# Recent Progress of Membrane Technology and Its New Application for Water Treatment

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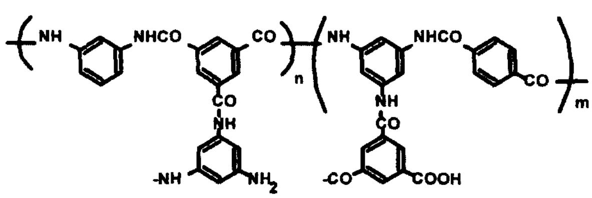
## 1. INTRODUCTION

Nowadays, membrane separation such as reverse osmosis (RO) and ultrafiltration (UF) play an important role in the industrial separation technology. Among desalination technologies available today, reverse osmosis is usually the most economical process for wide range of water salinity. Main applications include production of high purity water, desalination of seawater and brackish water for a drinking water supply, treatment of waste water for environmental protection, and recovery of precious materials from industrial waste water.

In the market of reverse osmosis membrane, thin film composite membranes have reached a major position, because of their outstanding membrane performance and durability [1]. In a typical thin film composite membrane, an ultra-thin salt barrier layer covers the surface of a porous polysulfone substrate. This salt barrier layer is formed by an in-situ interfacial polymerization reaction or an in-situ crosslinking reaction at the surface of the water soluble polymer layer. Figure 1 illustrates a typical structure of the thin film composite



T.Uemura,Y.Himeshima and M.Kurihara U.S.Pat. 4,761,234 (1988).

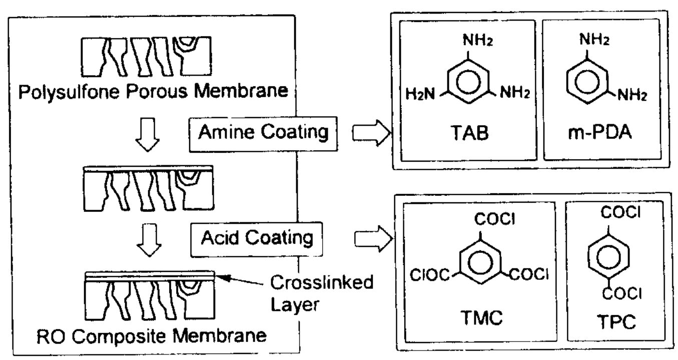
Figure 1. Toray's crosslinked fully aromatic polyamide Composite membrane (UTC-70)

membrane, Toray "UTC-70".

The diversity of application in an industrial market shapes the development of specialized membranes with its demands for unique performance characteristics. Such demands are represented as follows; (1) high selectivity, (2) high water permeability, and (3) tolerance for oxidizing agents.

High selectivity is a major requirement in seawater desalination to gain potable water with a high recovery rate, and in ultrapure water production for the electronics industry to remove low molecular weight Total Organic Carbon (TOC). High water permeability is necessary for low pressure, low running cost operation. Tolerance for oxidizing agents allows disinfection by chlorine, such that the membrane systems will operate dependably without biological fouling

To satisfy these requirements, much research has been done on membrane materials, structure and fabrication technology. In-situ interfacial polycondensation method (Figure 2) and in-situ crosslinking reaction at the surface of the water soluble polymer layer method were developed to obtain the high performance composite membrane [2],[3],[4],[5],[6]. With this method, crosslinked polyamide composite membranes, which meet the previously discussed requirements, have been produced commercially and have become one of the major reverse osmosis membrane types today.




T.Uemura, Y.Himeshima and M.Kurihara U.S.Pat. 4,761,234(1988).

Figure 2. In-Situ Interfacial Polycondensation

From the view point of operating pressure, synthetic low pressure composite membranes which can be used at around 1.5 MPa, became to be used in the field of desalination of brackish water and production of ultrapure water because of a high water permeability and a high solute rejection. Recently, ultra low pressure RO membrane which can be used at below 1.0 MPa, and loose RO (LRO) membrane or nanofiltration

(NF) membrane which has high water permeability and low NaCl rejection, are developed.

Also the membrane filtration technology continues to place great emphasis on the removal of contamination from various kind of process water, and more economical and reliable procedures are required. In order to satisfy these filtration membrane, we have developed a new type membrane. This new membrane and its modules are specially designed for reducing membrane fouling.

In this paper, we will mention membrane performance and these practical use focused on reverse osmosis membranes and ultrafiltration membranes recently developed by Toray.

