Focus on Membrane Technology for Water Treatment

Toray Industries, Inc. Dr. Masaru Kurihara

September 2003

CONTENT

1. World Water Problem

Water Treatment Membranes
 RO Membranes & NF Membranes

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

5. Immersed Membranes 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)

<Advanced Materials>

- Nanofibers
- High-performance Fibers

and Resins

<Core Technologies>

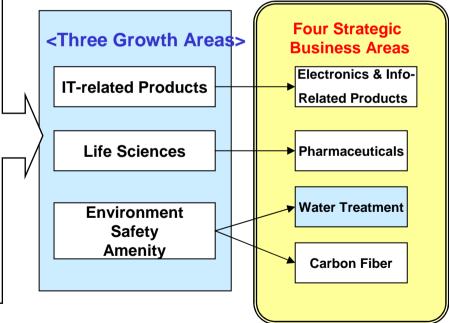
Organic Synthetic

Chemistry

Polymer Chemistry

Biochemistry

- Nano-alloy Materials
- Advanced Electronics Materials
- Biomaterials
- Separation Materials
- High-performance Composite Materials
- Recycling Materials



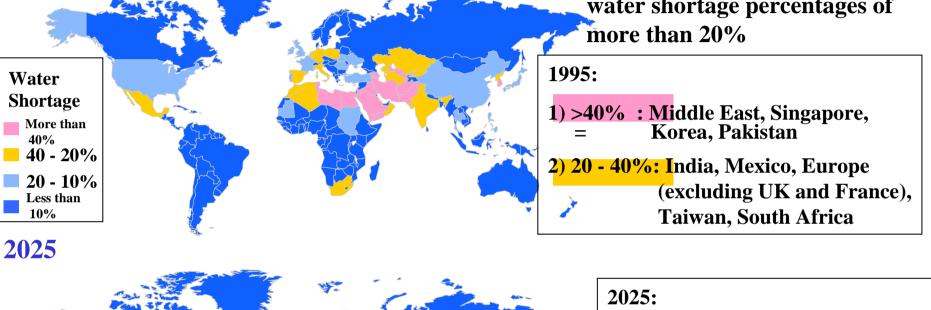
'TORAY'

World Water Shortage - Now and Future

1995

(WMO and others, 1996)

Main regions which have high water shortage percentages of



- 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, the U.S.A., and China by 2025

'TORAY' Water Problem and Membrane Technology

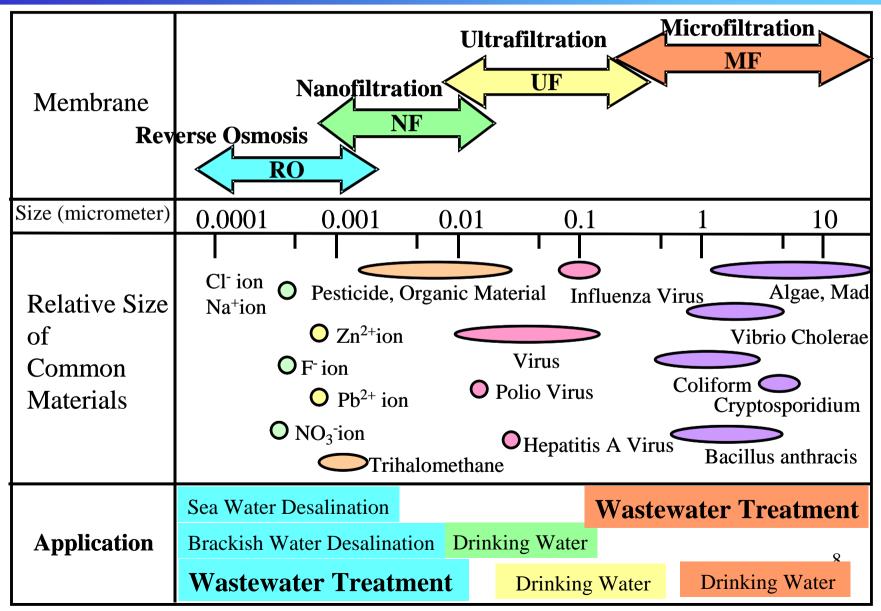
	Water Problem		Membrane Technology for Water Treatment			
Region, Country	Water Resource Shortage	Water Pollution	Fresh Water Treatment	Desalination	Wastewater Reuse & Reclamation	
United States	Problem	Problem	In operation	In operation	Construction	
Benelux		Problem	Being applied		In operation	
UK, 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 and wastewater.



