# Focus on Membrane Technology for Water Treatment

**Toray Industries, Inc.**
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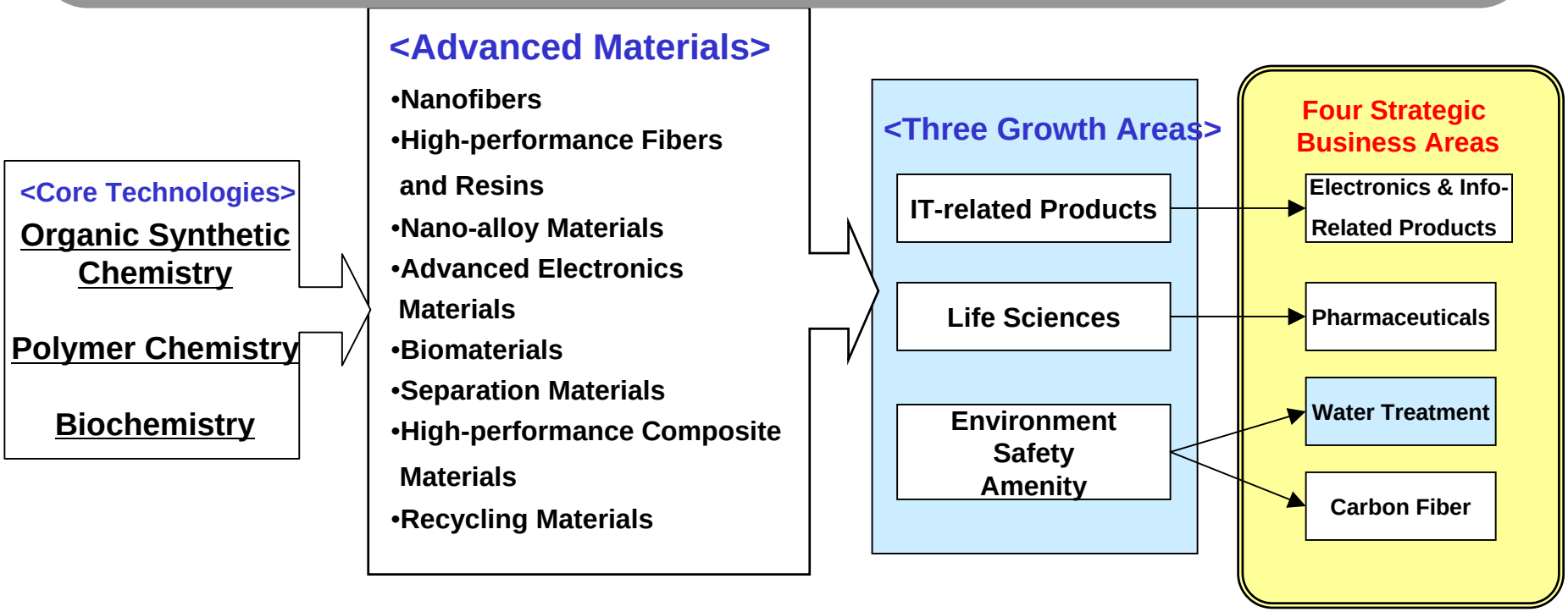
February 4, 2004

# CONTENT

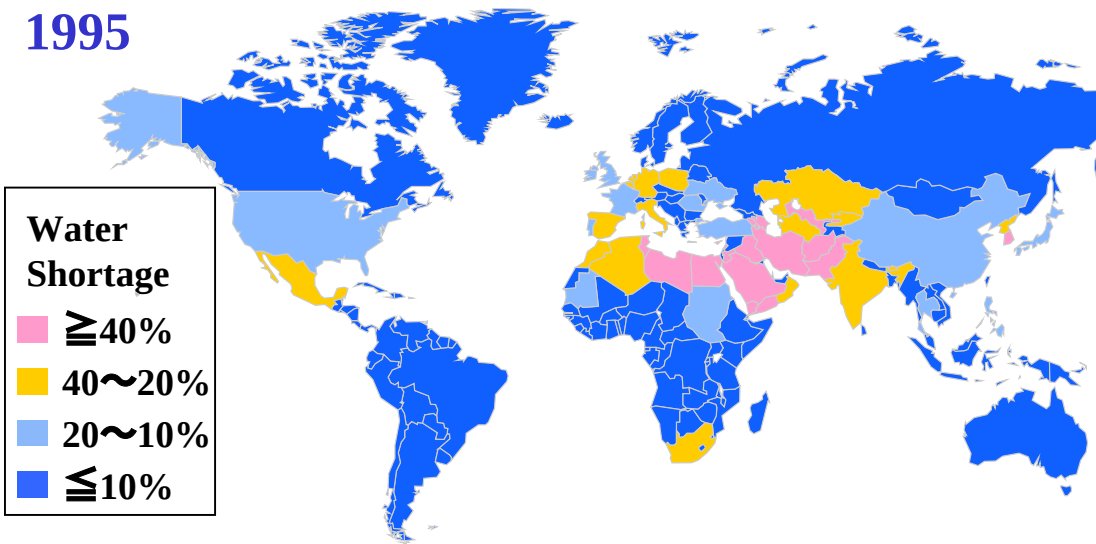
# Toray – The Leader in "Advanced Materials"

**Achieving High Growth by Constantly Supplying "Advanced Materials" – Developed with our Core Technologies – into our Three Growth Areas (an expansion of our four strategic business areas)**



# World Water Shortage - Now and Future (WMO and others, 1996)

1995



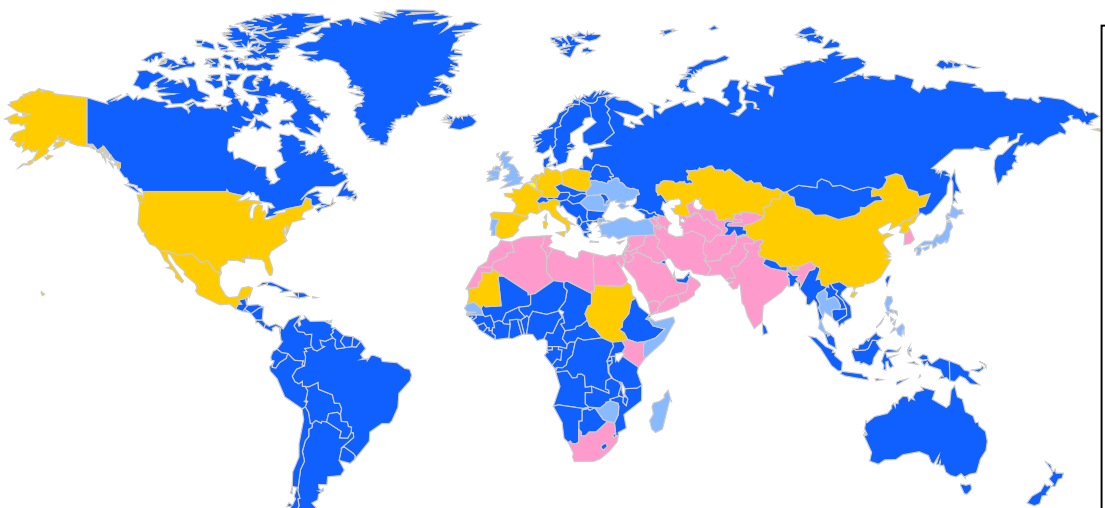

**Main regions which have high water shortage percentages of more than 20%**

**1995:**

**1) ≧40%：Middle East, Singapore, Korea, Pakistan**

**2) 20～40%：India, Mexico, Europe (excluding UK and France), Taiwan, South Africa**

2025



**2025:**

**1) ≧40%：Middle East, Korea, Pakistan, India, Algeria, South Africa, etc.**

**2) 20～40%：Mexico, China, USA, Europe (excluding UK)**

**Water shortage presumed to continue worldwide especially in Europe and the U.S.A., as well as throughout China by 2025**

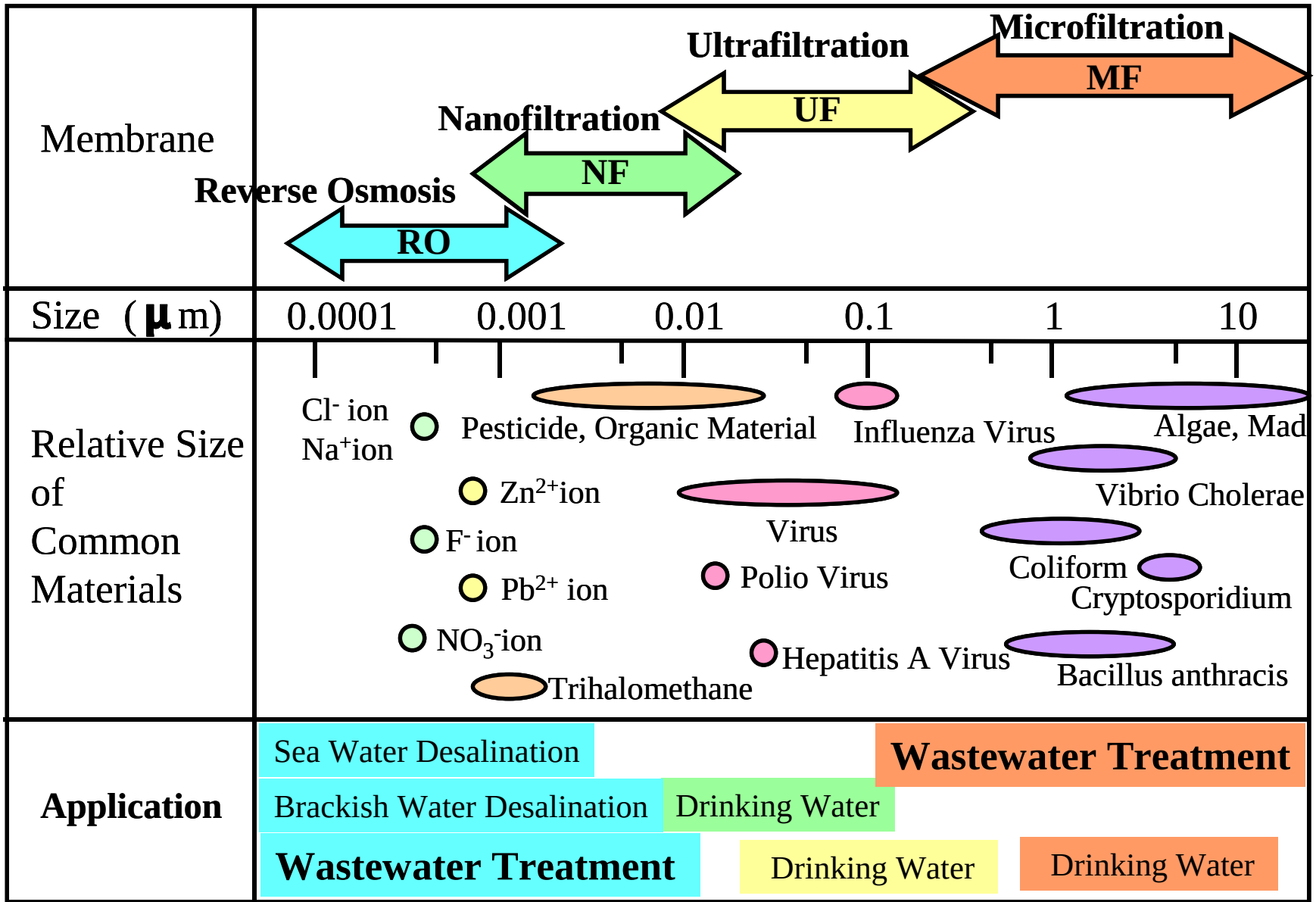
# Water Problem and Membrane Technology

| Region, Country | Water Problem | | Membrane Technology for Water Treatment | | |
|---|---|---|---|---|---|
| | Water Resource Shortage | Water Pollution | Fresh Water Treatment | Desalination | **Wastewater Reuse & Reclamation** |
| United States | Problem | Problem | In operation | In operation | **Construction** |
| Benelux | | Problem | Being applied | | **In operation** |
| UK, France | | Problem | In operation | | Being applied |
| Spain | Problem | Problem | Being applied | In operation | Being applied |
| Saudi Arabia | **Severe** | | | In operation | Planning |
| Kuwait | **Severe** | | | In operation | **Construction** |
| China | Problem | **Severe** | Being applied | Being applied | Planning |
| Singapore | **Severe** | | In operation | In operation | **In operation** |
| Japan | | Problem | In operation | In operation | |

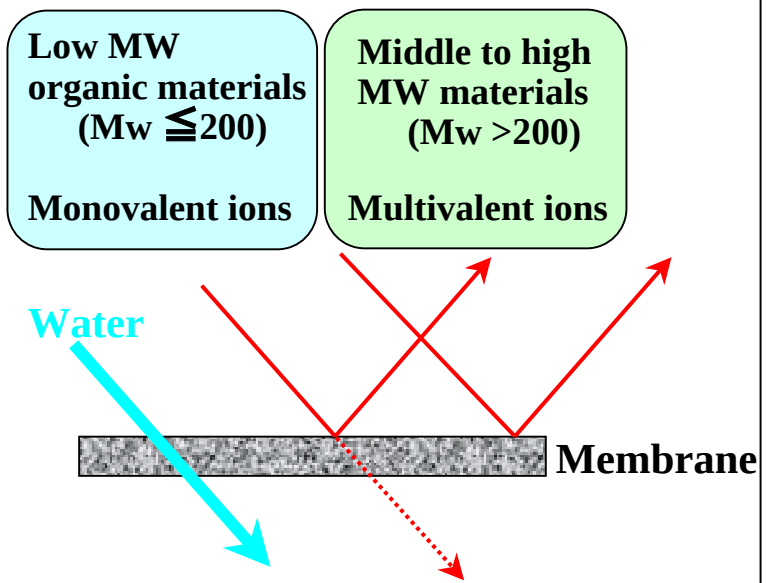
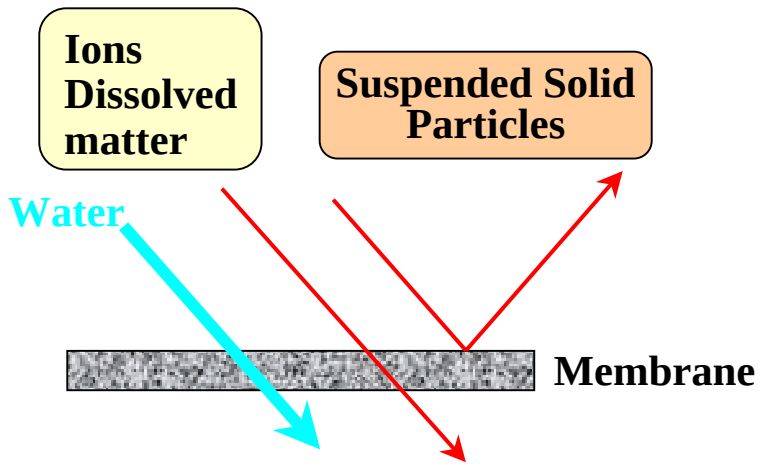
**Water resources are extending from fresh water to sea water & wastewater**

# Water Treatment Membranes

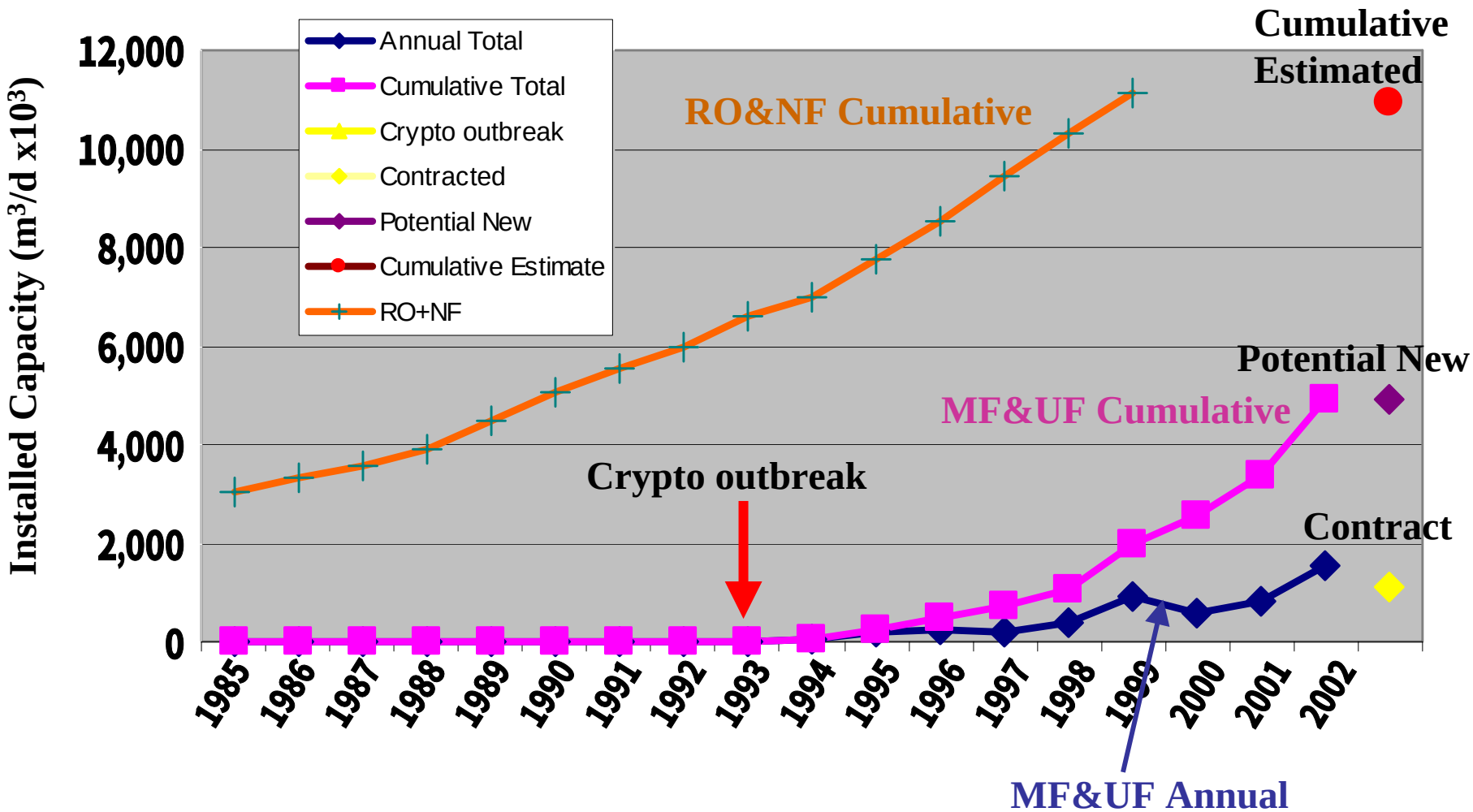
# Membrane and Relative Size of Common Materials



# Separation Characteristics of Various Membranes

| | RO/NF Membranes | UF/MF Membranes |
|---|---|---|
| Permeation and rejection |  |  |
| Separation mechanism | RO: Molecular interaction<br>Solution diffusion<br>Electric repulsion<br>NF: Size exclusion | MF: Dynamic separation<br>Size exclusion<br>UF: Electric repulsion |
| Pore size | RO: <1 nm<br>NF: 1~10 nm | UF: 10~100 nm<br>MF: >100 nm |

