VI. By-Products Recovery Techniques

6.1. Seawater Resources

Seawater is composed of about 96.5% water and 3.5% dissolved substances which contain various elements. The concentration of components of seawater by element is shown in Table 6.1-1.

Since the total volume of seawater on the earth is said to be 1.37×10^9 km^3, the quantity of principal substances contained in seawater is estimated as shown in Table 6.1-2.

According to a trial calculation, the reserves, static index of economic life, average growth rate of consumption and representative index of mineral resources in the world in 1969 are as shown in Table 6.1-3.

Table 6.1-3 indicates that the reserve of main mineral resources of the world is only enough for 20 - 100 years, even when the average growth rate of consumption is held to less than 5%. It is said that most mineral resources will be exhausted within 100 - 150 years even with additional reserves which might be discovered in the future. In contrast, seawater contains an incommensurably large amount of resources as shown in Table 6.1-2. However, most dissolved substances are low in concentration and only a limited number of resources are considered to have economic values.

Table 6.1-4 shows the value of dissolved substances per 1,000 tons of seawater which are economically extractable at present or in the future. As shown in the table, seawater has a high economic value beyond our expectation and may be considered as a very attractive industrial raw material in Japan which has a very few natural resources. In particular, drained brine, produced as a by-product of desalination of seawater with the evaporation process, has a concentration twice that of seawater and its value is considered to be double the value of seawater.

6.2. Use of Seawater at Present

(1) Magnesia and bromine

Industrial products manufactured on a large scale using seawater as raw material include, besides salt, magnesium salts and bromine.

(Magnesium Salt)

Except for products manufactured from bittern in small quantities, most magnesium salts are made from magnesium hydroxide which is formed by the direct reaction between seawater and milk of lime.

The Japanese chemical industry which uses seawater magnesium as raw material, is the largest in scale in the world and has an annual capacity of about 800 thousand tons in terms of MgO.

Magnesium in seawater is taken out in the form of magnesium hydroxide as a result of chemical reaction of seawater with milk of lime.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$$
$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow CaSO_4$$

Since seawater contains carbonate of about 100 ppm, the reaction of untreated seawater causes a mixture of calcium carbonate in products, thereby lowering the purity of the product. Therefore, the reaction should take place after decarbonation by either of the following methods.

Alkali method $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$
Acid method $Ca(HCO_3)_2 + 2H_2SO_4 \rightarrow CaSO_4 + 2CO_2 \uparrow + 2H_2O$

The magnesium hydroxide deposited by the reaction is clarified and concentrated by a thickner to concentrated slurry.

(Magnesium Hydroxide)

The slurry is then processed by washing, filtration, drying, grinding and sieving to become a magnesium hydroxide product, which is packed according to use and shipped to users.

Magnesium hydroxide is widely used as fertilizer and for various industrial purposes. As a fertilizer, it is used in the form of a simple magnesium hydroxide fertilizer and is also considered very effective as a high compound synthetic fertilizer, especially for soils lacking magnesia. In the industrial field, it is used as a raw material for inorganic chemicals, including magnesium carbonate and magnesium sulfate, and for manufacturing thermal insulators and as building materials. Recently, it has found a use in the manufacture of agents for desulfurization of stack gas and neutralization of acidic wastewater as a part of pollution control.

(Magnesia Clinker)

Magnesia clinker is manufactured from magnesium hydroxide slurry through such processes as washing, filtration, drying, light burning, granulation and dead burning.

Since the product is required to have a high density, the magnesium hydroxide is thermally decomposed to MgO in a light burning kiln, and is then formed into briquets under high pressure. Then the briquets are burned in a rotary kiln at a high temperature of over 1,800°C.

Magnesia clinker is used in large quantities as a raw material for basic fire bricks. Products of various standards in chemical composition such as CaO, SiO_2, Fe_2O_3, $A\ell_2O_3$, Cr_2O_3 and B_2O_3, have been developed by industries to meet requirements of dimensional stability and spalling and corrosion resistance at high temperatures.

Since the main use of basic refractories is in steel manufacturing, the demand for magnesia clinker is increasing with the increase of output of crude steel. The scale of this industry can easily be assumed from the fact that the largest manufacturer of clinker in Japan has a capacity of 420 thousand tons per year.

(Bromine)

In Japan, bromine is manufactured from seawater mainly by the blowing out process, which is employed by two companies, i.e. Asahi Glass Co. and Toyo Soda Co., and the production of the two companies accounts for over 90% of the total domestic production.

The blowing out process is divided into the sulfurous gas absorption and soda absorption methods according to the type of absorption liquids used in the absorption process. These two methods involve the following processes.

Reaction formula - (Fig. 6.2-3)

Br^- oxidation $2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$
Blowing out $Br_2\,(aq) \rightarrow Br_2\,(gas)$
Absorption $Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$
Distillation $2HBr + Cl_2 \rightarrow Br_2 + 2HCl$

Resction formula - (Fig. 6.2-4)

Absorption $6NaOH + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O$
Distillation $5NaBr + NaBrO_3 + 3H_2SO_4 \rightarrow 3Br_2 + 3Na_2SO_4 + 3H_2O$

Seawater is added with acid beforehand, to make its pH 3 - 4, and then chlorine is blown into it for oxidation. This acidification of seawater is required to prevent the following reaction.

$$3Br_2 + 3H_2O \rightarrow HBrO_3 + 5HBr$$

Blowing out process: Seawater is supplied to the tower from the top and a large volume of air is fed from the bottom with a blower to blow out bromine from the seawater. Because of the equilibrium vapor pressure, the blowing out rate improves with the rise of seawater temperature.

Absorption process: Each method uses a different type of absorption agent and has both marits and demerits in respect of size and type of materials of the tower.

Distillation process: Steam distillation is employed in both methods.

Purification process: Its purpose is to remove chlorine mixed in the product.

Up to the blowing out process (inclusive), the process is the same for both methods. In the blowing out and absorption processes, about 60 to 65 g/m^3 of bromine contained in seawater is concentrated about 2,000 to 4,000 times.

The manufacturing capacity for bromine in Japan is estimated at 16,000 tons per year. Globally, the U.S.A. has a capacity of 270,000 tons per year with the use of brine produced in Arkansas, and Israel, which uses water of the Dead Sea as raw material, is said to be increasing its capacity. These two countries are the largest bromine manufacturing countries.

Of the demand for bromine in the U.S.A., ethylene dibromide accounts for 64%, methyl bromide 8% and bromine compound 28%. Ethylene dibromide is used mainly as a scavenger together with tetraethyl lead, which is a petrol additive. At present, the demand for both tetraethyl lead and ethylene dibromide is said to be leveling off, but with increasing use of lead-free gasoline for automobiles in the future, the demand for bromine is expected to decrease from the present level. However, the use of bromine for manufacturing fire-retardants and calcium bromide for use in wells is being developed and the demand for bromine as a whole is expected to increase in the future, thereby offsetting the anticipated decrease in the demand for ethylene dibromide.

In Japan, there is no demand for ethylene dibromide as a petrol additive. It is used for manufacture of photographic agents, medicines, methylene bromide, dyestuff and agricultural and other industrial chemicals. In future, the growth of fire-retardants is expected to increase the demand for bromine.

As for the supply source of bromine in Japan, a large scale expansion of production facilities is not anticipated because of a steep rise of energy costs. Instead, the import of bromine and its compounds from the U.S.A. and the Middle East is expected to grow further.

(2) Salt and bittern

The salt manufacturing method in Japan was completely changed in 1971. That is, the salt farm method, which had been used for many years as a manufacturing process of brine, was replaced with the ion exchange membrane system. At present, most of salt is produced by this system and the capacity of seven plants (seven companies) in Japan is 1,122,000 tons of salt per year, with each plant having an annual production capacity of 160,000 tons on the average.

The brine extracting process by ion exchange membrane electrodialysis is shown in Fig. 6.2-5 and examples of dialyzers in actual use are shown in Photo. 6.2-1. As for raw material seawater, care is taken as to the geographical location of the intake to prevent seasonal changes and the effect of land water and rain water, and water is pumped from a depth of about 10 meters. The average quantity of seawater pumped up is 6,672 m^3 per hr. per plant. Since the suspensions of seawater affect the working ratio of dialyzers, a sand filter is provided for pretreatment of seawater. In some plants, two stage filters are provided or an other filter is inserted at the second stage in an effort to obtain seawater as clear as possible.

At present, dialyzers and membranes are manufactured by Asahi Chemical Industry Co., Asahi Glass Co. and Tokuyama Soda Co. The dialyzer made by the former two companies is called a clamping type and that by the last company a water bath type. The size of membranes ranges from 123 x 114 cm to 119 x 103 cm for the clamping type and 124.8 x 92.3 cm for the water bath type; the number of pairs of membranes inserted is 1,350 pairs (75 pairs x 18 stacks) and 1,800 pairs (300 pairs x 6 stacks) for the former type and 1,900 pairs (25 pairs x 38 groups x 2: compound baths) for the latter type; the gross working area of membranes is 340,000 m^3 and the average working time is 8,080 hours per annum. Although the dialysis condition in dializers differs from company to company and according to the type, current density is 2.20 to 4.15 A/dm^2 and the utilization rate (1 - drained water $C\ell^-$/taken in water $C\bar{\ell}$) ranges from 23 to 29%. The properties of brine produced differs accoring to the process used, operating conditions and seasonal changes, with the annual average being 163 to 182 g/ℓ in density of sodium chloride and 90 to 95% in the purity of salt $(Na^+ + K^+/C\bar{\ell})$. The net power consumption of the dialysis is 306 kWh/t - NaC as an average of various companies, which tends to decrease in the case of vessels now under test.

An evaporator is used to extract crystal salt from the brine concentrated in dializers. A line diagram of this process is shown in the flow sheet in Fig. 6.2-6. Most of the evaporators now in use are of forced circulation and outside heating type, and materials used are stainless clad steel for evaporating chambers and aluminium brass or stainless steel for heating pipes. The evaporating section is 5,000 to 7,000 mm in inside diameter and 9,950 to 22,800 mm in height, and the heating area is 700 to 1,100 m^2 per evaporator. Before being supplied to evaporators, the brine is conducted through a preheater, which is of the titan-plate type in many cases and several units of these preheaters, each having a heating area of 40 to 122 m^2, are in use at present. Evaporators are operated as vacuum type triple - or quadruple - effect evaporators and the vacuum device is made up of a barometric condenser, surface condenser or ejector. Dry salt of 99.5% in purity is produced by this method.

Auxiliary facilities of a salt factory, such as the generator which supplies power for electrodialysis, and the boiler, which supplies steam to drive turbines and steam as a heat source of evaporators, play an important role in the factory. The plant power generators have a capacity to supply 8,000 kW on the averag with part of the power requirement met by purchased power. The boilers installed are of such capacities as 62 t/h of rated evaporation and 72 kg/cm^2 of maximum pressure on the average.

The mother liquor, or bittern as it is called, drained from the last process of salt manufacture in various companies, is not always the same in quantity and composition because of the difference in the limit of concentration used by each company. But on the average, the specific gravity is 30.8° Be' and the amount of production is 46,500 Kℓ, or about 290ℓ per ton of salt. Magnesium chloride, a principal component of bittern, is solidified by concentration as a product, or it is separated as hydroxide through a chemical reaction and is processed further as such products as magnesia, magnesium carbonate and magnesium sulfate. Bromine extracted from bittern is superior in quality.

6.3. By-Products Recovery System

6.3.1. Basic Idea

In the seawater desalination process, drained brine of the same quantity as fresh water is concurrently produced as a by-product. As described in paragraph 6.1, the concentration of useful resources contained in this drained brine is twice that of seawater. Instead of wasting this drained brine, use of it in a combination of appropriate processes can recover such resources as magnesium, calcium, potassium, chlorine and bromine, including salt. Recovery of such resources is considered very significant for saving resources and reducing the cost of water production.

Because of the problem of environmental pollution caused by mercury, the salt electrolytic industry has been required to change its manufacturing process from the mercury system to the diaphragm system since 1973. In this connection, a possibility is to use condensed brine, which can be obtained through electrodialysis of drained brine, as raw material brine in the diaphragm system. This has an advantage that it leads to a way to attain self-sufficiency in industrial salt, which depends entirely on import at present.

Assuming that a seawater desalination plant is operated as a multi-purpose plant, utilities such as electricity, steam and water can be supplied to the process utilizing by-products at lower costs than a single purpose plant.

In view of such merits as described above, the process which utilizes by-products, such as drained brine, from a seawater desalination plant as raw material has been adopted for the extensive project undertaken by the Agency of Industrial Science and Technology, Ministry of International Trade and Industry, since fiscal 1969 and systematic joint research was carried out by the governmental, academic and private sectors. As a result, a by-product recovering system shown in Fig. 6.3-1 has been proposed.

Recovery of bromine and magnesia shown in the flow sheet, Fig. 6.3-1, is excluded from the present research because a process used to manufacture them economically from seawater has already been established. Utilization of salt for the soda industry and recovery of pottasium were selected as basic subjects of research since they were considered to bring about the greatest economic benefit and to be the easient way to shift from the existing technology. The present research covers, in particular, three processes, enclosed by heavy lines in the flow sheet, (namely, (1) electrodialysis, (2) production of chlorine, etc. and (3) recovery of potassium) and the main objective of research is to clarify the technical feasibility and economical efficiency of these processes.

6.3.2. Processes

(1) Electrodialysis

(a) Characteristics of electrodialysis

The electrodialytic method has been developed to use brine obtained through concentration of seawater as industrial salt for one of the principle objectives and has been put to practical use in table salt factories in Japan as a seawater concentrating process which has replaced the former solar salt field method.

Seawater is concentrated to about 16 to 17% by making use of permselectivity of ion exchange membranes and the power requirement of this process is 300 to 350 kWh per ton of salt. The characteristic of this technology is that the univalent ion selective permeability given to ion exchange membranes concentrates selectively Na and Cℓ ions contained in seawater while comparing them with bivalent ions, and that brine of high density can be obtained with smaller energy consumption.

Since the drained brine of seawater desalination with the multistage flash evaporating method has the following characteristics,

- pretreatment of seawater, including decarboxylation, is already completed;
- its concentration is about twice that of seawater;
- water temperature is almost constant throughout the year; and
- drained brine in the required quantity can be obtained continuously;

it is believed to be more economical than seawater for use as raw material for concentration by electrodialysis and has an advantage that, in particular, concentrated brine of high concentration containing a high content of sodium chloride can be obtained with low power consumption.

(b) Outline of research

Research on the concentration of brine drained from a multistage flash evaporator was carried out from 1970 to 1973. In the first year, the basic structure of the electrodialyzer used for concentration of seawater at table salt factories was examined for applicability to the present purpose. In subsequent years, the module of an electrodialyzer, of which specifications are shown in Table 6.3-1, was designed and manufactured on an experimental basis. The research focused on its operating test was conducted at the Chigasaki Marine Research Facilities of the Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

Elements of development in the research were

- to select an economical pretreatment procedure adapted to the properties of drained brine;

- to examine the structure of an electrodialyzer capable of withstanding operations at high current density;
- to confirm the durability of ion-exchange membranes, electrodialyzer and auxiliary equipment against high temperature, high concentration and high current density; and
- to establish operating conditions which enable the manufacture of concentrated brine of high concentration and high purity at a low cost.

As a result, the required information was obtained. In parricular, it has become clear that concentrated brine containing sodium chloride of about 250 g/ℓ is obtainable through concentration of drained brine from a multistage flash evaporator by electrodialysis at a current density of 6 - 7 A/dm^2, with the power requirement of electrodialysis being about 300 kWh/t NaCℓ, and that the total quantity of Ca^{2+} and Mg^{2+} ions in concentrated brine can be lowered to 0.03 in terms of equivalent ratio to $C\ell^-$ ions. Also, it has become possible to obtain these results steadily over a long period of time with the electrodialyzer in practical use.

In particular, stability of performance of the electrodialyzer in long-run continuous operation has been attained through partial improvement of the design of the electrodialyzer, and the durability of ion exchange membranes has also been confirm

The concentrated brine obtained in 1971 was sent to the Chiba Factory of Asahi Glass Co. as a sample for research on the production of chlorine, and adaptability to diaphragm electrolysis. An example of typical compositions of concentrated brine is shown in Table 6.3-2.

(c) Conceptional design

Based on the results of the research, a by-product utilizing process was designed on the basis of a desalination plant having a capacity of 100,000 m^3/day. As shown by the outline of the process in Fig. 6.3-2, the drained brine from a multi-stage flash evaporating apparatus is flocculated and filtered with an automatic backwash gravity type sandfilter and then supplied to an electrodialyzer arranged in two stages.

The capacity of this equipment is outlined in the following.

Production capacity at current density of 7 A/dm^2 and permselectivity of 0.97 for univalent cation on the basis of 330 working days per annum is 2,310,000 m^3/year of concentrated brine and 614,000 t/year of salt, and the power requirement for concentration is 320 kWh/t NaCℓ. Composition of concentrated brine passing to the next process is as follows.

Outlines of principal equipment to be used are as shown below.

Construction cost of this equipment is about 2,760 million yen at the price level of April to June of 1973. Prime cost of NaCℓ contained in concentrated brine is 2,506 to 2,781 yen/t, which is lower than the price of solid salt imported at that time.

(2) Production of chlorine, etc.

Research on this process was carried out at the Chiba Factory of Asahi Glass Co. over two years in 1970 and 1971.

The purposes, details and results of the research in each year are described in the following.

- 1970 -

(a) Purposes of research

The purpose of the research was to perform demonstration operations of three processes mentioned below at respective pilot plants in order to make clear the problems of the processes and find the solution to these problems. The processes were;

- saturating with salt and purifying process to obtain purified brine for electrolysis use;
- electrolytic process to obtain caustic soda solution containing potassium and salt and hydrogen by electrolyzing the above brine in a diaphragm electrolytic cell; and
- concentrating process to obtain caustic liquor of about 50% and salt crystals by evaporating and concentrating the above solution;

For raw materials, the above processes used concentrated brine (about 200 g/ℓ in terms of salt) obtained at that time through the research of the electrodialytic method.

(b) Details and results

(i) Refining process (Production scale of 200 ℓ/hr in purified brine)

Since concentrated brine obtained by the electrodialytic method contains various impurities, especially calcium and magnesium, of which absolute quantity is remarkably large as compared with brine dissolving industrial salt. With the latter contained in larger volume than the former, efforts were made to find an efficient purifying method.

As a result, it was discovered that the purpose can be achieved by devising a purifying method mainly by finding a method to add a purifying liquid agent to saturated brine and the optimum conditions of purifying were determined.

(ii) Electrolytic process

Tests were carried out using three electrolytic cells (1,000 A) of Nelson type at a feeding capacity of purified brine of about 14ℓ per hr per cell.

As a result, any special phenomenon which seems to be due to potassium and other traces of components (such as boron etc.) contained in concentrated brine was not observed, and it predicted the possibility to operate the system without hindrance under the conditions regarded as standard for the Nelson cell, including current efficiency, unit consumption of power, purity of produced gasses (chlorine and hydrogen), and others, in the same way as in the case of using brine made from industrial salt. Therefore, the desired purpose, i.e. actual proof of diaphragm electrolysis with the use of concentrated brine obtained by the electrodialytic method, was achieved in the main.

(iii) Concentrating process

A vacuum evaporator of Krystal-Oslo type, capable of evaporating water at a rate of 30 kg/hr, was used for the tests which were made with attention paid to concentration of potassium in purified brine, behavior of impurities with the progress of concentrating and particle properties of salt produced secondarily.

As a result, it was verified, after confirming the saturated concentration of potassium against caustic concentration, that there is absolutely no fear of potassium chloride, etc., being deposited during the concentrating process even when catholyte liquor (caustic solution), or its concentrate, from the diaphragm electrolytic cell is used to purify concentrated brine. Moreover, recovered salt obtained in the present test was of uniform crystals of comparatively large particle size, and could be separated easily.

(iv) Summary of results

The results described above enabled confirmation that this process, which starts with concentrated brine by the electrodialytic method to obtain chlorine and caustic solution of about 50%, can be established as a through process, having no problems which need any further special development.

- 1971 -

(a) Purposes of research

The research was conducted with concentrated brine prepared on the basis of the drained brine actually obtained by the multistage flash process for the purpose of collecting long-run operational data of this method under certain operating conditions. In the previous year, such concentrated brine was not available due to the schedule, and concentrated brine obtained by directly electrodialyzing seawater was used.

(b) Details and results

Concentrated brine prepared by the electrodialytic method using the drained brine of the multistage flash process at the Marine Research Facilities for Seawater Desalination of the National Chemical Laboratory for Industry was transported to the Chiba Factory of the Asahi Glass, where it was purified to be used for diaphragm electrolysis. Normal operation of electrolysis lasting for over one continuous month was conducted and operating data were collected and studied.

As a result, no special phenomena which might have been caused by trace components or their accumulation in the concentrated brine obtained based on drained brine from the multistage flash process were observed. Also, from the progress of the quantity of catholyte taken out, no difference was found compared with ordinary diaphragm electrolysis with industrial salt, and it was judged that continuous operation is feasible over a long time.

On the basis of the above result, the production process of chlorine and others was established in the case of a desalination plant capable of producing 100,000 m^3/day, and block diagrams of the process including the balance of principal materials and products are shown in Figs. 6.3-3 and 6.3-4.

(3) Recovery of potassium

Raw caustic solution of about 50% obtained in the preceding process for production of chlorine, etc., contains about 1% - 3% of non-reacted salt and potassium, respectively. If this solution diluted to 40% is heated, crystals of caustic soda - 3.5 water - salt ($NaOH \cdot 3.5H_2O$) are deposited. Since no salt or potassium exists in the crystals theoretically, refined caustic soda can be obtained by separating the crystals and the potassium in the solution can be condensed for recovery.

These crystalizing and separating processes are outlined in the following.

(a) Cross equilibrium of NaOH - KOH - NaCℓ - H_2O system

Cross equilibrium of NaOH - KOH - NaCℓ - H_2O system has been already investigated in detail by Hayano and others. As an example, here, a caustic solution of 40.3% in total dissolved solid (TDS) is shown in Fig. 6.3-5. The ratio of caustic potassium to TDS is represented on the axis of ordinate and the density of chlorine ion on the axis of abscissa. In the graph, the a - b line is the saturated density curve of NaCℓ and $NaOH \cdot 3.5H_2O$, the b - f - c line that of $NaOH \cdot 3.5H_2O$ and KCℓ and the b - d line that of NaC and KCℓ. Also, the dashed line represents the deposition temperature of $NaOH \cdot 3.5H_2O$.

Point e shows an example of composition when raw caustic solution is diluted to TDS 40.3%. If this solution is cooled below 13.5°C, then $NaOH \cdot 3.5H_2O$ deposits; with cooling proceeding $Cℓ^-$ and K^+ are concentrated to reach the saturation curve of KCℓ at f point where KCℓ begins to deposit. For the purpose of refining caustic soda, since it is desirable to keep KCℓ from depositing, crystalization of $NaOH \cdot 3.5H_2O$ is operate between e - f and this constitutes the refining process.

If cooling proceeds further below f point, $NaOH \cdot 3.5H_2O$ and KCℓ deposit concurrently, and the composition of the solution moves along f - c line during which KOH is concentrated in the solution. This f - c line constitutes the process to concentrate and recover potassium.

(b) Development of $NaOH \cdot 3.5H_2O$ crystalizing plant by direct contact method

For the efficient crystalization of $NaOH \cdot 3.5H_2O$ from a raw caustic solution, it is desirable to adopt the direct refrigerant contact method which cools the solution with the heat of vaporization obtained by spraying liquefied refrigerant directly into the crystalizer, because of the relatively high viscosity of caustic solution and low steam pressure. Any refrigerant for this purpose is required to satisfy the following conditions -

(1) that the refrigerant is insoloble in the solution; (2) that it is stabilized chemically; (3) that difference in the density between it and the solution enables the to separate easily; (4) that its operating pressure is approximate to atomospheric pressure as far as possible; and (5) that it is incombustible. Table 6.3-6 shows the characteristics of refrigerants which are deemed usable when the above conditions are taken into consideration.

Fig. 6.3-6 shows crystals of $NaOH \cdot 3.5H_2O$ separated from an $NaOH - KOH - NaC\ell - H_2O$ system applying freon 12 as a refrigerant. As seen from the figure, crystals grow large taking the shape of square plates, and if 24 to 43 minutes are given for residence time in a crystalizer, their grain size grows to 0.33 mm to 0.66 mm to become crystals of good quality which permit easy centrifugal separation.

(c) Flow sheet

According to the cross equilibrium chart shown in Fig. 6.3-5, the potassium recovering system is divided into three processes, caustic soda refining, potassium concentrating and potassium recovering, to organize a flow which uses crystalizers of a three-stage in-line arrangement. Since the organization of instruments is basically the same for these processes, Fig. 6.3-7 shows only a flow sheet from receiving the raw caustic solution to refining process, excluding the concentrating and recovering processes.

A slurry of $NaOH \cdot 3.5H_2O$ crystals produced in the crystalizer after refrigerant gas accompanying it from the deaeration tower having been removed, is sent to a centrifugal separator for separation into crystals and mother liquor. The crystals are melted to obtain refined caustic soda. The mother liquor is sent to the second stage, or potassium concentrating process for use as raw material.

As example of the material balance for each process of the potassium recovering process is shown in Table 6.3-7.

(4) Cost

For each of the three processes - electrodialysis, production of chlorine, etc. and recovery of potassium, costs were calculated on a trial basis in the form of processing expenses for each process (on the basis of the economic level in the first half of 1973) and the results of calculation were summarized as shown in Table 6.3-8. Ceilings were fixed for processing expenses in order to give some allowance, such as 2.5 to 3.3 yen/kWh in the unit price of electric power and 300 to 700 yen/t in the unit price of steam.

6.3.3. Conclusion

(1) Results of research

(a) Electrodialysis

This process, which produces raw brine for caustic soda elctrolysis by concentrating the drained brine produced secondarily in desalinating seawater with electrodialyzing equipment is required to reduce the amount of magnesium and calcium mixed in the concentrated brine. For the main subjects of research including monovalent ion selectivity exchange membranes, adoption of high temperature and high current density and the life of apparatus, the necessary data were obtained and solutions have been found. That is, concentrated brine of about 250 g/ℓ in density of salt was obtainable through concentration of drained brine at 35°C and 6 7 A/dm^2 in current density, and power consumption was about 300 kWh/t·NaCℓ. It was possible to reduce the total amount of calcium and magnesium ions in the concentrated brine to 0.03 in terms of equivalent ratio to chlorine ions, and the possibility of long stabilized operation of baths in practical use was confirmed.

The drained brine as a raw material stands at an advantage as compared with seawater in that its density is twice that of seawater, its temperature is as high as 35°C and it needs no pretreatment process. In the case of electrodialysis, the optimum conditions were determined by making use of this advantage, and the same applies to the manufacture of magnesia and bromine from drained brine.

(b) Production of chlorine, etc.

Chlorine and caustic soda are manufactured from the concentrated brine obtained through electrodialysis after being saturated with recovered salt and purified with the diaphram method. Since the concentrated brine contains a relatively large amount of impurities as compared with ordinary raw brine prepared from industrial salt, it was necessary to use an economical method to purify the salt solution. As a result of research, it was found that this problem could be resolved mainly through development of a method to add purifying agents to brine.

A problem still remains of how to deal with the mixed precipitates (the so-called salt solution purification mud) produced in the purifying process of the salt solution, and in this connection it is essential to improve further the technique of electrodialysis and find a way to make effective utilization of the said mud.

The research on the influence of impurities, such as potassium and boron contained in brine, on the electrolytic efficiency and the purity of caustic soda showed no major changes as compared with the conventional diaphragm method.

(c) Recovery of potassium

In the case of the diaphragm method, caustic soda of 50% obtained through concentration of catholyte contains potassium of 5 to 8% by weight in terms of solids. Therefore, purification is required according to the use of caustic soda. The research in this respect shows that if this caustic soda of 5% is diluted with water to 39% by weight and cooled below 15°C deposit and separate the crystals of $NaOH \cdot 3.5H_2O$, caustic soda of high purity may be obtained, and that the optimum method is to use hydrate prepared through concentration of caustic potassium in the mother liquor. Basic research and development of crystalizing apparatus associated with the above were also carried out.

The present research was limited to the recovery of potassium as a mixed alkali of caustic soda and caustic potassium, and the recovery of potassium as a single item was not covered. However, more efficient use and more effective potassium recovery methods should be developed.

One of the far-reaching effects of the know-how concerning the refining technique of caustic soda with the hydrate method is that it has paved the way for application to the separation and refining of salt, etc. contained in caustic soda (ordinary one) produced with the diaphragm method.

(2) Material balance and economical efficiency

The material balance and economical efficiency of the by-product recovering system was calculated on the assumption that a seawater desalination plant having a capacity of 100,000 m^3 per day uses 30% of salt contained in the drained brine. Details of calculation are given in paragraph 6.3.2. The production scale of a by-product factory is 430,000 tons per year (388,000 tons of chlorine and 2,100 tons of bromine are to be produced annually) in terms of caustic soda (reduced to a 100% basis) and such a scale is considered appropriate for a large caustic factory in the future.

On the other hand, the costs of electrodialysis and salt electrolysis facilities amounts to about 15,000 million yen (at prices in April to June of 1973) and the cost of potassium recovery and caustic soda refining facilities is about 8,000 million yen, for a total of 12,000 million.

Based on the above trial calculation, the economy of a by-products recovery system as a means of comprehensive use of seawater will be considered in the following.

Japan imports about 6 million tons of industrial salt annually, and the steep rise of the price in recent years presents a serious problem for the soda industry. The present research has clarified that the manufacturing cost of concentrated brine is only 5,000 yen per ton of salt (the price in the latter half of 1975). The price of imported salt delivered to a soda factory is 22 or 23 dollars, or 6,600 to 6,900 yen at an exchange rate of 300 yen to the dollar, leaving a difference of about 1,800 yen. Since the supply of industrial salt depends entirely on import, a further rise of salt price will be inevitable. Therefore, if even a part of the imported salt could be replaced with the concentrated brine dealt with by the present research, it will contribute to the restraint of salt prices, thereby leading the way to self-sufficiency.

Since the production scale of a by-product factory is 430,000 tons of caustic soda (reduced to a 100% basis) per annum as described above and the production capacity of caustic soda manufacturers of Japan is 4.5 million tons as of December 1976, the demand in Japan can be met if 10 by-product factories, or so, are established. On the other hand, the water shortage in 1985 is forecast to be at least 2,000 million m^3 per annum, or 5.5 million m^3 per day, which correspond to 50 water making plants of 100,000 m^3 per day in capacity. Although there is an imbalance between demand for by-products and for water, this means that a by-product factory of a seawater desalination plant can be selected for its most favorable location.

As for the recovery of potassium and the refining of caustic soda, it has been clarified that the processing cost is 2,900 yen per of caustic (reduced to a 100% basis) (as of October, 1975). This means that 9,000 tons of caustic potassium is obtainable annually from a by-product factory of the scale mentioned above, and thus the demand in Japan can be satisfied by 10 such factories. However, since caustic potash produced in the by-product factory is in the form of a mixture with caustic soda, it cannot be used as a substitute except for a special case. It may be appropriate to regard it as potassium fertilizer and use it for decomposing rock phosphate into potassic fertilizer. Japan imports 1 million tons of potassium salt annually, of which 90% is used for fertilizer.

As stated above, the utilization of salt and potassium contained in drained brine is inevitably associated with the recovery of other useful components such as bromine and magnesia, and the systematic combination of these components will open up the way to the comprehensive use of seawater. A triple purpose factory of steam power generation, seawater desalination and recovering of by-products is believed to reduce the cost of equipment, raw materials and utilities through comprehensive and intensified operation, thereby contributing to the improvement of the economic effect of the plant.

(3) Summary

(a) Systematic combination of the by-products recovery process with the recovery and use of unused resources contained in seawater is possible.

(b) Use of drained brine of high concentration and high temperature as a raw material results in a saving of energy as compared with seawater.

(c) Since the main part of the electrolytic process is the diaphragm salt electrolysis, there is no requirement for use of mercury. It is possible to combine this process with the supply of raw salt and brine for the ion exchange membrane electrolytic method developed recently.

(d) It is possible to save resources and energy and reduce the cost of products through concentration of factories in specific areas.

(e) Demand for industrial salt to be used in the salt electrolysis process can be met domestically without depending on import.

(f) Export of seawater desalination plants, including the by-product recovery process, to the countries of the Middle and Near East and Southeast Asia can be expected.

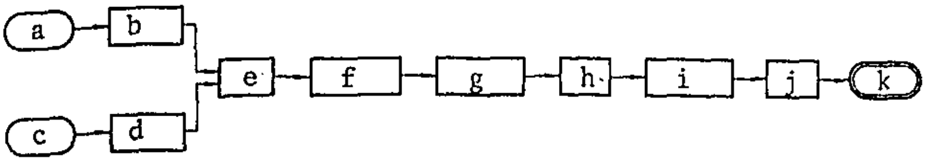


Fig. 6.2-1 Manufacturing process of magnesium hydroxide

Note:

a: Seawater
b: Decarbonation
c: Lime
d: Milk of lime
e: Reaction
f: Precipitation and thickening
g: Washing and separation
h: Drying
i: Grinding and sieving
j: Package
k: Magnesium hydroxide

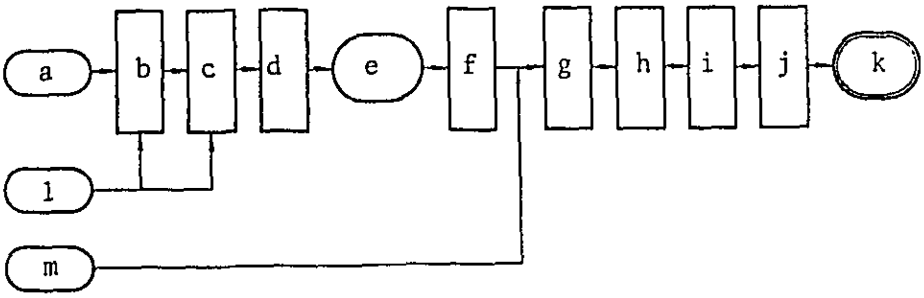


Fig. 6.2-2 Manufacturing process of magnesia clinker

Note:

a: Seawater
b: Decarbonation
c: Reaction
d: Precipitation and thickening
e: Magnesium hydroxide
f: Washing
g: Separation
h: Light burning furnace
i: Granulation
j: Dead burning furnace
k: Magnesia clinker
l: Milk of lime
m: Additives

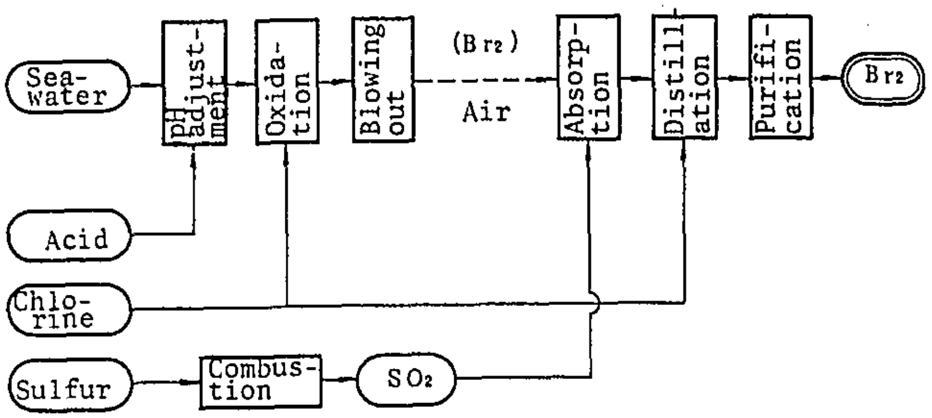


Fig. 6.2-3 Sulfurous gas absorption method

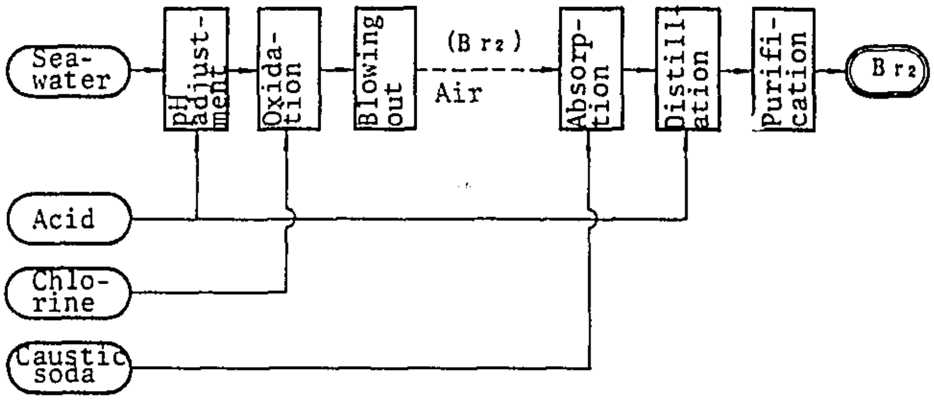


Fig. 6.2-4 Soda absorption method

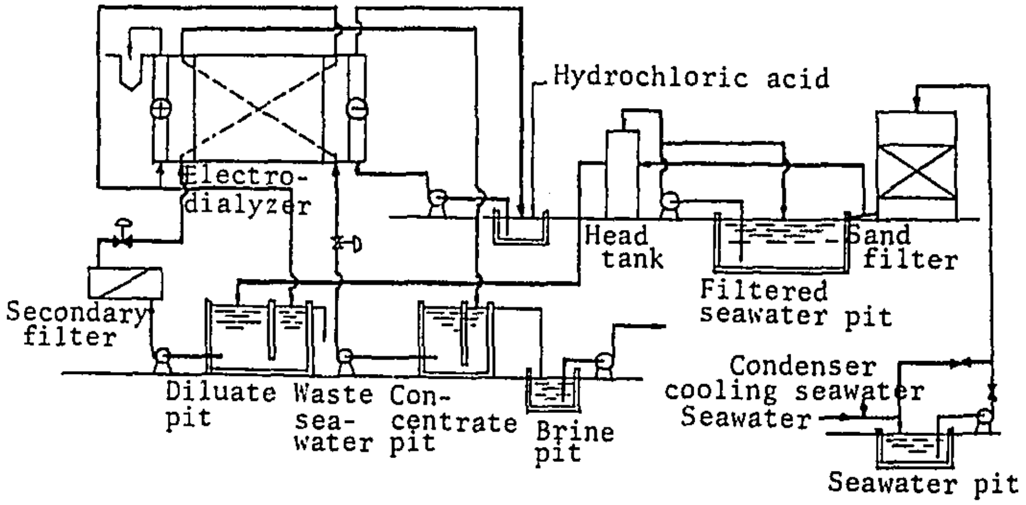


Fig. 6.2-5 Flow sheet of extacting process by ion

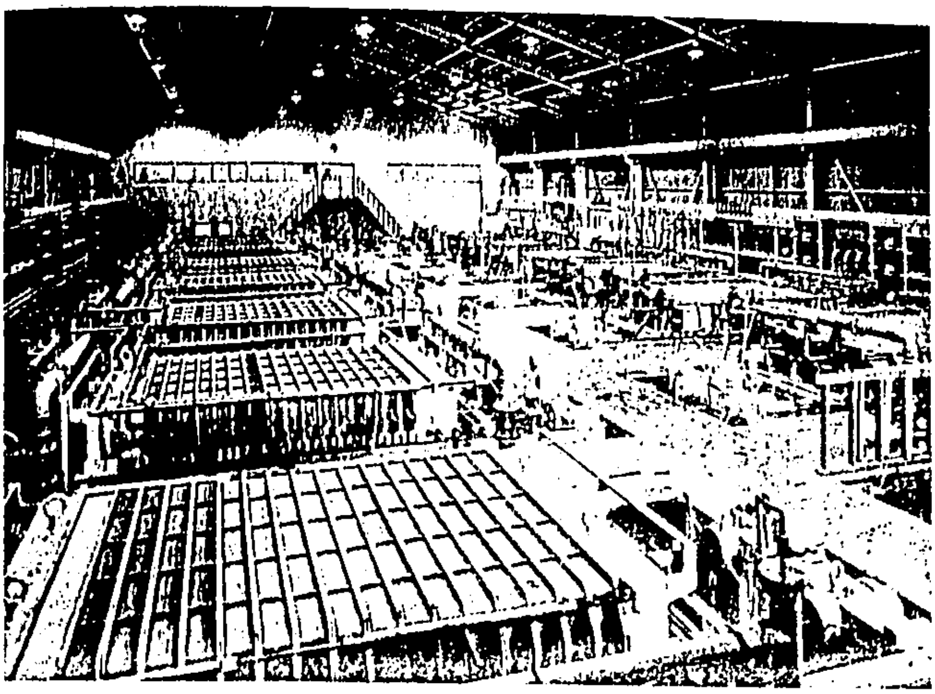


Photo. 6.2-1 Ion exchange membrane facility

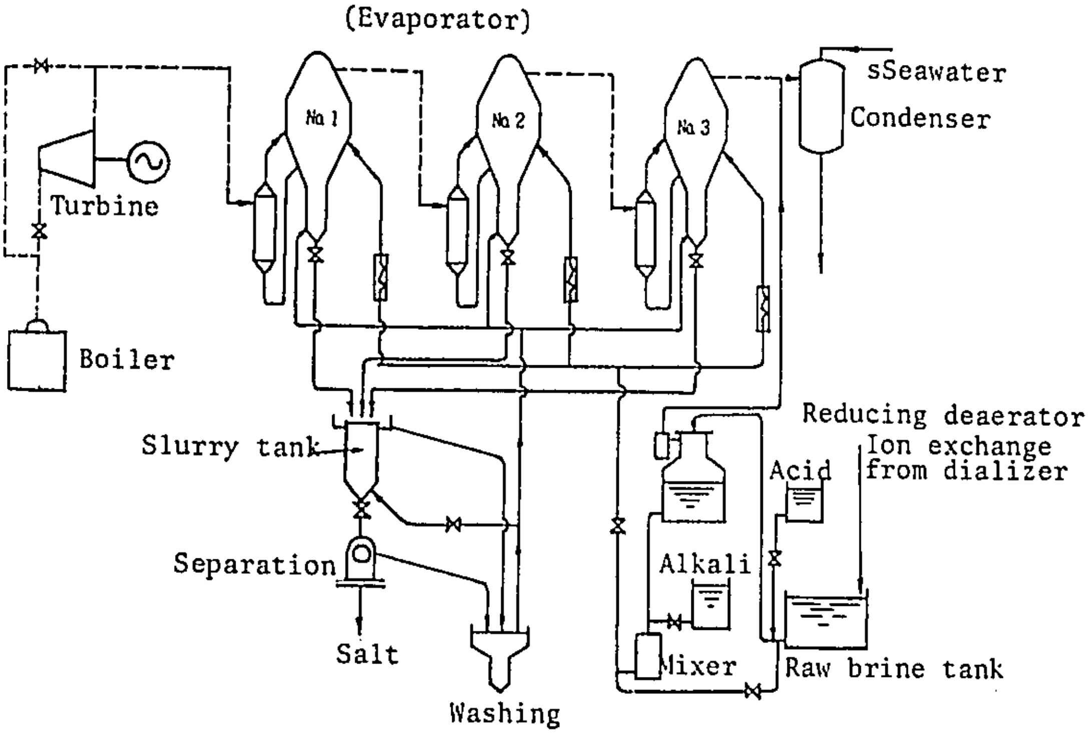


Fig. 6.2-6 Flow sheet of salt refining plant

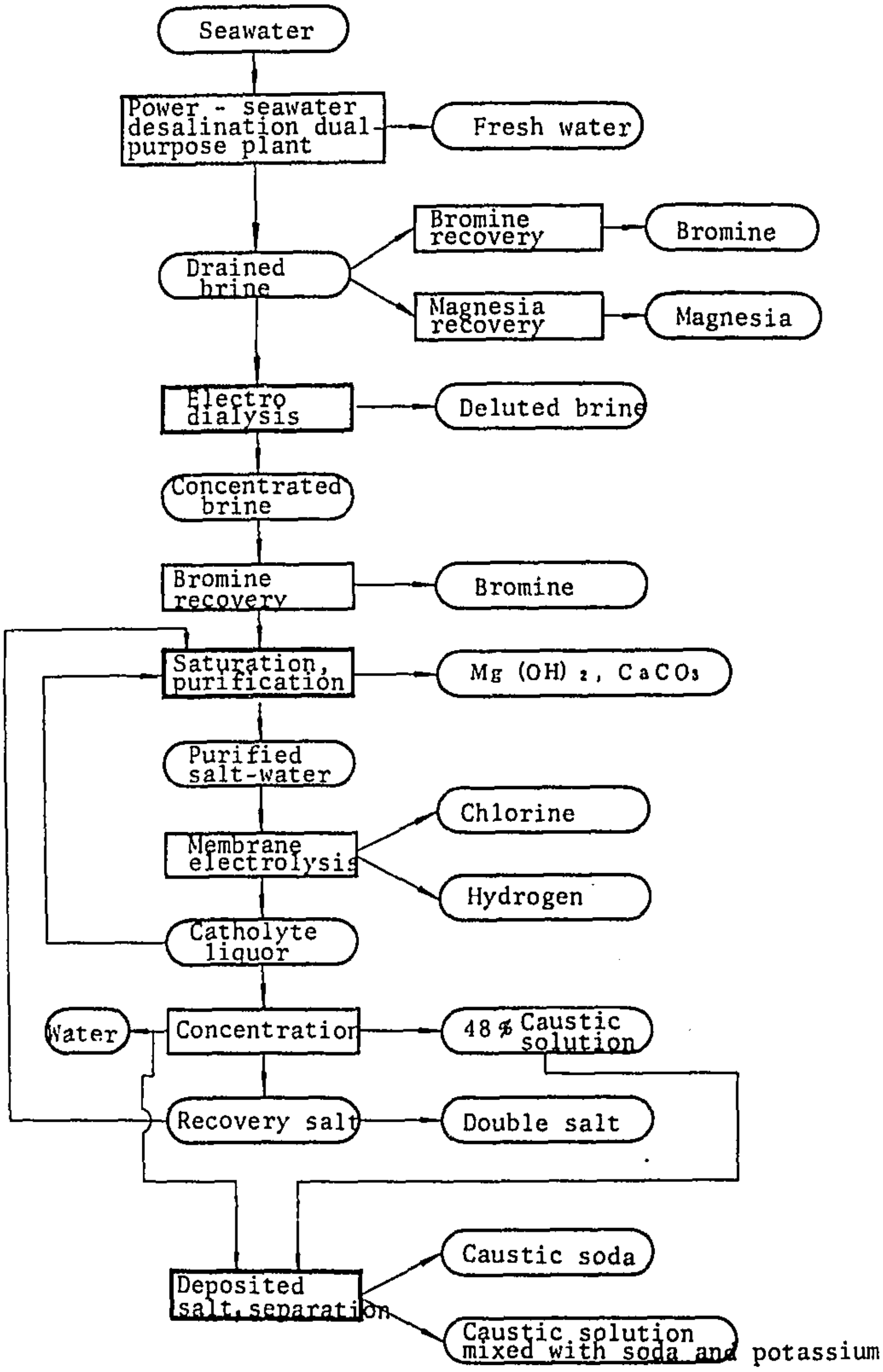


Fig. 6.3-1 By-product recovery system

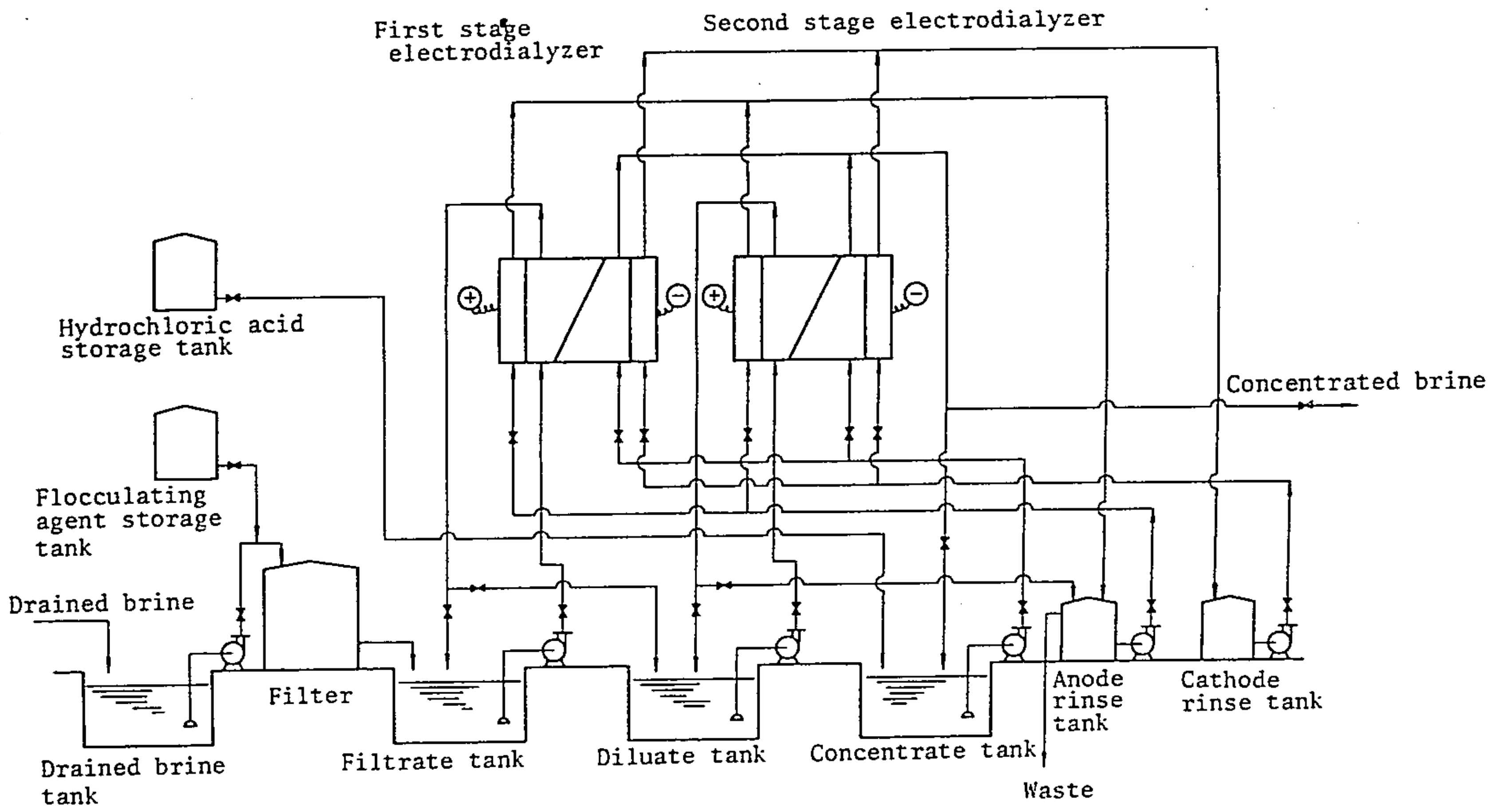
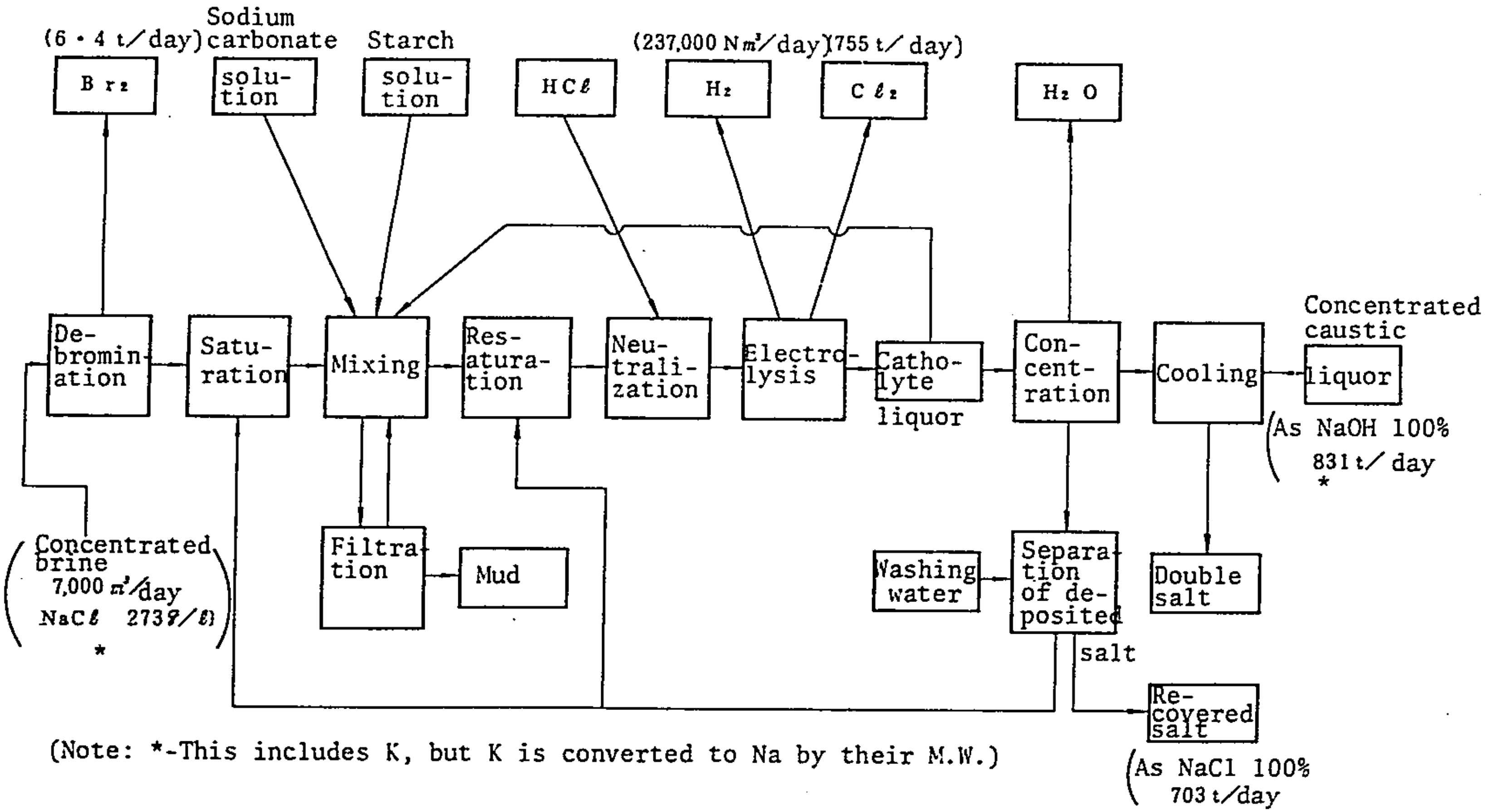


Fig. 6.3-2 Outline of electrodialysis process



(Note: *-This includes K, but K is converted to Na by their M.W.)

