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New Advancement of Seawater Desalination Reverse Osmosis Membranes (SWRO)

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Toray Industries, Inc.

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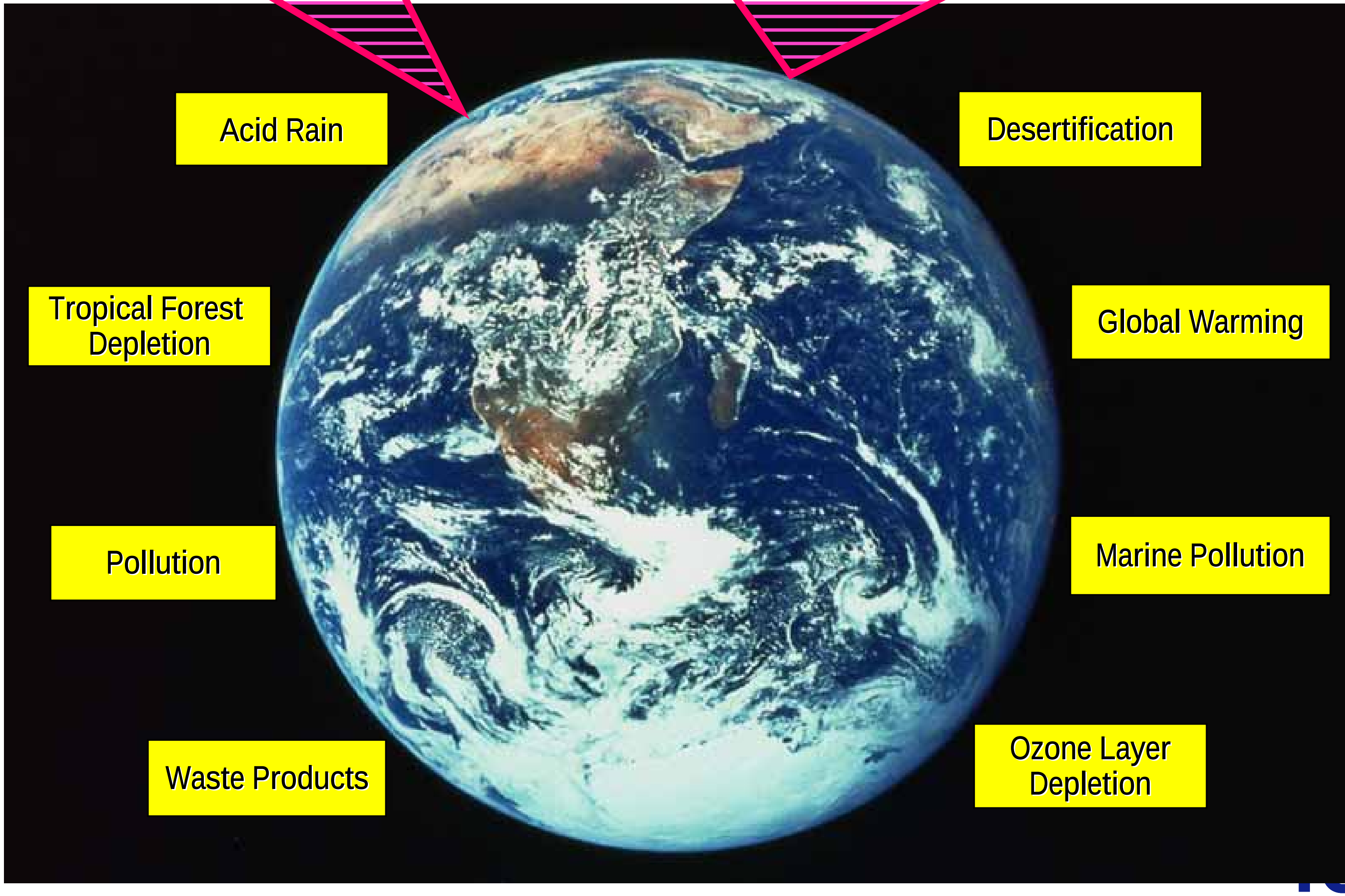
1. Trends on Seawater RO Desalination

The Global Environmental Issues
The "Carbon Dioxide Issue" and the "Water Issue"!