# Global Capacity of Membrane Filtration Plants



# Membrane applications - Conventional & new technologies

: New membrane products ( ) : in R & D

| Water treatment processes | | | | | Technical target | Toray's products |
|---|---|---|---|---|---|---|
| Desalination | Conventional | Sea-water | Multi Stage Flush (MSF) | Drinking water | Low cost (=High recovery) | RO membrane with high boron removal |
| | | | Single Stage SWRO | | | |
| | New | | NF → Multi stage flush (MSF) | | High quality (Low boron conc.) | NF membrane for scaling inhibition |
| | | | (NF) → Brine conversion Two-stage SWRO | | | RO membrane for brine conversion system |
| Drinking water production | Conv. | River Lake Ground | Coagulation & Sedimentation → Sand Filter | Drinking water | Security conservation | PAN hollow fiber UF membrane |
| | New | | (Coagulation & Sedimentation) → MF/UF membrane | | Removal of cryptosporidium | PVDF hollow fiber MF(UF) membrane |
| Wastewater treatment | Conv. | Sewage & Ind. | Activated Sludge → Sedimentation | Discharge | High quality for reuse and reclamation | PVDF MF/UF flat sheet membrane for MBR |
| | New | | MF/UF Membrane Bio-Reactor (MBR) → Low-fouling RO | Drinking water | | Low-fouling RO membrane |

# Toray's Membranes & Applications

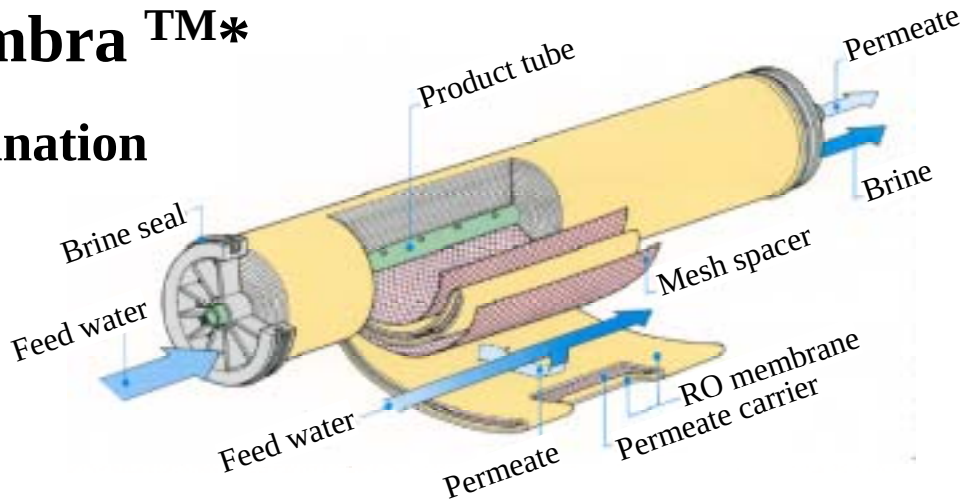
## 1. RO & NF Membrane Romembra ™*

1) Seawater & Brackish Water Desalination

2) Ultra Pure Water Production

3) Harmful Material Removal

4) Wastewater Reuse

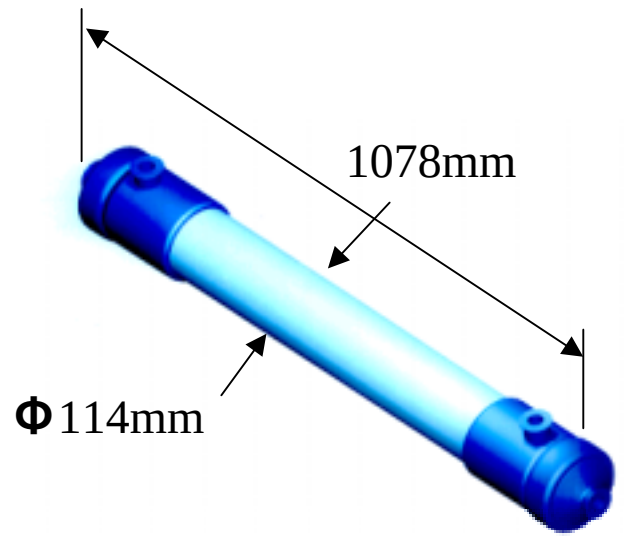



## 2. PAN Hollow Fiber UF Membrane Torayfil ™*

1) Industrial Process Water Production

2) Drinking Water Production

3) Wastewater Reuse

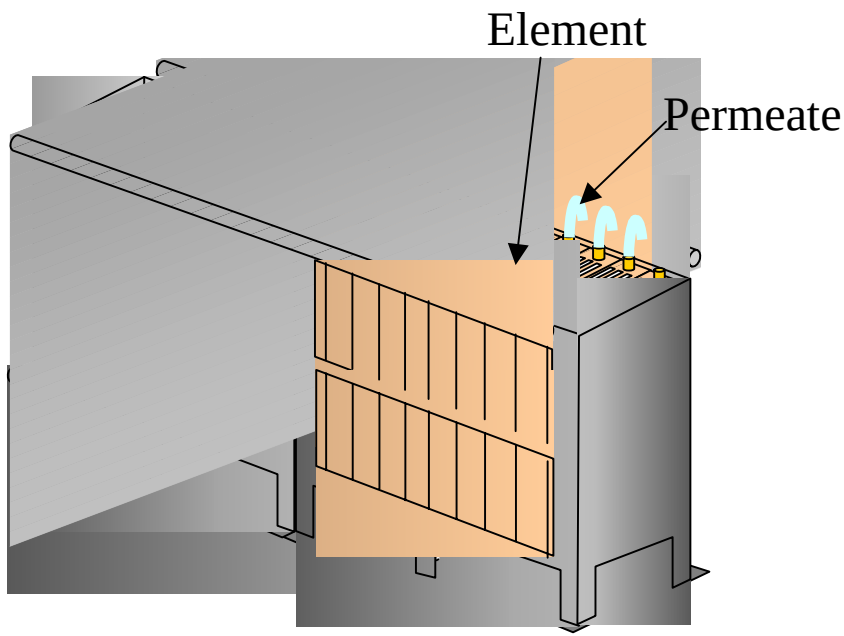


# Toray's Membranes & Applications

## 3. PVDF Hollow Fiber MF Membrane Torayfil-F ™*


1) Drinking water production
2) Industrial process water production
3) Pre-treatment for seawater desalination
4) Wastewater reuse

## 4. PVDF Flat Sheet MF Membrane for MBR




1) Municipal and industrial wastewater treatment
2) Municipal and industrial wastewater reuse

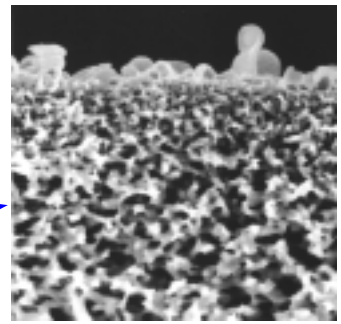
# RO Membranes & NF Membranes

# Structure of RO Membrane Element

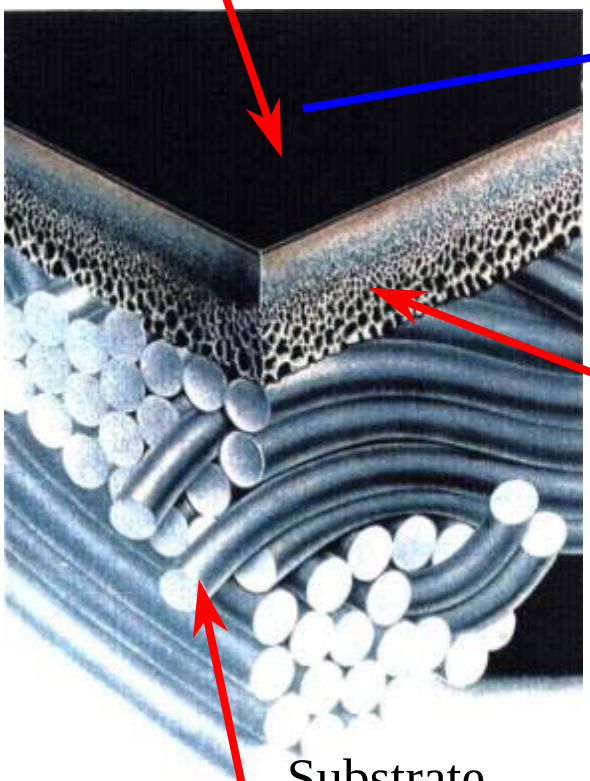
Separation Membrane

Feed

Crosslinked Aromatic Polyamide
**0.2 µm**



**Structure of RO Membrane**



Support Membrane

Polysulfone
**45 µm**

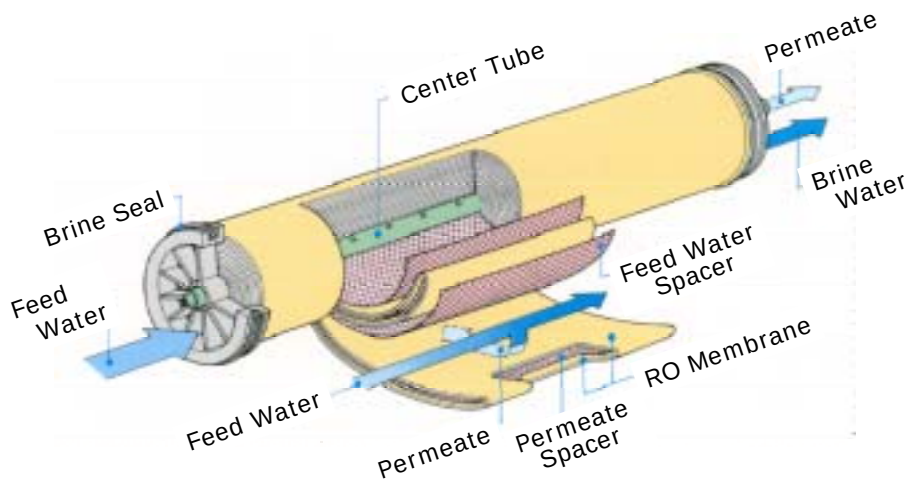
Substrate

Polyester Taffta
**150 µm**

Filtrate

**Structure of Composite Membrane**

**Structure of RO Element**



# Application of RO Membranes

## 1. Industrial

Ultra Pure Water

Industrial Process Water

Pure Water for Boilers

Recovery of Valuables

Food Industry Process Water

## 3. Wastewater Reuse & Reclamation

Industry

Agriculture

Indirect Drinking Water

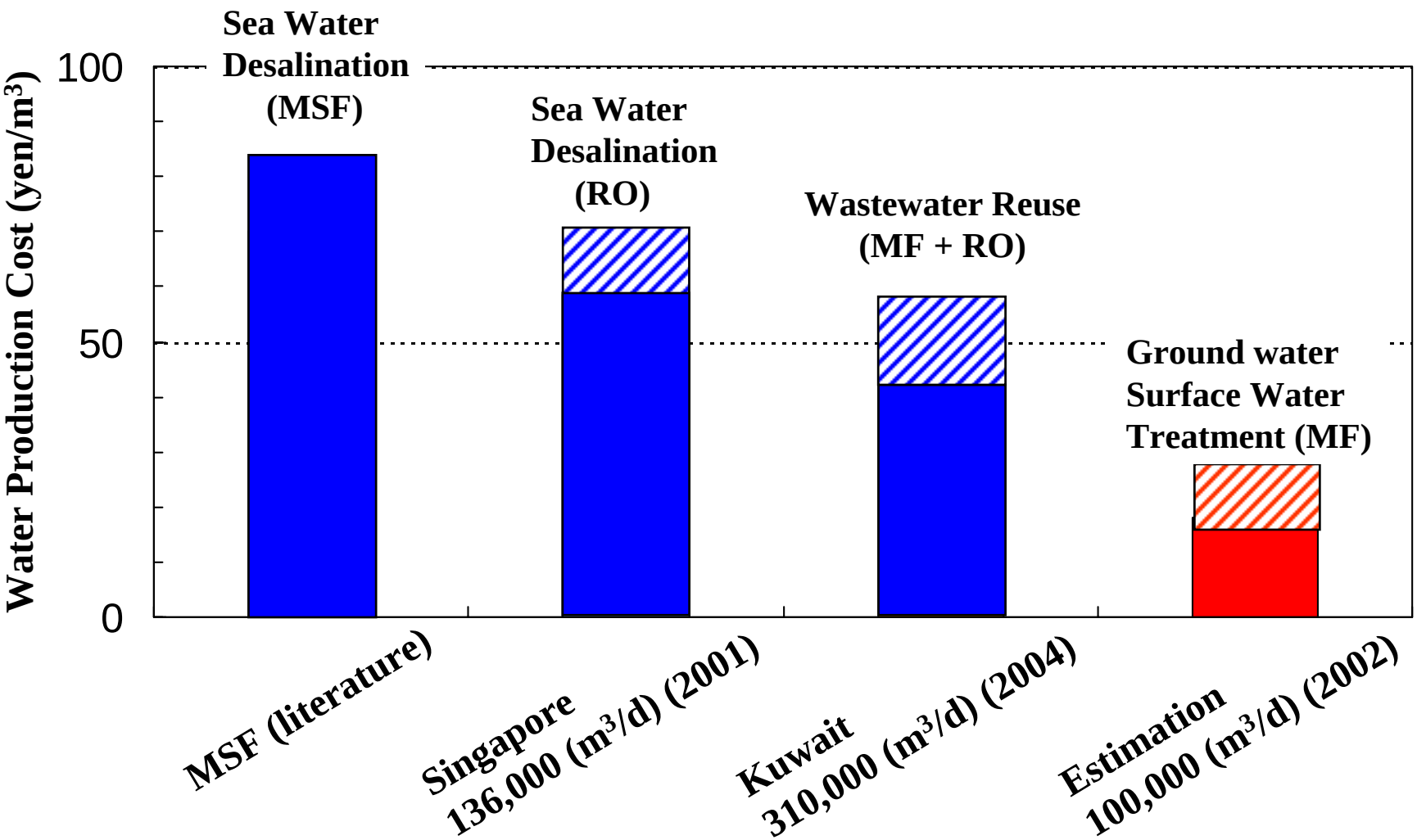
RO Membranes

## 2. Drinking Water

Sea Water Desalination

Brackish Water Desalination

# Water Production Cost




**Water Resource can be Chosen by Country**

# Progress of RO Seawater Desalination Plants

| | | 1980‘s | 1990‘s | 2000‘s |
|---|---|---|---|---|
| Recovery | % | 25 | 40 - 50 | 55 - 65 |
| Operational Pressure | psig (MPa) | 1,000 (6.9) | 1,200 (8.25) | 1,400 (9.7) |
| Product Water Quality (TDS) | mg/l | 500 | 300 | <200 |
| Energy Consumption | kWh/kgal ($kWh/m^3$) | 45 (12) | 21 (5.5) | 17.4 (4.6) |

I. Moch, Pre-prints of ADA Conference in Lake Tahoe (2000)

**Progress of Membrane Technology Realized**
**Good Quality & Energy Saving**

# Sea Water Desalination RO Membranes in Global Market

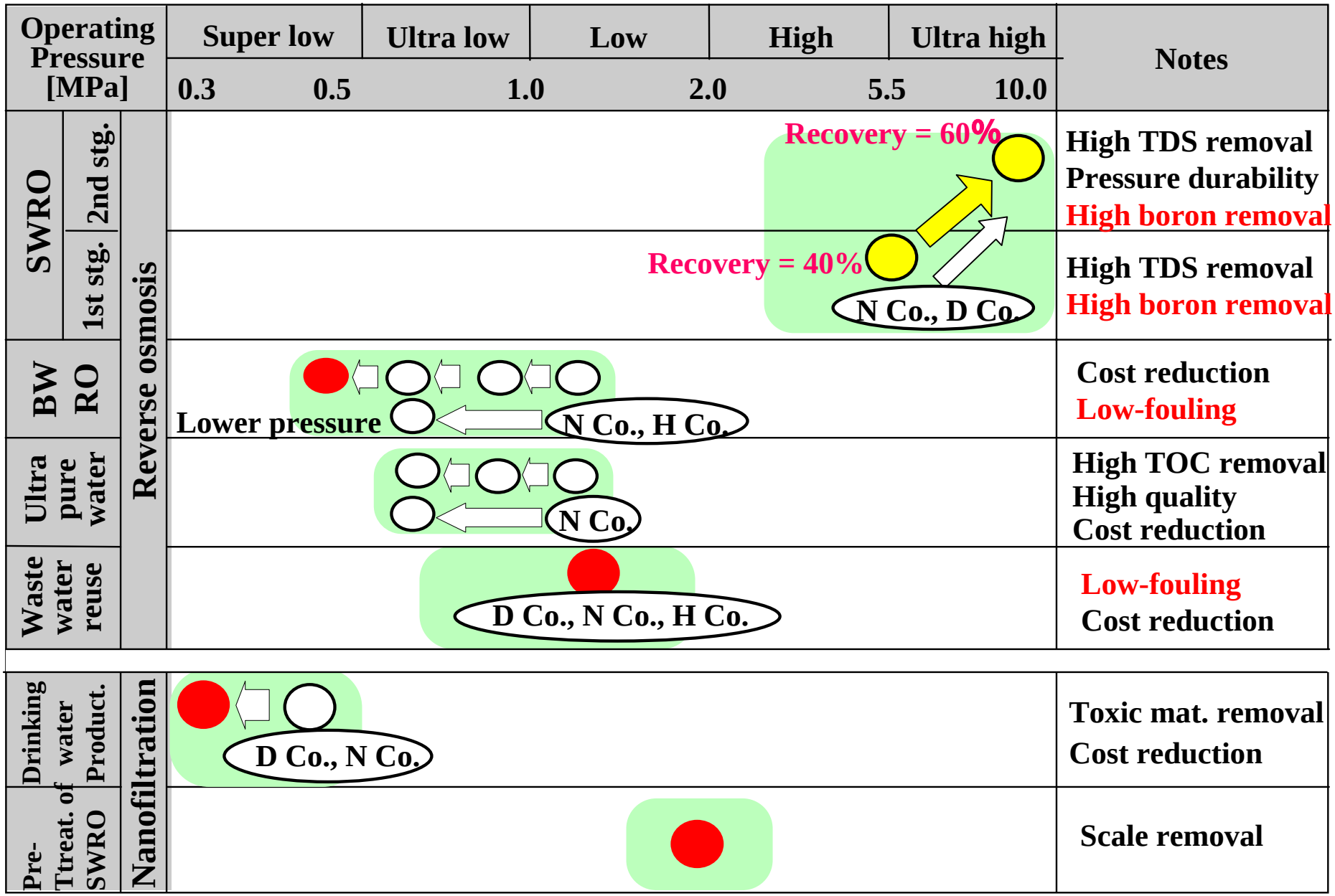
| Module Type | Supplier | Product | Material | Morphology |
|---|---|---|---|---|
| Spiral | Toray | SU-800 | Crosslinked Aromatic Polyamide | Composite Membrane |
| | Dow/ Filmtech | SW-30 | | |
| | Koch/ Fluidosystems | TFCL-HP | | |
| | Nitto Denko/ Hydranautics | NTR-SWC | | |
| Hollow Fiber | Toyobo | HOLLOSEP | Cellulose Triacetate | Asymmetric Membrane |