Fig. 6.3-3 Block diagram of concentrated brine purification and electrolysis process

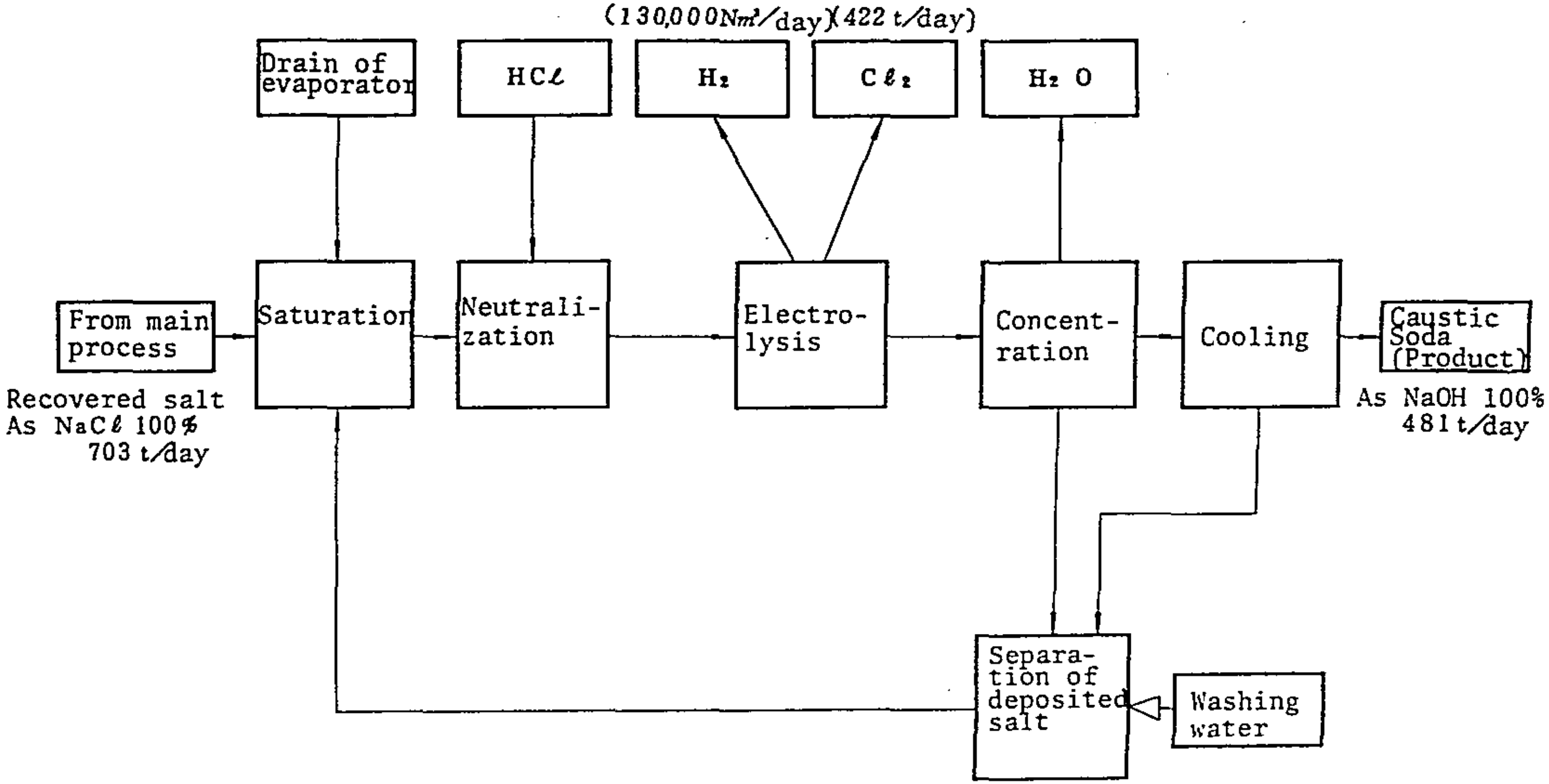


Fig. 6.3-4 Block diagram of recovered salt electrolysis process

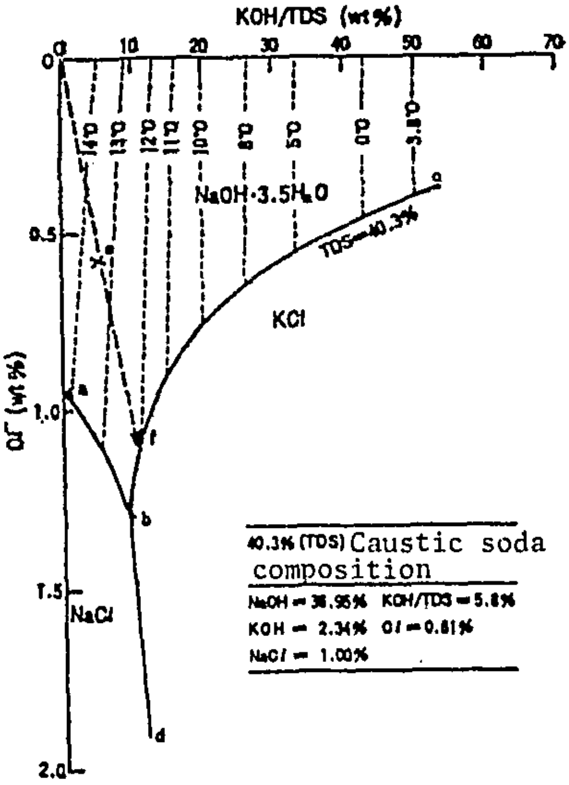


Fig. 6.3-5 Cross equilibrium diagram of NaOH-KOH-NaCl-H_2O system

Fig. 6.3-6 Microphotograph of NaOH·3.5H_2O

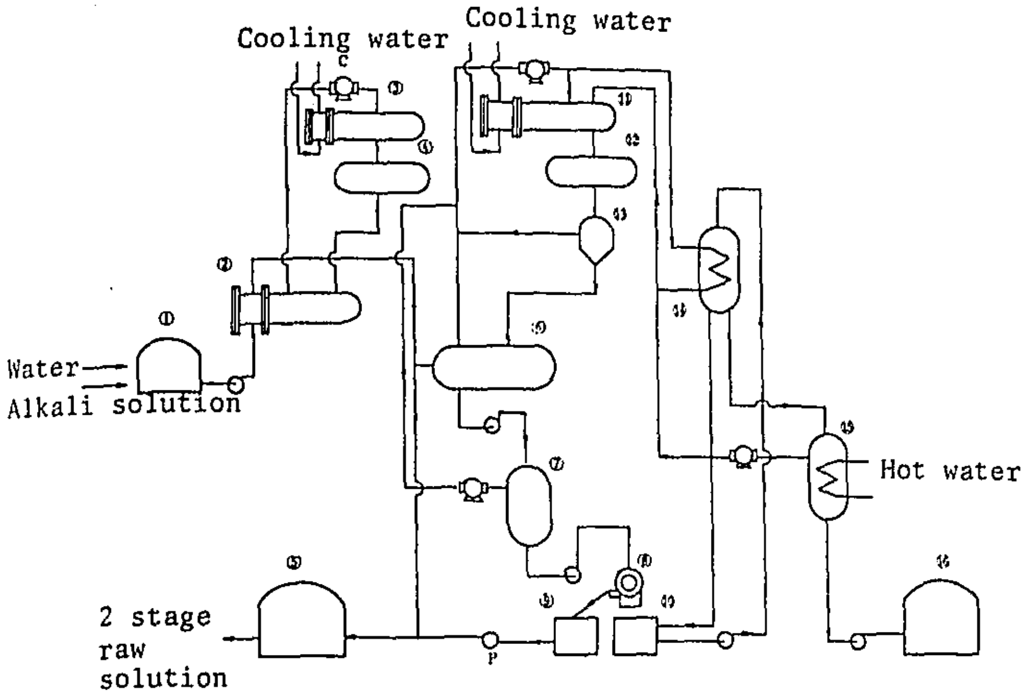


Fig. 6.3-7 Flow sheet of caustic soda refining process

Table 6.1-1 Concentration of components of seawater by element

Element	Concentration (mg/ℓ)	Element	Concentration (mg/ℓ)
H	108,000	N	0.5
He	5×10^{-6}	O	857,000
Li	0.17	F	1.3
Be	6×10^{-7}	Ne	1×10^{-4}
B	4.6	Na	10,500
C	28	Mg	1,350
Al	0.01	Ni	0.002
Si	3	Cu	0.003
P	0.07	Zn	0.01
S	885	Ga	3×10^{-5}
Cl	19,000	Ge	7×10^{-5}
A	0.6	As	0.003
K	380	Se	0.004
Ca	400	Br	65
Sc	4×10^{-5}	Kr	3×10^{-4}
Ti	0.001	Rb	0.12
V	0.002	Sr	8
Cr	5×10^{-5}	Y	3×10^{-4}
Mn	0.002	Zr	–
Fe	0.01	Nb	1×10^{-5}
Co	5×10^{-4}	Mo	0,01

Element	Concentration (mg/ℓ)	Element	Concentration (mg/ℓ)
Tc	–	Ce	5.2×10^{-6}
Ru	–	Pr	2.6×10^{-6}
Rh	–	Nd	9.2×10^{-6}
Pd	–	Pm	–
Ag	4×10^{-5}	Sm	1.7×10^{-6}
Cd	1.1×10^{-4}	En	4.6×10^{-7}
In	<0.02	Gd	2.4×10^{-6}
Sn	8×10^{-4}	Tb	–
Sb	5×10^{-4}	Dy	2.9×10^{-6}
Te	–	Ho	8.8×10^{-7}
I	0.06	Er	2.4×10^{-6}
Xe	1×10^{-4}	Tm	5.2×10^{-7}
Cs	5×10^{-4}	Yb	2.0×10^{-6}
Ba	0.03	Lu	4.8×10^{-7}
La	1.2×10^{-5}	Hf	–
Ta	–	Bi	2×10^{-5}
W	1×10^{-4}	Po	–
Re	–	At	–
Os	–	Rn	6×10^{-16}
Ir	–	Fr	–
Pt	–	Ra	1.0×10^{-10}
Au	4×10^{-6}	Ac	–
Hg	3×10^{-5}	Th	5×10^{-5}
Tl	$<1\times10^{-5}$	Pa	2.0×10^{-9}
Pb	3×10^{-5}	U	0.003

Table 6.1-2 Quantity of principal substances in seawater

Substance	Quantity (t)	Substance	Quantity (t)
$NaCl$	37,000兆	Mo	140億
SO_4	3,600 〃	Al	140 〃
MgO	3,100 〃	U	40 〃
KCl	990 〃	Cu_2-	40 〃
CaO	770 〃	Ni	30 〃
D_2O	240 〃	V	30 〃
Br_2	90 〃	Mn	30 〃
H_3BO_3	40 〃	Co	1 〃
$SrCO_3$	20 〃	W	1 〃
PO_4	3 〃	Cr	7,000万
Zn	140億	Ag	5,000 〃
Fe	140 〃	Au_2-	500 〃

Table 6.1-3 Reserve and economic life of main mineral resources

Mineral	Known reserve (t) (100 million)	* Static economic life (index) (Year)	Average growth rate	Representative index (Year)
Cr	7.03	408	2.6%	94
Co	0.02	109	1.5	65
Fe	877.43	226	1.8	90
Mn	7.22	97	2.9	46
Mo	0.05	78	4.5	34
Ni	0.67	157	3.4	54
W	0.01	39	2.5	27
V	0.09	92	4.4	37
Al	10.60	105	6.4	32
Cu	2.79	42	4.6	23
Zn	1.12	23	2.9	18
H_3BO_3	3.74	301	4.4	60
PO_4	606.45	1,312	4.7	96
SO_4	75.20	72	4.5	32

Table 6.1-4 Potential value of dissolved substances in seawater

(as of July 1977)

	Reserve (t)	Price(yen/kg)	Potential value(yen)
NaCl	27.35	6.5	178,000
MgO	2.15	143	307,000
KCl	0.738	39	29,000
Br_2	0.067	363	24,000
H_3BO_3	0.026	166	4,300
D_2O	0.175	38,000	6,650,000
U_3O_8	3.3×10^{-6}	19,000	63

Table 6.3 - 1

Name	Model CB-V electrodialyzer
Type	Filter-press type
Ion-exchange membrane	Selemion CMV and Selemion ASV
Size of membrane	2,000 mm × 1.120 mm
Effective membrane area	$1.93m^2$/sheet
Number of membrane installed	600 pairs
Membrane distance	0.8 mm
Flow rate of diluate	5 cm/sec
Current density	3 - $8A/dm^2$

Table 6.3-2 Examples of compositions of concentrated brine by means of electrodialysis

Item	Drained brine from multistage flash eveporator	Concentrated brine		
		1	2	3
(Current density)	–	($4.5 A/dm^2$)	($5.2 A/dm^2$)	($6.5 A/dm^2$)
Na (N)	0.86	3.76	3.90	4.35
K 〃	0.019	0.12	0.13	0.14
Ca 〃	0.040	0.10	0.11	0.08
Mg 〃	0.21	0.22	0.24	0.15
Cl 〃	1.02	4.20	4.38	4.72
SO_4 〃	0.11	0.005	0.005	0.004
Br 〃	0.0016	–	0.007	–
B(mg/ℓ)	8	4	5	6

Table 6.3 - 3

Name	Flow rate	Temperature	Concentration
Filtered brine	100,000 m^3/day	35 ℃	Cl^- 39.4 g/l
Concentrated brine	7,000 〃	〃	〃 170 〃
Diluted brine	93,000 〃	〃	〃 29.8 〃

Table 6.3 - 4

Na	104.6	g/l
K	5.0	〃
Ca	1.0	〃
Mg	1.2	〃
Cl	169.9	〃
SO_4	0.6	〃
Br	1.0	〃

Table 6.3 - 5

Filtration equipment	Type	Automatic backwash gravity type sand filter
	Unit of installation	4 units
	Dimension	Filtration area 12,500 mmϕ
	Filtering velocity	8.94 m/hr
Electro dialyzer	Model	CB - V
	Unit of installation	34 units
	Arrangement	2 stages × 17 lines
	Ion-exchange membrane	Selemion CMV and Selemion ASV
	Size of membrane	2,000 mm × 1,120 mm
	Effective membrane area	1.93 m^2/sheet
	Number of membrane installed	1,200 /unit
Rectifier	Type	Thyrister type
	Unit of installation	1 set
	Output	D.C. 460 V 1,800A × 34 lines
	Input	3 phase A.C. 6.6 KV

Table 6.3-6 Characteristics of refrigerant

Refrigerant	Boiling point (℃)	Pressure (0℃) Kg/cm²	Vapor temp.(°C) kcal/kg	Density (0℃) kg/l	Dissolve wt%(25℃)	Toxic (U.G.N*)	Explosive Vol.% (in air)
R-11(CCl_3F)	23.77	0.409	45.48	1.534	0.11	5 A	no
R-12(CCl_2F_2)	−29.79	3.147	36.18	1.397	0.028	6	no
R-22($CHClF_2$)	−40.80	5.074	49.05	1.285	0.30	5 A	no
n − Butane	− 0.50	1.055	91.78	0.604	0.022 (0℃.1 A.P.)	5	1.5~8.5
iso − Butane	−11.70	1.631	85.01	0.582	-	5	1.8~8.5
Propane	−42.3	4.778	94.56	0.530	0.012 (0℃.0.9 A.P)	5	2.3~7.3
Ammonia	−33.3	4.2	301.5	0.82 (−79℃)	88.9 (0℃)	2	16~25

40%aq NaOH, density=1.45(1 °C), viscosity=70=100cp, Crystallization heat of $NaOH \cdot 3.5H_2O$=53 cal/g

*U.G.N.: National Fire Underwriter's group number.

Table 6.3-7 Example of material balance*1

	Refining caustic soda	Prerefining*2 caustic soda	Concentrate potassium solution
NaOH (t/day)	470.6	294.4	16.8
KOH (t/day)	1.7	20.5	27.4
NaCl (t/day)	0.74	18.6	1.8
H_2O (t/day)	745.6	525.8	72.4
Total (t/day)	1218.6	859.3	118.4

*1 Assumption to be 100,000m³/day by seawater desalination

*2 Dissolved thing of crystal obtained by concentration or recovery process

Table16.3-8 By-product recovery process

Process	Electrodialysis	Production of chlorine	Potassium recovery
1. Plant scale	Concentrated brine 2,310,000m^3/year NaCl 614,000t/year	NaOH mixed with potassium 272,000t/year NaOH 158,000/year Cl_2 388,000/year Br_2 2,110t/year	Treatment NaOH mixed with potassium 272,000t/year
2. Facility	2,760 million yen	12,030 million yen	827 million yen
3. Personnel	24	60	14
4. Land	83m × 16m=13,280m^2	220m×250m=55,000m^2	80m×105m=8,400m^2
5. Product quality (Cl_2, Br_2, H_2 -- except ordinally)	Concentrated brine (to next process) g/ℓ g/ℓ a 104.6 Cl 169.9 K 5.0 SO_4 0.6 Ca 1.0 Br 1.0 Mg 1.2	NaOH (mixed K--to next process) NaOH 46.0% KOH 2.9 NaCl 1.2 NaOH (normal) NaOH 48.0% NaCl 1.0	Refining NaOH (eliminate)K, Cl) NaOH 38.63%(on KOH 0.14 100% NaCl 0.06 basis) 155,000t/year By-product (a) (mixed K, Cl) NaOH 34.2% KOH 2.4 NaCl 2.2 284,000t/year By-product (b) (mixed K, Cl) NaOH 14.2% KOH 23.1 NaCl 1.5 39,000t/year
6. Main product treatment cost per ton	Concentrated brine ton/NaCl on 100% basis 2,510 ∿ 2,780 yen	Total NaOH pair ton on 100% basis (include Cl_2 0.9t Br_2 4.9kg) 21,480∿26,000 yen	Raw material NaOH (mixed K) ton/on 100% basis 1,500 ∿ 1,610 yen

VII. Reverse Osmosis

7.1. Theory

7.1.1. Introduction

As is well known, the reverse osmosis method employs what is called a semi-permeable membrane. It has appeared as a conception on the stage of physical chemistry since a fairly long time ago and has been used principally to explain osmotic balance and osmotic pressure. Prof. Reid of the Florida University, who received a hint from osmotic balance, thought of applying the reverse osmosis method to the desalination of seawater in 1953. When a pressure higher than osmotic pressure is applied to the salt solution side barriered with a semi-permeable membrane, pure water comes out from that side passing through the membrane. Thus the reverse osmosis method has made an entrance as a desalination method. The question was whether such a semi-permeable membrane existed in fact and, if so, whether it was fit to be put to practical use.

This question was answered by the advent of a cellulose acetate membrane originated in 1960 by Loeb and Sourirajan, and the reverse osmosis method has grown as seen today. Here the membrane will be briefly dealt with since it is considered in detail in the next section. The development of new membranes is still actively carried on and bewildering progress is continuing with new products produced one after another. Many meetings of academic societies and symposiums were organized to discuss the matter and the arrangement of information from them alone constitutes an enormous task.

Search for a membrane relates closely to the mechanism of separation, that is, why a membrane is semi-permeable, or why it allows water to pass through but does not allow the solute of low molecular weight such as inorganic salt to do so. As a result of tests made on various membranes at the Florida University after the reverse osmotic method was suggested, it was found that the cellulose acetate membrane produced by Du Pont was semi-permeable but the rate of passage was very low. Then, as a guideline to improve the membrane, the mechanism of separation was considered.

In general, it is said that although cellulose acetate is inferior in its crystallinity compared with regenerated cellulose, its crystallization is furthered if water exists. This is due to the fact that as the molecules of water are small, hydrogen bonds are formed between the molecules of acetate adjoining each other; thus the molecules of cellulose acetate become as if bridged by those of water and it is inferred that this augments the crystallinity. Reid and others concluded, judging from such a structure, that the following two types of diffusion take place. First, ions and molecules which do not form a hydrogen bond diffuse through pores formed in coarsely bridged regions (hole-type diffusion). On the other hand, water and molecules which form hydrogen bonds move on successively to the sites of the bonds to diffuse (alignment-type diffusion). In this way, ions etc. diffuse slowly through pores slightly formed on the membrane of cellulose acetate which is in a condition as if bridged by water and water passes through the bridged parts at a higher rate. It was concluded that the difference in the rate of passage produces semi-permeability. Based on this, the problems will be solved by finding a better membrane which has many sites for hydrogen bonds and a skeleton appropriately bridged and of a suitable size and also which is dissoluble to water and stabilized chemically. Though efforts were made, such a membrane could not be discovered easily and the researches at the Florida University ended with no result.

Sourirajan et al of Los Angeles Campus of the University of California started their approach to a membrane based on a different idea. The essence of their idea was to use a membrane prepared with a material which absorbs water selectively when placed in a salt solution and to press the water out by applying pressure to it. This idea is also supported by the fact that although a cellophane membrane does not separate salt, it separates when silicone grease is coated on it. Eventually, this comes to the cellulose acetate membrane, and the cause for the success of Sourirajan, et al. was that they manufactured a membrane by preparing a membrane making solution by themselves, instead of employing membranes on the market. Details in this connection will be omitted, but this led to the discovery of a membrane making solution of a four-component system consisting of cellulose acetate, acetone, magnesium perchlorate and water, and with this the rate of passage was increased very much.

Another important point discovered during these processes was the fact that the performance of a membrane can be varied in many ways by dipping the membrane in hot water, that is by heat treatment. Based on this fact and a guiding principle leading to the discovery of the composition of a membrane making solution, Sourirajan presented a model as shown in Fig. 7.1-1. Water selectively absorbed by the membrane comes out through suitable pores, and if the diameter of pores is large the original solution passes through it and if the diameter is small the solution ceases to pass through with separation improved; in this connection, it is thought that the diameter of pores is adjustable by the temperature of heat treatment and if the temperature is raised the diameter is reduced.

Bean and Glueckauf also have suggested the same idea as that mentioned above which presumes the existence of pores but, on the contrary, there is an idea which maintains that no pores exist and the membrane is homogeneous, with no definite conclusion having been reached. This is because arguments are about tiny pores that cannot be observed even through an electron microscope.

The above arguments on the mechanism of separation principally concern the separation of inorganic salts, but the separation of organic substances requires different arguments. In general, cellulose acetate membranes separate alcohol and carbozylic acids of low molecular weight and, on the contrary, phenols are concentrated in the permeated solution. Although many studies have been made by Matsuura and Sourirajan on the arrangement of data on the separation of organic substance, their presentation will be omitted here.

7.1.2. Transport Equations

In arranging the data of experiments on the reverse osmosis method, data such as those simply showing how much quantity was separated are not satisfactory. If a comparison of performance is to be made among different membranes, the data need to be arranged in the form of coefficients. Nevertheless, since respective researchers differ in their opinions as to the equations of membrane transmission which constitute the basis of the comparison, such rearrangement is not effected so much in general. Since 1965, the author and others have consistently devised a method of arrangement, by which many data have been arranged. Since so far no extraordinary result has been produced from it, the method will be explained in the following.

The concentration distribution near the membrane of water and solute which pass through that membrane is as shown in Fig. 7.1-2. Of the water and solute transferring toward the membrane from the left of the Figure, the solute of which a small quantity is allowed to pass through the membrane due to selectivity becomes accumulated near the surface of the membrane. With this the concentration of C_2 near by the surface of the membrane becomes higher compared with the concentration of C_1 of the solution proper. This phenomenon is generally called concentration polarization. Accumulated solute return to the solution proper due to the difference between the density C_2 and C_1. As described above, in the case of membrane permeation, the transport phenomenon in the laminar film (1) near the surface of membrane and that in the true membrane are connected in a series and thus it is needed to consider them individuall

First, when the transport phenomenon in a laminar film is considered the following equation is valid.

$$J_v C - D\frac{dc}{dz} = J_v C_3 \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

Wherein, D = diffusion coefficient ($cm^2/sec.$) and Jv = volume flow ($cm^3/cm^3 sec.$). If this equation is solved assuming that $C = C_1$ when $Z = 0$ and $C = C_2$ when $Z = 1$, the following equation is obtained.

$$\frac{C_2 - C_3}{C_1 - C_3} = e^{J_v/k} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

It is value defined here by $k = D/l$, and this value is ordinarily called individual film coefficient of mass transfer in chemical engineering. This value depends on the flow conditions of the solution near the surface of a membrane and, in general, it becomes higher when the solution is disturbed very much in the vicinity of the surface of a membrane and C_2 takes a value approximate to C_1 as seen from the equation (2). In this connection, attention should be paid to the fact that the consumption of energy increases due to it.

For another transport phenomenon as to membrane permeation, the equations to be applied include those (3) and (4) shown below.

$$Jw = A[\Delta P - [\pi(C_2) - \pi(C_3)]] \cdots\cdots\cdots \quad (3)$$

$$Js = \left(\frac{D_{AM}}{K\delta}\right)(C_2 - C_3) \cdots\cdots\cdots \quad (4)$$

Wherein, ΔP is the difference of mechanical pressure, $\pi(C)$ is the osmotic pressure of the solution of density C, and A and $(D_{AM}/K\delta)$ are the transport coefficients respectively of water and solute. Jw and Js show flux respectively of water and solute.

As against equations (3) and (4), those (5) and (6) are deduced as to a general film phenomenon

$$Jv = Lp(\Delta P - \sigma \Delta \pi) \cdots\cdots\cdots \quad (5)$$

$$Js = W \Delta \pi + (1 - \sigma) \bar{C} Jv \cdots\cdots\cdots \quad (6)$$

Besides the Lp and ω values respectively corresponding to A and $(D_{AM}/K\delta)$, these equations involve the value σ which is called reflexion coefficient. When these equations are applied to the reverse osmosis method, the average concentration C involved in the equation (6) raises a problem. Thus, there have been proposed the following equations which are obtained by rewriting the equation (6) in the differential form and integrating this in the direction of a thicker membrane.

$$R = \frac{C_2 - C_3}{C_2} = \frac{\sigma(1 - F)}{1 - \sigma F} \cdots\cdots\cdots \quad (7)$$

$$F = \exp\{-Jv(1 - \sigma)/P\} \cdots\cdots\cdots \quad (8)$$

Wherein P is transmission coefficient and R is rejection the solute. If the equatins (7) and (8) are expanded assuming 1, they become as the equation (9)-

$$R \doteqdot \frac{Jv}{Jv+P/\sigma} = \frac{Jv}{Jv+(D_{AM}/K\delta)} \cdots\cdots\cdots\cdots (9)$$

but, if R is calculated by the equations (3) and (4) it takes the form on the right side of the equation (9), resulting in the same. In general the σ value is extremely approximate to 1 for an ordinary membrane, making it difficult to find it accurately, though it can be found by using data obtained by changing the pressure.

Based on the above, all the transport phenomena of reverse osmosis can be expressed by combining three equations (2), (3) and (4). The A and $(D_{AM}/K\delta)$ values can be also found by arranging the data of experiments, and this serves for the arrangement of data.

7.1.3. Design of Process

In general, if the properties of a membrane are given, it becomes possible to calculate what performance the membrane will display according to the conditions of its use and design a process. The following relations are obtained between C_1 and C_3 by rearranging the equations (2), (3) and (4).

$$\begin{aligned} C_1 &= C_3 \left[1 + \frac{1}{(\gamma C_3+\theta)} \cdot \exp\left\{ - \frac{1}{\lambda(\gamma C_3+\theta)} \right\} \right] \cdots\cdots\cdots (10) \\ &= C_3 \cdot q \end{aligned}$$

wherein,

$$\theta = (D_{AM}/K\delta)/(A \cdot \Delta P)$$

$$\lambda = k/(D_{AM}/K\delta)$$

$$\gamma = m/\Delta P, \quad \pi(c) = mC$$

θ represents the selectivity of a membrane, the influence of concentration polarization and γ that of osmotic pressure. Where these values are determined the relation between C_1 and C_3 can be found by the equation (10). Although it needs a method of trial and error to find the C_3 value from the C_1 value, it becomes $\gamma C_3 \ll \theta$ where a solution is so dilute that any influence of osmotic pressure can be ignored, making the calculation easier. Also, it will become simple if $\lambda \to \infty$ is assumed, and there is a method to start approximation from this. Details will be found elsewhere.

On the other hand, due to a solution of lower concentration coming out through the membrane, the concentration C_1 of the solution proper increases gradually. As a result, C_3 also increases. Where the flow rate of solution on the high pressure side is designated as L, according to material balance-

$$d(CLC_1) - C_3\,dL = 0 \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (11)$$

By the intergration of the equations (10) and (11) combined together, recovery through the membrane and average concentration of the solution can be found. As this calculation is complicated, if the recovery is small it will be sufficient to calculate assuming that the bath can be regarded as a perfect mixing bath as shown in Fig. 7.1-3.

If a solution of the density $C_1{}^o$ supplied to this bath is drained at $\bar{C}_1$ and that of the density $\bar{C}_3$ comes out from the membrane, putting the recovery at Δ,

$$C_1^o = \bar{C}_1(1-\Delta) + \bar{C}_3\,\Delta \quad \cdots\cdots\cdots\cdots\cdots \quad (12)$$

If $\bar{C}_1$ is related to $\bar{C}_3$ by the equation (10), then

$$C_1^o = \bar{C}_3\,[\,q(1-\Delta)+\Delta\,] \cdots\cdots\cdots\cdots\cdots \quad (13)$$

On the other hand, the relation between the recovery Δ and length of membrane x differs according to the shapes of modules and individual examinations are required.

Thus in practice, it is difficult in many cases to satisfy both the desired rejection and recovery with only one module. This necessitates providing a multistage module or make the solution recycle. The recovery $\Delta\gamma$ when the solution is recycled is as expressed by the following equation based on Fig. 7.1-4 and it becomes higher with an increase in the recycle rate.

$$\Delta_r = \Delta\left(1 + \frac{rL}{F}\right) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (14)$$

The Relation between the concentration C of feed solution and that, C_3, of solution transmitted is,

$$C_F = \overline{C}_3 \left[q - (q-1) \triangle \left(1 + \frac{rL}{F}\right) \right] \cdots\cdots \quad (15)$$

and if γ increases $\overline{C}_3$ also increases.

A multistage system which connects in series the appratuses shown in Fig. 7.3-1 is ordinarily known as that of Christmas tree type and is much adopted in general. Another multistage system is of the cascade type and the 2-stage desalination of seawater is outlines in Fig. 7.1-5 It is an interesting problem how to establish various conditions for s such a multistage system, and this needs future examination and actual proof.

7.2. Membrane and Module

7.2.1. Membrane

(1) Necessary conditions

(a) High salt removing capacity

The quantity of principal components dissolved in seawater is 34,000 to 35,000 ppm in terms of T.D.S. and, on the other hand, although the standard concentration of drinking water is inaccurate, the value T.D.S. 500 ppm determined by the United States Public Health Service has been adopted as the standard. To meet this, membranes used to obtain drinking water from seawater need to have the capacity to remove about 99% of salt. As a salt removing rate for practical purposes, the membrane should be capable of removing about 99.5% of salt, if the recovery of plain water from seawater fed is taken at around 50%, and account is taken of the facts that the concentration of salt in the seawater becomes densified twice in the vicinity of the outlet in the reverse osmotic system and concentration polarization occurs on the surface of membrane.

(b) High-pressure resistance

The osmotic pressure which seawater develops is about 25 Bar, and if the recovery of plain water is taken at around 50% it rises to about 50 Bar. With the concentration polarization on the surface of the membrane added to this, the difference of osmotic pressure between both surfaces of the membrane is estimated to rise to as much as 60 Bar, and eventually a practical operating pressure of at least 60 Bar will be required.

(2) Limits and countermeasures of Loeb-Sourirajan membrane

The asymmetric membrane of 2.5 cellulose acetate discovered by Loeb-Sourirajan is of a structure with a porous support layer lapped over it with a fine layer of 1μ or less in thickness. Where seawater is desalinated using this membrane under an operating pressure of about 100 Bar, plain water of less than T.D.S. 500 ppm can be obtained at first; but with an elapse of time, the flux passing through the membrane diminishes gradually and at the same time the salt concentration in the plain water rises to over 500 ppm. This phenomenon is called compaction phenomenon and a part of it is due to increase in fluid resistance caused by the elastic compression of the porous supporting layer and another part is due to increase in the pure water transport coefficient caused by the increased thickness of the fine layer. The former is a phenomenon of relatively short duration, or a few hours, and has the property that it recovers when the application of pressure is ceased. The latter never recover and reduces permanently the flux, to constitute a serious defect of the Loeb-Sourirajan membrane. Where the flux at the initial hour to be designated as J_{vo} and flux after t hours as J_v, the relation

$$\frac{Jv}{Jvo} = \left(\frac{t}{to}\right)^{-m}$$

is valid, and the value of m is called the coefficient of compaction. The smaller this value is, the less compaction is.

The value of the coefficient of compaction of a 2.5 cellulose acetate membrane becomes smaller the higher the temperature of heat treatment is and the lower the operating pressure is. Fig. 7.2-1 shows the relation between the initial transport coefficient of membrane A'_o [g/cm^2·sec.·bar] and the value m for membranes treated at three levels of temperature by applying pressure changed from 102 to 68 and to 40 $) Bar. Since no correction is made for concentration polarization and osmotic pressure in calculating the transport coefficient of the membrane, accurate data cannot be obtained but it is possible to understand the general tendency described above. It has been found that the value m is about 0.1 at 102 Bar and about 0.05 at 68 Bar. Where $m = 0.1$, flux reduces to 40% and where $m = 0.05$, to 65% respectively after one year.

Since the compaction phenomenon seems eventually to be caused by creeping flow of macromolecules, it is supposed that with a rise in the temperature of feed solution the membrane becomes soft with its pressure resistance decreasing. Fig. 7.2-2 shows the relation between the temperature of the feed solution and the value m, which becomes larger the higher the humidity is, showing that compaction is furthered. In the case of long-term operation, the control of the temperature of the feed solution becomes absolutely indispensable.

As described so far, the asymmetrical membrane of 2.5 cellulose acetate was found to have a serious defect in using it to desalinate seawater. Due to this, the desalination of seawater on a practical basis, which was the original object, was delayed considerably. Various methods were devised to overcome such a defect for successful desalination of seawater by applying the reverse osmosis method. First, a search was made for a way which somehow enables the use of the asymmetrical membrane of 2.5 cellulose acetate. Economical desalination seems feasible if a membrane which permits large flux can be used even at the cost of the separation ratio to a certain extent. For example, if a membrane of 90 to 95% in salt rejection is employed, it is possible to obtain flux two to three times as large as that of a 99.5% membrane. In return for it, as the concentration of salt in the permeated solution becomes 3,500 ppm to 5,000 ppm, reverse osmotic treatment must be conducted by using a reverse osmotic membrane once again. In short, the direction of efforts was changed toward the search for the possibility of a 2-stage process. In particular, the second stage can utilize entirely the method of desalination which has been established already for brine, and since the operating pressure is 20 to 30 Bar, there is no possibility for compaction to become a practical problem. The 2-stage process enables the second stage to compensate for any lowered capacity of the first stage, and this augments the reliability considerably and the future is very promosing.

Although searches were made in order to obtain a membrane of high compaction resistance, using 2.5 cellulose acetate for a one-stage process, by adding to it various agents or devising methods to make membranes, the efforts did not pay off after all. Then membrane making was tried in various ways including the manufacture of blended membranes of cellulose 2.5-acetate and cellulose triacetate and membranes of various cellulose esters such as cellulose acetete butyrate. As to details on this point, reference is made to, Chapter III, "Formation of Membrane". The typical examples are shown in Table 7.2-1. At present, blended membranes and asymmetric membranes of cellulose triacetate have come to be used for the first stage of the 2-stage process of seawater desalination. Also cellulo triacetate has been recognized to have superior separation characte istics but, as its flux is small, it is used as modules of ultra-thi or hollow system membranes.

Subsequently, investigations were made as to whether synthetic macro molecules of non-cellulic material can be applied to reverse osmotic membranes. The investigations were made, as classified roughly, on water soluble macromolecules bridged, copolymer of hydrophilic and hydrophobic monomer, homogeneous polymer from polar monomer, hydrophobic polymer added with hydrophilic group, and aromatic heterocycl condensation product. Their outlines are shown in Table 7.2-2.

Eventually, aromatic polyamide has been found to be the best for the present as a material to use for single stage desalination of seawater. However, since the membrane of asymmetric structure provided little flux, it was necessary to make a membrane in the type of a hollow fiber system to increase its area. The properties of polymer made it impossible to make an ultra-thin membrane. Apart from the Loeb-Sourirajan method in which a proper material is once melted and then cast to make an asymmetric membrane, a method to make a composite membrane has been developed; that is, a thin layer of membrane having a separation function is formed on the surface of a porous supporting layer which has been prepared beforehand.

To summarize above, the blended membrane of cellulose 2.5 acetate and cellulose triacetate is used in the first stage of the 2-stage desalination process. The best membrane for the single stage process is aromatic polyamide membranes and composite membranes prepared by the new method of membrane making. In particular, due to the spiral module of PA-300 to be mentioned later being capable of standing against high temperature, it has been determined to use the module to construct a seawater desalination plant of 12,000 m^3/day in capacity in Jedda of Saudi Arabia and the manufacture of the module is now under way. If this plant is successful, all the seawater desalination plants in the Near East are expected to convert their method from evaporation to reverse osmosis, because the construction period for the latter is remarkably shorter than for the former.

7.2.2. Composite Membrane

In order to overcome the problems such as compaction and the limitation of operating temperature which occur where membranes of cellulose acetate are used to desalinate seawater, as described in the preceding paragraph, two directions were indicated for the research and development search for new materials and manufacture of composite membranes. Since compaction is a phenomenon caused by creep of macromolecules, any membrane obtained by a making method based on the usual Loeb-Sourirajan's technique will not relieve the problem of compaction even if a new material can be obtained. Accordingly, research was started on ultra-thin membranes consisting solely of an active layer for the asymmetric membrane which takes part in separation. If an ultra-thin membrane is formed over a porous supporting layer of high pressure resistance, the thickness of the active layer hardly changes with the elapse of time and thus the flux continues to keep a fixed value.

(1) Initial research

Riley and others of Gulf General Atomic Co. (renamed as Gulf Environmental System Co. and then to the present Universal Oil

Products Co.) have continued the research on ultra-thin membranes of cellulose triacetate. In the initial period, an ultra-thin membrane formed on a glass plate was moved on to a membrane filter layer. A subsequently developed technique has enabled casting directly on the porous supporting layer obtained from a blend of cellulose nitrate and cellulose monoacetate and continuous membrane making has been successful and a prototype module of spiral type has been published.

(2) Plasma polymer membrane

Yasuda and others of the Research Triangle Institute has conducted research on a composite membrane obtained by making polymer impalpable powder just polymerized deposit on the porous supporting layer In the gas plasma produced by electrodeless glow discharge, various monomers (even benzene and toluene) become radical and simple polymerization initiating reaction takes place. Living polymer obtainable in this was is made to deposit on a milli-pore filter or polysulfone membrane or porous glass tube to form a composite membrane. Interestingly enough, where this membrane is used as a reverse osmotic membrane it has characteristics that both the flux and the rejection of salt increase with the elapse of time. A great problem remaining to be solved is how to equip apparatuses where it is intended to manufacture membranes in a large quantity.

(3) NS-100, NS-200, PA-100 and PA-300 Composite membranes

As a result of researches on reverse osmotic membranes of non-cellulose systems, it has been found that the following 4 points are important to improve the reverse osmotic characteristics of membranes. (1) It is necessary to keep a balance between hydrophobic and hydrophilic groups in order to increase flux while maintaining the rejection of salt. (2) Polymer must be hard in order to prevent compaction, increase flux and suppress the diminishing tendency of the flux. (3) Formation of asymmetric membranes having a thin active layer must be possible in order to increase flux. (4) It needs to have resistance against deterioration due to chemicals and micro-organisms existing in a feed solution.

The above conditions can be satisfied by forming the condensation polymer of polyamine and polycarboxylic acid chloride or isocyanate directly on porous supporting layers. For example, urea bond is hydrophilic and stabilized chemically and structurally. On the other hand, hydrophobicity is increased by the use of reactants containing aromatic cycle and heterocycle and the structural strength of membranes is also improved. However, since these condensation polymers are insoluble to most solutions, it is impossible to obtain asymmetric membranes by the Loeb-Sourirajan technique. The methods described hereunder as to a series of membranes are those to obtain asymmetric membranes by forming insoluble condensation polymers directly on the surface of porous supporting layers. NS-100 and NS-200 have been developed by Rozelle and others of North Star Research Institute.

(a) NS-100: Porous polysulfone supporting membrane is dipped in 1 to 2% aqueous solution of polyethylene imine (PEI). After having been drained, the membrane is made to react with 0.5 to 1% hexane solution of tolylenediisocyanate (TDI) for a short time at the normal temperature, and then heat-treated at 115 to 120°C for 10 to 15 minutes. The structure is as shown in Fig. 7.2-3. Where seawater is processed at 102 Bar by reverse osmosis, values obtained are around 99.4% in the rejection and 18 gfd in flux.

(b) NS-200: Porous polysufone supporting membrane is dipped in solution composed of (isoproyl alcohol, 20g + 1% aqueous solution of dodecile sulfate of soda, 76g + sulfuric aid, 2g + furfuryl alcohol, 2g) for 5 minutes; then after having been drained, the membrane is wrapped with aluminum foil to be heat-treated at 150°C for 15 minutes; then it is cooled in 10% aqueous ammonia. The structure is as shown in Fig. 7.2-4, and the reverse osmotic characteristics against seawater are 99% in the rejection at below 68 Bar and 18 to 20 gfd in flux.

(c) PA-100: Porous polysulfone supporting membrane is dipped in 1.5 to 2.5% aqueous solution of PEI. After having been drained, the membrane is made to react with 0.6 to 2.0% hexane solution of isophthaloy/chloride (IPC) for 5 to 120 seconds. Heat treatment is conducted at 60 to 120°C. The structure is as shown in Fig. 7.2-5, and the reverse osmotic characteristics against seawater were 99% in the rejection at below 68 Bar and 15 gfd in flux.

(d) PA-300: Porous polysulfone supporting membrane dipped in 10% epiamine aqueous solution for 30 minutes is air-dried for 30 minutes after having been drained. Then the membrane dipped in the same solution for another 20 minutes is air-dried for 3 to 5 minutes after having been drained. Then it is made to react with 1.1% hexane solution of IPC for 30 seconds. Then the membrane heat-treated at 105°C for 10 minutes is covered with 8% PVA aqueous solution for another heat treatment at 105°C for 5 minutes. The structure is as shown in Fig. 7.2-6. It is possible to store PA-300 membranes in a dried state. Its reverse osmotic characteristics against seawater at 54 Bar were 98.5% in the rejection and 19 gfd in flux. Based on the results of actual tests made with a spiral module, it may be said that the coefficient of consolidation is virtually zero as shown in Fig. 7.2-7.

7.2.3. Modules

The use on an industrial scale of membranes suitable for seawater desalination requires resolving various technological problems including concentration polarization, etc. and solving a difficult question of how to support satisfactorily extremely delicate semipermeable membranes under conditions of high pressure. Moreover, these membranes must be assembled into apparatuses of high reliability which can be produced in a large quantity and at low cost so that they can be applied as a module. The progress of modules starts with a small plane membrane on a laboratory scale, of which enlarged types are known as spiral and pressure resistance plate types. Also the membranes are shaped into tubes known as tubular and hollow fiber types. For the purpose of comparison, the characteristics of respective modules are shown in Table 7.2-3. As seen from the table, each module has characteristics of its own.