Water Treatment Membranes

Membranes and Relative Size of Common Materials



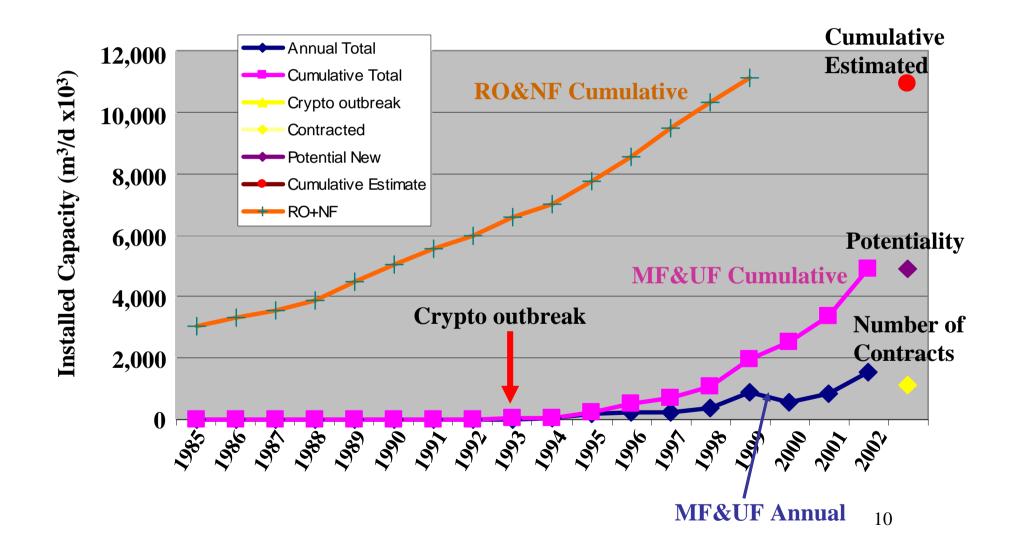


Separation Characteristics of Various Membranes

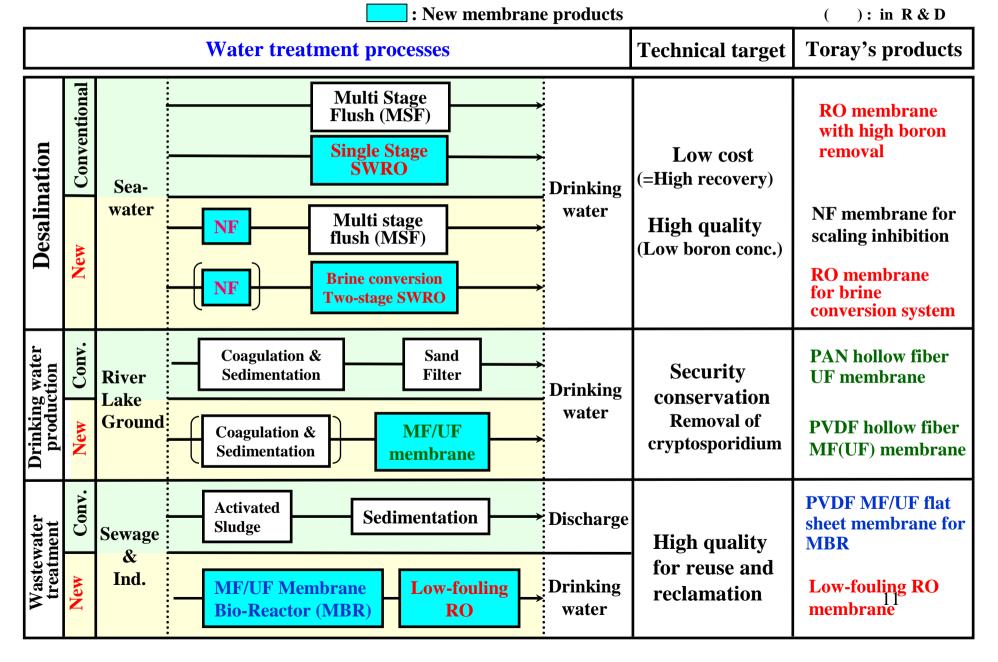
	RO/NF Membranes	UF/MF Membranes		
Permeation and Rejection	Low MW organic materials (Mw ≤ 200) Monovalent ions Water Water Membrane	Ions Dissolved Matter Water Water Membrane		
Separation Mechanism	RO:Molecular interactionImage: Constraint of the sector o	MF: Dynamic separation Size exclusion UF: Electric repulsion		
Pore Size	RO: <1 nm NF: 1~10 nm	UF: 10~100 nm MF: >100 nm 9		



Global Capacity of Membrane Filtration Plants



TORAY Membrane Applications - Conventional & New Technologies



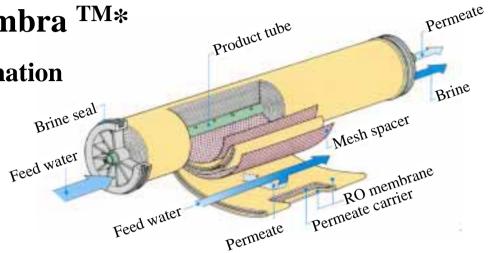
Toray's Membranes & Applications

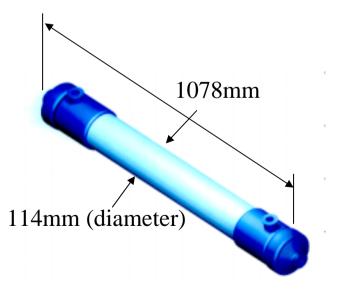
1. RO & NF Membrane Romembra TM*

- 1) Seawater & brackish water desalination
- 2) Ultra pure water production
- 3) Harmful material removal
- 4) Wastewater reuse



- 1) Industrial process water production
- 2) Drinking water production
- 3) Wastewater reuse

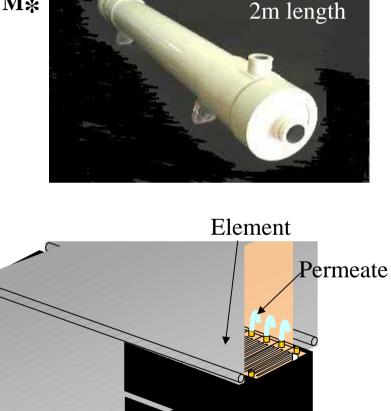




8 inches

Toray's Membranes & Applications

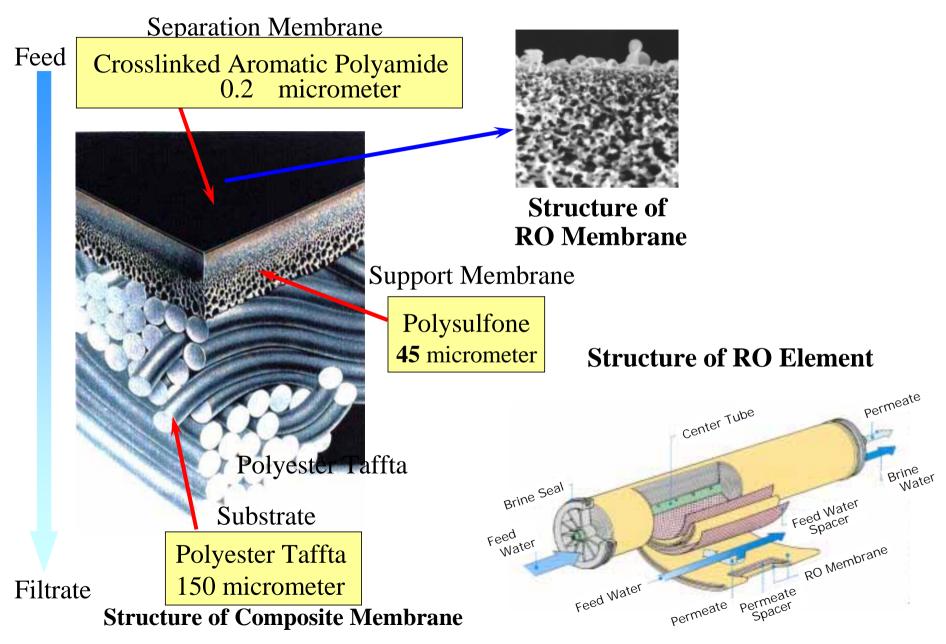
- **3. PVDF Hollow Fiber MF Membrane** Torayfil-F TM*
 - 1) Drinking water production
 - 2) Industrial process water production
 - 3) Pre-treatment for seawater desalination
 - 4) Wastewater reuse
- 4. PVDF Flat Sheet MF Membrane for MBR
 - 1) Municipal and industrial wastewater treatment
 - 2) Municipal and industrial wastewater reuse



