Focus on Membrane Technology for Water Treatment

Toray Industries, Inc.
Dr. Masaru Kurihara

September 2003
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4. UF Membranes & MF Membranes
   - Drinking Water Production -

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   for Wastewater Treatment

6. Conclusion
Introduction of Doctor M. Kurihara

Title:

Toray Industries, Inc. Senior Director
In charge of Water Treatment Division, Technology Center (Water Treatment Technology Center), and Research & Development Division
Director of International Desalination Association (IDA)
Vice President of Japan Desalination Association (JDA)
Director of Japan Membrane Society, Part-time lecturer at Kyoto University

Personal History:

1963  Joined Toray Ind., Inc.
1970  Doctoral Dissertation at the University of Tokyo
      Membrane Research with Prof. J.K. Stille at the University of Iowa as Post-Doctoral Fellow
1991  General Manager, Polymers Research Labs

Awards:

1992  Chemical Society of Japan Technical Award
2002  International Desalination Association Presidential Award
2003  Okochi Memorial Production Prize
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)

(Core Technologies)
- Organic Synthetic Chemistry
- Polymer Chemistry
- Biochemistry

<Advanced Materials>
- Nanofibers
- High-performance Fibers and Resins
- Nano-alloy Materials
- Advanced Electronics Materials
- Biomaterials
- Separation Materials
- High-performance Composite Materials
- Recycling Materials

<Three Growth Areas>
- IT-related Products
- Life Sciences
- Environment Safety Amenity

Four Strategic Business Areas
- Electronics & Info-Related Products
- Pharmaceuticals
- Water Treatment
- Carbon Fiber
World Water Shortage - Now and Future

(WMO and others, 1996)

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

1) >40% : Middle East, Singapore, Korea, Pakistan
2) 20 - 40%: India, Mexico, Europe (excluding UK and France), Taiwan, South Africa

Water shortage presumed to continue worldwide especially in Europe, the U.S.A., and China by 2025:

1995:
1) >40% : Middle East, Singapore, Korea, Pakistan
2) 20 - 40%: India, Mexico, Europe (excluding UK and France), Taiwan, South Africa

2025:
1) >40% : Middle East, Korea, Pakistan, India, Algeria, South Africa, etc.
2) 20 - 40%: Mexico, China, USA, Europe (excluding UK)
## Water Problem and Membrane Technology

<table>
<thead>
<tr>
<th>Region, Country</th>
<th>Water Problem</th>
<th>Membrane Technology for Water Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water Resource Shortage</td>
<td>Water Pollution</td>
</tr>
<tr>
<td>United States</td>
<td>Problem</td>
<td>Problem</td>
</tr>
<tr>
<td>Benelux</td>
<td>Problem</td>
<td></td>
</tr>
<tr>
<td>UK, France</td>
<td>Problem</td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td>Problem</td>
<td>Problem</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>Severe</td>
<td></td>
</tr>
<tr>
<td>Kuwait</td>
<td>Severe</td>
<td></td>
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<tr>
<td>China</td>
<td>Problem</td>
<td>Severe</td>
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<tr>
<td>Singapore</td>
<td>Severe</td>
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<td>Japan</td>
<td>Problem</td>
<td></td>
</tr>
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</table>

Water resources are extending from fresh water to sea water and wastewater.
Water Treatment Membranes
## Membranes and Relative Size of Common Materials

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Reverse Osmosis (RO)</th>
<th>Nanofiltration (NF)</th>
<th>Ultrafiltration (UF)</th>
<th>Microfiltration (MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Membrane</strong></td>
<td><strong>RO</strong></td>
<td><strong>NF</strong></td>
<td><strong>UF</strong></td>
<td><strong>MF</strong></td>
</tr>
<tr>
<td><strong>Size (micrometer)</strong></td>
<td><strong>0.0001</strong></td>
<td><strong>0.001</strong></td>
<td><strong>0.01</strong></td>
<td><strong>0.1</strong></td>
</tr>
</tbody>
</table>

### Relative Size of Common Materials

| Size (micrometer) | 0.0001 | 0.001 | 0.01 | 0.1 | 1 | 10 |

- **Cl⁻ ion Na⁺ ion**
- **Pesticide, Organic Material**
- **Zn²⁺ ion**
- **F⁻ ion**
- **Pb²⁺ ion**
- **NO₃⁻ ion**
- **Trihalomethane**
- **Hepatitis A Virus**
- **Polio Virus**
- **Virus**
- **Influenza Virus**
- **Algae, Mad Vibrio Cholerae**
- **Coliform Cryptosporidium**
- **Bacillus anthracis**