## 2. ULTRA LOW PRESSURE RO MEMBRANE

Today, as a much lower pressure operation is required from a view point of energy saving, improvement of a water productivity of membrane element is one of the technological trends in the field of low pressure RO membrane elements. Such improvement had been achieved by means of expanding nominal active membrane surface area or improving water flux of the membrane. Consequently a few kinds of ultra low pressure RO membrane elements which can be used below 1.0 MPa has become commercially available [7],[8].

Toray's UTC-70 membrane [9] is a low pressure RO membrane which can be used at around 1.5 MPa and UTC-70L membrane is a ultra low pressure membrane which can be used at around 1.0 MPa. They are crosslinked fully aromatic polyamide ultra-thin composite membranes manufactured by in-situ interfacial polymerization reaction. They have a high water permeability, a high salt rejection, a high organic solute rejection and a high silica rejection, which is suitable for desalination of brackish water. They are commercially available as a spiral-wound element SU-700 and SU-700L from 1987 and 1988 respectively.

Recently, we have developed a new crosslinked fully aromatic polyamide ultra low pressure composite RO membrane (UTC-70UL) which can be used at around 0.75

MPa. UTC-70UL has approximately two times higher water flux than UTC-70 keeping the high solute rejection of UTC-70 [10].

## 3. ULTRA LOW PRESSURE RO MEMBRANE ELEMENTS FOR BRACKISH WATER DESALINATION

SUL-G20 element is a 8 inch diameter spiral-wound element for brackish water desalination using UTC-70UL membrane, which has a high productivity and a high solute rejection same as the conventional membranes and elements (SU-720L: 8 inch diameter spiral-wound element using UTC-70L membrane; SU-720: 8 inch diameter spiral-wound element using UTC-70 membrane) at ultra low pressure 0.75 MPa (Table 1,2).

Table 1. Historical Performance Changes of TORAY's Brackish Water RO Element

| Items | | SU-720 (1987) | SU-720L (1988) | SUL-G20 (1996) |
|---|---|---|---|---|
| Performance | | | | |
| Salt Rejection | (%) | 99.4 | 99.0 | 99.3 |
| Water Permeability | ($m^3$/day) | 26.0 | 22.0 | 30.0 |
| Test condition | | | | |
| Operating Pressure | (MPa) | 1.47 | 0.98 | 0.74 |
| Temperature | (°C) | 25 | 25 | 25 |
| Feed Conc. | (mg/l as NaCl) | 1500 | 1500 | 500 |
| Brine Flow Rate | (l/min) | 80 | 80 | 80 |
| Recovery | (%) | 12 | 12 | 12 |
| Measurement | | | | |
| Diameter | (mm) | 201 | 201 | 201 |
| Length | (mm) | 1016 | 1016 | 1016 |
| Weight | (kg) | 16.5 | 16.5 | 16.5 |

Table 2. Organic Compounds Separation Performance of UTC-70 series Membrane

| Compounds (Molecular Weight) | Rej. (%) UTC-70 | UTC-70L | UTC-70UL |
|---|---|---|---|
| Methyl Alcohol (32) | 14 | 8 | 4 |
| Ethyl Alcohol (46) | 54 | 40 | 42 |
| Isopropyl Alcohol (60) | 96 | 91 | 92 |
| Urea (60) | 63 | 46 | 49 |
| Acetone (58) | 70 | 55 | 58 |
| Acetic Acid (60) | 55 | 41 | 46 |
| Ethylenediamine (60) | 95 | 84 | 83 |
| Operating Pressure (MPa) | 1.47 | 0.74 | 0.74 |

Test Condition : 1000ppm, 25°C, pH6.5

## 4. ULTRA LOW PRESSURE RO MEMBRANE ELEMENT FOR ULTRAPURE WATER PRODUCTION

Table 3. Historical Performance Changes of TORAY's RO Membrane Element for Ultra Pure Water Production

| Items | | SU-710P (1990) | SUL-G10P (1996) |
|---|---|---|---|
| Performance | | | |
| IPA Rejection | (%) | >89.0 | >93.0 |
| Water Permeability | ($m^3$/day) | 8.0 | 6.5 |
| Test condition | | | |
| Operating Pressure | (MPa) | 1.47 | 0.74 |
| Temperature | (°C) | 25 | 25 |
| Feed Conc. | (mg/l as IPA) | 1000 | 1000 |
| Brine Flow Rate | (l/min) | 20 | 20 |
| Recovery | (%) | 12 | 12 |
| Measurement | | | |
| Diameter | (mm) | 101 | 101 |
| Length | (mm) | 1016 | 1016 |
| Weight | (kg) | 4.3 | 4.3 |

SUL-G10P element is a 4 inch diameter spiral-wound element especially designed for ultrapure water production, which has a high productivity and a high solute rejection and a start-up characteristic better than the conventional element (SU-710P [11]: 4 inch diameter spiral-wound element for ultrapure water production) (Table 3, Figure 3).

