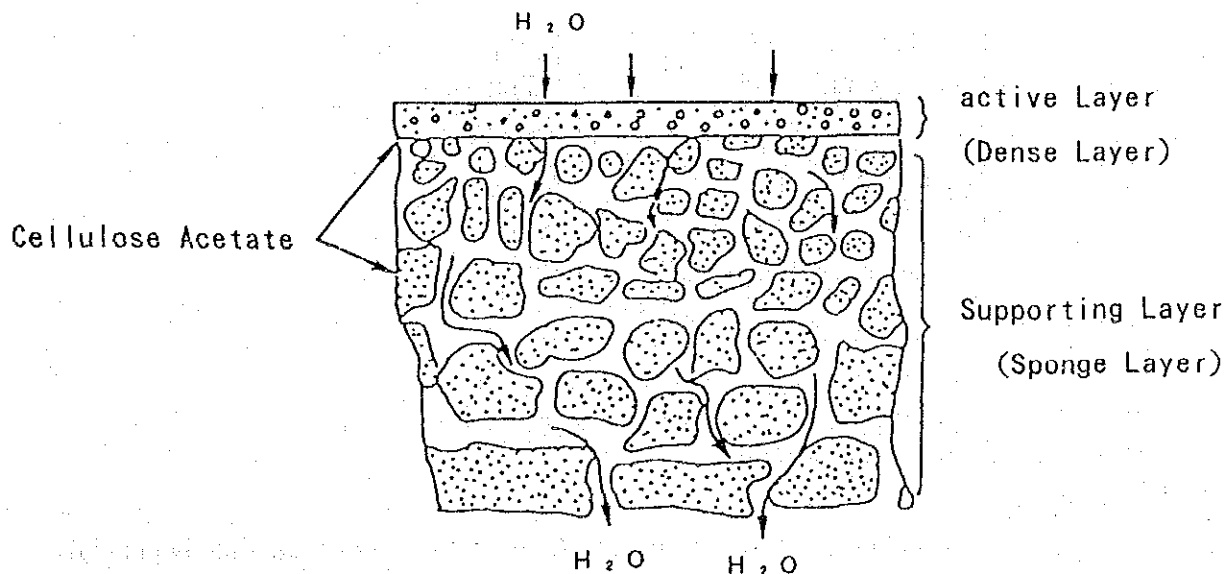


Fig.3.6.1 Cross-section Drawing of Reverse Osmosis Cellulose Acetate Asymmetric Membrane<sup>9</sup>

### (1) Membrane Manufacturing Process

The manufacturing process of cellulose acetate membranes is shown in Fig. 3.6.2<sup>8</sup>. By weight ratio, 25 of cellulose acetate, 45 of acetone, 30 of formamide are first mixed together in order to prepare a casting solution which is then poured on to a glass plate and made to spread so that its thickness will become 100 microns, with the acetone evaporating within 20 to 60 seconds. Next the glass plate is dipped in icy water for more than an hour with the casting liquid still on it, and in this process the remaining acetone and formamide are dissolved in the water so that the solution is transformed into a gel state and becomes a generally opaque film, which is then removed from the glass surface. After a thorough wash, it is heat treated so that it finally becomes a membrane with the desired membrane permeability.

### (2) Products

Examples of cellos acetate membranes are shown in Table 3.6.1<sup>9</sup>.

Table 3.6.1 Examples of Cellulose Acetate membranes<sup>9</sup>

Maker	Model No.	Element Configuration
Toray	SC-1000, SC-3000	Spiral
UOP	ROGA-4160	Spiral
Du Pont	C-1	Spiral
Hydronautics	400b-1620CA	Spiral
DSI	8054-98	Spiral

### (3) Characteristics

- 1) Rejections ratios ranging from 95 to 98%.
- 2) Easily hydrolyzed.

The hydrolysis rate is minimum at around pH 4 to 6 and increases outside this range. This speed is also temperature dependent and increases as temperature rises. This phenomenon is shown in Fig. 3.6.3<sup>4</sup>.

- 3) A narrow range of suitable operating pH 5 to 7.0. The suitable pH range means the range of pH Values at which they show resistance against hydrolyzing action. Thus, they cannot be

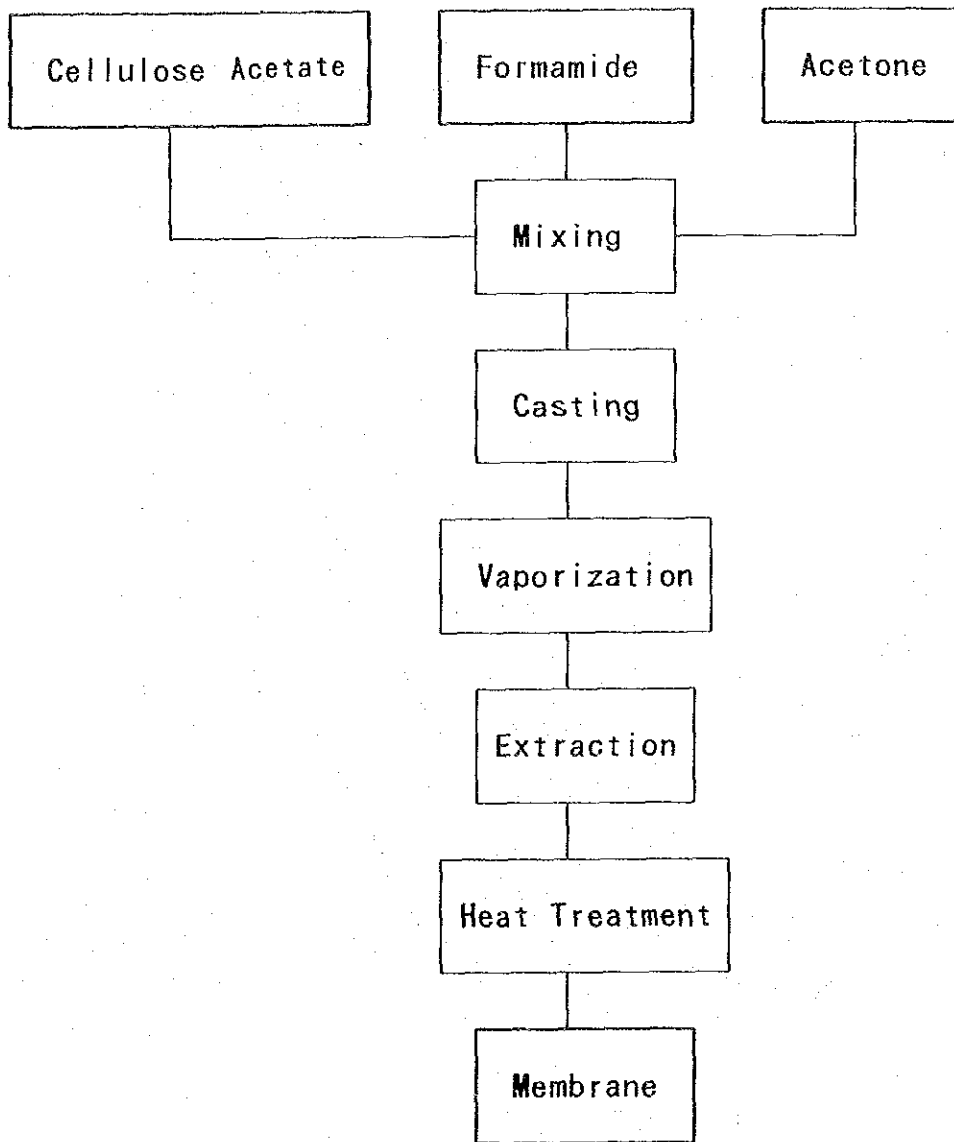


Fig.3.6.2 Membrane Casting Process<sup>8</sup>

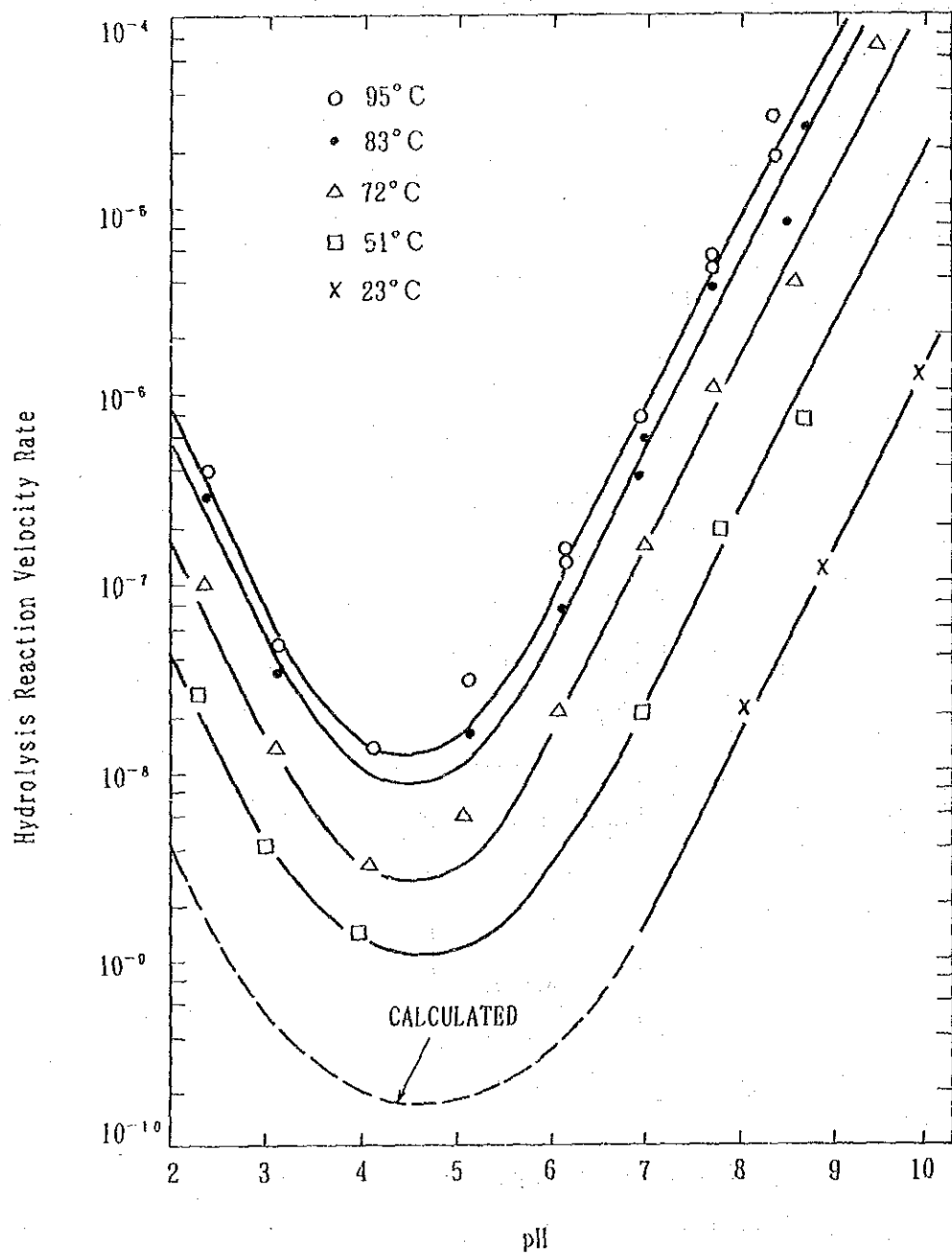


Fig.3.6.3 Effect of pH for Hydrolysis Reaction Velocity of Cellulose Acetate<sup>4</sup>

used for strong acids or weak alkalines.

- 4) Low bacteria resistance (bacteria attacking)<sup>6</sup>, brockgradable.

This is because the bacteria's enzyme action hydrolyzes the membrane materials.

- 5) Easily dissolved in various organic solvents (such as alcohols, organic acids, ketones, aldehydes and amides)<sup>7</sup>.

- 6) High chlorine resistance.

The range of free chlorine resistance is 0 to 2.0ppm<sup>5</sup>.

- 7) Limited heat resistance, actual operating range 0-0.5 ppm.

This is because hydrolyzing action becomes accelerated at high temperatures.

#### (4) Catalog Data

Table 3.6.2 shows Toray's catalog data<sup>24</sup>:

### 3.6.2 Cellulose Triacetate Membranes (Asymmetric Membranes)

These are improvements to cellulose acetate derivative membranes and are so-called asymmetric membranes. Only the hollow fiber configuration has been put to practical use. This membrane material is one of few membrane material which are capable of a single stage desalination of seawater and is being recognized as a good membrane material with a long service record.

#### (1) Membrane Manufacturing Process<sup>25</sup>

Manufacturing process and membrane characteristics of cellulose triacetate membranes are shown in Table 3.6.3.

#### (2) Products<sup>3</sup>

Examples of cellulose triacetate membranes are shown in Table 3.6.4.

Table 3.6.4 Examples of Cellulose Triacetate Membranes<sup>3</sup>

Maker	Model No.	Element Configuration
Toyobo	Hollosep	Hollow Fiber
Dow	Dowex	Hollow Fiber

Membrane Type	Cellulose Acetate													
Element Configuration	Spira Wound													
Model No	SC 1100	SC 1200	SC 2100	SG 2200	SG 3100	SC 3200	SC 4100	SC 4200	SC 5100	SC 6200	SC 8100	SG 8200	SC L100R	SC L200R
Performance Specification														
Salt Rejection %	95		95		97		97		98		96		85	
Average	94		92.5		96		96		97		95		76	
Product Flow Rate	5.8		8.8		17.6		6.8		5.3		2.2		6.2	
Average	(1530)		(2320)		(4640)		(1800)		(1400)		(580)		(1640)	
Minimum	23.2		35.2		4.4		27.2		22.0		8.8		24.8	
m <sup>3</sup> /day (gpd)	(6120)		(9280)		(1160)		(7200)		(5840)		(2320)		(6560)	
Product Flow Rate	5.2		7.6		4.0		22.0		4.3		8.0		5.3	
Minimum	(1370)		(2010)		(1060)		(5840)		(1130)		(2120)		(1400)	
Test Conditions of Performance Specification														
Pressure	30													
kg/cm <sup>2</sup> (psi)	(430)													
Temperature	25													
°C (°F)	(77)													
Feed Concentration mg/l NaCl	1500													
pH Range	5-6													
Brine Flow Rate	10		40		10		40		10		40		10	
l/min (gpm)	(2.65)		(10.6)		(2.65)		(10.6)		(2.65)		(10.6)		(2.65)	
Dimensions and Weight														
Diameter	100.5		201		100.5		201		100.5		201		100.5	
mm (in)	(4)		(8)		(4)		(8)		(4)		(8)		(4)	
Length	1016													
mm (in)	(40)													
Weight	6.3		22.0		6.3		22.0		6.3		22.0		6.3	
kg (lb)	(13.9)		(48.5)		(13.9)		(48.5)		(13.9)		(48.5)		(13.9)	

Table 3.6.2 Typical performance of TORAY's membrane 8

Table 3.6.3 Comparison of Membrane Characteristic and Cellulose Acetate Casting Method 25

Membrane Composition	Cellulose Acetate	Cellulose Triacetate
Element Configuration	TUBULAR SPIRAL Wound	Hollow Fiber
Casting Process		
Polymer Concentration	LOW	HIGH
Drawing	NILL ~ LITTLE	BIG
Heat Treatment Temperature	LOW	HIGH
Membrane Characteristic		
Dense Rate	LOW	HIGH
Orientation	LOW	HIGH
Product Flow Rate (m <sup>3</sup> /d)	1.0 ~ 0.6*	0.2*
Salt Rejection (%)	94 ~ 98	98
Applications	Brackish Water Desalination Pure Water	Pure Water Aceptic Water Brackish Water Desalination
	Sea Water Desalination (Double Stage)	Sea Water Desalination (Single Stage)
	0.3** 94 ~ 96	0.05** 99.8

\* Test Condition : 1,500ppm NaCl, 25°C, 30kg/cm<sup>2</sup>

\*\* Test Condition : 35,000ppm NaCl, 25°C, 55kg/cm<sup>2</sup>

### (3) Membrane Characteristics

#### 1) High rejection.

They are also capable of the single stage desalination of seawater.