**Crosslinked aromatic polyamide/spiral module is global standard.**

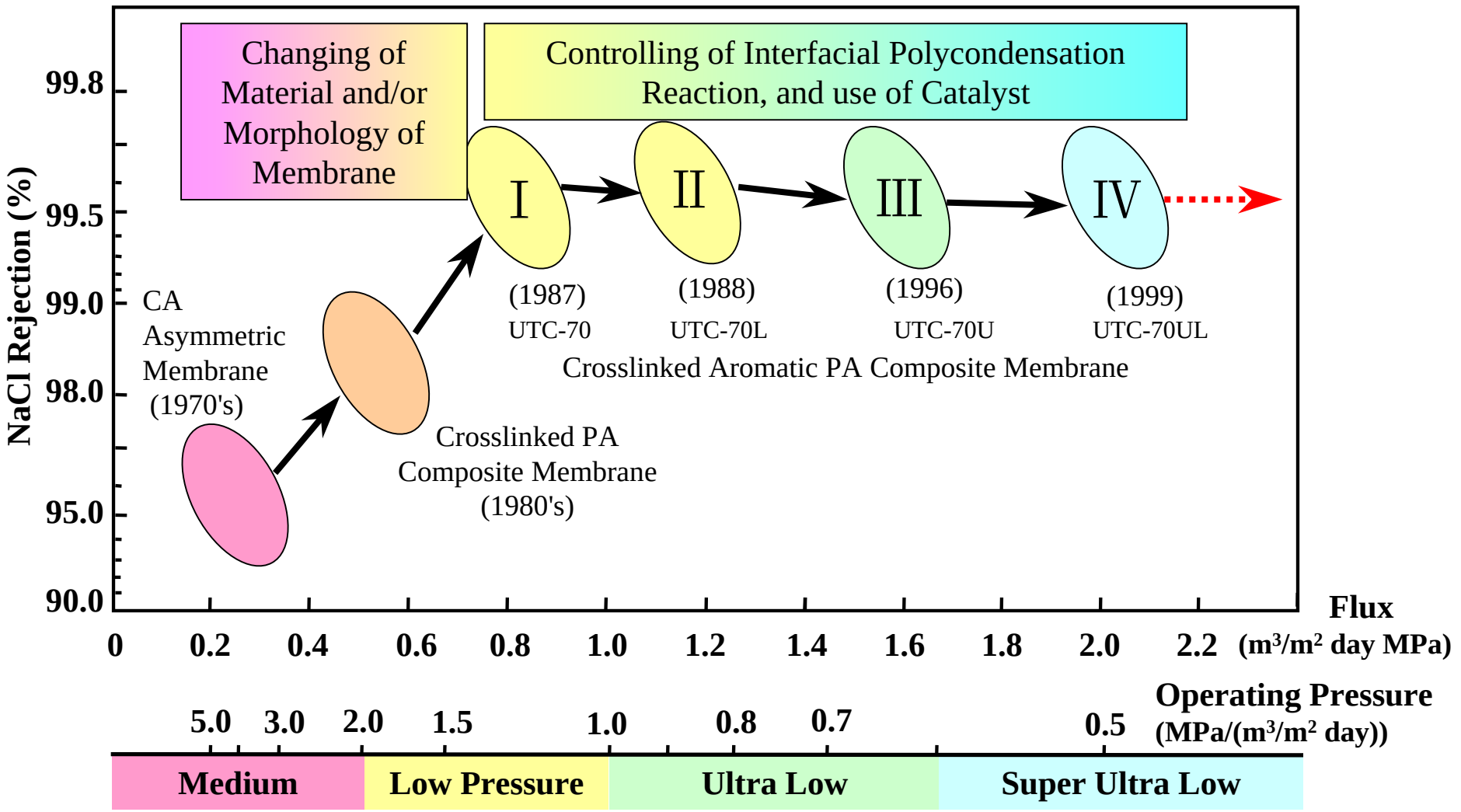
**Toyobo is the only hollow fiber module supplier.**

**DuPont withdrew from the hollow fiber RO module business in March 2001.**

# Technological Trends of RO/NF Membranes

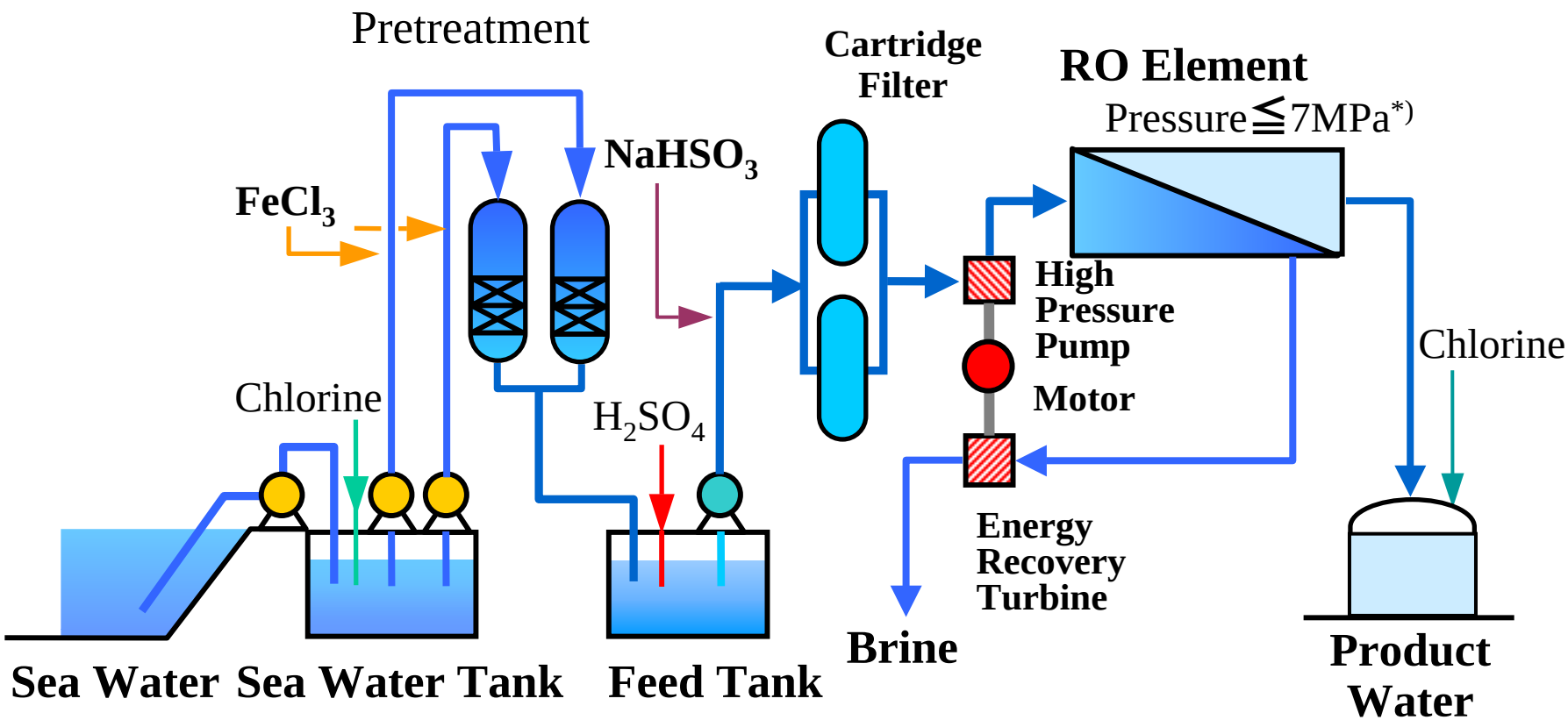


# Progress of RO Membrane Performance




**World's No. 1 Membrane Performance**

# Conventional One-Stage RO Sea Water Desalination System




*) Spiral element

# Okinawa Sea Water Desalination Plant

## (Capacity: 40,000 m³/d, 1996)

**40,000m³/d: Tap water for 160,000 people**

RO Module Installation
(each unit produces 5,000m³/d)

**Toray Module is used in Japan's Largest Plant**

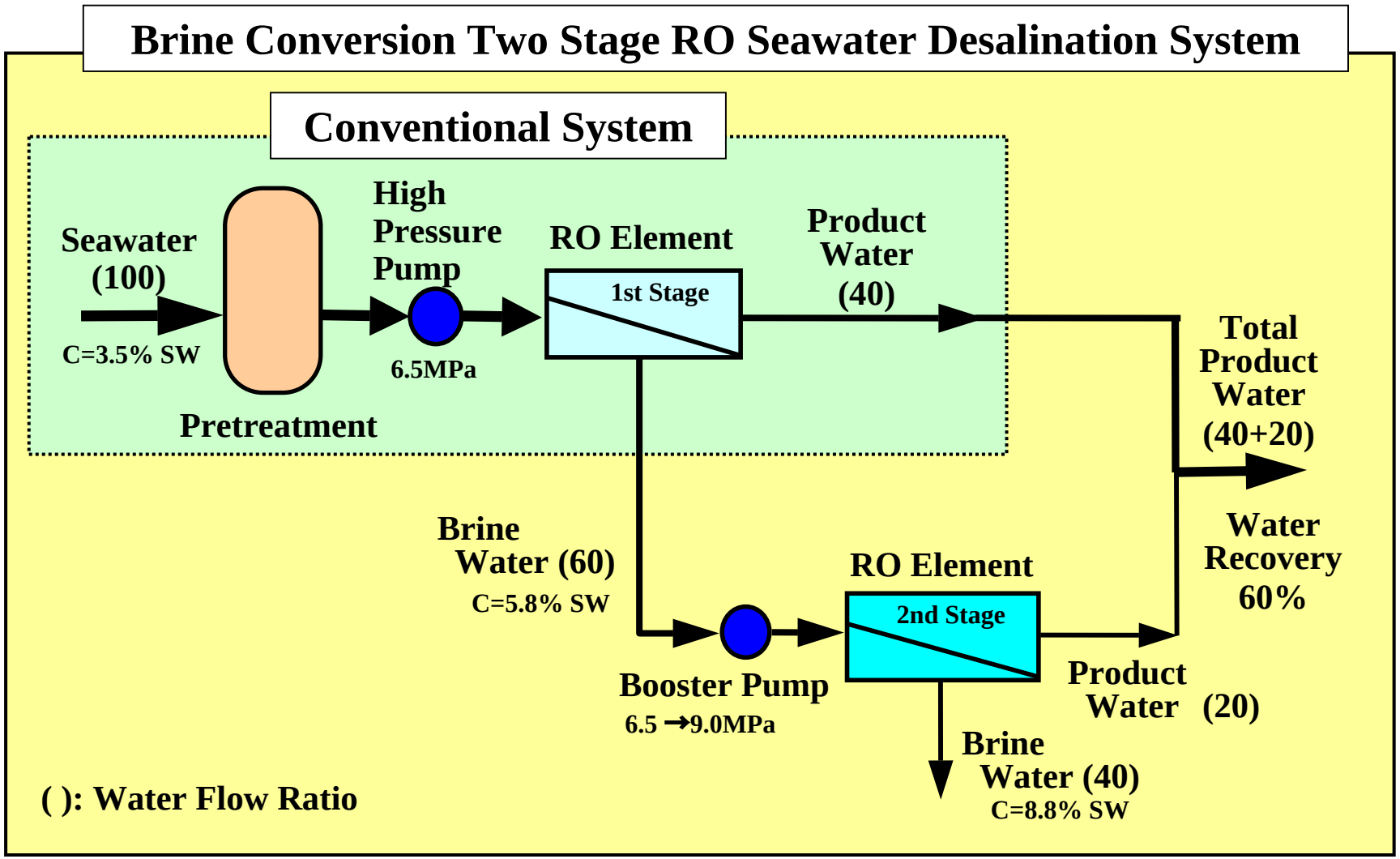
# Largest Sea Water Desalination Plants in the World

| | Country | Location | Capacity (m3/d) | Operation (year) | Plant Supplier | Membrane Supplier |
|---|---|---|---|---|---|---|
| 1 | Israel | Ashkelon | 272,520 | 2004 | OTID/ IDE/ OTV | Dow |
| 2 | UAE | Taweelah | 227,300 | 2006 | Toray/ Mitsui/ Veolia | Toray |
| 3 | UAE | Fujairah | 170,000 | 2003 | ONDEO | Hydra |
| 4 | Israel | Ashdod | 137,000 | 2004 | Ionics | Toray |
| 5 | Trinidad and Tobago | Point Lisa | 136,000 | 2002 | Ionics | Toray |
| 5 | Singapore | Tuas | 136,000 | 2004 | Hyflux | (Toray) |
| 7 | Mexico | Hermosillo | 128,690 | 2004 | IDE/ IL | - |
| 8 | Saudi Arabia | Yanbu | 128,000 | 1995 | Mitsubishi | Toyobo |
| 9 | Spain | Carboneras | 120,000 | 2001 | ABENS/ONDEO/PRI | Hydra |
| 10 | USA | Tampa | 94,625 | 2003 | COVANTA | Hydra |
| 11 | Saudi Arabia | Al Jubail III | 90,909 | 2000 | PWT | DuPont/Toray |

*** DuPont withdrew from RO business in 2001**

**RO sea water desalination seems very difficult in theArabian Gulf, because troubles occurred at all of DuPont's RO plants.**
**Al Jubail III is the first successful plant.**

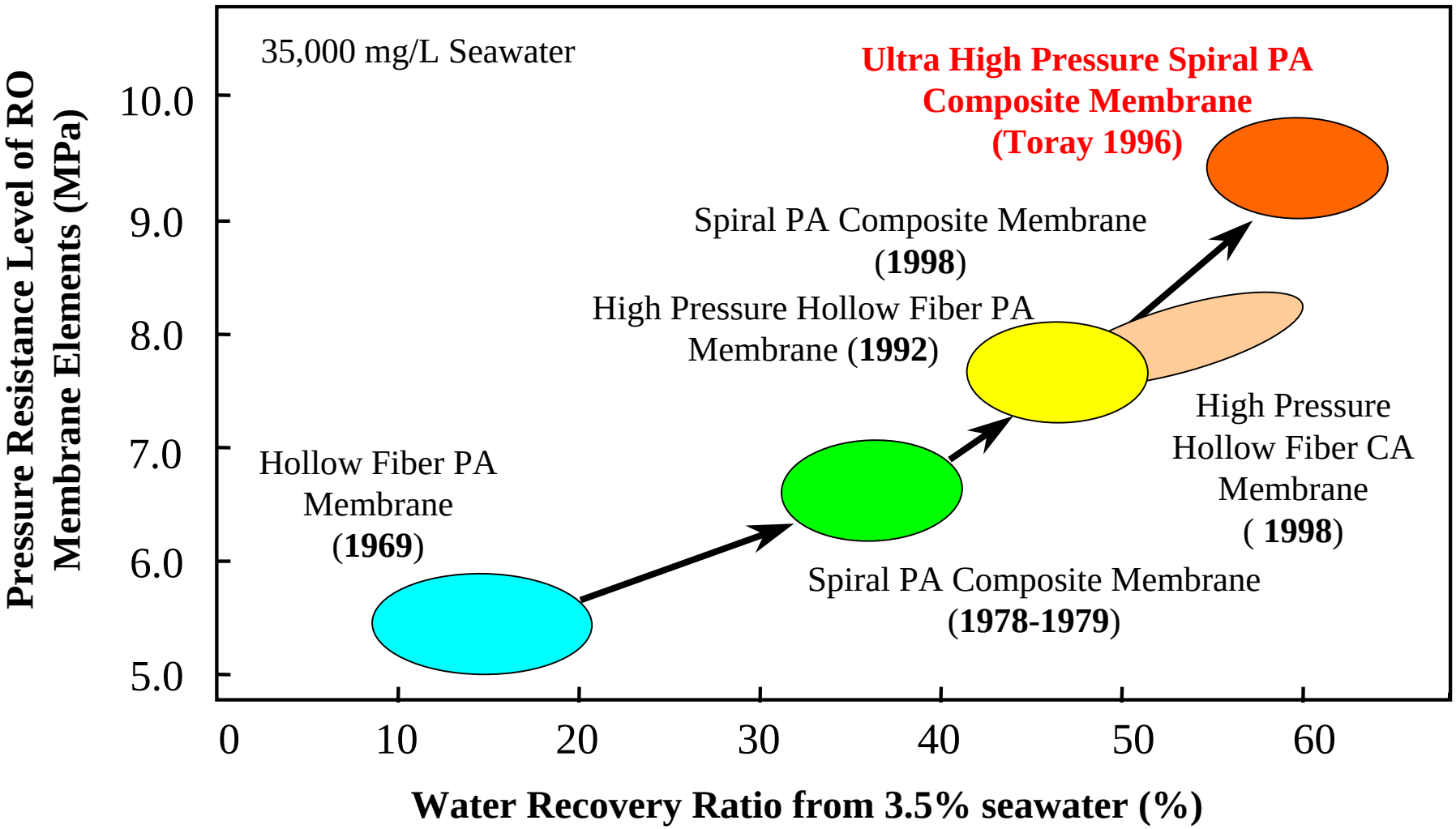
# Typical Flow Diagram of Brine Conversion Two Stage RO Seawater Desalination System




**Toray's Patent:**

**Japanese Patent Application 1994-245184(1994), US: 6187200(2001), CA: 216033(2001), RC: 302294(1997), AU: 691649(1998), EU(granted 2002), KR: 204608(1999), Pending - JP, CH**

# Performance Trends of RO Membranes for Seawater Desalination




**World No. 1 Membrane Performance for Sea Water Desalination**

# Global Installations of Toray Sea Water Desalination ROs

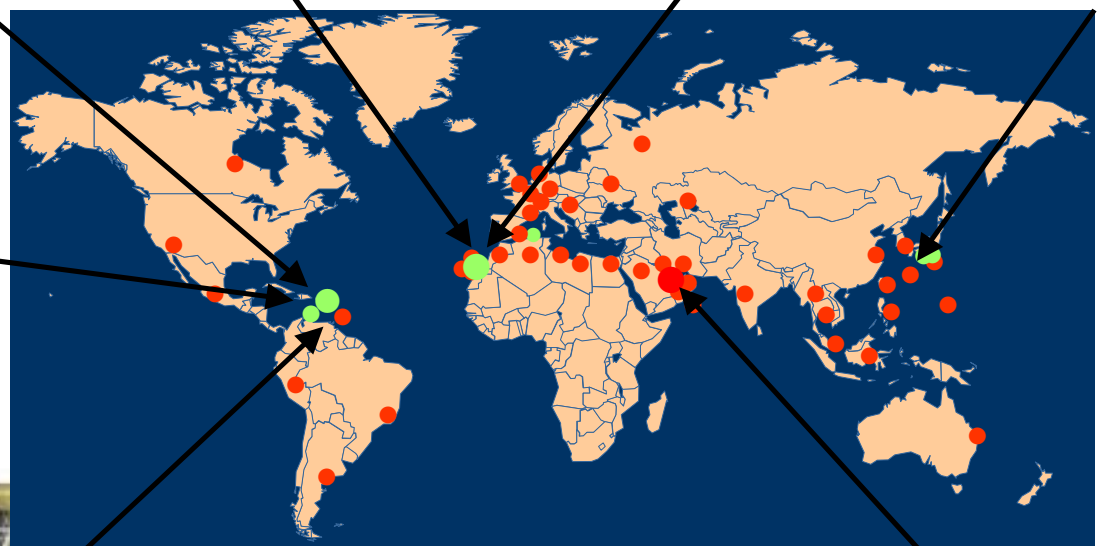
KAE Curacao
(Netherlands Antilles)
11,400 (m3/d)

Mas Palomas
(Spain Canary Island)
No. 1 Plant 4,500 (m3/d)

Mas Palomas
(Spain Canary Islands)
No. 2, 3 Plant 9,000 (m3/d)

Okinawa
(Japan)
40,000 (m3/d)

Tortola
(British Virgin Islands)
690 (m3/d)



● :Toray's 2-Stage RO Systems
● :Conventional RO Systems

Trinidad and Tobago
136,000 (m3/d)