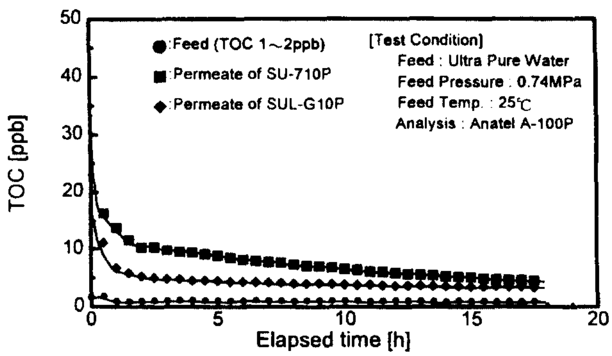


Figure 3. Start-up Characteristics of TOC with SUL-G10P and SU-710P

## 5. LOOSE RO MEMBRANE

Loose RO membrane (LRO), which also called nanofiltration (NF) [12],[13], has been developed and become commercially available. Most of loose RO (LRO) membrane are crosslinked piperazine polyamide ultra-thin composite membranes manufactured by in-situ interfacial polymerization reaction (Figure 4). This membrane has

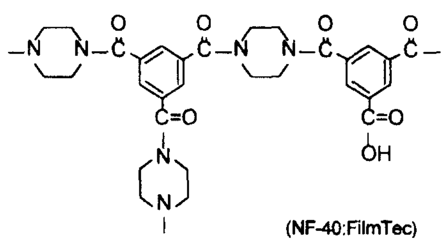

(NF-40:FilmTec)

Figure 4. Chemical structure of crosslinked piperazine polyamide (typical lose RO membrane)

intermediate separation performance between RO membrane and UF membrane. Based on its unique separation performance, loose RO (LRO) membrane has been used wide range of application. Its main applications are softening of water and concentration of organic materials and desalination of organic materials in production process of food, medicine or biological industry. Recently it has been developed that the application of loose RO (LRO) membrane for high grade purification of drinking water. Also application of loose RO (LRO) membrane for high level of drinking water purification has been investigated on a project named "Membrane Aqua Century 21" in Japan. Main objects of this project are (1) reducing of byproduct of disinfection, (2) reducing of agricultural chemical or smelling material, (3) rejection of viruses, (4) treatment of waste water [14].

UTC-20 and UTC-60 membrane are such loose RO membranes, having high water permeability and solute selectivity. They are crosslinked piperazine polyamide ultra-thin composite membranes. Typical separation performance of UTC-20 and UTC-60 membrane are shown in table 4. UTC-20 is an anionic membrane and UTC-60 is a cationic membrane [15].

Table 4. Performance of TORAY's Loose RO Membranes Elements

| Items | | SU-220[1) (1985)] | SU-620 (1988) [2)] |
|---|---|---|---|
| Performance | | | |
| Salt Rejection | (%) | 60* | 55* |
| Water Permeability | ($m^3$/day) | 44.0 | 18.0 |
| Test condition | | | |
| Operating Pressure | (MPa) | 0.74 | 0.34 |
| Feed Conc. | (mg/l as NaCl) | 500 | 500 |

1)M.Kurihara,T.Uemura,Y.Nakagawa,T.Tonomura, Desalination, 54, 75(1985).
2)T.Sasaki,H.Fujimaki,T.Uemura,M.Kurihara, U.S.Pat. 4,758,343 (1988).
* Low Salt Rej. means the loose RO Membrane

Table 5 represented agricultural chemicals separation performance through UTC-20 and UTC-60 membrane compared to low pressure RO membrane (UTC-70L). In this experiments simazine and atrazine were added to feed water as a typical agricultural chemicals. And concentration