#### 2) Easily hydrolyzed : A relatively narrow range of suitable operating pH 2 to 9.<sup>5</sup>

#### 3) A narrow range of suitable operating pH 5 to 7. They cannot be used for strong acids or medial alkalis.<sup>5</sup>

#### 4) Low bacteria resistance (bacteria attacking), and biodegradable.<sup>6</sup>

This is because bacteria's enzyme action hydrolyzes the membrane material.

#### 5) High chlorine resistance (an allowable free chlorine concentration range of 0 to 2.0ppm and actual operating range of 0 to 0.5ppm).<sup>5</sup>

#### 6) Limited heat resistance.

This is because hydrolyzing action become accelerated at high temperature.

### (4) Catalog Data<sup>25</sup>

Typical operation data of cellulose triacetate membranes are shown in Table 3.6.5–3.6.8.

### ***3.6.3 Linear Fully-Aromatic Polyamide Membranes(Asymmetric Membranes)***

Linear fully-aromatic polyamide RO membranes are so-called asymmetric membranes (classic membranes). Only the hollow fiber configuration has been put to practical and commercial use. With an outer and inner diameter of some 85 and 42 microns, respectively, a typical hollow fiber of this type is a very fine tube, thinner than human hair, with a dense layer approximately 0.1 microns thick formed on its exterior as part of an asymmetric membrane structure. The raw water, while being subjected to a high pressure, is fed to the membrane from outside so that the water is filtered by the membrane's dense layer, with the permeate collected inside the hollow fiber.

This membrane material is also one of those few which are capable of the single stage desalination of seawater and is also still widely used, especially in the field of the desalination of seawater, and is being recognized as a good membrane material with a long service record.

#### (1) Products<sup>3</sup>

Commercial linear aromatic polyamide membranes are shown in Table 3.6.9

### (2) Membrane Characteristics

#### 1) High rejection ratios.

They are also capable of the single stage desalination of seawater.<sup>8</sup>



Table 3.6.5 Typical Operation Data of Cellulose Triacetate Membranes 25

Table 3.6.6 Typical Operation Data of Cellulose Triacetate Membranes 25

## SPECIFICATION OF HOLLOSEP

## HA SERIES

Table 3.6.5

Type		Low Pressure	
Model		HA3110	HA5110
Module			
Number of Element		1	1
Size, Diameter	mm	90	140
Length	mm	420	420
Weight, Filled with Water	kg	4	11
Materials			
Vessel		FRP	FRP
End Plates		SUS304	SUS304
Connection, Female *1			
Feed		PT $\frac{1}{2}$	PT $\frac{1}{2}$
Product		PT $\frac{1}{2}$	PT $\frac{1}{2}$
Concentrate		PT $\frac{1}{4}$	PT $\frac{1}{2}$
Product Flow Rate *2			
Nominal	m <sup>3</sup> /D	0.9	2.5
Minimum	m <sup>3</sup> /D	0.6	2.0
Salt Rejection *2, *3			
Nominal	%	94	94
Minimum	%	92	92
Test Conditions			
Feed Water, NaCl Solution	ppm	500	500
Pressure	kg/cm <sup>2</sup> G	10	10
Temperature	°C	25	25
Recovery ratio	%	30	30
Operating Conditions			
Max. Pressure	kg/cm <sup>2</sup> G	15	15
Temperature Range	°C	5~35	5~35
Concentrate Flow Rate Range *5	m <sup>3</sup> /D	1~4	3~12
Feed Water Qualities			
Max. Fouling Index		4.0	4.0
pH Range *6		3~8	3~8
Residual Chlorine	ppm	0.2~1.0	0.2~1.0

Table 3.6.6

High Flux		
HA5230	HA5330	HA8130
1	1	1
150	150	295
840	1240	1320
21	31	100
FRP SUS304	FRP SUS304	FRP SUS304
PT $\frac{1}{2}$	PT $\frac{1}{2}$	PT $\frac{1}{4}$
PT $\frac{1}{2}$	PT $\frac{1}{2}$	PT $\frac{1}{4}$
PT $\frac{1}{8}$	PT $\frac{3}{8}$	PT $\frac{1}{4}$
15	24	60
11	20	54
94	94	94
92	92	92
1500	1500	1500
30	30	30
25	25	25
75	75	75
40	40	40
5~35	5~35	5~35
7.5~60	10~90	25~150
4.0	4.0	4.0
3~8	3~8	3~8
0.2~1.0	0.2~1.0	0.2~1.0

- \*1. According to your request, the female connections are changeable to NPT threads in same fitting size.
- \*2. The product flow rate and the salt rejection indicate minimum values obtained under the test conditions two hours after putting the module into the initial operation.
- \*3. The salt rejection defines the product quality, being indicated in the following formula.  

$$\left(1 - \frac{\text{salt concentration in product water}}{\text{salt concentration in feed water}}\right) \times 100.$$
- \*4. The material used for the parts which are in contact with high salinity water is SUS316.
- \*5. The concentrate flow rate range is limited by the quality and the temperature of feed water.
- \*6. pH range is limited by the feed water quality.

Table 3.6.7 Typical Operation Data of Cellulose Triacetate Membranes 25

Table 3.6.8 Typical Operation Data of Cellulose Triacetate Membranes 25

HR SERIES

Table 3.6.7

Table 3.6.8

Type		High Rejection			
Model		HR5155	HR5255	HR5355	HR8355
Module					
Number of Element		1	1	1	1
Size, Diameter	mm	153	210	210	305
Length	mm	444	816	1216	1330
Weight, Filled with Water	kg	13	30	40	125
Materials					
Vessel		FRP	FRP	FRP	FRP
End Plates		FRP	SUS316	SUS316	SUS316
Connection, Female *1					
Feed		PT $\frac{1}{2}$	PT $\frac{1}{2}$	PT $\frac{1}{2}$	PT $\frac{3}{4}$
Product		PT $\frac{1}{2}$	PT $\frac{1}{2}$	PT $\frac{1}{2}$	PT $\frac{3}{4}$
Concentrate		PT $\frac{3}{4}$	PT $\frac{3}{4}$	PT $\frac{3}{4}$	PT $\frac{3}{4}$
Product Flow Rate *2					
Nominal	m <sup>3</sup> /D	1.2	3.0	5.0	12
Minimum	m <sup>3</sup> /D	0.9	2.4	4.0	10
Salt Rejection *2, *3					
Nominal	%	99.4	99.4	99.4	99.4
Minimum	%	99.2	99.2	99.2	99.2
Test Conditions					
Feed Water, NaCl Solution	ppm	35000	35000	35000	35000
Pressure	kg/cm <sup>2</sup> G	55	55	55	55
Temperature	°C	25	25	25	25
Recovery ratio	%	30	30	30	30
Operating Conditions					
Max. Pressure	kg/cm <sup>2</sup> G	60	60	60	60
Temperature Range	°C	5~40	5~40	5~40	5~40
Concentrate Flow Rate Range *5	m <sup>3</sup> /D	2~10	3~60	5~90	15~150
Feed Water Qualities					
Max. Fouling Index		4.0	4.0	4.0	4.0
pH Range *6		3~8	3~8	3~8	3~8
Residual Chlorine	ppm	0.2~1.0	0.2~1.0	0.2~1.0	0.2~1.0

High Rejection	
HM8255	HM9255
2	2
298	360
2640	2665
205	310
FRP	FRP
SUS304**	SUS304**
PT1	PT1
2-PT $\frac{3}{4}$	2-PT $\frac{3}{4}$
PT1	PT1
27.5	35
25	32
99.4	99.4
99.2	99.2
35000	35000
55	55
25	25
30	30
65	70
5~40	5~40
35~120	50~150
4.0	4.0
3~8	3~8
0.2~1.0	0.2~1.0

\* The above specifications are understood to be subject to change without prior announcement.

## GENERAL PRECAUTIONS

- Keep the HOLLOSEP away from direct sunshine.
- Since the HOLLOSEP is filled with preservative solution to keep its performance, be sure to discharge perfectly the solution prior to use.
- Do not freeze or dry the HOLLOSEP at all times.

Table 3.6.9 Examples of Aromatic Polyamide Membranes 3

Maker	Model No.	Element Configuration
Du Pont	Permasep B-9, B-10	Hollow Fiber
	Permasep B-15	Spiral

2) A wide range of suitable operating pH 3 to 11<sup>5</sup>. Although they have a high resistance against alkalis, they cannot be used for strong acids or strong alkali.

3) Very low chlorine resistance (an allowable free chlorine concentration range of 0 to 0.1ppm).

(3) Catalog Data

Du Pont's catalog data on their linear aromatic polyamide membranes are shown in Table 3.6.10<sup>35</sup>.

**3.6.4 Crosslinked Fully-aromatic Polyamide Membranes(Composite Membranes)**

While the membranes thus far mentioned have all been asymmetric, only composite membranes will be discussed henceforth.

(1) Chemical Structure of the Membranes<sup>13</sup>

Chemical structure of crosslinked aromatic polyamide membranes are shown in Fig.3.6.4.

(2) The Membrane Manufacturing Process

Crosslinked fully aromatic polyamide skin layers are formed with the "in situ" polymerization method based on the Schotten-Baumann interfacial reaction between water-soluble multi-functional amines and oil-soluble multi functional acid chlorides. These are so-called interfacial polymerization type composite membranes.

The manufacturing process of FT-30 (BW-30) from Film Tec, for example, is as follows.

First of all, a polyester non-woven fabric is finished on a polishing machine to give it a strong and smooth surface onto which a polysulfone microporous layer is then cast, with its

Table 3.6.10 DuPont's linear aromatic polyamide membranes 26



**PRODUCT SPECIFICATIONS FOR PERMASEP\* PERMEATORS AND REPLACEMENT BUNDLES**

APPLICATION	SEAWATER				BRACKISH							
PRODUCT TYPE	B-10 <sup>1,2</sup>				B-9							
MODEL NO.	6410T	6440T	6845T	6845TR	0410	0420	0440	0840	0840R	0040	0040R	
<b>PHYSICAL CHARACTERISTICS</b>												
MEMBRANE TYPE	ARAMID				ARAMID							
MEMBRANE CONFIGURATION	Hollow Fine Fiber				Hollow Fine Fiber							
DIAMETER, NOMINAL, cm (in)	11.7 (5)	11.7 (5)	21.6 (8)	21.6 (8)	10.2 (4)	10.2 (4)	10.2 (4)	20.3 (8)	20.3 (8)	25.4 (10)	25.4 (10)	
APPROX. LENGTH <sup>3</sup> , cm (in)	58 (23)	126 (50)	150 (59)	150 (59) <sup>1</sup>	43 (17)	64 (25)	119 (47)	122 (48)	89 (35) <sup>3</sup>	135 (53)	89 (35) <sup>3</sup>	
APPROX. SHIPPING WEIGHT kg (lb)	10 (22)	32 (70)	122 (270)	30 (66)	7 (15)	11 (25)	23 (50)	66 (145)	34 (75)	113 (250)	53 (117)	
CONNECTIONS - FEMALE NPT FEED	1/2"	1/2"	3/4"	NA	1/2"	1/2"	1/2"	3/4"	NA	1-1/2"	NA	
PRODUCT	1/2"	1/2"	3/4"	NA	1/2"	1/2"	1/2"	3/4"	NA	1"	NA	
BRINE	3/8"	3/8"	3/4"	NA	3/8"	3/8"	3/8"	3/4"	NA	1"	NA	
SAMPLE	1/8"	1/8"	3/8"	NA	1/8"	1/8"	1/8"	3/8"	NA	3/8"	NA	
<b>OPERATING SPECIFICATIONS</b>												
PRODUCT WATER CAPACITY m <sup>3</sup> /day (GPD) Nominal <sup>4</sup>	2.46 (650)	6.81 (1800)	26.5 (7000)	26.5 (7000)	5.30 (1400)	9.08 (2400)	15.90 (4200)	60.57 (16,000)	60.57 (16,000)	94.64 (25,000)	94.64 (25,000)	
RANGE	2.09/2.83 (552/747)	5.40/7.80 (1500/2100)	22.52/30.48 (5950/8050)	22.52/30.48 (5950/8050)	4.77/6.09 (1260/1540)	8.18/10.22 (2160/2640)	14.31/18.17 (3780/4620)	54.51/66.62 (14,400/17,600)	54.51/66.62 (14,400/17,600)	85.17/104.10 (22,500/27,500)	85.17/104.10 (22,500/27,500)	
SALT REJECTION (%) Nominal <sup>4</sup>	99.2	99.2	99.2	99.2	94	94	92	92	92	92	92	
MINIMUM	98.7	98.7	98.7	98.7	90	90	90	90	90	90	90	
OPERATING PRESSURE RANGE KPa (psig)	(5515-8274) 800-1200				2415-2760 (350-400)							
OPERATING TEMPERATURE RANGE °C (°F)	0-40 (32-104)				0-40 (32-104)							
pH RANGE, CONTINUOUS EXPOSURE	4-9				4-11							
BRINE RATE, l/min (gpm) MAXIMUM	9.9 (2.6)	39.4 (10.4)	105.2 (27.8)	105.2 (27.8)	6.4 (1.7)	12.5 (3.3)	25.4 (6.7)	65.9 (17.4)	65.9 (17.4)	106.0 (28.0)	106.0 (28.0)	
MINIMUM SEAWATER	1.1 (0.3)	5.3 (1.4)	15.9 (4.2)	15.9 (4.2)	NA	NA	NA	NA	NA	NA	NA	
HIGH BRACKISH	2.3 (0.6)	8.3 (2.2)	26.5 (7.0)	26.5 (7.0)	NA	NA	NA	NA	NA	NA	NA	
BRACKISH	NA	NA	NA	NA	2.3 (0.6)	4.2 (1.1)	8.3 (2.2)	26.5 (7.0)	26.5 (7.0)	43.5 (11.5)	43.5 (11.5)	
<b>STANDARD CONDITIONS</b>												
FEED, mg/l NaCl	35,000				1,500							
PRESSURE, KPa (psig)	6895 (1000)				2760 (400)							
TEMPERATURE °C (°F)	25 (77)				25 (77)							
CONVERSION %	35				75							

\*Du Pont's registered trademark for its reverse osmosis products.  
NA = Not applicable

<sup>1</sup>Seawater and High Brackish applications  
<sup>2</sup>All B-10 permeators are also available on special orders as "TA" models, i.e. B-10T bundles equipped with shell assemblies rated for 1000 psig  
<sup>3</sup>Bundle length without shipping container  
<sup>4</sup>Nominal values are for design purposes

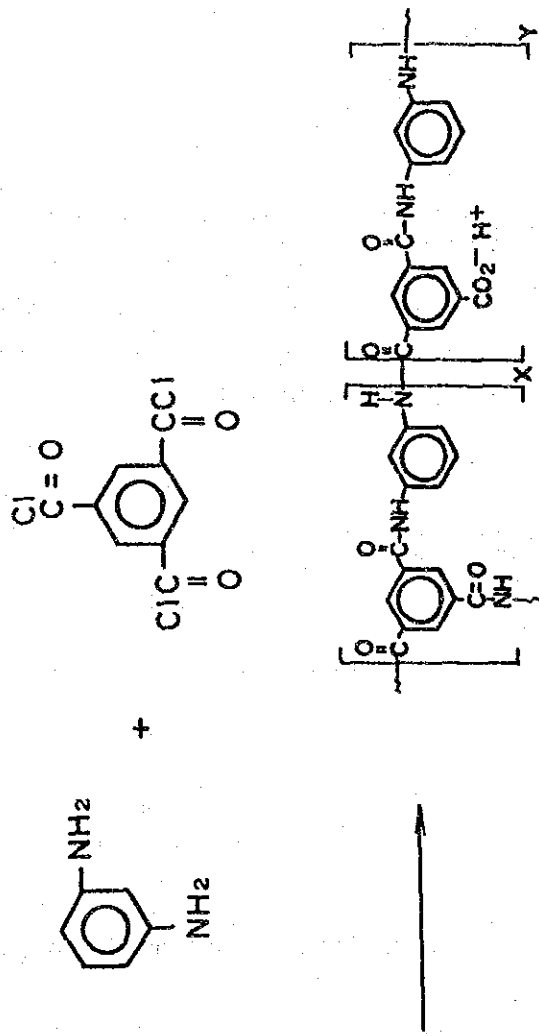


Fig. 3.6.4 Chemical Structure of the Fully Aromatic Polyamide

porosity controlled to be around 150Å. The membrane is completed by coating this polysulfone layer, used as a support layer for its high compaction resistance, with a skin layer approximately 2500Å thick<sup>3</sup>.