### Application

- **Sea Water Desalination**
- **Brackish Water Desalination**
- **Wastewater Treatment**
- **Drinking Water**
## Separation Characteristics of Various Membranes

<table>
<thead>
<tr>
<th>Permeation and Rejection</th>
<th>RO/NF Membranes</th>
<th>UF/MF Membranes</th>
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</thead>
<tbody>
<tr>
<td></td>
<td><strong>Membrane</strong></td>
<td><strong>Membrane</strong></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>Water</td>
</tr>
<tr>
<td>Low MW organic materials (Mw ≤ 200)</td>
<td>RO: Molecular interaction</td>
<td>MF: Dynamic separation</td>
</tr>
<tr>
<td>Monovalent ions</td>
<td>Solution diffusion</td>
<td>Size exclusion</td>
</tr>
<tr>
<td></td>
<td>Electric repulsion</td>
<td>UF: Electric repulsion</td>
</tr>
<tr>
<td>Middle to high MW materials (Mw &gt;200)</td>
<td>NF: Size exclusion</td>
<td></td>
</tr>
<tr>
<td>Multivalent ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water permeating</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore Size</td>
<td>RO: &lt;1 nm</td>
<td>UF: 10~100 nm</td>
</tr>
<tr>
<td></td>
<td>NF: 1~10 nm</td>
<td>MF: &gt;100 nm</td>
</tr>
</tbody>
</table>
Global Capacity of Membrane Filtration Plants

- **Installed Capacity (m³/d x 10⁴)**
  - 12,000
  - 10,000
  - 8,000
  - 6,000
  - 4,000
  - 2,000
  - 0

- **Global Capacity of Membrane Filtration Plants**
  - **RO&NF Cumulative**
  - **MF&UF Cumulative**

- **Crypto outbreak**
- **Number of Contracts**

- **Potentiality**
- **Cumulative Estimated**

- **Annual Total**
- **Cumulative Total**
- **Crypto outbreak**
- **Contracted**
- **Potential New**
- **Cumulative Estimate**
- **RO+NF**

Years:
- 1985
- 1986
- 1987
- 1988
- 1990
- 1991
- 1992
- 1993
- 1994
- 1995
- 1996
- 1997
- 1998
- 1999
- 2000
- 2001
- 2002

**MF&UF Annual**
<table>
<thead>
<tr>
<th>Water treatment processes</th>
<th>Technical target</th>
<th>Toray’s products</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Desalination</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desalination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea-water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>Multi Stage</td>
<td>RO membrane</td>
</tr>
<tr>
<td>New</td>
<td>Flush (MSF)</td>
<td>with high boron</td>
</tr>
<tr>
<td></td>
<td>**Single Stage</td>
<td>removal</td>
</tr>
<tr>
<td></td>
<td>SWRO</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desalination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>Multi stage</td>
<td>NF membrane for</td>
</tr>
<tr>
<td></td>
<td>flush (MSF)</td>
<td>brine</td>
</tr>
<tr>
<td></td>
<td>Brine conversion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Two-stage SWRO</td>
<td>conversion system</td>
</tr>
<tr>
<td>Desalination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td></td>
<td></td>
</tr>
<tr>
<td>River Lake Ground</td>
<td>Coagulation &amp;</td>
<td>PAN hollow fiber</td>
</tr>
<tr>
<td>Conv.</td>
<td>Sedimentation</td>
<td>UF membrane</td>
</tr>
<tr>
<td>New</td>
<td>Sand Filter</td>
<td></td>
</tr>
<tr>
<td>Desalination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drinking water production</td>
<td>Coagulation &amp;</td>
<td>PVDF hollow fiber</td>
</tr>
<tr>
<td>Conventional</td>
<td>Sedimentation</td>
<td>MF(UF) membrane</td>
</tr>
<tr>
<td>New</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desalination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seawater</td>
<td>Activated Sludge</td>
<td></td>
</tr>
<tr>
<td>Desalination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wastewater treatment</td>
<td>Sedimentation</td>
<td>PVDF MF/UF flat</td>
</tr>
<tr>
<td>Conventional</td>
<td></td>
<td>sheet membrane</td>
</tr>
<tr>
<td>New</td>
<td></td>
<td>for MBR</td>
</tr>
<tr>
<td>Wastewater treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drinking water</td>
<td></td>
<td>Low-fouling RO</td>
</tr>
<tr>
<td>Wastewater treatment</td>
<td></td>
<td>membrane</td>
</tr>
<tr>
<td>New</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Water treatment processes**:
- **Multi Stage Flush (MSF)**
- **Single Stage SWRO**
- **Brine conversion Two-stage SWRO**
- **Coagulation & Sedimentation**
- **MF/UF membrane**
- **Activated Sludge**
- **MF/UF Membrane Bio-Reactor (MBR)**
- **Low-fouling RO**