Table 5. Agricultural chemicals and silica separation performance of UTC-20, UTC-60 and UTC-70L membrane

| | Items | UTC-20 | UTC-60 | UTC-70L |
|---|---|---|---|---|
| | Flux($m^3/m^2hr$) * | 1.23 | 1.22 | 0.55 |
| Rejection (%) | 5ppb simazine | 88.1 | 36.7 | 98.6** |
| Rejection (%) | 5ppb simazine +100ppmNaCl | 78.5 | 52.5 | - |
| Rejection (%) | 5ppb atrazine | 94.9 | 86.1 | 98.8 |
| Rejection (%) | 50ppm$SiO_2$ | 18.9 | 18.0 | 99.4 |

Test conditions : 0.54MPa,pH6.5,25°C
* 500ppmNaCl **40ppb simazine

of each agricultural chemicals in feed or permeate were determined by ELISA method. Simazine (CAT: 2-Chloro-4,6-bis-ethylamino-S-triazine) and atrazine (2-Chloro-4-ethylamino-6-isopropylamino-S-triazine) have similar molecular weight, 201.6 and 215.7 respectively, and similar molecular structure, which has one chloride and two amino groups on a triazine ring (Figure 5). From these chemical structure, it seems that these agricultural chemicals has week base characteristic. Simazine and atrazine rejection of UTC-20 membrane are higher than that of UTC-60. Especially, atrazine rejection of UTC-20 is nearly 95%. Because of this high rejection, UTC-20 will be able to use for reducing of atrazine concentration in water, in case of low atrazine concentration feed. Simazine rejection of these membrane changed with concentration of sodium chloride in the feed water. This phenomena seems to be caused by separation mechanism of membrane. Simazine rejection of UTC-20 membrane is even lower than 90%. It is necessary to improve rejection, to practical use of these membrane for high level drinking water treatment.

simazine Mw 201.6 atrazine Mw 215.7

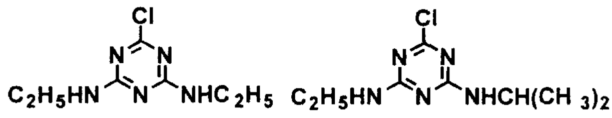



Figure 5. Molecular weight and chemical structure of agricultural chemicals

## 6. SEAWATER DESALINATION MEMBRANE

UTC-80 membrane, specified for seawater desalination has been developed by utilizing and expanding the technology of UTC-70. SU-820 spiral wound membrane element, using UTC-80 membrane, exhibits excellent high salt rejection characteristic, average of 99.75%, and high water

Table 6. Performance of SU-820 Membrane Element

| Items | | | SU-820 |
|---|---|---|---|
| Performance | | | |
| Salt Rejection | (%) | Average | 99.75 |
| | | Minimum | 99.60 |
| Water Permeability | ($m^3$/day) | Average | 16 [illegible] |
| | | Minimum | [illegible] |
| Test condition | | | |
| Operating Pressure | ($kg/cm^2$) | | 56 |
| Temperature | ( °C) | | 25 |
| Feed Conc. | (% as seawater) | | 3.5 |
| Brine Flow Rate | (l/min) | | 80 |
| Recovery | (%) | | 12 |
| Measurement | | | |
| Diameter | (mm) | | 201 |
| Length | (mm) | | 1016 |
| Weight | (kg) | | 16.5 |

productivity of 16m$^3$/day at conditions described in Table 6 [17]. Table 7 shows typical water quality and performance at a practical seawater desalination plant. The data shows that the TDS of permeate is 85 ppm in the condition of feed water TDS being 34,810 ppm at a practical seawater desalination using SU-820 element, and which is low enough for the Ministry of Health and Welfare's new Standard of Water Quality (500 ppm as TDS).

Recently maximum concentration of total THM (0.1 ppm) and bromoform (0.09 ppm) have been added to the Ministry of Health and Welfare's new Standard of Water Quality. Accordingly the removal of THM should be very important in both seawater and brackish water desalination technology.