Where membranes liable to compaction are used, the plate type which permits easy exchange of membranes will be advantageous. Where pretreatment is not conducted, it will be profitable to adopt the tubular type which does not become plugged and can be easily washed even if plugged. Except the above cases, the spiral or hollow fiber type will be advantageous in terms of price. However, since the hollow fiber type is extremely liable to be plugged, its use requires sufficient pretreatment. The price of modules is heavily denpendent on the structure of support, density of membranes inserted and membrane flux. If mechanized mass production of modules is started, its benefits will be the greatest with the hollow fiber type and to the spiral, pipe and plate types in a lesser degree.

(1) Plate type

It is equally called Plate & Frame type and corresponds to the filter press of a filter. Historically, it is the earliest type which became available since plane membranes could be used.
But, different from the filter press, higher pressure is required, raising problems in designing and thus it has gradually disappeared. The greatest characteristic of this plate type compared with modules of other types is that its structure is very simple and thus membranes alone can be exchanged and such ability of easy exchange can

reduce running costs. Simple structure makes it easy to build a strong apparatus which is highly reliable against any change in pressure and in respect of field operations. As shown in Fig. 7.2-8, since the structure is such that membranes, passage guiding plates of raw solution and those on the permeated solution side are stacked alternately, it is relatively easy to make compact the cubic volume of apparatuses. Where the quantity of permeating solution is increased, it needs only to increase the stacks. However, since the fluid sealing is maintained usually by a mechanical pressure, higher accuracy of various parts must be secured with an increase in the number of stacks and the size of apparatus, and this constitutes a factor to raise installation costs in spite of the simpleness of apparatus.

Fig. 7.2-8 shows the modules manufactured by DDS Co. of Denmark and types 20 and 40 use plane membranes respectively of 20 cm and 40 cm in diameter. In the case of the 30 type, pipes for raw and concentrated solutions are formed near its center, by the stacking up of respective frames. A frame provided with a feeding stage of raw solution by cutting off a part of the raw solution pipe and a frame provided with a taking out mouth of concentrated solution by cutting off a part of the concentrated solution pipe perform the same role as that of the middle flanges of 20 and 40 types, and this arrangement dispenses with the middle flanges and outside piping which cost a lot and reduce the area of membrane per module. Assembly is as shown in Fig. 7.2-8(c), frames being bound tight around the center shaft with the end flange.

(2) Tubular type

Membranes of the tubular type are formed by a tube-shaped support fitted with a semipermeable membrane on its inside or outside surface. Various kinds of membranes of this type have been developed and commercialized according to the structure of the support or the method of fitting a semipermeable membrane, the method of feeding raw solution and taking out permeated solution.

The first tubular membrane was devised by Havens; the membrane is cast on the inside of a tube which is formed by weaving glass fiber impregnated with resin. This system has been further developed and, today, membranes made by it, known as those of internal pressure type, and used widely for practical purposes. Tubular membranes are bundled in the multitubular system to form a module. At the inside of the module, membrane tubes are connected in a series or in parallel so as to increase the conversion rate of the module to the volume of the feed solution. In addition, the passage inside of some modules is narrowed, or a turbulence accelerating mechanism is provided.

As a characteristic of the tubular type, the passage of the solution to be treated is generally large enough to be seldom plugged even without pretreatment and the surface of membranes permits washing with chemicals as well as physical washing with a sponge.

As an example of the internal pressure system, Fig. 7.2-9 shows a type which has been developed by Loeb and others since about 1964. Tubular membranes of 22.9 mm in outer diameter are formed by casting and their outside surface is rolled up with nylon cloth. Then they are inserted in steel pipes of 25.4 mm in outer diameter and 0.89 mm thick which are provided with fine holes of 1.6 mm in diameter for taking out the permeated solution and their ends are expanded to tighten with gaskets for sealing. A number of such tubular membranes of about 3 m long are connected with U-shaped bands.

Fig. 7.2-10 shows the type devised in 1965 by the membrane department of American Standard Co. (absorbed and taken over by Afcor Co.). Tubes of membrane are filled with plastic balls as a turbulence accelerator.

As an example of the external pressure system, the type called Ropak which was produced in 1971 by Raypak Co. is shown in Fig. 7.2-11. The membrane is cast directly on the outside of a hollow ceramic tube of about 1 m long and 15 mm in diameter and 7 or 19

pieces of such tube bundled and fixed to tube board are set in a cylindrical case of stainless steel. The outside of the membrane is wound up with a plastic coil as a turbulence accelerator.
A type of external pressure system called "spaghetti" has a support of smaller diameter, constituting an intermediate structure as betwe the hollow fiber type. An example is shown in Fig. 7.2-12.

(3) Spiral type

The spiral type was developed by Gulf General Atomic Co. (the presen UOP, ROGA Division). As shown in Fig. 7.2-13, two semipermeable membrane sheets are placed on both sides of a porous support (which becomes the passage of the solution permeated through the membrane); their 3 edges are glued to form an envelope; then the last edge remaining open is connected to the intake pipe of the solution to constitute one leaf; and generally, leaves in two - or three-ply are rolled in spirally. As shown in the figure, separators are provided between membranes and it is so structured that while the feed solution is flowing in parallel with the intake pipes these separators work as turbulence accelerators reducing concentration polarization and the velocity of flow can be kept uniform at every part on the surface of the membrane.

Toho Rayon's module is different from UOP module in the direction of flow of the raw solution as shown in Fig. 7.2-14. Raw water flows spirally into the interior of the module from the outer periphery.

(4) Hollow fiber type

The pressure resistance of a tube is virtually determined by the ratio of outer to inner diameter but the absolute value of thickness has no influence. Therefore, if a semipermeable membrane is formed into a tubular shape, the pressure resistance of the membrane is improved dispensing with a support. The hollow fiber membrane is a semipermeable membrane which does not need any support due to the pressure resistance given to the tubular semipermeable membrane itself. The actual hollow fiber membranes are 40 to 250μ in outer diameter and 2 - 4 in the ratio of outer to inner diameter.

Du Pont Co. sent a reverse osmotic module of the hollow fiber type called B-5 in 1967 and B-9 in 1970. It put on the market modules made of aromatic polyamide for general desalination of seawater in 1973. Fig. 7.2-15 shows the section of B-10.

Dow Co. has been intending to manufacture modules of hollow fiber membrane of cellulose triacetate and it has been published that the module for low density purpose is 250μ and 125μ respectively in outer and inner diameter and that for the desalination of seawater 90μ and 40μ respectively in outer and inner diameter.
Fig. 7.2-16 shows the section of DOWEX-4K and -20K.

7.3. Pretreatment

In order to carry out the desalination of seawater on a practical basis, there should be established methods of pretreatment and membrane washing suitable for the modules to be used.

7.3.1. Method to Indicate Low Turbidity

Although, as a tentative standard of water, turbidity allowed for modules of spiral type has been 0.5 JTU or less and that for those of hollow line type 0.3 JTU or less, many questions have been posed as to whether such accurate values of low turbidity can be obtained by the analytical method adopted thus far, causing a bottleneck for the use of modules. So, recently, a more direct method has been devised to measure the low turbidity. That is, a micro-filter (or membrane filter) of 0.45μ in average pore diameter manufactured by Millipore Co. is used to measure the rate of plugging caused by microscopic substances contained in feed water and to use such rate as an index of turbidity. Usually, a membrane filter of 0.45μ in pore size and 42.6 cm in effective diameter (47 cm in nominal diameter; HAWPO 4700, Type HA) is used and measurement is made under a pressure of 2.1 kg/cm^{2}G to find (1) firstly, the time t_i in which the first 500 cc of water passes through the filter; and (2) the time t_f in which another 500 cc passes through after 15 minutes have elapsed from the start of pressure. (3) The value calculated by the following formula is the quantity called "plugging index", or PI for short.

$$\text{PI (15 min., 2.1 KG)} = (1 - t_i/t_f) \times 100\ (\%) \qquad (7.3.1)$$

If PI = 100%, the filter will become completely plugged and if 0%, there will be no plugging. (4) The value calculated by the following formula is the quantity called "fouling index" (or silting index), or FI (or SI) for short.

$$\text{FI (15 min., 2.1 KG)} = \text{PI}/15 \qquad (7.3.2)$$

FI (15 min., 2.1 KG) is the average rate per hour of PI and that it takes the values 0 to 6.7 is clear from the meaning of the formula (7.3.2). Attention should be given to the fact that, as a matter of course, if the interval between the measurement of t_i and that of t_f or the pressure to be applied is changed, PI and FI will change accordingly. For example, if the interval is reduced from 15 to 5 minutes, FI will take the values 0 to 20. Although it is complicated in the case of PI, the correlation diagram of PI 15 and PI 5 has been obtained for seawater, for example, as shown in Fig. 7.3-1. As to the relation with the method to indicate turbidity, it is seen from Fig. 7.3-2 that although FTU changes little, PI does considerably.

7.3.2. Troubles in Reverse Osmotic Process

Where it is intended to separate water and salts by the reverse osmosis membrane, (1) suspended solids and, in many cases, (2) colloids and soluble substances of macromolecules existing in seawater accumulate on the surface of membranes as a matter of course, to reduce the performance of membranes. Also, with the progress of concentration polarization and concentration, substances dissolved in the initial stage come to accumulate on the surface as (3) deposited solids. Further, there are restraints in respect of (4) the limits of usable temperature and of pH and the maximum allowable density of chemical species, and such problems as (5) the deterioration of membranes due to microorganisms and the generation of slime from metabolic products. The phenomenon of deterioration in the performance of membranes may be broadly classified into deteriorated function of a membrane itself and deteriorated performance of a module due to solids stuck to the surface of a membrane.

The operation of the reverse osmosis system requires control of these troubles. The methods for this include pretreatment and membrane washing. Although it depends on the types of modules, if the value FI (15 min., 2.1 KG) is 3 or less the system can be operated relatively smoothly but if not, pretreatment must be conducted.

7.3.3. Pretreatment

It is desirable to remove factors which are likely to cause troubles from raw seawater in advance of feeding it to the reverse osmosis system. With the extent of the removal approaching to perfection, the performance of the module deteriorates less and long-run stabilized operation of the reverse osmosis system is possible, but the installation and running costs of pretreatment become higher. Therefore, it is necessary to select the optimum method of pretreatment as a part of the total system, taking into account the life of the reverse osmosis membrane, cost of pretreatment and other factors. Thus, for practical purposes, planning and selection are made in each case. However, as a tentative standard, measures for each cause of trouble will be considered in the following.

(1) Adjustment of temperature

There are certain limits of temperature applicable to membranes. If the temperature of raw seawater is higher than the limit it becomes necessary to cool the seawater by a suitable heat exchanger, including a cooling tower. Where it is excessively low, the flux passing through the membrane reduces, causing uneconomical operation. A more economical way is to blow waste steam directly into raw seawater or utilize waste heat of low temperature in order to raise the temperature of the seawater to about 25°C before feeding it to the reverse osmosis system.

(2) Adjustment of pH

Tolerance for pH exists in membranes and if pH in raw seawater exceeds it, as a general practice, some chemicals are impregnated in the seawater to adjust it. It is desirable for membranes to be operated rather on the acidic side. As an acidic additive, in general, sulfuric acid is preferable where account is taken of the separation of membranes, but hydrochloric acid is more preferable if account is taken of the precipitates.

(3) Measures against microorganisms and seaweeds

The most effective measure is to add chlorine. It is added in the form of soda hypochlorite produced when seawater is electrolyzed, on the upstream side whenever practicable, so that its density will become 1 to 5 ppm. However, since the upper limit for the density of residual chlorine is fixed for some membranes, the density of chlorine at the inlet of the membrane module needs to be kept within the specified values.

(4) Suspended solids

Suspended particles and colloids are most liable to cause troubles. Although it depends on the properties and electric charge of colloids themselves, the stability of colloids changes with the progress of concentration and, in many cases, colloids having begun to aggregate begin to accumulate on the surface of the membrane. Where such accumulation starts, the state of flow in the module changes, accelerating the accumulation further.

Since colloids consist of extremely fine particles, they cannot be removed by ordinary filters (two-layer sand, cartridge and diatomaceous sand filters and membrane filter of 1μ or more, etc.). Thus, it becomes most important to make colloids aggregate and flock so that their size is increased to an extent which permits the ordinary technique to deal with them. Colloids are ordinarily charged with possitive or negative electricity, and those of the same electric charge exist stably repulsing each other. If the electric charge of colloids is neutralized electrically, colloids collide and aggregate to become larger particles which can be caught more easily. For this purpose, polyelectrolyte is added as flocculant. Electrolyte containing aluminum and iron ions is used from the stand point of price. In one method, electrolyte is added successively at the midpoint of the piping and processing is done by an ordinary filter; and in another method, most of the colloids are sedimented and separated beforehand in a flocculator* and processing is done by an ordinary filter. Recently, a filtration system has been tested using across current ultrafiltration membrane (or microfilter). Compared with conventional filtration of various systems, the accuracy of filtration is far better and thus it may be the best processing method for the pretreatment for reverse osmosis modules.

* Although various names are given to it, all of the systems are devised so that colloids and flocks aggregate effectively during the contact process of the solid and liquid taking place when the raw water rises as a counter current to the settling direction of flocks aggregated. It is most effective when the ascending current and the settling particles balance to produce a misty layer (which is called a blanket) and the point of the device is to form such layer. Flocks, of which the settling velocity is higher than the balanced velocity, descend naturally and accumulate in the bottom to be discharged as sludge.

(5) Soluble inorganic matter
(which can become sediment)

Where the rate of recovery is 50%, the concentration becomes doubled even by simple calculation. In this connection, special consideration is required to be given to substances passing the solubility limit. Calcium carbonate and calcium sulfate are particularly liable to produce sediment. The simplest pretreatment is to add acid, and other methods include the adding of chelating agents (such as organic system macro-molecule electrolyte and hexametaphosphoric acid soda), exchange with soluble ions (softening by ion exchange resin) and chemically forced sedimentation (removal of carbonate and silica by lime).

(6) Iron and manganese

There is no problem so long as both iron and manganese exist stabilized in the dissolved state. However, if they come as insoluble colloids or slime as ferric hydroxide and manganese oxide, they constitute a serious problem for membranes. The density of iron allowable for membranes is usually around 0.1 to 0.05 ppm, though it differs considerably depending on pH and dissolved oxygen. Therefore, where corrosive steel pipes (even stainless steel pipes) are used as material for piping for a long time, the piping corrodes, if dissolved oxygen exists sufficiently, and iron dissolves out to cause trouble. Methods to remove iron and manganese which are frequently used involve aeration oxidation filtering and catalytic oxidation filtering. To prevent iron from scaling, DDS Co. has suggested adding sulfite to remove dissolved oxygen and prevent oxidation of iron.

(7) Soluble organic matter

Different from colloidal organic mass, organic matter which does not sediment or aggregate in the ordinary pretreatment stage not only deteriorates but even melts membranes with the progress of concentration. As countermeasures, (1) most colloidal and suspended matter are removed by oxidation with the use of chlorine or hypochlorous acid. Although strong oxidizing agents such as ozone and permanganic acid are more preferable, they have a demerit in that they cost a lot. (2) Filtration by the use of active carbon is an effective means to remove almost all soluble organic matter. Since used active carbon is reclaimable, eventually it costs little.

7.3.4. Post-treatment

Post-treatment for the reverse osmosis system varies widely according to what purpose the treated water is used for. The ratios of dissolving ions which the reverse osmosis system removes differ by membrane, and since polyvalent ions are almost completely removed, the water produced contains Na^+, $C\ell^-$ and HCO_3^- ions as its principal components, scarcely containing hardness components. Also, since the operation is conducted with acid impregnation, the water produced is a little acidified and contains carbonic acid gas freed and formed. Therefore, the water as it is has more corrosive tendency compared with natural water of the same density of dissolving solid matter, and it may cause unexpected corrosion depending on its use. Thus, carbon dioxide is removed by a gas separating operation, etc., or use is made of the method of readjusting pH by adding alkali.

7.3.5. Results of Marine Tests

(1) Data of OWRT

OWRT is carrying on researches on the pretreatment methods for rever osmosis at Wrightville Beach. R & DP Report No. 891 of OSW evaluated seven kinds of combinations of various treating methods and recommen "addition of chlorine; chemical aggregation and settling; sand filte ing; and obsorption by active carbon" as the first selection and "addition of chlorine; sand filtering; and obsorption by active carbo as the second selection. Based on these results, in 1975, it constru a central pretreatment system having the capacity to treat 1,635 m^3 o seawater per day, i.e. a design value based on the flow shown in Fig. 7.3-3. The round-shaped clarifier has a treatment capacity of 90 m^3/ and is about 8 m in diameter at its top, 3.2 m in depth, 70 minutes i average residence time and 2 m/hr in ascending velocity.

The inclined-plate type clarifier of the same treatment capacity as the above is of a rectangular parallel pipe of 6.1 m long, 3.4 m wid and 3.2 m high, with average residence time being 36 minutes and ascending velocity 8 m/hr. The dual sand filter is 2.44 m in diameter and 1.83 m high, with the layer of anthracite (0.8 to 1.2 mmø) being 46 cm thick and that of sand (0.35 to 0.45 mmø) 23 cm thick. The zeolite filter is 1.7 m in diameter and the layer of manganess treate greensand (0.32 to 0.34 mmø) is 68 cm thick. The activated layer tan is 1.83 m respectively in diameter and height and the layer of active carbon is 91 cm thick.

The minimum quantity of aluminium added is 25 ppm and the turbidity of the clarified solution was 2 to 4 FTU, but in the case of the inclined-pipe type, it is about twice the former, or 4 to 8 FTU. The average value of PI is 75 at the outlet of the two-layer filter; it is 90 immediately after back washing, then fell to 75 after 6 hours and to 50 to 75 after 2 days. A zeolite filter is used for finishing and the average value of PI at its outlet is 45. Where an iron ion is used as coagulant in place of aluminium sulfate, it functions as zeolite. An activated carbon filter is used for removing residual chlorine, with no lowering of PI caused.

In the case of in-line impregnation and coagulation sand filtering and finishing filtering, the quantity of added aluminium sulfate is 10 ppm and PI becomes 60, but the life of the two-layer sand filter is 12 hours. On the other hand, where a clarifier is used the said life is 4 to 5 months.

It has been found with reference to the results of tests carried out in Ocean City, N.J., by Du Pont Co., mentioned later, that the use of sulfite of soda instead of the activated carbon layer for removing chlorine is more effective to avoid various troubles entailed by the use of active carbon and to reduce costs. Therefore, the final pretreatment system for reverse osmosis will be as shown Fig. 7.3-4.

(2) Data of tests in Ocean City, N.J.

Du Pont Co. established its Marine Test Institute in Ocean City, N.J. in order to develop the DP-1 membrane for desalination of seawater and to make researches on the B-10 hollow line membrane module to put it to practical use.

The pretreatment system is of a treating capacity of 50 ppm and turbidity is reduced from 75 FTU to 1 FTU or less by sand filtration and further to 0.5 FTU by diatomaceous earth filtration. In order to remove microorganisms, 20 ppm of chlorine is added. Feeding temperature to the reverse osmotic system is 20°C or over. Sulfuric acid is added to prevent contamination by iron and pH is kept at 5 to 5.5. Operation was started in 1972 on the above design basis, and Fig. 7.3-5 shows the final flow chart.

The sand filter is 1.8 m in diameter and 76 cm high, and the maximum flow rate is 6 m/hr. The diatomaceous earth filter, of which the filtration area is 9.3 m^2, is used by the precoating method. The active carbon filter is a tank of 1.2 m respectively in diameter and depth, which is filled with 1.4 m^3 of active carbon.

The quantity of aluminium sulfate added is 20 to 30 ppm. At first, active carbon was used to keep to content of chlorine in the feed water to the aromatic polyamide membrane at 0.1 ppm or less. However, its life was about 6 months and, in addition, since colloidal silica of around 2 ppm came out in the active carbon pretreated seawater, more frequent exchange of the guard filter was necessitated. Also, finer particles having passed through the guard filter accumulated on the surface of the membrane, thus contaminating the module. As it became clear that active carbon cost unexpectedly much, it was replaced with impregnation of thiosulfate of soda.

(3) Ultrafiltration membrane

The pretreatment system on a large scale as described above costs a lot to operate as a small-sized desalination system of seawater by reverse osmosis which has a capacity of less than 500 m^3/day and is not always economical. Thus the applicability of ultrafiltration membranes is under investigation. Materials examined include polysulfone, polyacrylonitrile, polyurea and cellulose acetate. Under the condition that 85 to 90% is recovered at 1.7 to 3.4 Bar, the initial flux of 30 to 70 gfd reduces to 20 50 gfd after 4 to 5 hours. The flux is recovered by washing with

100 to 200 ppm aqueous solution of sodium hyposulfite for 4 to 5 minutes. PI becomes 50 or less and this method seems to be very effective, though it is not yet established as an economical and reliable technique both in terms of the life and the price of a module.

(4) Data of water reuse promotion center

The flow-chart of the pretreatment systems for the hollow fiber (A) and spiral types constructed in 1975 are shown in Fig. 7.3-6. The pretreatment system for the spiral type is composed of a coagulation settling tank and dual media sand filter as shown in the figure. The operating conditions are as shown in Table 7.3-1 and the value FI is 3 or less. The operating conditions of the hollow fiber (A) type are as shown in Table 7.3-2 and although the value FI is around 3, the frequency of regeneration of the sand filter is twice as much as that of the spiral type, showing that only with aggregation the filter is liable to be plugged as a matter of course and the provision of a precipitating tank is necessitated.

Based on the above operating data, the pretreatment system for general purposes as shown in Fig. 7.3-7 was constructed in 1976. The specifications of apparatuses are shown in Table 7.3-3. The operating conditions are shown in Table 7.3-4 and the value FI at the outlet of the polishing filter is 2 or less.

7.4. Design of Plants

7.4.1. Pretreatment Plants in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility

Reverse osmotic plants of spiral and hollow fiber (A) types were constructed in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility in 1974 and, at the same time, two kinds of pretreatment plants shown in Fig. 7.3-6 were built for exclusive use for the former plants.

The following information has been obtained from the basic experiments about pretreatment, including operation of the plants and jar tests made in parallel with the operation.

(1) $FeC\ell_3$, sulfuric acid band, PAC and electrolytic aluminium were tested to be used as flocculants for flocculation - precipitation methods, and $FeC\ell_3$ has been found to be the best based on a wide range of pH, strength of flocks and superior sedimentation. A sufficient quantity of $FeC\ell_3$ to be added is 2 to 3 ppm.

(2) In the process of the spiral type, the prescribed quality of pretreated water could be attained with out using active carbon or two-layer filters.

(3) Addition of a few ppm of PAC is effective for direct flocculation-filtration in the case of the hollow fiber (A) type.

(4) Although nearly satisfactory values can be obtained for the quality of treated water by the direct flocculation-filtration system, back washing of filters is necessary every one or two days.

(5) For polyamide membranes, treatment by active carbon, etc. is necessary to remove residual chlorine. It is preferable to place an active carbon filter before a sand filter because the former becomes a breeding place for microorganisms.

(6) Complete supression of growth of bacteria by adding hypochlorous acid soda has a favorable influence also on flocculation - precipitation or sand filtration.

(7) It is necessary to reduce the value pH of seawater to 5 to 6 by the addition of chlorine or sulfuric acid, taking into account the optimum region of flocculating reaction, prevention of reverse osmotic membranes from hydrolyzing, and conversion of carbonate in seawater into soluble type.

Based on the above results of the experiments, a "pretreatment plant for general use" capable of feeding seawater to respective reverse osmotic plants in common was constructed in March, 1976. It has been made possible, by this plant, to adjust pH in seawater, chlorinate and, at the same time, remove turbid components almost completely, and also arrangement has been made for each reverse osmotic plant to place a cartridge filter and a device to remove residual chlorine, etc. as occasion demands. (See Fig. 7.3-7 and Table 7.3-3).

The maximum processing capacity of the plant is 300 m^3/day. Three kinds of chemicals can be added to seawater before entering the flocculator - precipitator and, ordinarily, 80 to 100 ppm of sulfuric acid (75%), 2 to 3 ppm (in terms of $C\ell_2$) of hypochlorous acid soda (10%) and 2 to 3 ppm (interms of Fe) of ferric chloride are injected.

The flocculator - precipitator is a clarifier of sludge circulating type and basic experiments, including jar tests, are necessary to determine residence time. Also, it is necessary to prevent agitation caused by wind and convection due to changes in the temperature of water, in order to protect the layer of sludge in the tank from being disturbed.

The two-layer filter consisting of anthracite and sand is a descending flow filter of a pressure system to which automatic back washing is applicable. Back washing is carried out by the aid of a timer in the order: filtration → water draining → back washing by air → back washing by water → washing by passing water → filtration. The frequency of back washing initially scheduled was once every two days, but since the flocculator - precipitator has been far more effective than expected it is sufficient to perform back washing once every 2 to 4 weeks. Although duration of washing of 5 to 8 minutes suffices both for air and water washing, considerable time is required until the quality of filtered water becomes stabilized after back washing. It is necessary to allow 2 to 3 hours for washing by passing water.

Back washing by water is performed using filtered water, of which the quantity per time of washing is 30 m/hr (velocity of back washing flow) x 2.5 m^2 (sectional area) x 0.2 hr (back washing time) = 7.5 m^3, necessitating a filtered water tank of considerably large capacity.

Mud in seawater is almost completely removed during the processes up to and including this two-lay filter. The polishing filter constituting the last process is filled with sand of fine grain size. The filter is effective for processing seawater to be used to wash the two-layer filter by passing water.

This pretreatment system has been operating for about $1\frac{1}{2}$ years to date, and the quality of treated water attained is approximately the same as the prescribed quality (2 or less in the value FI).

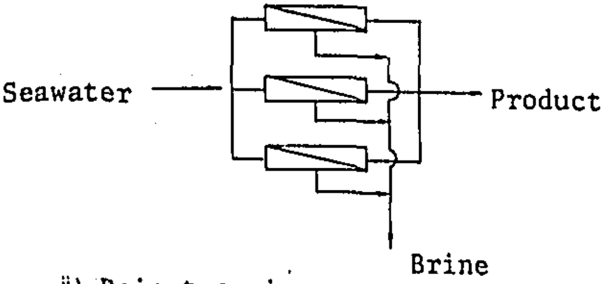
It is preferable not to use iron, as far as possible, for the material of apparatus for the pretreatment system. Seawater corrodes remarkably and the iron has an adverse effect on reverse osmotic membranes. Usually, use is made of vinyl chloride piping, plastic tanks, epoxy coating and rubber lining.

7.4.2. Reverse Osmotic Plants

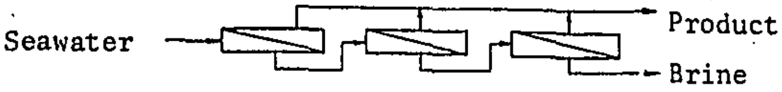
(1) Reverse osmotic modules

In a plant for practical use, the number of required modules are determined based on the quantity of water needed to be produced. The required number of modules are arranged in various ways as shown below.

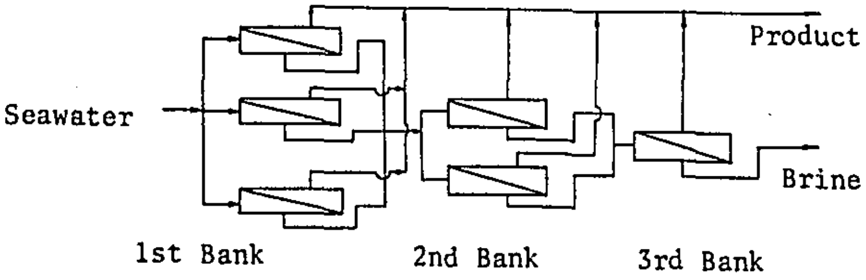
i) Parallel



ii) Reject series



iii) Christmas tree



Of course, there are many cases where these arrangements are mixed. The optimum method of arrangement is determined so as to satisfy the specified minimum linear velocity of brine and pressure loss, etc., based on the scale of the system, required rate of desalination and rate of recovery.

For example, 1) parallel arrangement is the simplest system. If the units of the module are increased to improve the rate of recovery, it becomes impossible to secure the minimum linear velocity of brine per unit, and sometimes the velocity becomes lower than the value designated in the specifications. The arrangement of 2) reject series is exactly inverse, and the prescribed rate of recovery can be attained by arranging the required number of modules in series, but at the cost of increased pressure loss as a whole. Also, with progress to the later stages, the density of brine increases and linear velocity decreases, resulting in worsened quality of and reduced quantity of desalinated water. 3) the Christmas tree arrangement which is used most widely is similar to the reject series. It enables keeping the linear velocity of brine in the later stages at the same as in the initial stage and restrains occurrence of a condensation polarization phenomenon.

Arguments have been made for a long time as to how many stages should be provided for desalinating seawater. Both one-and two-stage methods have merits and demerits and no conclusion has been drawn thus far. Although, in view of the final object of technical development, it will have to settle for the adoption of the one-stage method due to the simplicity of the system, the present level of technology necessitates considering the two-stage method.

In the two-stage process, as shown in Fig. 7.4-1, the density of seawater once having decreased to around TDS 2,000 to 3,000 ppm is further desalinated to 200 to 300 ppm by the second stage of reverse osmosis.

As a matter of course, the two-stage method requires two sets of high pressure pumps, a reverse osmotic module and instrumentation. However, since the second stage which processes seawater of lower density than the first stage can be operated at lower pressure, a sufficient capacity for the high pressure pump is about 1/3 in flow rate x 1/2 in pressure = 1/6. That is, the second stage is about 1/6 in scale compared with the first stage. Therefore, the installation cost is about 1.2 to 1.3 times that of the one-stage method.

There is an opinion that the two-stage method is not inferior to the one-stage method in terms of energy. However, engineering for the optmization of the required area of membranes and the conditions of operation present fairly difficult problems. For example, thorough examination is needed in designing as to the adjustment of the rate of recovery in the second stage where the total quantity of water having passed through the first stage is fed to the second stage.

(2) Test plants of reverse osmosis in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility

Descriptions will be made of several reverse osmotic plants installed in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility for experimental purposes.

(i) One-stage desalination plants

Outlines of the one-stage desalination plants are shown in Table 7.4-1.

a) Module of spiral type

Modules are of CTA Thin Film Composite rolled up into a spiral type of 2 inches in diameter. Different from previous asymmetric membranes, this composite membrane, which has been developed by UOP for use in the one-stage desalination of seawater, is formed by coating an ultra-thin membrane of cellulose triacetate on a porous support composed of cellulose nitrate and cellulose acetate (CN-CA), so as to increase the quantity of transmitted water and the rate of removed salt. The test plant is composed of high pressure containers arranged in 2 parallel x 10 series, each vessel containing 2 modules (40 modules in total), and the design output of water is 3.8 m^3/day.

b) Hollow fiber (A) type

The test plant is composed of a Permasep B-10 permeator developed by the Du Pont Co. for use in one-stage desalination.

In this system, one standard 4-inch module and one half size module, which is half both in length and output of water, are connected in reject series. That is, pretreated seawater is firstly fed to the standard module by a high pressure pump, and then concentrated effluent water from this module is led into the half size module. Transmitted water from respective modules flows together to constitute water produced. The production capacity of this plant is 8.3 m^3/day.

This plant was modified partly and since April, 1977, it has been operated composed of one 8-inch B-10 module. The capacity of water production is 5,000 GPD (18 m^3/day) and the rate of recovery is 30%.

c) Hollow fiber (B) type

This is the test plant of a hollow fiber module made from cellulose triacetate which has been developed by the Dow Chemical Corp. for one-stage desalination of seawater, and is composed of one 8-inch module, one three-throw plunger pump and instrumentation. The capacity of water production is 9.4 m^3/day.

(ii) Two-stage desalination plants

Outlines of 2-stage desalination plants are shown in Table 7.4-2.

a) Spiral type

Modules are of the spiral type developed by the Toho Rayon Co. and 2 modules are loaded in a high pressure container 4 inches in diameter. The first stage has 12 modules arranged in a Christmas tree of 6-4-2 and the second stage 4 modules arranged in reject series. The design capacity of this plant is 10 m^3/day in the quantity of water produced from the second stage, and the quality of produced water is 200 ppm or less in TDS. All the concentrated water discharged from the second stage modules is returned to the feeder tank for the first stage so that the rate of recovery can be improved.

b) Tubular type

Modules of this plant are of the internal pressure developed jointly by Kobe Steel, Ltd. and the Nitto Electric Industrial Co. Each module consists of an outer tube of 11 cm ø x 2.67 m filled with 18 tubes of 1/2 inch ø arranged in series. Membranes are made from two kinds of materials including cellulose diacetate and a blend of cellulose diacetate and cellulose triacetate. The material of supports is FRP.

This plant has the capacity to produce 1.7 m^3/day of water, the rate of recovery ranging from 25% to 30% and the quality of produced water being 300 ppm or less in TDS. Piping is provided so that pretreated water, for general purposes, and raw seawater can be fed as material water. A part of the brine discharged from the second stage flows back to the first stage and the remainder circulates in the second stage in order to secure the flow rate of water to be fed to this stage. The first stage has 12 modules arranged in 4 parallels x 3 reject series and the second stage 3 modules in 2 x 1.

Since the tubular module is structurally simple, suspended matter in the raw water plugs the passages to a small extent and simplification as far as possible of pretreatment has little influence on the performance of membranes. Therefore, in this plant, an arrangement is made to feed raw seawater pretreated only by making it pass through the cartridge filter.

c) Hollow fiber type

The plant uses hollow fiber modules of cellulose acetate developed by the Toyobo Co. In the first stage, 5 modules are arranged in parallel and in the second stage, 1 module is placed. Design values for the second stage of this plant are 10 m^3/day in quantity and 250 ppm or less in quality of produced water. Brine discharged from the second stage flows back to the first stage in the same way as the above-mentioned type.

(3) High pressure pumps and recovering

It is said that the desalination of seawater by reverse osmosis requires 8 to 9 kWh of electric power to obtain 1 m^3 of fresh water, and these values of power are influenced considerably by the efficiency of high pressure pumps. If the energy which the high pressure concentrated water has is recovered, the consumption of power will be reduced to about 5 kWh/m^3.

Considerable tests and experience are necessary to select kinds and anti-corrosive materials for high pressure pumps. In general, pumps of the plunger type, which develop high pumping efficiency, are used for small-scale plants producing 50 m^3/day or less of water (200 m^3/day in terms of the flow rate of seawater). Pumps of this type are produced by many pump manufacturers in Japan and have long-standing actual results in the transportation of fluid other than seawater. However, due to the high corrosiveness of seawater and use of pumps under high flow rate and high pressure, check valves, grand packings and plungers provided in front of and behind a pump are liable to be damaged.

Multistage centrifugal pumps are frequently used if plants are of low capacity and the pressure is 40 kg/cm^2 or less. Where high pressure is needed, as in the desalination of seawater, these pumps must be used by two-stage boosting. Recently, one-stage centrifugal pumps of small capacity and high lift such as sunflow pump (Niiso Co.) and rotojet pump (Kobe Co., U.S.A.) have come onto the market.

Plants of large capacity producing 100 m^3/day or more will use one-stage or multistage pumps. It is said that the pumping efficiency of centrifigal pumps increases as the scale does, and pumps of 100 m^3/h or more will probably attain 70% or more in efficiency, including that of motors.

Components of large-sized reverse osmotic plants include recovering systems for energy. The system is intended to recover energy possessed by the high pressure concentrated water discharged from the reverse osmotic plant in order to use it as an auxiliary driving force for the high pressure pump.

As recovering systems for energy, reciprocating, Pelton wheel and turbine types are now under investigation. According to the results of research by the Dynatech Co., the Pelton wheel type is regarded as most promising for plants of 100,000 GPD (380 m^3/day) or more. However, devices on the market which are not designed to deal with seawater cannot be used as they are. Since strong force are transmitted to the buckets, it is needed to develop a special material. It is said that, in the case of a plant of 100,000 GPD, about 40% of energy can be recovered on an economical basis.

Oil refineries and petrochemical factories widely apply the recovery of energy to such high pressure reactors as added water desulferization systems. Hydraulic turbines are frequently used for this purpose of recovering motive power and their application to plants of seawater desalination is conceivable if the problem of ustable materials is examined.

7.5. Operation and Maintenance

7.5.1. Operation and Maintenance of Pretreatment Plant

A necessary condition of seawater fed to reverse osmotic plants of the hollow fiber and the spiral types is that is should contain almost no turbid matter. Therefore, analysis and control of pretreatment water constitute extremely important problems. As to methods of water analysis, reference is made to paragraph 8.1-3.

Turbidity is indicated by the MF (membrane filtration time) and FI (fouling index) values where it is 0.5 ppm or less as in the case of pretreated water for reverse osmosis.

Interrelation of turbidity and MF and FI values is not so clear. The relation between turbidity (FTU) and FI values (shown as PI values, and PI values x $\frac{1}{15}$ = FI values) is shown in Fig. 7.5-1, and that between the values MF and FI which were actually measured in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility is shown in Fig. 7.5-2. Within a range of minute turbidity as in the case of reverse osmotic feed water, any slight change in turbidity is detected as FI value but the value shown as turbidity is constant.

As a yardstick of turbidity for reverse osmotic feeding, the Seawater Desalting and By-Products Recovery Chigasaki Test Facility set the FI values at 3 or less in accordance with the designation for the hollow fiber modules and operation and control were performed with these values for a guide. A part of the experimental data on this plant (property values of raw seawater included) is shown in Fig. 7.5-3. It is seen from this figure that the FI value of treated water from the outlet of the polishing filter is maintained at 3 or less, in spite of changes in turbidity or the MF values of raw seawater.

Seawater changes in its properties according to the seasons. In spring, the propagating power of microorganisms becomes high and although turbidity increases only in some measure, the MF values indicate extremely high degrees and the membrane filters are colored green. An effective means to cope with this is to add hypochlorous acid soda of higher density than usual. However, it must be controlled so that the concentration of residual chlorine will have no adverse effect on the reverse osmotic membranes. In autumn, the sea is liable to be agitated by typhoons, and, where this happens, both the turbidity and the MF values increase and the membrane filter is colored mud yellow. Where the turbid matter contains many inorganic components, as in this case, it seems that the pretreatment plant can be operated relatively well with the addition of chemicals in the same quantity as usual.

In the following, the operational and control problems of the pretreatment plant are discussed by apparatus.

Flocculation - precipitation tank - It is most important to maintain its flock layer in a stabilized state. The formation of this flock layer takes 4 to 7 days after the start of operation. Also, it is necessary to prevent the flock layer formed from being destroyed and flowing out and the water from being agitated by strong wind. To this end, the water surface is covered with a vinyl sheet in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility. The optimum conditions should be confirmed beforehand as to kinds of flocculant, concentration and range of pH and thoroughly controlled operation be conducted in order to form a flock which sediments adequately and is of high-power. Once a day, sludge is extracted from the bottom of the sedimentation tank watching the surface level of the flock layer. Although the influence of hupochlorous acid soda added for sterilization on the flocculating mechanism is not clear, such addition seems to contribute to improve flocculating performance.

Two-layer filter - The cycle of automatic back washing is determined based on various data, as shown in Fig. 7.5-4, collected on the relation of operating hours to the pressure damage to filters and the quality of filtered water. A problem is the fact that, immediately after back washing with water, it takes 3 to 4 hours until the quality of filtered water become FI 3 or less. The water is discharged but not led into the treated water tank (a practice known as washing by passing water) for about one hour after back washing. But after that, such discharge is forced to be discontinued due to the capacity of tank, even though the quality of water is somewhat inferior. Therefore, it is necessary to place a polishing filter as mentioned below.

Polishing filter - Ordinarily, since this filter is fed with water of 3 or less in FI value from the two-layer filter, it almost does not function to reduce the FI values further. However, immediately after the two-layer filter is washed by passing water as mentioned above, filtered water of 3 or more in FI value from the two-layer filter flows in the polishing filter, and the quality of that water becomes stabilized by passing through the latter filter. The filtration mechanism of this filter seems to be approximate to surface filtration, and, due to small quantity of flock capture, there is little increase of pressure damage, with the intervals of back washing being twice that of the two-layer filter.

Increased size of a pretreatment plant increases back washing water drained from the filter and the volume of sludge from the flocculation - precipitation tank. Taking as an example a pretreatment plant capable of processing 2,000 m^3 of seawater per day (500 m^3/day in terms of desalinated water), about 10 kg of solid materials are discharged per day (or 1 ton including the water content of 99%), presuming the turbidity of seawater to be 2 ppm and the addition of flocculant to be 3 ppm of Fe.

This suggests the necessity to plan a method to dispose of them.

7.5.2. Operation and Maintenance of Reverse Osmotic Plants

(1) Collection of operational data

It is necessary to measure the flow rate of feed water, desalinated water and concentrated water, electric conductivity, water temperature, pH and pressures at inlet and outlet of modules.

The performance of modules is judged based on the quantity of desalinated water, rate of desalination and rate of recovery obtained by operation under the fixed conditions of operating pressure and of quantity of feed water. The rate of recovery is given by the following expression.

$$\text{Rate of recovery} = \frac{\text{quantity of desalinated water (l/h)}}{\text{quantity of feed water (l/h)}} \times 100 \;\ldots\ldots\ldots \quad (1)$$

Desalination of seawater is usually operated so as to attain about 30%. The following expression is valid between the rate of recovery and the density of brine, assuming the density of desalinated water to be negligible.

$$\text{Density of brine/density of feed water} = \frac{100}{100 - \text{rate of recovery (\%)}} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The multipliers of concentration (density of brine/density of feed water) increase in proportion to the increase in the rate of recovery. Where the said rate is 50%, or concentration is twice, there is a possibility of calcium carbonate being deposited. Also, the osmotic pressure of the brine becomes 50 atm, necessitating operation at a high pressure of 70 kg/cm^2 or over. Since the quantity of desalinated water increases with a rise in the water temperature, the rate of recovery may increase excessively and thus caution should be used for operation, especially during the summer.

The rate of desalination is expressed in many ways. The following expression adopted here is that which takes into account the rate of recovery in any way.

$$\text{Rated of desalination} = \left\{1 - \frac{2 \times \text{density of desalinated water}}{(\text{density of feed water} + \text{density of brine})}\right\} \times 100 \;\ldots\ldots\ldots\ldots \quad (3)$$

Where the rate of recovery is especially high, a different method of indication will be required to be examined. Salinity (TDS) is frequently used to indicate density. Usually, the relation of electric conductivity, which can be measured most esily, to TDS or the density of chlorine ions is studied beforehand and TDS is found from the observations of electric conductivity. TDS is not proportionally related to electric conductivity and it can be assumed that TDS = EC x 0.75 for seawater and brine and TDS = EX x 0.5 for desalinated water. Sometimes, the rate of desalination is found by using EC itself which is regarded as each density for simplicity's sake, and in that case attention needs be given to the fact that the values found are somewhat lower than the rate of desalination based on TDS.

As for the quantity of desalinated water, with the rise in its temperature the water reduces its viscosity and passes more easily through membranes, resulting in an increase in the apparent quantity of water. Therefore, it is necessary for comparison to convert the values into those at a fixed temperature, and that usually selected for this purpose is 25°C. Although methods suggested for this correction include conversion by the coefficient of viscosity and the molecular diffusion coefficient, it is most preferable to observe the quantities by conducting transmission tests of pure water by varying water temperature for each module. At Chigasaki, the correction factors of temperature ($f = A_{25}/At$) for the A values of pure water transmission coefficient have been calculated for each module and an example is shown in Fig. 7.5-5. Results obtained differ by module, and there are many cases where change in quantities due to temperature exceed the amount corrected by the coefficient of water molecular diffusion. Conversion into the quantity of desalinated water at 25°C is expressed as follows.

$$\frac{Q_{25}}{Q_t} = \frac{A_{25}}{A_t} \times \left(\frac{P - \pi(C_{25})}{P - \pi(C_t)}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Q_{25}, Q_t = quantities of desalinated water respectively at 25°C and t°C

To be exact, it is needed to correct the osmotic pressure π on the surface of the membrane, though it is calculated simply by $Q_{25} = f \times Q_t$, assuming that, for convenience sake, the concentration (or the rate of recovery) almost does not change due to water temperature.

Water temperature and module pressure must be measured correctly as they have considerable influence on the quantity of desalinated water. Since it is impossible to detect the temperature on the surface of membranes, although desirable, to obtain water temperature, that of desalinated water is usually used. However, attention should be given to the fact that water temperature may be influenced by atmospheric temperature, depending on the location of sampling and the quantity of water sampled.

Pressure is usually measured with a Bourdon-tube guage. Since some errors may develop during operation of long duration, the guage should be inspected periodically. Where the pressures at the inlet and outlet of the module differ considerably, their mean value is adopted as operating pressure.

(2) Analysis of experimental data

In order to confirm the durability of reverse osmotic modules, it is needed to fix the operating conditions such as quantity of feed water, operating pressure, rate of recovery and water temperature, to know changes in the quantity of desalinated water (in terms of that at 25°C) and the rate of desalination. However, as these conditions are extremely difficult to keep constant, it is important to calculate the coefficients of membranes themselve which are not influenced by those factors. An analytical method for this purpose is computer analysis by Oya-Sourirajan models which take into account the flowing state of water for each module. In the Seawater Desalting and By-Products Recovery Chigasaki Test Facility, the A values of the pure water transmission coefficient and the B values of the salt transmission coefficient have been calculated by the following expressions for simplicity's sake.

$$Jw = A[\triangle P - (\pi(C_2) - \pi(C_1))] \cdots\cdots \quad (5)$$

$$J_S = B(C_2 - C_3) \cdots\cdots \quad (6)$$

$$\frac{C_2 - C_3}{C_1 - C_3} = \exp\left(\frac{Jv}{k}\right) \cdots\cdots \quad (7)$$

$$\pi(c) = 1.24[Cl] + 0.0045 \cdot t \cdot [Cl] \cdots\cdots \quad (8)$$

For designations, see paragraph 7.1.

During continuous operation to process seawater, transmission tests of pure water are conducted at about 500-hour intervals to find the A values. The mass transfer coefficient (k) is calculated from the test data of seawater obtained before and after the above tests, using the expressions (5), (7) and (8). In analyzing the tests of seawater, the A and B values are calculated assuming the k value to be constant.

Usually, assuming that the following expression is valid empirically for durability resulting from consolidated membranes, the m value of the reducing coefficient (equally called the log flux decline rate) is used.

$$m = -\frac{\log A_1 - \log A_2}{\log t_1 - \log t_2} \cdots\cdots \quad (9)$$

A_1 and A_2 are the transmission coefficients of pure water respectively after t_1 and t_2 hours from the start of operation.

The declining rates of this m value and the quantity of desalinated water after a lapse of one year are shown in Fig. 7.5-6. Where m = 0.04, the quantity of desalinated water reduces by about 35% after one year. However, gradual increase of pressure enables adjustment of the quantity of water and an m value of this order may said to be suitable for practical use.

(3) Control of factors affecting the performance of modules

Since the turbidity, hardness, iron, pH, residual chlorine and temperature of feed water have much influence on reverse osmotic membranes, adequate attention must be given to the operation and control of modules in conformity with respective specifications.

Adherence of turbid matter to the surface of membranes and deposition of hardness components have been mentioned already. Such matter and components are thoroughly removed by pretreatment and, on the other hand, cartridge filters of about 5 to 10μ are placed at the inlets of modules for final protection. Iron eluted as divalent ions from piping and containers is oxidized by dissolving oxygen and residual chlorine in the seawater and those deposited on the surface of membranes. Iron as deposits not only reduces the quantity of desalinated water but changes chemically and deteriorates the membranes by its catalytic action. High pressure containers of SUS 316 type are used widely. However, this SUS 316 type is liable to sustain clearance corrosion in its sealing parts and screw joints. It is desired to develop a technique to apply FRP to containers of modules.

Polyamide membranes can be used in a relatively wide range of pH, but cellulose acetate membranes are limited in their pH range (around pH 5 to 7) as they are subjected to hydrolysis. The adjustment of pH is carried out in the pretreatment plant by the acid qualitative pump and on-off control.

Residual chlorine has a bad influence upon polyamide membranes in particular. Methods to remove residual chlorine, include absorption by active carbon and reduction by chemicals, both of which have advantages and disadvantages as mentioned below.

a) Method of absorption by active carbon

  - May actual results have been given and almost 100% of chlorine can be removed.
  - Installation cost is high.
  - As the active carbon tower becomes a breeding place of microorganisms, it is necessary to place a precision filter, etc.

- There is a risk that active carbon is disintegrated by chlorine of high density.
- Since the chlorine saturation absorption quantity of active carbon is 0.7 g $C\ell_2$/g carbon, its renewal is necessary.

b) Method of reduction by chemicals

- The plant is simple and can be installed at a low cost.
- Another chemical injection pump is required as a spare unit from the stand-point of safety.
- Where bisulfate of soda is used, more than 10 ppm of $NaHSO_3$ is necessary to decompose 0.6 ppm of residual chlorine compety (because decomposition occurs due to dissolving oxygen) and thus the operating cost is some what higher. However, as the dissolved oxygen in seawater is removed, corrosiveness reduces.
- Chlorine cannot be removed completely, if it takes the form of chloramine.
- Where thiosulfate of soda is used, free sulfur generates due to heterogeneous reaction with an increase in pH and may be become slime.