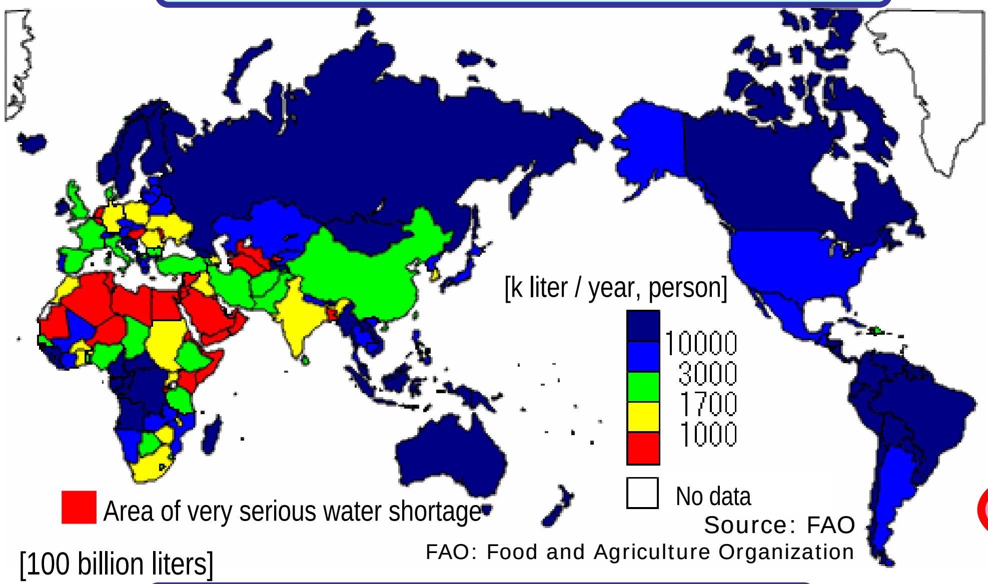
CO_2 Emissions

Issues of Shortage and Pollution of Water Environments

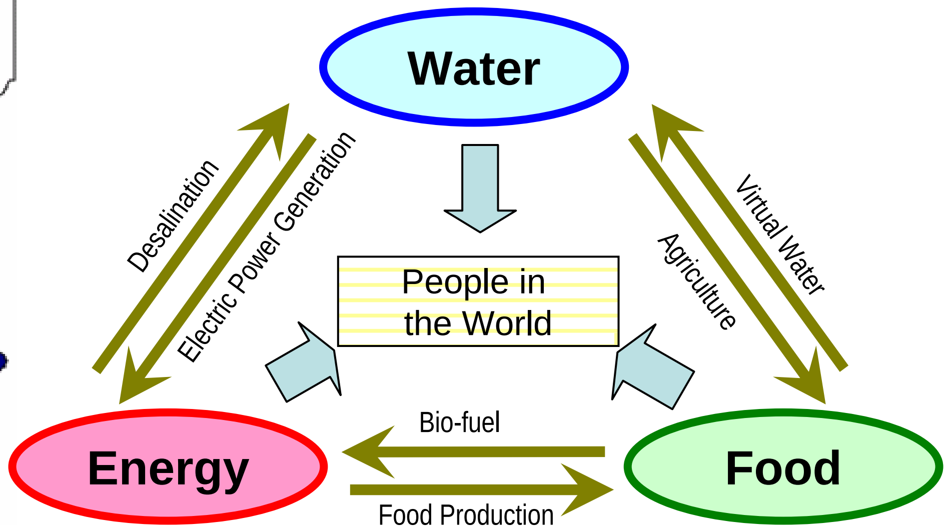


World Water Resources and Water Issues

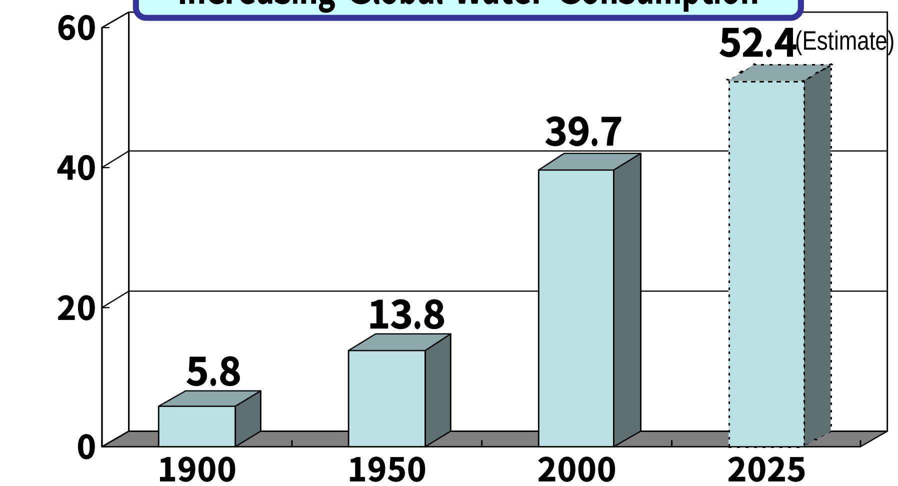
Annual Per Capita Water Resources



Relationship between Water, Energy and Food



Increasing Global Water Consumption



Source: UNESCO

The Water Issue is a Global Challenge

- UN Target: "Halve the proportion of people without access to drinking water or sanitation facilities" - Not yet achieved.
- The water issue is a global challenge required to be resolved together with the food and energy issues.
- The water issue is a global challenge that should be dealt with on the same basis as the carbon dioxide issue.