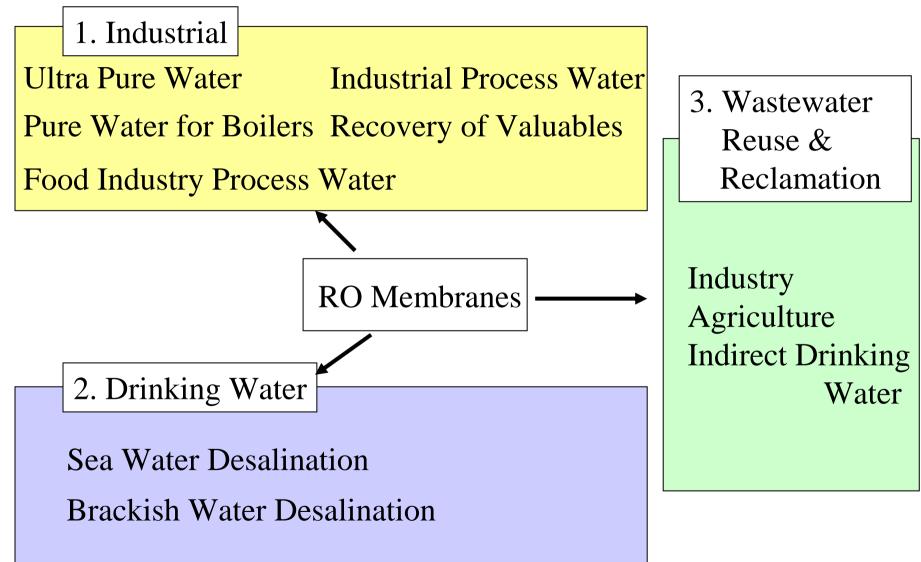


RO Membranes & NF Membranes

Structure of RO Membrane Element

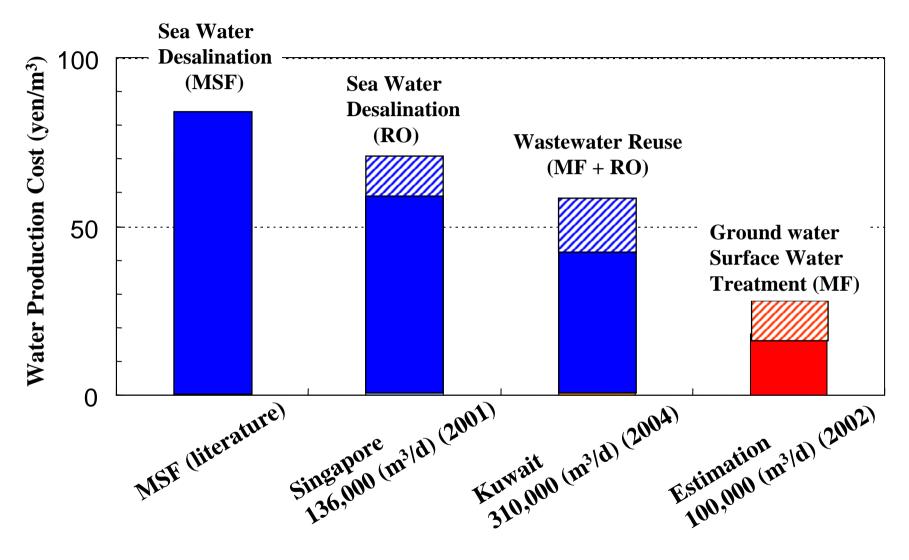


Application of RO Membranes





Water Production Cost



Water resource can be chosen by country.

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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 and energy saving.

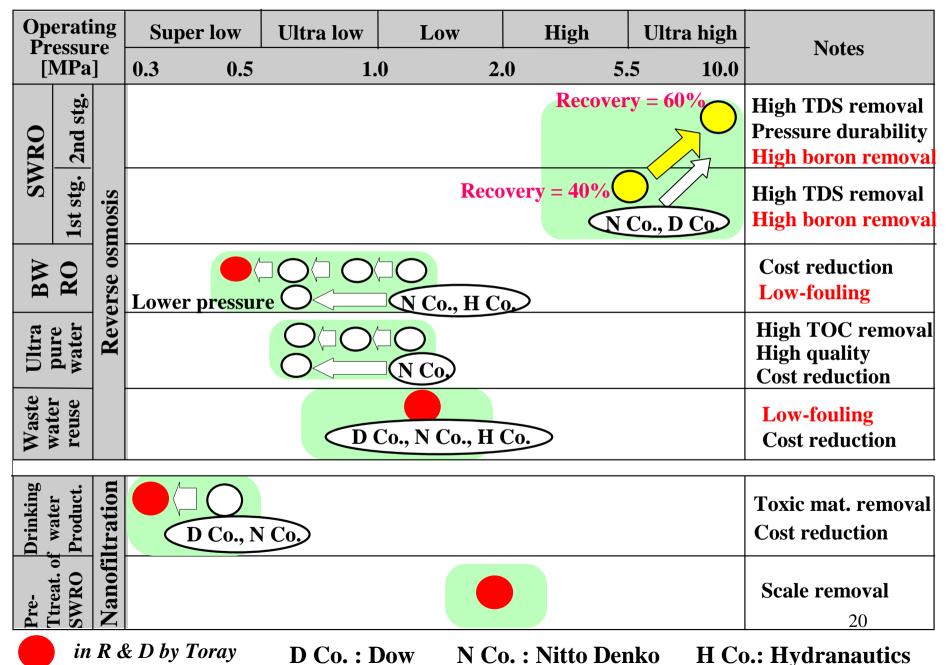
TORAY Sea Water Desalination RO Membranes in Global Market

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

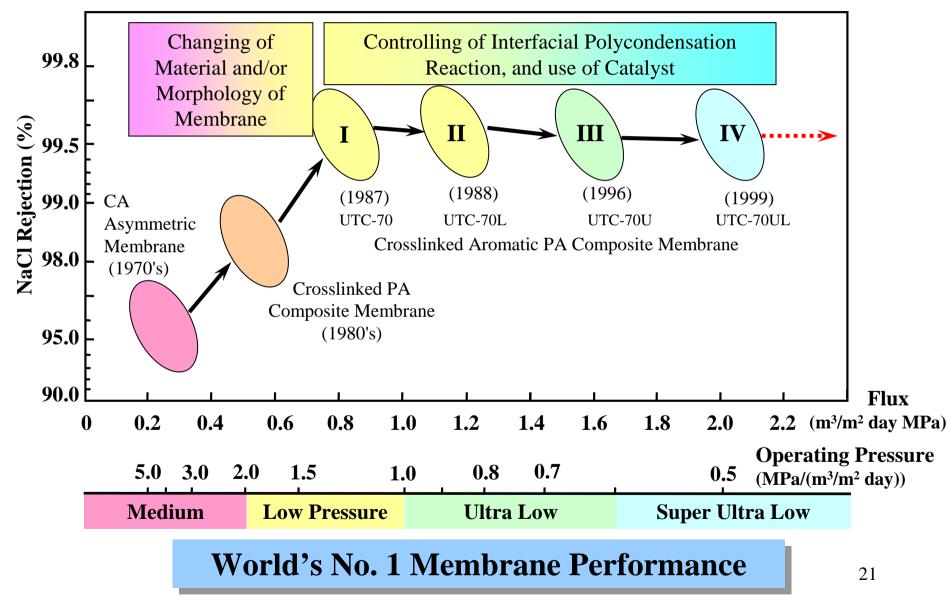
Crosslinked aromatic polyamide/spiral module is global standard. Toyobo is the only hollow fiber module supplier. DuPont withdrew from the hollow fiber RO module business in March 2001.

Technological Trends of RO/NF Membranes

TORAY

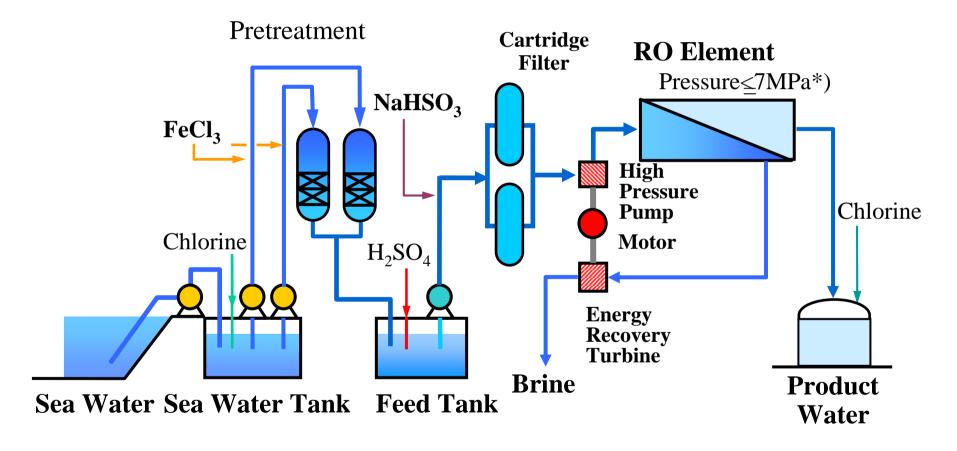


Progress of RO Membrane Performance





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.