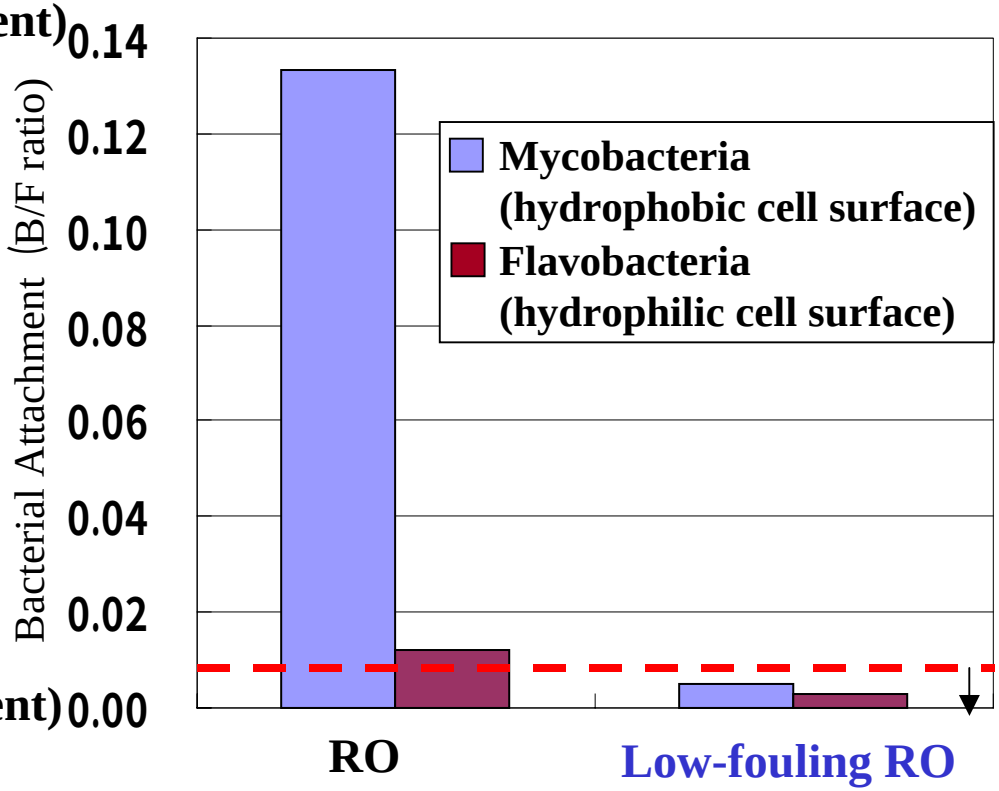
Al Jubail
(Saudi Arabia)
91,000 (m3/d)

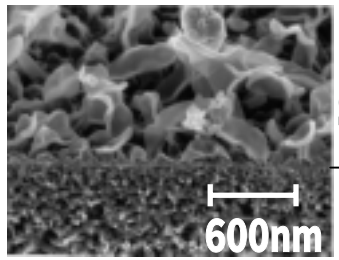
# Results of Membrane Biofouling (MBP) Assay

(Orange County water district: Dr.Ridgway)

Bad
(High attachment)

Good
(Low attachment)

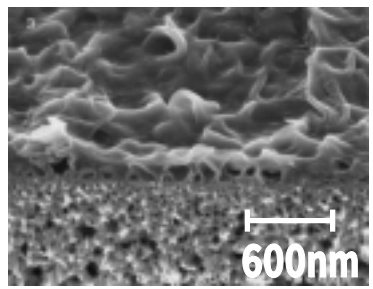



Surface

Cross section

RO




Surface

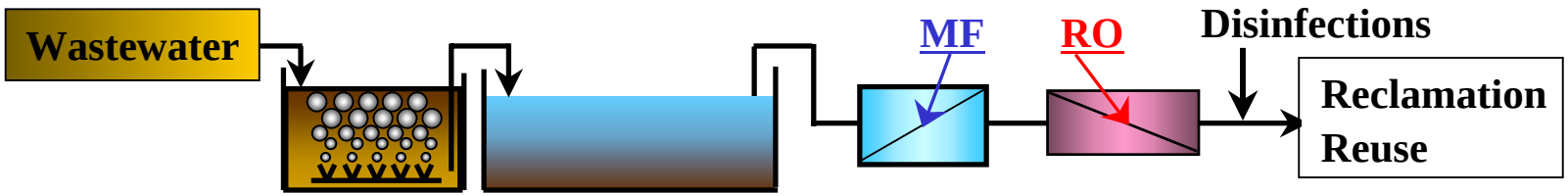
Cross section

Low-fouling RO

**Fouling : Deterioration of membrane performance caused by stains**

**Toray less-fouling RO membrane has extremely low bacteria attachment**

# Wastewater Reclamation & Reuse Plants




| | Country | Location | Capacity (m3/d) | Operation Year | Plant Supplier | Membrane Supplier |
|---|---|---|---|---|---|---|
| 1 | Kuwait | Sulaibiya | 300,000 | 2003 | IONICS | Toray |
| 2 | USA | CA Fountain Val | 264,950 | 2004 | PROJECT | |
| 3 | Singapore | Ulu Pandan | 140,000 | 2004 | | |
| 4 | India | Chennai | 135,000 | 1999 | CAMP DRESSER | |
| 5 | USA | CA San Diego | 75,000 | | | |
| 6 | Spain | Almeria | 42,000 | 2001 | PRIDESA/INIMA | PERMETEC ES |
| 7 | Singapore | Kranji | 40,000 | 2003 | VEOLIA | Hydranautics |
| 8 | Singapore | Bedok | 32,000 | 2003 | HYFLUX | Hydranautics |
| 9 | Saudi Arabia | Jeddah | 30,000 | 1990 | BIWATER GB | DuPont |
| 10 | Korea | | 26,182 | 1996 | IONICS US | Dow/Filmtec |
| 11 | Singapore | Seletar | 24,000 | 2003 | HYFLUX | Toray |
| 12 | Japan | | 22,984 | 1983 | KURITA JP | Toray |
| 13 | USA | AZ Scottsdale | 22,710 | 1998 | ADVANCED ES USA | Koch |

(Nov. 2003 :Based on IDA Inventory Report 2002)

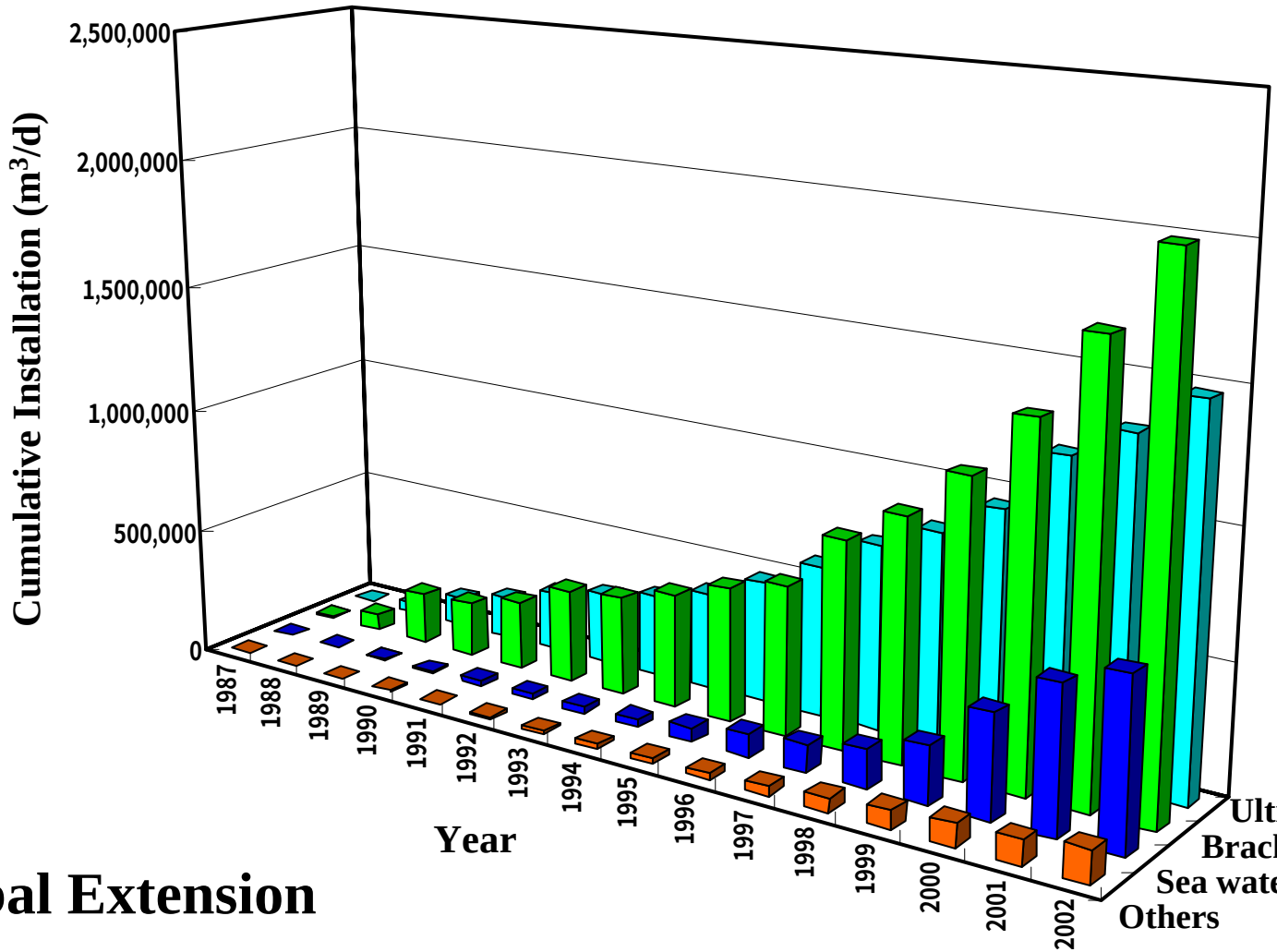
**Toray less-fouling RO was selected at the world's largest RO plant**

# List of Large Water Treatment Plant using RO membrane (under operation or construction)

| | Country | Location | Capacity (m3/d) | Raw Wate | User | Operating Year | Plant Supplier | Mmbrane Supplier |
|---|---|---|---|---|---|---|---|---|
| 1 | Kuwait | Sulaibiya | 310,000 | Waste | Irrigation | 2004 | Ionics | Toray |
| 2 | USA | AZ Yuma | 276,672 | Brackish | Discharge | 1983 | Fluid System | Koch |
| 3 | Israel | Ashkelon | 272,520 | Sea | Municipal | 2004 | OTID IDE OTV | Dow/Film Tec |
| 4 | USA | CA Fountain Val | 264,950 | Waste | Municipal | 2004 | Project | sellecton |
| 5 | UAE | Taweelah C RO | 227,300 | Sea | Municipal | 2006 | Toray/Mitsui/Veolia | Toray |
| 6 | UAE | Fujairah | 170,000 | Sea | Municipal | 2003 | ONDEO | Hydranautics |
| 7 | Spain | Malaga | 165,000 | Brackish | Municipal | 2003 | ABENSUR/ONDO | unkown |
| 8 | USA | FL Boca Raton | 151,400 | River | Municipal | 2003 | ADVANCED EWT | unkown |
| 9 | France | Mery-sur-Oise | 140,000 | River | Municipal | 1999 | OTV VIVENDI | Dow/FilmTec |
| 10 | Singapore | Ulpandan | 140,000 | Waste | Municipal | 2004 | PUB | selection |
| 11 | Israel | Ashdod | 137,000 | Sea | Municipal | 2004 | OTV/Ionics | Toray |
| 12 | Singapore | Tuas | 136,380 | Sea | Municipal | 2004 | Hyflux | (Toray) |
| 13 | Oman | Sharqiya | 136,000 | Sea | Municipal | 2004 | Project | selection |
| 14 | Trinidad Tobago | Point Lisas | 136,000 | Sea | Industry | 2002 | Ionics | Toray |
| 15 | India | Chennai | 135,000 | Waste | Industry | 1999 | Camp Dresser | unkown |
| 16 | Mexico | Hermosillo | 128,690 | Sea | Municipal | 2004 | IDE IL | selection |
| 17 | Saudi Arabia | Medina/Yanbu II | 128,000 | Sea | Municipal | 1995 | Mitsubishi | Toyobo |
| 18 | Spain | Carboneras | 120,000 | Sea | Municipal | 2001 | ABENS/ONDEO/PRI | Hydranautics |
| 19 | Saudi Arabia | Hail | 105,980 | Brackish | Municipal | 1996 | EMCO | SIDMAS |

(Nov. 2003 ; Based on IDA Inventory Report 2002)

# Cumulative Installations of Toray ROs by Application




(thousand $m^3/d$)

| | |
|---|---|
| Ultra pure water | 1,470 |
| Brackish water | 2,940 |
| Sea water desalination | 650 |
| Others | 13 |

## Global Extension

**Ultra pure water production**
**Brackish water desalination**

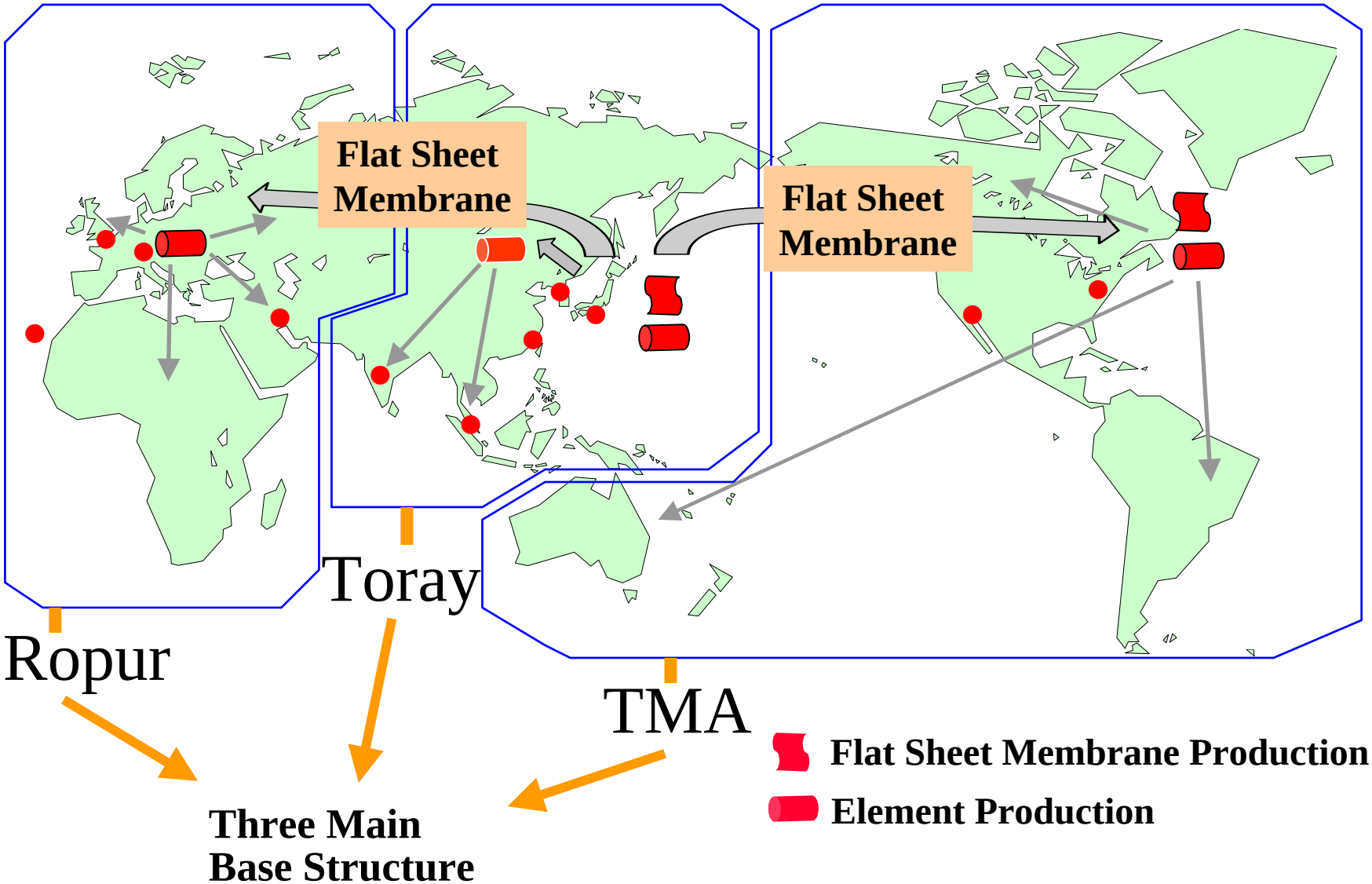
➡

**Sea water desalination**

➡

**Wastewater reuse & reclamation**

# Toray Group's Business Bases and Global Operations



# Conclusion – RO•NF Membranes

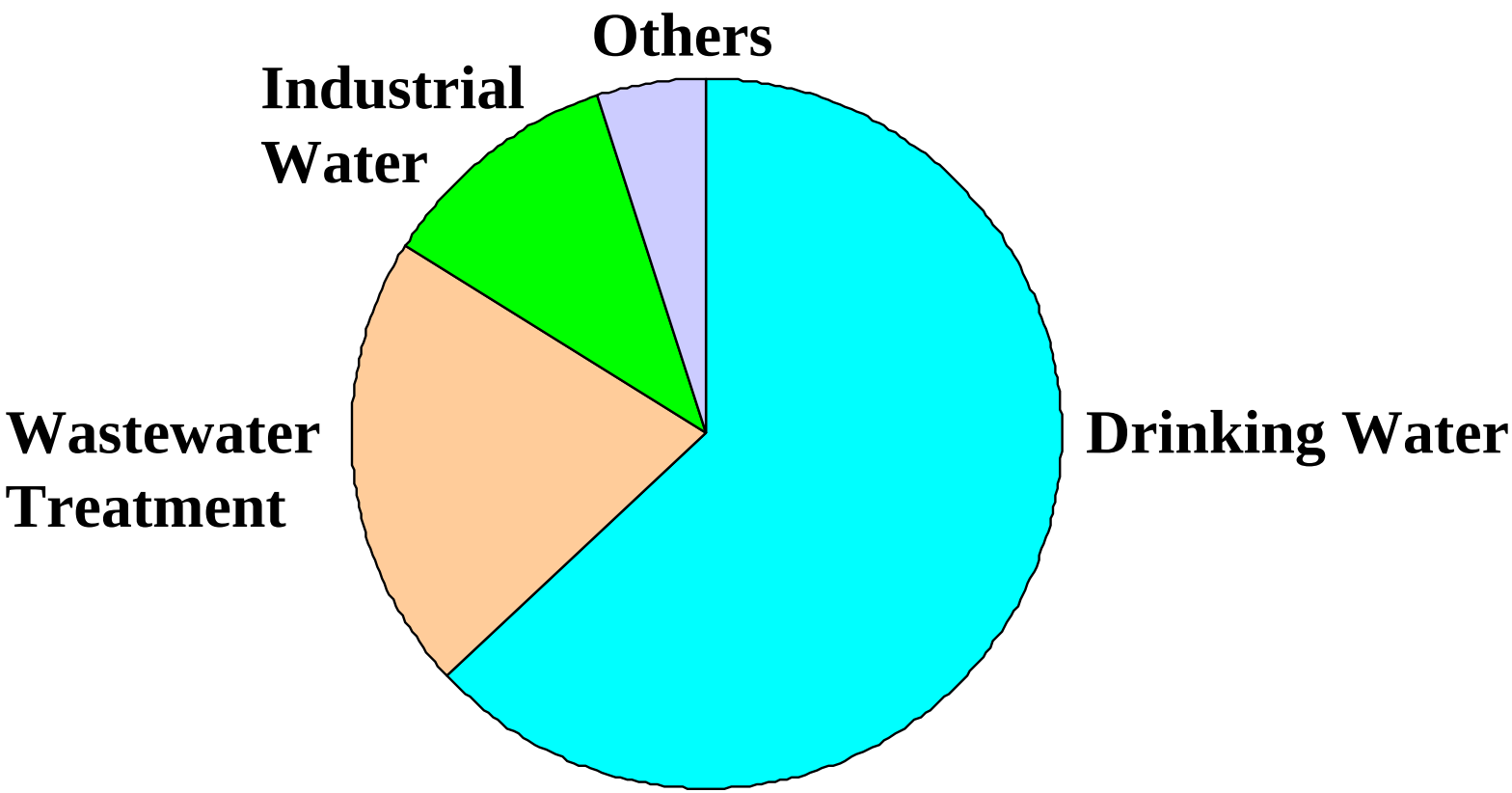
1. The RO seawater desalination system has entered a stable growth stage and the business is expanding steadily.