Table 7. Typical Water Quality and Performance at a Practical Seawater Desalination Plant

| Constituent | | Feed Water | Permeate | Rej. (%) |
|---|---|---|---|---|
| Total Dissolved Solid (TDS) | (ppm) | 34,810 | 85.00 | 99.77 |
| Sodium | (ppm) | 10,200 | 30.00 | 99.72 |
| Potassium | (ppm) | 380 | 2.50 | 99.35 |
| Calcium | (ppm) | 310 | 0.25 | 99.92 |
| Magnesium | (ppm) | 1,210 | 0.89 | 99.93 |
| Chloride | (ppm) | 20,900 | 61.60 | 99.71 |
| Bicarbonate | (ppm) | 1,400 | 7.30 | 94.79 |
| Sulfate | (ppm) | 2,660 | 2.27 | 99.92 |
| Total Hardness as $CaCO_3$ | (ppm) | 5,960 | 4.30 | 99.93 |
| pH | | 6.8 | 5.7 | |

Operating Conditions: 5.5 MPa,25 °C, Brine Flow Rate 80 l/min

THM separation performance were measured for UTC-80 membrane mentioned above, and Toray's SC-8000 membrane which is the double stage seawater cellulose acetate membrane.

Testing was conducted as follows. The closed-loop feed water flow containing 3.5% sodium chloride was held constant with a temperature of 25°C and a pH of 6.5. The feed water was fed into membrane test cells at a pressure of 5.5MPa. After measurement of salt separation performance, several THM compounds were dissolved in the feed solution. Membranes were equilibrated in operation for 1.5 hr before measurement. Concentration of each THM component in the feed and the permeate

Table 8. THM Separation Performance of UTC-80 Membrane Compared to that of Cellulose Acetate Membrane

| Material Names of Trihalomethane | Feed (ppb) | UTC-80 Perm. (ppb) | UTC-80 Rej. (%) | Toray's CA Membran Perm. (ppb) | Toray's CA Membran Rej. (%) |
|---|---|---|---|---|---|
| Chloroform | 190 | 9.5 | 95.0 | 190 | 0 |
| Chlorodibromomethane | 195 | 1.4 | 99.3 | 150 | 23 |
| Bromodichloromethane | 175 | 3.7 | 96.0 | 150 | 14 |
| Bromoform | 145 | < 1 | >99.3 | 120 | 17 |
| Dichloroacetic Acid | 130 | <10 | >92.0 | - | - |
| Trichloroacetic Acid | 190 | 3 | 98.0 | - | - |
| Chloroacetonitrile | 170 | 69 | 59.0 | - | - |
| Chloral Hydride | 190 | 6.4 | 97.0 | - | - |
| Trichloroethylene | 150 | < 1 | >99.3 | 88 | 41 |
| Trichloroethane | 130 | < 1 | >99.2 | 95 | 27 |
| Tetrachloroethylene | 135 | <0.5 | >99.6 | 60 | 56 |
| Membrane Performance | | 99.67%-0.55m$^3$/m$^2$day | | 97.1%-0.49m$^3$/m$^2$day | |

were measured by gas chromatography and the rejection for each THM compounds were calculated (Table 8).

In the permeate of UTC-80 membrane, most THM components were detected less than 10 ppb. For example, chloroform and bromoform were detected 9.5 ppb and less than 1 ppb respectively. The rejection for each compounds were calculated to be 95% and at least 99.3%. On the other hand, when the membrane is SC-8000, the rejection for chloroform and bromoform were 0% and 17% respectively. These results reveal that the crosslinked fully aromatic polyamide ultra-thin composite membrane had a extremely higher THM rejection comparing to cellulose acetate membrane.

The affinity of trihalomethane with membrane materials are presumed to cause such a difference of trihalomethane rejection. The solubility parameter of cellulose acetate is smaller than that of aromatic polyamide, and is closer to that of THM (Figure 6). It could be easily considered that THM has stronger affinity with cellulose acetate than aromatic polyamide. So THM should be easily absorbed in cellulose acetate membrane and could permeate through the membrane.

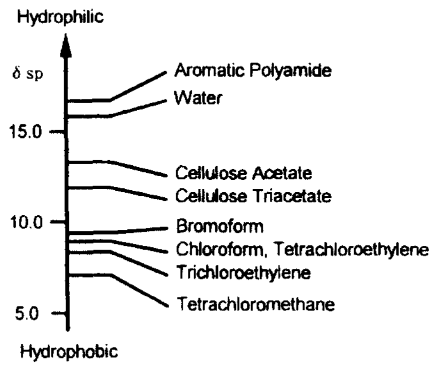


Figure 6. Solubility Parameter of Membrane Materials and THM

SU-820 series membrane elements have been used at various RO seawater desalination plants in Europe and Japan. It has been already demonstrated that SU-820 elements are stable in the 240 $m^3$/day desalination plant at Kitadaitou island of Okinawa prefecture in Pacific Ocean for over 3 years period. They are used at the 7,000$m^3$/day RO seawater desalination plant located in Ibiza island (Spain), and they are stable over one year period. Recently they are used at the 30,000$m^3$/day (total water productivity is planned 40,000$m^3$/day) RO seawater desalination plant located in Okinawa prefecture, which is the largest RO seawater desalination plant in Japan.