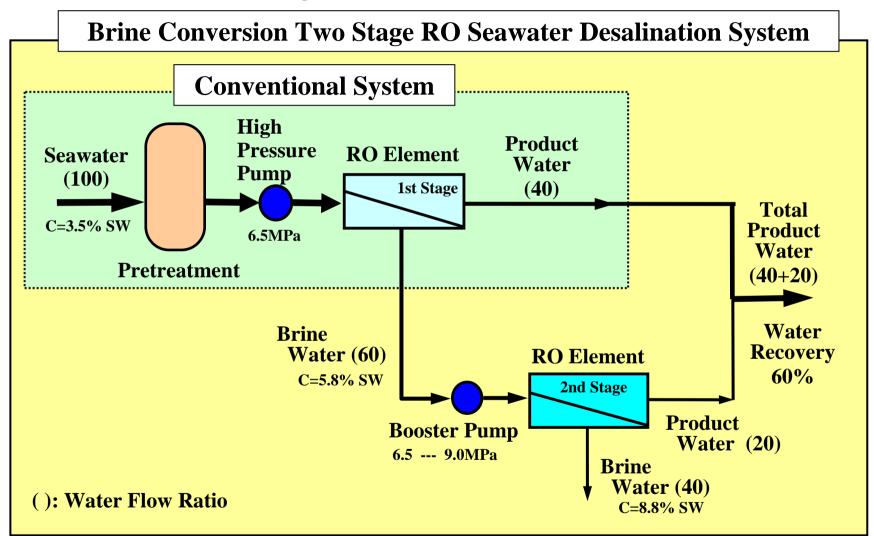
TORAY Largest Sea Water Desalination Plants in the World

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

* 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.

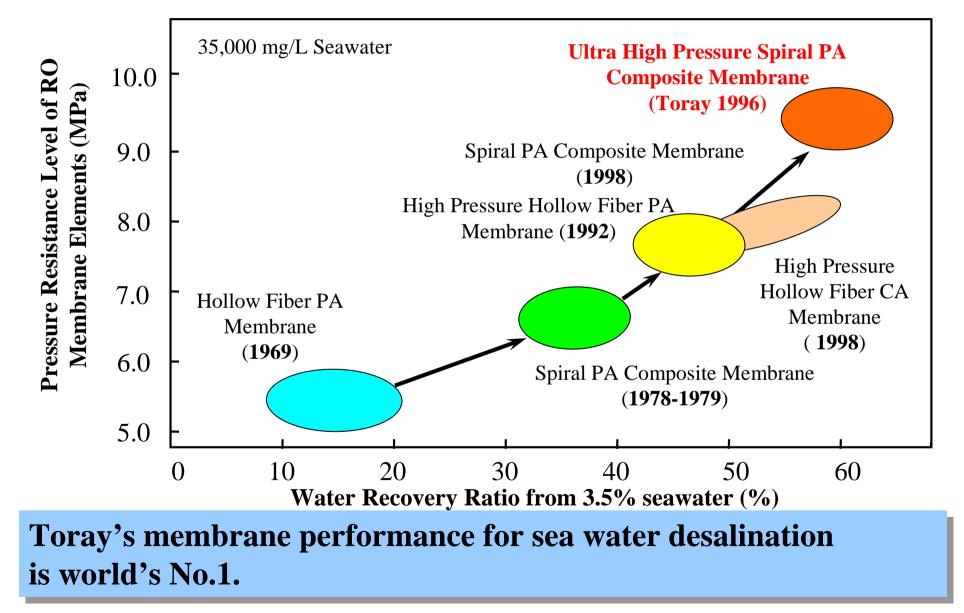
Typical Flow Diagram of Brine Conversion Two Stage RO'TORAY' Seawater Desalination System



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



'TORAY' 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) No. 2, 3 Plant 9,000 (m3/d)



Mas Palomas (Spain, Canary Islands)



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



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



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

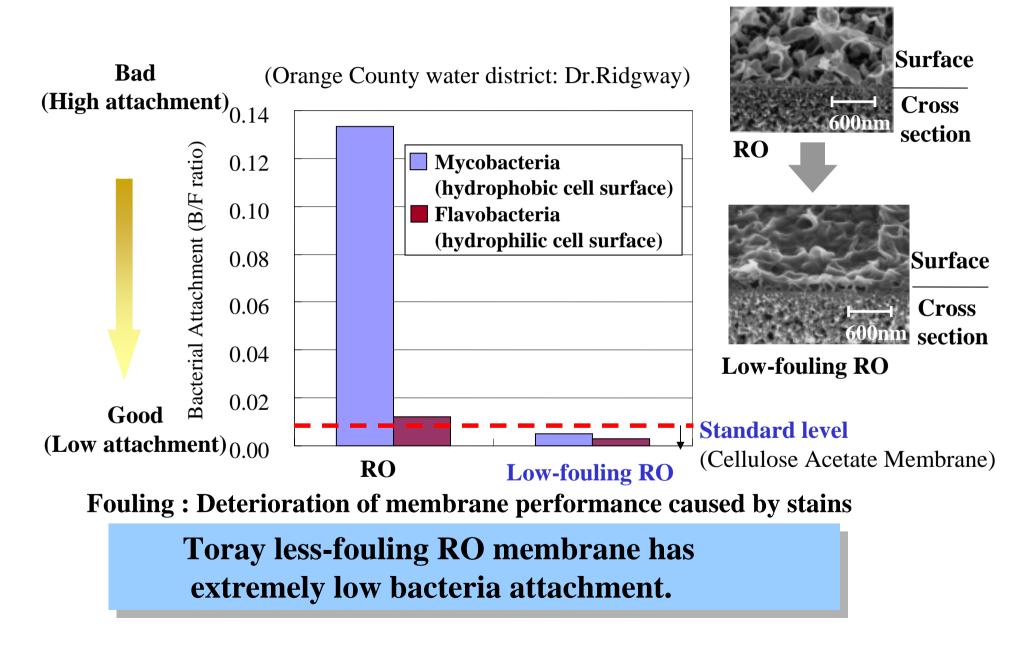
Trinidad and Tobago 136,000 (m3/d)

Al Jubail (Saudi Arabia) 91.000 (m3/d)