**Technical target**:
- Low cost (=High recovery)
- High quality (Low boron conc.)
- Security conservation Removal of cryptosporidium
- High quality for reuse and reclamation

**Toray’s products**:
- RO membrane with high boron removal
- NF membrane for scaling inhibition
- RO membrane for brine conversion system
- PAN hollow fiber UF membrane
- PVDF hollow fiber MF(UF) membrane
- PVDF MF/UF flat sheet membrane for MBR
- 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 TM*
   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

- **Feed Water**
- **Filtrate**

**Structure of RO Membrane Element**

- **Separation Membrane**
  - Crosslinked Aromatic Polyamide
  - 0.2 micrometer

- **Support Membrane**
  - Polysulfone
  - 45 micrometer

**Structure of Composite Membrane**

- Polyester Taffta
  - Substrate
  - 150 micrometer
Application of RO Membranes

1. Industrial
- Ultra Pure Water
- Industrial Process Water
- Pure Water for Boilers
- Recovery of Valuables
- Food Industry Process Water

2. Drinking Water
- Sea Water Desalination
- Brackish Water Desalination

3. Wastewater
- Reuse & Reclamation

Industry Agriculture
Indirect Drinking Water
Water Production Cost

- Sea Water Desalination (MSF)
- Sea Water Desalination (RO)
- Wastewater Reuse (MF + RO)
- Ground water
- Surface Water Treatment (MF)

Water resource can be chosen by country.
## Progress of RO Seawater Desalination Plants

<table>
<thead>
<tr>
<th></th>
<th>1980’s</th>
<th>1990’s</th>
<th>2000’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery</td>
<td>%</td>
<td>25</td>
<td>40 - 50</td>
</tr>
<tr>
<td>Operational Pressure</td>
<td>psig (MPa)</td>
<td>1,000 (6.9)</td>
<td>1,200 (8.25)</td>
</tr>
<tr>
<td>Product Water Quality (TDS)</td>
<td>mg/l</td>
<td>500</td>
<td>300</td>
</tr>
<tr>
<td>Energy Consumption</td>
<td>kWh/kgal (kWh/m³)</td>
<td>45 (12)</td>
<td>21 (5.5)</td>
</tr>
</tbody>
</table>


Progress of membrane technology realized good quality and energy saving.
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

<table>
<thead>
<tr>
<th>Operating Pressure [MPa]</th>
<th>Super low</th>
<th>Ultra low</th>
<th>Low</th>
<th>High</th>
<th>Ultra high</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td></td>
<td></td>
<td>1.0</td>
<td>2.0</td>
<td>5.5</td>
<td>10.0</td>
</tr>
</tbody>
</table>

### SWRO

- **1st stg.**
  - Low pressure
  - N Co., H Co.
- **2nd stg.**
  - N Co., D Co.

### BW RO

- **Reverse osmosis**
  - Lower pressure
  - N Co., H Co.

### Ultra pure water

- High TOC removal
- High quality
- Cost reduction
- Low-fouling

### Waste water reuse

- Low-fouling
- Cost reduction

### Drinking water

- Toxic mat. removal
- Cost reduction

### Nanofiltration

- Scale removal
- 20

*in R & D by Toray*

D Co. : Dow  
N Co. : Nitto Denko  
H Co.: Hydranautics
Progress of RO Membrane Performance

- Changing of Material and/or Morphology of Membrane
- Controlling of Interfacial Polycondensation Reaction, and use of Catalyst

I. UTC-70 (1987)
II. UTC-70L (1988)
III. UTC-70U (1996)
IV. UTC-70UL (1999)

Crosslinked Aromatic PA Composite Membrane

Crosslinked PA Composite Membrane (1980's)

CA Asymmetric Membrane (1970's)

NaCl Rejection (%)

0.90 0.95 0.99 0.995 0.998

Flux (m³/m² day MPa)

0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2

Operating Pressure (MPa/(m³/m² day))

0.5 0.7 1.0 1.5 2.0 3.0 5.0

Medium Low Pressure Ultra Low Super Ultra Low

World’s No. 1 Membrane Performance
Conventional One-Stage RO Sea Water Desalination System

- Pretreatment
  - FeCl₃
  - Chlorine
  - H₂SO₄
  - NaHSO₃

- RO Element
  - Pressure ≤ 7MPa
  - High Pressure Pump
  - Motor
  - Energy Recovery Turbine

- Product Water
  - Chlorine
  - Brine
  - Water Feed Tank
  - Sea Water Tank

*) Spiral element
Okinawa Sea Water Desalination Plant

(Capacity: 40,000 m³/d, 1996)