### (3) Products

Commercial crosslinked aromatic polyamide membranes are shown in Table 3.6.11.

Table 3.6.11 Examples of Crosslinked Aromatic Polyamide Composite Membranes

Maker	Model No.	Element Configuration
Film Tec	TW, BW-30, NF-50, NF-70, SW, HR-30	Spiral
DDS		Plate & Frame
PCI		Tubular
Toray	SU-700, SU-800, SU-900, UTC-70	Spiral
Nitto Denko	NTR-759HR, NTR-704WC	Spiral
Toyobo	HS5230, HS5530	Hollow Fiber

### (4) Membrane Performance

- 1) A variety of RO functions incorporated with good balance. These are the membranes with the best future prospect.
- 2) A high degree of cross-linking and hydrophilicity.
- 3) Low operating pressures.
- 4) High rejection.  
The salt rejection of UTC-70 is shown in Table 3.6.12<sup>3</sup>.
- 5) High flux.
- 6) A wide range of suitable operating pH 3 to 11<sup>5</sup>. Although they exhibit a high alkali resistance, they cannot be used for strong acids or strong alkali.
- 7) High oxidation resistance (durability).
- 8) Very low chlorine resistance (an allowable free chlorine resistance range of 0 to 0.1ppm).

Table 3.6.12 Rejection of inorganic materials(By UTC-70)  
 NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, MgSO<sub>4</sub><sup>3</sup>

		NaCl	Na <sub>2</sub> SO <sub>4</sub>	MgCl <sub>2</sub>	MgSO <sub>4</sub>
Rejection (%)	Cation	99.48	99.87	99.88	99.93
	Anion	99.53	99.94	99.75	99.94
(m <sup>3</sup> /day)		7.0	7.5	6.7	7.3

Test conditions

Concentration : 1500 ppm  
 Operating Pressure : 15 kg/cm<sup>2</sup> (214 psi)  
 Water Temperature : 25 °C (77°F)  
 pH : 6.5  
 Brine flow rate : 20 l/min (5.28 gpm)

The followings are possible counter-measures to this:

- a) A shift to disinfectants with few effects on the membrane (such as chloramine) from chlorine.
- b) The use of chlorine maintained but its contact with the membrane avoided.
- c) Chlorine sterilization carried out only intermittently.
- 9) High hydrogen peroxide resistance.
- 10) High bacteria resistance.
- 11) High SiO<sub>2</sub> rejection.
- 12) High TOC rejection.

Table 3.6.13 shows the TOC rejection of UTC-70.

Table 3.6.13 Organic Rejection of Low Pressure Type Membrane(Rej.%)

Solute	Mw	UTC-70	BW-30
Methanol	32.04	13.9	11.1
Ethanol	46.07	54.1	52.7
Iso-propanol	60.10	96.2	90.8
Acetone	58.08	69.5	66.9
Formaldehyde	30.03	32.3	28.9
Urea	60.06	63.0	58.7
Acetic Acid	60.05	55.0	54.4
Citric Acid	210.14	99.0	99.0
Ethylene Diamine	60.10	95.0	91.0
Sucrose	342.30	99.79	99.71

Feed Conc. 1000ppm, Press. 15Kg/cm<sup>2</sup>, Temp.25°C

(5) Catalog Data

- 1) Data concerning commercial crosslinked aromatic polyamide membrane, FT-30 made by Film Tec. Co., Ltd. are shown in Table 3.6.14.
- 2) Data concerning commercial crosslinked aromatic polyamide membrane made by TORAY Co., Ltd. are shown in Table 3.6.15 and Table 3.6.16.
- 3) Data concerning commercial crosslinked aromatic polyamide membrane made by Nitto Denko Corporation are shown in Table 3.6.17 and Table 3.6.18.



Table 3.6.14 Data concerning commercial crosslinked aromatic polyamide membrane, FT-30 made by Film Tec. Co., Ltd.

	FT-30	FT-40	FT-50
Pressure, PSI	200	200	150
Flux, GFD	22-26	30-35	70-80
Rejection			
Sodium Chloride	98%	55%	55%
Magnesium Sulfate	99%	95%	95%
Glucose	>99%	95%	95%
Sucrose	>99%	99%	99%
Raffinose	>99%	>99%	>99%
Maltotetrose	>99%	>99%	>99%
Colloids	>99%	>99%	>99%
Chlorine Tolerance	Fair	Good	Poor

Table 3.6.15 Data concerning commercial crosslinked aromatic polyamide membrane made by TORAY Co., Ltd.

			SU-810	SU-820
Performance	Salt Rejection* %	Average	99.4	99.4
		Minimum	99.2	99.2
	Product Flow Rate m <sup>3</sup> /day(gpd)	Average	4.0 (1055)	16.0 (4220)
		Minimum	3.5 (925)	14.0 (3700)
Test Conditions	Operating Pressure	kg/cm <sup>2</sup> (psi)	56 (800)	56 (800)
	Temperature	°C(°F)	25(77)	25(77)
	Feed Concentration	%asNaCl	3.5	3.5
	Brine Flow Rate	ℓ/min(gpm)	20(5.3)	80(21.2)
Measurement	Diameter	mm(in)	101(4)	201(8)
	Length	mm(in)	1016(40)	1016(40)
	Weight	kg(lb)	4.5(9.9)	16.5(36.4)

\*99.6% in case of 3.5% Seawater.

Table 3.6.16 Data concerning commercial crosslinked aromatic polyamide membrane made by TORAY Co, Ltd.

	SU-710	SU-720		
<b>Performance</b>	Salt Rejection %	Average Minimum	99.4 99.0	99.4 99.0
	Product Flow Rate m <sup>3</sup> /day (gpd)	Average Minimum	6.5 (1720) 5.5 (1460)	26 (6880) 22 (5840)
<b>Test Conditions</b>	Operating Pressure	kg/cm <sup>2</sup> (psi)	15 (215)	15 (215)
	Temperature	°C (°F)	25 (77)	25 (77)
	Feed Concentration Brine Flow Rate	mg/l NaCl l/min (gpm)	1500 20 (5.3)	1500 80 (21.2)
<b>Measurement</b>	Diameter	mm (in)	101 (4)	201 (8)
	Length	mm (in)	1016 (40)	1016 (40)
	Weight	kg (lb)	4.5 (9.9)	16.5 (36.4)

Note: Specifications are based on the expected average value for 100 or more elements.

Table 3.6.17 Data concerning commercial crosslinked aromatic polyamide membrane made by Nitto Denko Corporation

PRODUCT TYPE		NTR-759HR		
MODEL NO.		S2	S4	S8
OPERATING SPECIFICATIONS				
SALT REJECTION Nominal	%	99.5		
PRODUCT WATER CAPACITY Nominal	m <sup>3</sup> /day	1.6	7.0	30
OPERATING PRESSURE Maximan	kg/cm <sup>2</sup>	30		
OPERATING TEMPERATURE Maximan	°C	40		
FEED FLOW RATE	ℓ/min	25	42	200
FEED SDI		<4		
ALLOWABLE CHLORINE CONC.	ppm	<1		
pH RANGE		2-10		
PRESSURE DROP	1element kg/cm <sup>2</sup>	0.8		
	6element kg/cm <sup>2</sup>	4.2		
STANDARD CONDITIONS				
FEED, mg/l NaCl	%	0.15		
PRESSURE	kg/cm <sup>2</sup>	15		
TEMPERATURE	°C	25		
pH	—	6.5		
CONVERSION	%	10-20		

Table 3.6.18 Data concerning commercial crosslinked aromatic polyamide membrane made by Nitto Denko Corporation

PRODUCT TYPE		NTR-70SWC	
MODEL NO.		S4	S8
OPERATING SPECIFICATIONS			
SALT REJECTION Nominal	%	99.5	
PRODUCT WATER CAPACITY Nominal	m <sup>3</sup> /day	4.3	18.8
OPERATING PRESSURE Maximum	kg/cm <sup>2</sup>	70	
OPERATING TEMPERATURE Maximum	°C	45	
FEED FLOW RATE	l/min	80	284
FEED SDI		<4	
ALLOWABLE CHLORINE CONC.	ppm	0.1	
pH RANGE		3-10	
PRESSURE DROP	1element kg/cm <sup>2</sup>	0.56	
	6element kg/cm <sup>2</sup>	3.36	
STANDARD CONDITIONS			
FEED, mg/l NaCl	%	3.2	
PRESSURE	kg/cm <sup>2</sup>	56	
TEMPERATURE	°C	25	
pH	-	6-7	
CONVERSION	%	7	

### 3.6.5 Aryl-Alkyl Polyamide/Polyurea Membranes

#### (1) Chemical Constitution of Membranes

Fig. 3.6.5 shows typical examples of skin layers of aryl-alkyl polyamide/polyurea composite membranes.

#### (2) Membrane Manufacturing Process.

Aryl-alkyl polyamide/polyurea skin layers are formed using the "in situ" polymerization based on the Schotten-Baumann interfacial reaction. These are so-called interfacial polymerization type composite membranes.

#### (3) Products<sup>3</sup>

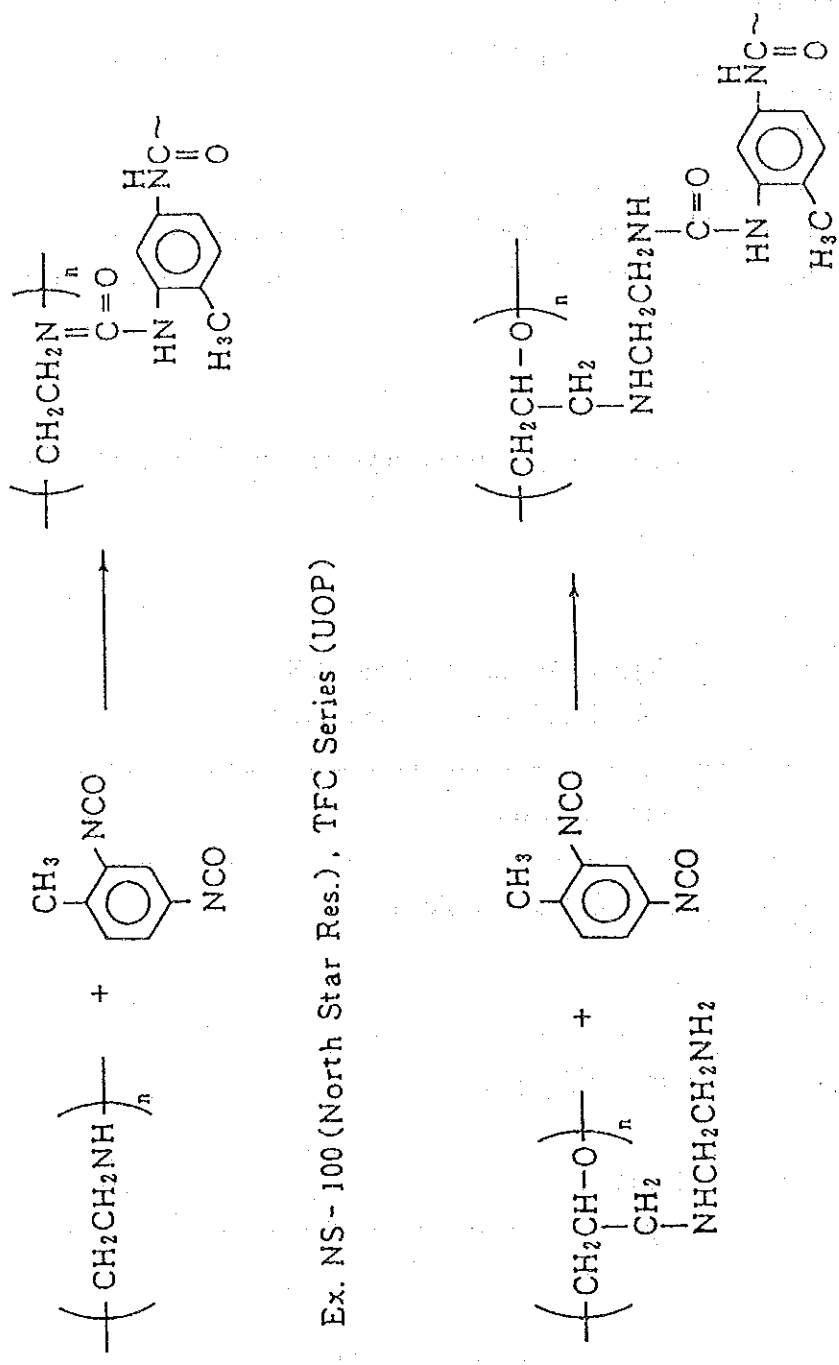
Typical commercial aryl-alkyl polyamide/polyurea composite membranes are shown in Table 3.6.19.

Table 3.6.19. Typical Commercial Aryl-alkyl Polyamide/polyurea Composite Membranes <sup>3</sup>

Maker	Membrane No.	Module Type
UOP	RC-100, PA-300, TFC	Spiral
Hydronautics	CPA	Spiral
Nitto Denko	NTR-7197, NTR-739HF	Spiral
Dupont	Permasep A-15	Spiral

#### (4) Membrane Characteristics

Membrane characteristics of aryl-alkyl polyamide/polyurea composite membranes are summarized below:



Ex. NS-100 (North Star Res.), TFC Series (UOP)

Fig.3.6.5 Chemical structure of aryl-alkyl polyamide/polyurea composite membrane 13

- 1) High rejection ratios : A similar level to those of cross-linked fully-aromatic membranes.
- 2) High flux.
- 3) Very low oxidation resistance (durability).
- 4) High TOC rejection : A similar level to those of crosslinked fully-aromatic polyamide membranes.
- 5) High SiO<sub>2</sub> rejection : A similar level to those of crosslinked fully-aromatic polyamide membranes.

(5) Catalog Data

Nitto Denko's data on their aryl-alkyl polyamide/polyurea composite membranes are shown in Table 3.6.20<sup>32</sup>.

### 3.6.6 Piperazine Polyamide Membranes (Composite Membranes)

The greatest advantage of piperazine polyamide membranes is its excellent chlorine resistance. Piperazine polyamide was originally investigated by Montedison for use in asymmetric membranes as chlorine resistance linear polymers<sup>21</sup>. After that, J.F. Cadotte succeeded in applying this material to composite membranes<sup>22</sup> and as a result these membranes have been put to practical use as so-called "loose RO" membranes which lie midway between reverse osmosis and ultrafiltration in terms of separation performance.

(1) Chemical Structure of Membranes

Fig. 3.6.6 shows typical examples of chemical structure of skin layers incorporated in piperazine polyamide membranes.