## 7. HOLLOW FIBER ULTRAFILTRATION MEMBRANE

The hollow fiber membrane is prepared from specially polymerized polyacrylonitrile (PAN), which molecular weight is about three times larger than that of commercially available PAN, by means of Toray's polymer technology [18][19][20][21]. It brings sufficient mechanical strength of the hollow fiber membrane for practical membrane cleaning and air scrubbing procedures. The membrane shows low absorption level of against fouling components.

The membrane morphology is designed to be asymmetric, with skin layer on the outer feed side surface. The pore size on the skin layer (about 0.01 to 0.03 micrometers) is smaller than that of usual microfiltration membranes, and small enough compared with most of fouling components such as suspended solids and microorganisms. Such fouling components are to be remained on the outer surface without sticking into the interior of the membrane. These characteristics allow the fouling components on the membrane to be removed very easily by simple membrane cleaning procedures as air scrubbing.

Two types of membrane modules (simple type module and tank type module), have been developed and started to be used in many applications. Simple type module is an 4 inches diameter membrane module, which membrane area is 12 $m^2$ and can be easily installed in the apparatus. Tank type module consists of some 4 inches cartridge type membrane elements and tank-type module in which these elements are installed. The tank type module are suitable for large volume water treatment and its membrane area is chosen from about 80 to 600 $m^2$. The specifications of the modules are sown in Table 9 and Figure 7.

Table 9. The specifications of the modules

| Capacity | ($m^3$/d) | 70 | 200 | 500 |
|---|---|---|---|---|
| Number of Elements | | 7 | 19 | 48 |
| Membrane Area | ($m^2$) | 84 | 228 | 576 |
| Diameter (D) | (cm) | 45 | 75 | 120 |
| Height (H) | (cm) | 200 | 230 | 250 |

Membrane modulcs can be operated for more than 2 to 3 years, with physical and chemical cleaning procedures. Among some physical cleaning procedures, air scrubbing procedurc which is carried out every one to eight hours is effective. In air scrubbing procedure, hollow fibers are moved and scrubbed each other by feeding air bubbles, and fouling components are easily floated up and removed from membrane surface into the outside water to be drained afterwards. Though usual fouling components are removed by air scrubbing, some fouling components might be deposited on membrane surface during long term operations. At in these cases, fouling components are expected to be removed by chemical cleaning using proper chemicals such as oxalic acid, citric acid, sodium hydroxide, sodium lauryl sulfate, sodium hypochlorite.

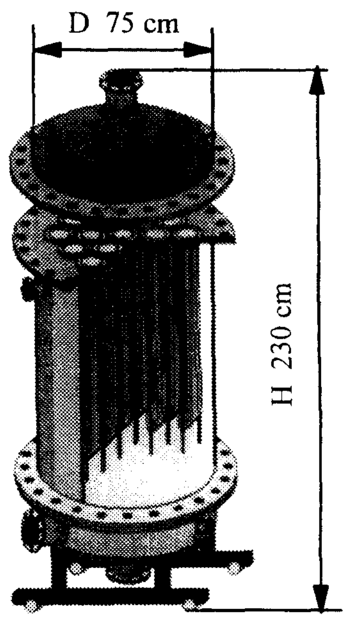


Figure 7. Tank-Type module unit

The performance of the above mentioned membrane modules are proved to be in good conditions, through long term field tests, and actual operations in various applications. Though the performance of the hollow fiber membrane is affected by filtration velocity, feed water contents, temperature, cleaning conditions, and so on, it is found that good performance can be obtained by determining the operating conditions properly. Nowadays, many studies and research activities, such as Membrane Aqua Century 21 project (MAC21) in Japan, for obtaining safe drinking water from river surface water by membrane filtration. In the MAC21 project, this membrane modules have been successfully operated b⋅ ɔme water treatment companies. Toray's above mentioned membrane module (simple type module) have got a certificate for this purpose from Japan Water Research Center on January 1996.

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