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

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

Toray module is used in Japan’s largest plant.
Largest Sea Water Desalination Plants in the World

<table>
<thead>
<tr>
<th>No.</th>
<th>Country</th>
<th>Plant Site</th>
<th>Capacity (m³/d)</th>
<th>Number of Units</th>
<th>Contract (year)</th>
<th>Operation (year)</th>
<th>Plant Manufacturer</th>
<th>Membrane Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Trinidad</td>
<td>Trinidad</td>
<td>136,000</td>
<td>8</td>
<td>99</td>
<td>2002</td>
<td>Ionics</td>
<td>Toray</td>
</tr>
<tr>
<td>2</td>
<td>Saudi Arabia</td>
<td>Yanbu RO2</td>
<td>128,000</td>
<td>15</td>
<td>92</td>
<td>98</td>
<td>MHI</td>
<td>Toyobo</td>
</tr>
<tr>
<td>3</td>
<td>Saudi Arabia</td>
<td>Al Jubail III</td>
<td>91,000</td>
<td>15</td>
<td>93</td>
<td>2000</td>
<td>Preussag</td>
<td>DuPont, Toray</td>
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<tr>
<td>4</td>
<td>Saudi Arabia</td>
<td>Jeddah RO1</td>
<td>56,800</td>
<td>10</td>
<td>86</td>
<td>89</td>
<td>MHI</td>
<td>Toyobo</td>
</tr>
<tr>
<td>4</td>
<td>Saudi Arabia</td>
<td>Jeddah RO2</td>
<td>56,800</td>
<td>10</td>
<td>91</td>
<td>94</td>
<td>MHI</td>
<td>Toyobo</td>
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<tr>
<td>6</td>
<td>Spain</td>
<td>Marbella</td>
<td>56,400</td>
<td>10</td>
<td>97</td>
<td>99</td>
<td>Inima</td>
<td>DuPont</td>
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<tr>
<td>7</td>
<td>Malta</td>
<td>Penbroke</td>
<td>54,000</td>
<td>10</td>
<td>-</td>
<td>94</td>
<td>Polymetric</td>
<td>DuPont</td>
</tr>
<tr>
<td>8</td>
<td>Bahrain</td>
<td>Al Dur</td>
<td>45,000</td>
<td>8</td>
<td>84</td>
<td>89</td>
<td>Weirwest garthge</td>
<td>DuPont</td>
</tr>
<tr>
<td>9</td>
<td>Spain</td>
<td>Bl Mallorca</td>
<td>42,000</td>
<td>6</td>
<td>96</td>
<td>98</td>
<td>Degremont</td>
<td>DuPont, Toray</td>
</tr>
<tr>
<td>10</td>
<td>Japan</td>
<td>Okinawa</td>
<td>40,000</td>
<td>8</td>
<td>94 - 95</td>
<td>96 - 97</td>
<td>Kurita, etc.</td>
<td>Toray, Nitto</td>
</tr>
</tbody>
</table>

* DuPont withdrew from RO business in 2001

RO sea water desalination seems very difficult in the Arabian 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

Conventional System

Seawater (100)

C=3.5% SW

Pretreatment

High Pressure Pump

6.5MPa

RO Element

1st Stage

Product Water (40)

Total Product Water (40+20)

Water Recovery 60%

Brine Water (60)

C=5.8% SW

Booster Pump

6.5 --- 9.0MPa

RO Element

2nd Stage

Product Water (20)

Brine Water (40)

C=8.8% SW

( ): Water Flow Ratio

Toray’s Patent:
Performance Trends of RO Membranes for Seawater Desalination

Toray’s membrane performance for sea water desalination is world’s No.1.
Global Installations of Toray Sea Water Desalination:

- **KAE Curacao** (Netherlands, Antilles): 11,400 (m$^3$/d)
- **Mas Palomas** (Spain, Canary Island):
  - No. 1 Plant: 4,500 (m$^3$/d)
  - No. 2, 3 Plant: 9,000 (m$^3$/d)
- **Tortola** (British, Virgin Islands): 690 (m$^3$/d)
- **Trinidad and Tobago**: 136,000 (m$^3$/d)
- **Okinawa** (Japan): 40,000 (m$^3$/d)
- **Al Jubail** (Saudi Arabia): 91,000 (m$^3$/d)
Results of Membrane Biofouling (MBP) Assay

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

Fouling: Deterioration of membrane performance caused by stains

Toray less-fouling RO membrane has extremely low bacteria attachment.
## Wastewater Reclamation & Reuse Plants