As a result of investigations conducted on both methods in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility, the method of reduction by $NaHSO_3$ has been believed to be better in view of the simplicity of the plant and operation.

It is generally said that consolidation and hydrolysis of membranes are accelerated if water temperature exceeds 35°C. Although the temperature of seawater is around 28°C even in mid-summer, it will rise up to 30°C to 32°C due to long residence time in the pretreatment plant and water tanks of various kinds on the land. Moreover, since the water temperature at the inlet of module may exceed 35°C where high pressure centrifugal pumps, which are low in efficiency, are used or the quantity of recycle is large, attention needs to be given to the control of water temperature. PA-300 membranes, which have been produced recently by UOP, are said to have thermal resistance against temperatures up to 55°C, and it is desired to develop membranes having greater thermal resistance with the aim of exporting the technique to the Middle and Near East.

(4) Operating results of various modules in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility

(a) One-stage desalination plant of spiral type (CTA and TFC membranes manufactured by UOP)

The changes on desalination performance are shown in Fig. 7.5-7. The operating conditions were approximately the same except where the rate of recovery was increased in Run No.4 and the quality of feed water was worsened in Run No.5. The rate of desalination was approximately constant throughout this operating period and water of 290 to 470 ppm in TDS was obtained as desalinated water. In particular, it is conspicuous that the rate of desalination was rather improved where seawater of about 5 in FI value, having been processed only through the sand filter, was run in Run No.5.

The quantity of desalinated water reduced by about 20% due to the consolidation of membranes in the initial 100 hours of operation, after which it was relatively stabilized. The m value found by logarithmic plotting of both the quantity of desalinated water and the elapsed time is $m = 0.057$.

In the modules of spiral type, considerably worsened quality of feed water, as in the case of Run No.5, only results in somewhat decreased quantity of desalinated water and the modules are very stabile against variations in turbidity. Also, these composite membranes have been found to have better desalinating performance and pressure resistance, compared with the previous asymmetric membranes.

(b) One-stage desalination plant of hollow fiber (A) type
(Du Pont B-10 Permeater)

Operation was continued from Run No.4 to Run No.7 for about 6,300 hours without replacing any module.

The experiments were carried out by increasing the operating pressures gradually from 51.7 kg/cm^2 in the initial operation to ultimate 56.0 kg/cm^2, so as to maintain the rate of recovery (the target being 30%) and the quantity of desalinated water constant as far as possible. As shown in Fig. 7.5-8, the quantity of desalinated water was 300 to 320 ℓ/hr (in terms of quantity at 25°C) showing an approximately constant value and the rate of recovery maintained 28 to 30%.

The rate of recovery lowered gradually with the passage of operating hours. However, the rate of desalination was improved considerably due to treatment by PTB (Post Treatment B), a recovering agent of membrane performance developed by the Du Pont Co., conducted when the quality of desalinated water reached to target value (1,000 μ℧/cm in electric conductivity for initial 3,500 hours and 700 μ℧/cm thereafter) and the prescribed quality of desalinated water was attained throughout the whole operating period. Although the intervals of the treatment differed somewhat according to the water temperature, they were once per 500 to 1,000 hours.

The m value calculated from the changes in the volume of transmitted water was about 0.041. Therefore, decrease in the quantity of desalinated water is very little even if operation is done under constant pressure.

(c) One-stage desalination plant of hollow fiber (B) type
(XFS 416707 Module of Dow Chemical Corp.)

Results have been reported on the operation of this module carried out for 2 years (6,000 hours in the total) at the

Wrightsville Beach Research Facilities of OWRT, U.S.A. In the experiments made in the Seawater Desalting and By-Products Recovery Chigasaki Test Facility, a similar phenomenon was that membrane performance worsened in operation of short duration made on 4 modules. The typical results (Run No.1, No.2 and No.4) are shown in Fig. 7.5-9. As seen from this figure, the TDS density of desalinated water increased gradually to exceed 800 ppm at the end of 800 hours of operation in Run No.2. The operation was suspended at this time and treatment was tried with XF-4273 (supposed to be a kind of vinyl acetate), a recovering agent of membrane performance which had been sent from the Dow Chemical Corp., at the biggining of Run No.4. Although the rate of desalination recovered with this treatment, the quantity of desalinated water decreased by about 20% on the other hand. The treatment by the said recovering agent was tried twice in subsequent operation, but the third treatment in particular had almost no effect on membrane performance.

(d) 2-stage desalination plant of spiral type (SC-5000 A and B manufactured by Toho Rayon Co.)

Operation has been continued for about 4,500 hours and Fig. 7.5-10 shows changes in the membrane performance of the first and second stages in the initial 2,500 hours in the total for Run No.1 and No.2.

The quantity of desalinated water was very stabile in both the first and second stages but the rate of desalination in the first stage had a tendency to decrease somewhat. However, the plant exceeded the design capacity even after 2,500 hours of operation and 16 m^3/day in quantity, and 120 ppm or less in TDS in quality of desalinated water were attained. Calculation of the m value indicates that m = 0.027 (data measured under 50 kg/cm^2) to 0.039 (56 kg/cm^2) for the first stage and m = 0.00 for the second stage, with almost no decrease in the quantity of water.

A conceivable cause of the reduced rate of desalination in the first stage is that the membranes deteriorated due to iron eluted from the high pressure containers and residual chlorine of high density.

(e) 2-stage desalination plant of tubular type

In Run No.1, water was fed from the general - purpose pretreatment plant in order to grasp the basic characteristics of modules. In Run No.2 and No.3, water was run to the modules solely through the cartridge filters respectively of 30 and 75 micra, assuming that treatment for a plant for practical use is made solely through a microstrainer.

The changes in the quantity of desalinated water in each Run and stage are shown in Fig. 7.5-11. The quantity of desalinated water in the first stage was relatively stabile in Run No.1, but its decrease was slightly larger in Run No.2. The level of the quantity reduced in Run No.2 was maintained intact in Run No.3. The m values calculated from the first stage from the changes in the quantity of desalinated water from the start of operation of respective Runs were m = 0.031, m = 0.041 and m = 0.015 or so respectively for Run No.1, No.2 and No.3. As to the second stage, since one module was replaced at the start of operation respectively for Run No.2 and No.3, the m value calculated only for Run No.1 was m = 0.036

Also, the membranes were washed with an aqueous solution of oxalic acid at the beginning of each Run and it was seen in Run No.2 and No.3 that the quantity of desalinated water recovered by about 10%, compared with that before washing.

The rate of desalination was recognized to have lowered somewhat in Run No.1 and No.2. Investigations into the causes of this revealed that membranes of diacetate are comparatively more liable to deteriorate. The membranes of diacetate were replaced with mixed membranes when the third operation was completed and the fourth and subsequent operations have been progressing smoothly.

Judging from the above results, although the simplified pretreatment applied to the tubular modules worsen somewhat the lowering rate of the quantity of desalinated water, these modules seem to be fairly promising if washing of membranes is combined with it.

7.6. Cost of Water Production

Since a plant of seawater desalination by reverse osmosis has not yet been realized on a scale for practical use, any trial estimation of the cost of water production is inevitable to be merely desk calculation. The cost varies to a great extent depending on the details of a plant including methods of pretreatment, one-stage or 2-stage processing, and recovery of energy. Unit prices of electric power and chemicals also differ by country and by year. Thus far, many reports on the cost of water production have been published but the cost estimated varies according to calculators.

As an example of the cost of water production, Table 7.6-1 shows trial estimates of the cost of plant construction and the cost of water production which have been prepared recently by OWRT. According to their trial calculations, where recovery of energy is included, the construction cost is 1.5 to 2.5 dollars/1 GPD (120 to 200 thousand yen/ 1 m^3/day) and total cost of water production is 1.5 to 2.0 dollars/ 1,000 gallons (120 to 160 yen/m^3) and they have reported that the cost of water production is considerably lower than that of the MSF evaporation plant which presently exists in U.S.A. The above figures have been calculated using 30% as the rate of energy recovery, and with an increase in the rate to 35% and 40% the cost of water production reduces accordingly.

Among other trial estimates of the cost which have been published by different manufacturers of modules, an example of the Dow Chemical Corp. is shown in Table 7.6-2. Figures are larger than those provided by OWRT and this may be due to differences in the scale of plant, recovery of energy (no account is taken of it by Dow) and methods to calculate personnel and insurance expenses. The price of a module is put at 1 dollar/1 GPD (79,000 yen/1 m^3/day).

Recent cost of water production in Japan is summarized in the research report of Nihon Kaisui Gakkai. The cost has been worked out based on figures calculated on a trial basis by several private manufacturers under a unified standard of costing. The following information on seawater desalination by reverse osmosis is cited from the said report.

(a) Total amount of plant and equipment investment

Where the plant has a maximum production capacity of water ranging 5,000 m^3/day to 18,000 m^3/day, the investments are 272 thousand to 394 thousand yen, or 313 thousand yen on the average, per 7 m^3/day of produced fresh water.

(b) Cost of water production and its breakdown

The cost of water production ranges from 324 to 375 yen per 1 m^3 of fresh water, or 354 yen on the average, of which ratios accounted for by respective cost items are shown in Table 7.6-3.

(c) Service life

In many cases, service life is 3 years for membranes and 15 to 18 years for plant.

(d) Consumption of energy per 1 m^3 of fresh water

Consumption of electric power is put at 8 to 8.4 kWh. Recovered energy from discharged brine corresponds to 2.2 to 2.9 kWh.

As seen from the above data, the cost of water production in Japan is higher than that in the U.S.A. This may be caused by the fact that the unit price of electric power in Japan is twice that in the U.S.A. and where modules imported from abroad are used, prices of modules become fairly high due to transport cost, duties, etc.

It is seen from the data of trial estimates in Japan and U.S.A. that expenses of power, membrane replacement and equipment depreciation acount for 75 to 85% of the cost of water production, each sharing one third. The recovery of energy is effective to reduce the power expense and thus improvement in the rate of recovery is needed. To this end, it is desired to develop membranes of higher permeability. The expense of membrane replacement has much weight and this is due to short durability of membranes and a high unit price of modules. Achievement of longer durability is required to clear up causes which deteriorate membranes and it is necessary to strive for the technical development of plants, operation and control related to washing and revitalization of membranes. Reduction in the depreciation expenses of equipment necessitates decreasing installation cost through simplified pretreatment and increased size of reverse osmotic modules and improving the service life of plants through the use of anticorrosive materials.

Compared with other techniques of seawater desalination, reverse osmotic methods consume the least quantity of energy per unit of produced fresh water and, in future, it will be diffused widely as an "energy-saving" technique, as it is called. Many reports have been published also on the required quantity of energy. Table 7.6-4 shows the quantities of energy comparing the MSF evaporation methods having a water production ratio of 10 with reverse osmotic methods operated under a pressure of 70 kg/cm^2 by using various kinds of energy sources.

Reverse osmotic methods are more profitable than evaporation m methods in any case and their required quantities of energy are 40% or less of those of the latter methods, except where gas turbines are used as a power source. In case "C" where a plant of energy recovery is provided, the said quantities are about one fourth of those of evaporation methods.

The required quantities of energy shown in the table for reverse osmotic methods are 8.25×10^3 $Kcal/m^3$ which seems reasonable in the main.

Since reverse osmotic methods are generally composed of assembling small modules, it is said that the cost of water production does not reduce so much by increase in the size of plants. The electric power, membrane replacement and chemical expenses accounting for two thirds of the total cost of water production are almost fixed regardless of the size of plants. However, since the law of the 0.7th power, which is used for ordinary plants, is valid for the equipment cost accounting for the remaining one third, the scale merit becomes effective.

Taking a high pressure pump as an example, a pump of 1,000 m^3/h in capacity can be manufactured and a plant capable of producing 8,000 m^3/day of water can be operated with one such high pressure pump. Also, one set of instrumentation suffices for the operation. Expenses of pretreatment plants, modules and annexed facilities as construction costs are almost the same. In proportion with the increase in the capacity of pretreatment plants, the construction cost per unit quantity of produced fresh water reduces. The results of calculations shown below are those published as trial estimates in the report of Nihon Kaisui Gakkai aforementioned.

Capacity of water production	2,000 m^3	5,000 m^3/d	10,000 m^3/d	30,000 m^3/d
Cost of water production, in year /m^3	353	333	320	310

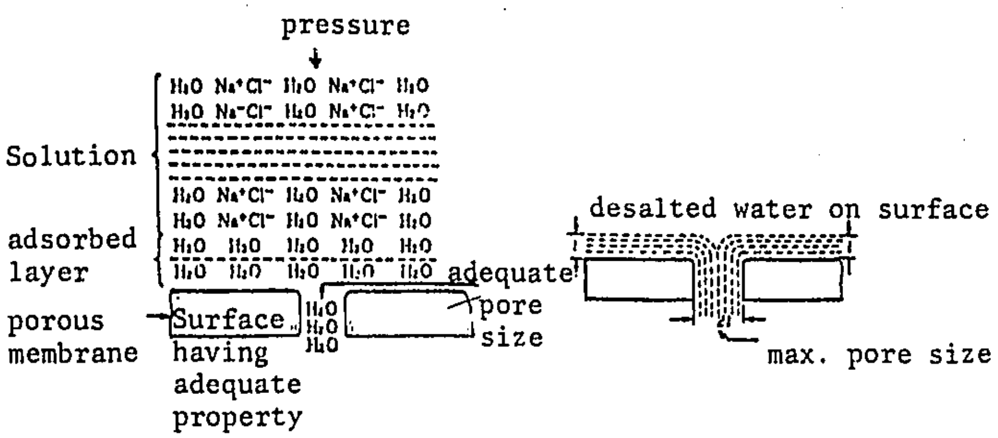


Fig. 7.1 - 1 Sourirajan's reverse osmosis model

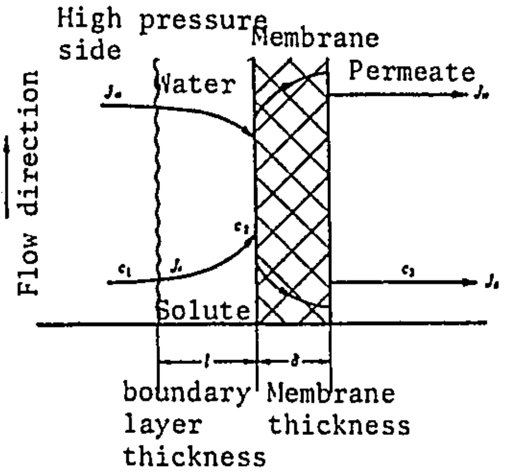


Fig. 7.1-2 Concentration distribution neighboring membrane

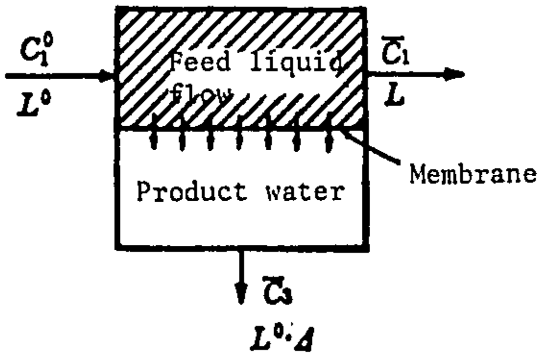


Fig. 7.1-3 Model of Module

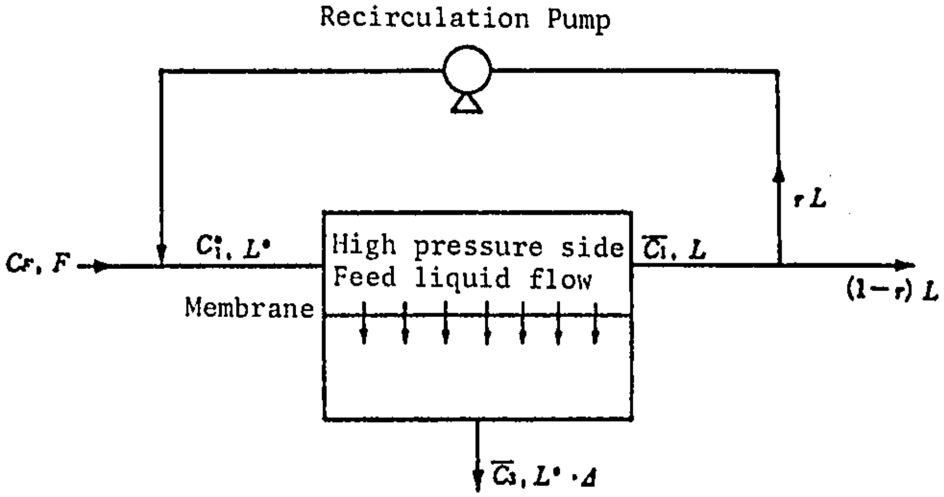


Fig. 7.1-4 Model of Module in recirculation flow

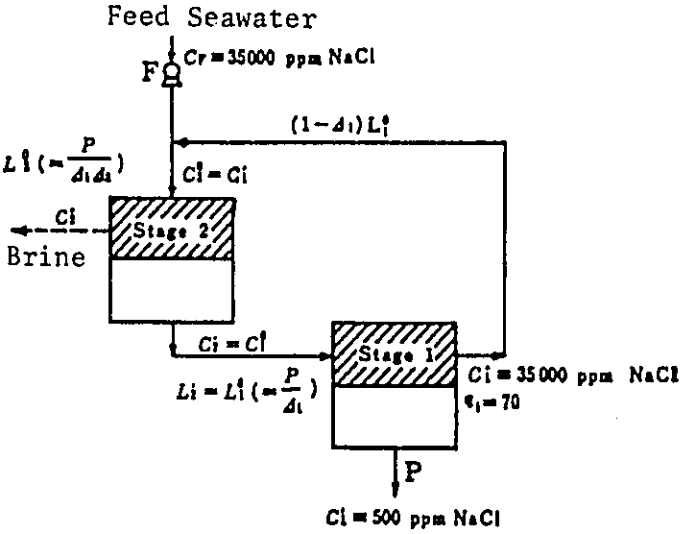


Fig. 7.1 - 5 Two Stage Seawater Desalination

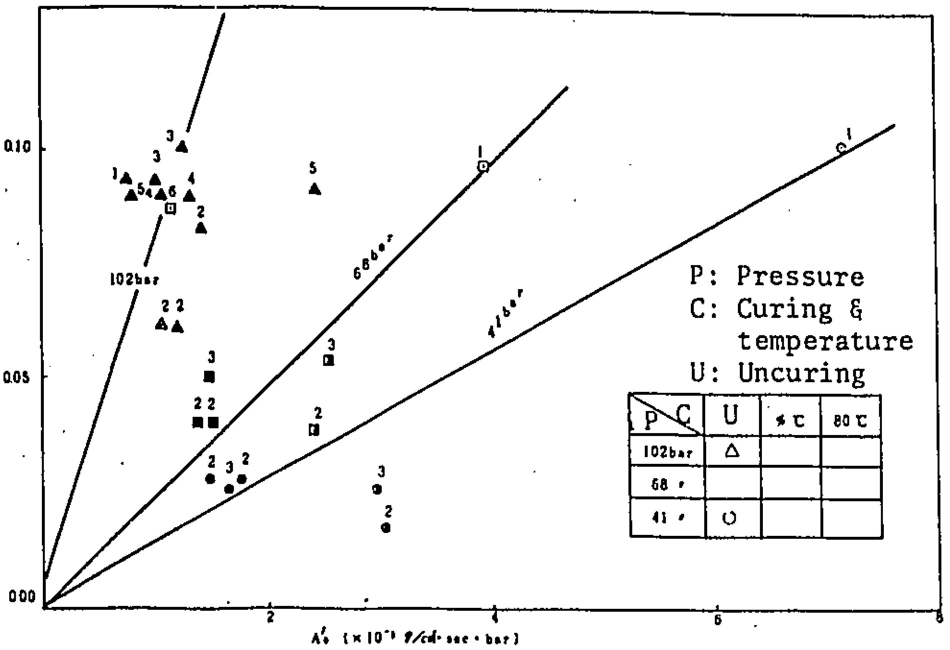


Fig. 7.2-1 Initial Membrane Permiability Coefficient and Compaction Coefficient

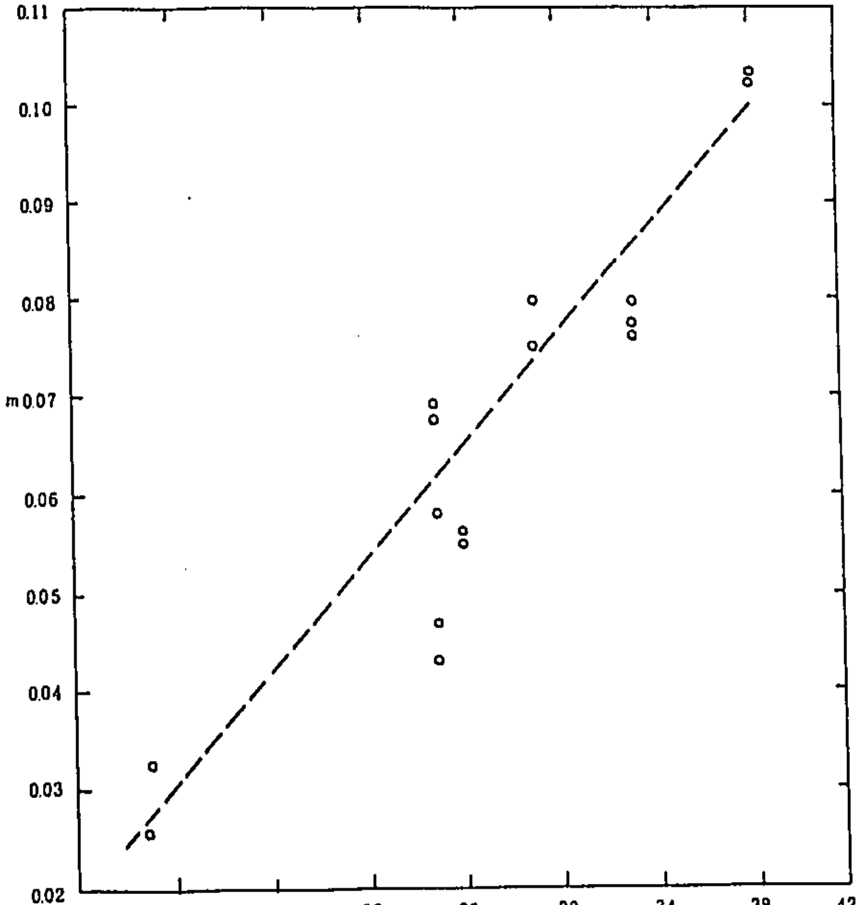


Fig. 7.2-2 Increase of Membrane Compaction Coefficient by Liquid Temperature

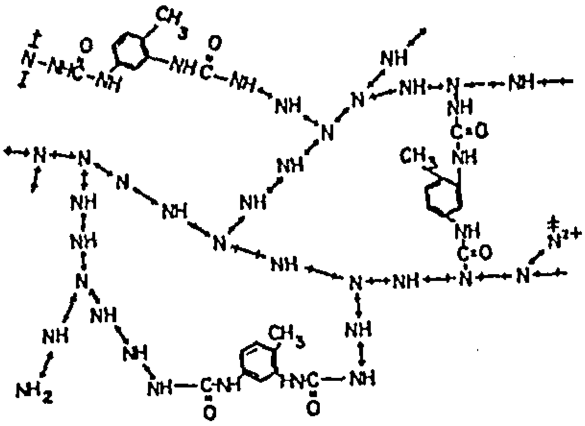


Fig. 7.2-3 Presumed Structure of NS-100
++: $-CH_2$ $-CH_2$

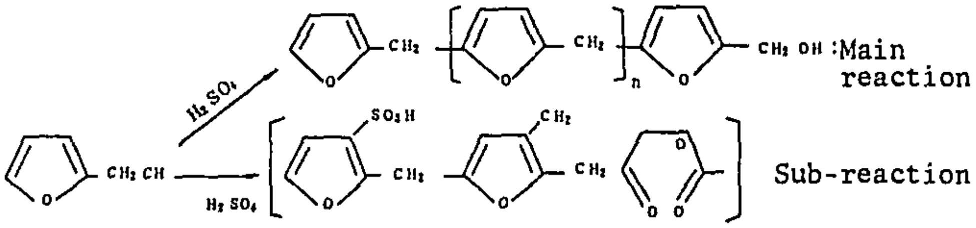


Fig. 7.2-4 NS-200 Reaction Formula

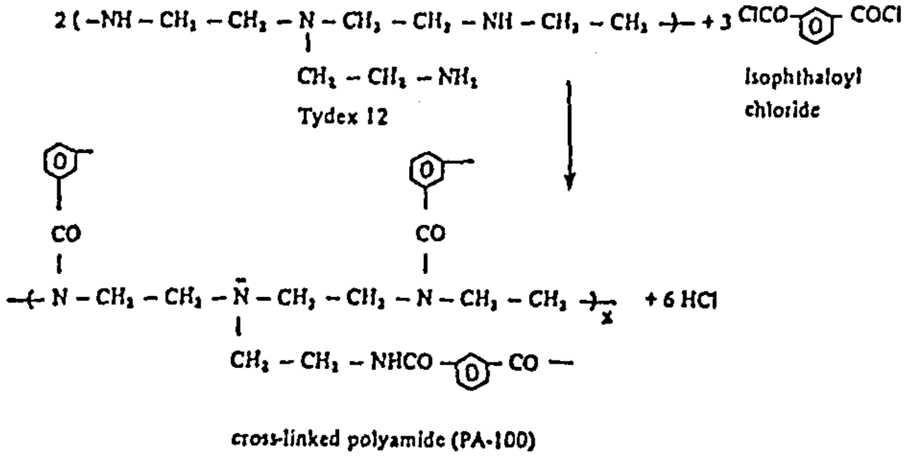


Fig. 7:2-5 Reaction and Constitutional Formula of PA-100

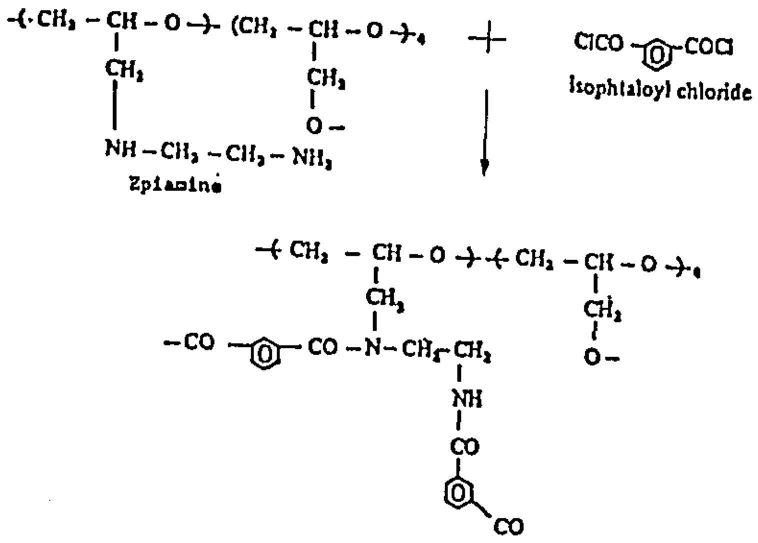


Fig. 7.2-6 Reaction and Constitutional Formula of PA-300

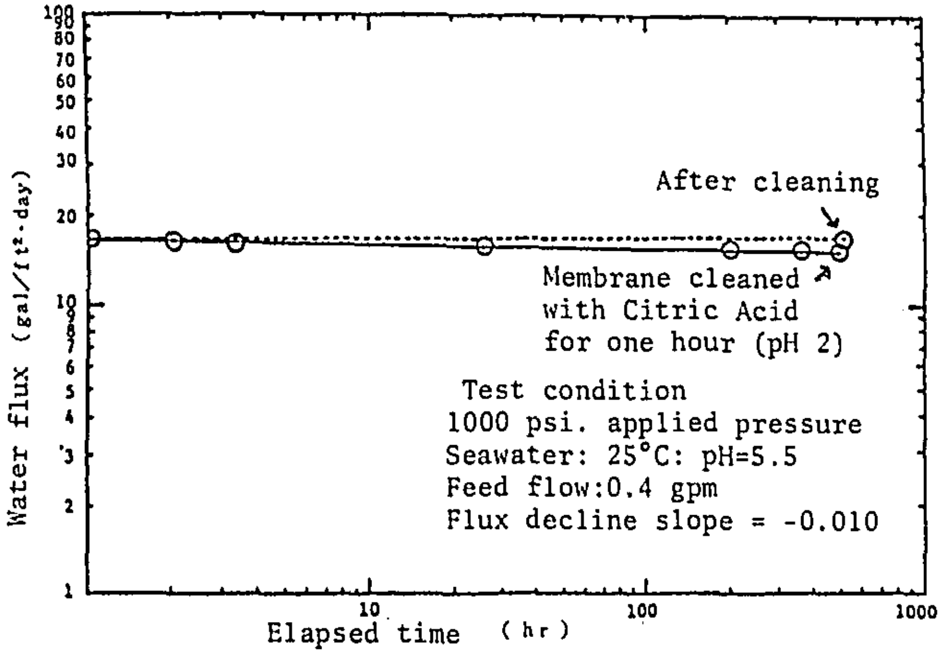
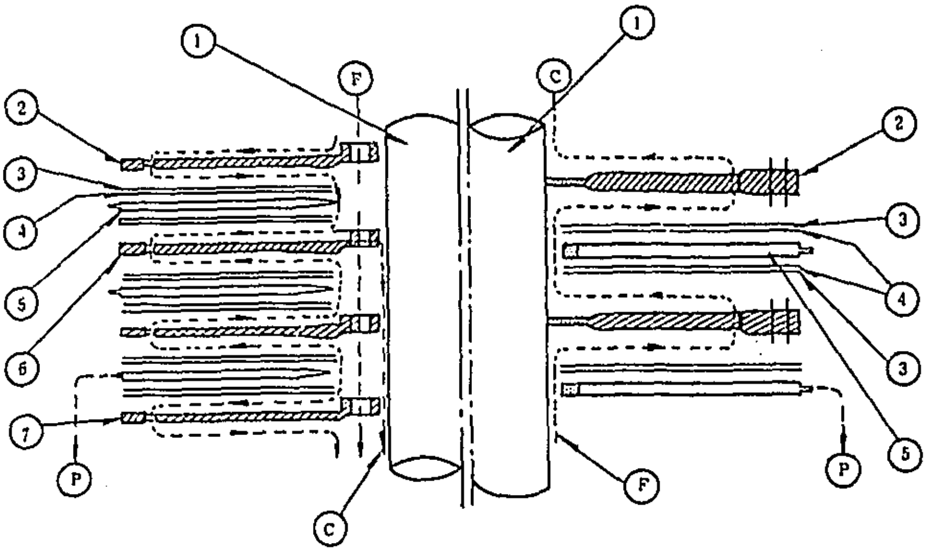
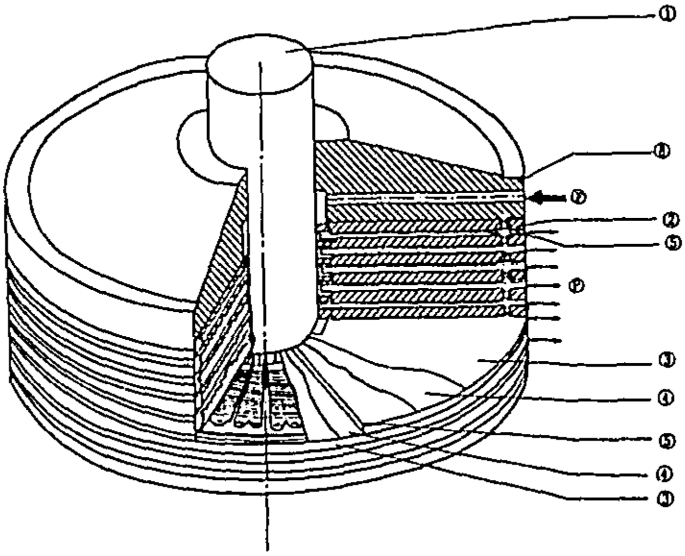


Fig. 7.2-7 Flux decline performance of PA-300 poly (ether/amide) thin-film composite membrane as a function of time



(b) 30 Type (a) 20,40 Type



(c)

Fig. 7.2-8 DDS Module Configuration

1 : Center bolt, 2 : Frame, 3 : Membrane, 4 : Filter paper
5 : Plate, 6 : Brine outlet, 7 : Raw water inlet, 8 : End frange
F : Raw water, C : Brine, P : Permeate

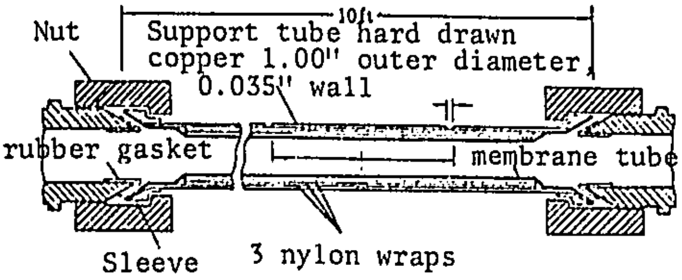


Fig. 7.2-9 Schematic diagram of UCLA type tubular assembly

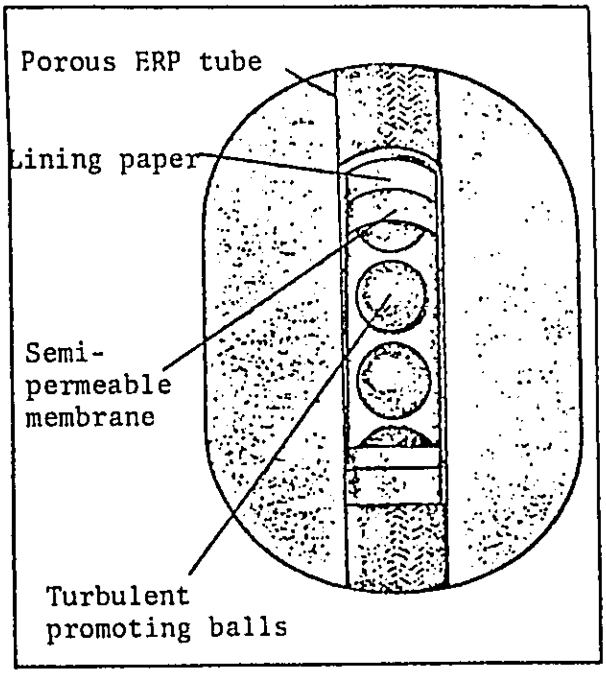


Fig. 7.2-10 Structure of American Standard type membrane

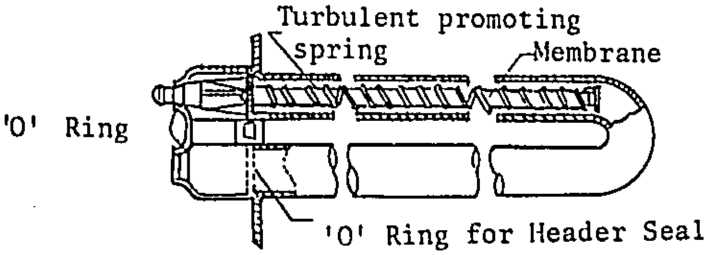


Fig. 7.2-11 Structure of Ropak

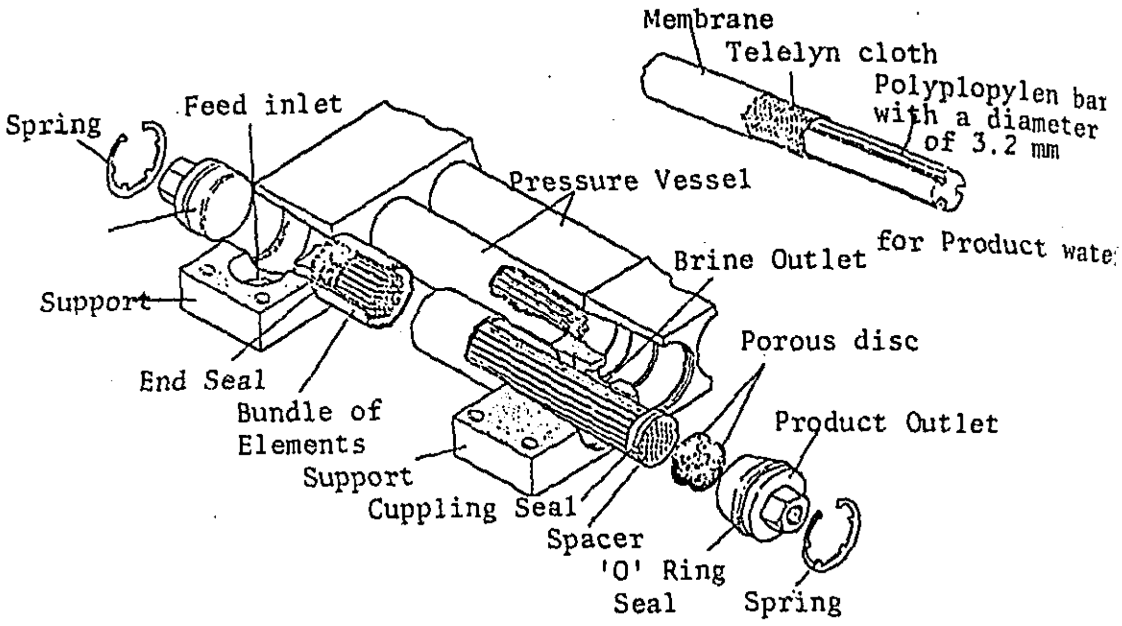


Fig. 7.2-12 Spageti Type

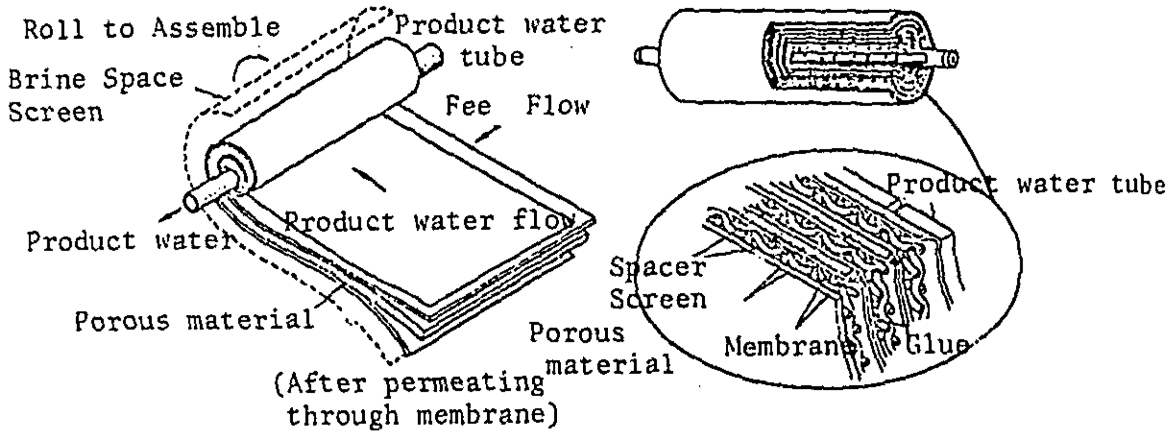


Fig. 7.2-13 Spiral Wound Module

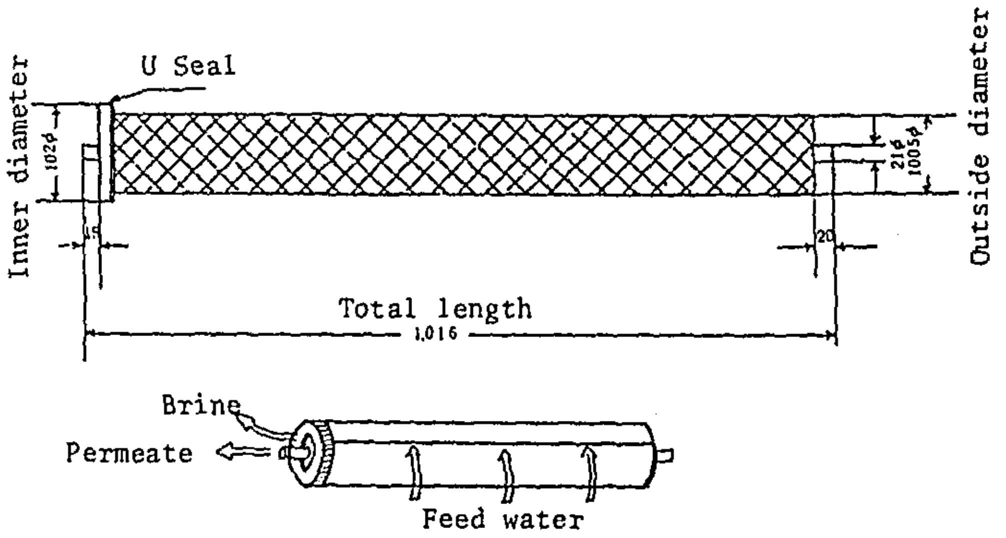


Fig. 7.2-14 Toray Spiral Wound Module

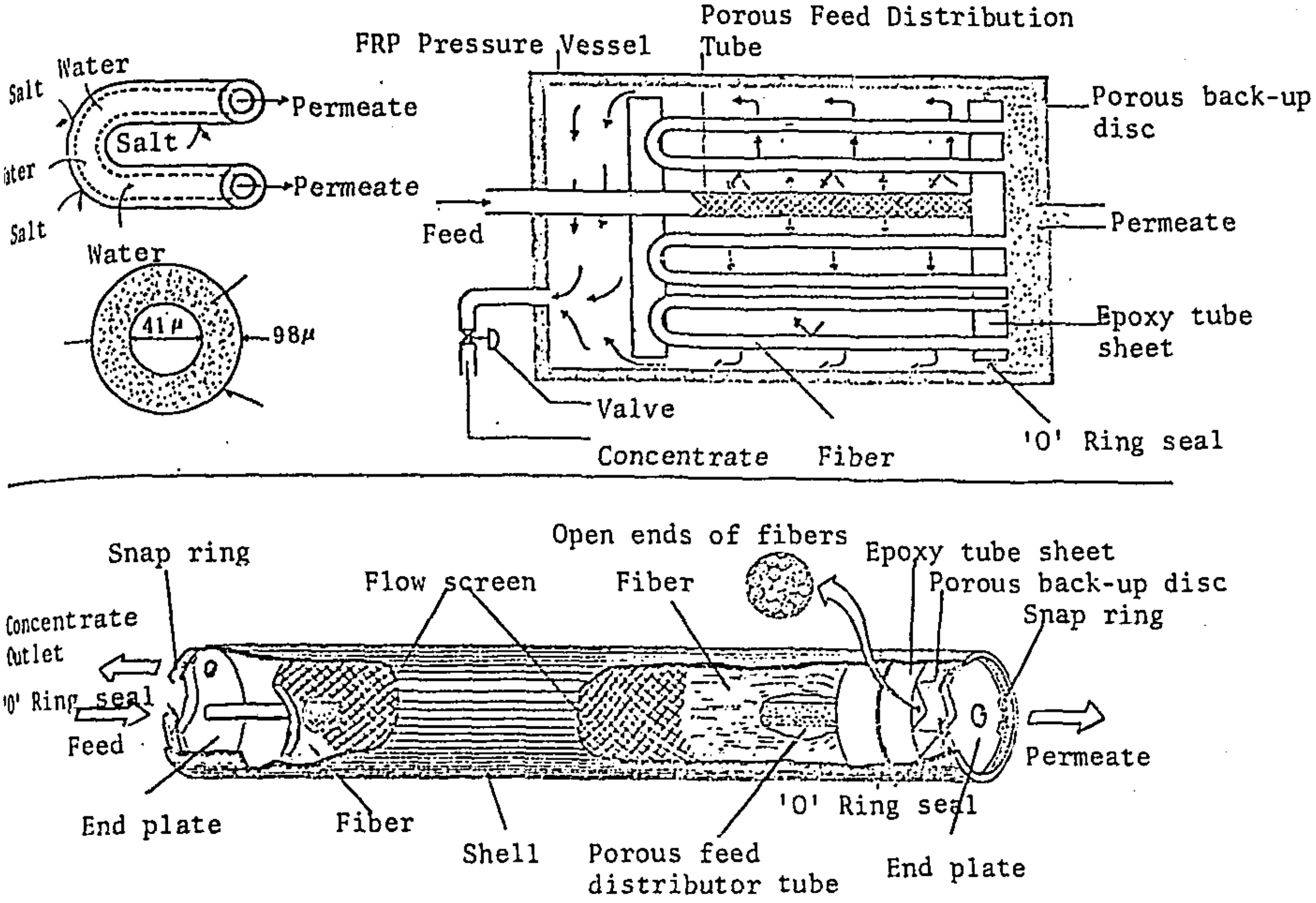


Fig. 7.2-15 B-10 Permeator

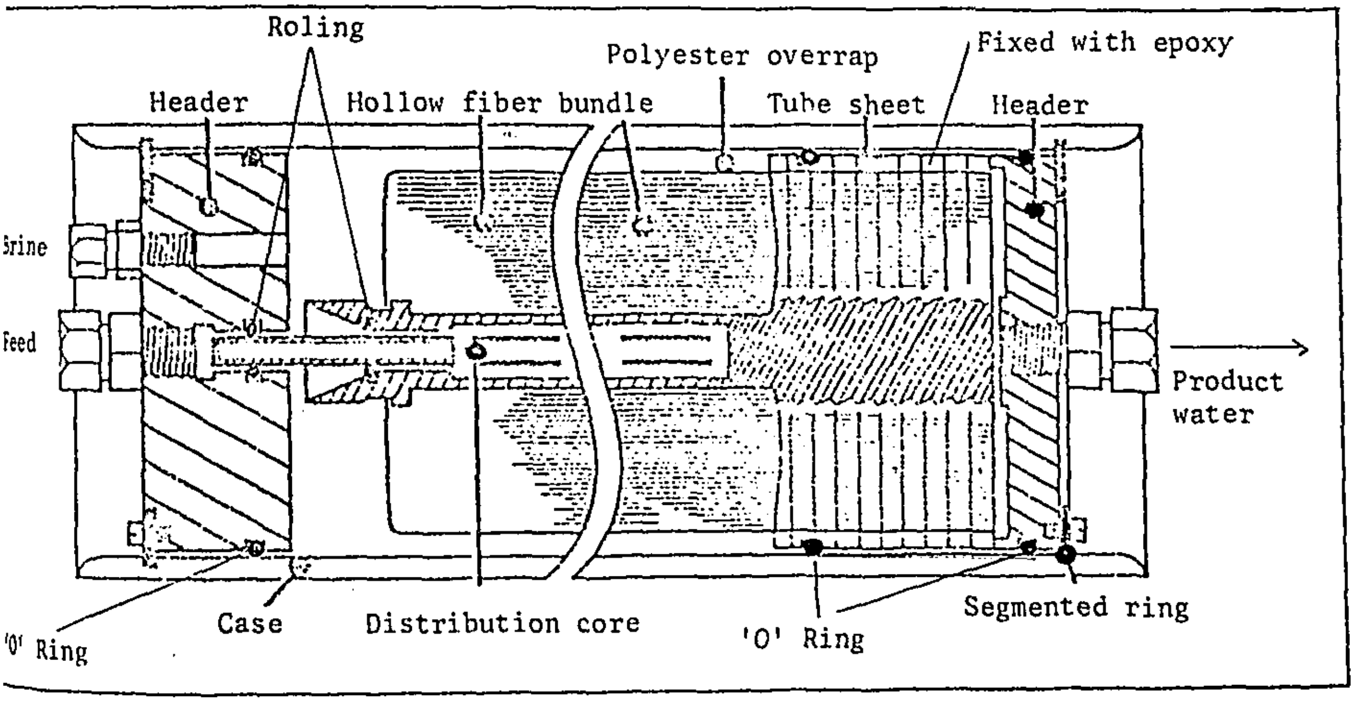


Fig. 7.2-16 DOWEX4K and 20K Reverse Osmosis Permeater

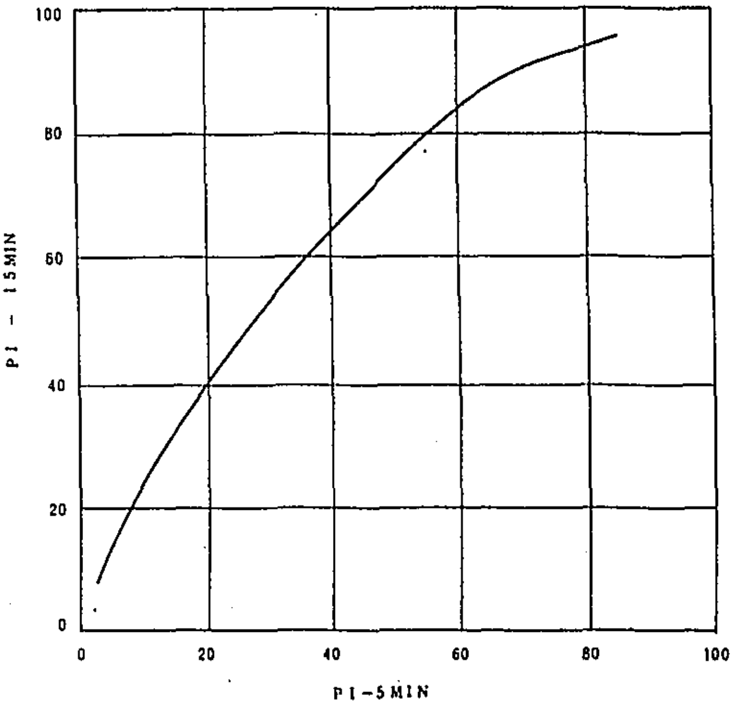


Fig. 7.3-1 PI_5 and PI_{15}

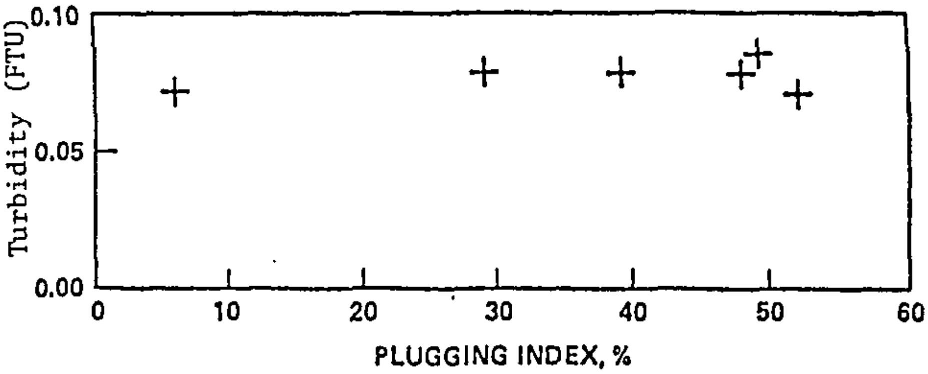
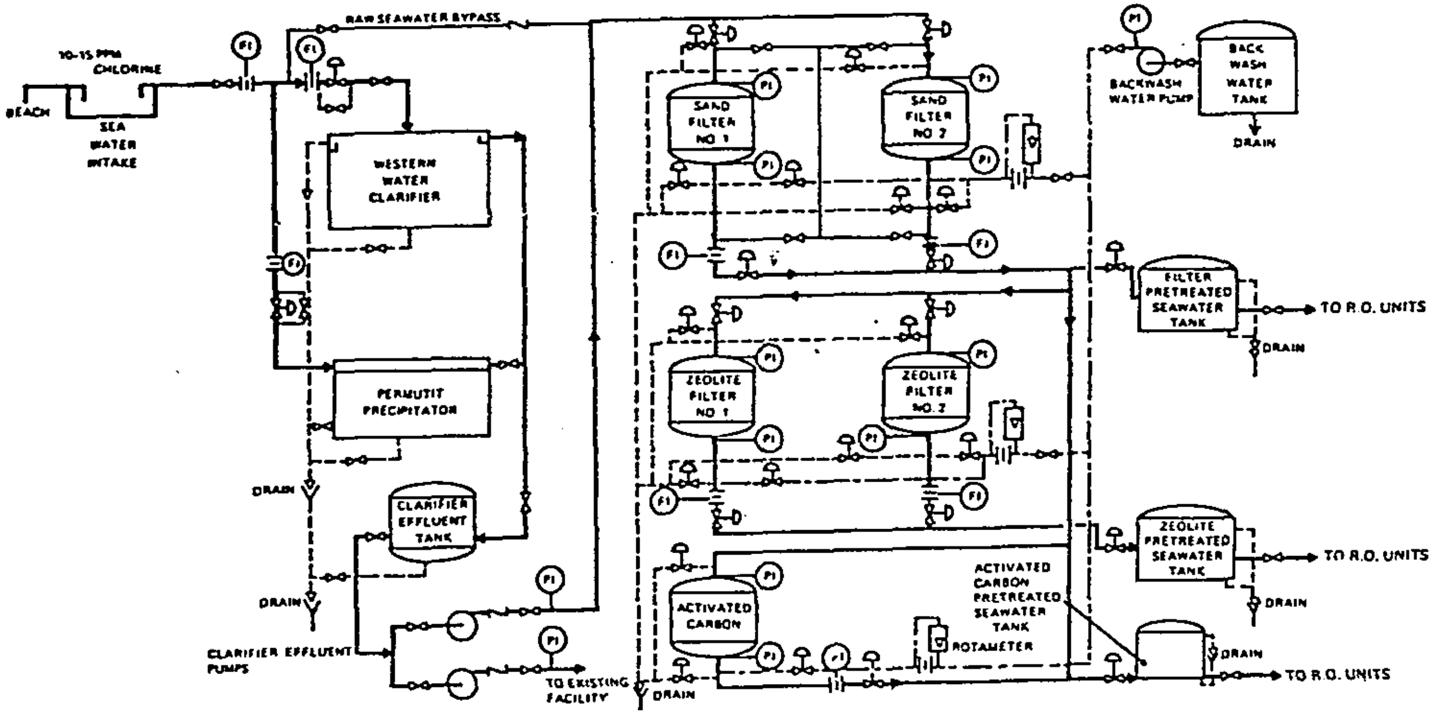