Results of Membrane Biofouling (MBP) Assay



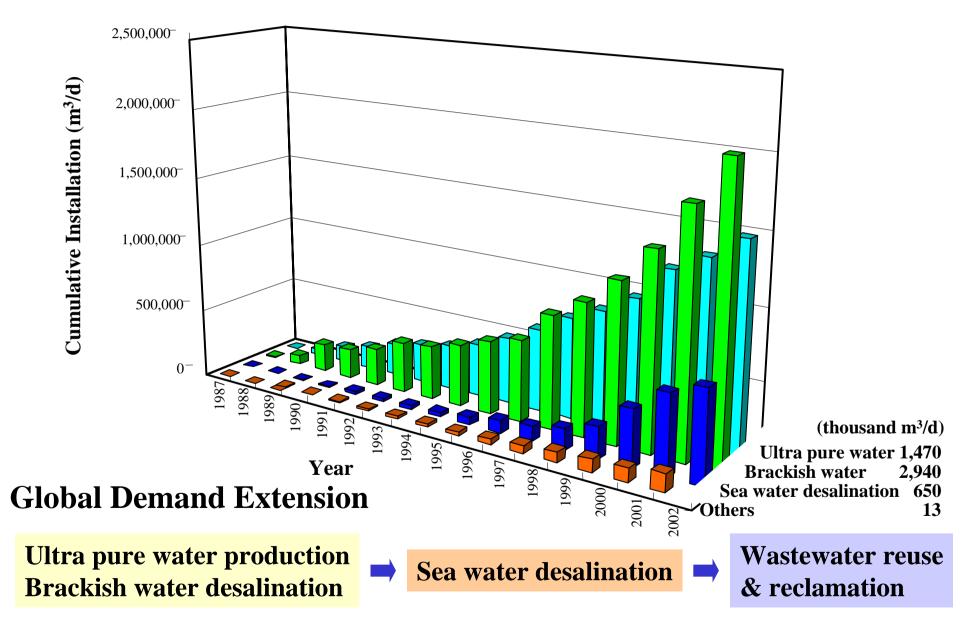


Wastewater Reclamation & Reuse Plants

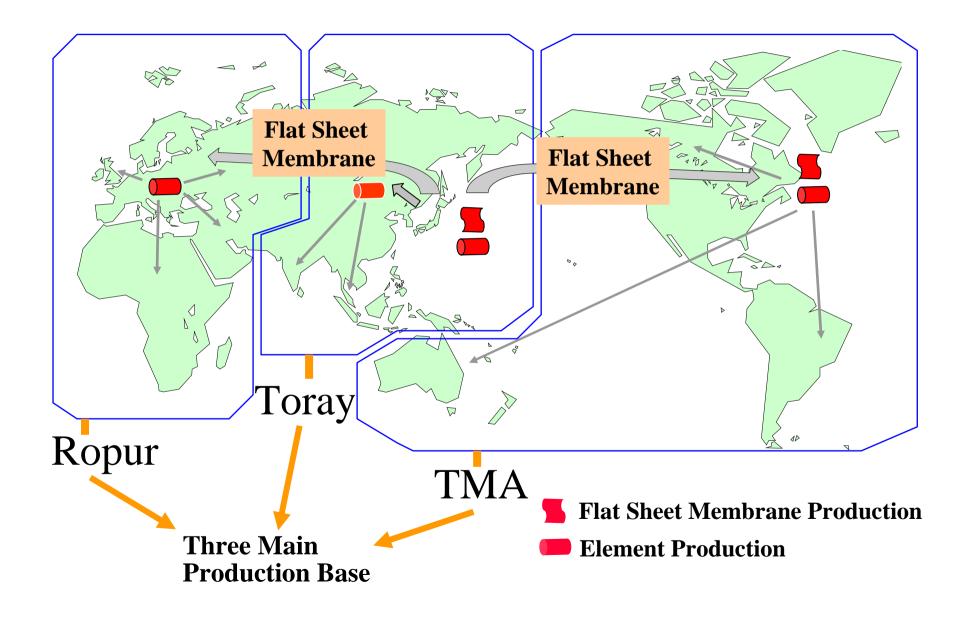
Wa	astewater	Γ		RO ↓	fections Reclamation Reuse
	Plant (Country)	Capacity	Installation	MF/UF	RO
		(m^{3}/d)		Supplier	Supplier
	Jewel (Singapore)	30,000	2000		Dow
	Luggage Point (Australia)	14,000	2000	Pall	Dow
	Bedok (Singapore)	10,000	2000	US Filter	Hydranautics
	Bedok (Singapore)	32,000	2003	Zenon	Hydranautics
	Kranji (Singapore)	40,000	2003	US Filter	Hydranautics
	Seleta (Singapore)	24,000	2003	Hyflux	Toray
	Sulaibiya (Kuwait)	310,000	2004	Norit	Toray
	Orange County (USA)	220,000	2004	US Filter	Piloting
	Ulpandan (Singapore)	140,000	2004	Piloting	Piloting

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

'TORAY' Cumulative Installations of Toray ROs by Application



'TORAY' Toray Group's Business Bases and Global Operations





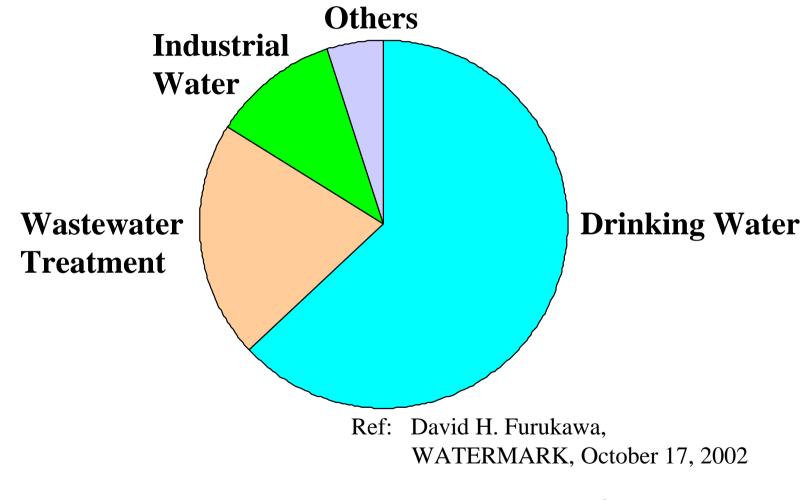
Conclusion – RO•NF Membranes

- 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.



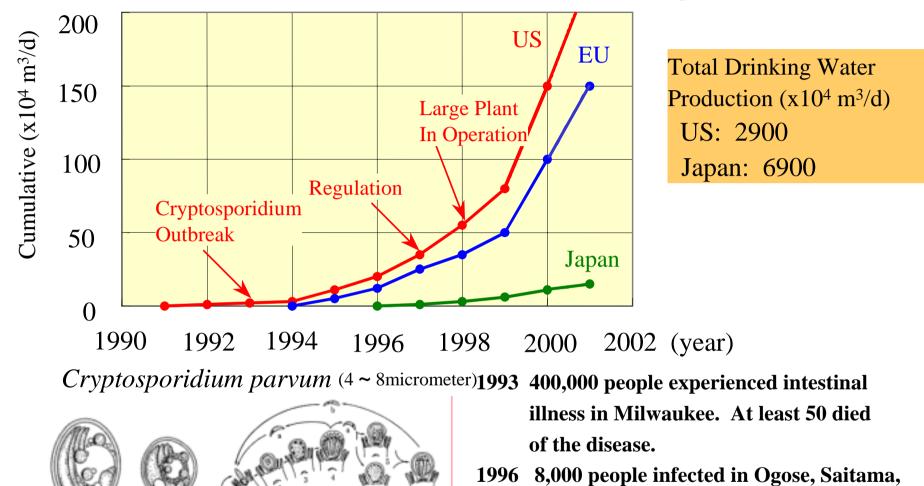
UF Membranes & MF Membranes - Drinking Water Production -

TORAY UF & MF Membranes – Breakdown of World Applications -



Total Water Production: 4.9 million m³/d

TORAY Market for Hollow-fiber Membranes for Drinking Water Production



Japan

1998 Enhanced regulations of surface water treatment

Enhancement of Pathogen Regulations caused market expansion.