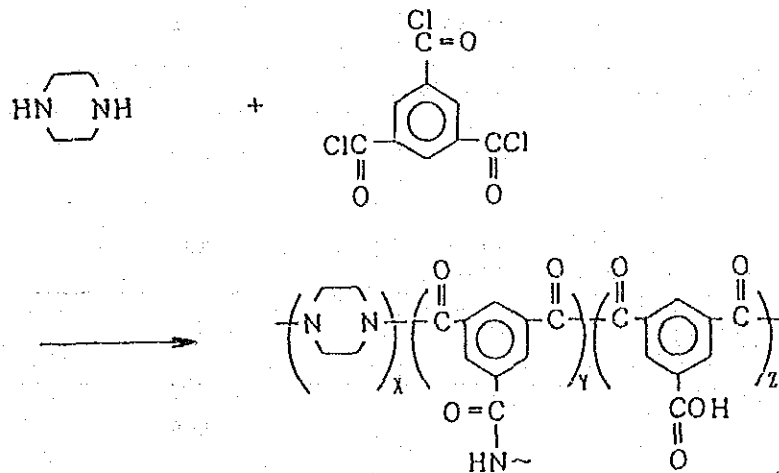


Fig.3.6.6 Chemical Structure of Piperazine Polyamide 13

Table 3.6.20 Nitto Denko's data on their aryl-alkyl polyamide/polyurea composite membranes

PRODUCT TYPE MODEL NO.		NTR-7197		
		S2	S4	S8
OPERATING SPECIFICATIONS				
SALT REJECTION Nominal	%	98		
PRODUCT WATER CAPACITY Nominal	m <sup>3</sup> /day	1.6	6.8	30
OPERATING PRESSURE Maximum	kg/cm <sup>2</sup>	42		
OPERATING TEMPERATURE Maximum	°C	40		
FEED FLOW RATE	l/min	25	42	200
FEED SDI		<4		
ALLOWABLE CHLORINE CONC.	ppm	0.00		
pH RANGE		4-11		
PRESSURE DROP	1element kg/cm <sup>2</sup>	0.8		
	6element kg/cm <sup>2</sup>	4.2		
STANDARD CONDITIONS				
FEED, mg/l NaCl	%	0.2		
PRESSURE	kg/cm <sup>2</sup>	30		
TEMPERATURE	°C	25		
pH	—	6.5		
CONVERSION	%	10-20		



## (2) The Manufacturing Process

Piperazine polyamide skin layers are formed using the "in situ" polymerization based on the Schotten-Baumann interfacial reaction. These are so-called interfacial polymerization type composite membranes.

## (3) Products<sup>3</sup>

Example of commercial piperazine polyamide composite membranes is shown in Table 3.6.21.

Table 3.6.21 Examples of Commercial Piperazine Polyamide Composite Membranes<sup>3</sup>

Maker	Membrane No.	Model Type
Film Tec	NF-40, NF-40HF	Spiral
Nitto Denko	NTR-7250, NTR-729HF	Spiral
Toray	SU-200, 500, 600	Spiral

## (4) Membrane Characteristics<sup>3</sup>

As the fact that they are dubbed "loose RO" implies, these membranes do not exhibit high rejection for low molecular weight organic compounds. Nevertheless expectations are high for their application in the food area, since they can remove most of the organic compounds with molecular weight greater than those of sucrose (molecular weight 342) or similar.

The following is a summary of membrane characteristics of piperazine polyamide composite membranes:

- 1) High flux
- 2) High chlorine resistance
- 3) High hydrogen peroxide resistance
- 4) Low rejection -> loose RO membranes: an application for food industry.

## (5) Catalog Data

Nitto Denko's data on their piperazine polyamide composite membrane are shown in Table 3.6.22<sup>32</sup>:

Table 3.6.22 Nitto Denko's data on their piperazine polyamide composite membrane 23

PRODUCT TYPE	NTR-7250			NTR-729HF		
MODEL NO.	S2	S4	S8	S2	S4	S8
OPERATING SPECIFICATIONS						
SALT REJECTION % Nominal	60			93		
PRODUCT WATER CAPACITY m/day Nominal	3.6	12	48	3.6	12	54
OPERATING PRESSURE Kg/cm <sup>2</sup> Maximum	30			30		
OPERATING TEMPERATURE °C Maximum	40			40		
FEED FLOW RATE l/min	25	42	200	25	42	200
FEED SDI	<4			<4		
ALLOWABLE CHLORINE CONC. ppm	<1			<1		
pH RANGE	2-8			2-8		
PRESSURE DROP 1element Kg/cm <sup>2</sup>	0.8			0.8		
6element Kg/cm <sup>2</sup>	3.2			3.2		
STANDARD CONDITIONS						
FEED, mg/l NaCl %	0.15			0.15		
PRESSURE Kg/cm <sup>2</sup>	5			10		
TEMPERATURE °C	25			25		
pH	6.5			6.5		
CONVERSION %	30-35			15-25		

### 3.6.7 Sulfonated Polysulfone Membranes (Composite Membranes)

The material of these membranes was developed in the process of developing RO membranes with high durability, which took an approach of introducing hydrophilic functional groups into hydrophobic polymers. Classified as an above-mentioned 'loose RO', their characteristics include 10 % or so NaCl rejection, sharp cut-off molecular weight characteristics, and peculiar behaviors exhibited in their solute separation performance, common among RO membranes with cationic ion exchangeability.

For these reason, their application has been sought in areas where sterilization with high concentration chlorine or cleaning with strong acids or strong alkali is conducted, such as the food industry.

Although these membranes were originally developed by Rhone-Poulenc, ICI, Albany, etc., they are presently commercialized by Milipore, DSI and Nitto Denko.

#### (1) Chemical Structures of Membranes

Fig. 3.6.7 shows typical examples of chemical structures of skin layers incorporated in the sulfonated polysulfone composite membranes.

#### (2) The Membrane Manufacturing Process

In contrast to skin layers made of crosslinked fully-aromatic polyamide, aryl-alkyl polyamide/polyurea and piperazine polyamide, which are all formed using the in situ polymerization based on the Schotten-Baumann interfacial reaction, sulfonated polysulfone skin layers, being linear polymers, are formed using the thin film formation process. Thus they are so-called polymer coating composite membranes.

#### (3) Products<sup>3</sup>

Example of sulfonated polysulfone membranes are shown in Table 3.6.23.

Table 3.6.23 Example of sulfonated polysulfone membranes<sup>3</sup>

Maker	Membrane No.	Module Type
Millipore	PSRP	Spiral
DSI	Desal Plus	Spiral
Nitto Denko	NTR-7410, NTR-7450	Spiral

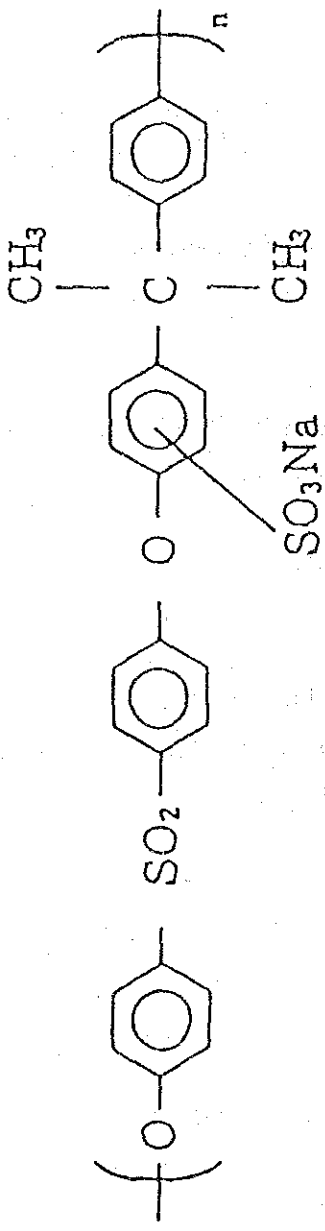


Fig.3.6.7 Representative chemical structure of sulfonated polystyrene

#### (4) Membrane Characteristics

In addition to being heat resistant, sulfonated polysulfone is a chemically stable polymer, with resistance against electrophilic substitution reaction due to the electron withdrawing property of sulfonic acid groups.

Membrane characteristics of sulfonated polysulfone composite membranes are summarized below:

- 1) High heat resistance
- 2) Low rejection -> Loose RO membranes
- 3) High Chlorine resistance -> Food industry application

#### (5) Catalog Data

Nitto Denko's data on their sulfonated polysulfone composite membranes are shown in Table 3.6.24.

### 3.6.8 Crosslinked Polyether Membranes (Composite Membranes)

Marketed in the early 1980's, PEC-1000 (Toray) achieved a NaCl rejection rate of 99.9%, which is still one of the world's best records, capable of full single stage seawater desalination.

#### (1) The Membrane Manufacturing Process

Crosslinked polyether skin layers are formed using in situ polymerization where polymerization catalysts and monomers are deposited or dip-coated on the support layer with subsequent polymerization by heating. These are so-called monomer polymerization composite membranes.

#### (2) Products<sup>3</sup>

Example of crosslinked polyether membranes is shown in Table 3.6.25

Table 3.6.25 An example of crosslinked polyether composite membranes<sup>3</sup>

Maker	Membrane No.	Model Type
Toray	PEC-1000	Spiral

Table 3.6.24 Nitto Denko's data on their sulfonated polysulfon composite membranes

PRODUCT TYPE		NTR-7410		NTR-7450	
MODEL NO.		S2	S4	S2	S4
OPERATING SPECIFICATIONS					
SALT REJECTION Nominal	%	10		50	
PRODUCT WATER CAPACITY Nominal	m <sup>3</sup> /day	8	25	4.5	13
OPERATING PRESSURE Maximum	kg/cm <sup>2</sup>	30		30	
OPERATING TEMPERATURE Maximum	°C	40		40	
FEED FLOW RATE	ℓ/min	25	42	25	42
FEED SDI		<4		<4	
ALLOWABLE CHLORINE CONC.	ppm	<100		<100	
pH RANGE		2-11		2-11	
PRESSURE DROP	1element kg/cm <sup>2</sup>	0.8		0.8	
	6element kg/cm <sup>2</sup>	4.2		4.2	
STANDARD CONDITIONS					
FEED, mg/l NaCl	%	0.2		0.2	
PRESSURE	kg/cm <sup>2</sup>	5		10	
TEMPERATURE	°C	25		25	
pH	—	6.5		6.5	
CONVERSION	%	50		50	

### (3) Membrane Characteristics

- 1) A super high rejection (NaCl rejection 99.9%) capable of full single stage seawater desalination.
- 2) Very low oxidation resistance → Low resistance against dissolved oxygen and chlorine after dissolved oxygen.
- 3) The possibility of enhancing their heat and chemical resistance by introducing segments with such properties.
- 4) Sharp cut-off molecular weight characteristics for compounds with molecular weights of around 500, as shown in Fig. 3.6.8<sup>3</sup>.

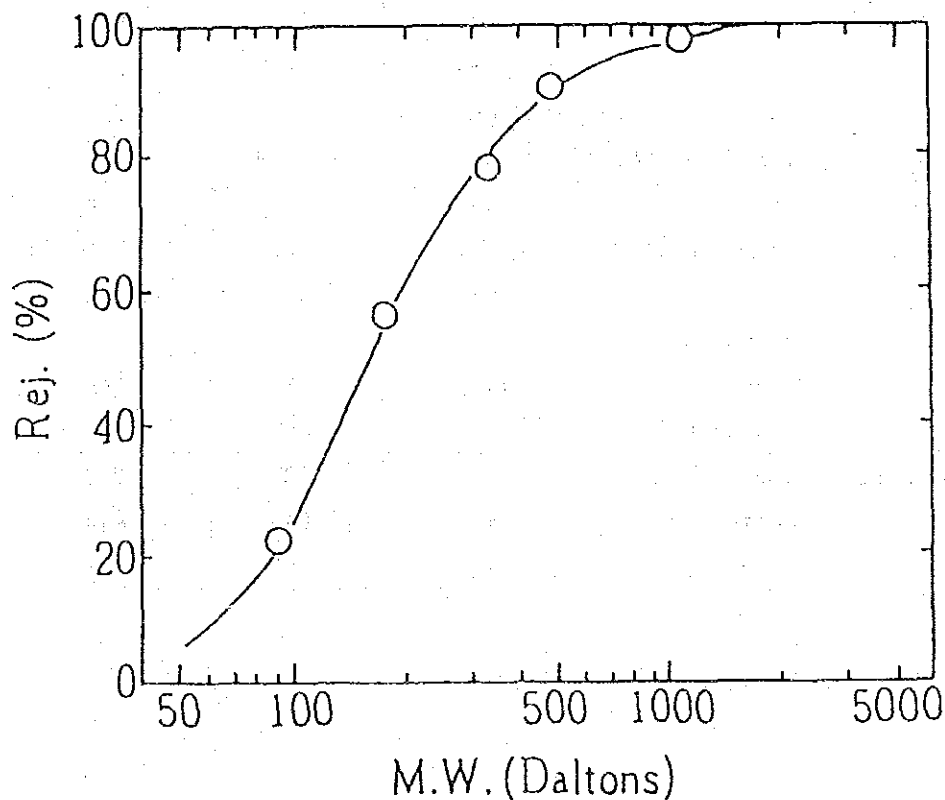


Fig.3.6.8 Separation performance of crosslinked polyether composite ultrafiltration membrane <sup>3</sup>

(4) Catalog Data

Toray's catalog data on their crosslinked polyether RO membranes are shown in the Table 3.6.26<sup>3</sup>.

Table 3.6.26 Specification for PEC-1000 Module <sup>3</sup>

Membrane Type Element Type		Synthetic Composite Membrane Spiral Type <SP Series>		
Model No.		SP-110	SP-120	
PERFORMANCE	Rejection	Ave. (%)	99.7	99.7
		Min. (%)	99.5	99.5
	Product	Ave. (m <sup>3</sup> /day)	2.25	9.0
	Flow Rate	Min. (m <sup>3</sup> /day)	1.9	7.6
Test Condition	Pressure	(kgf/ cm)	56	56
	Temperature	(°C)	25	25
	Feed Concentration	(ppm)	35,000	35,000
	Brine Flow Rate	(ℓ /min)	10	40
	Dimensions& Weight	Dimeter	(mm)	101
Length		(mm)	1,016	1,016
Weight		(kg)	6	22

**3.6.9 Summary**

Classification of RO membranes according to their chemical structures and the membrane characteristics of each membrane, which have so far been discussed, are summarized in Table 3.6.27<sup>3</sup>.



Table 3.6.27 Classification of commercial RO Membrane by Chemical Structure<sup>3</sup>

membrane type/maker	name of goods	module type
Crosslinked fully aromatic polyamide FilmTec (DDS) (PCL) Toray Nitro Denko	TW/BW/SW/HR-30* HR-95*, HR-99* ZF-99* SU-700*, SU-800*, SU-900*, UTC-70 NTR-759*, NTR-70SWC	spiral plate & frame tubular spiral spiral
Linear fully aromatic polyamide Dupont DuPont	Permasep B-9, B-10 Permasep B-15	hollow fine fiber spiral
aryl-alkyl polyamide/ polyurea UOP Hydranautics Nitro Denko DuPont North Star Res.	RC-100 (and PA-300)*, TFC CPA* NTR-7197*, NTR-739HF* Permasep A-15* NS-100	spiral spiral spiral spiral
Polypiperazine amide FilmTec Nitro Denko Toray	NF-40*, NF-40HF* NTR-7250*, NTR-729HF* SU-200*, SU-600*, SU-500*	spiral spiral spiral
Cellulose acetate Toray UOP Hydranautics DSI DuPont	SC-1000, 3000 ROGA-4160 400B-1620CA 8054-98 C-1	spiral spiral spiral spiral spiral
Cellulose triacetate TOYOBO	Hollosep	hollow fiber
Crosslinked polyether Toray	PEC-1000*	spiral
Polyacrylnitril Sumitomo chemical	Solrex	tubular, spiral
Polybenzimidazolone TEIJIN	PBIL	tubular, spiral
Sulfonated polysulfon DSI Millipore Nitro Denko	Desal Plus* PSRO* NTR-7410, 7450*	spiral spiral spiral

### 3.7 High Heat-Resistance RO Membranes

Table 3.7.1 shows commercial RO membranes with a heat resistance of 35°C or more.