Fig. 7.3-2 PI and Turbidity



FLOW SCHEMATIC OF THE CENTRAL
PRETREATMENT SYSTEM

OFFICE OF WATER RESEARCH AND TECHNOLOGY
SEA WATER TEST FACILITY, WRIGHTSVILLE BEACH,
N. CAROLINA

Fig. 7.3-3 Pretreatment Flow Diagram of OSW Wrightville Beach Facility

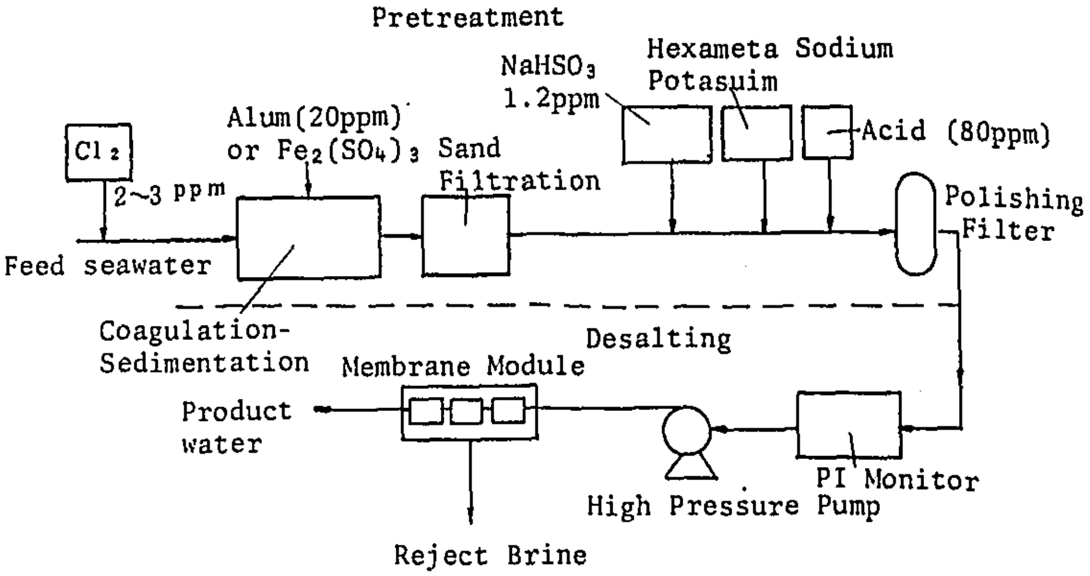


Fig. 7.3-4 Pretreatment of Reverse Osmosis System

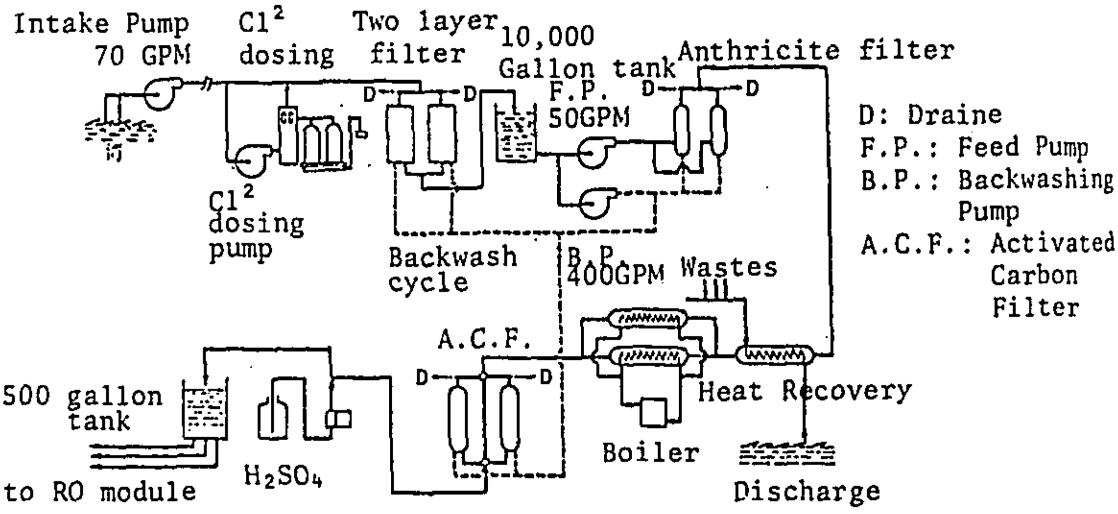
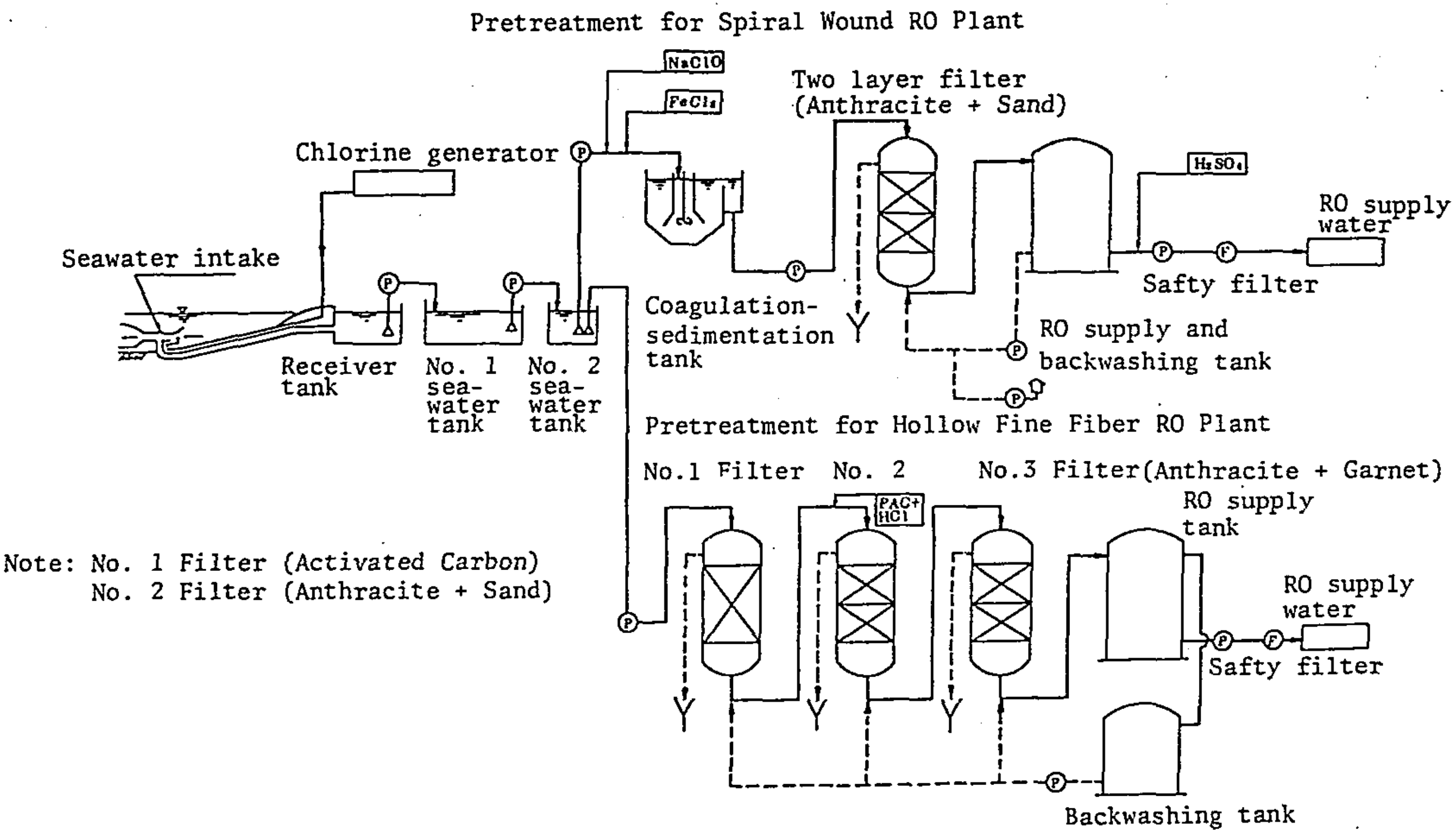
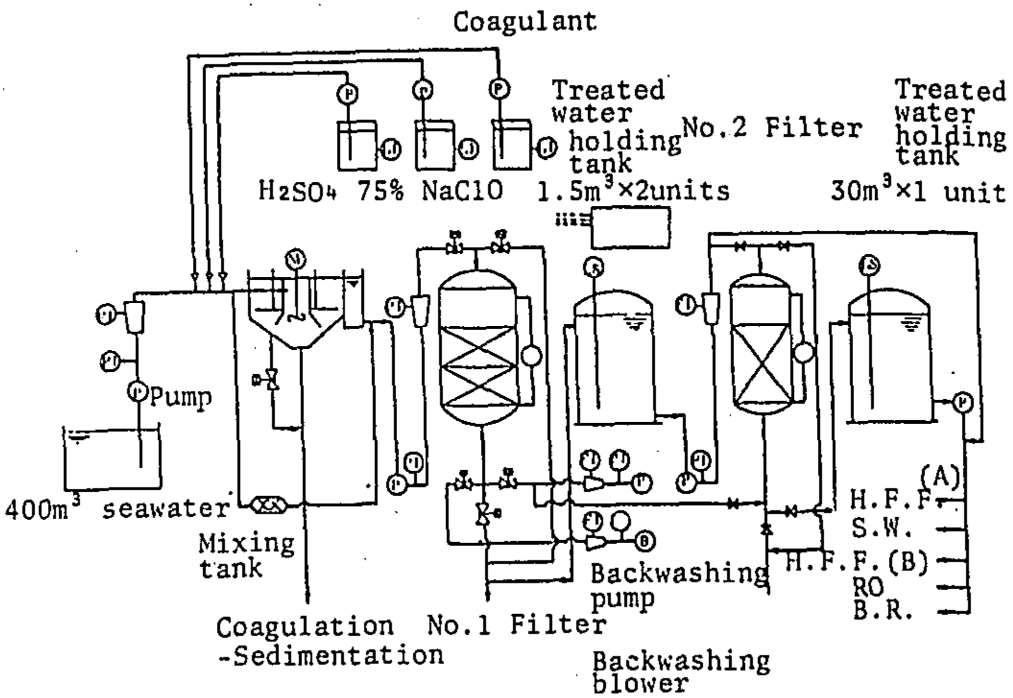


Fig. 7.3-5 Pretreatment (Du Pont Co., Ocean City, N.J.)



Note: No. 1 Filter (*Activated Carbon*)
No. 2 Filter (Anthracite + Sand)

Fig. 7.3-6 Flow Diagram of RO Pretreatment at Water Re-Use Promotion Center in Chigasaki



Note: H.F.F.(A) : Hollow Fine Fiber (A)
S.W. : Spiral Wound
H.F.F.(B) : Hollow Fine Fiber (B)
RO : RO Test Facility
B.R. : Basic Research

Fig. 7.3-7 Flow diagram of pretreatment at Water Re-use Promotion Center in Chigasaki

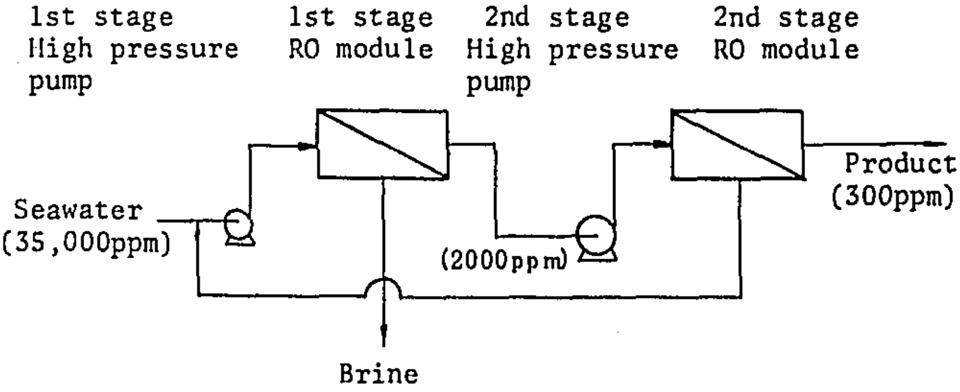


Fig. 7.4-1 Flow diagram of two stage desalination

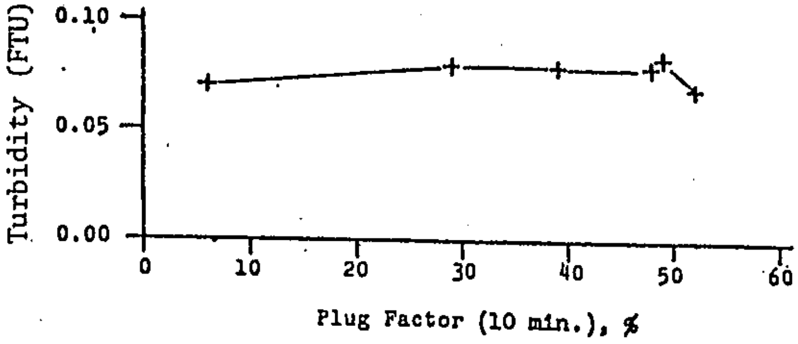


Fig. 7.5-1 Turbidity (FTU) and Plugging index

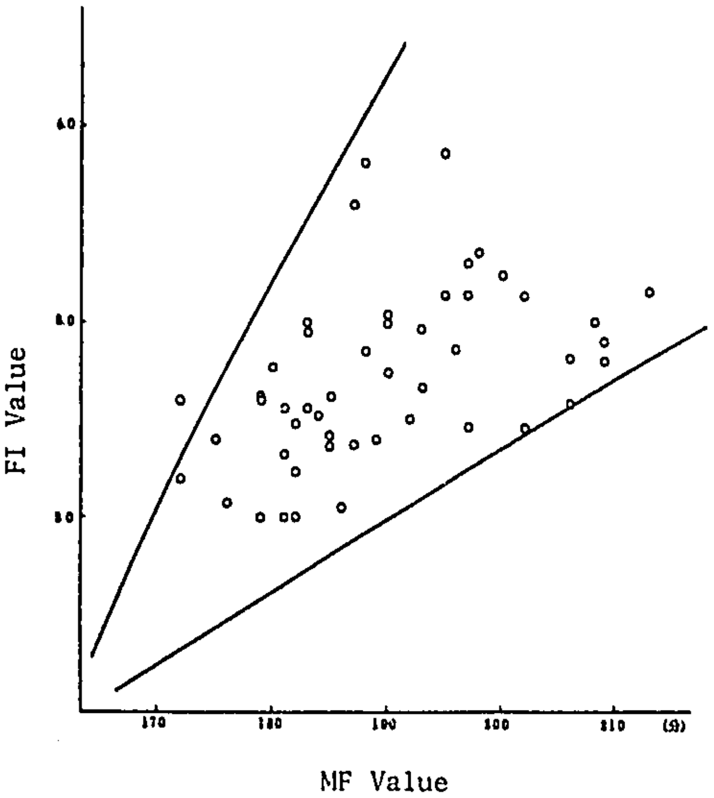


Fig. 7.5-2 FI Value and MF Value

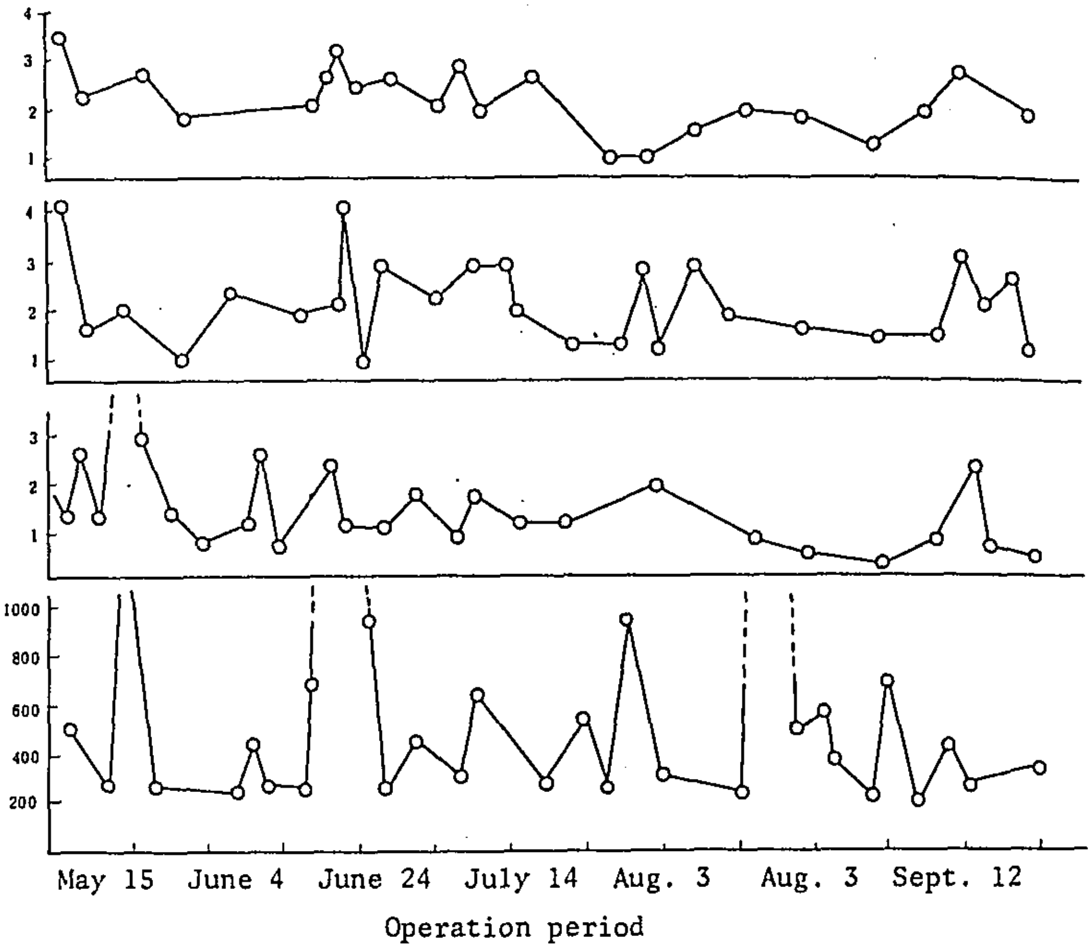


Fig. 7.5-3 Water quality of raw seawater and pretreated water

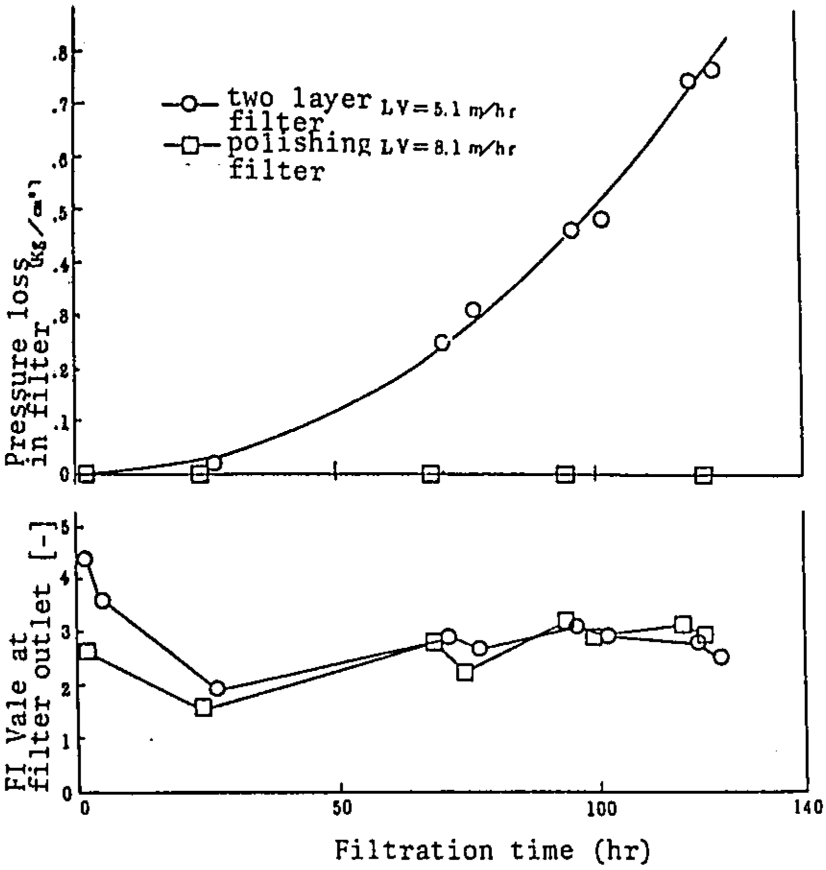


Fig. 7.5-4 Pressure loss, FI value and filtration time

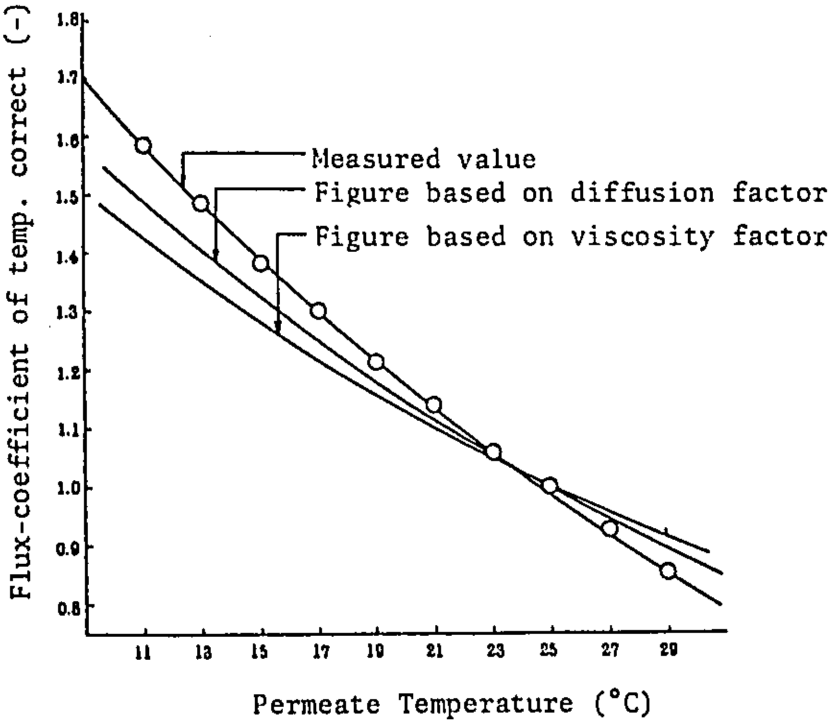


Fig. 7.5-5 Water flux-coefficient of temperature adjustment (Hollow fine fiber (A) type)

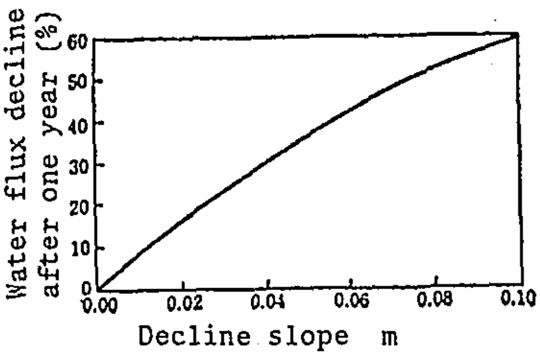


Fig. 7.5-6 Water flux decline after one year

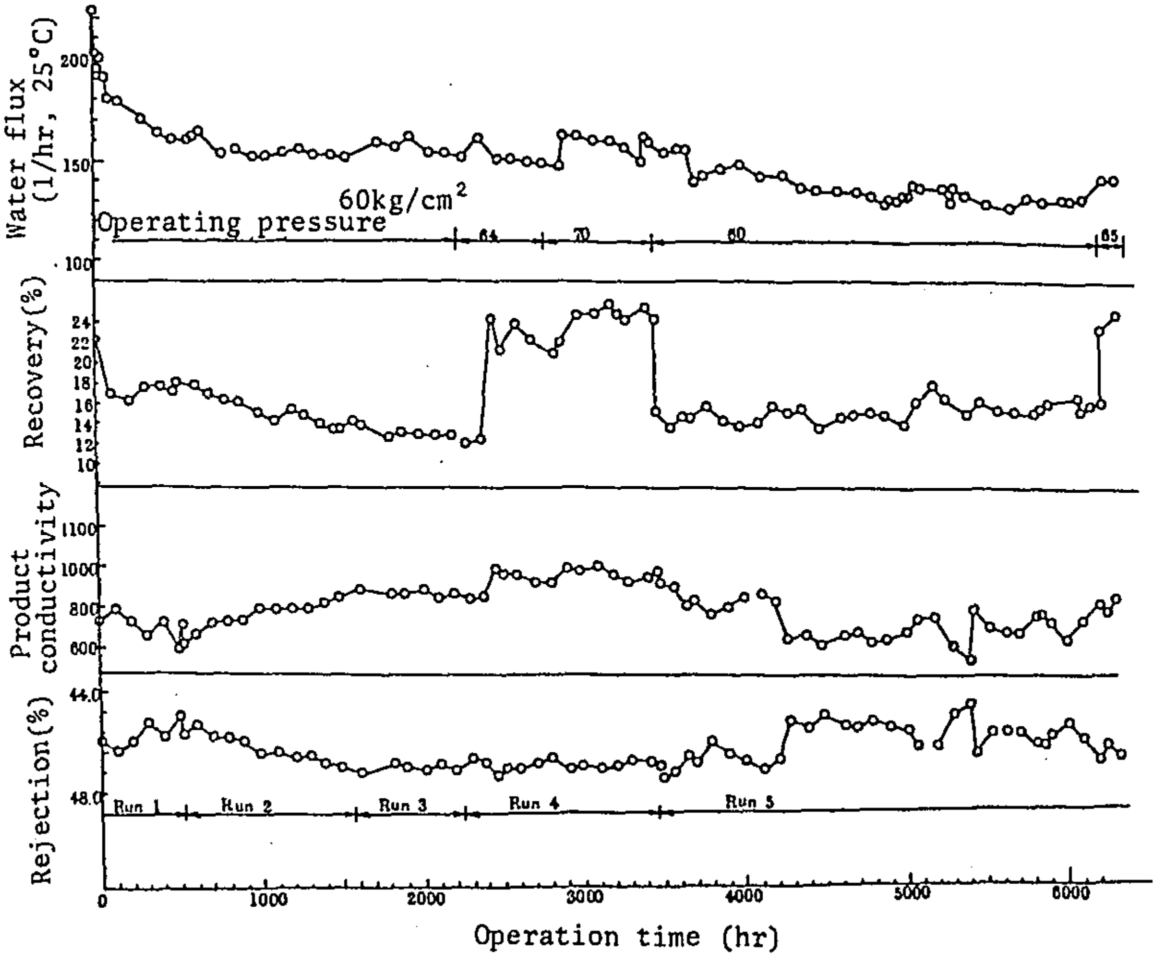


Fig. 7.5-7 One stage spiral wound RO performance result as a function of time

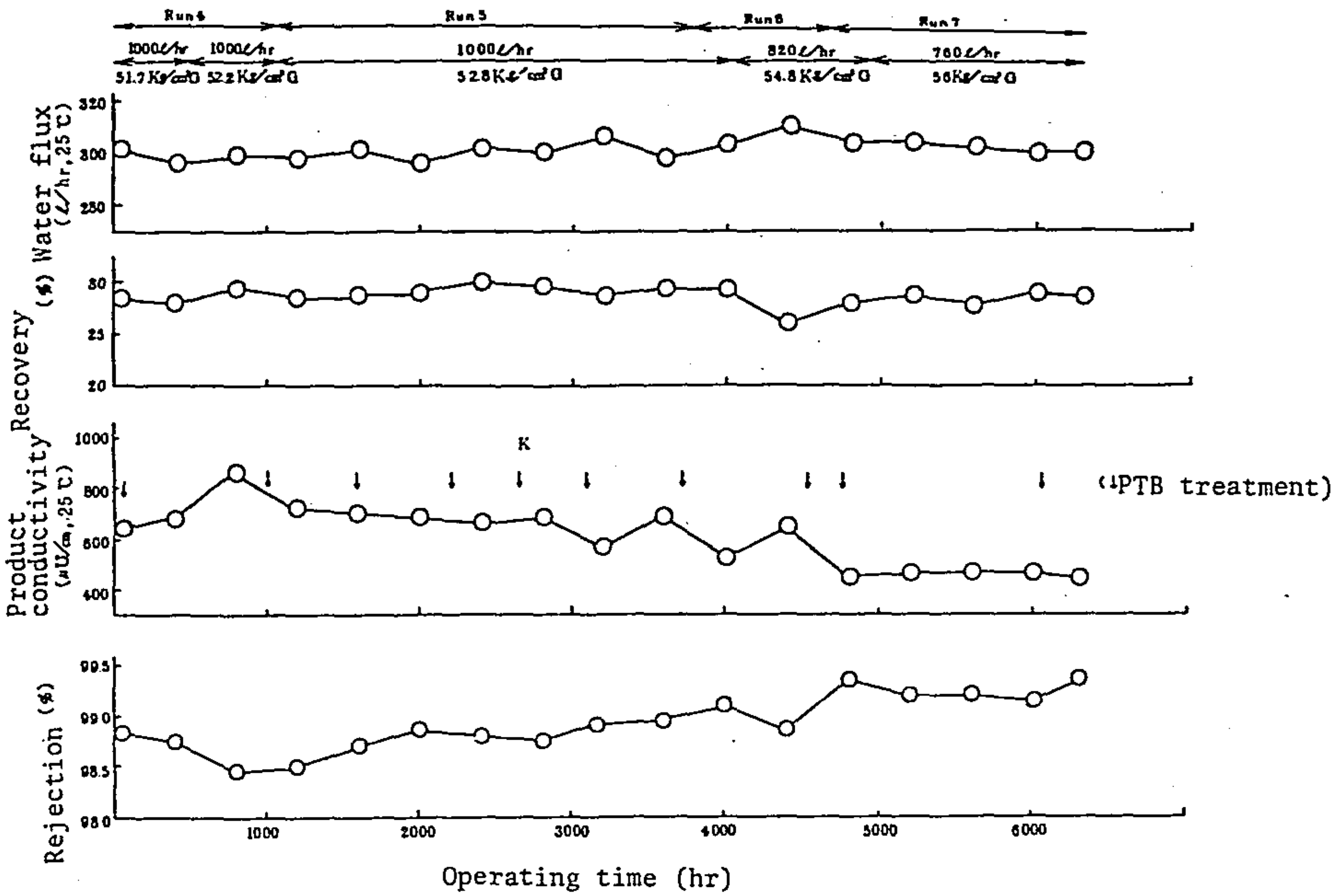


Fig. 7.5-8 Performance result of hollow fine fiber (A) type module as a function of time

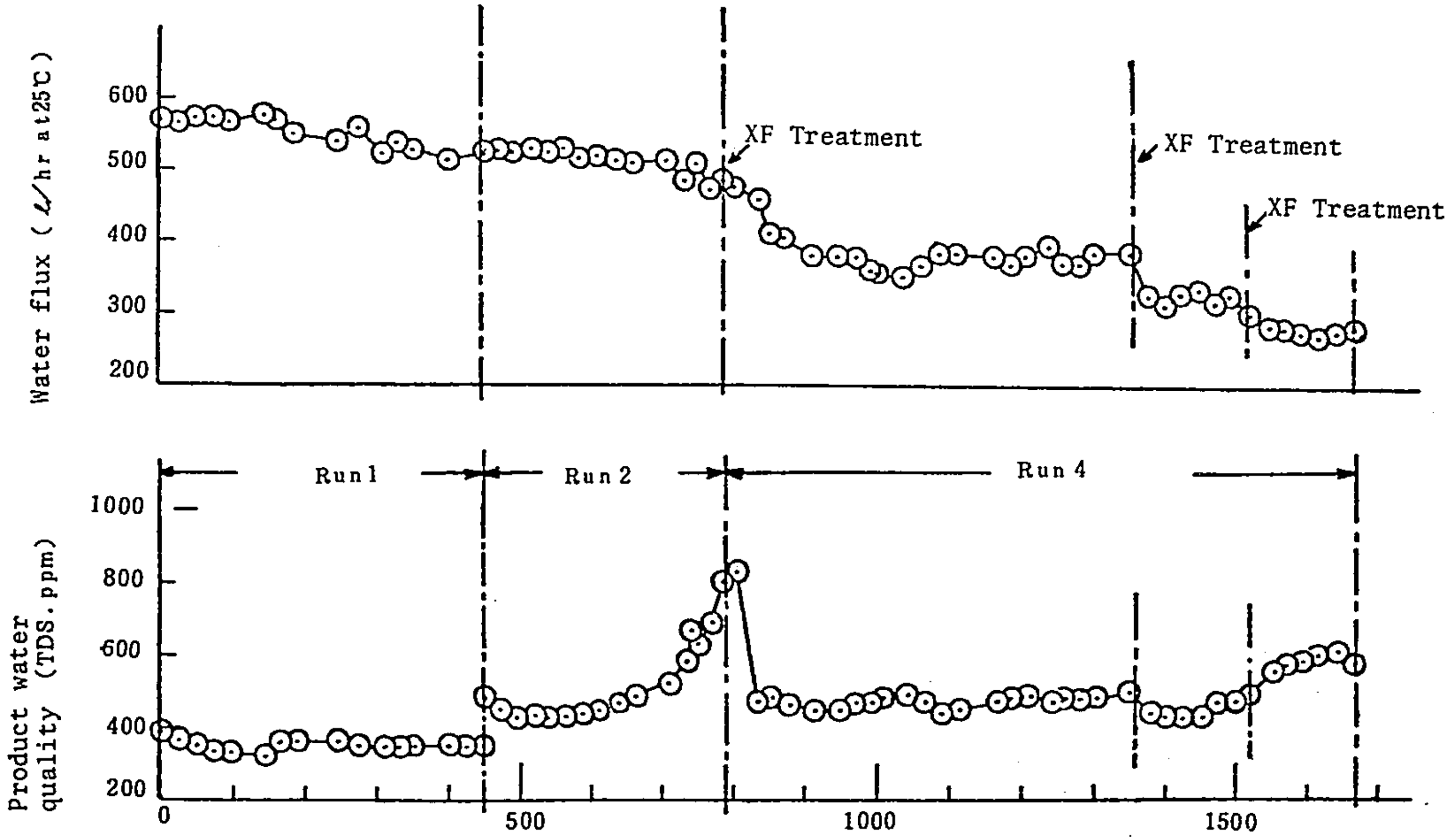


Fig. 7.5-9 Performance result of hollow fine fiber (B) No. 1 module as a function of time

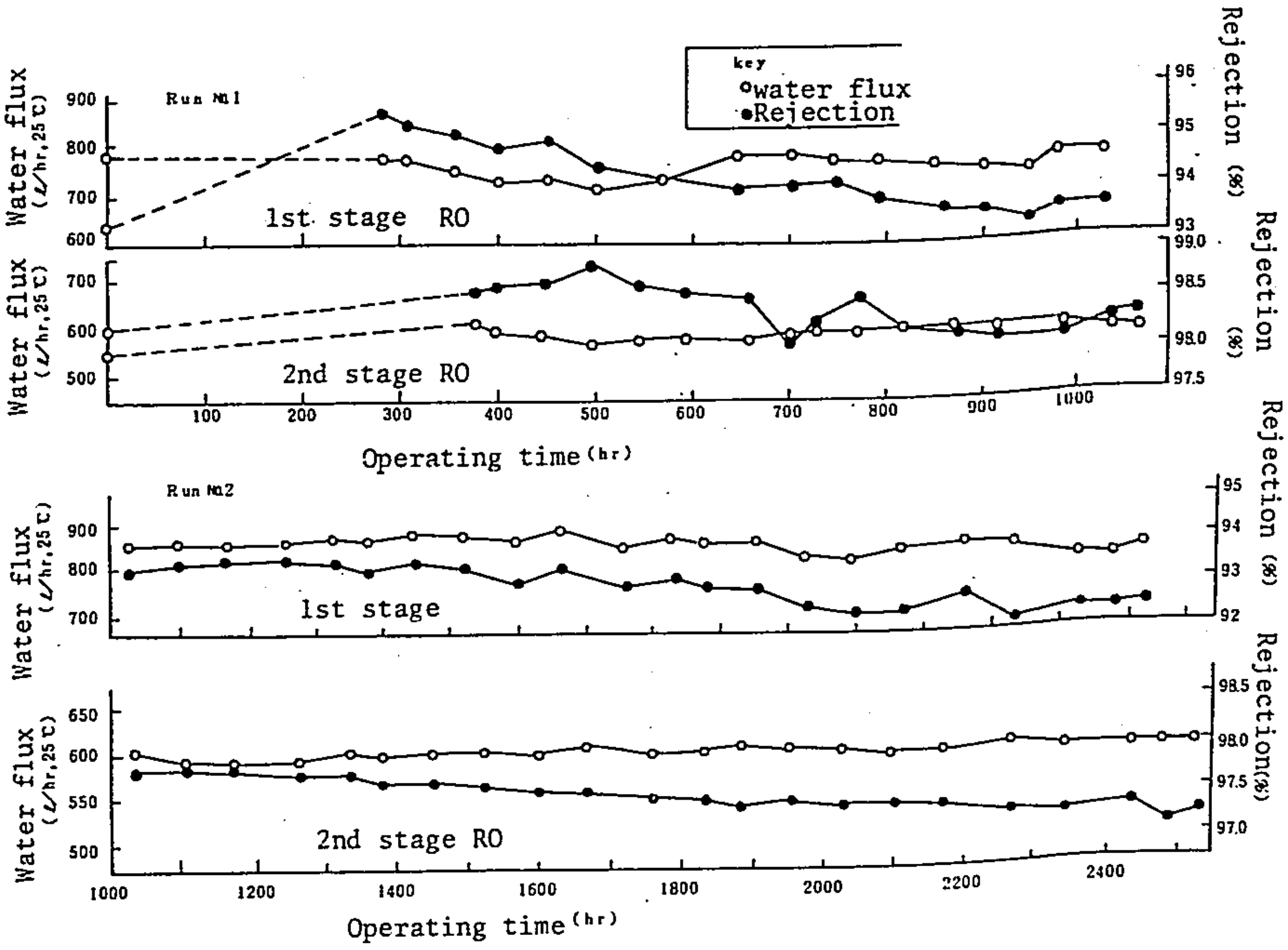


Fig. 7.5-10 Toray spiral wound module performance as a function of time

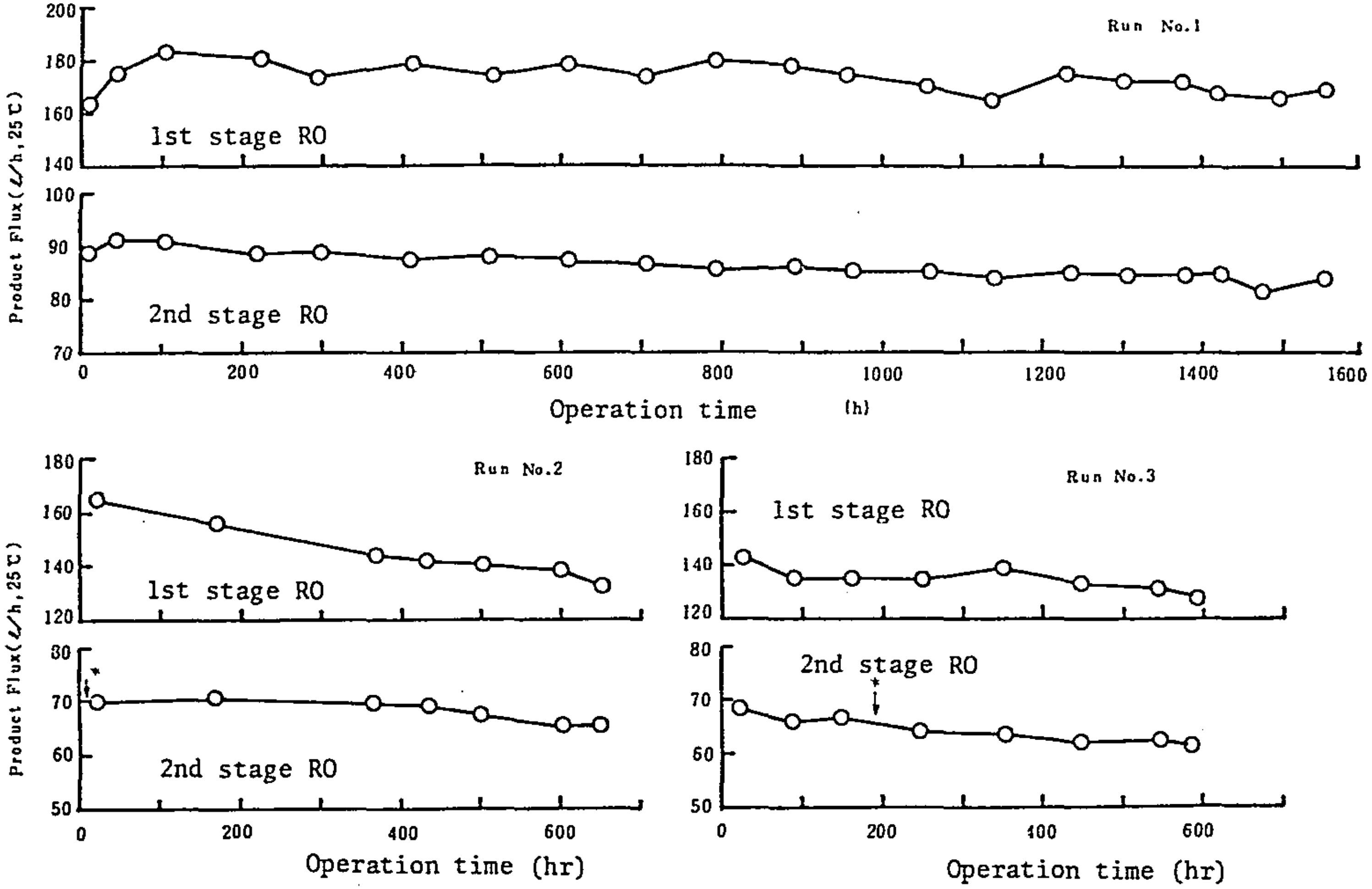


Fig. 7.5-11 Tublar type module performance result as a function of time

* Replacement of module (1 element)

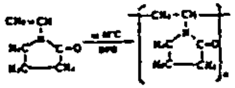
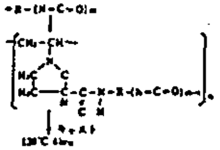
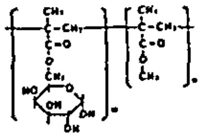
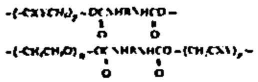
Table 7.2-1 Riverse Osmosis Membrane and Efficiency