IN HOST

OUTSIDE HOST

 $2 \alpha m$

'TORAY'

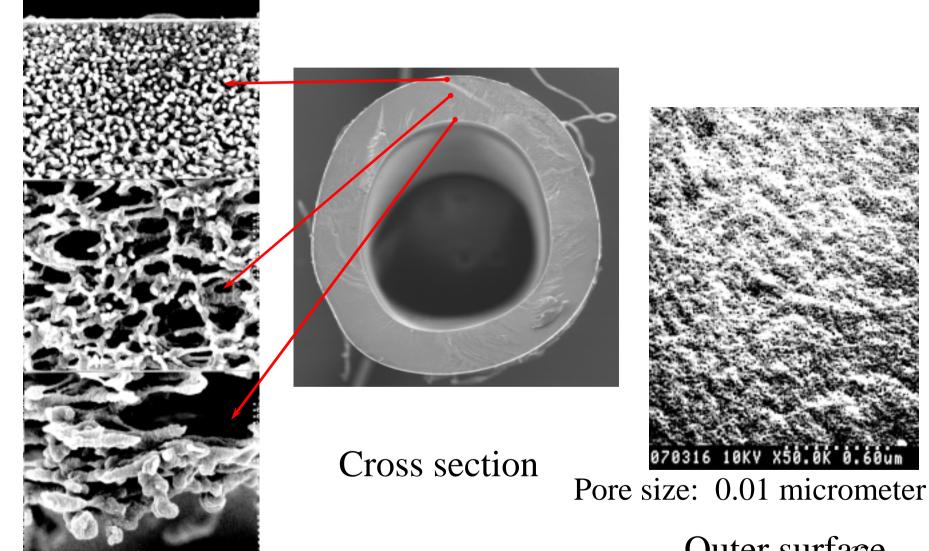
Membrane Filtration Plants for Drinking Water in Japan

Capacity	Location	Engineering	Membrane	Installation
(m³/d)			Supplier	(Year)
4,000	Saitama, Ogose	Kurita	Kuraray (UF)	1998
6,200	Hokkaido, Nishisorachi	Orugano	Daiseru (UF)	1999
2,400	Ooita, Notsu	Hitachi	Toray (UF)	1999
10,000	Tochigi, Imaichi	Orugano	Daiseru (UF)	2000
1,900	Fukui, Miyazaki	Suido Kiko	Asahi Kasei (UF)	2000
1,600	Fukushima, Aizuwakamatsu	Orugano	Daiseru (UF)	2000
6,000	Miyagi, Onagawa	NKK	Memcore (MF)	2001
5,000	Mie, Kiho	Ebara	Mitsubishi (MF)	2001
1,900	Fukui, Eiheiji	Maezawa	Toray (UF)	2001
4,500	Gifu, Ena	Suido Kiko	Asahi Kasei (UF)	2001
1,900	Gunma, Showa	Suido Kiko	Asahi Kasei (UF)	2001
5,000		Suido Kiko	Toray (MF)	2002
8,000		Suido Kiko	Toray (MF)	2003

Application of UF/MF membranes is expanding in Japan. Cumulative installations are 200,000 (m³/d) as of June 2003.

'TORAY'

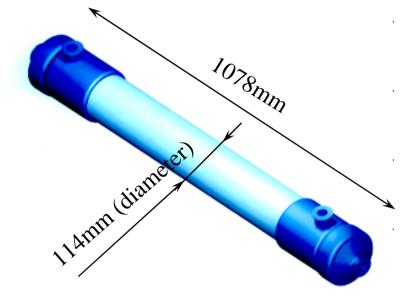
PAN-based Hollow Fiber UF Membrane

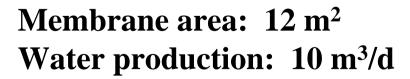


Outer surface



Casing Type Module



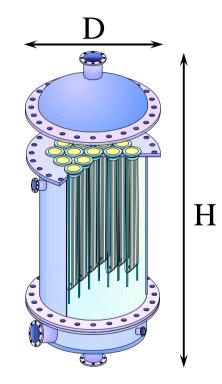




Drinking water production plant

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 ⁴⁰



Toray PVDF Hollow Fiber Membrane

	Spinning Method	Feature	Outer surface Lumen
Spinning	Extraction Melt spinning with pore formation agent and extraction	High Strength High Cost	
Melt Spin	Drawing Melt spinning and drawing	High Strength Low Cost	
Spinning	Non-solvent Induced Phase Separation Polymer solution is coagulated by non-solvent	UF/MF Applicable Low Cost Permeability and High-strength inconsistent	Water flow
Solution S	Thermally Induced Phase Separation Polymer solution is cooled down to phase separation temperature	High Strength High Flux Low Cost	41



Comparison of Hollow Fiber Membrane with Other Companies

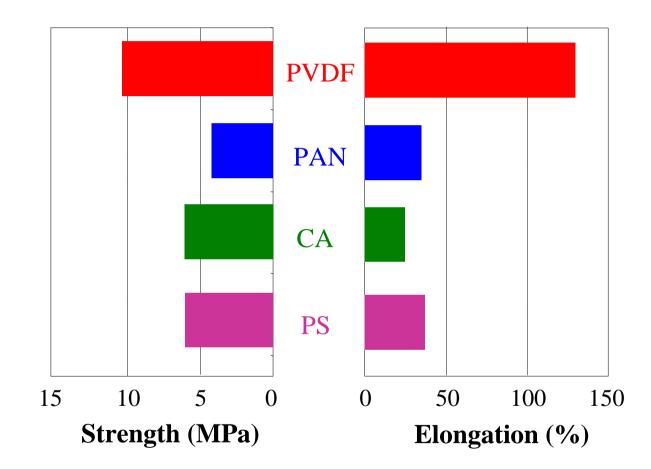
* Pure Water, at 50 kPa

Supplier	U Coi	mpany	Z Company	N Company	A Company	Toray
Material	PP	PVDF	PVDF	PES	PVDF	PVDF
Permeability* (m ³ / m ² -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)

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-

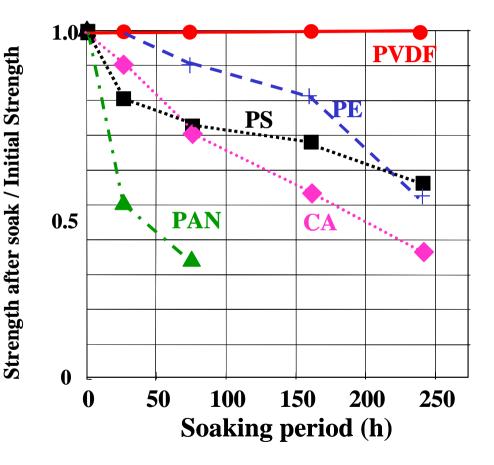
Purpose: Confirmation of stability against strong oxidation agent

Accelerated oxidation

- 1. Evaluation of membrane configuration
- 2. Evaluation under cleaning condition
- (5,000 ppm as 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

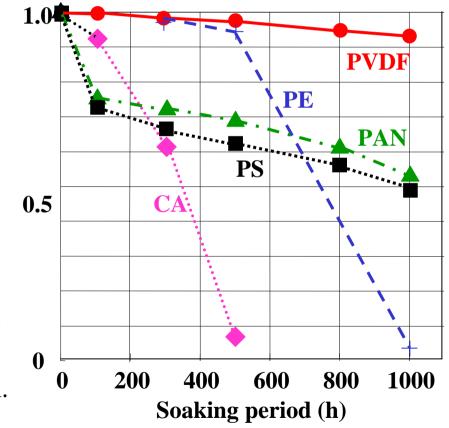
Purpose: Confirmation of stability against chlorine

Evaluation condition

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

Results

- Elongation after soak / Initial Elongation 1. PVDF MF membrane is very stable in a concentrated chlorine solution.
- 2. PVDF-MF membrane can be cleaned with a concentrated chlorine solution.