Table 3.7.1 Example of Heat Resisting Membrane

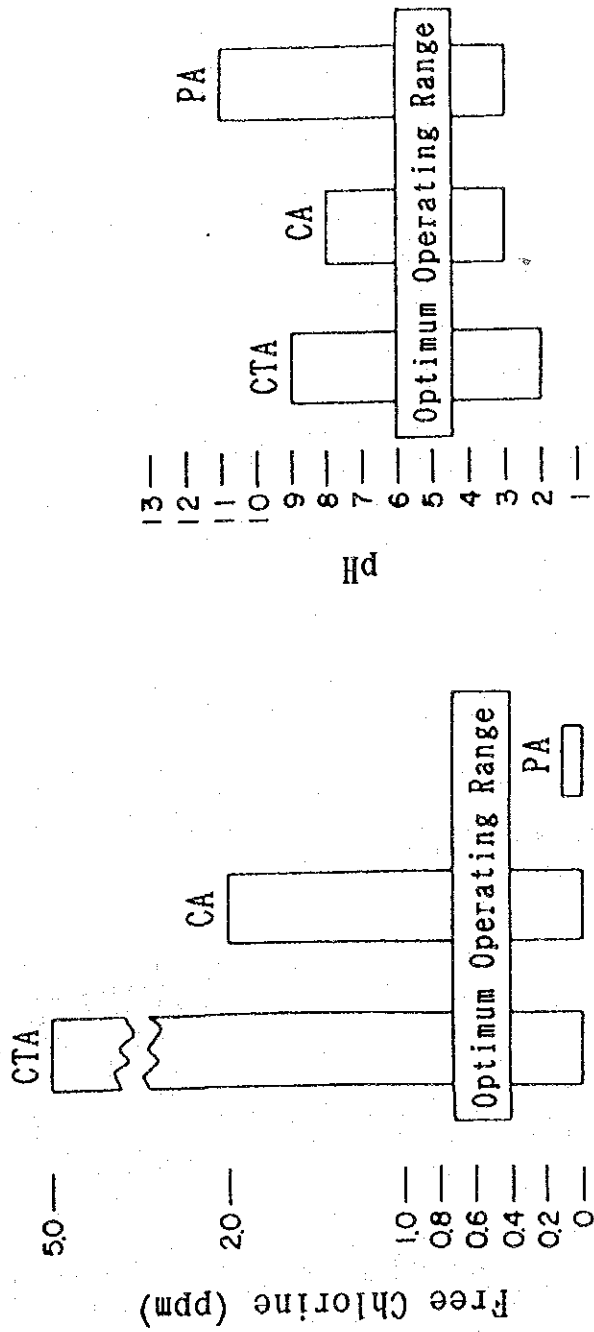
Manufacturer	Membrane	Heat Resistance(°C)
TEIJIN	PBIL	60
North Star Research	NS-100	>35
North Star Research	NS-200	>35
FilmTec.	FT-30	50
UOP	PA-300	45
TOYOBO	Hollosep	40
Toray Industries	SU-800	45
DuPont	B-10	40

### 3.8 Chlorine Resistance Characteristics and Operating pH Ranges of RO Membranes

Chlorine resistance characteristics and operating pH ranges of various RO membranes are shown in Fig.3.8.1.

### 3.9 Cross-Comparison of Various RO Membranes

- (1) A performance diagram (a diagram plotted to give a correlation between rejection and flux for each membrane) for various RO membranes under the operating conditions of 0.5W% NaCl, 42kg/cm<sup>2</sup> and 25°C is shown in Fig. 3.9.1.
- (2) Fig.3.9.2 below shows a performance diagram for various RO membranes under these operating conditions: raw water containing 0.2 W% NaCl; an operating pressure of 30kg/cm<sup>2</sup>; and an operating temperature of 25°C.
- (3) Fig.3.9.3 below shows a performance diagram for various RO membranes under these operating conditions: raw water containing 0.15 W% NaCl; an operating pressure of 15kg/cm<sup>2</sup>; and an operating temperature of 25°C.



CTA: Cellulose Triacetate  
 CA : Cellulose Acetate  
 PA : Polyamide

Fig.3.8.1 Chlorine Resistance and Optimum pH Range for Various Type of Membranes 5

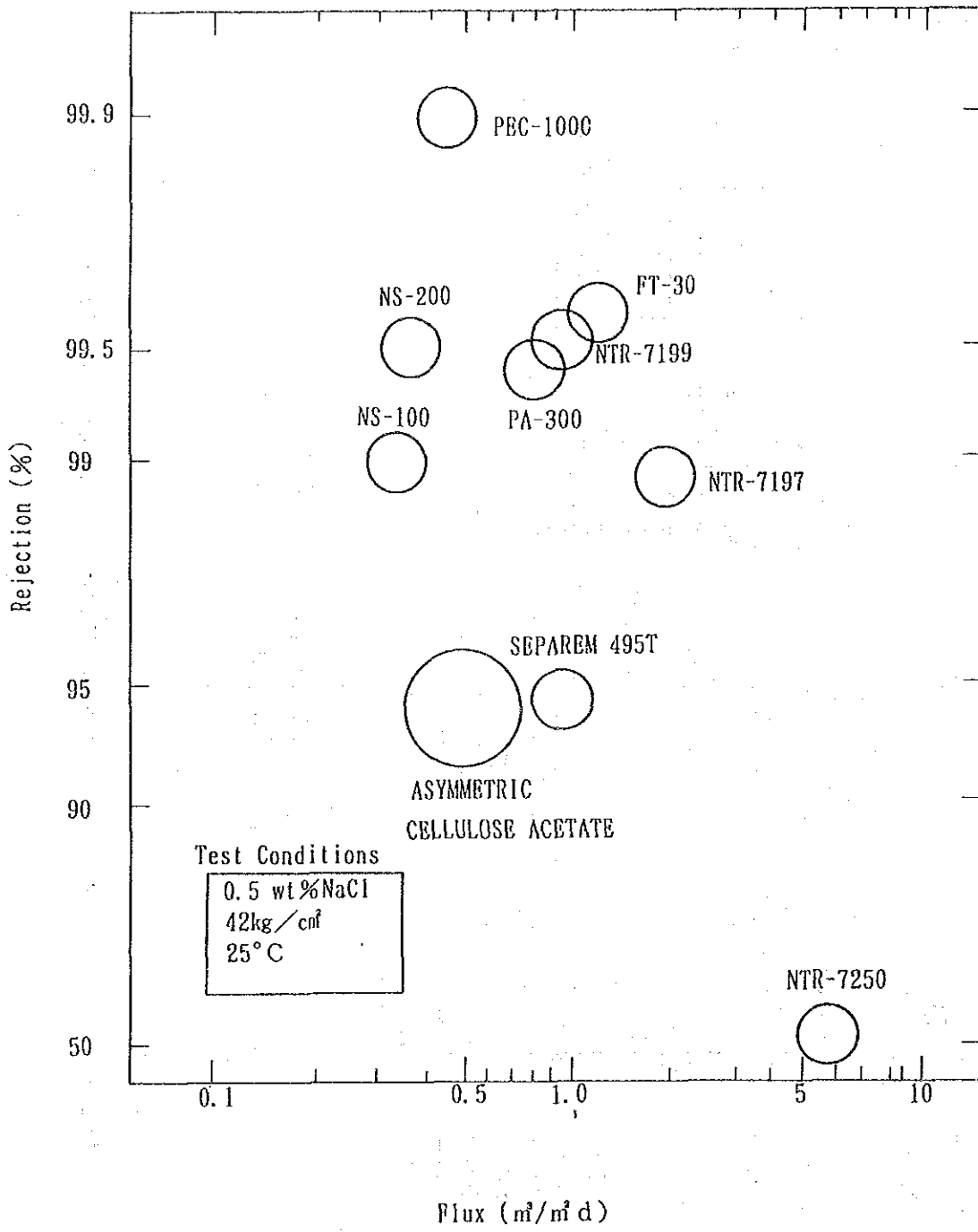


Fig.3.9.1 RO Performance of Various RO Membranes <sup>11</sup>

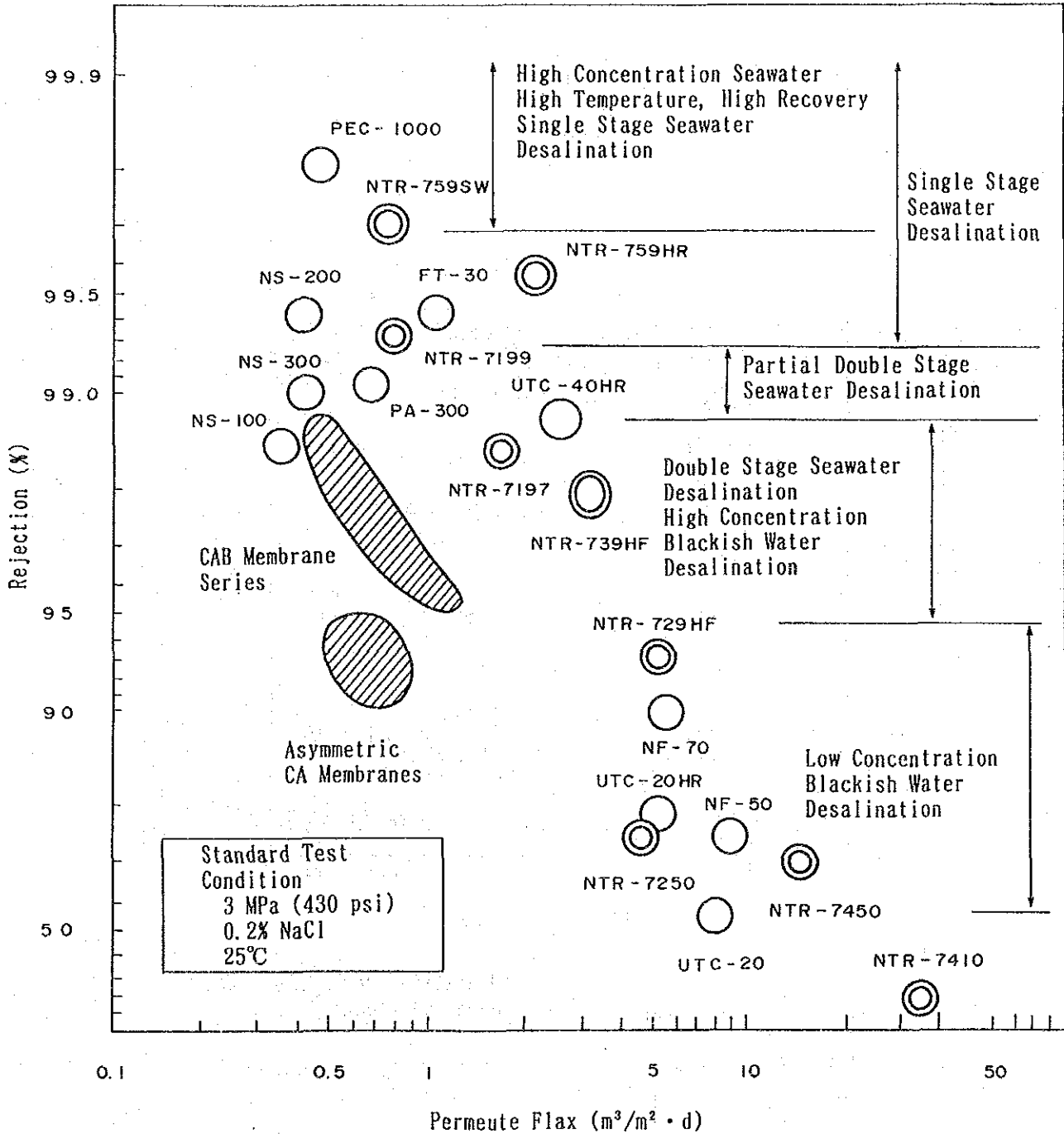
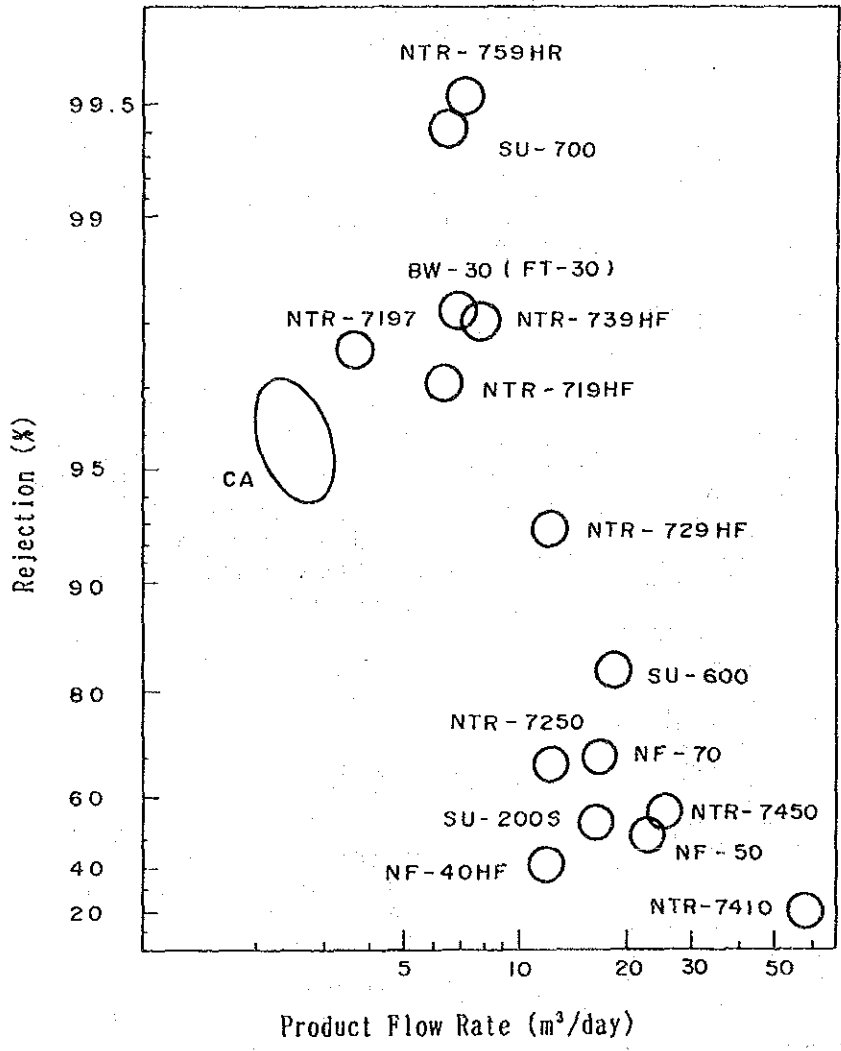


Fig. 3.9.2 Distribution of RO membrane (spiral-wound type) performance under the standard test condition <sup>23</sup>



(Quotation from Various Maker's Goods Catalogues)

$\phi 4 \times 40(L)$  in Element  
 0.15% NaCl  
 1.5 MPa (15 kgf/cm<sup>2</sup>)  
 25°C

Fig. 3.9.3 Performance diagram of membranes <sup>20</sup>

- (4) Table 3.9.1 shows a comparison of membrane characteristics of various RO membranes under these operating conditions: raw water containing 4 W% NaCl; an operating pressure of 59kg/cm<sup>2</sup>; and an operating temperature of 25°C.
- (5) Table 3.9.2 shows a comparison of various Japanese spiral-wound type RO membranes--

### **3.10 List of RO Membranes**

Examples of commercial RO membranes are shown in Table 3.10.1

### **3.11 RO Membranes for the Desalination of Seawater**

Since the desalination of seawater is one of the fields where the technical requirements are most stringent, membranes applicable to this field are not many and limited to those shown in Table 3.11.1.