Reference: Council for Science and Technology Policy, 67th Meeting (held on May 18, 2007)
Material 3: Recent Trends of Science and Technology "Japanese Technologies Contributing to the World – An Example of Japanese Water Treatment Technologies —"1

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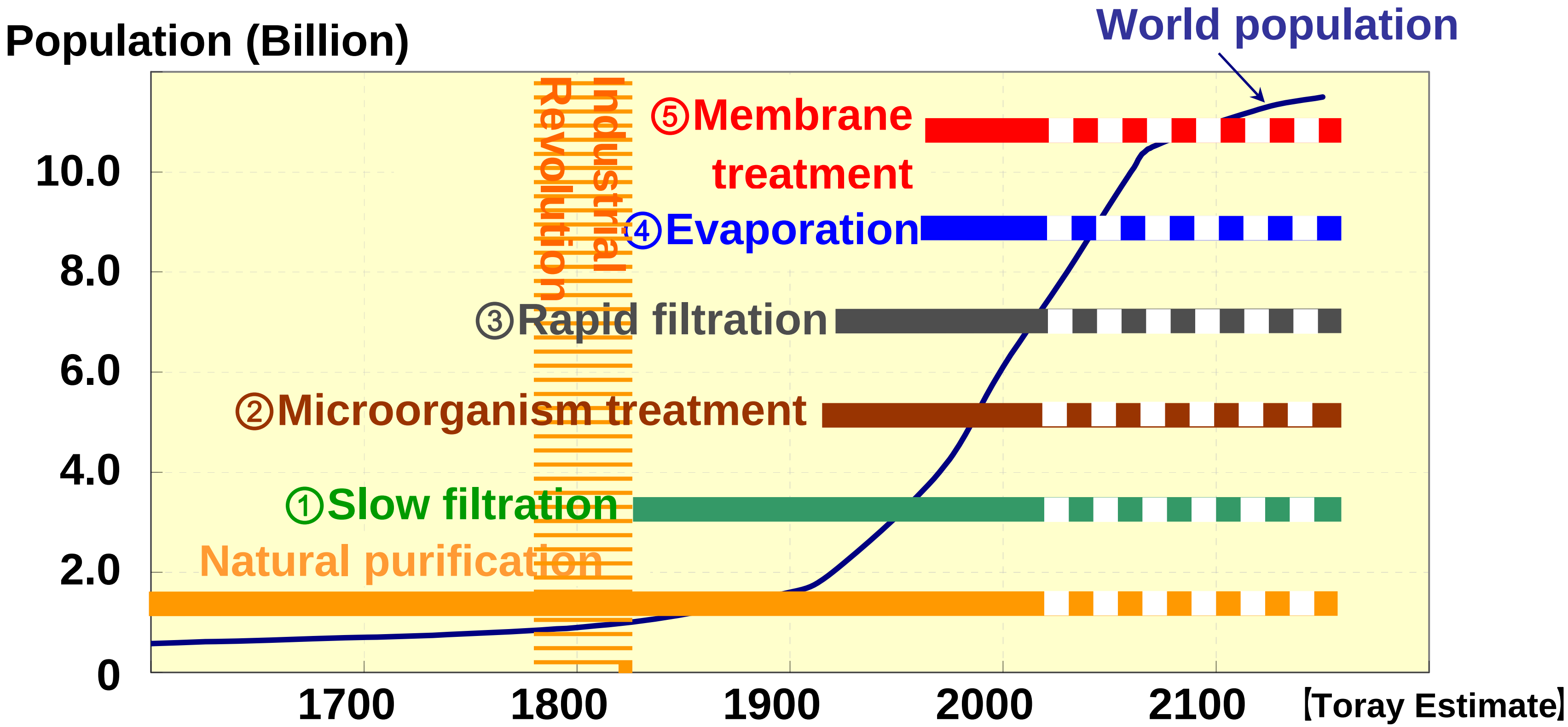
Increase of World Population and Development of Water Treatment Technologies