**Image:** Flowchart showing wastewater reclamation and reuse processes.

<table>
<thead>
<tr>
<th>Plant (Country)</th>
<th>Capacity (m³/d)</th>
<th>Installation</th>
<th>MF/UF Supplier</th>
<th>RO Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seleta (Singapore)</td>
<td>24,000</td>
<td>2003</td>
<td>Hyflux</td>
<td>Toray</td>
</tr>
<tr>
<td>Sulaibiya (Kuwait)</td>
<td>310,000</td>
<td>2004</td>
<td>Norit</td>
<td>Toray</td>
</tr>
<tr>
<td>Orange County (USA)</td>
<td>220,000</td>
<td>2004</td>
<td>US Filter</td>
<td>Piloting</td>
</tr>
<tr>
<td>Ulpandan (Singapore)</td>
<td>140,000</td>
<td>2004</td>
<td>Piloting</td>
<td>Piloting</td>
</tr>
<tr>
<td>Bedok (Singapore)</td>
<td>32,000</td>
<td>2003</td>
<td>Zenon</td>
<td>Hydranautics</td>
</tr>
<tr>
<td>Bedok (Singapore)</td>
<td>10,000</td>
<td>2000</td>
<td>US Filter</td>
<td>Hydranautics</td>
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<tr>
<td>Luggage Point (Australia)</td>
<td>14,000</td>
<td>2000</td>
<td>Pall</td>
<td>Dow</td>
</tr>
<tr>
<td>Jewel (Singapore)</td>
<td>30,000</td>
<td>2000</td>
<td>Pall</td>
<td>Dow</td>
</tr>
<tr>
<td>Kranji (Singapore)</td>
<td>40,000</td>
<td>2003</td>
<td>US Filter</td>
<td>Hydranautics</td>
</tr>
</tbody>
</table>


**Note:** Toray less-fouling RO was selected at the world’s largest RO plant.
Cumulative Installations of Toray ROs by Application

Global Demand Extension

Ultra pure water production
Brackish water desalination
→ Sea water desalination
→ Wastewater reuse & reclamation

Cumulative Installation (m$^3$/d)

Year

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

(thousand m$^3$/d)
Toray Group’s Business Bases and Global Operations

Three Main Production Base

Flat Sheet Membrane Production

Ropur

Toray

TMA

Flat Sheet Membrane Production

Element Production
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 -
Total Water Production: 4.9 million m³/d
Market for Hollow-fiber Membranes for Drinking Water Production

Total Drinking Water Production (x10^4 m^3/d)
US: 2900
Japan: 6900

Enhancement of Pathogen Regulations caused market expansion.

Cryptosporidium parvum (4 ~ 8 micrometer)

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
Membrane Filtration Plants for Drinking Water in Japan

Application of UF/MF membranes is expanding in Japan. Cumulative installations are 200,000 (m$^3$/d) as of June 2003.

<table>
<thead>
<tr>
<th>Capacity (m$^3$/d)</th>
<th>Location</th>
<th>Engineering</th>
<th>Membrane Supplier</th>
<th>Installation (Year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,000</td>
<td>Saitama, Ogose</td>
<td>Kurita</td>
<td>Kuraray (UF)</td>
<td>1998</td>
</tr>
<tr>
<td>6,200</td>
<td>Hokkaido, Nishisorachi</td>
<td>Orugano</td>
<td>Daiseru (UF)</td>
<td>1999</td>
</tr>
<tr>
<td>2,400</td>
<td>Ooita, Notsu</td>
<td>Hitachi</td>
<td>Toray (UF)</td>
<td>1999</td>
</tr>
<tr>
<td>10,000</td>
<td>Tochigi, Imaichi</td>
<td>Orugano</td>
<td>Daiseru (UF)</td>
<td>2000</td>
</tr>
<tr>
<td>1,900</td>
<td>Fukui, Miyazaki</td>
<td>Suido Kiko</td>
<td>Asahi Kasei (UF)</td>
<td>2000</td>
</tr>
<tr>
<td>1,600</td>
<td>Fukushima, Aizuwakamatsu</td>
<td>Orugano</td>
<td>Daiseru (UF)</td>
<td>2000</td>
</tr>
<tr>
<td>6,000</td>
<td>Miyagi, Onagawa</td>
<td>NKK</td>
<td>Memcore (MF)</td>
<td>2001</td>
</tr>
<tr>
<td>5,000</td>
<td>Mie, Kiho</td>
<td>Ebara</td>
<td>Mitsubishi (MF)</td>
<td>2001</td>
</tr>
<tr>
<td>1,900</td>
<td>Fukui, Eiheiji</td>
<td>Maezawa</td>
<td>Toray (UF)</td>
<td>2001</td>
</tr>
<tr>
<td>4,500</td>
<td>Gifu, Ena</td>
<td>Suido Kiko</td>
<td>Asahi Kasei (UF)</td>
<td>2001</td>
</tr>
<tr>
<td>1,900</td>
<td>Gunma, Showa</td>
<td>Suido Kiko</td>
<td>Asahi Kasei (UF)</td>
<td>2001</td>
</tr>
<tr>
<td>5,000</td>
<td></td>
<td>Suido Kiko</td>
<td>Toray (MF)</td>
<td>2002</td>
</tr>
<tr>
<td>8,000</td>
<td></td>
<td>Suido Kiko</td>
<td>Toray (MF)</td>
<td>2003</td>
</tr>
</tbody>
</table>
PAN-based Hollow Fiber UF Membrane