#### **3.11.1 RO Membranes for Standard Seawater**

Table 3.11.2 shows an average plant fed with 3 to 4.5% (average 3.5%) salt-concentration seawater. According to past service records, Du Pont's B-10 has the largest installed processing capacity.

#### **3.11.2 RO Membranes for High Salinity Seawater**

The seawater in the Middle and Near East differs drastically from standard seawater. For example, the salt concentration is 4.25% for the Red Sea seawater and 4.3 to 5.0% for the Arabian Gulf seawater and the desalination of these high salt-concentration seawater is greatly different from that of standard seawater. Table 3.11.3 shows service records of some plants.

Also, Du Pont's B-10 is intended to treat seawater above 4.0 % in salt concentration using the partial single stage process. In case of 4.2 % saline seawater, the expected quality of the product is some 720 ppm in TDS, with a recovery rate of 30 %. At actual plants (in Albirk and Tanajib, Saudi Arabia) the two stage process is used with a 30 % recovery rate for 4.2 and 4.4 % saline seawater.

With Toray's PEC-1000 product, qualities of 350 and 250 ppm have been achieved for simulated Near and Middle East seawater with salt concentrations of 5.1 and 4.1 % respectively at a 35 % recovery rate, while those less than 500 ppm have been obtained from 4.4 % seawater at their actual plant in Saudi Arabia (2,300 m<sup>3</sup>/d) using the single stage with a recovery rate of 40 %.

#### **3.11.3 RO Membranes for the Single Stage Process**

The single stage method refers to the RO process used for the desalination of seawater which desalinates seawater with a salt concentration of 35,000 mg/liter after one pass through a single process to obtain a product less than 500 mg/liter. The raw water is fed to a membrane

Table 3.9.1 Comparison of Various RO Membranes

(4wt%, 59 kg/cm<sup>2</sup>, 25 °C)

Element	Flux per Unit Volume (GPD/ft)	Salt Rej (%)	Chlorine Resistance	Other Oxidizing Agents Resistance	Max Operating Temp. (°C)	Tolerance pH Range
<u>Spiral Wound</u>						
FT-30	2400	98.5	Fair	Good	50	2 - 11
PA-300	1600	98.1	Poor	Good	45	2 - 11
PEC-1000	1200	99.2	Poor	Poor	40	1 - 12
SU-800	2100	99.4	Poor	Good	45	2 - 10
<u>Hollow Fine Fibers</u>						
B-10	1400	98.4	Poor	Fair	35	4 - 9
Toyobo CTA	900	99.0	Good	Good	40	5 - 7

Performance after one year on 40,000 ppm seawater at 850 PSI, 25°C and 30% recovery.



Table 3.9.2 Comparison of various Japanese spiral-wound type RO membranes 14

Model No.	INTERMEDIATE PRESSURE TYPE			LOW PRESSURE TYPE				
	SC-3200	NTR-7197	SU-220S	SU-720	NTR-7250	NTR-729HF	NTR-739HF	
Maker	TORAY	NITTO	TORAY	TORAY	NITTO	NITTO	NITTO	
Material	CELLULOSE ACETATE	POLYAMIDE COMPOSITE MEMBRANE	POLYAMIDE COMPOSITE MEMBRANE	POLYAMIDE COMPOSITE MEMBRANE	POLYVINYLALCOHOL COMPOSITE MEMBRANE	POLYVINYLALCOHOL COMPOSITE MEMBRANE	POLYVINYLALCOHOL COMPOSITE MEMBRANE	
Performance pressure (kg/cm <sup>2</sup> )	30	30	7.5	15	20	10	10	
permeate flow (m <sup>3</sup> /d)	17.6	35	44	26	60	36	22	
Operating condition								
Max pressure (kg/cm <sup>2</sup> )	42	42	15	42	30	30	30	
pH	3~8.5	4~11	3~9	3~9	2~8	2~8	2~8	
Max temperature °C	40	40	40	40	40	40	40	
Free chlorine (ppm)	1	0	0.2	0	1	1	1	
Salt rejection(%)								
NaCl	97	98	60	99.4	50	92	95	
MgSO <sub>4</sub>	—	—	99	99.9	98	—	99	
Organic rejection(%)								
Methanol	5	19	0	14	9	—	—	
Ethanol	9	51	12	54	26	25	30	
IPA	36	90	23	96	43	70	75	
n-butanol	11	77	—	—	27	52	64	
Ethylene glycol	42	81	—	—	50	—	—	
Glycerol	92	95	37	—	67	—	—	
Phenol	0	64	0	—	5	—	—	
Glucose	99<	98<	96	99<	94	97	97	
Saccharose	99<	99<	99	—	98	99	99<	
Raffinose	99<	99<	—	—	99	—	—	
Acetic acid	6	34	4	54	9	—	—	
Oxalic acid	68	—	35	—	36	—	—	
Citric acid	99	97	86	99<	92	—	—	
Urea	26	52	10	63	11	—	—	
Formaldehyde	33	33	—	32	20	—	—	
Ethylendiamine	76	—	67	95	—	—	—	

Table 3.10.1 List of RO Membranes <sup>10</sup>

Maker Product	Material	NaCl Rejection(%)	Element Configuration
Asahi Glass MVP	polyethyleneimine		SPIRAL
Alvac-service RM-97, -89 RM-90S, -30S, -15S	Cellulose Acetate	97, 98 (Sucrose, 90, 30, 15)	Flate Sheet
Sumitomo Solcon P	polyacrylnitryl	80, 90, 95, 98	TUBULAR
Daicel DRS-97, -95, -90 DRA-99, -98 DRS-10	Cellulose Acetate synthetic polymer Cellulose Acetate	97, 95, 90 99, 98 10~20	TUBULAR SPIRAL, Flate Sheet PLEAT
Teijin PBIL TL	polybenzimidapyrone polyether amide	98 98	TUBULAR, SPIRAL
TOYOBO Hollow Sep -HR -HM, -HA	Cellulose Triacetate	99, 90	HOLLOW FAIBER
TORAY CA PEC-1000	Cellulose Acetate crosslinked polyether composite membrane	95, 97, 98 99.7	SPIRAL SPIRAL
SU-800, -700	crosslinked aromatic polyamide composite membrane	99.4	SPIRAL
NITTO NTR-1500	Cellulose Acetate	97, 95, 90, 70 50, 30, 10	TUBULAR
NTR-7100, 7200	polyimide	99, 97, 50	SPIRAL
Mitsubishi Rayon Engg 6048, 60410, 60412 20834, 20843, 20852	Cellulose Acetate	98, 97, 96 98, 97, 96	SPIRAL SPIRAL SPIRAL
Celanese	polybenzimidazol		HOLLOW FAIBER
DDS HR-98, 95	Cellulose Acetate		Flate Sheet plate and frame
Desalination System B-400, B-800	Cellulose Acetate synthetic polymer composite membrane	95, 98 98.5	SPIRAL SPIRAL
Dow Chemical Dowex 4K Dowex 20K	Cellulose Acetate Cellulose Acetate	98.7 90	HOLLOW FAIBER HOLLOW FAIBER
Du Pont B-9, -10, -15 C-1	crosslinked aromatic polyamide Cellulose Acetate	90, 99 96 96~98	HOLLOW FAIBER SPIRAL SPIRAL
Elgastat Spectrum SC-30, -31, -32	polyamide		SPIRAL

Table 3.10.1 List of RO Membranes

Maker Product	Material	NaCl Rejection(%)	Element Configuration
Envirogenics CTA	Cellulose Triacetate	95, 97	SPIRAL TUBULAR
Film Tech SW-30, -30HR BW-30, TW-30 NF-40, -40HF	composite membrane composite membrane composite membrane	99, 99.5 98 45, 98	SPIRAL SPIRAL SPIRAL
GE	sulfonated phenylene oxide		
Hydronautics CPA, spv	Cellulose acetate	95, 98, 99	SPIRAL
Kalle Film UO-98, -97, -95	Cellulose Acetate	98, 97, 95	Flate Sheet TUBULAR HOLLOW FAIBER
Monsanto Montedison	Cellulose Acetate poly(piperazine amide)		
North Star Research NS-100	polyethyleneimine -toluen diisocyanate		TUBULAR SPIRAL
NS-101	polyethyleneimine -acid chloride		
NS-200, -300	sulfonated poly fulfryl alcohol	99	SPIRAL
Nuclepore Nuclepore-RO	Cellulose Triacetate	95	
Osmonic SEPA-CA PR, SR, HR	Cellulose Acetate Cellulose Acetate	90, 95, 97.5	SPIRAL SPIRAL
Paterson Candy Type B-1 ZF-99	Cellulose Acetate		TUBULAR TUBULAR
Polymetrics T, S L, H	polyamide polyamide	85, 90 95, 99	HOLLOW FAIBER SPIRAL HOLLOW FAIBER
L, N, H, J N, J, H TFC	Cellulose Acetate Cellulose Acetate composite membrane	90 95 95	SPIRAL SPIRAL SPIRAL
Ray Pak	Cellulose Acetate		TUBULAR
Rhone-Poulance Universal Water UOP	sulfonated polysulfon Cellulose Acetate	95~97	plate and frame TUBULAR
ROGA-SD, -LP, -HR -MP	Cellulose Acetate	95, 5, 97, 98, 98.5	SPIRAL SPIRAL
4600, 8600, 4101 PA-100, -300	Cellulose Acetate polyether amide composite membrane	98, 5, 96 95, 98	SPIRAL SPIRAL
RC-100 OSMOTIK-320, -420 -520, -620	polyether urea Cellulose Acetate		SPIRAL TUBULAR
LP-300	sythetic composite membrane	62~80, 88 ~94 95~97, 97 ~98.4	SPIRAL
Westinghouse	Cellulose Acetate		TUBULAR

**Table 3.11.1 Membranes Applicable to Desalination of Seawater**

<b>Maker</b>	<b>Membrane No.</b>	<b>Module Type</b>
Du Pont	B-10	Hollow Fiber
UOP	PA-300(RC-100)	Spiral
Film Tec	FT-30(BW-30)	Spiral
Toray Industries	SU-800	Spiral
TOYOBO	Hollosep(HR5355)	Hollow Fiber
Nitto Denko	NTR-70SWC	Spiral

Table 3.11.2 Plant Performance of Standard Concentration Seawater <sup>14</sup>

Element	Location	Plant	Seawater Concentration (%)	Recovery (%)	Process	Water Quality of Permiate (ppm)	
B-10	VENEZUELA	3,000	m <sup>3</sup> /d	3.98	30	Double Stage	580
	U.S.A	11,000	m <sup>3</sup> /d	3.8	30	Single Stage	370
	ITALY	20,000	m <sup>3</sup> /d	3.65	33	Single Stage	380
PA-300	U.S.A	—		3.6	40	Double Stage	150
		24.5	m <sup>3</sup> /d	3.2	25	Single Stage	866
FT-30	U.S.A	—		3.2	5	Single Stage	400
Hollosep	JAPAN	800	m <sup>3</sup> /d	3.5	40	Single Stage	300
PEC-1000	JAPAN	800	m <sup>3</sup> /d	3.5	40	Single Stage	<160

Table 3.11.3

Examples of Plant Performance of High Concentration  
Seawater RO Desalination (Saudi Arabia) 19

Element	Location	Plant Capacity (m <sup>3</sup> /D)	Seawater Concentration (%)	Recovery (%)	Process	Permeate Quality (ppm)
PA-300	Jeddah	12,000	4.2	30	Double stage	900
B-10	Al Birk	2,300	4.2	30	Double stage	250
-	Tanajib	13,700	4.4	30	Double stage	<500
Hollosep (HM10255)	Jeddah	56,800	4.2	35	Single stage	(150-1200)
Hollosep (HM8255)	Haql	4,400	4.2	30	Double stage	<500
Hollosep (HM8255)	Duba	4,400	4.2	30	Double stage	<500
PA 1501	Umm Lujj	4,400	4.2	30	Double stage	<500

process with a rejection of more than 99 % at a high pressure of 60 to 80 kgf/cm<sup>2</sup>. (salt rejection =  $1 - 500/35000 = 0.986$ )

Considering both the quality of the permeate and a rise in osmotic pressure due to increased concentration of the seawater, the concentration ratio, i.e., ratio of TDS of reject to TDS of feed should be limited within the range of some 1.3 to 1.4, or 0.23 to 0.29 in terms of recovery rate.

(1) A Flow Diagram of The Single Stage Process

A flow diagram of the single stage process is shown in Fig.3.11.1.

(2) Membranes Suitable For The Single Stage Process

RO membranes suitable for the single stage seawater desalination are few and shown below:

- <1> CTA hollow fiber membranes: Hollosep (HR-8350), a rejection of more than 99.5%.
- <2> Linear aromatic polyamide membranes: B-10.
- <3> Cross-linked fully-aromatic polyamide membranes: BW-30, SU-810, SU-820, NTR-70SWC-S4.
- <4> Cross-linked polyether membranes: PEC-1000, a rejection of 99.8 %.
- <5> Aryl-alkyl polyamide/ polyurea membranes: PA-300, NTR-7199

(3) A Performance Diagram of RO Membranes for the Desalination of seawater

A performance diagram of RO membranes for the desalination of seawater is shown in Fig.3.11.2. The diagram reveals that RO membrane must have a minimum NaCl rejection of 99.3% for it to be capable of single stage seawater desalination.

**3.11.4 RO Membranes for the Two Stage Process**

The two stage method refers to the RO process for the desalination of seawater which desalinates seawater with a salt concentration of 35,000 mg/liter after going through two processes, each using a membrane with a rejection (solute removal rate) of 90 to 95 %, to obtain a product less than 500 mg/liter. The raw water is fed to the first membrane process at a pressure of 50 to 70 kgf/cm<sup>2</sup> to obtain a first stage product with a salt concentration less than 3000 - 4500 mg/liter (salt rejection =  $1 - 3000 \text{ to } 4500 / 35000 = 0.871 \text{ to } 0.914$ ), which is then fed to the second membrane process at a pressure of 20 to 40 kgf/cm<sup>2</sup> to obtain the final product (salt rejection =  $1 - 500 / 3000 \text{ to } 4500 = 0.838 \text{ to } 0.888$ ).