2. Wastewater reuse and reclamation is expected to be a new RO application.

3. Expansion of the NF membrane businesses is expected in the pretreatment of seawater desalination, and in highly efficient water purification systems.

# UF Membranes & MF Membranes
# - Drinking Water Production -

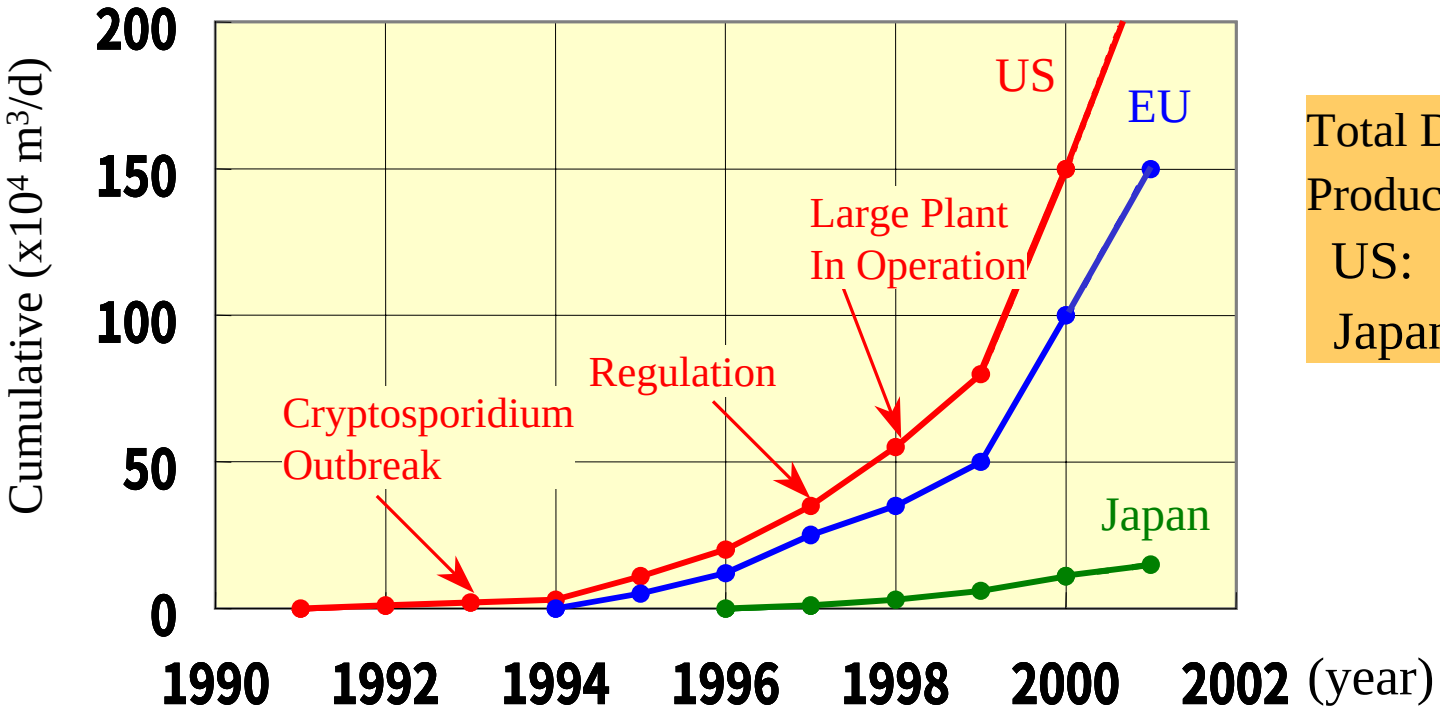
# UF & MF Membranes – Breakdown of World Applications -




Ref: David H. Furukawa,
WATERMARK, October 17, 2002

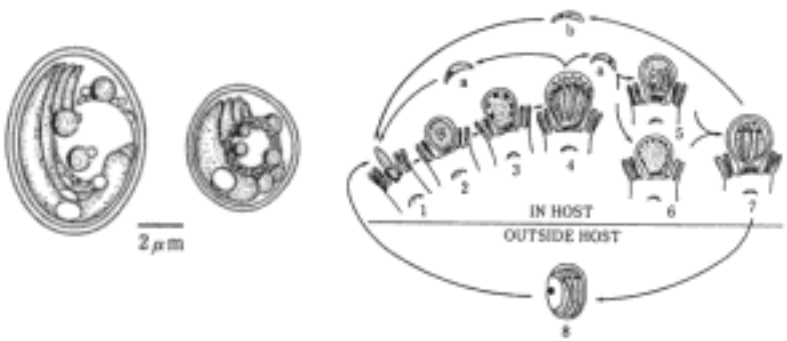
**Total Water Production: 4.9 million $m^3/d$**

# Market for Hollow-fiber Membranes for Drinking Water Production




Total Drinking Water Production (x10⁴ m³/d)
US: 2900
Japan: 6900

*Cryptosporidium parvum* (4～8 μm)




**1993 400,000 people experienced intestinal illness in Milwaukee. At least 50 died of the disease.**

**1996 8,000 people infected in Ogose, Saitama, Japan**

**1998 Enhanced regulations of surface water treatment**

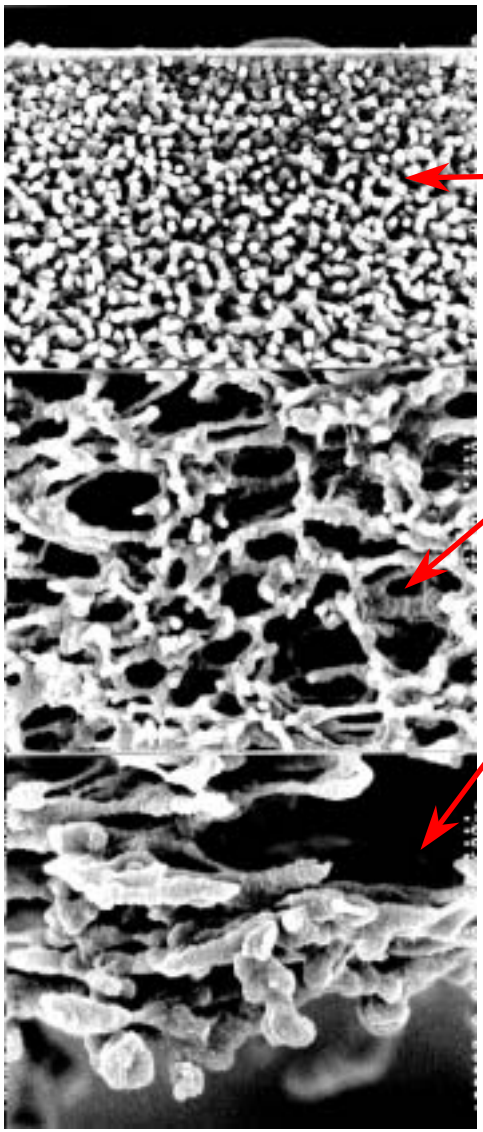
**Enhancement of Pathogen Regulations caused Market Expansion**

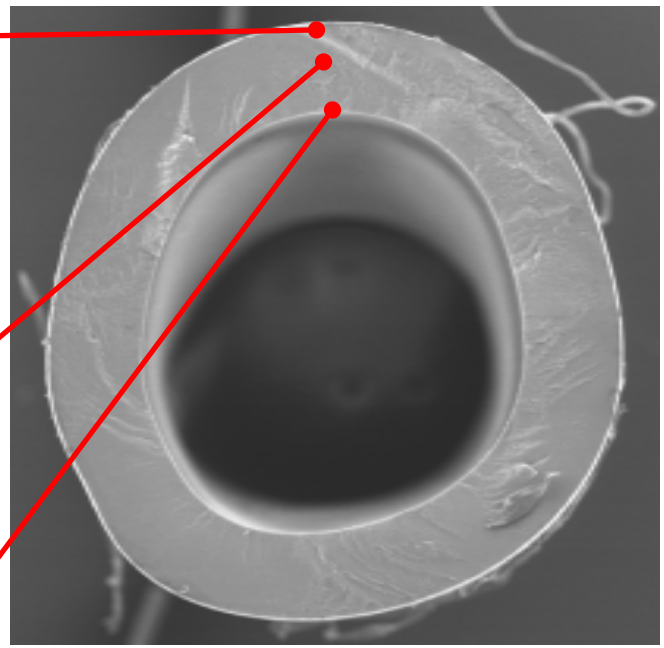
# Membrane Filtration Plants for Drinking Water in Japan

| | Capacity ($m^3/d$) | Location | Engineering | Membrane Supplier | Installation (Year) |
|---|---|---|---|---|---|
| 1 | 27,500 | Tokyo, Hamura | Suido Kiko | Kuraray | 2004 |
| 2 | 10,000 | Tochigi, Imaichi | Orugano | Daiseru (UF) | 2000 |
| 3 | 8,000 | | Suido Kiko | Toray (MF) | 2003 |
| 4 | 6,200 | Hokkaido, Nishisorachi | Orugano | Daiseru (UF) | 1999 |
| 5 | 6,000 | Miyagi, Onagawa | NKK | Memcore (MF) | 2001 |
| 6 | 5,320 | Aichi, Shinshiro | Orugano | Daiseru (UF) | 2003 |
| 7 | 5,000 | | Suido Kiko | Toray (MF) | 2002 |
| 7 | 5,000 | Mie, Kiho | Ebara | Mitsubishi (MF) | 2001 |
| 9 | 4,500 | Gifu, Ena | Suido Kiko | Asahi Kasei (UF) | 2001 |
| 10 | 4,000 | Saitama, Ogose | Kurita | Kuraray (UF) | 1998 |
| 11 | 2,400 | Ooita, Notsu | Hitachi | Toray (UF) | 1999 |
| 12 | 1,900 | Fukui, Eiheiji | Maezawa | Toray (UF) | 2001 |
| 13 | 1,900 | Gunma, Showa | Suido Kiko | Asahi Kasei (UF) | 2001 |
| 14 | 1,900 | Fukui, Miyazaki | Suido Kiko | Asahi Kasei (UF) | 2000 |

**Application of UF/MF membranes is expanding in Japan**
**Cumulative installations are 210,000 ($m^3/d$) as of June 2003**

# PAN-based Hollow Fiber UF Membrane



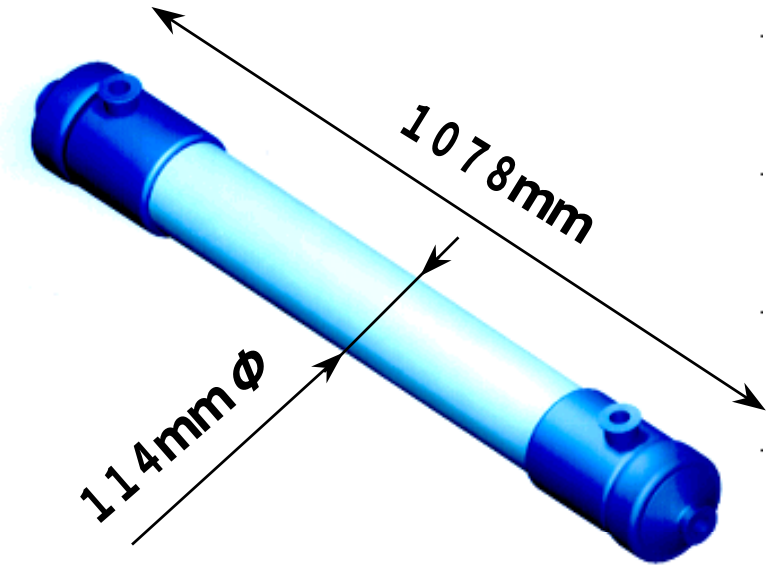


Cross section

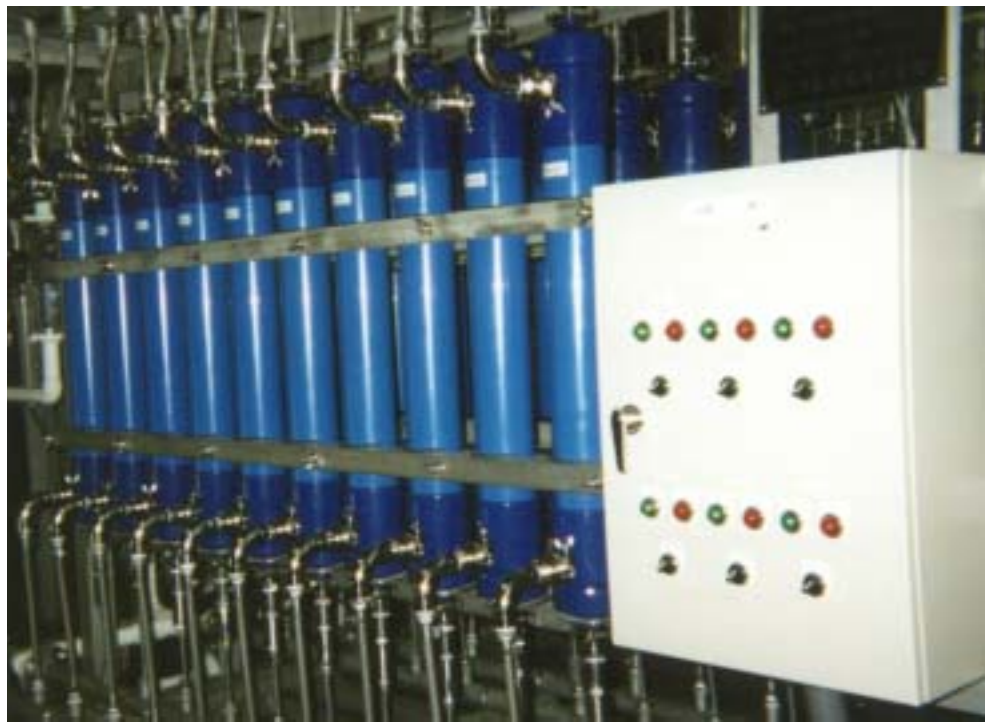

Pore size: 0.01 micrometer

Outer surface

# Casing Type Module

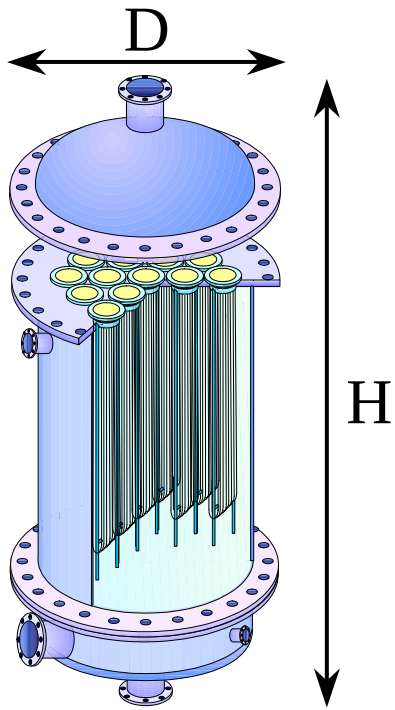



**Membrane area: 12 $m^2$**
**Water production: 10 $m^3$/d**



**Drinking water production plant**

# Tank Type Module




## Merit

- Low Initial Cost
- Small Footprint
- Easy Maintenance

| Flux ($m^3/d$) | 70 | 200 | 500 | 800 |
|---|---|---|---|---|
| Membrane area ($m^2$) | 84 | 228 | 576 | 960 |
| Diameter (D) (cm) | 45 | 75 | 120 | 150 |
| Height (H) (cm) | 200 | 230 | 250 | 250 |

# Design Concept of PVDF Hollow Fiber MF Membrane

**Operation**

1. High Water Flux
2. Low Operational Pressure
3. Frequent Physical Washing
4. Frequent Chemical Rinse

**Functional Requirement**

1. High Water Permeability
2. Precise Pore Size
3. High Physical Stability
4. Good Chemical Resistance

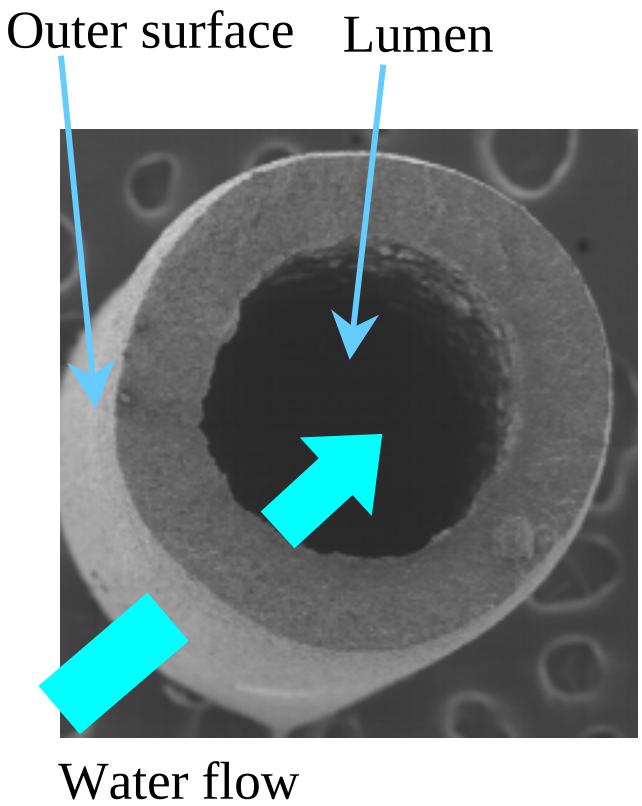
**PVDF(Poly Vinylidene Fluoride) polymer is suitable**

Performance of hollow fiber membrane depends highly on spinning process → Proprietary spinning process

**High Permeability & High Physical Strength**

# Toray PVDF Hollow Fiber Membrane

| | Spinning Method | Feature |
|---|---|---|
| Melt Spinning | **Extraction**<br>Melt spinning with pore formation agent and extraction | High Strength<br>High Cost |
| | **Drawing**<br>Melt spinning and drawing | High Strength<br>Low Cost |
| Solution Spinning | **Non-solvent Induced Phase Separation**<br>Polymer solution is coagulated by non-solvent | UF/MF Applicable<br>Low Cost<br>Permeability and High-strength inconsistent |
| | **Thermally Induced Phase Separation**<br>Polymer solution is cooled down to phase separation temperature | High Strength<br>High Flux<br>Low Cost |