Cross section

Pore size: 0.01 micrometer

Outer surface
Casing Type Module

Membrane area: 12 m²
Water production: 10 m³/d

Drinking water production plant
Tank Type Module

<table>
<thead>
<tr>
<th>Flux (m³/d)</th>
<th>70</th>
<th>200</th>
<th>500</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane area (m²)</td>
<td>84</td>
<td>228</td>
<td>576</td>
<td>960</td>
</tr>
<tr>
<td>Diameter (D) (cm)</td>
<td>45</td>
<td>75</td>
<td>120</td>
<td>150</td>
</tr>
<tr>
<td>Height (H) (cm)</td>
<td>200</td>
<td>230</td>
<td>250</td>
<td>250</td>
</tr>
</tbody>
</table>

Merit
- Low Initial Cost
- Small Footprint
- Easy Maintenance
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

High Permeability & High Physical Strength
# Toray PVDF Hollow Fiber Membrane

<table>
<thead>
<tr>
<th>Spinning Method</th>
<th>Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Extraction</strong></td>
<td>High Strength</td>
</tr>
<tr>
<td>Melt spinning with pore</td>
<td>High Cost</td>
</tr>
<tr>
<td>formation agent and extraction</td>
<td></td>
</tr>
<tr>
<td><strong>Drawing</strong></td>
<td>High Strength</td>
</tr>
<tr>
<td>Melt spinning and drawing</td>
<td>Low Cost</td>
</tr>
<tr>
<td><strong>Non-solvent Induced</strong></td>
<td>UF/MF Applicable</td>
</tr>
<tr>
<td>Phase Separation</td>
<td>Low Cost</td>
</tr>
<tr>
<td>Polymer solution is</td>
<td>Permeability and</td>
</tr>
<tr>
<td>coagulated by non-solvent</td>
<td>High-strength</td>
</tr>
<tr>
<td><strong>Thermally Induced</strong></td>
<td>High Strength</td>
</tr>
<tr>
<td>Phase Separation</td>
<td>High Flux</td>
</tr>
<tr>
<td>Polymer solution is</td>
<td>Low Cost</td>
</tr>
<tr>
<td>cooled down to phase separation temperature</td>
<td></td>
</tr>
</tbody>
</table>
Comparison of Hollow Fiber Membrane with Other Companies

<table>
<thead>
<tr>
<th>Supplier</th>
<th>U Company</th>
<th>Z Company</th>
<th>N Company</th>
<th>A Company</th>
<th>Toray</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>PP</td>
<td>PVDF</td>
<td>PVDF</td>
<td>PES</td>
<td>PVDF</td>
</tr>
<tr>
<td>Permeability* (m³ / m²-d)</td>
<td>4.8</td>
<td>-</td>
<td>1.5</td>
<td>3.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Membrane Area (m²)</td>
<td>30</td>
<td>-</td>
<td>56</td>
<td>35</td>
<td>50</td>
</tr>
</tbody>
</table>

* Pure Water, at 50 kPa

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

Toray’s hollow fiber membranes are World’s No.1 in permeability and the 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 H₂O₂ with FeSO₄)

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

Soaking period (h)

Strength after soak / Initial Strength

0 50 100 150 200 250

PVDF  PS  PE  PAN  CA
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.
PVDF MF Membrane 8” Module

Specifications

<table>
<thead>
<tr>
<th>Items</th>
<th>Toray 8B Module</th>
</tr>
</thead>
<tbody>
<tr>
<td>Module Size [mm]</td>
<td>216 (8B) dia. x 2,160L</td>
</tr>
<tr>
<td>Membrane Area [m2]</td>
<td>72</td>
</tr>
<tr>
<td>Flux (pure water) [m3/h/50kPa]</td>
<td>20</td>
</tr>
<tr>
<td>Temperature [deg.]</td>
<td>0 – 40</td>
</tr>
</tbody>
</table>
### HFM-2020 Standard Operational Conditions