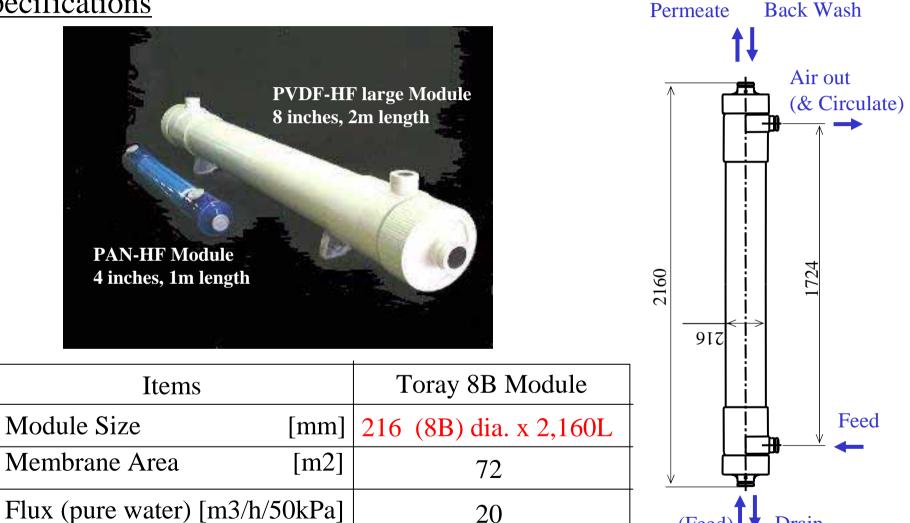
Comparison of Chlorine Resistance

PVDF MF Membrane 8" Module

[deg.]

Specifications

Temperature



20

0 - 40

(Feed)

&Air

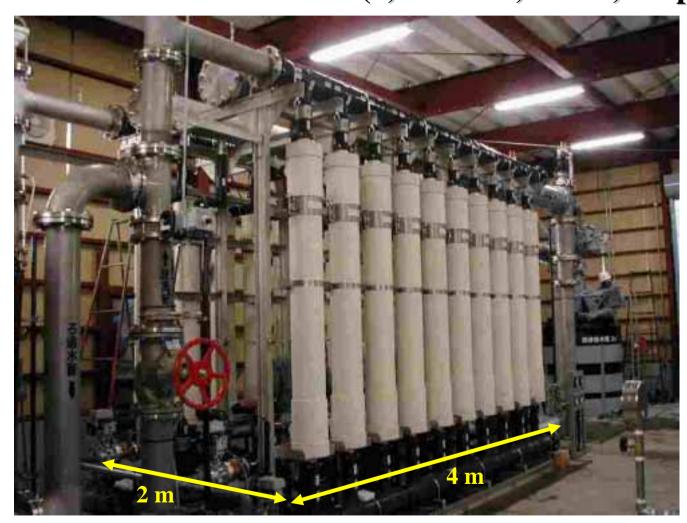
Drain

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HFM-2020 Standard Operational Conditions

Feed Water Type	Pretreated Water 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 Chlorine dosing: 1 - 10 ppm Time: 30 – 60 sec. Frequency: every 0.3 – 2 h	
Scrubbing Condition	Air flow: 4 – 10 Nm ³ /h/Module Time: 30 – 120 sec. Frequency: every 0.3 – 2 h	
Operation Temp. (degrees C)	≦ 40	
Operation pH	1 – 10	
Chemical Cleaning	Chemical Cleaning(1) CIP (Clean In Place): every 3 - 6 month (2) Trans-Membrane pressure (3 - 5 times of initial, or 150 H (3) Chemicals: 1N-HCl + 3,000 ppm NaCh	

Large Scale Ground Water Filtration Plant (5,000 m³/d, for 20,000 people)



Compact and High Productivity

Outline of Suido Kiko Kaisha, Ltd.

Profile

Established Net Sales Function

- : 1936
- : 200 million dollars
- : 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) 49



Toray Collaboration with Suido Kiko



- 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 Technology₅₀

Water Treatment Related National Projects

Year	Title	Toray's R&D Theme
1992	Project Membrane Aqua Century 21	
1993	(MAC21)	
1994	New Membrane Aqua Century 21	- Highly efficient water purification system
1995	(MAC21)	utilizing NF membranes (Toray Engineering Co.)
1996		
1997	Advanced Aqua Clean Technology for the 21 st	[Search for New Technology Application of Membrane Filtration] - Development of efficient coagulation and sedimentation technology to
1998	Century (ACT21)	be applied in the UF pretreatment
1999		-Development of operational stability during the NF advanced water purification process
2000		[Development of Advanced Water Purification System of River Water] - Technological examination of combination of conventional water
2001		purification systems and membrane filtration
2002	Environmental, Ecological, Energy Saving and	Group 1: Development of large-capacity membrane filtration
2003	Economical Water Purification System (e-Water)	technology (Kawai,Yokohama/Shinishikawa,Okinawa) Group 2: Total water purification system
2004		(Ayase, Yokohama/Otogane, Fukuoka) Group 3: Observation technology at the drinking water supply
		source 51

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 June/03 - Mar/05	Fresh Water	 Comparative Experiments of 6 Groups, including Ebara <u>Case Trial - 200,000 m³/d</u> 	 Toray/Suido Kiko Joint Team Toray; Experiment Supervisor, Basic Design, Manufacture of Experimental Facility, Follow-up of Operations
Ayase, Yokohama Aug/03 - Mar/05	Fresh Water	- Examination of Appropriate Operating Conditions	 Co-R&D of 38 Companies Toray; Basic Design, Supply of PVDF Modules
Otogane, Fukuoka Sept/03 - Mar/05	Fresh Water	 Comparative Experiments of 5 Groups including Maezawa and Shinko Pantec <u>Case Trial - 110,000 m³/d</u> 	 Suido Kiko as the Supervisor Toray; Supplies PVDF Modules, Supports System Examination
Ishikawa, Okinawa Oct/03 - Mar/05	Fresh Water	 MF Pretreatment+NF Membrane (to confront Ozone + Activated Carbon Method) Only Successful Group to actually demonstrate use of membranes <u>Case Trial - 50,000 m³/d</u> 	 Nishihara; Supervisor, Joint Team of Suido Kiko, Ebara, Kubota, and Toray Toray; Basic Design and Supply of PVDF and NF Modules 52



Conclusion - UF/MF Membranes for Drinking Water

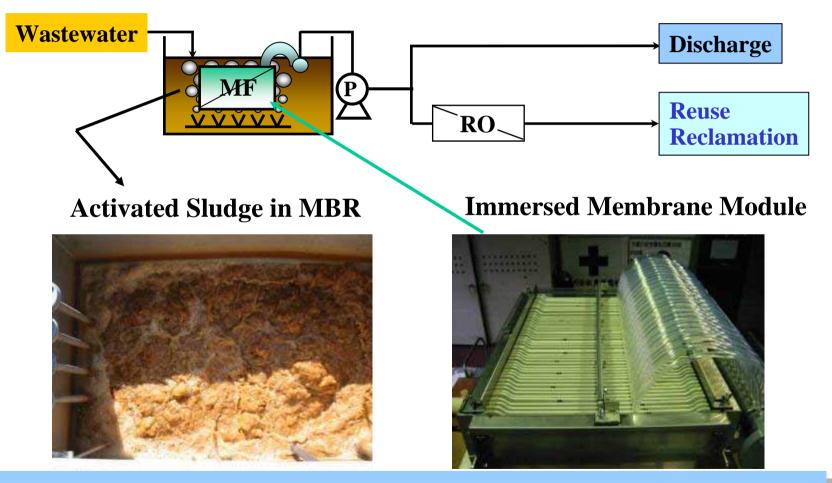
- 1. The Drinking Water Production Market is expanding rapidly, centering on the U.S. and Europe.
- 2. Toray has developed highly water-permeable and highly stable PVDF hollow fiber large modules suitable for drinking water production.
- **3.** Although still in the experimental stage, Toray's technology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