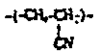
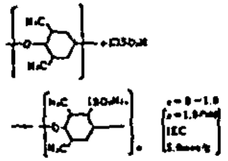
Membrane material	Components of casting liquid (wt.Ratio)		Membrane performance					Ref.
			Solution	(wt.%)	Applied measure (kg/cm^{2}G)	Rejection (%)	Flux (gal/ft^2.day)	
Cellulose Acetate (CA)	CA	22.1	NaCl	0.5	41	95.0	29.4	10)
	Acetone	51.4						
	Glycelin	6.6						
	n-propyl alcohol	19.9						
Cellulose Acetate (CA)	CA	10	NaCl	1.101	57	97.7	25.5	15)
	Acetone	20						
	Water	3						
	Propionamid	6						
Cellulose Acetate (CA)	CA	10	NaCl	3.5	102	98.6	10.8	16)
	Acetone	30		0.5	51	92.7	35.5	
	Water	5						
	Tartaric Acid	2.5						
Cellulose Acetate (CA) $d_s = 2.61$	CA	10	NaCl	3.5	102	99.56	13.3	17)
	Acetone	22						
	Formamid	8						
	Maleic Acid	2						
Cellulose Acetate (CA) $d_s = 2.61$	CA	10	NaCl	3.5	102	99.5	11.0	18)
	Acetone	15~20						
	Formamid (or Methanol)	5~12						
	Maleic Acid	1~5						
Cellulose Acetate (CA) Blending	- do. -							
$d_s = 2.45$			NaCl	3.5	102	98.7	12.0	18)
$= 2.55$						99.0	12.0	
$= 2.63$						99.0	11.9	
$= 2.64$						99.7	10.7	
$= 2.67$						99.5	11.1	
$= 2.71$						99.5	11.7	
$= 2.74$						99.6	9.1	
$= 2.79$						98.7	6.8	
$= 2.86$						98.7	4.5	
Cellulose Acetate (CA) Blending	CA ($d_s = 2.86$)	8	NaCl	1.0	57	99.0	14.3	17)
	CA ($d_s = 2.41$)	12	Sea water		102	99.46	10.4	
	Dioxane	55						
	Acetone	35						
	Methanol	9						
	Maleic Acid	3						
Cellulose Acetate (CA) Cellulose Tri-acetate (CTA)	CA	10	NaCl	3.5	102	99.2	12.0	16)
	CTA	10						
	Dioxane	60						
	Acetone	35						
	Methanol	9						
	Maleic Acid	4						
Cellulose Acetate (CA) Composite membrane	--				102	99.54	13.3	19)
Cellulose Acetate (CA) Tublar type	Triethylene glycol & Methyl carbitol 1 : 1		NaCl	0.5	41	96.8	2.3	20)
				3.5	41	96.1	0.45	
Cellulose Acetate (CA) Tublar type	CA	30	NaCl	0.3	17	76.0	6.4	21)
	Acetone	28				86.0	5.3	
	Formamid	42				88.0	2.0	
						98.0	1.6	
				1.0	34	99.0	0.6	
Cellulose Tri-acetate (CTA)	CTA	10	NaCl	0.5	41	97.4	12.5	22)
	Acetone	12						
	Dioxane	75.5						
	Tri-acetin	2.5						
Cellulose Acetate Propionic Acid (CAP)	CAP	10	NaCl	3.5	102	99.1	13.4	16)
	Acetone	29						
	Formamid	9						
	Maleic Acid	2						

Table 7.2-1 Riverse Osmosis Membrane and Efficiency (Cont'd)

Membrane material	Components of casting liquid (wt. Ratio)			Membrane performance				Ref.
				Solution (wt.%)	Applied measure (kg/cm^{2}G)	Rejection (%)	Flux (gal/ft^2.day)	
Cellulose Acetate Propronic Acid (CAP) $d_s = 2.5$	CAP Acetone Formamid (or Methanol) Maleic Acid	.10 15∿20 5∿12 1∿ 5	NaCl	3.5	102	99.5	11.8	18)
Cellulose Acetate Butylic Acid (CAB)	CAB Acetone Formamid Maleic Acid	10 20 7 4	NaCl	3.5	102	99.3	10.6	16)
Cellulose Acetate Butylic Acid (CAB)	CAB Acetone Formamid (or Methanol) Maleic Acid	10 15∿20 5∿12 1∿ 5	NaCl	3.5	102	99.8	8.7	18)
Cellulose Acetate Butylic Acid (CAB) Hollow Fiber	CAB Acetone Triethyl Phosphate n-propyl Alcohol Glycerine	32 39.17 21.83 5.23 1.77	NaCl	0.3	17	98.0	0.18∿0.31	21)
Cellulose Acetate Metaclylic Acid (CAM)	CAM Acetone Formamid Maleic Acid	10 20 9 3	NaCl	3.5	102	99.21	10.3	16)
Cellulose Acetate Metaclylic Acid (CAM) $d_s = 2.62$	CAM Acetone Formamid (or Methanol) Maleic Acid	10 15∿20 5∿12 1∿ 5	NaCl	3.5 1.0 1.0	102 54.5 54.5	99.7 90.0 81.0	7.6 34.4 81.0	18)
Cellulose Acetate Metaclylic Acid (CAM)	CAM Acetone Formamid Maleic Acid	10 16.7 9 3	NaCl	3.5	102	99.6	9.2	17)
Cellulose Acetate Benzonic Acid (CABen)	CABen Acetone Formamid Maleic Acid	10 30 10 5	NaCl	3.5	102	97.5	8.1	16)
Ethyl Cellulose (EC)	EC Acetic Methyl Methanol Formamid 70% Perchloric Acid	10 48 12 15 3	NaCl	3.5	102	94.5	4.25	22)
Ethyl Cellulose (EC)	EC Pyridine Dioxane Formamid	22 35.1 23.4 19.5	NaCl	1.0	54.5	96.7	4.2	23)

Table 7.2 - 2 Outline of Non-cellulosic Reverse Osmosis Membrane

Polymer	Membrane preparation	Test condition of RO	Salt rejection	Flow-rate	ref.
Poly vinyl alcohol	MW Ca 37,000 18 wt% aq. → membrane annealing temp. 140 160°C, cross-linking	0.5% NaCl 1000 psi	22~64%	un-known	1,2
Poly vinyl pyrrolidone 	Pyridine: N-dimethylformamide = 1:1 Soln. 13.5% PVP + 13.5% MDI (13.5% PMPI) 		$[(D_{AM}/K\delta),A] = 5 \times 10^{-4}, 1.7 \times 10^{-9}$ ~ $5 \times 10^{-5}, 1.1 \times 10^{-10}$ assuming thickness = 100μ		3
Styrene-Vinylpyrrolidone copolymer	3% Chloroform Soln. 50°C 24 hrs. Drying	1% NaCl 1500 psi	98%, Decrease with time ↓	68 gfd, Increase with time ↑	23
Ethylacrylate-Vinylpyrrolidone copolymer	3% Chloroform Soln. 50°C 24 hrs. Drying	1% NaCl 1500 psi	80%, Decrease with time ↓	11 gfd, Increase with time ↓	
Galactose methacrylate-methacrylic acid copolymer 	Chloroform: ethanol = 50:50 drying in room temperature >1 hr	1% NaCl 1500 psi	1:m/n % 1:12 97.5 1: 9 97 1: 6 89 1: 4 73	gfd 0.026 0.055 0.15 0.63	
	asymmetric membrane acetone, chloroethanol, acetone-aq. acetone-DMF, chloroethanol-aq. $Mg(ClO_4)_2$, $ZnCl_2$ 1 30 min. evap.	1% NaCl 68 atm.	thickness >20μ symmetric 33% 93%	 40 gfd 0.2 gfd	7
	1:m/n = 1 : 9 Acetone-formamide = 90:10, 20% Soln. 20 casting, 1 min. evap. 20 water immerse >24 hrs. 70 10 min.	1% NaCl 800 psi	77%	2.9 gfd	
Polyethylene-oxide-Vinylmonomer copolymer 	PEO/Stylene, PEO/methacrylic acid ...cyclohexanone 2.5~5% PEO/Acrylonitrile ...dimethylformamide 2.5~5% thickness 0.02" Re-casting after 24 hrs. - 52 2 hrs.→water immersing CH_2XY X = H, Me, Y = Ph, COOH, CN	1% NaCl 600 psi " 2000 psi	thickness(μ) % gfd STY PEO% (75) 65 6.8 2.9 " (75) 41 15.9 1.75 " (56) 35 31.2 0.21 MAM (50) 35 1.50 6.0 " (—) 24 6.2 50.2		10
Ethylenglycol-monomethacrylate-Ethylenglycol-dimethacrylate copolymer	Monomer immersing in filter paper (or nylon cloth)→ copolymerization 250 300μ	4% NaCl 1800 psi	80%	0.01 m/day	11

Polymer	Membrane preparation	Test condition of RO	Salt rejection	Flow-rate	ref.
Acrylic Acid (AAc)-n-Methylol Acrylamide (NMA)-Ethyl Acrylic Acid (EA) copolymer	Teflon copolymerization →150µ	1% NaCl 1500 psi	AAc-NMA-EA (75 %,	0.15 gfd)	12
			~		
			(64 %,	0.4 gfd)	
AAc-NMA-Tri-metacryl Tri-methylol Propane copolymer (TPT)			AAc-NMA-TPT(98.5%,	0.03 gfd)	
			~		
			(91 %,	0.2 gfd)	
Polyvinylene carbonate 	DMF (DMSO) 75.6%, PVCa 15.8% Mg (ClO$_4$) 1.3%, Water 7.3% 60°C20 21 min. distillation (5 min. in DMF)→ ice water → 85°C 5 minutes	3.5% NaCl 1500 psi	DMSO 32 %,	9.2 gfd	13
			DMF 28 %,	6.4 gfd	
			" 83 %,	0.2 gfd	
Polyacrylnitoril  $-(CH_2-\underset{CN}{CH})-$		3.5% NaCl 1500 psi	25 %,	200 gfd	14
			17 %,	284 gfd	
PPO-SO$_3$H membrane 	Chloroform/Methanol = 2/1 ~ 20/1 4 ~ 10 wt % drying: more than 1 hour per 0.1 mil	1500 ppm NaCl 800 psi	IEC 1.60 2/1 90 %	14 gfd	16
			1.36 91	6	24
			1.27 91	5	
			1.60 20/1 95	6	28
			1.36 97	3	
			1.27 98	1	
Polyethylene membrane + Hydrophilic monomer grapht	Polyethlene membrane (thickness:1mm) + 25% monomer immersing Co-60 0.012 M rad/hr total 0.815 M rad	2500 ppm NaCl 400 psi	Metaacrylic Acid 52.2%	5.72gfd	17
			4-Vinyl pyridine 67.7	1.42	
			61.2	3.66	
			Acrylic Acid 53.2	5.46	
			68.2	1.47	
			Acrylic Acid + 4-Vinylpyridine 82.7	1.24	
Nylon membrane	10 25% Formic Acid Solution → (16 ~ 20 hrs. drying), (under depression 85°C, 20 60 min.), (90 150°C, 10 50 min. drying in room temperature)	10000ppm NaCl 800 psi	4-Nylon 86%	0.45gfd-mil	19
			4-Nylon blend		
		600	25% 6-Nylon 90	0.09	
		150	50% 6-Nylon 72	0.22	
		200	75% 66-Nylon 90	0.02	
		600	50% 66-Nylon 62	0.10	
		1000	6-Nylon 55	0.02	
		250	66-Nylon 76	0.02	

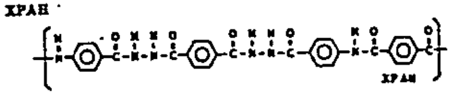
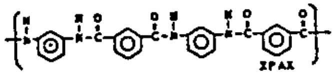
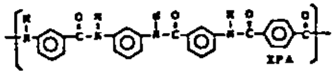
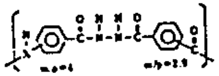
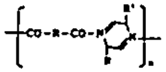
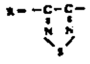
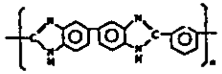
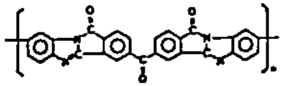
Polymer	Membrane preparation	Test condition of RO	Salt rejection	Flow-rate	ref.
Aromatic Polyamide XPAH 	5 ~15% DMSO DMF DMAc	35000ppm,NaCl 1500psi	XPAH 92.8% 98.0	8.3 gfd 1.6	19
XPAX 	room temp. 150°C 0 5 min. Ice water immersing 100°C 2.5 min. (water)	m≒0	XPAX 99.5 99.6	7.0 6.1	
XPA 			XPA 99.5 99.7	6.7 6.1	
DP-1 	DP-1, 15%, $LiNO_3$ 4.5%, DMAc 80.5% 15 mil 80°C 15 ~ 20 min. distillation → water	$J_v = k_1(\Delta p - \Delta\pi) + k_3\Delta p$ $J_s = k_2\Delta\pi + k_3\Delta p C_0$	k_1= 3.5 6.8 k_2= 1.2 3.0 k_3= 0.97 1.5	10^{-1} l/cm^2sec psi 10^{-12}mol NaCl/cm^2sec psi 10^{-12}l/cm^2sec psi	29
XPAH, XPA	(XPAH:6%, XPA:12%) $CaCl_2$ +DMAc XPAH 40 100°C 15 min. annealing	5,000ppm, NaCl 41 atm,	XPAH 69% 98 XPA 93.2 97.5	28 gfd 40°C } annealing temp. 2.5 100 3.1 15 min. } Distillation time 6.1 240	31,32
Polypyperadinamid 	Formic Acid (Chloroform-Methanol), (Chloroform-Methylen chloride 5 10 wt % 30°C Distillation → Ice water	10,000ppm,NaCl 80atm	 49% 84 R'=R''=CH_3 98	6,000 l/m^3day 2,250 ~ 600	34 44
Poly Benz Imidasol (PBI) 	PBI 23% (LiCl 1.5%, DHAc) → DMAc diluting 23 ~ 140°C casting 3 min. distillation 20 min. Ice water Ethylene glycol 180°C 10 min. annealing	5,000ppm, NaCl 600psi	95% hollow fiber 96	14 16 gfd 2.07	45 48
Poly Imidasopylolon 	Thickness 2.5 ~ 30μ from monomer	0.5% NaCl 1,500 psi 3.5% NaCl 1,500 psi	> 99% 94%	0.2 gfd 4.2 gfd	49 50

Table 7.2-3 Module Type and Characteristics

Type	Using	Membrane concentration	Support	Plugging	Easiness of cleaning	Membrane replacement
Flat type		Mediate	Complicate	Easy	Easy	Very easy
Tublar type	Internal	Small	Simple	Impossible	Very easy	Easy
	External	Small	Complex	"	Difficult	Difficult
Spiral type		Large	Simple	Easy	"	Impossible
Hollow Fine Fiber	Internal	Very large	"	Very easy	Very difficult	"
	External	"	"	"	"	"

Table 7.3-1 Operating

Operation period	July, 1975 - March, 1976
Product water	3.0 m^3/hr
Flow rate	2.2 m/hr
Coagulant	$FeCl_3$ (0.7% as Fe) 1.6~5.0 ppm as Fe
pH	7.8~8.1
pH control agent	Non
Cleaning time	120 min
Service	140~160 hrs
Backwashing water	6 m^3
Backwashingfflow rate	22 m/hr
Air backwashing	1.5 m^3/min (0.3 Kg/cm^2) × 15 min
Water backwashing	10 min
Air backwashing	15 min

Table 7.3-2 Continuous Filter Operation for Hollow Fine Fiber (A)

Operating period	July, 1975 ∿ March, 1976
Product water	2.0 m^3/hr
Flow rate	6.7 m/hr
Coagulant	PAC 0.2% as Al_2O_3, 2.5 ∿ 10 ppm as Al_2O_3
pH	6.0 ∿ 6.5
pH Control	HCl (2.3%)
Cleaning time	30 ∿ 60 min
Service time	12 ∿ 48 hrs
Backwashing water	4.5 m^3 (No.1 Filter: 1.3 m^3, No.2 Filter: 1.7 m^3, No.3 Filter: 1.5 m^3)
Backwashing flow rate	No.1 Filter: 53 m/hr, No.2 Filter: 66 m/hr, No.3 Filter: 60 m/hr
Backwashing time	5 min for each Filter
Backwashing water	Pretreated water

Ref: Coagulant dosing

1) When raw seawater quality is good: Inlet of No.2 Filter only

2) When raw seawater quality is degraded: Inlets of No.2 & No.3 Filters

Table 7.3-3 Specification of General Pretreatment Plant

Coagulation-sedimentation tank

Type : Slurry recirculation clarifier

Size : 3600 mmø x 2500 mmH

Up-flow rate : 1.6 m/hr

Detention time : 1.5 hrs

Material : Carbon steel with epoxy coating inside

No.1 Filter

Type : Pressurized two-layer filter,
Automatic backwashing

Size : 1800 mmø x 2440 mmH

LV : 5.5 m/hr

Filter media : Anthricite (0.9 mmø) 40 cm,
Sand (0.45 mmø) 40 cm

Material : Carbon steel with gum lining inside

No.2 Filter

Type : Pressurized mono-layer filter

Size : 1400 mmø x 3050 mmH

LV : 9 m/hr

Filter media : Sand (0.40 mmø) 70 cm

Material : Carbon steel with gum lining inside

Table 7.3-4 Continuous Operating Condition and Backwashing Condition of Filter

Operating period		May 15∿Sept. 22, 1976	Nov. 1∿Dec. 20, 1976	Jan. 8∿March 23, 1976
Process for water amount	Coagulation & sedimentation tank	7.0 m^3/hr	8.0∿10.0 m^3/hr	7.0 m^3/hr
	Two-layer filter	6.0 m^3/hr	7.0∿ 9.0 m^3/hr	6.0 m^3/hr
	Polishing filter	5.0 m^3/hr	6.0∿ 8.0 m^3/hr	5.5 m^3/hr
Surface water loadings	Coagulation & sedimentation tank	0.83 m^3/m^2.hr	0.95∿1.2m^3/m^2.hr	0.83 m^3/m^2·hr
Flow rate	Two-layer filter	2.4 m/hr	2.8 ∿3.5 m/hr	2.4 m/hr
	Polishing filter	3.3 m/hr	4.0 ∿5.2 m/hr	3.6 m/hr
Service time	Two-layer filter	200∿ 940 hrs	150∿300 hrs	120 hrs
	Polishing filter	150∿1900 "	200∿430 "	200∿900 hrs
Backwashing water amount	Two-layer filter	15.0 m^3		
	Polishing filter	15∿23 m^3		
Backwashing flow rate	Two-layer filter	30 m/hr		
	Polishing filter	30 m/hr		
Backwashing	Two-layer filter	1.0 hrs		
	Polishing filter	2.0 hrs		
Air	Two-layer filter	2.0 m^3/min (0.4 kg/cm^2)		
Backwashing time by air	Two-layer filter	10∿15 min		
Backwashing time by water	Two-layer filter	10 min		
	Polishing filter	20∿30 min		
Coagulants (ppm as Fe)		2.0∿3.0	1.0∿4.0	2.4∿2.6
Chlorine (ppm as Cl_2)		1.0∿4.0	1.0∿3.5	0.9∿1.8
pH		5.8∿6.6	6.0∿6.5	5.8∿6.1
pH adjustment		75% H_2SO_4		

Table 7.4-1 Module Specification for One-Stage RO Module

Type	Spiral	Hollow fiber (A)	Hollow fiber (B)
Maker	UOP (U.S)	Du Pont (U.S)	Dow Chemical (U.S)
Name of module	ROGA-2B-TF	Permasep B-10	XFS416708
Material	Tricellulose acetate	Poliamide	Tricellulose acetate
Module size	2" x $10\frac{3}{4}$"	$5\frac{1}{2}$"O.D x $4\frac{5}{8}$"I.D x 47"	$8\frac{5}{8}$" x 40"
Element No./module	40 elements	Full size 1 element Half size 1 element	1 element
Membrane area/module	1 leaf about 4 ft^2 (0.36 m^2)	98μ x 46μ 1500 ft^2(139 m^2)	90μ x 40μ 335 m^2
Water flux/module	32GPD (120 ℓ/day)	1500GPD (5.5 m^3/day)	2500GPD (9.4 m^3/day)
Rejection rate (as NaCl)	98.5%	98.5%	98.7%
Applied pressure	60 kg/cm^2	56 kg/cm^2	56 kg/cm^2
Applied temperature	$\leqq$ 35°C	$\leqq$ 35°C	$\leqq$ 35°C
pH range	4 ∿ 7.5	5 ∿ 9	4 ∿ 7.5
Residual chlorine	< 1.0 ppm	< 0.1 ppm	< 1.0 ppm

Table 7.4-2 Module Specification for Two-Stage Desalination

Type	Spiral wound	Tablar	Hollow fine fiber
Maker	Toray	Kobe Seiko - Nitto Denko	Toyobo
Name	Toray SC 5000A,B	Nitto NRO-A,B	HR-5350, HR-5330S
Membrane material	Cellulose acetate	Cellulose acetate	cellulose acetate
Module size	4"ø x 1 m	109 mmø x 2674 mm	140 mm(O.D) x 1200 mm
Membrane area	6.8 m^2	1.75 m^2, 12.5 mm(I.D) x 18 pcs.	65 m^2
Applied temperature	< 35°C	< 35°C	
pH	4∿7	4∿7	3∿7
Residual Cl^-	< 1 ppm	< 1 ppm	< 1 ppm
Water flux	SC-5000A: 2.0 m^3/day SC-5000B: 3.2 m^3/day	NRO-A: 0.74 m^3/day NRO-B: 0.56 m^3/day	HR-5350 : 2.5 m^3/day HR-5330S: 10 m^3/day
Rejection rate	SC-5000A: 95% SC-5000B: 98%	NRO-A: 96.5% NRO-B: 97.5%	HR-5350 : > 90% HR-5330S: > 90%
Module performance	A: NaCl 38,000 ppm Pressure 50 kg	A: 5,000 ppm 40 kg	HR-5350 : 35,000 ppm 50 kg
Measuring condition	B: NaCl 30 kg Pressure 16,000 ppm	B: 5,000 ppm 40 kg	HR-5330S: 2,000 ppm 30 kg

Table 7.6-1 Desalination Water Cost for Fresh Seawater with RO Method
(OWRT Calculation example) \$1.00 = ¥300

Calculation Criteria

Plant capacity : 1 MGD (3,800 m^3/day)

Plant type : One-stage desalination

Operating condition: Pressure : 800 psi (56 kg/cm^2)
Recovery rate: 80%

Energy recovery : Exist

Membrane life : 3 year, Power consumption: 6 Yen/kWh

Interest : Interest 8%
Insurance: 0.25%/year
Tax : 1%/year

Construction Cost

Pretreatment	90,000 (x 10^3 Yen)
Intake facility	60,000
Low pressure pumps	6,000
High pressure pumps, Energy recovery	90,000
RO modules	210,000
Piping & Valving	60,000
Tanks	18,000
	534,000 x 10^3 Yen

Operation & Maintenance Cost

Plant amortization cost	34 Yen
Maintenance cost	4
Repairing cost	14
Personel expenditure	8
Chemicals	11
Power consumption	38
Membrane replacement	33
	142 Yen/m^3

Amortization cost (20 years)	32 Yen
Tax, Insurance, General	45
Total:	399/317/290
Membrane life	1 year/2 years/3 years

Table 7.6-2 Desalination Water Cost by Dow Chemical
(200 m^3/day capacity)

- Construction cost Yen 5.4 million
- Operating ratio 90%
- Standard price for middle of 1975

Overhead (Operationg & Maintenance)	¥26
Cartridge filter	3
Chemicals	13
Pretreatment amortization cost (Sand filter, 20 years)	34
Membrane replacement cost (one/two/three years of life)	164/83/55
Material cost for maintenance	8
Power consumption (60% efficiency, ¥6/kWh)	75

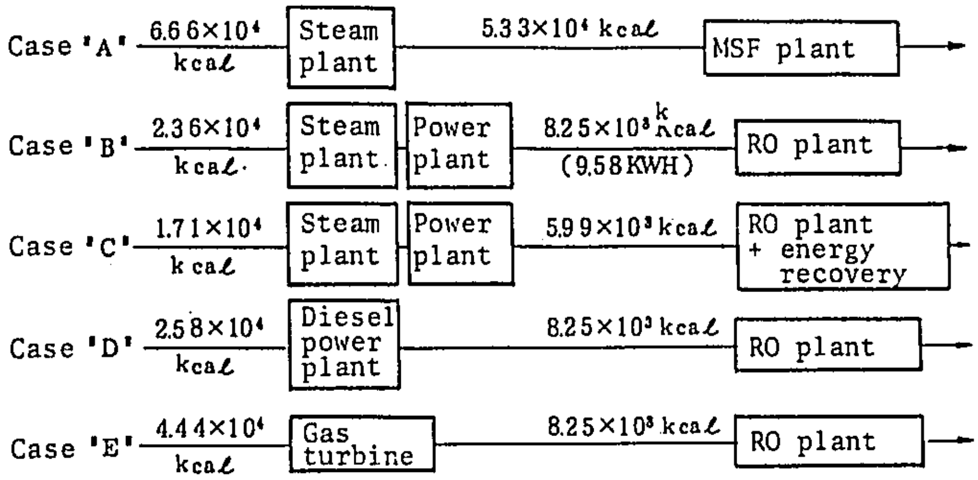
Table 7.6-3 Cast study of Desalination Water Cost in Japan 3)

	Ratio (%)	Amount (Yen)
(1) Amortization cost	29.3	104
(2) Maintenance material cost	1.4	5
(3) Operating cost		
Power cost	27.4	97
Steam cost	7.3	26
Operation man power	1.3	5
Membrane replacement	28.8	102
General administration	2.7	10
Chemicals	3.8	13
(4) Insurance	0.6	2
Total	100.0	354

Table 7.6-4 Comparison of energy consumption between reverse osmosis and distillation

Condition

MSF plant : Ratio 10
RO plant : 70 atm, Recovery rate 25%
Steam plant: 80% EH.
Power plant: 56% EH.
Diesel : 32% EH.
Energy requirement/m^3 product water



Product-water	2,000 m^3/d	5,000 m^3/d	10,000 m^3/d	30,000 m^3/d
Product-water cost yen/m^3	353	333	320	310

VIII. Methods of Seawater and Freshwater Analysis

8.1. Methods of Seawater Analysis

8.1.1. General Analysis

In analyzing seawater, the most important item for general analysis is to determine chlorinity. It is because, as already stated in the section 2, Properties of Seawater, this analysis makes clear various physical properties of seawater and also enables approximate estimation of the contents of other principal constituents. Further, it enables grasping of various characteristics of water mass under different conditions, for example, influences of land water such as river water. However, among those included in principal components, strontium (Sr), boron (B) and fluorine (F) have little importance to the desalination of seawater and, therefore, reference is only made to literature on the methods of analysis regarded to be most suitable for them. On the other hand, nutritive salts, dissolved oxygen and suspended substances are included in the items of analysis as they have relevance in general.

(1) Principal constituents

(a) Chloride ions ($C\ell^-$)

Chloride ions are determined by either of the first two methods described below where high accuracy (0.01% or less) is required but, in general, salinometer methods are applied.

(i) Salinometer methods

Measurement is made with sample water to calculate the chlorinity with an induction-type electric conductometer, of which temperature and specific conductivity dials are set beforehand based on standard seawater (in general, the seawater contained in an ampul which has been verified by the Ocean Research Institution of Denmark, with its chloride ions indicated down to the third decimal place). The method is suitable for measurement principally where influences of ocean water and river runoff are not conspicuous, since it develops the highest accuracy within a range of 17 to 21% in chlorinity and accuracy decreases with increasing departure from this range.

(ii) Knudsen method (improved method)

Operation is approximately the same as in Mohr's method mentioned below. The quantity of sample seawater is measured with the Knudsen pipet 10 mℓ and titration with a silver nitrate solution of relatively high concentration (about 0.353 N) is performed using a piston buret, of which capacity can be read down to 0.01 mℓ. Standardization of this solution is made by the standard seawater. Different from the method (i), it can be applied to sample water of low salinity which is almost the same as fresh water.

(iii) Mohr's method

25 mℓ of sample water diluted 10 times is mixed with 1 mℓ of a potassium chromate solution and around 25 mℓ of pure water and titration is made with a silver nitrate solution of 0.1 N. Titrating is continued until the point, that is the end point, when the suspended solution ceases to change its color after having discolored from yellow to orange, and the chlorinity at this end point is calculated from the titration value. Separately from the above, 50 mℓ of pure water added with 0.5 g of calcium carbonate powder not including chloride ions is operated on in the same manner as above and this titration value is used to correct the former titration value. The silver nitrate solution of 0.1 N to be used must be standardized based

on sodium chloride (a standard reagent). Although this method is somewhat less accurate as analysis compared with the above two methods, it does not need special apparatuses and is suitable for routine work.

However, as the chlorinity determined by any of these methods includes bromide ions (Br^-), values obtained multiplying the values of bromine ions determined separately by 0.444 are deducted for correction where the values only of chloride ions ($C\ell^-$) are required.

* Where chloride ions are expressed by chlorinity it is indicated as $^0/_{00}$ more frequently, though it is usually indicated as g/ℓ in the method (iii).

(b) Sulfate ions ($SO_4{}^{2--}$)

Methods to determine sulfate ions include, in addition to the gravimetric method, EDTA titration and iodometer titration with barium chromate, among which the gravimetric method is the most reliable in view of accuracy. The basis of the methods is to add a solution of barium chloride to precipitate barium sulfate ($BaSO_4$).

50 mℓ of sample water mixed successively with 230 mℓ of pure water, 10 mℓ of saturated solution of picric acid and 5 mℓ of hydrochloric acid is heated to a temperature of about 90°C. Then warmed 10% solution of barium chloride is added to the sample while being agitated sufficiently and the warming is continued. Then, precipitates taken on a fine quantitative filter paper are washed with warm water and, after having dried together with the filter paper, burned in a platinum crucible to be reduced to ashes, which are ignited at 800°C for about 2 hours, allowed to cool in a dessicator and weighed. Values obtained are multiplied by 0.4115 to determine sulfate ions. Where a fritted silica

filter is available, it is preferable to use it, and after filtering, washing and heating at 100°C for 30 minutes, igniting is performed in the same way as above.

(c) Bromide ion (Br^-)

At present, the only reliable method is to oxidize bromide ions by a solution of sodium hypochlorite to form bromate ions (BrO_3^-) which are determined by iodometric titration.

10 mℓ of sample water mixed successively with 10 mℓ of 10% solution of sodium chloride, 10 mℓ of 5% solution of sodium dihydrogenphosphate and 2 mℓ of 1 N solution of sodium hyphchlorite is increased to about 40 mℓ by adding pure water. The sample prepared is heated on a hot plate and immediately after having boiled for 5 seconds it is taken down from the hot plate, 5 mℓ of 50% solution of sodium formate is added while being agitated, and then cooled to the normal temperature. After the sample has 0.25 g of potassium iodide, several drops of 3% solution of ammonium molybdate and 10 mℓ of 6 N sulfuric acid added, having been left as it is for 30 seconds, it is titrated with 0.002 N sodium thiosulfate and, when it is colored light yellow, a 1% solution of α starch is added to continue the titration until the sample is decolored. A titration value separately obtained from 10 mℓ of pure water operated in the same way as above is deducted from the former titration value to obtain the required value. 1 mℓ of 0.002 N sodium thiosulfate corresponds to 0.02663 mg of bromide ion.
A solution of sodium thiosulfate is obtained from 0.1 N solution prepared beforehand and standardized with the standard 0.1 N solution of pottasium iodate. The solution is diluted to a 0.002 N solution each time to use for analysis.

(d) Boron $[B(OH)_3]$ and fluoride (F^-) ions

As these ions are to be determined in the electrolysis and reverse osmosis processes, analytical methods and literature adoptable in these cases are listed here. The mannite alkali titration method is applicable to boron and absorptiometry by alizarin complexion to fluorine. The former method is not so sensitive but reliable values can be obtained.

(e) Calcium ion (Ca^{2+})

There are two methods, the EGTA method of high accuracy and the EDTA method. These are chelatemetric titrations. Since strontium ions are determined together with calcium ions by these methods, the former ions are measured separately to use for correction if necessary. Methods for this measurement are omitted here and literature is given instead [Anderson, Hume: Analytica Chim. Acta 40, 207 (1968)].

(i) EGTA method

10 mℓ of sample water is mixed with 95% of the expected quantity of the standard solution of 0.01 M - EGTA and agitated. Then the sample is mixed 4 mℓ of 0.05% GHA solution and the same quantity of sodium borate buffer is agitated for 3 minutes to forma Ca - GHA complex, which is extracted by adding 7 mℓ of n - butyl alcohol. Then the titration is continued with the standard solution of EGTA until the end point indicated by the organic solvent layer turning from red to completely colorless. In this case, the titration is arranged so as to be complete within 15 minutes because the complex is unstable. 1 mℓ of 0.01 M - EGTA corresponds to 0.4008 mg of calcium ion.

(ii) EDTA method

5 mℓ of sample water is mixed with 4% solution of sodium hydroxide drop by drop while being violently agitated until white precipitate is formed and pH becomes 11.5 or higher. Then, the sample is mixed with about 30 mg of pottasium cyanide, 1 mℓ of 5% solution of hydroxylamine hydrochloride and 0.7 g of NN diluted powder reagent is titrated with the standard solution of 0.01 M EDTA until the end point when the sample changes its color completely from reddish purple to blue. 1 mℓ of 0.01 M EDTA corresponds to 0.4008 mg of calcium ion.

(f) Magnesium ion (Mg^{2+})

10 mℓ of sample water is mixed successively with 5 mℓ of pH 10 buffer solution of ammonium chloride - aqueous ammonia, 1 mℓ of 5% solution of hydroxylamine hydrochloride and 0.2% EBT solution is titrated with the standard solution of 0.01 M EDTA while being agitated, avoiding direct rays of the sun, until the end point when its color changes from red to blue completely. 1 mℓ of the standard solution corresponds to 0.2431 mg of magnesium ion. Since this titration value includes both calcium and strontium ions expressed as content, the value of calcium ions separetely determined must be deducted from it to calculate the quantity of magnesium ions. Also, the colorimetric titration method at a wavelength of 640 mm which aims at high precision determination and direct colorimetry of magnesium ions by thymolphthalein complexone may be applied but their procedure is rather complicated.

(g) Potassium ions (K^+)

Flame photometric and hexyl methods can be used to determine potassium ions, but the flame method when applied to seawater has a defect that it is subjected to much interference from sodium ions, and the hexyl method may cause irregularity in composition depending upon conditions. Therefore, the gravimetric method by tetraphenyl boron which is the most reliable is applied frequently.

10 mℓ of sample seawater, to which is added 0.5 mℓ of hydrochloric acid, has 10 mℓ of 0.6% solution of tetraphenyl boric acid sodium added drop by drop while being agitated. The solution, having been left intact for a few minute, is filtered through a fine glass filter, washed throughly with a washing solution, dried at 105°C for 30 minutes and weighed. The value obtained is multiplied by 0.1091 to obtain the quantity of potassium ions. In this method, ammonium ions are determined together and this quantity is corrected where the sample water contains many ammonium ions, that is, 18.7 mg reduced from the weighed value per 1 mg of ammonium ions.

(h) Sodium ions (Na^+)

Methods to determine sodium ions include gravimetry by sodium zine uranyl acetate and flame photometry. However, as both the methods are not very accurate, direct determination is not performed ordinarily and the residual value of combined calculation of salts from the determined values of other various ions is taken as that of sodium ions in many cases.

(i) Alkalinity

Alkalinity is a small part of alkaline substances, that is, bicarbonate, carbonate, hydroxide ions and boron compounds, expressed as meq/ℓ or emp and the greater part constitutes the indices of quantities of bicarbonate ions. Methods to measure alkalinity include the precise pH method, which finds it from pH obtainable under certain conditions, and the titration method which is somewhat simpler.

(i) pH method

Precisely 25 mℓ of 0.070 N standard solution of hydrochloric acid put in a thoroughly washed flask with ground stopper of 125 mℓ in capacity has accurately added 100 mℓ of sample water and is agitated sufficiently and the indication of the pH meter is read to the 2nd decimal place and the salinity is found from the following expression and annexed table. First, C^{H+} is calculated by the following expression based on the pH reading.

$$pH = -\log C^{H+} \cdot f^{H} . f^{H+}$$

Wherein f^{H+} is the activity coefficient of H^{+} and is found from the following table because it varies with the quantity of chlorinity.

Chlorinity (‰)	10	12	14	16	18	20
f^{H+}	0.755	0.752	0.752	0.754	0.754	0.758

Alkalinity (meq/ℓ = 2,500 - (1,250 x C^{H+})

(ii) Titration method

100 mℓ of sample water in which a complex electrode connected to a pH meter of 0.03 or less in accuracy is inserted, is placed on a magnetic agitator and titrated with 0.01 N standard solution of hydrochloric acid until pH indicates exactly 4.80; then the volume is read down to 0.01 mℓ and the alkalinity (meq/ℓ) is found from this titration value. Although rather less accurate, the alkalinity can be found, instead of using the pH meter, by performing titration with an ethyl alcohol indicator containing methyl red of 0.02% and bromocresol green of 0.7% until the solution becomes yellowish green.

(2) Nutritive Salts

In general, nutritive salts include nitrogen in the forms of ammonium, nitrite and nitrate, phosphorus as phosphate and silicon as silicate state, each of which is expressed as mg·at/ℓ in many instances. Sometimes, respective ions are shown as mg/ℓ.

(a) Ammonium ions (NH_4^+)

50 m of sample water is mixed with 2 mℓ of 2.5% solution of phenol containing a trace of nitroprusside and mixed thoroughly. Then the sample has added 2 mℓ of solution of sodium hypochlorite - sodium hydroxide containing free chlorine of about 0.1% and mixed up, and after having left as it is for around 4 hours its supernatant is taken out to apply obsorptiometry at a wavelength of 630 mm. The same operation is separately performed with pure water for correction purposes.

(b) Nitrite ion (NO_2^-)

50 mℓ of sample water is mixed with exactly 1.0 mℓ of 1.2 N hydrochloric acid solution of sulufanilamide and made to react for several minutes. Then, the sample is mixed with 1.0 mℓ of 0.1% solution of N-(1-naphthyl) ethylenediamine hydrochloride and in between 10 minutes and 2 hours after that, absorptiometry is applied at a wavelength of 535 mm. The same operation is separately performed with 50 mℓ of pure water for correction purposes.

(c) Nitrate ion (NO_3^-)

A column filled with cadmium powder coated with copper is washed in advance by passing fresh water and then about 0.7% EDTA solution to prepare a column to use for reduction.

About 100 mℓ of sample water is mixed with 1 mℓ of the EDTA solution above-mentioned and is made to pass through the column at a rate of about 10 mℓ per minute. After washing 30 to 40 mℓ of the initial runoff, 50 mℓ of the sample is taken from the subsequent runoff to perform the analytical operation in accordance with that for nitrite ions.

(d) Phosphate ions (PO_4^{3-})

50 mℓ of sample water is mixed with 50 mℓ of mixed reagent, and in between 3 minutes and 3 hours after that, absorption photometry is applied at a wavelength of 885 mm. The same operation is separately performed with pure water for correction purposes.

(e) Silicic acid [$Si(OH)_4$]

10 mℓ of 0.8% solution of ammonium molybdate - hydrochloric acid is put in a measuring cylinder 50 mℓ in capacity, with a ground stopper, in which it has been confirmed that no elution of silicic acid is found. 25 mℓ of sample water which was contained in a polyethylene bottle in advance is added to and mixed with the above solution and left as it is for 10 minutes. Then, a mixed reagent of methol - sodium sulfite - oxalic acid is filled to the mark of 50 mℓ and after the sample having been left as it is for 2 to 3 hours, absorptiometry is applied at a wavelength of 810 mm. The same operation is seperately performed with 25 mℓ pure water for correction purposes.

(3) Suspended substances and dissolved oxygen

Suspended substances include mainly clay minerals, animal and plant plankton and its disintegrated material and also solid pollutants. As they are mixtures of varied materials and, in addition, their particle sizes are indeterminate, their quantities are generally determined by gravimetric methods. Dissolved oxygen is generally determined by a method similar to the iodine titration method by Winkler.

(a) Suspended substances (SS)

A certain quantity of seawater (preferably a quantity not exceeding 5 mg in a weight) is passed through organic synthetic fiber or glass fiber of 0.45 to 0.9 in pore size by using a filter provided with a fritted glass plate for exclusive use. Then vacuum suction washing with pure water is applied to the fiber filter until the adhering salts become traces; then the filter is removed and dried at 105°C to 110°C; and the gain in weight of the filter is the content of suspended substances which is expressed as ppm or mg/ℓ.

(b) Dissolved oxygen

Although the process is similar to that of Winkler, a part of it is changed in compliance with the caution given in JIS K-0102-(1974) 17-17-4 and the determination is made by the amended Winkler - sodium azide method, as it is called. A container, known as an oxygen bottle, of 100 mℓ in capacity is carefully filled to the brim with sample water so that air is not contained in it and 0.5 mℓ of 40% solution of manganese chloride and 0.5 mℓ of mixed solution of about 10% potassium iodide - about 8 N sodium hydroxide are injected into the sample. Then it is bottled up immediately excluding any air from entering it and after having been tumbled up and down about 30 times, it is left as it is for several hours. First, 5 to 10 mℓ of supernatant is taken in a beaker and the sample in the bottle is added 3 N hydrochloric acid to dissolve precipitate and then transferred into the beaker to be titrated with iodine according to the normal process.

8.1.2. Analysis in Distillation Process

(1) Scale

In plants of multistage flash type which are most frequently used at present among the desalination plants of distillation process, scale or sludge deposited on the insides of heat transfer tubes of respective stages may be roughly classified into three types. As shown in Table 8.1-1, since scale differs in the regions of temperatures in which it deposits, adhesiveness to tube walls and agents used to dissolve and remove it, caution should be exercised in sampling. In particular, where multistage flash-type plants use heat transfer tubes of a long type, examinations should be made taking into account the fact that quantities and components of scale vary according to the parts even in the same condenser tube due to differences in the steam temperatures in respective flash stages.

As the components and adhering conditions of scale are also influenced by preventive methods, any analysis of scale is required to be made knowing which method is applied from among conventional methods which use polymer phosphate scale inhibitors, pH control methods which use sulphuric acid and methods to inject carboxylate additive which have been increasingly adopted in recent times.

The chemical analysis of scale extracted from plants starts with the decomposition of samples, and the operation of quantitative determination is simplified by dividing it into two systems according to the chemical properties of elements to be analyzed as shown in Fig. 8.1-1. In the first system, CO_3^{2-} is determined from the gas generated when a sample is dissolved with hydrochloric acid alone and C is measured from residues. In the second system, Ca, Mg and others are determined from a sample solution which is prepared by dissolving scale into mixed acid of hydrochloric acid and nitric acid (sulfuric acid cannot be used because Ca and SO_4 is contained in scale) and perchloric acid which have strong dissolving power.

Methods to measure qualitatively the coposing elements of scale include fluorescence X-rays analysis and emission spectrometrical analysis.

As it is difficult to establish standard methods of analysis uniformly for a substance such as scale of which constituents and limits of composition are not necessarily defined, analytical methods of scale themselves are not prescribed in any JIS. ASTM D2331-73 Water-Formed Deposit is suggestive of methods of sample decomposition, and JIS K0101 Methods of Industrial Water Test and JIS G1211 Determination of Carbon in Iron and Steel are instructive for determination after the sample is converted into a solution. Methods of determination shown in Table 8.1-2 are those suitable for analyzing the components of scale.

(2) Corrosion (Analysis of dissolved oxygen)

As started already, the quantity of dissolved oxygen in brine or seawater in various parts of a desalination plant constitutes an important factor which has direct influence on the corrosion of metal materials. The brine passing through a plant of multistage flash type usually contains dissolved oxygen ranging from several ppm to tens of ppb according to operating conditions and respective parts in the plant, and a concentration of this order is sufficient to cause corrosion if the temperature of the brine is high. Therefore, methods of oxygen analysis must be those capable of measuring 5 ppb or less with certainty. In recent times, in particular, there are some cases where deaeration by the injection of reducing agents is used jointly with vacuum deaeration and this practice may require analysis of higher precision.

In general, as the concentration of oxygen during operation changes delicately depending on the way of operation in many cases, it is desirable that a concentration as low as 1 ppb or less can be continuously recorded if possible. To meet these requirements, instrumental methods of analysis as described below can be applied but, although they are very convenient methods, handling of them requires a fair amount of skill.

(a) Methods of chemical analysis

Chemical analysis of dissolved oxygen is performed ordinarily by the iodine method (the Winkler method) which the advantage that it is not influenced by dissolved substances except oxidant such as residual chlorine or reductant such as organic matter. Where trace dissolved oxygen of 0.01 ppm or less is measured, a method of potentiometric or amperometric titration, a subdivision of the above method, is applied.

(b) Dissolved oxygen meter

There are dissolved oxygen meters of electrochemical, electric conductometric and heat conductometric types. The meter shown in Fig. 8.1-2 as an example is one of the meters of conductometric type. When a sample solution (an electrolytic solution) into which two electrodes, one of platinum and the other of gold, are inserted is fed with hydrogen gas, the platinum electrode is polarized by hydrogen. Oxygen in the sample, having arrived there, reacts with hydrogen on the surface of the gold electrode and is converted into water, and thus an electric charge corresponding to the reaction moves to the platinum electrode through an exterior circuit, producing a potential difference proportional to the quantity of oxygen. From this difference, the oxygen can be determined.

This device is capable of continuously measuring the quantity of trace oxygen in seawater and also verifying by the standard eletrolysis cell, and thus it is especially convenient for research purposes.

Recently, sensors of a probe type have come to be used fairly widely for continuous measure. This is a variety of the electrochemical type which utilizes polarography and was originally used as a on-line meter for the feed water of boilers. Therefore, where there is a fear of pollutant being mixed in the seawater, dirt adhering to the surface of teflon membranes which permeate gas should be watched and the membranes must be renewed at proper times. The limits of measurement are 0 to 200 ppb and the accuracy is within ±1% of the full scale.

(3) Pollution

Of ammonium, COD and sulfide ions (S^{2-}) which are the important indices of polluted seawater, the first two are dealt with in the general analysis, and methods of analysis for trace sulfur ions are described in the following.

In JIS K0101, colorimetric methods are adopted which use p - phenylenediamine. On the other hand, where a large number of samples of low concentration are measured, reliable results cannot be obtained unless sulfide ions are fixed because they are unstable. However, in the JIS method, fixing agents interfere with coloring, making it difficult to find accurate values. The National Chemical Laboratory for Industry has obtained satisfactory results by using dimethyl - p - phenylenediamine as a color reagent and zinc acetate as a fixing agent. The limit of determination for sulfide ions is 8 μg in the JIS method, but it has become possible to measure trace sulfide ions down to 0.25 μg (6.5% in the standard rate of deviation) at all times and as low as 0.08 to 0.10 μg if the extracting method by nitrobenzene is used jointly.

The operating process developed is as outlined in the following: A sample is added with an aqueous solution of zinc acetate to fix sulfide ions, and the sample is adjusted approximately to a fixed quantity by adding water. Then the sample is mixed with dimethyl - p - phenylenediamine (p - aminodimethylaniline), a color reagent, and an aqueous solution of ferric chloride and is shaken thoroughly. The sample having adjusted accurately to the fixed quantity is left as it is for a fixed time and after that absorptiometry is applied at a wavelength of 660 µm. If the coloring is weak in the above operation, the sample is extracted by nitrobenzene and the absorbance of the nitrobenzene phase is measured.

Sulfate ions in seawater and interstitial water of bottom mud was measured in the Tokyo Bay and Ototsu Port of Oita Prefecture and the results of the measurement are shown in the following table.

8.1.3. Analysis in Membrane Methods

Methods of operation control and, in particular, pretreatment of raw feed water are most important to maintain the performance of reverse osmosis plants in a stable condition for a long period.

Here, a brief description is given about items to indicate and methods to measure the quality of water fed to reverse osmosis plants (RO feed water) and methods to select and test flocculant necessary to obtain water of the standard quality, these methods being used in general.

(1) Methods of water quality measurement

(a) FI value (Fouling Index)

Although SS measurement and turbidity meters are generally used as the methods to measure turbidity in water, the tolerance limits of fine turbid substances in the RO feed water are below the lower limit value which can be measured with conventional turbidity meters and thus it is necessary to find a new method of measurement. The FI values are one of indicators which express the quantity of traces of turbid substances existing in RO feed water.

Method of measurement. The device shown in Fig. 8.1-3 is generally used as a measuring instrument. About 20ℓ of the sample solution contained in a pressure storage tank is filtered under a fixed pressure (2.1 kg/cm^{2}G) through a membrane filter of 0.45μ (of HA type manufactured by Milipore Co.). At the start of filtration, the time (t_0 seconds) taken to filter the first 500 mℓ is measured and then after the filtration having continued for 15 minutes the time (t_{15} seconds) taken to obtain 500 mℓ of filtered solution is measured. The FI value is calculated by the following expression.

$$FI = \left(1 - \frac{t_0}{t_{15}}\right) \times 100/15$$

Pressure
gage

The standard of the FI values is generally 3 or less for the feed water to the modules of hollow fiber type, but an FI value of 5 to 6 will suffice for those of spiral type.

(b) MF values

This method measures fine turbid substances in the RO feed water using the membrane filter in the same manner as the FI method.

Method of measurement. The time (t seconds) taken to filter 1ℓ of sample water through the membrane filter of 0.45μ (of HA type manufactured by Milipore Co.) in the vacuum of 500 mmHg is measured using a suction bottle as shown in Fig. 8.1-4, to find MF filtration time. As the MF filtration time is influenced by water temperature, it is expressed at a standard temperature of 25°C. It makes little difference that the conversion factor of temperature is in inverse proportion to the coefficient of viscosity of water. The standard of MF filtration time for RO feed water is 300 seconds or less. A strong point of this method is that the quantity of fine turbid substances captured on the membrane filter can be roughly indicated based on a coloring degree (MF coloring degree), and the standard of such a degree for RO feed water is generally 15 or less.

The method of MF measurement is mainly used to evaluate water fed to the RO modules of the spiral type and is comparatively simpler than the method of FI value measurement. Also it is a convenient method capable of measurement covering a wide range of high turbidity which can be measured with an ordinary turbidimeter for very clear water (3 or less in FI values).