<table>
<thead>
<tr>
<th>Feed Water Type</th>
<th>Pretreated Water Cleaning Ground Water</th>
<th>River &amp; Lake Surface Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtration Flux (m³/m²/d)</td>
<td>2 – 5</td>
<td>1 - 2</td>
</tr>
<tr>
<td>Backwash Condition</td>
<td>Flux: 1 - 2 times of filtration flux</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chlorine dosing: 1 - 10 ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time: 30 – 60 sec.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Frequency: every 0.3 – 2 h</td>
<td></td>
</tr>
<tr>
<td>Scrubbing Condition</td>
<td>Air flow: 4 – 10 Nm³/h/Module</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time: 30 – 120 sec.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Frequency: every 0.3 – 2 h</td>
<td></td>
</tr>
<tr>
<td>Operation Temp. (degrees C)</td>
<td>≤ 40</td>
<td></td>
</tr>
<tr>
<td>Operation pH</td>
<td>1 – 10</td>
<td></td>
</tr>
<tr>
<td>Chemical Cleaning</td>
<td>(1) CIP (Clean In Place): every 3 - 6 months</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2) Trans-Membrane pressure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3 - 5 times of initial, or 150 kPa)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) Chemicals: 1N-HCl + 3,000 ppm NaClO</td>
<td></td>
</tr>
</tbody>
</table>
Large Scale Ground Water Filtration Plant
(5,000 m³/d, for 20,000 people)

Compact and High Productivity
Profile

Established: 1936
Net Sales: 200 million dollars
Function: One of the largest water system and equipment companies in Japan

Alliance with Toray: Toray owns 20% of shares
- Joint water business venture
- Development of new systems and membrane products
- Sharing and exchange of technical and business information

Domestic position

Positioned in 15th place as a water treatment company, second, behind Ebara, in the drinking water production business, and first in membrane filtration systems (Orugano second, Ebara third)
Toray Collaboration with Suido Kiko

Suido Kiko’s Advantages
- Pioneer and first-ranking manufacturer in the drinking water systems business
- Experience in Government and Public Businesses

Toray’s Advantages
- Capable of meeting diverse demand with a wide range of products from MF to RD membranes
- Operating businesses in Japan, the U.S., and Europe

Development into an Overall Water Treatment System Business

Japan : Supplies Membranes to Suido Kiko
Korea/China : Jointly Launched Business -
Toray Supplies Membrane Technology,
Suido Kiko Offers Engineering Technology
# Water Treatment Related National Projects

<table>
<thead>
<tr>
<th>Year</th>
<th>Title</th>
<th>Toray’s R&amp;D Theme</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>Project Membrane Aqua Century 21 (MAC21)</td>
<td>[Search for New Technology Application of Membrane Filtration] - Development of efficient coagulation and sedimentation technology to be applied in the UF pretreatment - Development of operational stability during the NF advanced water purification process</td>
</tr>
<tr>
<td>1994</td>
<td>New Membrane Aqua Century 21 (MAC21)</td>
<td>- Highly efficient water purification system utilizing NF membranes (Toray Engineering Co.)</td>
</tr>
<tr>
<td>1995</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1996</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1997</td>
<td>Advanced Aqua Clean Technology for the 21st Century (ACT21)</td>
<td>Group 1: Development of large-capacity membrane filtration technology (Kawai,Yokohama/Shinishikawa,Okinawa) Group 2: Total water purification system (Ayase,Yokohama/Otogane,Fukuoka) Group 3: Observation technology at the drinking water supply source</td>
</tr>
<tr>
<td>1998</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>Environmental, Ecological, Energy Saving and Economical Water Purification System (e-Water)</td>
<td></td>
</tr>
<tr>
<td>2001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## 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