# Comparison of Hollow Fiber Membrane with Other Companies

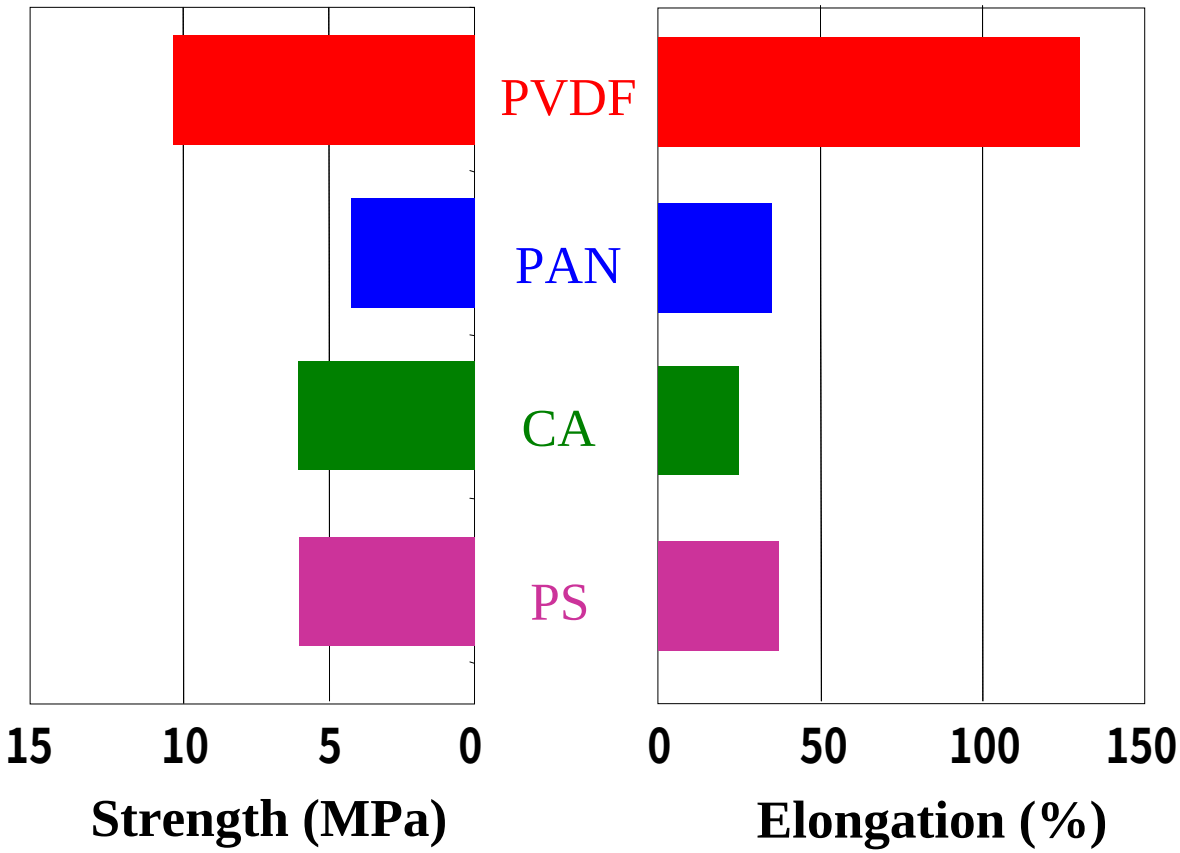
* Pure Water, at 50 kPa

| Supplier | U Company | | Z Company | N Company | A Company | Toray |
|---|---|---|---|---|---|---|
| Material | PP | PVDF | PVDF | PES | PVDF | PVDF |
| Permeability* ($m^3/m^2 \cdot d$) | 4.8 | – | 1.5 | 3.0 | 5.3 | 6.7 |
| Membrane Area ($m^2$) | 30 | – | 56 | 35 | 50 | 72 |
| Module |  | |  |  |  |  |

PP: Polypropylene, PVDF: Poly (Vinylidene Fluoride), PES: Poly (Ether Sulfone)

**World's No. 1 Permeability and Largest Module**

# Comparison of Strength & Elongation - Membrane Material -




**Physical property depends highly on material & spinning method**

# Comparison of Chemical Stability of PVDF Hollow Fiber

## -Accelerated Oxidation-

**Purpose: Confirmation of stability against strong oxidation agent**

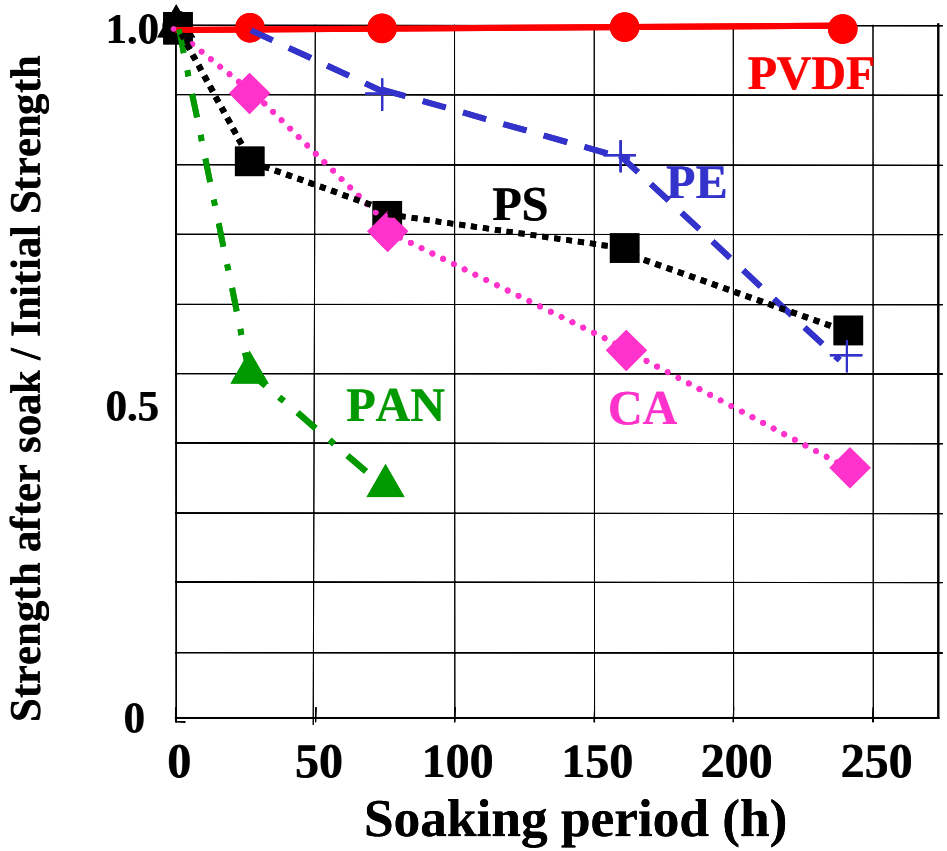
**Accelerated oxidation**

1. Evaluation of membrane configuration
2. Evaluation under cleaning condition

**(5,000 ppm as $H_2O_2$ with $FeSO_4$)**

**Results**

1. PVDF-MF membrane is very stable under strong oxidation conditions.
2. PVDF-MF membrane can be cleaned with a concentrated oxidation agent.




**Comparison of Oxidation Resistance**

# Comparison of Chlorine Resistance of PVDF Hollow Fiber

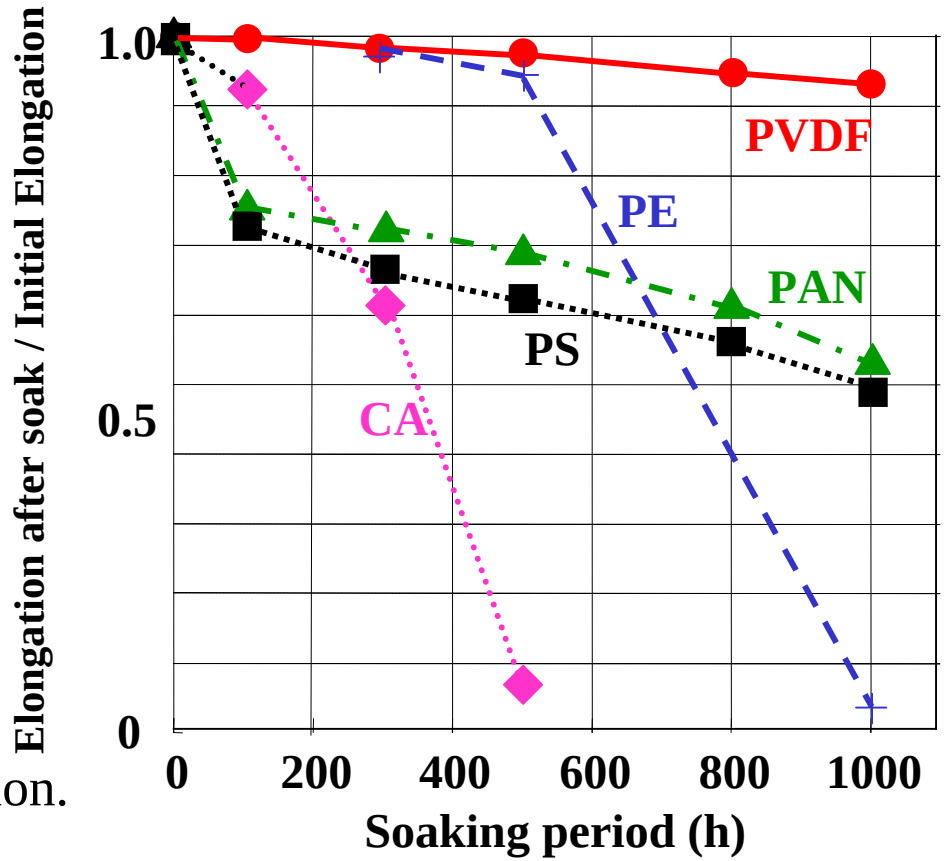
## Purpose: Confirmation of stability against chlorine

**Evaluation condition**

1. Evaluation of membrane configuration
2. Evaluation **under cleaning condition**
   (1,000 ppm as Chlorine, **pH=10**)

**Results**

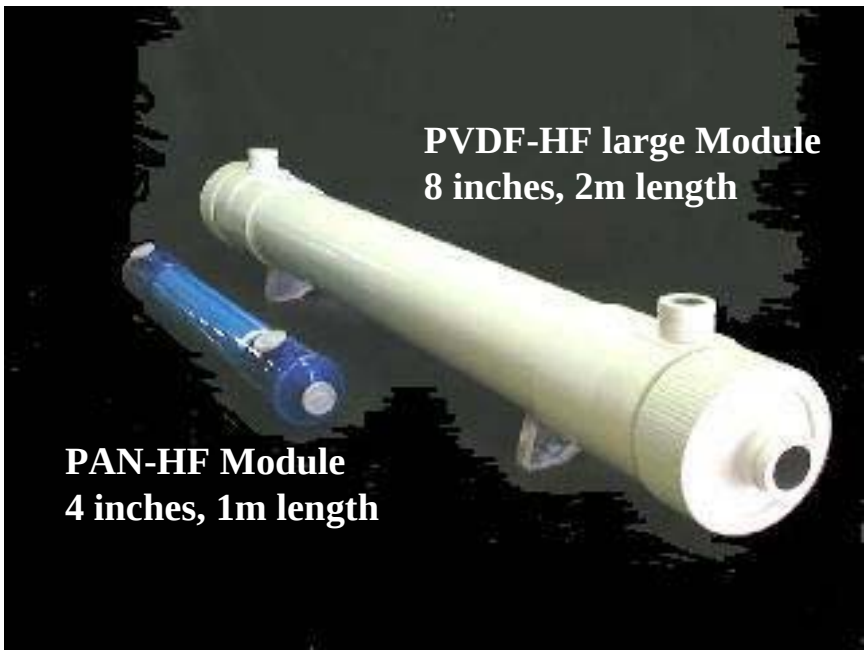
1. PVDF MF membrane is very stable in a concentrated chlorine solution.
2. PVDF-MF membrane can be cleaned with a concentrated chlorine solution.



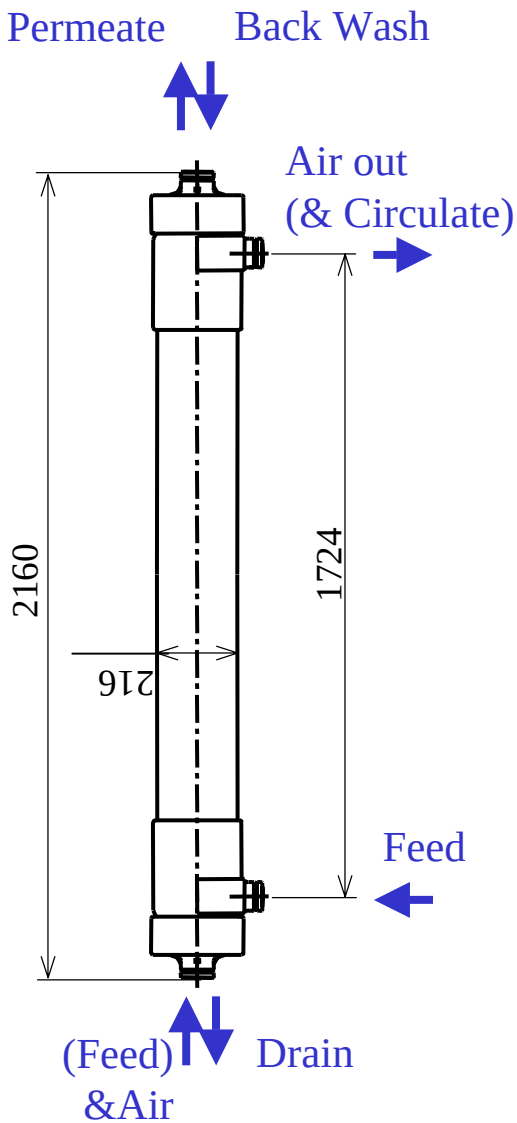

Comparison of Chlorine Resistance

# PVDF MF Membrane 8” Module

## Specifications




| Items | | Toray 8B Module |
|---|---|---|
| Module Size | [mm] | 216 (8B) dia. x 2,160L |
| Membrane Area | [m2] | 72 |
| Flux (pure water) [m3/h/50kPa] | | 20 |
| Temperature | [deg.] | 0 – 40 |

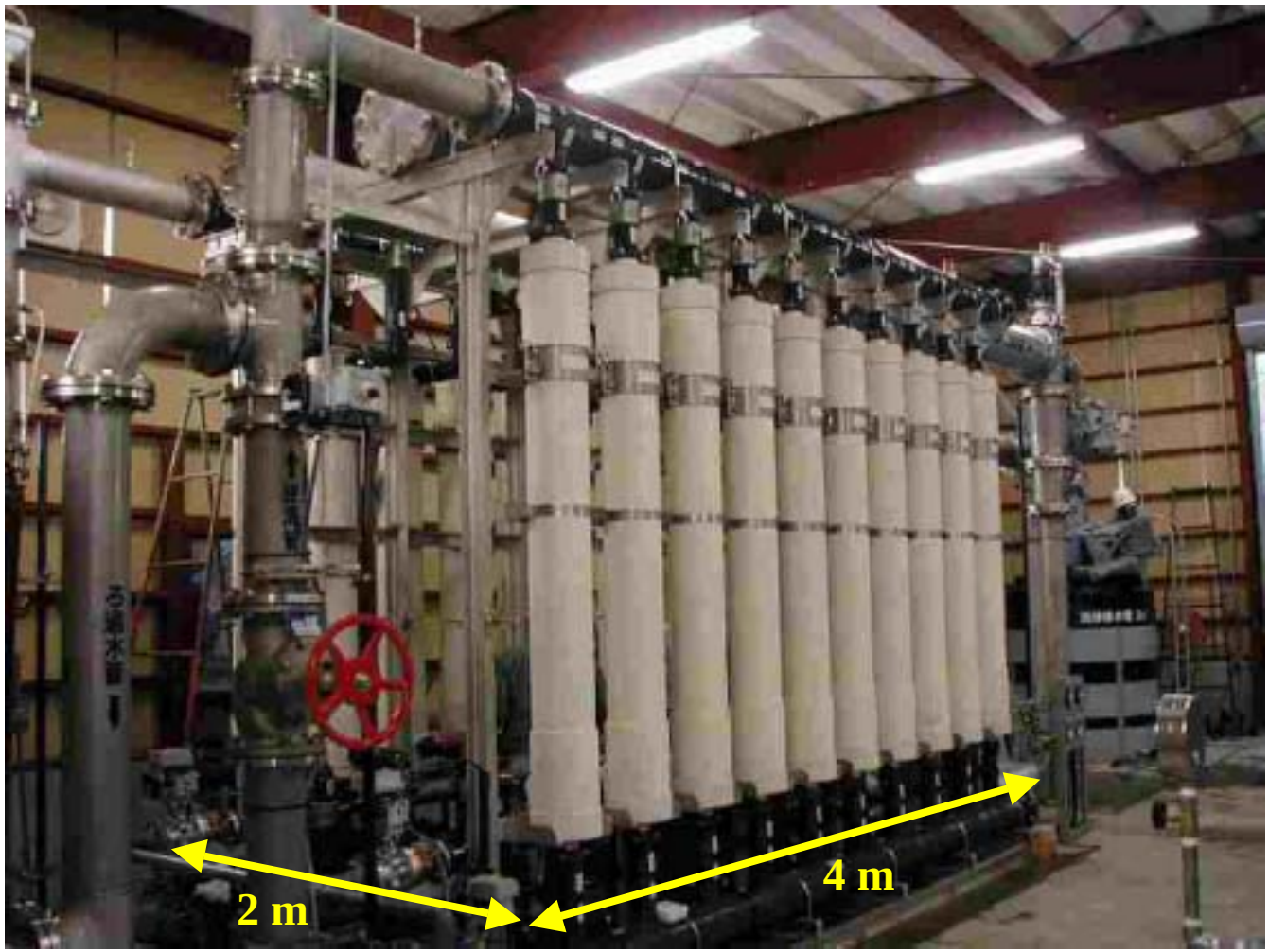


# HFM-2020 Standard Operational Conditions

| Feed Water Type | Pretreated Water<br>Clean Ground Water | River & Lake Surface Water |
|---|---|---|
| Filtration Flux ($m^3/m^2/d$) | 2 - 5 | 1 - 2 |
| Backwash Condition | Flux: 1 - 2 times of filtration flux<br>Chlorine dosing: 1 - 10 ppm<br>Time: 30 – 60 sec.<br>Frequency: every 0.3 – 2 h | |
| Scrubbing Condition | Air flow: 4 – 10 $Nm^3/h$/Module<br>Time: 30 – 120 sec.<br>Frequency: every 0.3 – 2 h | |
| Operation Temp. (degrees C) | ≦ 40 | |
| Operation pH | 1 – 10 | |
| Chemical Cleaning | (1) CIP (Clean In Place): every 3 - 6 months<br>(2) Trans-Membrane pressure<br>(3 - 5 times of initial, or 150 kPa)<br>(3) Chemicals: 1N-HCl + 3,000 ppm NaClO | |

# Large Scale Ground Water Filtration Plant

## (5,000 $m^3$/d、for 20,000 people)




**Compact and High Productivity**

# Water Treatment Related National Projects

| Year | Title | Toray's R&D Theme |
|---|---|---|
| 1992<br>1993 | Project Membrane Aqua Century 21 (**MAC21**) | |
| 1994<br>1995<br>1996 | New Membrane Aqua Century 21<br>(**MAC21**) | ・Highly efficient water purification system utilizing NF membranes<br>(Toray Engineering Co.) |
| 1997<br>1998<br>1999<br>2000<br>2001 | Advanced Aqua Clean Technology for the 21st Century<br>(**ACT21**) | 【Search for New Technology Application of Membrane Filtration】<br>・Development of efficient coagulation and sedimentation technology to be applied in the UF pretreatment<br>・Development of operational stability during the NF advanced water purification process<br>【Development of Advanced Water Purification System of River Water】<br>・Technological examination of combination of conventional water purification systems and membrane filtration |
| 2002<br>2003<br>2004 | Environmental, Ecological, Energy Saving and Economical Water Purification System<br>(**e-Water**) | Group 1: Development of large-capacity membrane filtration technology (Kawai,Yokohama/Shinishikawa,Okinawa)<br>Group 2: Total water purification system (Ayase,Yokohama/Otokane,Fukuoka)<br>Group 3: Observation technology at the drinking water supply source |