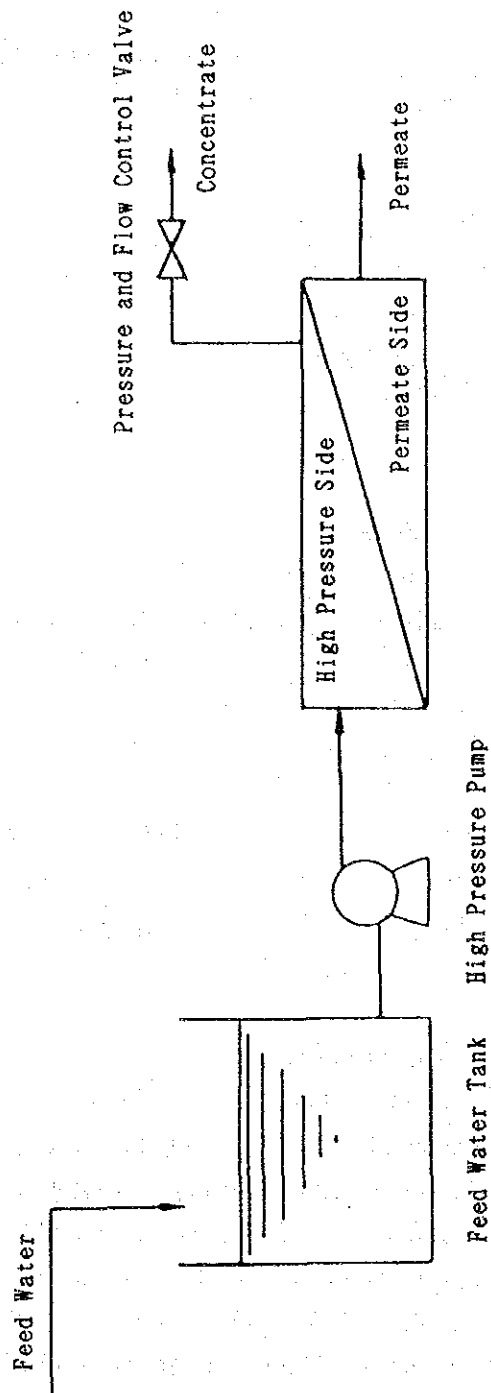


Fig.3.11.1 Flow Sheet of Single Stage Process 8



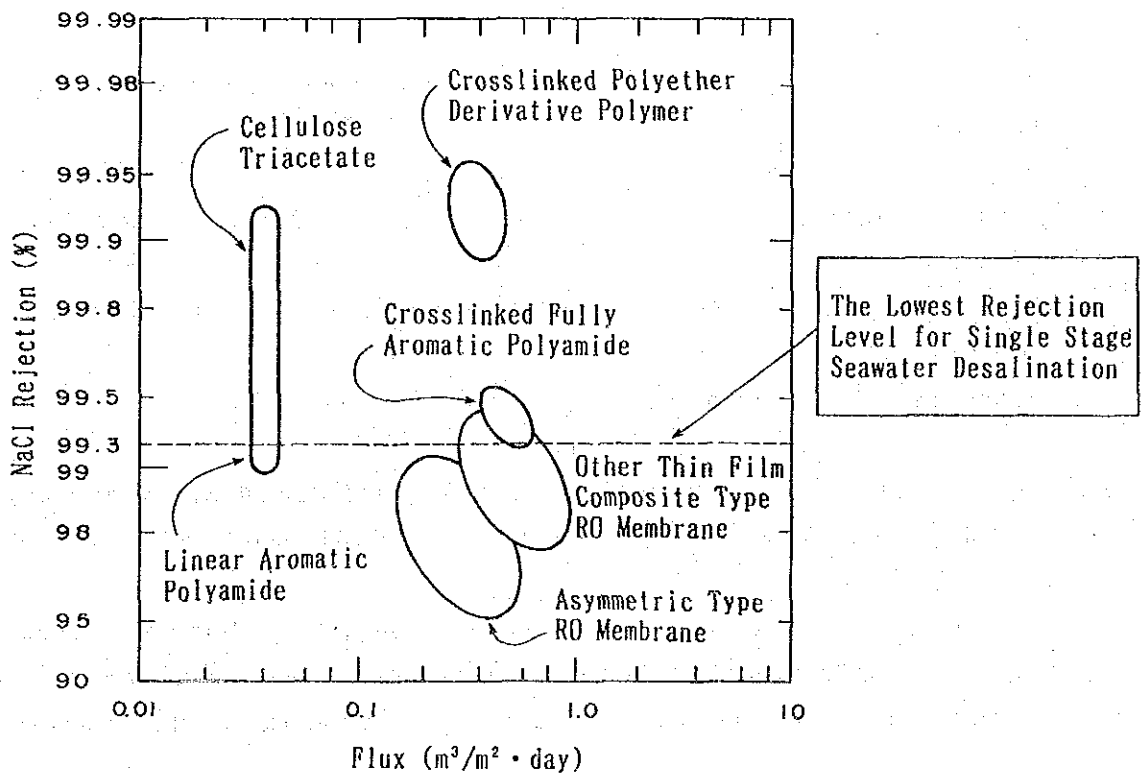


Fig. 3.11.2 Performance distribution comparisons of RO membrane

Feed Water—seawater, 56kgf/cm<sup>2</sup>, 25°C<sup>23</sup>

### (1) A Flow Diagram of the Two Stage Process

Flow diagram and material balance of two stage process are shown in Fig.3.11.3 and Fig.3.11.4.

### (2) The Characteristics Of The Two Stage Process

The characteristics of the two stage process of seawater desalination are summarized below<sup>8</sup>.

- <1> Reliable in operation.
- <2> High cost and operating complication due to the increase in the number of processes to two. Maintenance is also complicated.
- <3> Total energy consumption higher than the single stage process.
- <4> A decrease in membrane compaction rate and increase in membrane life due to low operating pressures.
- <5> The possibility of using membranes with long service records for the desalination of brackish water without modifications.
- <6> Improving product quality, plant stability and recovery ratio.

### ***3.12 A Summary of RO Membrane Characteristics for the Desalination of Seawater***

Finally, the membrane characteristics of some typical RO membranes for the desalination are shown in Table 3.12.1.

In order to determine the selection criteria for optimum performance membranes in seawater desalination, general characteristics of RO membranes were summarized and the performance of the desalination RO membranes currently in practical use over the world was investigated.

#### **I. RO Membranes in Practical Use**

The OSW has been carrying on its vigorous research and development activities for nearly 40 years. During this period, various types of RO membrane have appeared and disappeared, leaving only three types of membrane;

- a. cellulose membrane
- b. fully-aromatic polyamide membrane
- c. piperazine derivative membrane

The RO process is often applied to brackish water desalination for which spiral-wound

Flow Sheet of Double Stage

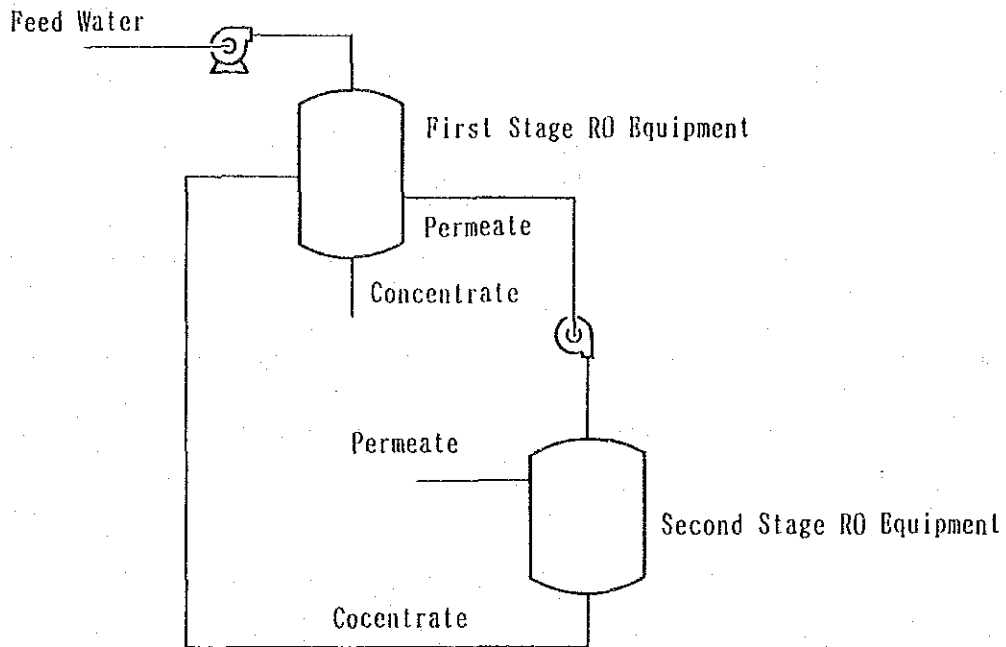


Fig.3.11.3 Flow diagram of two stage process <sup>8</sup>

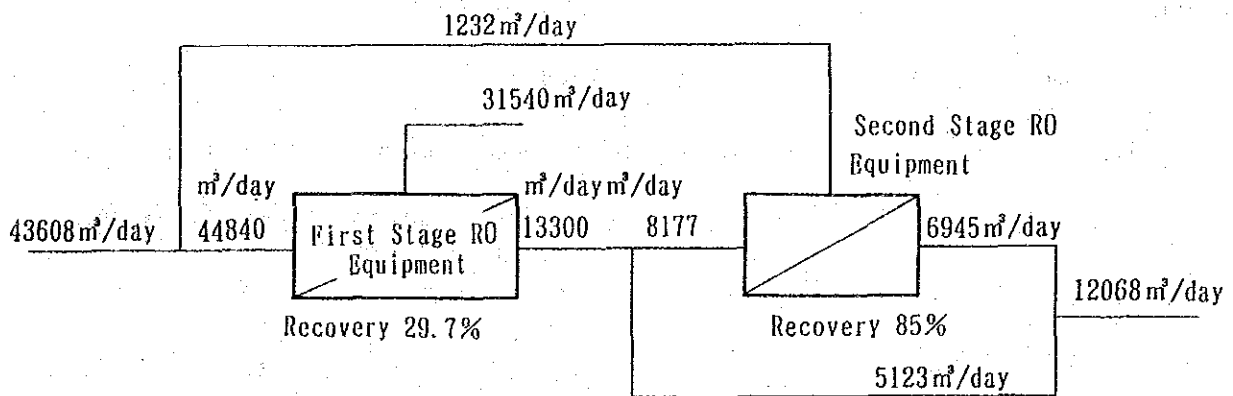


Fig.3.11.4 Material balance of two stage process <sup>8</sup>

**Table 3.12.1 Performance of Typical RO  
Membrane for Seawater Desalination**

Membrane Maker	Fluid system Allid signal(UOP)	Nitto Denko	Toray Industries	Film Tec	TOYOBO	Du Pont
Type	SPIRAL	SPIRAL	SPIRAL	SPIRAL	HOLLOW FIBER	HOLLOW FIBER
Model No.	1501 PA (2031 HF)	NTR-70SWC	SU-820	SW30HR-8040	HR5355	6840T
Size (mm) (Diameter×Total Length)	203×1524	203×1016	201×1016	203×1016	210×1216	203×1500
Membrane Material	Polyamide Urea	Polyamide Polysulfone	Polyamide Polysulfone	Polyamide Polysulfone	Cellulose Acetate	Polyamide  (B-10)
Rejection (%)	99.3	99.5nominal	99.4	More than 99.2	99.4nominal	99Ave.
Permeate Flux (m <sup>3</sup> /day)	34.8	18.9	16	15	5	18.9
<b>Operating Condition</b>						
Feed Water SDI	4	4	5	Max. 5	4	3
pH	2-11	2-11	1-12	2-11	3-8	4-9
Cl <sub>2</sub> (mg/l)	0	Less than 0.1	0	Less than 0.1	0.2-1.0	Less than 0.01
DO (mg/l)		No Limit	Max. 0.5	No Limit	No Limit	No Limit
Max Temperature(°C)	40	45	40	45	40	40
Pressure (kgf/cm <sup>2</sup> )	70	70	70	70	60	56-84

type CA and polyamide membranes are becoming the most utilized membranes.

The market of RO membranes for seawater desalination has not matured, and many types of membranes are still in their early stages of development. The choice of membranes has been limited to fully aromatic polyamide and TCA in terms of materials and spiral wound and hollow-fiber in terms of form. Although the hollow-fiber type still outnumbers the spiral-wound in application of membranes to existing plants, the performance of spiral-wound has improved yearly and use of spiral-wound is increasing.

As mentioned above, in brackish water desalination where RO membranes are most extensively used, the spiral-wound type has emerged as the definite favorite choice and the hollow-fiber type is only utilized in some special applications. It is therefore necessary to pay close attention to the development of the situation.

The seawater desalination RO membranes currently on the market are:

- <1> spiral-wound type, cross-linked fully-aromatic polyamide membranes
- <2> hollow-fiber type, TCA membranes
- <3> hollow-fiber type, fully-aromatic polyamide membranes.
- <4> spiral-wound type, polyamide-urea composite membranes

It is expected that the performance of the above membranes will continue to improve in the future. Before commencing with further research on membranes however, it is recommended that the focus of research subjects should be narrowed bearing in mind the following:

Some large scale plants equipped with membranes of type <2> and type <3> mentioned above are already in operation in Saudi Arabia, and any problems associated with these membranes have been thoroughly investigated. Of these however, experience with the type <2> membrane is limited because the large scale plants equipped with this membrane have been operating for a relatively short time.

Nevertheless this provides a theme for research including measures to minimize the oxidation degradation of membranes and low-soluble fouling matter such as silt. As for the type <3> membranes, ample past records exist therefore it would be sufficient to investigate the existing plant conditions in detail, and there is no need for a repetition of research.

Although the type <1> membranes are largely employed in brackish water desalination plants, compared to the membranes of type <2> and type <3>, they are a relatively new introduction in seawater desalination with no instances of practical application in Saudi Arabia, thus continued investigation and research are required. In this connection, know-how of brackish desalination and investigation results for membranes of type <3> above will provide useful data, despite the differences in conditions involved, brackish water/seawater, and hollow-fiber/spiral-wound.

The performance of membranes continues to improve year after year, and it is thus neces-

sary to proceed with investigations and research keeping in mind the establishment of standard evaluation methods for the following :

- a. Membrane: Durability (heat resistance, pressure tightness)  
Chemical resistance
- b. Module: Durability (heat resistance, pressure tightness)  
Recoverability from fouling (cleaning, sterilization, etc.)

The investigation and research should not be limited to the evaluation of existing membranes.

For stable operation of a desalination plant, the largest disadvantage of the RO-based desalination process is degradation in performance resulting from the fouling of membranes (fouling caused by inorganic colloided matter and bacteria). This problem is further complicated due to the fact that the nature of fouling varies in time depending on the quality of the feed water even within the same plant. Research and study of these problems, as well as the process to artificially change the properties of seawater are thus required.

## II. Future improvements in Performance of RO Membrane for Seawater Desalination

To maintain the economic and technical advantage of the RO membrane equipment seawater desalination, it is necessary to continue research in the following fields:

- a. Improvement in performance and quality of membranes and membrane modules
- b. Establishment of optimum operation conditions suitable for the properties of the raw seawater

With the understanding that all technologies are continually making progress, the following suggestions are given:

### 1) Evaluation of Membrane Material Which Resists Higher Pressure Operation

Development of a membrane material which resists higher pressure operation is required in order to completely desalinate high salinity seawater in the Middle East with single stage desalination.

The recovery rate is raised with high pressure operation and that makes the operation more economical.

### 2) Evaluation of a Membrane Module Which Resists High Temperature Operation

There already exists membranes which resist seawater of 40°C in the desalination process, but there is no membrane which can resist both high pressure and high temperature operation. Heat resistant parts for the membrane module are especially demanded. If an RO membrane

which can resist high pressure and high temperature over long period of operation is developed, desalination will become more economical.

3) Evaluation and Development of a Membrane with High Oxidation Resistance

RO membranes become fouled with the growth of microorganism in seawater, and the permeate flow rate of the membranes diminishes. As a measure, disinfectant containing a strong oxidation agent is added, however the membranes of high desalination capacity normally have low oxidation resistance. If an RO membrane with high oxidation resistance and high desalination capacity can be developed, the system of RO membranes and the control of the system operation will be simplified, thus eventually the cost will be reduced.

4) Evaluation and Development of a Module Equipped with the New Type of Membrane

Spiral wound and hollow-fiber type membranes are largely used at present, and a module which can minimize the fouling of membrane is under development. Development of a module suitable for the desalination of high temperature and high salinity seawater is awaited.

5) Establishment of Optimum Operation Conditions for the Desalination of High Temperature and High Salinity Seawater

It is necessary to optimize the overall system (pretreatment filtration, disinfection and operation pressure for the desalination of seawater) in order to suit membranes newly installed in the module.