(c) Constituents of scale

In order to prevent scale from depositing on the surface of reverse osmosis membranes, it is necessary to analyze beforehand the constituents of scale dissolved in RO feed water and keep the concentration within the deposition limits of scale. The constituents of scale generally include $CaSO_4$, $CaCO_3$ and SiO_2, and as to the method for analyzing scale, reference is made to section "8.1 - Methods of Seawater Analysis".

(d) Residual chlorine

In order to prevent bacterial growth in the modules of reverse osmosis membranes, it is necessary to sterilize RO feed water by the injection of chlorine. Residual chlorine in RO feed water is ordinarily adjusted to be 0.3 to 0.5 ppm as $C\ell_2$.

Method of measurement. - Reference is made to JIS K0102-1974 26 "Residual Chlorine".

In general, since residual chlorine easily passes through RO membranes, it is detected respectively from RO feed, permeate, and brine water approximately in the same quantity. As membrane of aromatic polyamide is easily affected by residual chlorine, it is necessary to remove such chlorine completely from the water fed to them.

(e) Bacteria

In order to confirm whether chlorination of RO feed water is performed sufficiently, it is necessary to count at times the number of bacteria respectively in RO feed, permeate, and brine water. Methods of bacteria count are described in detail in JIS K0101 "Bacteria Test" and ASTM "60 - 68" and the following method is frequently used as a simplified method of counting bacteria of RO feed water.

Method of measurement. - A case from the Total-Count^{TM} sampler manufactured by the Milipore Co. (Product No. MT 0000025) is taken out and is filled with sample water up to the line marked on it. Then the sampler, after having been dipped in the sample water for 30 seconds, is taken out and excess water is shaken off. Water in the case is emptied and the sampler is put in the emptied case. Then cultivation is performed with the filter surface of the sampler placed downside in an incubator (at 35°C) for 24 hours. Colonies generated on the filter of the sampler are counted, and the number of colonies is generally regarded as the number of bacteria (piece/mℓ).

(2) Selection tests of flocculant

In securing stable performance of RO plants keeping the measured MF and FI values of feed water within the standard values, it is most important to select a flocculant which is used in the pretreatment process and to determine the conditions of fluocculation. A jar test device is ordinarily applied for the latter determination.

Jar test. - Sample raw water is put in several beakers of 500 to 1,000 mℓ in capacity and different quantities of flocculant of prescribed pH are added to respective beakers. Then the jar test devices are agitated briskly (at 150 rpm) for the first 5 minutes or so, and then slowly (at 50 rpm) for about 10 minutes.

After letting the devices stand still, observation is made of the size of flocks, state of formation, time taken to precipitate and conditions of supernatant to compare the results of tests under different conditions. Based on the results of observation, the optimum kinds of flocculant and the quantity to be added as well as assistance of polymer additives if necessary, are selected to determine the accurate conditions of flocculation and filtration for plants of practical use.

8.2. Methods of Fresh Water Analysis

8.2.1. Drinking Water

In analyzing drinking water, items and methods of analysis and standards of judgement on drinkableness are determined principally from the sanitary point of view. In general, the analysis is apt to be considered to be easy because drinking water contains far less impurities compared with mineral water, industrial waste and sewage. But, on the other hand, not only considerably higher accuracy is demanded in the analysis, but also any error in the results can never be allowed. However, the methods of analysis can be applied as well to water other than drinking water and are used to analyze fresh or medium-contaminated water, and also many items are common to those of analysis for other purposes.

If desalinated seawater is supplied as drinking water to a specific area, legally it will be treated as tap water. Therefore, legally speaking, the suitability as drinking water depends upon whether or not the said water satisfies the requirements of water standards for tap water (Ordinance No.11, 1966, of the Ministry of Health and Welfare; see data at the end of this book). Actually, the public health centers and others in various places in the country apply these water standards to judge the drinkableness of well water, etc. other than tap water.

These standards specify the methods of examinations respectively for 26 quality items and the tolerance limits of values measured by the examinations. However, as 11 years have passed since their promulgation, today they have become unsuitable for the realities of the society in some respects and their defects have been covered by the administrative guidance of the ministry of Health and Welfare and the efforts of various self-governing communities, as a result of which it is intended to revise them almost completely in the near future.

Table 8.2-1 lists the methods of examination for each item of the present water standards and reference is made to the Ordinance of the Ministry of Health and Welfare for further information.

These methods of tests can be easily applied in inadequately equipped water laboratories in general and those laboratories which are adequately equipped and excellent in technique can adopt other methods which they think more suitable. However, where the results of examination concern legal issues, the methods prescribed by the Ordinance will have to be used.

Notifications of the Ministry of Health and Welfare issued after the promulgation of the said Ordinance provided guidance standards specifying the content of cadmium to be 0.01 ppm (KANKOKO No. 9098, Nov. 11, 1966, and KANSUI 81, July 26, 1974) and that of mercury 0.001 ppm or less (KANSUI 51, Apr. 19, 1974) and also recommended to apply, in measuring the total quantity of mercury, reducing vaporization atomic absorptiometry which includes pretreatment to resolve organic matter by using potassium permanganate and potassium persulfate. As regards radioactivity in water, the allowable quantity specified is 10^{-7} μCi/mℓ where the nuclides of radioactive isotopes are not known (Notification No.22 of the Science and Technology Agency). As for various harmful organic compounds (PCB, ester phthalate, organic chlorine compounds and agricultural chemicals, etc.) which are recent issues debated by the press, various methods of analysis are proposed, including gas chromatographic analysis in the main, although any legal obligation is not charged for their examination because there is almost no probability that they are contained in drinking water. Besides the methods for the examination of general drinking water specified in the Ordinance of the Ministry of Health and Welfare, such methods and sanitary chemical standards of drinking water are prescribed in the Methods of Sanitary Examination agreed on with the Pharmaceutical Society. Some literature, including the above, which is pertinent to the analysis of drinking water is listed below.

8.2.2. Feed Water of Boilers

Water produced in desalination plants also contains various impurities which, when brought into boilers, cause corrosion of them, turn into scale to adhere to heating surfaces interfering with heat conduction or are carried over in steam, exerting harmful influences in some form or other upon them. Therefore, feed water must be selected cautiously, taking into consideration various conditions of each boiler.

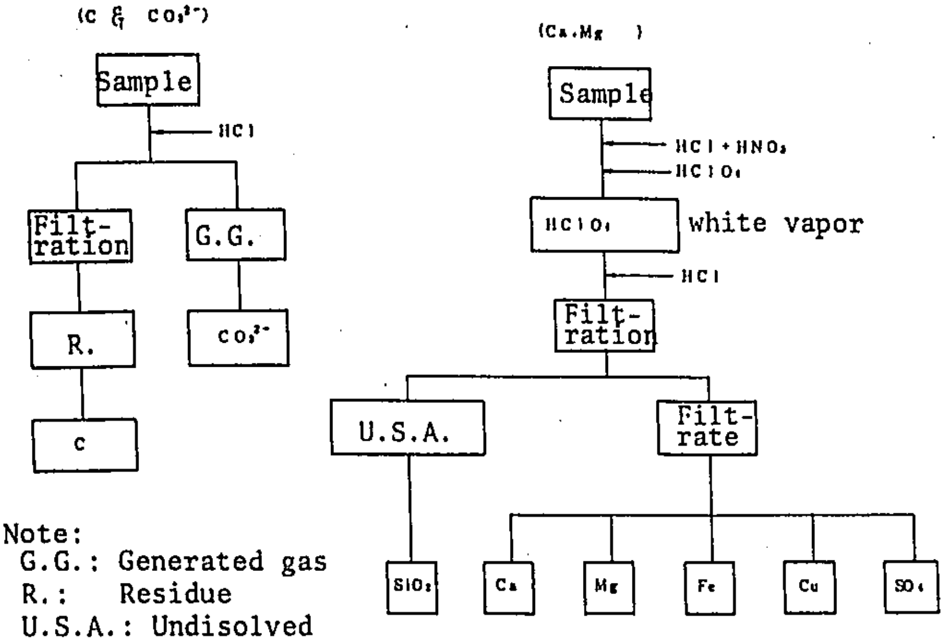
Although boilers generally require different qualities of water according to their types, pressures and operating conditions, the quality of water must be controlled so as to be within fixed limits and the standard and those values which provide bases for such control are specified in JIS B8223, Water Conditioning for Boiler Feed Water and Boiler Water. For boilers of the once through type in particular, in which almost all feed water is converted into steam, stricter restrictions are imposed generally on feed water compared with boilers of the circulating type. In any case, the intention common to both cases is that, as conditions which all feed water for boilers should satisfy, it is required to keep pH at 7 or more, hardness, suspended solids and fats and oils at approximately 0, and to restrain dissolved residual matter and dissolved oxygen to a level as low as possible.

Supplementary feed water is water to make-up from outside any shortage in required quantity of feed water and is not such water itself, but its qualities must satisfy those required by respective boilers. If the blow rate of boiler water and the rate of supplementary feed are given, the quality standards of make-up feed are decided secondarily.

Any of the items of analysis required to be made in order to judge whether water used as supplementary feed for boilers conforms to the quality standards decided as above cannot be ignored in view of its influences on the boilers. The relation between these items and principal interferences to boilers caused by water may be arranged as shown in Table 8.2-3.

Since make-up feed and feed water of boilers are approximately the same in quality, it is desirable to analyze them in conformity with JIS B8224, Testing Methods for Boiler Feed Water and Boiler Water. Reference is made to the above JIS for further information on the procedure of analysis, and here only the methods of determination for the items of analysis and the ranges of determination are arranged as shown in Table 8.2-4.

As some items of analysis are influenced by the time of sampling, air, containers and piping, special attention should be given in measuring dissolved oxygen, pH and electric conductivity.



Note:
G.G.: Generated gas
R.: Residue
U.S.A.: Undisolved substance by acid

Fig. 8.1-1 Scale analysis procedure

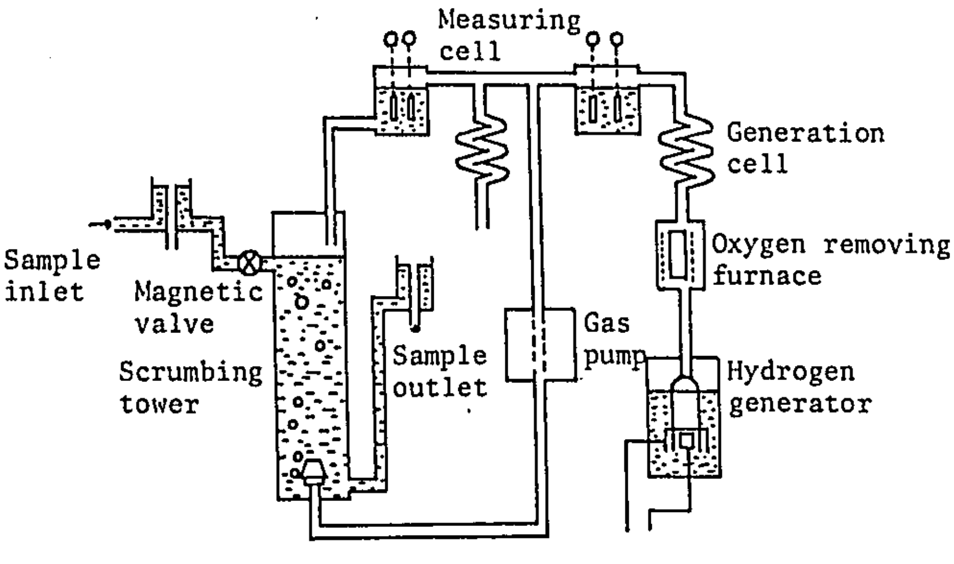


Fig. 8.1-2 Disolved oxygen meter

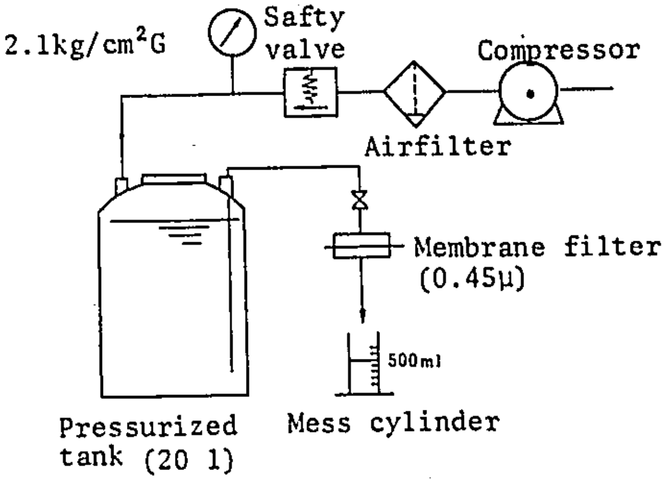


Fig. 8.1-3 Measurement

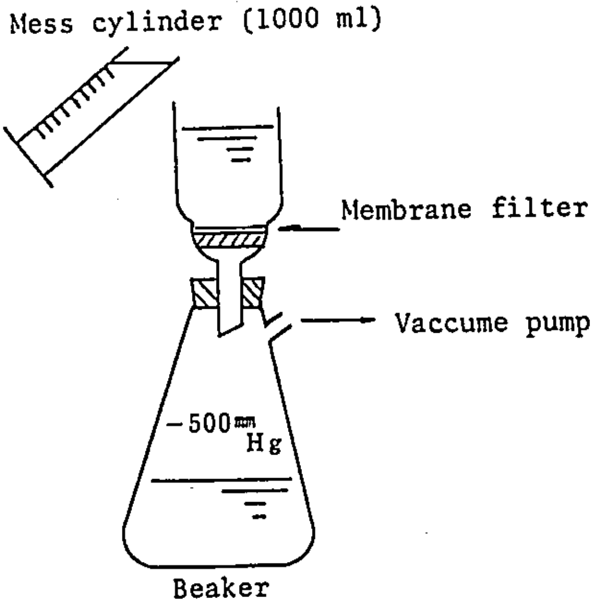


Fig. 8.1-4 MF Measurement

Table 8.1-1 Precipitation of scale or sludge (twice concentration)

Brine Tem.	Precipitating material	Form	Sampling
>120°C	$CaSO_4$	hard and stick	Dissolving with dil-HCl (high temp.)
90~120℃	$Mg(OH)_2$	Soft precipitate	Dissolving with dil-HCl (low temp.)
60~ 90℃	$CaCO_3$	Soft precipitate	〃
40~ 70℃	Fe_2O_3, Al_2O_3, SiO_2	Sludge	Mechanical scraping

Table 8.1-2 Quantitation analysis of scale components

Items	Method	Minimum analysis	Ref.
Ca	Titrimetric with EDTA	>0.04㎎	JISK0101
Mg	Titrimetric with EDTA	>0.025㎎	〃
CO_3	Gravimetric	>7.5㎎	JISG1211
	Titrimetric with acid	> 0.75㎎	〃
SO_4	Gravimetric	>10㎎	JISK0101
Fe	Photometric, Orthophenanthroline atomic absorption	0.005~0.5㎎ 0.03~0.35㎎/100㎎	〃 〃
Cu	Photometric, diethyldithio carbamate atomic absorption	0.002~004㎎ 0.005~0.4㎎/100㎎ >10㎎	〃 〃 〃
SiO_2	Gravimetric Photometric(Molybdenum Blue)	0.02~0.3㎎ > 7.5㎎	〃 JISG1211
C	Combustion-volumetric Combustion-titrimetric	> 0.75㎎	〃

Table 8.1-3 Analysis data on S^{2-}

Data	Place *	Temperature(℃)		S^{2-} (ppm)	
		Seawater	Sludge	Seawater	Supernatant of sludge
July,'75	Tokyo-2	23.7	19.9	0.023	2.8
〃	Tokyo-5	25.2	21.3	0.020	8.8
Aug.,'75	Tokyo-2	28.0	26.5	<0.017	25.8
〃	Tokyo-5	27.7	26.9	〃	61.8
Sept.'75	Tokyo-2	26.2	25.3	〃	24.7
〃	Tokyo-5	25.9	25.4	〃	31.3
〃	Arakawaguchi	26.4	25.9	〃	0.63
Aug.,'75	Ozu	26.8	20.8	〃	0.089
March'75	Ozu	11.5	11.0	〃	0.015

Ref.* Tokyo-2,5, indicate 2 and 5 kilometers offshore from Tokyo Bay and Arakawaguchi indicates the mouth of River Arakawa.

Table 8.2-1 Test Items and Methods of Potable Water

Test Item	Test Method
Ammoniacal nitrogen	Nessler method (qualitative test)
Nitrogen nitrite	Grease-Romen reagent method (qualitative test)
Nitrogen nitrate	Brucine-sulfanilic acid method
Chlorine ion	Silver nitrate titration
Organic matters (potassium permanganate consumption)	Acid oxidation method
Ordinary bacillus	
Colon bacilli	
Cyanide ion	Phenolphthalein method (qualitative test)
Mercury	Dithizone method (qualitative test)
Organic phosphorus	Diazotization and para-nitrophenol method (qualitative test)
Copper	Colorimetric with diethyl-dithiocarbamic acid
Iron	Orth-phenanthroline method
Manganese	Ammonum persulfate method
Zinc	Colorimetric with zincon
Lead	Dithizone method
Sexivalent chrome	Diphenyl-carbazit method
Arsenic	Colorimetric with diethyl-ditheocarbanic acid
Fluorine	Spance method
Calcium, magnesium (hardness)	Titrimetric with EDTA
Residue on evaporation	

Phenolic substances	4-amino-antipyrin method
Anion activator	Colorimetric as methylene blue
Hydrogen ion concentration	Colorimetric method
Odour Taste	Odour and taste at temperatures of 40 - 50°C (qualitative test)
Chromaticity	Platinum chloride cobalt method
Turbidity	Perspective nephelometry

Note: Water served to a population less than 100 is not classified as municipal water under the law except the case in which water is provided by water supply business (building water supply and small water supply system, for example).

Table 8.2-2 Quality of Make-up Water and Boiler Water

	Type of Boiler	Cycle Boiler			Once through boiler
		Cylindrical boiler	Water tube boiler		
Classification	Max. allowable working pressure (kg/cm2)	-	More than 20 and less than 30	More than 75 and less than 100	More than 75 and less than 100
	Evaration rate of heating surface (kg/m2'hr)	More than 30 and less than 60	-	-	-
Make-up water	pH (25°C)	7 - 5	7 - 9	8.5-9.5	8.8-9.5
	Hardness, CaCO3 (ppm)	Less than 2	0	0	0
	Oils (ppm)	To be held to 0	To be held to 0	To be held to 0	-
	Oxygen (ppm)	To be held low	Less than 0.1	Less than 0.007	Less than 0.007
	Total Fe (ppm)	-	-	Less than 0.03	Less than 0.03
	Total Cu (ppm)	-	-	Less than 0102	Less than 0.01
	Hydrazine (ppm)	-	More than 0.2	Less than 0.01	More than 0.01
	Electric conductivity (25°C) (μS/cm)	-	-	-	Less than 0.03 (1)
	Silica (ppm)	-	-	-	Less than 0.04(2)
Boiler water	pH (25°C)	11.0-11.8	10.5-11.0	9.0-9.8	
	M-alkalinity CaCO3 (ppm)	100-800	Less than 150	-	
	P-alkalinity CaCO3 (ppm)	80-600	Less than 120	-	
	Total residual matter (ppm)	Less than 3000	Less than 700	Less than 100	

		Electric conductivity (25°C) (uS/cm)		Less than 4500	Less than 1000	Less than 150
		Chlorine ion	(ppm)	Less than 500	Less than 100	Less than 10
		PO_4^{3-} ion	(ppm)	20-40	5-15	2-6
		Hydrazine	(ppm)	0.1-0.5	-	-
		Silica	(ppm)	-	Less than 50	Less than 2

Notes: (1) Water is tested through hydrogen type strong acidic ion exchange resin.

(2) Applied to boilers with a separator.

Table 8.2-3 Type and Cause of Boiler Trouble

Type of trouble	Items of analysis
Corrosion	pH (or P-alkalinity) Dissolved oxygen Cl^- ion
Scale deposition	Total residual matter (or electric conductivity) Hardness Silica Oils
Carry-over	Total residual matter (or electric conductivity) Silica M-alkalinity

Table 8.2-4 Methods Used for Analysis of Boiler Make-up Water

Items of analysis	Quantitative analysis	Quantitative limits	Accuracy
pH (1)	Glass electrode method	-	Within ±0.05 for normal measurement
Hardness	Titrometric with EDTA	More than 1 ppm	-
Oils	Hexane extracts method	Two methods: one for less than 5 ppm and the other for 5-200 ppm	±50%
Dissolved oxygen	(1) Iodine method		
	(a) Thiosulfate titration-starch indicator method A	More than 0.1 ppm	±0.003 ppm
	(b) Thiosulfate titration-starch indicator method B	More than 0.005 ppm	±0.004 ppm
	(c) Potentionetric end point method	Less than 0.01 ppm	±0.002 ppm
	(d) Amperometric titration method	Less than 0.01 ppm	±0.002 ppm
	(2) Colorimetric method		
	Colorimetric-indigo carmine method	Less than 0.02 ppm	-
Total Fe	(1) Absorptiometric method		
	(a) O-Phenanthroline method	More than 0.05 ppm	±10%-±2%
	(b) Bathophenanthroline method	0.0025-0.05 ppm	±10%-±2%
	(c) TPTZ method	0.0025-0.1 ppm	±10%-±3%
	(2) Atomic absorption spectrophotometry	0.3-3.5 ppm	Repeatability 2%-10% (standard deviation %)

Total Cu	(1) Absorptiometric method		
	(a) Colorimetric with diethyl-dithiocarbamic acid	More than 0.01 ppm	±10%–±3%
	(b) Colorimetric with zincon	0.0025–0.05 ppm	±10%–±3%
	(c) Colorimetric with neocuproine	0.0025–0.08 ppm	±10%–±3%
	(2) Atomic absorption spectrophotometry	0.05–4 ppm	Repeatability 2%–10% (standard deviation %)
Electric conductivity (2)	Wheatstone bridge method	-	±1%
M-alkalinity	Titrimetric with wulfuric acid	-	-
P-alkalinity	Titrimetric with sulfuric acid	-	-
Total residual matter	Evaporation method	More than 5mg as total residual matter	-
Chlorine ion	(1) Absorptiometric method		
	Mercuric thiocyanate method	0.025–0.5 ppm	±10%–±2%
	(2) Mercurimetric titration	1–50 ppm	±10%–±2%
	(3) Silver nitrate titration	More than 40 ppm	-
	(4) Ion electrode method	5–100 ppm	Repeatability 5–20% (standard deviation %)
Silica	Absorptiometric method		
	(1) Colorimetric as molybdenum yellow	2–20 ppm	±10%–±2%

(2) Colorimetric as molybdenum blue		
(a) Sodium sulfate reduction method	2-30 ppm	±10%-±2%
(b) 1-amino, 2-naphthol, 4-sulfonic acid	0.01-1.5 ppm	±10%-±2%

Notes: (1) Since pH changes according to the temperature, care should be taken when the temperature of test water deviates from 25°C. The electrode potential, which changes according to the temperature of test water, may be compensated with a temperature compensator attached to pH meter. However, the temperature compensator does not compensate the change of hydrogen ion concentration due to the change in the degree of dissociation of electrolyte. For this reason, pH of test water decreases by about 0.037 when the temperature rises 1°C. It is desirable, therefore, to maintain the temperature exactly at 25°C when measuring pH of test water.

(2) Since solids dissolved in normal water are inorganic salts which easily dissociate, their concentrations can be estimated by measuring electric conductivity of the water. With the water which can be used as boiler make-up water, about half of the value of electric conductivity (µS/cm) is the total salt concentration (ppm).

-REFERENCES-

1. Desalting Plants of the World

(1) Changes in the Number of Desalting Plants of the World

	Jan. 1, 1970		Jan. 1, 1972		Jan. 1, 1975		*Jan.1, 1977	
	No. of plants	Plant capacity (MGD)	No. of plants	Plant capacity (MGD)	No. of plants	Plant capacity (MGD)	No. of plants	Plant capacity (MGD)
Distillation	662	231.9	714	325.0	644	447.0	717	732.0
Single-stage flash	49	6.6	49	7.1	57	8.0	64	10.0
Multi-stage flash	196	158.4	218	226.0	285	352.0	337	625.0
Thin film vertical tube	102	30.4	113	49.5	104	51.0	90	50.0
Vapor compression	22	2.9	36	4.4	67	5.0	103	10.0
Thin film horizontal tube	-	-	4	1.3	12	5.0	19	19.0
Vertical tube/ multi-stage flash	-	-	1	3.0	1	3.0	1	3.0
Submerged tube	293	33.5	293	33.6	138	23.0	103	15.0
Membrane	47	12.4	94	4.0	370	77.0	597	164.0
Electrodialysis	44	12.2	61	18.7	75	26.0	90	27.0
Reverse osmosis	3	0.2	33	4.0	268	45.0	421	122.0
Electrodialysis/ Reversing	-				27	6.0	86	15.0
Freezing	3	0.3	4	0.4	2	-	-	-
Total	712	244.6	812	348.0	1,036	526.0	1,314	896.0

Source: US OWRT Inventory Report No. 3 - 5.

Notes:
1. * indicates the survey by the Agency of Industrial Science and Technology.
2. MGD = One million US gallons/day = 3,785 m^3/day

2. Desalting Plants (95 m^3/ day or over) by Location

Region		As of Jan.1972		As of Jan.1975		Distribution rationby location as of Jan. 1975 (%)	
		No. of plants	Plant capacity $10^3 m^3$/day	No. of plants	Plant capacity $10^3 m^3$/day		
North America	United States	321	193	346	257	13.0	19.1
	United States territories	17	49	26	76	3.8	
	North America excluding USA and territories	14	34	41	45	2.3	
Central & South America	Caribbean	39	98	39	121	6.0	7.2
	South America	27	23	24	23	1.2	
Europe	Great Britain and Ireland	64	61	69	61	3.0	16.0
	Other European countries	117	193	149	257	13.0	
Near-middle East	Africa	65	114	104	216	10.8	38.6
	Arabian Peninsula and Iran	96	413	153	553	27.8	
Asia, Oceania	Asia and Indonesia	33	23	68	257	13.0	13.4
	Australia and the Pacific	6	4	10	8	0.4	
Union Soviet Socialist Republic		13	114	7	114	5.7	
All locations		812	1,317	1,038	1,991	100.0	

Source: US OWRT Inventory Report No. 4 - 5.

(3) Export of Distillation - Desalting Plants by Japan (excluding plants with capacities of less than 200 m³/day).

(As of Oct. 1977 surveyed by National Chemical Laboratory for Industry)

Year of installation	Country	Type	Water production capacity (Volume × No. of units)m³/day
1966	Saudi Arabia	M S F	1,900
〃	Saudi Arabia	〃	2,300
1968	Kuwait	〃	36,400(9,100×4)
1969	Iran	〃	905
〃	Lebanon	〃	520
1970	Kuwait	〃	18,200
1971	Hongkong	〃	228
〃	Lebanon	〃	520
〃	Saudi Arabia	〃	2,300
〃	Algeria	〃	960
1972	Malta	〃	3,000
1973	East Germany	〃	3,600
〃	East Germany	〃	7,680(3,840×2)
〃	Saudi Arabia	〃 (L)	1,300
〃	Saudi Arabia	〃	550
〃	Saudi Arabia	〃	1,100
〃	Saudi Arabia	〃	1,630
〃	Mexico	〃	720(360×2)
〃	Bahrain	〃 (L)	3,400(1,700×2)
〃	Peru	〃	3,120
1974	Algeria	M E F	380
〃	Peru	M S F	1,500
〃	Libia	〃 (L)	13,500(4,500×3)
1975	Kuwait	〃	44,000(22,000×2)
〃	Hongkong	〃	180,000(30,000×6)
〃	Saudi Arabia	〃	3,260(1,630×2)
〃	Saudi Arabia	〃	2,300
1976	Algeria	〃	24,000(8,000×3)
Sub-total		45 units	359,273
Under construction	Saudi Arabia	M S F(L)	44,000(11,000×4)
	Singapore	M E F	3,000
	Saudi Arabia	M S F	9,810(3,270×3)
	Saudi Arabia	〃	2,016(672×3)
	Abu Dhabi	〃	109,200(18,200×6)
	Kuwait	〃	81,900(27,300×3)
	Dubai	〃	67,500(13,500×5)
	Kuwait	〃	109,200(27,300×4)
	Ras Al Khaimah	〃	27,300(13,650×2)
	Saudi Arabia	〃	136,200(22,700×6)
Sub-total		37units	590,126
Total		82units	949,399

Note: MSF; Multistage flash (L): Indicates long tube type, others short
MEF: Multiple effect flash

(4) Desalting Plants in Japan

(As of Nov. 1977 - surveyed by National Chemical Laboratory for Industry)

	Year of commission	Operator	Location	Type	Plant capacity (m^3/day)	Water feed	Use
Distillation	1967	Matsushima Coal Mining Co. Ltd.	Nagasaki-Ikejima	MSF	2,650	Seawater	Domestic water
	1969	Kansai Ele. Power - Himeji No. 2 Thermal Power	Hyogo - Himeji	MSF	1,200	Seawater	Boiler water
	1971	Hitachi Shipbuilding & Engineering Co. Ltd.	Hiroshima Innoshima	MEF	500	Seawater	Industrial
	1974	Kansai Ele. Power Obishi Nuclear Power	Fukui - Obishi	MEF	1,300	Seawater	Boiler water
	1974	Kansai Ele. Tanagawa No. 2 Thermal Power	Wakayama-Tanagawa	MSF	2,000	Seawater	Boiler water
	1974	Chubu Ele. Power Nishi-Nagoya Thermal Power	Aichi-Nagaya	MEF	1,000	Seawater	Boiler water
	1975	Ieshima Town, Hyogo prefecture	Hyogo-Ieshima	MSF (L)	1,000	Seawater	Domestic water
	1975	Shikoku Ele. Power Ikata Nuclear Power	Ehime-Ikata	MSF (L)	1,000 × 2	Seawater	Boiler water
	1976	Kansai Ele. Power Obishi Nuclear Power	Fukui-Obishi	MSF	1,300	Seawater	Boiler water
	1976	Kansai Ele. Power Tanagawa No. 2 Thermal Power	Wakayama Tanagawa	MSF	2,000	Seawater	Boiler water
	1976	Water Bureau of Uwajima City	Ehime-Hiburi shima	MES	200	Seawater	Domestic water
		Total		12 units	15,150 m^3/day		

Reverse Osmosis	1971∿ 1975	Sumitomo Metal Industries, Ltd.	Ibaragi-Kashima	14,900	Brine	Industrial
	1972	Showa Sangyo Co. Ltd.	Ibaragi-Kashima	720	Brine	Industrial
	1973	Kashimakita-Joint Power	Ibaragi-Kashima	9,600	Brine	Boiler water
	1973	Arakawa Rinsan Chemical Industry	Ibaragi-Kashima	120	Brine	Industrial
	1973	Izumiya	Hyogo Takarazuka	100	-	Drinking water
	1974	Vivasta Tosho	Nagasaki	400	Brine	Drinking water
	1974	Mitsubishi Electric Corporation	Kumamoto	480	Brine	Industrial
	1974	Dainippon Ink & Chemicals Inc.	Ibaragi-Kashima	720	Brine	Industrial
	1974	Kashima Oil	Ibaragi Kashima	5,300	Brine	Industrial
	1974	Kanegafuchi Chemical Industry Co. Ltd.	Ibaragi Kashima	1,000	Brine	Industrial
	1974	Texas Instruments	Saitama Kawaguchi	290	-	Industrial
	1974	Hitachi	-	175	-	Industrial
	1974	Nippon Electric Co. Ltd.	Kanagawa Yokohama	240	-	Industrial
	1975	Sumikin Kako	Ibaragi Kashima	1,500	Brine	Industrial
		Total	15 units	35,545 m^3/day		
Electro Dialysis	1970	Shikine-shima	Tokyo Shikine-shima	200	Brine	Domestic water
	1971	Asahi Sweep	Miyazaki	300	Brine	Industrial
	1972	Izu-Oshima	Tokyo-Izu Oshima	1,000	Brine	Domestic water
	1973	Nihon Ryoko	Chiba Kujukuri hama	200	Brine	Domestic water
	1973	Hatsushima	Shizuoka Hatsushima	200	Brine	Domestic water
	1974	Izu-Ohshima	Tokyo-Izu Oshima	1,000	Brine	Domestic water
	1974	Nojima	Yamaguchi Hofu City	120	Seawater	Domestic water
	1975	Tokyo Ele. Power Kashima Thermal Power	Ibaragi Kashima	2,000	Brine	Boiler water
	1975	Tokyo Ele. Power Kashima South Joint Power Plant	Ibaragi Kashima	12,000	Brine	Boiler water
		Total	9 units	17,020 m^3/day		
		Grand Total	36 units	67,715 m^3/day		

Note: MSF: Multistage flash; (L) Indicates long tube type
others are short tube type.
MEF: Multiple Effect Flash

2. Typical Specifications of Desalting plant

(1) Multistage Flash Distillation Plant (with capacity of 1,000 m^3/day or over)

(a) Japan, Asia

Operator	Location	Year commissioned	No. of units	Capacity of single unit (m^3/day)	Type	Performance ratio	Feed seawater		No. of stage	
							Temperature (°C)	Concentration (%)	Heat recovery section	Heat rejection section
Matsushima Coal Mining Co. Ltd.	Ikeshima (Nagasaki)	1967	1	2,650	Short tube	3.0	-	3.5	6	2
Kansai Ele. Power Himeji No. 2 power plant	Himeji city (Hyogo)	1969	1	1,200	Short tube	2.8	30	3.5	4	2
National R & D project of the Agency of Industrial Science & Technology	Chigasaki city (Kanagawa)	1971 - 1974	1	3,000	Long tube	11.0	25	3.5	36	3
Ieshima Town, Hyogo Prefecture	Ieshima (Hyogo)	1975	1	1,000	Long tube	12.0	26	3.5	30	3
Kansai Ele. Power No. 2 Tanagawa power plant	Misaki-cho Tanagawa (Osaka)	1974	1	2,000	Short tube	6.0	30	3.5	15	3
Shikoku Ele. Power Ikata power plant	Ikata-cho (Ehime)	1975	2	1,000	Long tube	8.0	30	3.4	24	3
Kansai Ele. Power Obishi power plant	Obishi-cho (Fukui)	1976	1	1,300	Short tube	6.0	30	3.5	15	3
Hongkong Government	Hongkong	1975	6	30,300	Short tube	10.5 (13.8)*	28	3.5	25	3
Kansai Ele. Power No. 2 Tanagawa power plant	Tanagawa (Osaka)	1976	1	2,000	Short tube	6	30 - 25	3.5	15	3

* ; Indicates actual values

Literature: (1) Survey by the Agency of Industrial Science and Technology. (2) Chemical Association of Japan, Chemical Handbook, Applied Chemistry P. 1530 (1973). (3) Metal (extra edition) 1976, July Issue.
(4) Bulletin of the Society of Seawater Science, Japan, Vol.28, 288 (1974)
(5) Thermal and atomic power generation, Vol. 28, 243 (1977)

Brine Temperature (°C)		Amount of heating steam (Kg/h)	Brine concentration	Heating tube material		Scale prevention	Purpose	Plant maker	Literature
Max.	Min.			Heat recovery section	Heat rejection section				
88	40	36,800	2.0	Alumi-brass	Alumi-brass	Chemical injection	Domestic water Boiler water	Sasakura IHI	(1)
101 - 105	44	18,000	2.0	"	Alumi-brass and 90/10 Cu-Ni	"	Boiler water	Sasakura	(1)
121	34	11,400	2.0	"	Alumi-brass	pH control by sulphuric acid injection	For experiment	"	(2)
120	36	3,470	2.0	"	Alumi-brass and titanium	"	Domestic water	"	(1)
104	40	13,890	2.0	"	Titanium	"	Boiler water	"	(3)
116	34	5,210	2.0	"	90/10 Cu-Ni	"	"	"	(3)
104	40	9,030	2.0	"	Titanium	"	"	"	(3)
121	-	(95,000 - 96,000)*	1.74	"	Alumi-brass	"	Domestic water	"	(4)
104	37 - 32	14,000	2.0	"	Titanium	"	Boiler water	Hitachi	(5)

Operator	Location	Year commi-ssioned	No. of units	Capacity of single unit (m³/day)	Type	Performance ratio	Feed seawater		No. of stage	
							Temperature (°C)	Concentration (%)	Heat recovery section	Heat rejection section
Porto Torres Petro-chemical complex	Sardinia (Italy)	1971	1	16,800	Long tube	8∿10	12∿ 31	3.8	30	3
"	"	1973	1	36,000	"	6.5∿8	"	"	28	3
Taranto steel Plant Italsider, S.P.a	Taranto (Italy)	1964	1	2,370	Long tube	4.1	-	3.5	20	
"	"	1964	1	2,370	"	"	-	3.5	20	
"	"	1968	1	2,880	Long tube	6.3	-	3.5	24	
"	"	1972	1	2,880	"	5.6	-	3.5	20	
PZEM. Waterplant	Terneuzen (Nether-lands)	1969	2	14,400	"	10.0	-	22.6	35	3
Eilat plant	Eilat (Israel)	1965	1	(3,505)*2 3,768	Short tube	8.0	-	4.6	26	4
"	"	1971		(3,125)*2 3,096	"	9.2	-	4.6	31	3
USSR	Shevchenko	1973	1	15,000	-	8.3	(Caspian sea)		31	3

* 1. SIR: Societá Italiá na Resine

* 2. Actual

References:
(1) Bulletin of the Society of Sea Water Science, Japan Vol. 30, 291 (1977)
(2) Bulletin of the Society of Sea Water Science, Japan Vol. 28, 278 (1974)
(3) Bulletin of the Society of Sea Water Science, Japan Vol. 31, 74 (1977)
(4) Proceedings of 5th International Symposium on Fresh Water from The Sea , Vol. 2, 71 (1976)

Brine temperature (℃)		Amount of heating steam (kg/h)	Brine concentration ratio	Heating tube material		Scale prevention	Purpose	Plant maker	Literature
Max.	Min.			Heat recovery	Heat rejection section				
90~115	—	—	1.8~2.0	Alumi-brass and 70/30 Cu-Ni	70/30 Cu-Ni	Sulphuric acid pH control	Industrial water	SIR*1	(1)
90~115	—	—	1.8~2.0	70/30 Cu-Ni	70/30 Cu-Ni	Sulphuric acid pH control	〃	〃	(1)
85	—	—	1.1	90/30 Cu-Ni		Darex 4D. Chemical injection	〃	Aqua-Chem	(2)
〃	—	—	1.1	〃		〃	〃	〃	〃
105	—	—	1.7	90/10 Cu-Ni		pH control	〃	Aqua-Chem (Italy)	〃
〃	—	—	1.7	Cu-Ni		〃	〃	Westing house	〃
(115) 120	37	—	2.0	90/10 Cu-Ni	70/30 Cu-Ni +1.5%Fe	pH control sponge ball	Industrial water Domestic water	Werkspoor (Netherlands)	〃
93	—	19,600	—	90/10 Cu-Ni and alumi-brass		Chemical injection (Belgard)	Domestic water	BLH	(3)
97	—	14,000	—	〃		〃	〃	Mekoroth Israel Power Co.	(3)
98~99	34~35	—	—	—	—		〃	—	(4)

Operator	Location	Year commi- ssioned	No. of units	Capacity of single unit (m^3/day)	Type	Performance ratio	Tempe- rature (°C)	Concent- ration (%)	Heat recovery section	Heat rejection section
US Office of Saline Water	San Diego (California)	Nov.1961 ~Feb.1964	1	3,780	Long tube	9.8~ 11.7	12~ 21	3.5	34	2
Virgin Island Water & Power Authority	St. Thomas	1962	1	1,040	"	5.2	26~ 28	4.0	24	4
"	"	1967	1	3,780	"	13.9	"	"	24	2
"	"	1969	1	9,450	"	7.0	"	"	38	3
Comision Federal De Electricidad	Tijuna (Mexico)	1969	2	14,194	"	10.8	16~ 23	3.6	40	4
The Florida Key Aqueduct Commission	Key West (Florida)	1969	1	10,000	"	14.0	26	3.4	48	2

Source: (1) OSW No. 102, No. 114, (2) Bulletin of the Society of Sea Water Science, Japan, Vol. 27, 59 (1973)

Brine Temperature (°C)		Amount of heating steam (Kg/h)	Brine concent- ration	Heating tube material		Scale prevention	Purpose	Plant maker	Literature
Max.	Min.			Heat recovery section	Heat rejection section				
93~ 121	28~ 34	14,607~ 20,664	1.7~ 2	Alumi-brass and 90/10 Cu-Ni + 1.7% Fe		pH control by chemical injection (Hagevap)	For experiment	Westing- house	(1)
91	-	-	2	90/10 Cu-Ni		pH control by sul- phuric acid injection	Multipurpose	Aqua-Chem	(2)
121	-	-	1.5	90/10 Cu-Ni		"	"	Westing- house	(2)
107	-	-	1.8	90/10 Cu-Ni		"	"	BLH	(2)
118	-	-	1.7	90/10 Cu-Ni		pH control by sul- phuric acid injection, sponge ball cleaning	"	Aqua-Chem	(2)
121	-	-	1.5	70/30 Cu-Ni	Titanium	pH control by sul- phuric acid injection	"	Westing- house	(2)

Operator	Location	Year commissioned	No. of units	Capacity of single unit (m³/day)	Type	Performance ratio	Feed seawater		No. of stage	
							Temperature (°C)	Concentration (%)	Heat recovery section	Heat rejection section
Shuaiba Power and Water Production	Shuaiba (Kuwait)	1965	1	4,550	Short tube	8.5	-	4.5	27	3
"	"	1968	1	9,100	"	8.0	-	4.5	21	3
"	"	1969	1	"	"	"	32	4.5	22	3
"	"	1972	1	22,730	"	"	-	4.5	-	-
"	"	1975	1	"	"	"	32	4.5	23	3
Shuwaikh Power and Water Production	Shuwaikh (Kuwait)	1957	1	2,270	"	3.0	-	4.82	3	1
"	"	1960	1	4,550	"	5.2	-	4.82	16	3
"	"	1968	1	9,100	"	8.3	-	4.82	21	3
"	"	1970	1	18,200	"	8.0	32	4.82	23	3
Tripoli West Thermal Power Plant	Tripoli (Libya)	1976	2	11,250	"	7.25	12∿ 31	3.87	20	3
Benghazi North Thermal Power Plant	Benghazi (Libya)	1976	8 4 units under construction	6,000	"	7.3	14∿ 27	3.87	17	3
Jeddah Phase-1	Jeddah (Saudi Arabia)	1970	2	11,250	Long tube	10.4	26∿ 29	4.1∿ 4.6	39	3

Source: (1) Bulletin of the Society of Sea Water Science, Japan, Vol. 28, 286 (1974)
(2) Bulletin of the Society of Sea Water Science, Japan, Vol. 30, 231 (1977)

Brine temperature (℃)		Amount of heating steam	Brine concentration ratio	Heating tube material		Scale prevention	Purpose	Plant maker	Literature
Max.	Min.			Heat recovery section	Heat rejection section				
90	—	—	—	Alumi-brass and 70/30 Cu-Ni	70/30 Cu-Ni	Chemical injection (Poly phosphates)	Domestic water	Weir-Westgarth	(1)
90	—	—	1.7	〃	〃	〃	〃	Westinghouse	〃
90	41.0	47,000	1.5	〃	Alumi-brass	〃	〃	IHI-Sasakura	〃
90	—	—	1.6	〃	70/30 Cu-Ni	〃	〃	Alsthom	〃
90	41.5	117,500	1.5	〃	〃	〃	〃	IHI	〃
90	—	—	1.9	70/30 Cu-Ni	〃	〃	〃	Westinghouse	〃
90	—	—	1.5	〃	〃	〃	〃	Weir-Westgarth	〃
90	—	—	1.7	Alumi-brass and 70/30 Cu-Ni	〃	〃	〃	Westinghouse	〃
90	40.0	94,000	1.45	〃	〃	〃	〃	IHI-Sasakura	〃
90	35.5	—	—	Alumi-brass	70/30 Cu-Ni	〃	Multi-purpose	Sidem	(2)
—	—	—	—	Alumi-brass and 70/30 Cu-Ni	90/10 Cu-Ni	〃	〃	〃	〃
121	40.0	—	—	90/10 Cu-Ni	70/30 Cu-Ni	pH control	〃	Aqua-Chem	〃

(2) Multiple Effect Seawater Deslination Plant

Operator	Location	Year commi-ssion-ed	Water produc-tion (m³/day)	Type	No. of effects	Amount of heating steam (kg/hr)	Brine con-centra-tion ratio	Brine concentration ratio	Scale prevention
US Office of Saline water	Free port Texas (U.S.A.)	1961~1965	3,628	(VTE) Vertical tube	12	14,143	10.7	3.01	Sulphuric acid injection pH control
U.S.S.R.	Shevchenko	1971	14,640~15,600	〃	10	78,000~82,000	8	3.7	
Public Works Dept.	Gibralter (Great Britain)	1973	1,365	〃	13	—	9.7~10	2.5	Acid treatment
—	st, Croix (U.S.A.)		3,400	〃	11	16,000	8.6	2.8	Sulphuric acid injection pH control
Toyo Engineering	Algeria	1972	380	Horizontal tube vertical type	6	3,500	4.5	2.5	〃
Chubu Ele. Power Nishinagoya Thermal Plant	Nagoya city	1974	1,000	〃	8	6,900	6	2.5	〃
Kansai Ele. Power Obishi Power Plant	Obishi (Fukui)	1974	1,300	(VTE) Vertical tube	8	9,000	6.0	2.6	pH control
Uwajima City Water Bureau	Hiburi shima (Uwajima)	1976	200	Thermal compression method is used jointly	6	830	10	1.65	Sulphuric acid injection pH control
Israel	Eilat (Israel)	1974	3,785	Horizontal tube	12	16,000	10	—	Chemical injection (Poly phosphates)

Reference: (1) OSW No. 123, (2) Proceedings of 4th International Sympozium on Fresh Water from the sea (Vol. 1), (3) Bulletin of the Society of Sea Water Science, Japan, Vol. 27, 65 (1973), (4) Survey by the Agency of Industrial Science and Technology, (5) Bulletin of the Society of Sea Water Science, Japan, Vol. 31, 77 (1977)

Total heat trans-fer area (m²)	Overall coefficient of heat transfer (Kcal/m² hr °C)	Heating steam tempe-rature (°C)	1st stage brine tempe-rature (°C)	Last stage brine tempe. rature (°C)	Feed seawater		Heat transfer tube	Purpose	Plant maker	Litera-ture
					Temperature (°C)	Concentration (%)				
6,220	1,900~3,400	115.4	109.9	47.7	—	3.5	Cross tube Al-brass	For experiment	W.L. Badger Assoc.	(1)
22,454	3,900~5,000	—	102.0	37~40	20	2.0	Fluttet tube Al-brass	Domestic water, boiler water	—	(2)
—	9,760	—	123.8	39.1	10~24	3.5	Double fluttet tube	Domestic water	Alton & Co.	(2)
—	—	138	107.0	40.0	30	〃	Ou-Ni	〃	Sterns Roger Corp.	(3)
—	—	(1Kg/m²G) 120	101.0	41.0	—	—	—	Construction water	Sasakura Engineering	(4)
—	—	〃	101.0	41.0	—	3.5	—	Boiler water	〃	〃
—	9,000	—	110.0	50.0	10~30	〃	Double fluttet tube Al-brass	Boiler water	Hitachi Shipbuilding & Engineering	〃
—	—	(10 A.P.) 101	97.0	60.0	—	—	—	Domestic water	Sasakura Engineering	〃
—	3,500	—	70.0	—	—	—	Aluminium alloy	〃	Israel Desalination Engineering	(5)

(3) Reverse Osmosis Desalting Plant

Operator	Location	Year commissioned	Capacity (m³/day)	Type of raw water	Salinity of raw water (μ℧/cm)	Concentration of product water (μ℧/cm)	Reverse osmosis module		
							Type	Membrane materials	modulo size (mm)
Sumitomo Metal Industries, Ltd. Kashima iron works	Kashima Ibaragi Prefecture	1971	1,000×3	Industrial water	670	52.9	Spiral ROOA 4100	Acetylcellulose	100φ×850L
	〃	1972	1,000×2		〃	〃	〃	〃	〃
〃	〃	1974	1,500×3	〃	2,445	73.2	Spiral ROOA 4160	〃	100φ×1015L
〃	〃	1974	1,500×2	〃	〃	〃	Spiral ROOA 4160	〃	100φ×1015L
〃	〃	1975	1,500	〃	1,180~1,730	1.4~8.4	Hollow fiber B-9	Polyamide	Pressure vessel 140φ×1200L
Kashima North Joint Thermal Power plant	〃	1973	2,000×2	〃	1,405	114.0	Spiral ROOA 4100	Acetylcellulose	100φ×1015L
〃	〃	1973	2,800	〃	971	34.7	Spiral ROOA 4160	〃	〃
〃	〃	1974	2,800	Air-conditioner waste water	〃	〃	〃	〃	〃
A company	Shiga prefecture	1977	330		TDS (ppm) 250 or over	TDS (ppm) 100 or less	Spiral Toray 80 3000	Acetylcellulose	100φ×980L
Sasakura Engineering	Yamaguchi Prefecture	1975	70	Sea-water	TDS (ppm) 35,000	TDS (ppm) 300	Hollow fiber B-10	Polyamide	Pressure vessel 140φ×1200L
B company	Saudi Arabia	1977	57	Sea-water	TDS (ppm) 45,000	TDS (ppm) 200~300	Spiral ROUA 6085 ROOA 4160	Acetylcellulose	150φ×1015L 100φ×1015L

Literature: (1) Thermal Power Generation No. 198 (March 1973)
(2) Thermal and Atomic Power Generation Vol. 26, No. 2, P-241 (1975)
(3) First Desalination Congress of The American Continent Mexico City, Oct. (1976)
(4) Survey by the Water Production Promotion Center

Reverse osmosis module		Operating pressure (Kg/cm^2)	Recovery rate (%)	Desalination rate (%)	Power consumption (KWh/m^3)	Pretreatment method	Cleaning method	Purpose	Plant maker	Literature
No. of modules	Effective area of membrane									
348 × 3 unit	$6m^2$/1 module	28∿35	75	90 or over	1.9	Coagulation-precipitation, double-screen filtration, pre-coat filt filter, pH control	Flashing chemical cleaning	Industrial water	Kurita Water Indsutries, Ltd.	(1)
do.	do.	do.	do.	do.	do.	do.	do.	do.	do.	(2)
432 × 3 unit	$7.6m^2$/1 module	do.	do.	do.	do.	do.	do.	do.	do.	(2)
432 × 2 unit	$7.6m^2$/1 module	do.	do.	do.	do.	do.	do.	do.	do.	(2)
144	-	28.1	do.	95	-	Coagulation-precipitation, sand filtra tion active charcoal, pH control	Chemical cleaning	do.	Sasakura Engineering	(3)
750 × 2 unit	$7.6m^2$/1 module	20∿30	do.	90 or over	1.9	Coagulation-precipitation, filtration, pH control	Flashing chemical cleaning	Boiler water	Kurita Water Industries, Ltd.	(2)(3)
do.	do.	do.	do.	do.	do.	do.	do.	do.	do.	(2)(3)
do.	do.	do.	do.	do.	do.	do.	do.	do.	do.	(2)(3)
-	$7.0m^2$/1 module	do.	90	97.7	-	Coagulation-precipitation, double-screen filtration, pH control	-	Recycle industrial water	Toray Industries, Inc.	(4)
17	$139m^2$/1 module	51∿56	30∿35	99	-	Coagulation-precipitation, filtration, dechlorination, pH control	-	For experiments	Sasakura Engineering	(4)
24	$17.1m^2$/1 module	50∿70	18∿28	99	10.3	Coagulation-precipitation, double-screen filtration, fine filtration, pH control, scale inhibitor	Flshing chemical cleaning	Potable water	Kurita Water Industries Ltd.	(4)
18	$7.6m^2$/1 module	25∿35								

(4) Electrodialysis Desalting Plant

Operator	Location	Year commi-ssioned	Capacity (m^3/day)	Raw water		Product water concent-ration (ppm)	Type of dialysis shell	No. of units (shells)	Membrane logarithm per unit Number	Membrane size (m)	Mem-brane inter-vals	Effective area per membrane (m^2)
				Type	Concent-ration (ppm)							
US OSW	Webster South Dakota	1962~ 1964	1,000	Brackish water (10°C)	1,500~ 1,800	350	4-stage one line	4	216	1.12 × 1.12	0.75	0.96
Mekoroth Water Co.	Mashabei-sade (Israel)	1972	2,400	Brackish water (38°C)	2,300	500	Two lines	-	300	-	-	0.56
Benghazi WaterB Bureau	Benghazi (Libya)	1972	19,200	Brackish water	1,980	650	WD15-5 2-stage one line	16×2	300	1.5 × 0.5	1.3	0.59
Atami City	Hatsushima	1973	200	Brackish water (15~25°C)	(Cl$^-$) 5,300	(Cl$^-$) 200	3-stage one line	3	150	1.0 × 1.35	1.0	1.0
Hofu City	Nojima	1974	120	Seawater	35,000	500	SS-O type	1	400	1.3 × 1.3	0.75	1.4
Izu-Ohshima South water Plant	Izu-Ohshima	1974	1,000	Brackish water (15~30°C)	1,500~ 2,500	500	SV-O type 4-stage one line	4	240	1.115 × 1.115	0.75	0.96
Tohoku Ele. Power Co. East Niigata Thermal Power plant	Niigata	1975	2,000	Industrial water	730	220	WD15-5 1-stage one line	6	300	1.5 × 0.5	1.3	-
Tokyo Ele. Power Co. Kashima Thermal Power plant	Kashima Kombinat	1975	2,000	Industrial water	(Cl$^-$) 845	190	DW-IV type 2-stage two lines	4	300	1.12 × 1.12	1.9	0.918
Kashima South Joint Thermal Power plant	Kashima Kombinat	1976	12,000	Industrial water	(Cl$^-$) 600	100	DW-IV type 3-stage six lines	18	300	1.12 × 1.12	1.9	0.918
Ministry of Mining and Industry, Iraq	Basrah (Iraq)	Under construc-tion 1978	10,000	River-water	(CaCO$_3$) 1,280	250	3-stage two lines	16	280	1.06 × 1.55	1.0	1.15

Literature: (1) Chemistry and Industry Vol. 16,696 (1963), OSW No. 101, 132.
(2) Bulletin of the Society of Sea Water Science, Japan, Vol. 28, 294 (1974).