# Participation in National Project (e-water)

## Water Drinking Production Plant Order Award Requirements:

1. Qualification of the Facility
2. Approval of Construction Work
3. Acquisition of National Licenses
4. Actual Experience in Plant Delivery

| Water Purification Plant | Feed Water | Subject | Participants/ Toray's Expected Role |
|---|---|---|---|
| Kawai, Yokohama<br>June/03 ～ Mar/05 | Fresh Water | ・Comparative Experiments of 6 Groups, including Ebara<br>・Case Trial - 200,000 $m^3/d$ | ・Toray/Suido Kiko Joint Team<br>・Toray; Experiment Supervisor, Basic Design, Manufacture of Experimental Facility, Follow-up of Operations |
| Ayase, Yokohama<br>Aug/03～Mar/05 | Fresh Water | ・Examination of Appropriate Operating Conditions | ・Co-R&D of 38 Companies<br>・Toray; Basic Design, Supply of PVDF Modules |
| Otogane, Fukuoka<br>Sept/03 ～ Mar/05 | Fresh Water | ・Comparative Experiments of 5 Groups including Maezawa and Shinko Pantec<br>・ Case Trial - 110,000 $m^3/d$ | ・Suido Kiko as the Supervisor<br>・Toray; Supplies PVDF Modules, Supports System Examination |
| Ishikawa, Okinawa<br>Oct/03 ～ Mar/05 | Fresh Water | ・MF Pretreatment+NF Membrane (to confront Ozone + Activated Carbon Method)<br>・Only Successful Group to actually demonstrate use of membranes<br>Case Trial - 50,000 $m^3/d$ | ・Nishihara; Supervisor, Joint Team of Suido Kiko, Ebara, Kubota, and Toray<br>・Toray; Basic Design and Supply of PVDF and NF Modules |

# Conclusion - UF/MF Membranes for Drinking Water

1. **The Drinking Water Production Market is expanding rapidly, centering on the U.S. and Europe.**
2. **Toray has developed highly water-permeable and highly stable PVDF hollow fiber large modules suitable for drinking water production.**
3. **Although still in the experimental stage, Toray's technology is highly appraised, and we are aiming to enter the market as soon as possible.**

# Immersed Membrane Modules for Wastewater Treatment

# Merit of Membrane Bio-reactor

1. Good permeate quality
   1) Low COD concentration
   2) Low total nitrogen and total phosphorous
   3) No suspended solid
   4) Removal of bacteria and viruses

2. Very space efficient design

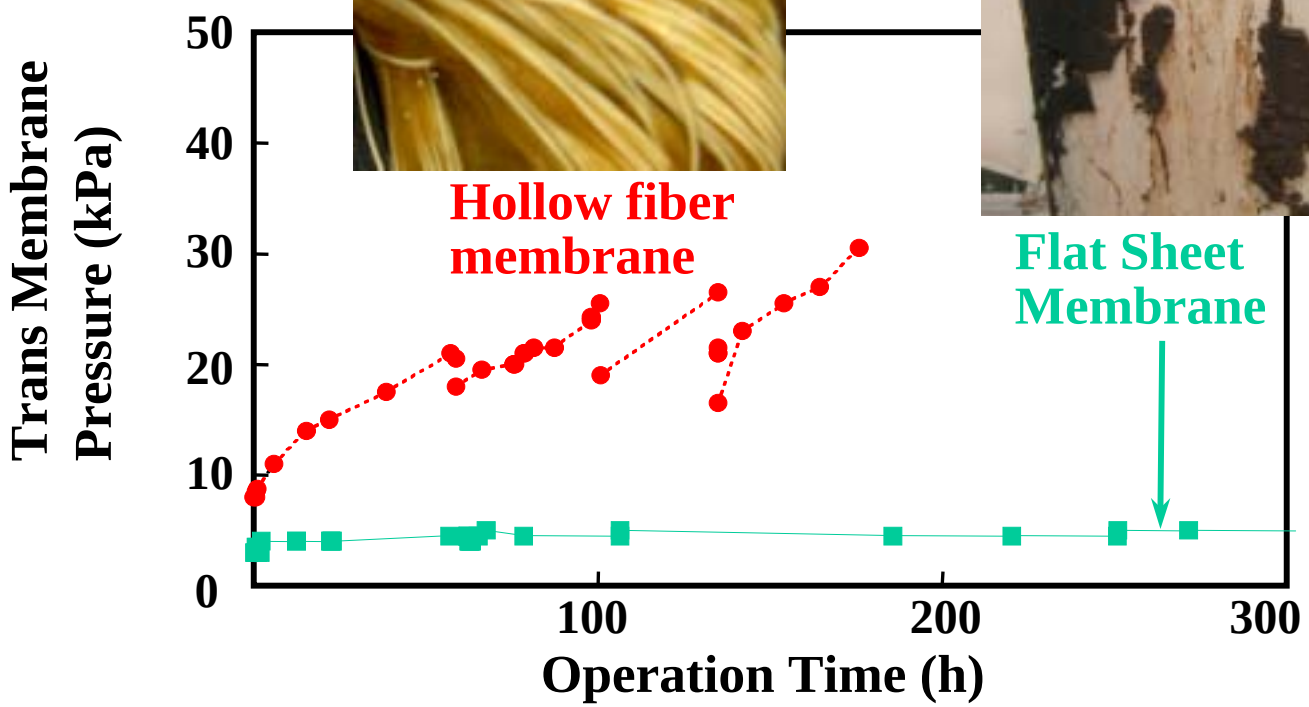
3. Considerable reduction of excess sludge

4. Reclamation of wastewater
   Integrated system with RO membrane

# Flat Sheet Membrane or Hollow Fiber Membrane

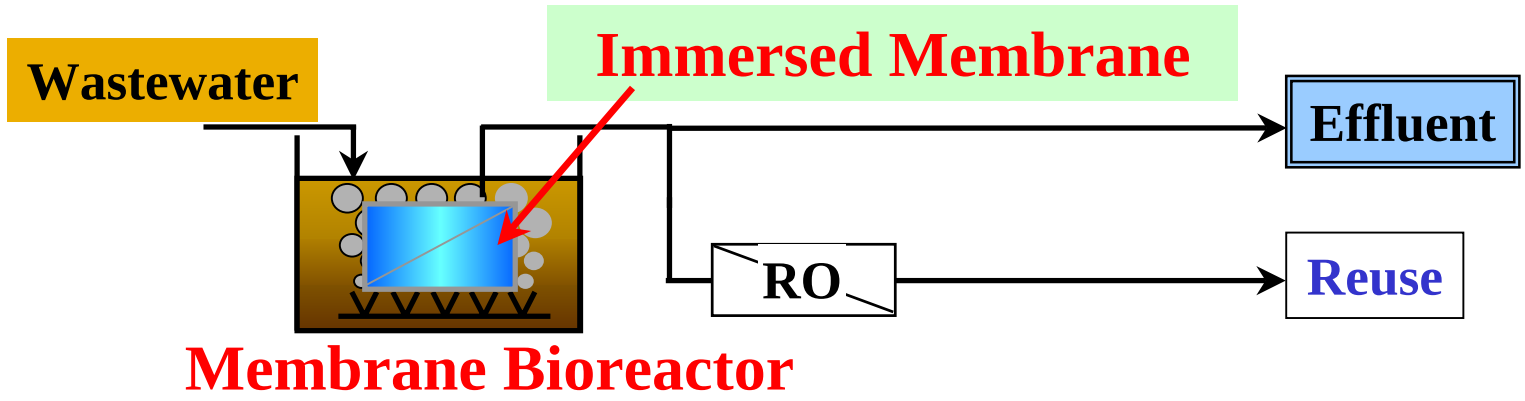
| Type | Merit | Demerit |
|---|---|---|
| Flat Sheet | Effective aeration per footprint<br>Ease to remove fouling substances<br>Less pressure loss<br>Small dead space | Small membrane area per volume<br>Difficulty for backwash |
| Hollow Fiber | Large membrane area per volume<br>Backwash cleaning | Inter-fiber fouling causes flux decline & fiber damage |

# Flat Sheet Membrane or Hollow Fiber Membrane

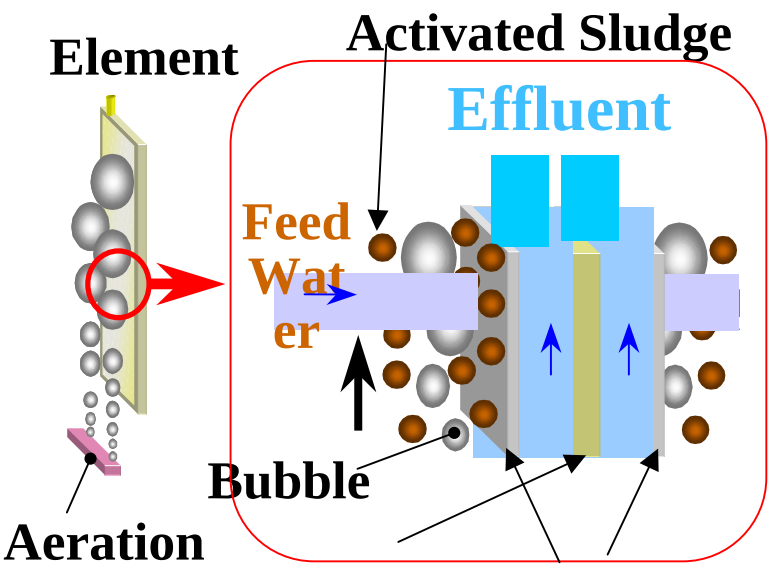



Industrial Wastewater Treatment Test

# Flat Sheet Membrane Bioreactor




Feed Water
(Activated Sludge)




Effluent

# Requirement and Design for Immersed Membrane

## Requirement

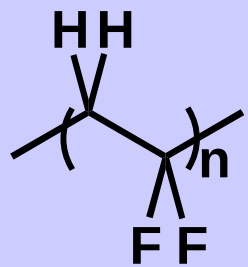
1. Chemical and physical durability
2. High water permeability and high permeate quality
3. Prevention for clogging

## Design Concept

1. Membrane material :

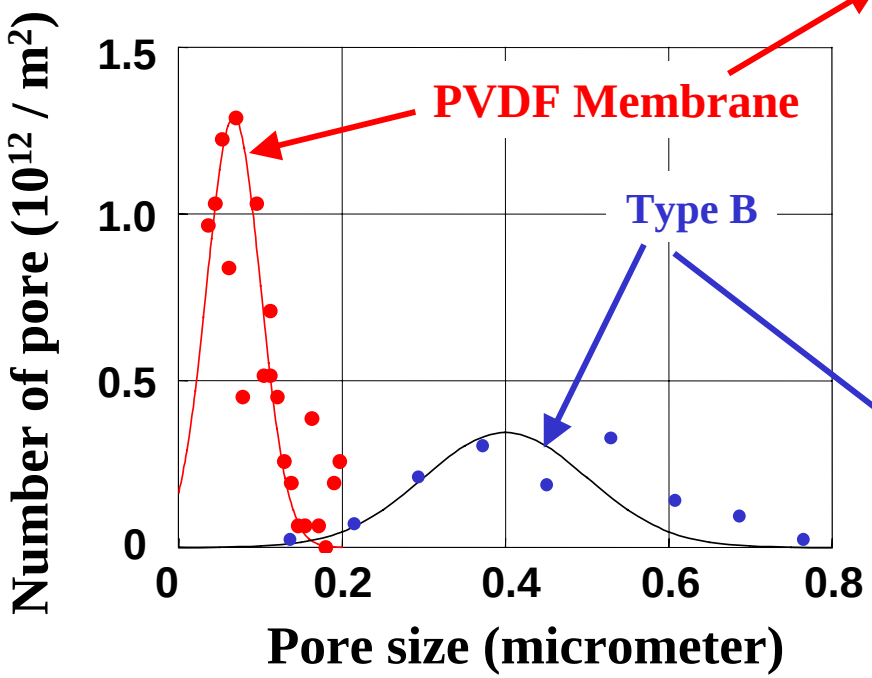
   Poly(vinylidene fluoride) (PVDF)

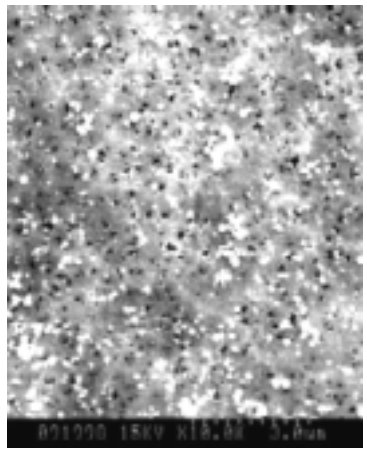
   High stability for chemicals and high physical strength



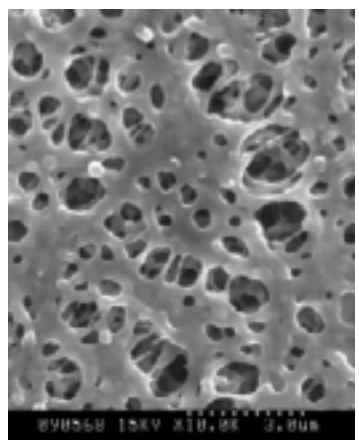

2. Membrane form : Fiber reinforced membrane
3. Surface pore : 1) Small pore size
   2) Narrow pore size distribution
   3) Large pore number

# Pore size of Flat Sheet Membranes



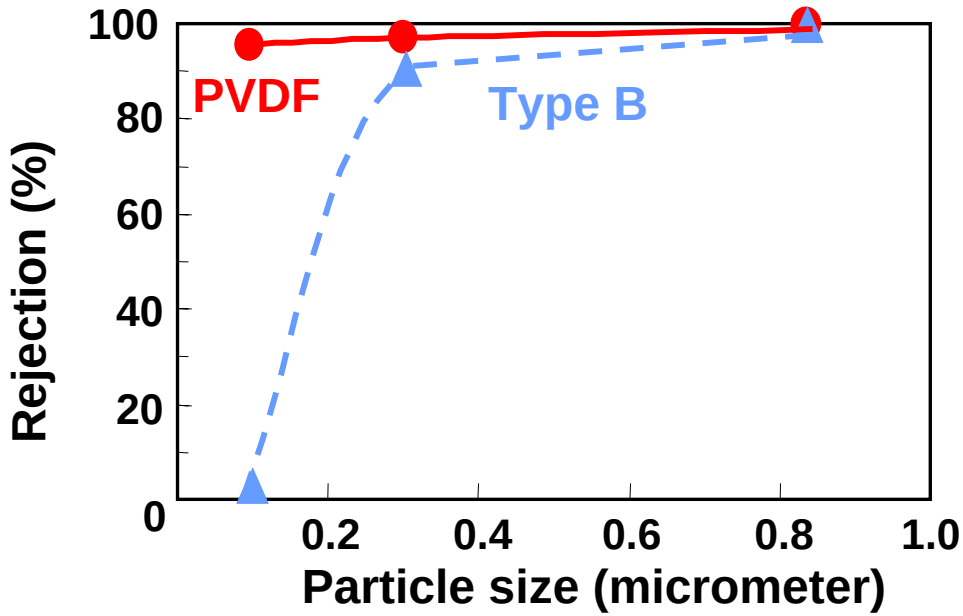
3.0 micrometer



3.0 micrometer

**Pore Size Distribution of Flat Sheet Membranes**

# PVDF Flat Sheet Membrane Performance



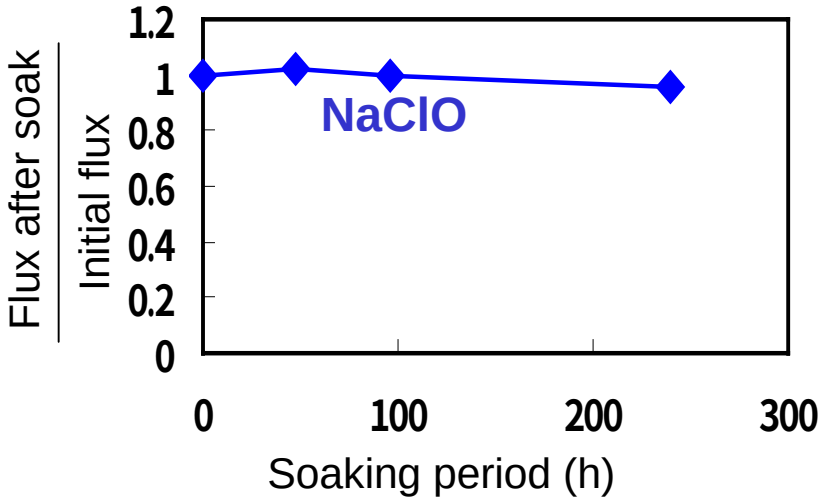

Rejection of PSt latex particles

| | PVDF | Type B |
|---|---|---|
| Average Surface Pore Size (micron) | 0.08 | 0.4 |
| Pure Water Flux ($m^3/m^2/h$, 10 kPa) | 1.44 | 0.90 |

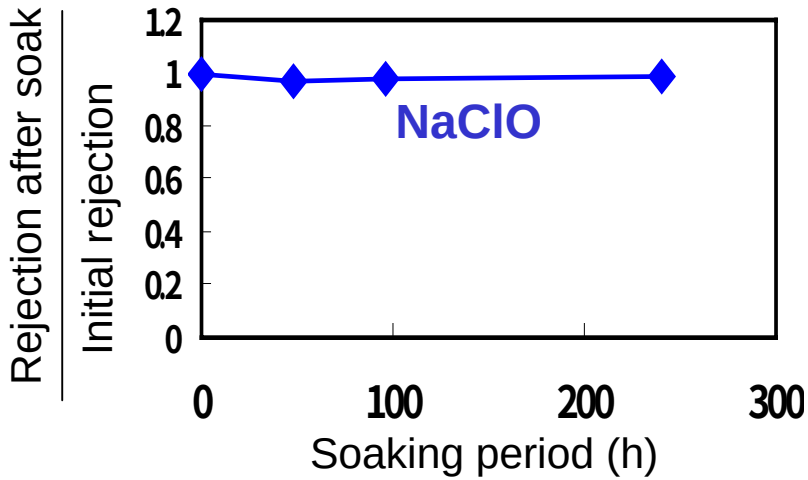
**PVDF membrane has small pore and high flux**

# Chemical Resistance of PVDF Flat Sheet Membrane

## Purpose: Confirmation of membrane stability for cleaning chemical




**Retention of Flux after soaking**




**Retention of PSt rejection after soaking**

## Evaluation condition

1. Membrane configuration
2. Under cleaning condition
   (1,000ppm as Chlorine , pH=10)

## Result

PVDF MF membrane

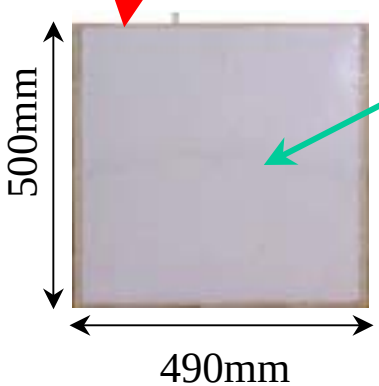
1. is very stable in concentrated chlorine solution
2. can be cleaned with concentrated chlorine solution

# Immersed Membrane Module

## Small Test Module

Membrane Module (10 elements)

Effluent




Membrane

Membrane Element (0.45m²)