6) Evaluation of Durability of Membrane Module

As a conclusion, the following is taken into consideration for development and selection of membranes:

To select a membrane, it is important to consider not only cost performance but also capacity to supply safe drinking water. In other words, it is necessary to select a membrane which has the capacity to remove even a trace quantity of harmful substances.

In order to further the development and selection of new membranes suggested above, it is necessary to establish a system for the exchange of latest information on membrane technologies and to work in cooperation.

## References

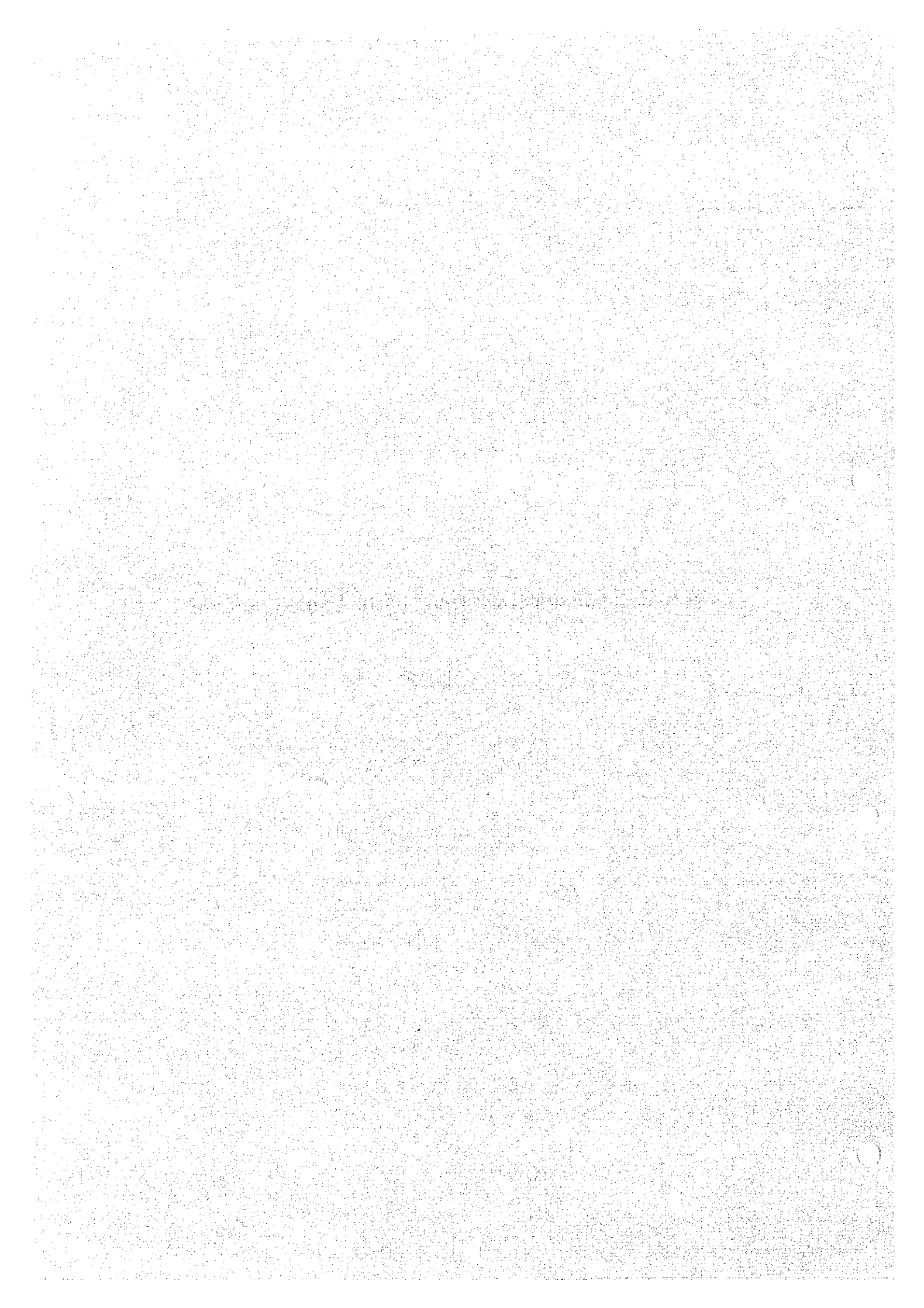
- 1) S. Loeb and S. Sourirajan, UCLA Rep. of Eng., Rept. No. 60 (1960)
- 2) 栗原優「機能性有機薄膜」、日本化学学会編、化学総説、No. 45, p30、学会出版センター (1983)  
Kurihara Masaaaru, "Functional Organic Membrane", Chemical Society, Japan, General Chemistry, No45, p30, Gakkai Shuppan Press, (1983)
- 3) 栗原優、表面、Vol. 129, No. 10, p836, (1991)  
Kurihara Masaru, "Surface", Vol., 129, No., 10, p836, (1991)
- 4) Vos, K. D., et al.; J. Appl. Polm. Sci., Vol. 10, p835 (1966)
- 5) R. E. Kessting, in S. Sourirajan, Reverse Osmosis and Synthetic Membranes Theory-Technology-Engineering, National Research Council Canada, Ottawa pp89, (1977)
- 6) H. Motomura, Y. Taniguchi, Symposium, Cellulose Division, ACS, Las Vegas (1980)
- 7) Lacey, R. E and Loeb, S.: Industrial Processing with Membranes, p138, Wiley Interscience, Tronto (1972)
- 8) 伊出哲夫「水処理工学」, p596, 技報堂出版 (1990)  
Ide Testuo, "Water Treatment Engineering", p596, Gihodo Press, (1990)
- 9) 大矢晴彦「純水・超純水製造法」、p57, 58, 61, 63, 幸書房 (1985)  
Ohya Haruhiko, "Pure and Ultra Pure Water Production Methods", p57, 58, 61, 63, Yuki-Shobo Press (1985)
- 10) 中垣正幸、「膜処理技術体系」(上巻) , p451, フジテクノシステム (1991)  
Nakagaki Masayuki, "Membane Treatment Tchnology System Vol. 1, Fuji-tekuno-System Press
- 11) E. Driori, Desalination, 63, p57, (1987)
- 12) 栗原優、液体膜による分離操作研究会第3講演討論会、化学工学協会、(1980. 7. 22)  
Kiri-hara Masasru, Conference of Separation Technology Using Liquid Film, Chemical Engineering Society, Japan, (22, July 1980)



- 13) R. J. Petersen, 1st Biennial, Conference of N. W. S. I. A., (1986)
- 14) 木村尚史他、「膜分離技術マニュアル」, p13, アイピーシー (1990)  
Kimura, Membrane Separation Manual, p13, IPC Press
- 15) 木村尚史、別冊化学工業、Vol. 34, No. 4, p324, (1990)  
Kimura, Vol. 34, No4, p34, (1990)
- 16) 横山晴一、日本海水学会誌、Vol. 32, p158, (1978)  
Yokoyama Haruichi, Bulletin of the Society of Sea Water Science,  
Japan, Vol. 32, p158, (1978)
- 19) 神沢千代志、日本海水学会誌、Vol. 40, p275, (1987)  
Kamisawa Chiyoshi, Bulletin of the Society of Sea Water Science,  
Japan, Vol. 32, p158, (1978)
- 20) 池田健一、化学装置、p88, No. 11, (1990)  
Ikeda Kenich, Chemical Equipment, No. 11, (1990), p88
- 21) L. Credali, A. Chhiolle, P. Parrini, Desalination, 14, 137 (1974)
- 22) J. E. Cadotte, M. J. Steuk, R. J. Petersoen. Resarch on In situ-Formed Condensation Polymer for Reverse Osmosis Membranes, NTIS Rport No. PB-288387 (1978)
- 23) 日東電工(株)カタログ  
Catalog of RO Membrane, Nitto Denco Co., Ltd.
- 24) 東レ(株)カタログ  
Catalog of RO Membrane, Nitto Denco Co., Ltd.
- 25) 東洋紡績(株)カタログ  
Catalog of RO Membrane, Toyobo Co., Ltd.
- 26) Du-Pont(株)カタログ  
Catalog of RO Membrane, Du-Pont Co., Ltd.



## **4.6 R-5 Chemical Cleaning of the Fouled Module**



**RO DESALINATION  
LITERATURE SURVEY NO.6, R-5**

**CHEMICAL CLEANING OF THE FOULED MODULE**

**JULY 1992**

**By**

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## **1. Introduction**

In the operation of the RO plants, prevention of membranes fouling is one aspect that must be given most attention. Fouling arises from the presence of certain substances in the feed, e.g. aluminium, iron, nickel, copper salts or ions etc., metal oxides found in water, colloidal and inorganic materials such as calciumsulphate. Bacterial and other micro-organisms, when found in the feed could also cause membrane biofouling.

The membranes that have been contaminated, may be recovered by adequate washing. Knowledge of the cause of membrane contamination definitely will help in establishing the best approach to membrane cleaning. However it is still necessary to develop the technology for suitable washing processes.

Recently, in the Arabian Gulf region as a result of the serious problems with pollution incurred in the Gulf War and from oil slicks, there is need for conducting experiments to establish the best method for abating oil pollution and for the prevention of membrane contamination by oil. Moreover, there is a need for a good cleaning method for oil contaminated membrane, a method that is capable of restoring membrane performance by removal of oil from the membrane surface.

## **2. Methods**

- (1) Investigation of the data and actual results offered from RO module suppliers in Japan and SWCC.
- (2) Study of literatures and patents by online data base survey (ex. DIALOG, STN, JOIS, PATOLIS) and investigation of those summaries and those full reports.
- (3) The followings show suggestions based on the results obtained from the above literature surveys.

- 1) Method for investigation of the causes of membrane degradation.
- 2) Experimental equipment for investigation of the causes of membrane fouling.
- 3) Experimental equipment for the testing of membrane fouling.
- 4) Analytical equipment for the investigation of the causes of membrane fouling matter and removal tests of those matter.
- 5) Test result evaluation method on removal of membrane foulants.
- 6) The schedule for the studies from basic to pilot scale.

## **3. Results**

### **3.1 Literature Survey**

#### **3.1.1 Results of Literature Survey**

(1) Information submitted by Japanese manufacturers

Almost all information concerning cleaning methods are in regard to fouling due to inorganic substances, and describe only surface active agents as the cleaning method against fouling due to oil.

However, the effect of oil fouling on the RO performance is not described quantitatively.

(2) Results of literature survey with online information retrieval system

(a) JOIS(JICST NETWORK)

Key word: Semi-permeable membrane, oil, Fouling, Cleaning

Number of retrieval operations=53

Number of acquired original reports=10

The authors, titles of paper and abstracts of acquired original 10 reports were shown as following:

1) Author: M.Farinas, J.M. Granda, L.Gurtubai, M.Villagra

Title: Pilot experiences on the recovery of polluted reverse osmosis membranes *Desalination*, Vol.66, p385-402, 1987.

Abstract: Calcium and magnesium precipitated on the DUPONT membrane can be removed by using EDTA. Oil can be removed by using 5% mixed detergent with a pH value of 11.8. Accumulated silica is hardly dissolved with chemicals. Iron can be removed easily by using 1 to 2% sodium hydrosulfite with pH values of 3.2 to 3.8. Ca and Mg are removed by dynamic cleaning more quickly.

2) Author: D.Ren

Title: Cleaning and regeneration of membranes, *Desalination*, Vol.62, p363-371, 1987.

Abstract: For the regeneration methods of membranes, there are physical one and chemical one. Others are the orange juice processing method and the electrical vibration method. As detergents, oxalic acid, citric acid, perborate and EDTA are introduced.

3) Author: T.Tanabe

Title: Practical state of plant cleaning technology — Cleaning and disinfection of membrane equipment, *Chemical Apparatus*, Vol.32, No.12, p38-42, 1990.

Abstract: There are four factors that influence cleaning: <1> Time; <2> Temperature; <3>

Mechanical force; <4> Chemicals. The effect of cleaning can be compared by the pure water flux pre and after treatment. Disinfection depends on the pH adaptability and the chemical resistance of membrane materials.

- 4) Author: Stanley F.Rak  
Title: Reverse osmosis membrane fouling and pretreatment considerations, *Ind. Water Eng.* Vol.21, No.4, p12-15, 1984.  
Abstract: Explanation of fouling by cause: <1>Scale Formation; <2> Biological Slime Formation; <3> Suspended Solids Formation; <4> Colloidal Fouling; <5> metal Oxide Deposition; <6> Oil and Grease Deposition. Oil and grease cover membrane surfaces and affect membrane performance. This is frequently irreversible.
- 5) Author: H.Nakanishi  
Title: Separation by RO method and Ultrafiltration method and their practical applications, *Chemical apparatus*, Vol.26, No.7, p50-58, 1984.  
Abstract: Outline of RO and UF  
Introduction of cleaning methods by foulant. The biggest problem in the treatment of effluent containing oil is the treatment of floating oil. The adhesion of floating oil to membranes rapidly reduces flux. In such a case, the cleaning by the circulation of alkali liquid should be performed in addition to cleaning by ordinary methods.
- 6) Author: D.D.Spatz  
Title: Multiyear experience with oily and organic chemical waste treatment using reverse osmosis, *ACS Symp. Ser.* No. 154, p221-236, 1981.  
Abstract: As the result of the 1000-hour pilot test, RO was employed for effluent treatment in the textile industry and cleaning was carried out every 8 hours. Though troubles due to the propagation of algae occurred, the permeability was recovered by adding chlorine to the detergent.
- 7) Author: O.Kutowy, W.L.Thayer, J.Tigner  
Title: Tubular cellulose acetate reverse osmosis membranes for treatment of oily waste water, *Ind. Eng. Chem. Prod. Res. Dev.*, Vol.20, No.2, p354-361, 1981.  
Abstract: The concentration of oil has a linear relationship with the turbidity(NTU) up to 120ppm. As the concentration of oil in feed water increase permeate decrease.

- 8) Author: R.G.Traeg  
 Title: Membrane cleaning, *Desalination*, Vol.71, No.3, p325–335, 1989.  
 Abstract: Detailed explanation of pretreatment and cleaning; According to the difference of membrane type, pH, temperature and chemicals are determined carefully. The study on cleaning is performed on a trial–and error basis.
- 9) Author: A.Ebrahim, A.Malik  
 Title: Membrane fouling and cleaning at DROP, *Desalination*, Vol.66, p201–227, 1987.  
 Abstract: Cleaning tests on UOP, DUPONT and STEINMULLER membrane were conducted by the method that was recommended by each membrane manufacturer. Though the cleaning with citric acid is common to all methods, cleaning conditions differ with membrane manufacturers.
- 10) Author: G.Peptow, F.Vernon  
 Title: Trace metal fouling and cleaning of seawater RO membrane, *Desalination*, Vol.66, p271–284, 1987.  
 Abstract: Metallic accumulations on membranes can be removed almost completely with citric acid. Though only the cleaning with strong acid can remove all metallic accumulations completely practical use of this technique is not approved.

(b) STN(JICST NETWORK)

Key word: Membrane, Oil, Cleaning, Seawater, Reverse Osmosis

Number of retrieval operations = 50

Number of acquired original reports = 6

The author, title of paper and abstracts of acquired original 10 reports was shown as following:

- 1) Author: Leitner, F.Gordon  
 Title: Oil field applications for water desalting, *Tech. Proc. Annu. Conf. Natl. Water Supply Improv. Assoc.*, 7th, Paper No.6, 17 page.  
 Abstract: Description of the economics of the RO process in oil fields.
- 2) Author: Grover, J.Rorer  
 Title: Improvements in or relating to the recovery of oil, *GB1520877*, 9 Aug., 1978  
 Abstract: Production of brine of 100,000ppm NaCl from seawater of 35,000ppm NaCl by