Immersed Membrane Modules for Wastewater Treatment

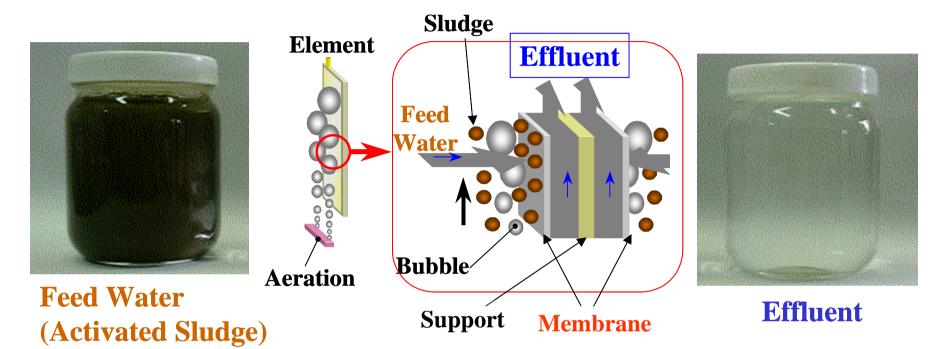
Immersed Membrane Module System

MBR (Membrane Bioreactor)



Features good water quality, small footprint, reduced excess sludge, and the market is yet undeveloped.

Filtration Mechanism and Required Characteristics



Requirement				
Stability	Physical Stability	Impact of bubble and sludge. Vibration.		
Stability	Chemical Stability	Chlorine, acid, oxidation agent, alkaline		
Dormoshility	Initial Permeability	High permeability		
Permeability	Durability	Prevention for clogging 56		



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Design Concept of Immersed Membrane

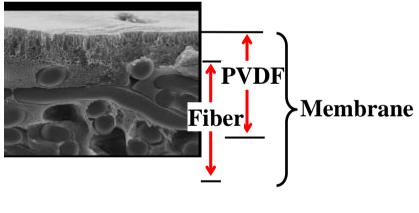
1. Membrane Material

Poly (Vinylidene Fluoride): PVDF

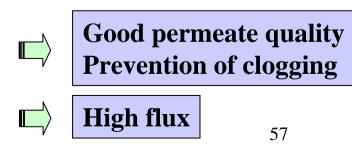
High stability for chemicals : fluorine polymerHigh physical strength: high molecular weight
(MW=300,000-400,000)

2. Membrane Form

Fiber reinforced (non-woven) flat sheet membrane

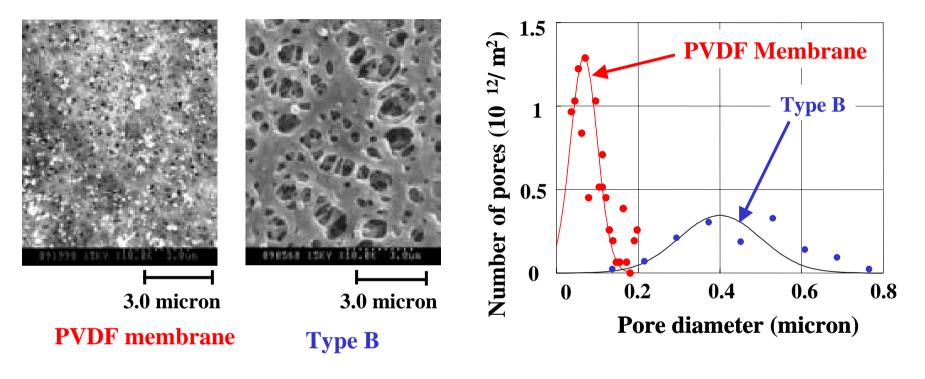


- **3. Surface Pore Diameter**
 - 1) Small pore diameter
 - 2) Narrow pore diameter distribution
 - **3) Numerous pores**





Basic Characteristics of Immersed Membranes



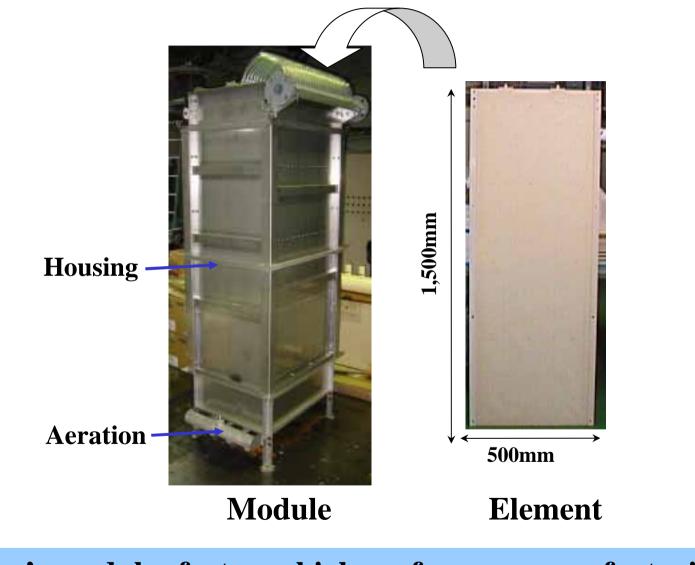
FE-SEM photographs of Flat sheet membrane surface

Pore diameter distribution of surface (Estimated from SEM photos)

Ideal membrane micro structure is achieved.



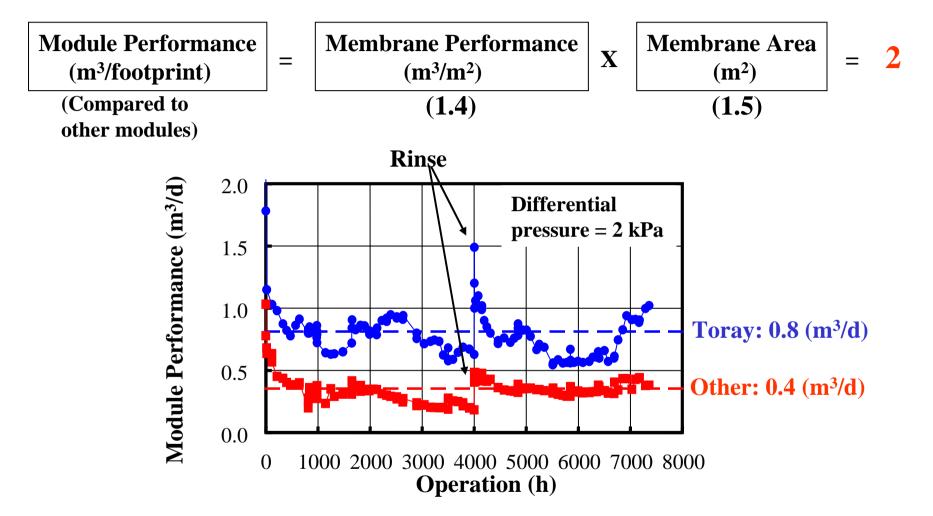
Immersed Membrane Element & Module



Toray's modules features high performance per footprint. 9



Comparison of Module Performance



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



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