## Large Size Module

Membrane Module (24m², 20 elements)

Housing

Diffuser


Membrane Element (1.2m²)

# Module Type and Standard Operation Condition

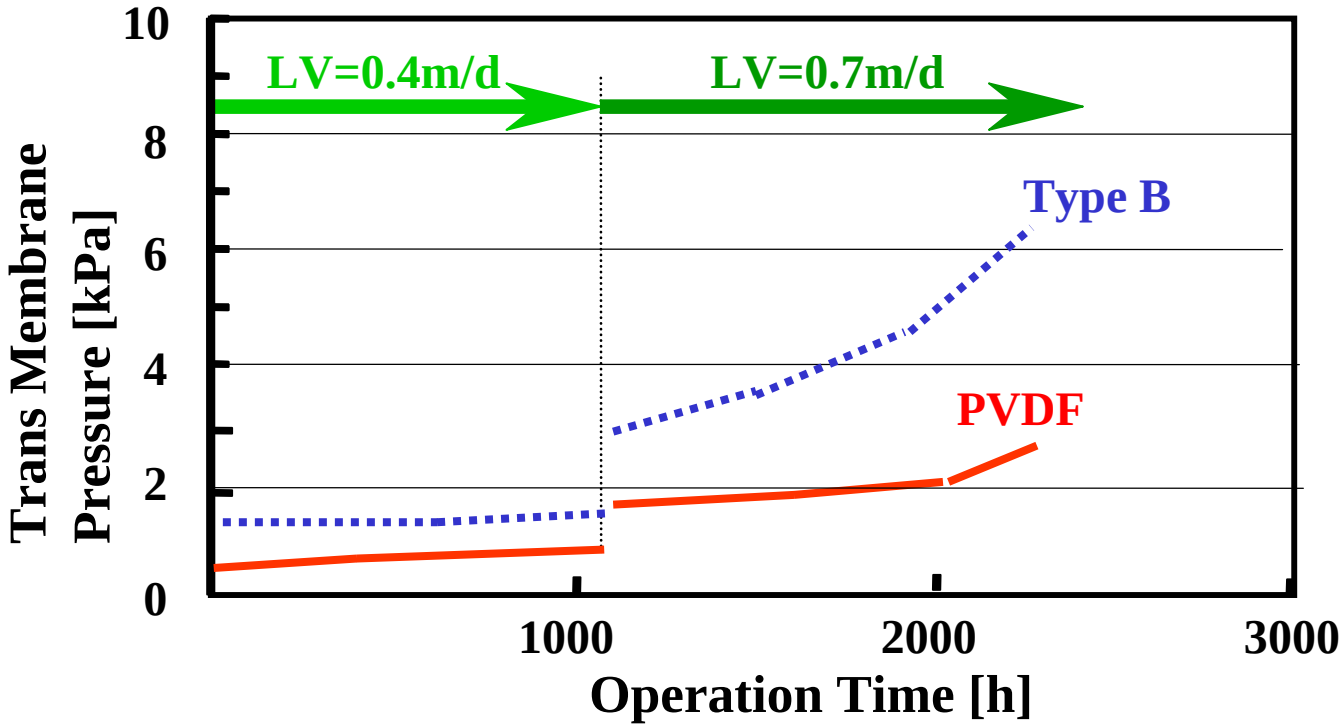
## Module Type

| Module type | | M1 | M2 | M3 |
|---|---|---|---|---|
| Dimension | Number of element | 50 | 100 | 200 |
| | Width (m) | 0.80 | 0.80 | 0.80 |
| | Depth (m) | 0.98 | 1.65 | 3.00 |
| | Height (m) | 2.20 | 2.20 | 2.20 |
| Material | Housing | SUS | | |
| | Permeate manifold | PVC | | |
| | Diffuser | PVC | | |

## Standard operation condition

| | |
|---|---|
| MLSS (mg/L) | 3,000 – 20,000 |
| Temperature (degree C) | 5 – 40 |
| pH | 2 – 12 |
| Operation flux ($m^3/m^2/d$) | 0.4 – 1.0 |
| Air flow (NL/min/Element) | 10 - 15 |
| Filtration pressure (kPa) | < 50 |

# Sludge Filtration Test (Small Test Module)




**Test Equipment**

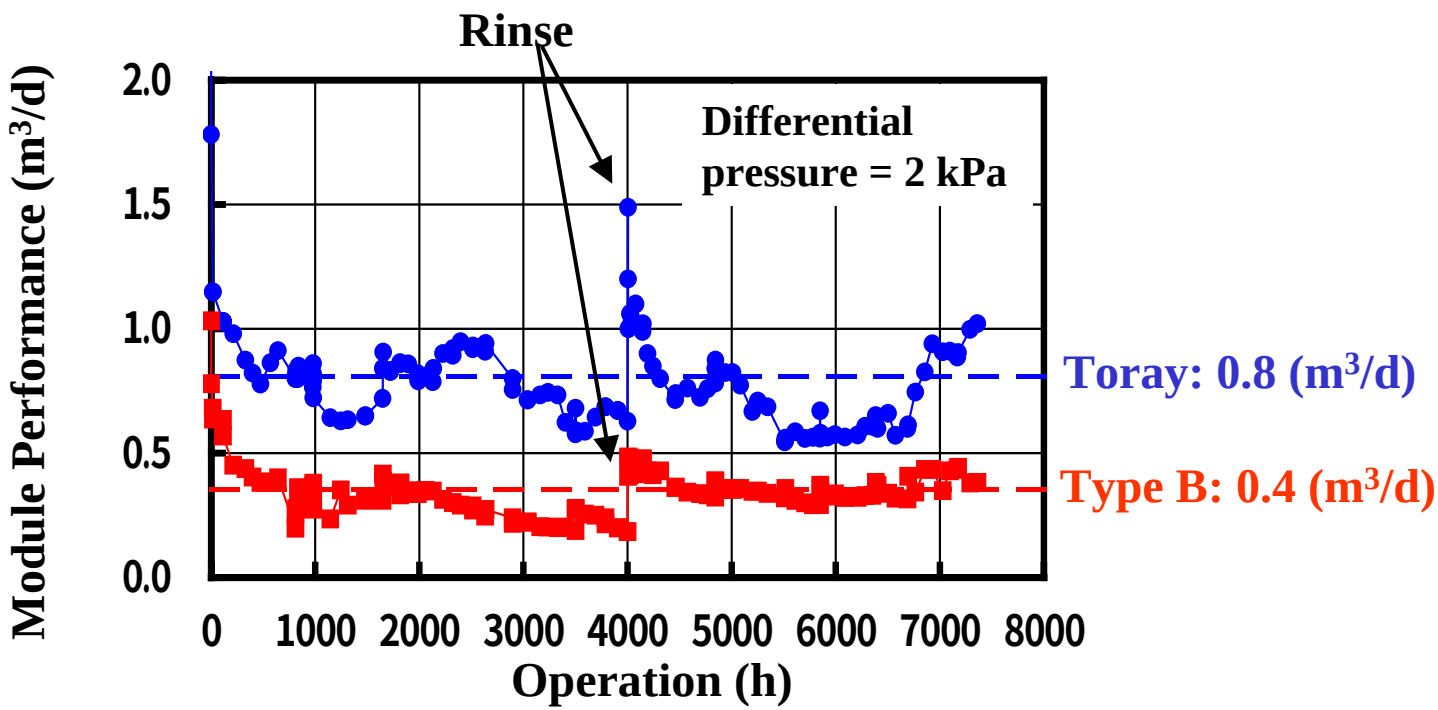
- MLSS : 3,000-4,000 (mg/L)
- Tank Size : 750L
- Membrane Area : 1.6 $m^2$

**Quality of Effluent**

| | PVDF | Type B | Conventional |
|---|---|---|---|
| Turbidity(NTU) | 0.20 | 0.21 | 1.25 |
| BOD (mg/L) | 3.5 | 3.4 | 3.8 |
| COD (mg/L) | 5.1 | 5.0 | 6.1 |

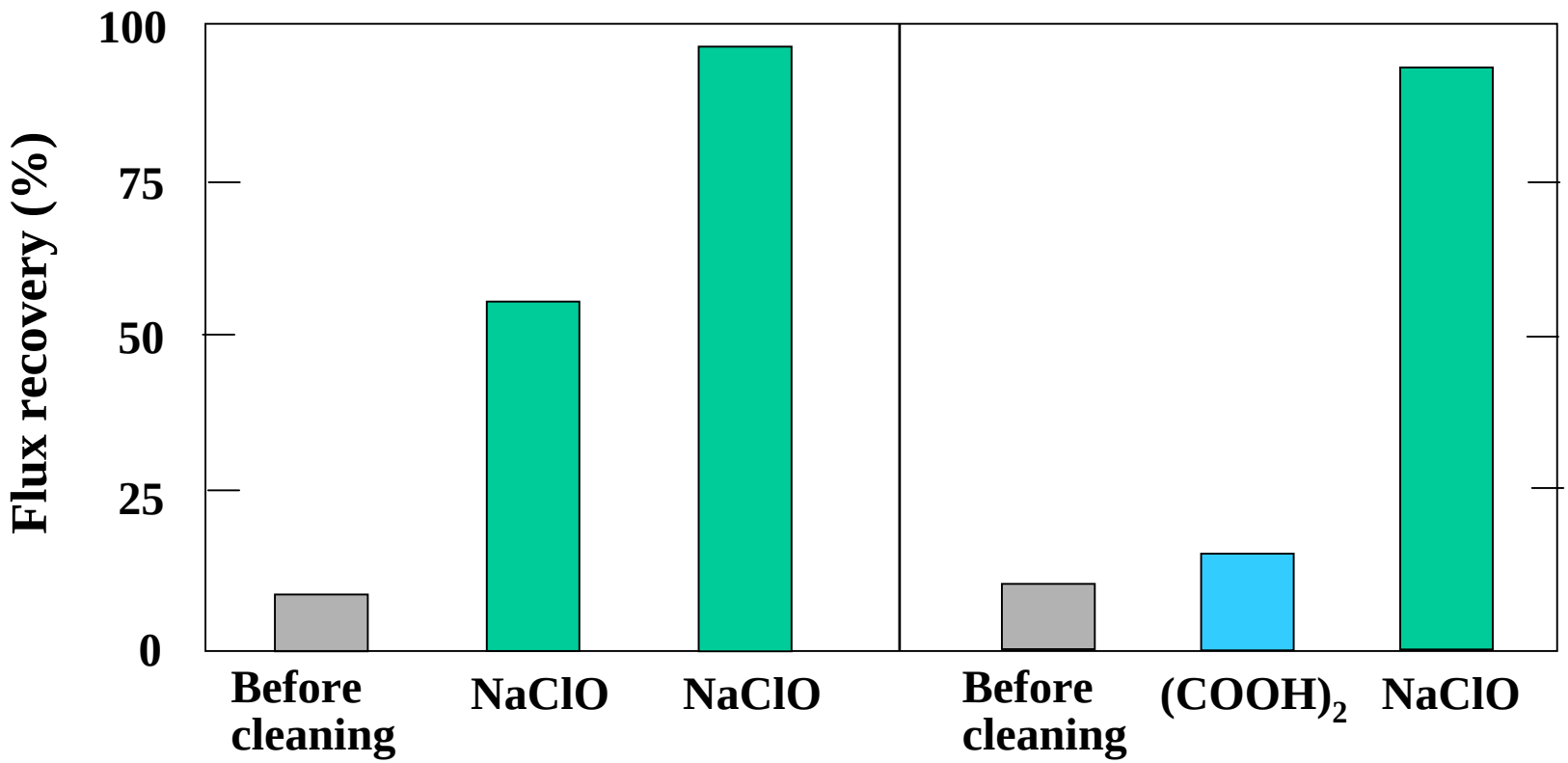
# Comparison of Module Performance

| Module Performance ($m^3$/footprint) | = | Membrane Performance ($m^3/m^2$) | × | Membrane Area ($m^2$) | = | 2 |
|---|---|---|---|---|---|---|
| (Compared to other modules) | | (1.4) | | (1.5) | | |




**Toray module performance is twice as competent as others**

# Chemical Cleaning of PVDF Flat Sheet Membrane




| Chemical | Concentration | Cleaning time (h) |
|---|---|---|
| Sodium hypochlorite | 1,000 – 5,000 (mg/L) | 2 – 5 |
| Hydrogen peroxide | 1,000 (mg/L) | 2 – 5 |
| Oxalic acid | 1 – 2 (%) | 1 - 3 |

# Pilot Test for Industrial Wastewater (Chemical plant)

## Test conditions

| Parameter | Unit | Value |
|---|---|---|
| Influent flow | $m^3/d$ | 41 ~ 68 |
| BOD of raw water | mg/l | 180 ~ 430 |
| MBR vessel capacity | $m^3$ | 5.5 |
| MLSS | mg/l | 12,000 ~ 20,000 |
| Membrane area | $m^2$ | 137 |
| Permeate water flux | $m^3/ m^2 /d$ | 0.30 ~ 0.50 |
| Scouring air flow | $Nm^3/min$ | 1.0 ~ 1.2 |
| Temperature | Degree C | 25 - 32 |

**Appearance of MBR**

## Influent and effluent quality

| Parameter | Unit | Influent | Effluent |
|---|---|---|---|
| pH | - | 7.6 | 7.4 |
| BOD | mg/l | 230 | 4.6 |
| COD | mg/l | 140 | 8.4 |
| SS | mg/l | 15 | None |
| Total nitrogen | mg/l | 18.6 | 2.3 |
| Total phosphorus | mg/l | 0.3 | 0.06 |

**Module installation**

# Pilot Test for Brewery Wastewater (Small test module)

## Operation Condition

| Parameter | Unit | Brewery |
|---|---|---|
| COD-Cr of raw water | mg/L | 3,000 |
| COD-Cr per sludge weight | kg-COD-Cr/kg-SS/d | 0.08 – 0.10 |
| MLSS | mg/L | 4,000 – 5,500 |
| Membrane area | $m^2$ | 6.0 |
| Permeate water flux | $m^3/m^2/d$ | 0.24 |
| Temperature | degree C | 12 - 15 |

## Result

1. COD removal was more than 95 %
2. Suspended solid was removed completely
3. TMP was stabilized

# Pilot Test for Municipal Wastewater

## Operation Condition

| Parameter | Unit | Municipal |
|---|---|---|
| COD-Cr of raw water | mg/L | 275 |
| COD-Cr per sludge weight | kg-COD-Cr/kg-SS/d | 0.15 – 0.22 |
| MLSS | mg/L | 7,800 - 5,000 |
| Membrane area | $m^2$ | 24 |
| Permeate water flux | $m^3/m^2/d$ | 0.53 |
| Temperature | degree C | 13 - 16 |

## Result

1. COD removal was about 90 %
2. Suspended solid was removed completely
3. TMP was stabilized

# Test for Municipal Wastewater

**Pilot test started at Beverwijk WWTP in March 2003, cooperated with Seghers Keppel Technology Group (SKG)**


**Toray**

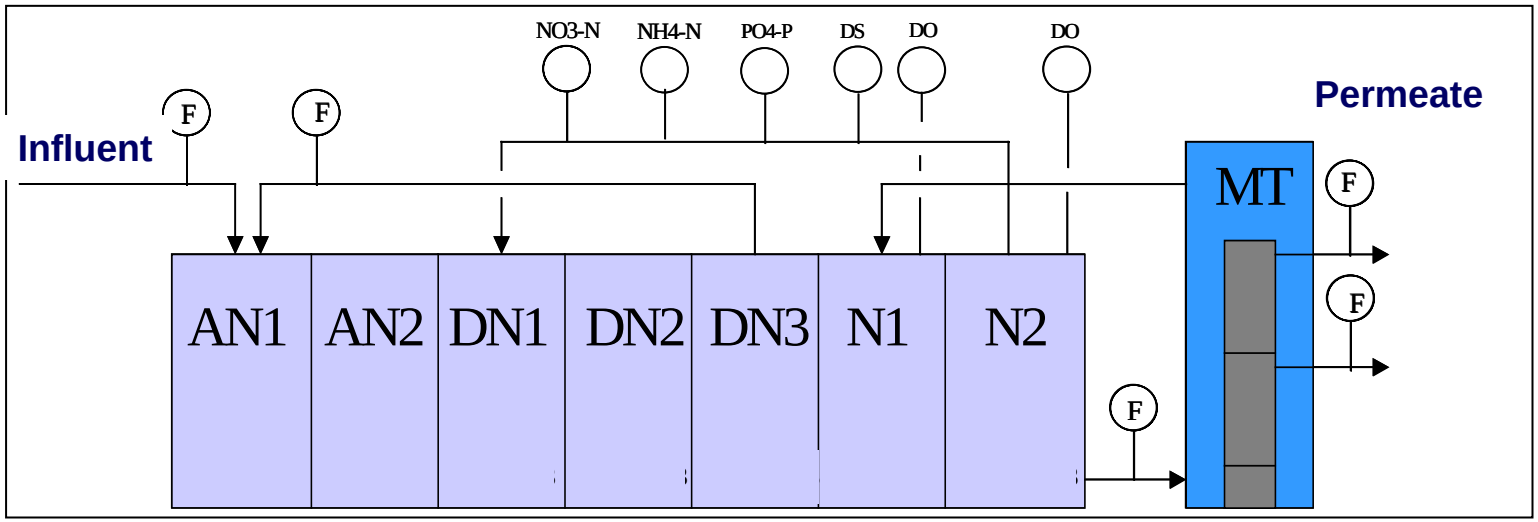
**Membrane element supply**

**SKG**

**MBR system design & build Operation**

# Test for Municipal Wastewater (Beverwijk WWTP)

## System Configuration




**AN= Anaerobic zone, DN= Anoxic zone, N= Nitrification zone, MT= Membrane tank**

| | |
|---|---|
| **Design capacity ($m^3$/d)** | **120** |
| **Membrane area ($m^2$)** | **137** |

# Test for Municipal Wastewater (Beverwijk WWTP)

1. After 6 months of operation, no fouling measured on membranes
2. No chemical cleaning necessary
3. Without dosing chemicals the following effluent limits is reached
   - $PO_4$-P : 0.35 (mg/l)
   - $NH_4$-N : 0.10 (mg/l)
   - $NO_3$-N : 3.5 (mg/l)
4. Permeability is still more than 1,200 ($l/m^2/h/bar$)
5. The following flux data were obtained compared with others

($l/m^2/h$)

| | Toray | A | B |
|---|---|---|---|
| Critical flux | 85 | 40 | 45 |
| Peak flux (Rain) | 70 | 30 | 35 |
| Average flux (Dry Weather) | 20 | 10 | 12 |

(based on “Membrantechnik in der Wasseraufbereitung und Abwasser be handlung, Aachen, 2003”)

# Conclusion

1. **Flat sheet type immersed membrane with high flux, small pore size and narrow pore size distribution has been developed.**
2. **Immersed membrane module was operated at low trans membrane pressure even in high activated sludge concentration.**
3. **Permeability was recovered after chemical cleaning and there was no damage of membrane.**
4. **Pilot tests were carried out at several WWTP plants and operations were stable.**

# Conclusion
## - Toray's Membrane Separation Technology for Water Treatment

1. Toray is a synthetic membrane manufacturer whose products cover all types - RO, NF, UF, and MF.

2. Placing top priority on seawater desalination, drinking water production, and wastewater treatment, Toray intends to expand its membrane technology business throughout the world.

3. High water quality and an Integrated Membrane System (IMS), a combination of several membranes, is required in the future market. Toray, possessing all types of membranes, is in an advantageous position in expanding business utilizing the IMS.

# Toray can contribute to ensuring sustainable water resources with membrane technology

River, Lake, Ground Water

Sea Water

Wastewater