<table>
<thead>
<tr>
<th>Water Purification Plant</th>
<th>Feed Water</th>
<th>Subject</th>
<th>Participants/ Toray’s Expected Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kawai, Yokohama</td>
<td>Fresh Water</td>
<td>- Comparative Experiments of 6 Groups, including Ebara</td>
<td>- Toray/Suido Kiko Joint Team&lt;br&gt;- Toray; Experiment Supervisor, Basic Design, Manufacture of&lt;br&gt;Experimental Facility, Follow-up of Operations</td>
</tr>
<tr>
<td>June/03 - Mar/05</td>
<td></td>
<td>- Case Trial - 200,000 m³/d</td>
<td></td>
</tr>
<tr>
<td>Ayase, Yokohama</td>
<td>Fresh Water</td>
<td>- Examination of Appropriate Operating Conditions</td>
<td>- Co-R&amp;D of 38 Companies&lt;br&gt;- Toray; Basic Design, Supply of PVDF Modules</td>
</tr>
<tr>
<td>Aug/03 - Mar/05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Otogane, Fukuoka</td>
<td>Fresh Water</td>
<td>- Comparative Experiments of 5 Groups including Maezawa and Shinko Pantec</td>
<td>- Suido Kiko as the Supervisor&lt;br&gt;- Toray; Supplies PVDF Modules, Supports System Examination</td>
</tr>
<tr>
<td>Sept/03 - Mar/05</td>
<td></td>
<td>- Case Trial - 110,000 m³/d</td>
<td></td>
</tr>
<tr>
<td>Ishikikawa, Okinawa</td>
<td>Fresh Water</td>
<td>- MF Pretreatment+NF Membrane (to confront Ozone + Activated Carbon Method)</td>
<td>- Nishihara; Supervisor, Joint Team of Suido Kiko, Ebara, Kubota, and Toray&lt;br&gt;- Toray; Basic Design and Supply of PVDF and NF Modules</td>
</tr>
<tr>
<td>Oct/03 - Mar/05</td>
<td></td>
<td>- Only Successful Group to actually demonstrate use of membranes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Case Trial - 50,000 m³/d</td>
<td></td>
</tr>
</tbody>
</table>
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
Features good water quality, small footprint, reduced excess sludge, and the market is yet undeveloped.
Filtration Mechanism and Required Characteristics

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Feed Water (Activated Sludge)</th>
<th>Aeration</th>
<th>Element</th>
<th>Sludge</th>
<th>Effluent</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Feed Water (Activated Sludge)</th>
<th>Aeration</th>
<th>Element</th>
<th>Sludge</th>
<th>Effluent</th>
</tr>
</thead>
</table>

**Stability**
- Chemical Stability: Chlorine, acid, oxidation agent, alkaline

**Permeability**
- Initial Permeability: High permeability
- Durability: Prevention for clogging

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Feed Water (Activated Sludge)</th>
<th>Aeration</th>
<th>Element</th>
<th>Sludge</th>
<th>Effluent</th>
</tr>
</thead>
</table>

[Table with requirements and descriptions]

56
### Design Concept of Immersed Membrane

#### 1. Membrane Material

**Poly (Vinylidene Fluoride): PVDF**

- High stability for chemicals: fluorine polymer
- High physical strength: high molecular weight (MW=300,000 – 400,000)

#### 2. Membrane Form

- Fiber reinforced (non-woven) flat sheet membrane

#### 3. Surface Pore Diameter

1. **Small pore diameter**
2. **Narrow pore diameter distribution**
3. **Numerous pores**

- Good permeate quality
- Prevention of clogging
- High flux
Basic Characteristics of Immersed Membranes

FE-SEM photographs of Flat sheet membrane surface

Pore diameter distribution of surface (Estimated from SEM photos)

PVDF membrane Type B

Pore diameter (micron)

Number of pores ($10^{12}/m^2$)

Ideal membrane micro structure is achieved.
Toray’s modules feature high performance per footprint.
### Comparison of Module Performance

<table>
<thead>
<tr>
<th>Module Performance (m³/footprint)</th>
<th>Membrane Performance (m³/m²)</th>
<th>Membrane Area (m²)</th>
<th>= 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Compared to other modules)</td>
<td>(1.4)</td>
<td>(1.5)</td>
<td></td>
</tr>
</tbody>
</table>

**Operation (h)**

**Differential pressure = 2 kPa**

- Toray: 0.8 (m³/d)
- Other: 0.4 (m³/d)

**Toray module performance is twice as competent as others.**
Operational Technology

1. Roll of Operational Technology

1) To maintain efficiency and stability of the performance of modules and module elements
2) To achieve module performance targets at low cost
3) Required as software in case of selling modules and module elements

2. Alliance with SKG*

1) Joint pilot tests in Europe and Singapore
2) Joint businesses in Europe, Singapore, and China

* SKG (Seghers Keppel Technology Group):
More than 200 Activated Sludge System installations Worldwide
Pilot Test at Beverwijk WWTP (the Netherlands)

Consulting company DHV conducts tests of MBR suppliers and immersed membranes.

The Absolute Group in Europe’s Wastewater Treatment Business

Pilot test is showing good performance.
Conclusion
- Immersed Membranes for Wastewater Treatment

1. Performances such as good water quality, small footprint, and reduced surplus sludge are expected in MBR technology, and the market is still globally new.

2. Toray has developed highly stable, highly permeable and reduced clog types of PVDF flat sheet membrane modules.

3. Toray making progress in pilot tests in Europe, Singapore, and China, and aiming at entering the market at an early stage.
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