Cation exchange membrane	Anion exchange membrane	Anode materials	Cathode materials	Voltage (V)	Current (A)	Current efficiency (%)	Power consumption ($KWhr/m^3$)	Pretreatment method	Purpose	Plant maker	Literature
Styren divinyl benzen type homegeneous membrane (Asahi Chemical Industry)		Graphite	Stainless steel	220 190 138 122	35 24 14 10	98.2 ~ 91.4	1.41	Addition of $KMnO_4$ manganese zeolite filtration	For experiment	Asahi Chemical Industry	(1)
Seremion CMV, AMV neocebuta CL25T, AV4T		-	-	540~ 600	-	-	3.6	Ion exchange resin	Domestic water	*Tahal Water* Planning	(2)
Neocebuta CL-25T	Seremion AMV	Titanium platinum plating	Titanium platinum plating	600 450	60 20	-	1.8	Ion exchange resin	do.	Bobby Co. (Great Britain)	(3)
Neocebuta CL-25T	ACH-45T	Titanium platinum plating	Stainless steel	90 70 70	150 51 17	90 or over	3.7	Sand filtration	do.	Ebara-Infilco, Tokuuama soda	(4)
Asiplex K-101	A-101	Graphite	Stainless steel	230~ 210	560~ 30	80~ 85	16.21	Sand filtration	do.	Asahi Chemical Industry	(4)
Asiplex K-101	A-101	Graphite	Stainless steel	100~ 110	20~ 30	-	1.6	Sand filtration	do.	Shinko Faudrau	(5)
Neocebuta CL-25T	AV4T	Titanium platinum plating	Titanium platinum plating	600	60	80~ 90	0.7	Sand filtration	Boiler water	Organo	(5)
Seremion CMV	AMV	Titanium platinum plating	Stainless steel	500 or less	(A/dm^2) 0.87 0.44	85 or over	2.90	Sand filtration, active charcoal	do.	Asahi	(4)
Seremion CMV	AMV	Titanium platinum plating	Stainless steel	600 or less	(A/dm^2) 0.66 0.39 0.25	85 or over	2.37	Sand filtration	Boiler water	Asahi Chemical Industry	(4)
Unirex XYC-30	XYA-51	Celite	Stainless steel	-	-	-	0.75~ 1.0	Coagulation-precipitation, sand filteration, active charcoal	do.	Mitsubishi Heavy Industries, Mitsubishi Petrochemical Engineering	(5)

3. Tables of Industrial Rights and Technical Know-how under the National R & D Project

(1) Table of Industrial Rights Applications

Reference No.	Date of application	Application number	Description	Registration		Remarks
				Date of registration	Registration number	
1	Sep.30,1971	46-75810	Salt water distillation process			
2	Nov. 1971	46-121191	Cascade decarboxylation apparatus	Aug.30,'76	1140993	Utility model patent
3	Dec.23,1971	46-121205	Cascade decarboxylation apparatus	Aug.30,'76	1140994	"
4	Dec.23,1971	46-121206	Same as above			
5	Jun.20,1972	47-61576	Heating tube scale removing method and apparatus			
6	Jun.28,1972	47-64051	Cascade decarboxylation apparatus	Mar.9,'77	847348	
7	Oct.3, 1972	47-98645	Scale prevention method and apparatus	Mar.31,'77	852771	
8	Oct.3, 1972	47-98615	Scale control method for multistage flash evaporator	Nov.18,'76	834644	
9	Dec.13,1972	47-124291	Flash distillation desalting plant			
10	Dec.15,1972	47-125280	Cascade decarboxylation apparatus	Nov.18,'76	834656	
11	Jan.22,1973	48- 8627	Seed agent circulation method and apparatus for desalting plant			
12	Feb.22,1973	48-20628	Scale prevention method			
13	Feb.21,1973	48-20228	Desalting plant with sponge ball circulation system			
14	Mar.7, 1973	48-26022	Multistage flash evaporator			
15	Mar.19,1973	48-30918	pH control method for desalination with multis age flash evaporator			
16	Jul.5, 1973	48-79312	Deaerator			Utility model patent
17	Sep.29,1973	48-108936	Scale prevention method (1)			
18	"	48-108937	Scale prevention method (2)			
19	"	48-108938	Scale prevention method (3)			
20	Dec.10,1973	48-136853	Vacuum deaerator			
21	Dec.26,1973	48-143903	Heating tube ball cleaning method for desalting plant			
22	Mar.6, 1974	49-025294	Fresh water post-treatment method			
23	May 24,1976		Cascade decarboxylation apparatus for desalting plant			
24	May 24,1977	52-059318	Flash distillation desalting plant			

(2) Table of Industrial Right Applications (Foreign Applicants)

Applying country	Application number	Description	Application number of the patent in Japan	(Date of registration) Registration number
U.S.A.	493480	Multi-Stage Flash Distillation Plant	1972-124291	(Jun.29, 1976) 3966562
U.S.A.	532814	Method of Preventing Scale from being Deposited in Case.	1973- 20628	(Jan.13, 1976) 3932224
U.S.A.	518616	Vacuum Deaerator.	1973-136853	(Jan.13, 1976) 3932150

(3) Table of Industrial Right Application by the National Chemical Laboratory for Industry

Application number	Date of application	Description of patent	Patent Number	Date of registration
1 44-61057	Aug.4, 1969	Method of recovering potassium from a mixed solution of sodium hydroxide and potassium hydroxide (Designation changed to the method of recovering potassium concentrate, Oct. 10, 1972)		
2 44-61058	Aug.4, 1969	Method of recovering caustic soda and caustic potash from a mixed solution of caustic soda containing salt as impurity and caustic potash		
3 45-11502	Feb.12,1970	Multistage flash distillation plant	754406	Jan.21,1975
4 45-12318	Feb.13,1970	Saline water desalination method	775794	Jul.16,1975
5 45-110102	Dec.12,1970	Electrolytic protection method	716074	Jan.31,1974
6 45-110103	Dec.12,1970	Electrolytic protection method	716075	Jan.31,1974
7 46-100125	Dec.13,1971	Electrolytic protection method using metal granules		
8 47-90314	Sep.11,1972	Process of refining caustic soda solution and recovering caustic potash with the secondary refrigerant direct contact crysta crystallization method		
9 47- 47—97702	Sep. 30, 1972	Salt water degassing plant		
10 47-107100	Oct.27,1972	Method of separating potassium from a mixed solution of sodium hydroxide and potasium hydroxide	775836 (Separate application)	Jul.23,1975
11 48-13685	Feb.5, 1973	Salt water decarboxylation plant		
12 48-67095	Jun.14,1973	Caustic soda solution refining plant		
13 (Utility model patent) 45-93607	Sep.22,1970	Vacuum mechanism of flash distillation plant		
14 (Utility model patent) 47-45155	Apr.18,1972	Salt water degassing plant		
15 USA-395072	Sep.7, 1973	Causting soda refining process	3922154	Nov.25,1975
16 UK-41532	Sep.4, 1973	Caustic soda refining process	1438360	Sep.29,1976
17 USA-113424	Jan.28,1971	Multistage flash distillation plant	3801471	Apr.2, 1976

(4) Table of Technical Know-how

Subject of research commissioned	Description of know-how	Know-how number
Research on heating tube materials	Estimation of useful life of heating tube materials	51-05-101
	Data related to heat transfer coefficient	51-05-102
	Method of cost calculation for tube bundle	51-05-103
Research on degassing, decarboxylation and scale prevention methods	Heating tube cleaning method	51-05-201
	pH and decarboxylation unit	51-05-202
	A comparison of decarboxylation characteristics between packed tower and shower tower	51-05-203
	Deaeration characteristics of spray nozzle	51-05-204
Research on the production of chlorine and others	Method of preparing alkali starch powder for refining salt water	51-05-301
	Saline water refining method	51-05-302
	Behavior of traces in electrolytic saline water	51-05-303
	Concentration after evaporation of caustic solution	51-05-304
Research on electrodialysis process	Removal of turbidity by pit	51-05-401
	Use of ball cleaning as a measure against the increase of turbidity of waste brine in desaling plant	51-05-402
	Improvement of electrodialysis shell	51-05-403
	Limit of selective permeability of univalent ion	51-05-404
	Durability of electrodialysis shell	51-05-405
	Concentration test data	51-05-406
	Economy of electrodialysis process	51-05-407
Research on concrete shell module	Proprtioning of concrete	51-05-501
	Structure of concrete shell	51-05-502
	Test pressure of concrete shell	51-05-503
	Allowable stress of concrete	51-05-504
	Extra coefficient for a combination of loads	51-05-505
	Allowable maximum crack width of concrete shell	51-05-506

Subject of research commissioned	Description of know-how	Know-how number
Research on concrete shell module	Protective covering of bars and PC wire in concrete shell	51-05-507
	Location of fixed bearing of concrete shell	51-05-508
	Airtight and protective treatment of fittings	51-05-509
	Analytical method for concrete shell	51-05-510
	Airtightness and airtight treatment of concrete shell	51-05-511
	Changes in properties of concrete shell in operation	51-05-513
	Analysis of water quality and scales in the plant using concrete shells	51-05-514
High flow rate long tube multi-stage flash distillation test plant	Prevention of steam leaks between stages	51-05-601
	Data sheet related to heat transfer coefficient	51-05-602
	Data sheet related to temperature difference between brine and generated steam	51-05-603
	Load change characteristics of plant	51-05-604
	Performance of steam separator	51-05-605
	Materials of plant equipment	51-05-606
	Sludge formation mechanism and sludge prevention method	51-05-607
	Data on deaeration by chemical injection	51-05-608
	Method of installing liquid level gauge	51-05-609
	Optimum cleaning method with ball cleaning	51-05-610
	Characteristics of intermittent acid injection method	51-05-611
	Performance of multistage deaerator	51-05-612
	Distilled water post treatment plant and its capacity	51-05-613
	Type and arrangement of flash mechanism under high flow rate	51-05-614
	Opening area of orifice and flow coefficient under high flow rate	51-05-615
	Engineering data on heat and mass transfer under high flow rate	51-05-616
	Operation control techniques under high flow rate	51-05-617
	Operation method of the plant using concrete shells	51-05-512

4. Oceanic and Meteorological Data

(1) Main Marine Meteorology in Japan[1]

Location	Annual mean Temp.	Annual mean humidity	Precipi-tation	Location	Annual mean Temp.	Annual mean humidity	Precipi-tation
Wakkanai	6.3℃	76 %	1212㎜	Saigo	13.8℃	77 %	1888㎜
Abashiri	5.9	78	848	Sakai	14.5	76	2082
Kushiro	5.5	80	1112	Tottori	14.3	77	2042
Nemuro	5.7	81	1077	Hamada	14.9	73	1702
Urakawa	7.6	78	1133	Shimonoseki	15.4	74	1724
Tomakomai	—	—	—	Hiroshima	14.8	75	1644
Hakodate	8.2	79	1143	Okayama	14.5	75	1218
Aomori	9.6	78	1424	Kobe	15.5	68	1367
Akita	10.9	77	1807	Osaka	15.6	71	1390
Miyako	10.4	72	1289	Wakayama	15.8	72	1455
Sakata	11.8	78	1954	Shiono-misaki	16.8	73	2785
Sendai	11.6	75	1245	Izuhara	15.1	72	2171
Onahama	12.8	76	1396	Fukuoka	15.7	75	1705
Wajima	12.9	78	2382	Saga	15.8	75	1893
Aikawa	13.0	75	1656	Ohita	15.3	76	1689
Niigata	13.0	76	1850	Nagasaki	16.6	74	1976
Kanazawa	13.7	77	2662	Kumamoto	15.9	75	1939
Toyama	13.3	79	2388	Kagoshima	17.0	77	2433
Mito	13.0	78	1377	Miyazaki	16.8	78	2594
Tsuruga	14.4	76	2559	Fukue	16.2	76	2358
Nagoya	14.7	73	1540	Matsuyama	15.4	74	1381
Choshi	15.1	77	1729	Takamatsu	14.9	76	1185
Tsu	14.8	74	1714	Kochi	16.1	74	2645
Hamamatsu	15.5	72	1905	Tokushima	15.5	74	1693
Tokyo	15.0	69	1503	Ashizuri-misaki	17.8	71	2545
Owashi	15.2	76	4158	Muroto-misaki	16.4	74	2533
Yokohama	14.8	73	1632	Naze	21.2	76	3039
Ohshima	15.0	77	3002	Naha	22.3	78	2118
Hachijojima	18.1	77	3284				

[1] Chronological Table of Science, 1977, meteorology 6~19

(2) Coastal Meteorology in South East Asia and Near Middle East2)

Country	District	Temperature (℃)	Humidity (%)	Precipitation (mm)
Korea		12.1	65	1279
	Inchon	11.1	73	1089
	Mokpo	13.4	73	1126
Taiwan	Taipei	22.1	83	2100
Peoples' Republic of China	Koshun	24.8	76	2462
	Luta	10.6	65	607
	Tienchin	12.5	59	533
	Shunto	12.2	73	658
	Shanghai	16.1	76	1135
	Shamen	22.0	77	1179
Hongkong	Hongkong	22.6	80	2265
Philippines	Aparri	27.6	80	2312
	Manila	27.3	78	1791
Vietnam	Tourane	25.7	82	1970
	Saigon	27.0	78	1808
Thailand	Bangkok	28.0	80	1492
Malaysia	Kola Bharu	27.0	80	2755
Singapore	Singapore	27.1	80	2282
Burma	Rangoon	27.3	74	2530
India	Calcutta	26.8	71	1582
Iran	Bandar	26.7	67	147
	Bushehr	24.2	74	274
Kuwait	Kuwait	25.0	60	130
Oman	Sharjah	25.9	68	107
	Muscat	28.6	72	99
Saudi Arabia	Salala	25.6	71	81
	Aden	28.9	70	39
	Tidda	28.1	56	64

2) Chronological Table of Science, 1977, Meteorology 106∿170

(3) Major Seas of the World[3)]

	Name of sea	Area (10^6 km^2)	Volume (10^6 km^3)	Max. depth(m)	Average depth(m)	Temperature(°C)	Salinity (‰)
Oceans	Pacific Ocean	165.246	707.555	11,034	4,282	3.73	34.91
	Atlantic Ocean	82.441	323.613	9,218	3,926	4.02	35.37
	Indian Ocean	73.443	291.030	7,450	3,963	3.82	34.81
	Total	321.130	1322.198	11,034	4,117	—	35.00
Mediterranean seas (Seas between Continents)	Arctic Ocean	14.090	16.980	5,440	1,205	-0.66	25.5?
	Australia-Asia Mediterranean sea	8.143	9.873	7,315	1,212	6.90	33.87
	American Mediterranean sea	4.319	9.573	7,238	2,216	6.60	35.95
	Mediterranean sea	2.966	4.238	4,595	1,429	13.35	34.85
	Hudson Bay	1.232	0.158	229	128	1.02	7.8
	Red Sea	0.438	0.251	2,212	491	22.69	38.8
	Baltic sea	0.422	0.023	427	55	3.91	26.0?
	Persian Gulf	0.239	0.006	91	25	24.0?	36.7
	Total	31.848	41.066	7,315	1,232	—	30.7
Coastal seas	Bering Sea	2.268	3.259	4,085	1,437	2.0	30.3
	Sea of Okhostsk	1.528	1.279	3,374	838	1.50	30.9
	East China Sea	1.249	0.235	2,681	188	9.29	32.1
	Japan Sea	1.008	1.361	3,610	1,350	0.90	34.1
	Andaman Sea	0.798	0.694	3,641	870	10.09	31.5
	North Sea	0.575	0.054	680	94	7.72	35.5
	Gulf of Californic	0.162	0.132	2,904	813	9.14	30.5
	St. Lawrence Bay	0.238	0.030	572	127	2.18	34.8
	Others	0.254	0.015	—	—	12.50	35.5
	Total	8.079	7.044	4,085	874 874	—	31.86
	Total of all seas	361.057	1370.308	11,034	3,795		

3) Chronological Table of Science, 1977, geography 42.

(4) Tidal constants in Japan[4]

Location	High water interual	Spring range	Near range
Sea of Okhostsk			
Esashi	2h 53m	0.5m	0.2m
Abashiri	3 19	0.5	0.2
Pacific Ocean			
Hokkaido			
Kushiro	3 37	0.8	0.5
Muroran	3 54	1.1	0.4
Hakodate	3 58	0.7	0.3
East coast of Honshu			
Hachinohe	3 48	0.9	0.4
Miyako	3 56	0.9	0.4
Nohagi	4 2	1.0	0.3
Hirakata (North Ibaragi)	3 58	0.9	0.3
Inobozaki	4 33	0.9	0.3
Katsuura	4 54	1.0	0.4
South Coast of of Honshu			
Tokyo Reiganjima	5 43	1.3	0.5
Yokohama	5 21	1.4	0.5
Uraga(Yokosuka)	5 8	1.1	0.4
Shimoda	5 27	1.2	0.4
Shimizu	5 52	1.2	0.4
Yokkaichi	6 12	1.9	0.7
Toba	6 8	1.5	0.6
Kushimoto	6 2	1.3	0.5
Wakaura (Wakayama)	6 39	1.3	0.4
Izu Island			
Hachijo-shima	5 21	0.9	0.3
Shikoku			
Urato (Kochi)	6 17	1.4	0.6
Uwajima	7 21	1.7	0.7
Kyushu			
Hososhima (Hyuga)	6 25	1.4	0.6
Utsumi (Miyazaki)	6 0	1.5	0.6
Nansei Shoto			
Kuji (Amami-Ohshima, Seto-uchi)	6 50	1.6	0.7
Naha	6h 51m	1.6m	0.7m
Ishigaki	6 41	1.3	0.5
Japan Sea			
Hokkaido			
Wakkanai	3 46	0.1	0.0
Otaru	3 58	0.1	0.0
Honsyu			
Tsuchisaki (Akita)	3 8	0.1	0.1
Niigara	3 25	0.1	0.1
Fushiki (Takaoka)	2 47	0.2	0.1
Tsuruga	2 27	0.2	0.1
Sakai	2 35	0.1	0.0
Hamada	12 12	0.2	0.1
Inland Sea			
Osaka	7 14	1.0	1.0
Kobe	7 21	1.0	0.3
Takamatsu	11 19	1.6	0.8
Onomichi	11 2	3.0	1.4
Ujina (Hiroshima)	9 46	2.9	1.2
Tokuyama	8 42	2.6	1.1
Moji (Kita-Kyushu)	9 0	2.0	0.8
Wakamatsu (Kita-Kyushu)	9 56	1.1	0.4
Tsushima Strait			
Fukuoka	9 34	1.6	0.6
Izuhara	8 39	1.6	0.6
East China Sea			
Sasebo	8 21	2.5	0.9
Nagasaki	7 56	2.2	0.9
Suminoe (Saga,Yamaguchi)	9 13	4.9	1.9
Miike (Omuta)	8 56	4.6	1.8
Misumi	8 46	3.5	1.5
Akune	7 33	2.3	1.0
Kagoshima	7 9	2.3	0.9

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4) Chronological Table of Science, 1977, Geography 47.

(5) SurfaceaMarine Meteoroligy around Japan[5)]

Location	Water temp. (°C)	Salinity (‰)	Oxygen (ml/L)	Concentration (σt)	Dgree of clearness	Location	Water temp. (°C)	Salinity (‰)	Oxygen (mL/L)	Concentration (σt)	Degree of clearness
Wakkanai	8.14	33.89	6.85	26.13	12^{m}	Tottori	20.25.	33.54	5.09	23.17	23^{m}
Abashiri	8.50	33.07	7.18	25.32	10	Hamada	19.35	32.66	—	23.84	17
Kushiro	9.60	32.91	7.55	25.16	11	Shimonoseki	19.23	33.87	5.39	24.01	—
Nemuro	10.02	32.92	7.83	24.55	8	Hiroshima	16.62	32.66	—	23.84	—
Urakawa	14.28	33.13	6.53	24.46	12	Okayama	18.02	31.94	5.51	22.81	—
Tomakomai	13.38	33.12	6.39	24.67	16	Kobe	17.85	29.07	5.97	20.62	—
Hakodate	17.00	33.68	6.06	24.23	16	Osaka	17.85	29.07	5.97	20.62	—
Aomori	16.01	32.57	5.97	23.72	14	Wakayama	22.53	34.22	5.10	23.44	20
Akita	16.26	33.56	5.01	24.10	19	Shionomisaki	22.53	34.22	5.10	23.44	20
Miyako	13.78	33.46	6.51	24.86	16	Izuhara	19.35	33.74	5.34	23.88	16
Sakata	18.99	—	5.70	24.62	21	Fukuoka	20.34	33.62	5.10	23.57	12
Sendai	15.80	33.31	6.33	24.37	15	Saga	20.34	33.62	5.10	23.57	12
Onahama	17.38	33.02	5.70	23.99	11	Ohita	17.88	32.80	5.62	23.61	5
Wajima	20.07	33.71	5.21	23.65	20	Nagasaki	21.12	33.70	5.24	23.44	16
Aikawa	17.19	33.86	5.53	24.43	19	Kumamoto	20.25	31.68	5.46	22.40	7
Niigata	19.99	29.04	—	19.98	—	Kagoshima	21.26	34.23	4.93	23.76	20
Kanazawa	24.77	32.38	5.05	21.37	19	Miyazaki	23.40	34.26	4.96	23.22	21
Toyama	19.60	33.17	5.32	23.53	17	Fukue	21.11	33.93	5.21	23.59	17
Mito	17.83	33.42	5.76	24.03	11	Matsuyama	22.45	33.54	5.65	22.95	12
Tsuruga	18.16	30.92	5.67	23.94	—	Takamatsu	18.02	31.94	5.51	22.81	9
Nagoya	—	32.99	5.84	—	—	Kochi	22.72	33.44	4.82	23.19	19
Choshi	17.83	33.42	5.76	24.03	11	Tokushima	18.02	31.94	5.51	22.81	9
Tsu	17.43	32.99	5.83	23.76	14	Ashizuri	23.94	33.95	5.23	22.87	19
Hamamatsu	19.76	34.20	5.17	24.13	18	Murotomisaki	22.14	33.16	5.28	22.84	19
Tokyo	18.45	—	5.81	—	—	Naze	24.12	35.59	4.81	—	26
Owashi	20.98	34.40	5.17	23.98	21	Naha	24.68	34.74	4.72	—	23
Yokohama	18.45	32.73	5.81	23.46	—	Makurazaki	—	34.23	4.93	23.76	20
Ohshima	20.45	34.42	5.31	24.17	18	Tanegashima	23.02	34.43	4.86	23.36	24
Hachijo	22.81	34.54	5.00	23.54	24	Yakushima	23.18	34.43	4.91	23.26	22
Saigo	20.98	—	4.99	23.22	21	Irozaki	21.72	34.48	5.09	23.86	22
Sakai	22.43	33.28	4.90	22.64	23	Ishigakijima	26.11	34.56	4.71	22.84	25

5) Estimated from data furnished by the Maritime Safety Agency.

5. Water Quality Standards

(1) Water quality standard under the Water Service Act

Table-1 Water quality standards (Ministry of Health and Welfare Ordinance No. 11, May 6, 1966)

Requirements under Article 4, paragraph 1, Item 1 of the Act. (Water shall not be contaminated by pathogenic organisms nor shall contain orgasnisms or substances which are suspected to have been contaminated by pathogenic organisms)	Ammoniacal nitrogen and nitrogen nitrite.	Shall not be detected simultaneously.
	Nitrogen nitrite	Shall be less than 10 ppm.
	Chlorine ion	Shall be less than 200 ppm.
	Organic matters (Potasium permanganate consumption)	Shall be less than 10 ppm.
	Ordinary bacillus	The number of bacterial colonies in 1 mℓ of test water shall be less than 100.
	Colon bacilli	Shall not be detected
Requirements under Article 4, paragraph 1, Item 2 of the Act. (Water shall not contain cyanide, mercury and other other harmful substances)	Cyanide ion	Shall not be detected.
	Mercury	Shall not be detected.
	Organic phosphorus	Shall not be detedted.
Requirments under Article 4, paragraph 1, Item 3 of the Act. (Contents of copper, iron, fluorine, phenol and other substances shall not exceed the allowable limit)	Copper	Shall be less than 1.0 ppm.
	Iron	Shall be less than 0.3 ppm.
	Manganese	Shall be less than 0.3 ppm.
	Zinc	Shall be less than 1.0 ppm.
	Lead	Shall be less than 0.1 ppm.
	Sexivalent chrome	Shall be less than 0.05 ppm.
	Arsenic	Shall be less than 0.05 ppm.
	Fluorine	Shall be less than 0.8 ppm.
	Calcium, magnesium (hardness)	Shall be less than 300 ppm.
	Residue on evaporation	Shall be less than 500 ppm.
	Phenolic substances	Shall be less than 0.005 ppm. in term of phenol.
	Anion activator	Shall be less than 0.5 ppm.
Requirements under Article 4, paragraph 1, Item 4 of the Act. (Water shall not show an abnormal tendency of acidity or alkalinity)	Hydrogen ion concentration	pH value shall be more than 5.8 and less than 8.6.
Requirements under Article 4, paragraph 1, Item 5 of the Act. (Water shall be free from abnormal odours, except for odours caused by disinfection)	Odour	Shall not have abnormal odours.
	Taste	Shall not have abnormal tastes.
Requirements under Article 4, paragraph 1, Item 6 of the Act. (Water shall be nearyy colorless)	Chromaticity	Shall be less than 5 degrees.
	Turbidity	Shall be less than 2 degrees.

(2) Standards of Industrial Water

Qualities required for industrial water differ according to the types of industry and the uses, which are arranged in Table-2 to show the standard qualities. As for water for boilers, the standards (JIS B-8223) are separately precribed by the Boiler Association.

Table-3 shows the standard values of water which can be supplied by industrial waterworks, determined taking into consideration the qualities of water desired by consumers. This standard of water does not necessarily satisfy all types of industry and uses, and thus some consumers may need to retreat the water to adapt it to their uses. These tables have been cited from the Report of the Committee on Establishment of Industrial Water Quality Standards, Japan Industrial Water Association (Mar., 1971)

Table-2 Standard Water Quality Required of Industrial Water by Industry and Purpose

Industry	Purpose	Turbidity (ppm)	pH	Alkalinity CaCO$_3$ (ppm)	Hardness CaCO$_3$ (ppm)	Residue on evaporation (ppm)	Cl^- (ppm)	Fe (ppm)	Mn (ppm)
Food industry	Cooling	10	7	35	50	75	30	0.1	0.1
	Cleaning	5	7	35	50	80	20	0.1	0.1
	Raw material	1	7	60	60	80	20	0.1	0.1
	Temperature & humidity control	10	7	50	50	80	30	0.1	0.1
	Product treatment	1	7	40	30	80	10	0.1	0.1
Textile industry (dyeing & finishing processes excluded) Aparrel and other textile products manufacturers	Cooling	20	7	60	50	200	30	0.1	0.1
	Cleaning	20	7	50	50	200	20	0.1	0.1
	Raw material	—	—	—	—	—	—	—	—
	Temperature & humidity control	20	7	60	60	150	20	0.1	0.1
	Product treatment	20	7	50	50	150	15	0.1	0.1
Dyeing and finishing operator	Cooling	20	7	50	50	100	100	0.1	0.1
	Cleaning	1	7	50	100	50	20	0.05	0.05
	Raw material	1	7	50	10	50	10	0.01	0.01
	Temperature & humidity control	1	7	50	20	50	10	0.05	0.05
	Product treatment	1	7	50	10	50	10	0.05	0.05
Timber and lumber Processing industry, furniture manufacturers	Cooling	20	7	60	50	200	30	0.1	0.1
	Cleaning	20	7	50	50	200	20	0.1	0.1
	Raw material	—	—	—	—	—	—	—	—
	Temperature & humidity control	20	7	60	60	150	20	0.1	0.1
	Product treatment	20	7	50	50	150	15	0.1	0.1

Industry	Purpose	Turbidity (ppm)	p H	Alkalinity OaOo$_3$ (ppm)	Hardness CaCo$_3$ (ppm)	Residue on evaporation (ppm)	Oℓ$^-$ (ppm)	Fe (ppm)	Mn (ppm)
Pulp, paper, paper product processing industries	Cooling	10	7.5	50	100	150	30	0.05	0.02
	Cleaning	5	7.5	30	30	100	10	0.05	0.02
	Raw material	5	7	50	80	80	30	0.05	0.02
	Temperature & humidity control	2	7	50	50	100	10	00.5	0.02
	Product treatment	5	7.5	40	50	100	50	0.05	0.02
Publication, printing industries and related industries	Cooling	20	7	60	50	200	30	0.1	0.1
	Cleaning	20	7	50	50	200	20	0.1	0.1
	Raw material	—	—	—	—	—	—	—	—
	Temperature & humidity control	20	7	60	60	150	20	0.1	0.1
	Product treatment	20	7	50	50	150	15	0.1	0.1
Chemical industry	Cooling	20	7	50	50	200	80	0.1	0.05
	Cleaning	10	7	50	50	80	20	0.1	0.05
	Raw material	10	7	40	40	70	10	0.1	0.05
	Temperature & humidity control	15	7	70	60	130	20	0.1	0.05
	Product treatment	10	7	50	50	100	15	0.1	0.05
Petroleum products and coal products manufacturers	Cooling	30	7	40	50	200	10	0.1	0.05
	Cleaning	6	7	40	50	200	5	0.05	0.01
	Raw material	6	7	40	50	150	5	0.05	0.01
	Temperature & humidity control	6	7	90	80	200	5	0.1	0.01
	Product treatment	1	7	50	50	100	5	0.05	0.01
Rubber industry, tannery, leather industry, fur manufacturer	Cooling	20	7	60	50	200	30	0.1	0.1
	Cleaning	20	7	50	50	200	20	0.1	0.1
	Raw material	—	—	—	—	—	—	—	—
	Temperature & humidity control	20	7	60	60	150	20	0.1	0.1
	Product treatment	20	7	50	50	150	15	0.1	0.1
Ceramic industry, earth & stone works	Cooling	15	7	100	70	200	30	0.1	0.1
	Cleaning	15	7	20	40	30	20	0.1	0.1
	Raw material	10	7	30	30	50	10	0.1	0.1
	Temperature & humidity control	10	7	100	70	200	30	0.1	0.1
	Product treatment	10	7	100	70	200	15	0.1	0.1

Industry	Purpose	Turbidity (ppm)	pH	$CaCO_3$ (ppm)	Hardness $CaCO_3$ (ppm)	Residue on evaporation (ppm)	Cl^- (ppm)	Fe (ppm)	Mn (ppm)
Steel industry	Cooling	30	7	100	200	300	100	—	—
	Cleaning	30	7	100	200	300	100	—	—
	Raw material	—	—	—	—	—	—	—	—
	Temperature & humidity control	20	7	100	100	200	50	—	—
	Product treatment	20	7	100	100	300	50	—	—
Non-ferrous metals manufacturing industry Metal goods manufacturing industry	Cooling	20	7	40	60	300	20	0.1	0.1
	Cleaning	16	7	40	50	300	10	0.1	0.1
	Raw material	20	7	40	60	200	10	0.1	0.1
	Temperature & humidity control	20	7	40	60	200	10	0.1	0.1
	Product treatment	20	7	40	50	300	10	0.1	0.1
General machinery manufacturers Electric equipment manufacturers Transport equipment manufacturers Precision machine manufacturers Munitions manufacturers	Cooling	20	7	40	60	300	20	0.1	0.1
	Cleaning	20	7	40	50	300	10	0.1	0.1
	Raw material	—	—	—	—	—	—	—	—
	Temperature & humidity control	20	7	40	60	200	10	0.1	0.1
	Product treatment	20	7	40	50	300	10	0.1	0.1

Table-3 Standard Water Quality of Industrial Water Supply

Use	Turbidity (ppm)	pH	Alkalinity $CaCO_3$ (ppm)	Hardness $CaCO_3$ (ppm)	Residue on evaporation (ppm)	Cl^- (ppm)	Fe (ppm)	Mn (ppm)
Standard values of industrial water supply	20	6.5~8.0	75	120	250	80	0.3	0.2

6. Measuring Unit Conversion Tables

(1) Length

(mm)	(cm)	(m)	(km)	(in)	(ft)	(yd)	(mile)
1	0.1	0.001	—	0.039370	0.00328	0.001093	—
10	1	0.01	0.00001	0.39370	0.032808	0.010936	—
1,000	100	1	0.001	39.370	3.2808	1.09361	0.00062137
—	100,000	1,000	1	39,370	3280.8	1093.6	0.62137
25.40	2.5400	0.02540	0.0000254	1	0.08333	0.027778	0.04157828
304.80	30.480	0.30480	0.00030480	12	1	0.33333	1.8939
914.402	91.4402	0.914402	0.00091440	36	3	1	0.00056818
—	160.935	1609.35	1.60935	63,360	5,280	1,760	1

1 Å (angstrom) = 10^{-8}cm, 1 μ(micron) = 10^{-3}mm = 10^{-4}cm

(2) Area

(m^2)	(a)	(km^2)	(in^2)	(ft^2)	(yd^2)	(ac)
1	0.01	0.000001	1550.1	10.7639	1.1959	0.0_32471
100	1	0.0001	15,501	1076.4	119.6	0.024710
1,000,000	10,000	1	—	10,764,000	1,196,000	247.1044
0.00064516	0.000006	—	1	0.0069444	0.03771605	—
0.092903	0.00092903	—	144	1	0.11111	0.0_422957
0.83613	0.0083613	0.0_68	1,296	9	1	0.0_320661
4046.849	40.46849	0.0040468	627,264	43,560	4,840	1

(3) Cubic volume

(m^3)	(ℓ)	(in^3)	(ft^3)	(yd^3)	U.S.A. (gal)	British (gal)
1	1,000	61,023	35.3147	1.30785	264.172	219.969
0.0010000	1	61.025	0.0353147	0.0013078	0.264172	0.219969
$0.0_4 16387$	0.016387	1	0.0357870	$0.0_4 21433$	0.0043290	0.003605
0.0283168	28.3168	1,728	1	0.037034	7.48053	6.22883
0.76456	764.56	46,656	27	1	202.0	168.17
0.0037854	3.78541	231.00	0.133681	0.004951	1	0.832674
0.0045461	4.54609	277.420	0.160543	0.005946	1.20095	1

1 barrel (petroleum) = 42 gal (US) = 35 gal (UK) = 158.99 ℓ

(4) Weight

(g)	(kg)	(t)	US (t)	UK (t)	UK (oz)	(lb)	(grain)
1	0.001	0.000001	—	—	0.035274	0.0022046	15.432
1,000	1	0.001	$0.0_3 98421$	0.0011023	35.274	2.2046	15432.4
1,000,000	1,000	1	0.984207	1.10231	35,274	2204.6	—
—	907.185	0.907185	1	0.892857	32,000	2,000	—
—	1016.05	1.01605	1.1200	1	35,840	2,240	—
28.3495	0.02835	$0.0_4 283495$	$0.0_4 3125$	$0.0_4 27902$	1	0.062369	437.5
453.592	0.453592	$0.0_3 45359243$	0.00005	$0.0_4 44643$	16	1	7,000
0.064799	0.000065	—	—	—	0.0022857	$0.0_3 14286$	1

1 carat = 200 mg
1 t (metric system) = 0.9842 ling ton (UK)
= 1.102 short ton (US)

(5) Density

(g/cm^3)	(g/ℓ) or (kg/m^3)	(lb/in^3)	(lb/ft^3)	(lb/gal US)	(lb/gal UK)	(grain/gal US)	(grain/gal UK)
1	1,000	0.036127	62.427	8.3454	10.022	58,417	70,155
0.001	1	$0.0_4 36127$	0.062427	$0.0_2 83454$	0.01002	58.417	70.155
27.6799	27679.9	1	1,728	231.00	277.39	—	—
0.0160185	16.0185	$0.0_3 57871$	1	0.133681	0.160544	935.763	1123.81
0.119826	119.826	0.004329	7.48049	1	1.20095	7,000	8406.65
0.099776	99.776	0.003605	6.2288	0.83267	1	5828.72	7,000
$0.0_4 17118$	0.017118	$0.0_6 6184$	0.0010687	0.0001429	0.0001716	1	1.2009
$0.0_4 14254$	0.014254	$0.0_6 5150$	$0.0_3 88986$	0.0001189	0.0001429	0.83268	1

(6) Pressure

(bar)	(kg/cm^2)	(lb/in^2)	(atm)	Mercurial column (0°C)		Water column (15°C)	
				(m)	(in)	(m)	(in)
1	1.01972	14.5038	0.986923	0.750062	29.5300	10.2064	401.825
0.980665	1	14.2233	0.967841	0.735559	28.9590	10.0090	394.056
0.068948	0.070307	1	0.0680460	0.0517149	2.03602	0.703704	27.705
1.01325	1.03323	14.6959	1	0.760	29.9213	10.3416	407.149
1.33322	1.35951	19.3368	1.31579	1	39.3701	13.6074	535.723
0.033864	0.0345316	0.491154	0.0334211	0.02540	1	0.345627	13.6074
0.097978	0.09991	1.42105	0.096697	0.0734896	2.89329	1	39.3701
0.002489	0.0025377	0.03609	0.002456	.0.0018666	0.0734895	0.0254	1

1 lb/in^2 = 1 psia (pound per square inch absolute)

1 mm Hg = 1 Torr,

(7) Speed

(m/sec)	(m/min)	(m/hr)	(km/hr)	(ft/sec)	(ft/min)	(mile/hr)
1	60	3,600	3.6	3.2808	196.850	2.23693
0.016667	1	60	0.06	0.054681	3.2808	0.037282
$0.0_{3}2778$	0.01667	1	0.001	$0.0_{3}9114$	0.05468	$0.0_{3}6214$
0.2778	16.667	1,000	1	0.91134	54.6807	0.62137
0.30480	18.288	1,097.28	1.09728	1	60	0.68182
0.005080	0.30480	18.287	0.018287	0.016667	1	0.011364
0.44704	26.8224	1,609.34	1.60934	1.46667	88	1

1 knot = 1 kair /hr = 6080 ft/hr

(8) Flow rate

(ℓ/sec)	(m^3/hr)	(m^3/sec)	(galUS) /min)	(gal UK) /min)	(ft^3/hr)	(ft^3/sec)
1	3.6	0.001	15.8503	13.1985	127.133	0.035315
0.27778	1	$0.0_{3}27778$	4.4029	3.6663	35.315	$0.0_{2}9810$
1,000	3,600	1	15,850.3	13,198.5	127,133	35.3147
0.06309	0.2271	$0.0_{4}6309$	1	0.8325	8.0208	$0.0_{2}2228$
0.075766	0.27276	$0.0_{4}75775$	1.2009	1	9.6323	$0.0_{2}2676$
$0.0_{2}7866$	0.02832	$0.0_{5}7866$	0.11247	0.1038	1	$0.0_{3}2778$
28.3153	101.941	0.02832	448.831	373.741	3,600	1

1000 GPD (US) = 3.785 m^3/day, 1 MGPD (US) = 3,785 m^3/day
1000 GPD (UK) = 4.546 m^3/day, 1 MGPD (UK) = 4,546 m^3/day
(GPD = gallon per day, MGPD = megagallon per day)

(9) Viscosity

(kg/m·hr)	(c p)	(p=g/cm·sec)	(kg/m·sec)	(lb/ft·sec)	(kg·sec/m²)	(Lb·sec/ft²)
1	0.2778	0.002778	0.0002778	0.00018667	$0.0_{4}2833$	$0.0_{5}5801$
3.60	1	0.01	0.001	0.0006720	0.00010197	$0.0_{4}20886$
360	100	1	0.1	0.06720	0.010197	0.0020886
3,600	1,000	10	1	0.6720	0.10197	0.020886
5,357	1,488.1	14.881	1.4881	1	0.15175	0.031081
35,304	9,806.65	98.0665	9.80665	6.5898	1	0.20482
172,368	47,880	478.80	47.880	32.174	4.8824	1

p = poise, cp = centi poise

(10) Work Energy and Calory

($joul_{ads}$)	(lb·ft)	(kg·m)	(ℓ·atm)	(Btu $_{60°F}$)	(kcal $_{15°C}$)	(kW·hr)
1	0.737562	0.101972	0.00986896	$0.0_{3}948281$	$0.0_{3}238920$	$0.0_{6}277778$
1.35582	1	0.132255	0.0133805	0.00127570	$0.0_{3}323833$	$0.0_{6}376616$
9.80665	7.23301	1	0.0967814	0.00929946	0.00234300	$0.0_{5}272407$
101.328	74.7356	10.3326	1	0.0960874	0.0242093	$0.0_{4}281466$
1,054.54	777.789	107.533	10.4072	1	0.251951	$0.0_{3}292928$
4,185.50	3,087.07	426.80	41.3065	3.96903	1	0.00116264
3.6×10^{6}	2.65522×10^{6}	3.67098×10^{5}	3.55282×10^{4}	3,413.81	860.112	1

1 erg = 1 dyn·cm = 10^{-7} $joul_{ads}$, 1 Watt·sec = 1 VA·sec = 1 $joul_{ads}$, 1 Btu (British thermal unit) $_{60°F}$ = Calory required to raise the temperature of 1 lb of water from 60°F to 61°F, 1 kcal 60°C = calory required to raise the temperature of 1 kg of water from 14.5°C to 15.5°C, 1 chu (centigrade heat unit)/lb = 1 kcal 15°C/kg

(11) Motive power

(kW)	(HP)	(PS)	(Btu/min)	(kg·m/sec)	(cal/sec)	(ft·lb/sec)
1	1.34102	1.35962	56.868	101.972	238.92	737.56
0.74570	1	1.01387	42.406	76.040	178.163	550.00
0.73550	0.58632	1	41.826	75.000	175.726	542.48
0.0175965	0.023597	0.023925	1	1.79435	4.2042	12.9785
0.0098067	0.0131509	0.0133333	0.55769	1	2.34302	7.2330
0.0041897	0.0056185	0.0056964	0.238260	0.42723	1	3.0902
0.00135582	0.00181818	0.00184340	0.077103	0.138255	0.32393	1

(12) Specific heat

(cal/g·℃)	(kcal/kg·℃)	(Btu/lb·℃)	(Chu/lb·℃)	(Joul/g·℃)
1	1	1	1	4.1868
0.238846	0.238846	0.238846	0.238846	1

(13) Heat flow rate

(cal/cm^2·sec)	(W/cm^2)	(cal/cm^2·hr)	(Btu/ft^2·hr)	(kcal/m^2·hr)
1	4.1868	3,600	13,272.1	36,000
0.238846	1	859.845	3,169.98	8,598.45
0.000277778	0.00116300	1	3.68669	10
0.0000753461	0.000315459	0.271246	1	2.71246
0.0000277778	0.00011625	0.1	0.368669	1

(14) Heat conductivity

(cal/cm·sec·℃)	(Joul/cm·sec·℃)	(W/cm·℃)	(Btu/ft·hr·°F)	(kcal/m·hr·℃)
1	4.18140	4.18140	241.75	360
10.23901	1	1	57.780	86.044
0.0041365	0.017307	0.017307	1	1.48817
0.0027778	0.0116296	0.0116296	0.67196	1

(15) Heat transfer coefficient

(kcal/m²hr·℃)	(Btu/ft²·hr·°F)	(Btu/in²·hr·°F)	(kcal/m²·sec·℃)	(cal/cm²·sec·℃)
1	0.20481	0.00142231	0.00027778	0.000027778
4.8825	1	0.0069444	0.0013562	0.00013562
703.08	143.998	1	0.19530	0.019530
3,600	737.308	5.1203	1	0.1
36,000	7,373.08	51.203	10	1

(16) Temperature conversion formula

t [℃] = (t [°F] − 32)/1.8

t [°F] = 1.8 × t [℃] + 32

T [°K] = t [℃] + 273.15

T [°R] = t [°F] + 459.67 = 1.8 × T [°K]