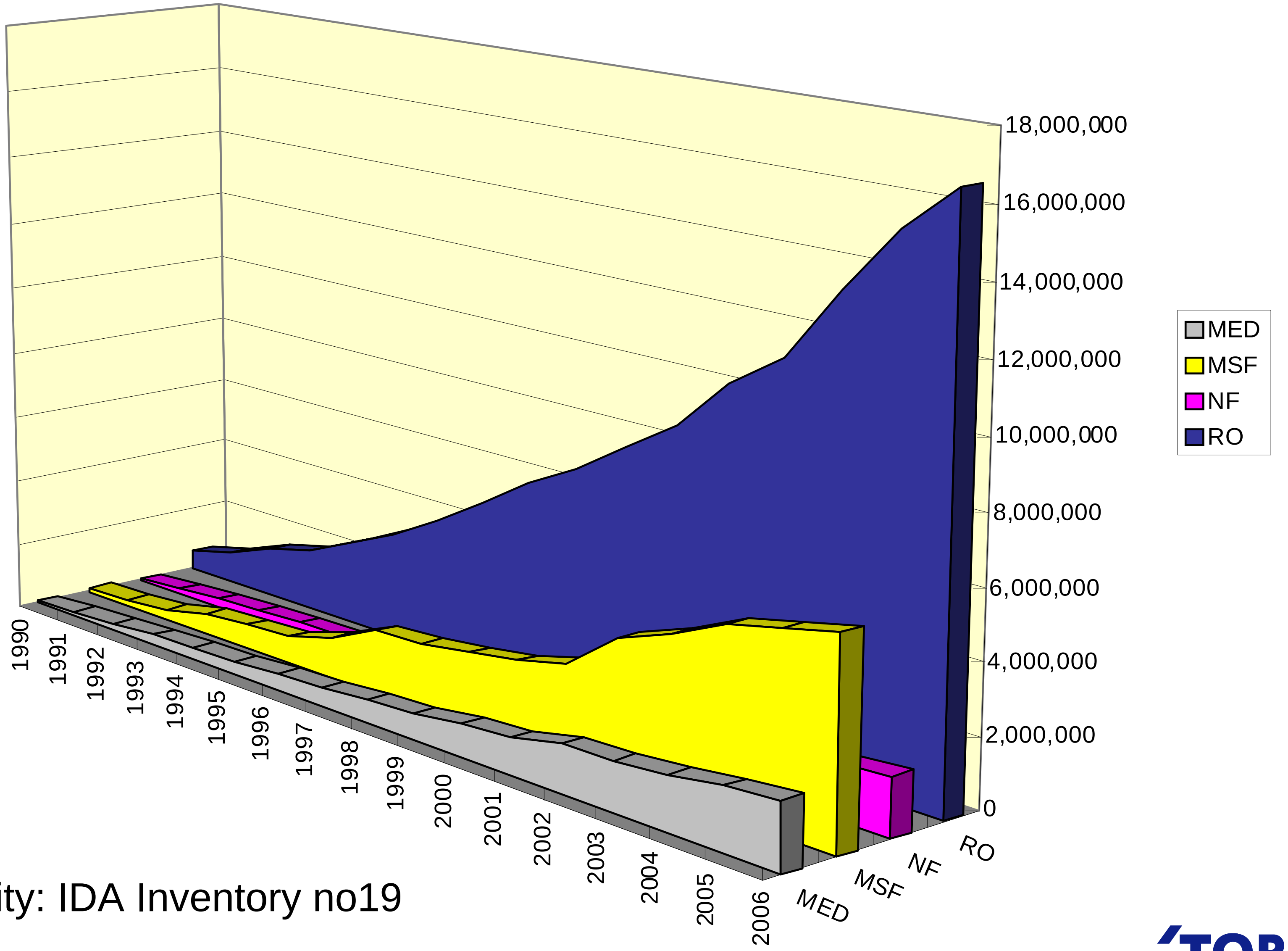


Difficult to secure volume and quality of water only by natural purification due to the increase of rapid increase of population

Membrane treatment technology, which enable control of high precise water quality and high speed treatment, is essential in 21 century

Reference: Tambo, N. et. ; "Infrastructure Development under Decreasing Population" - A Design from Expansion to Shrink -. Japan Society of Civil Engineers. 2002, p.10. (Japanese)

Trend of Cumulative Capacities of Water Production Facilities by Technology



Authority: IDA Inventory no19

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Types of Membranes and Toray's Membrane Products

Size	0.001 ㎛	0.01 ㎛	0.1 ㎛	1 ㎛	10 ㎛

Separation materials

- Ion, Low molecule weight organics
- High molecular weight polymer
- Colloid
- Clay
- Trihalomethane
- Agricultural & Organic Material
- Virus
- Coliform
- Cryptosporidium
- Bacteria
- Monovalent Ions
- Multivalent Ions

Types

RO (Reverse Osmosis) | NF (Nanofiltration) | UF (Ultrafiltration) | MF (Microfiltration)

Toray's membrane products

RO	NF	UF	MF	MBR
Ultrapure Water, Seawater Desalination, Advanced Water Treatment	Softening, Removal of Toxic substance	Municipal Drinking Water, Reuse of Wastewater, Pretreatment for RO Process	Municipal Drinking Water, Reuse of Wastewater, Pretreatment for RO Process	Sewage Water Treatment

RO membrane

NF membrane

HF membrane (PVDF Hollow Fiber)

MF membrane (PVDF Hollow Fiber)

PVDF Immersed membrane for MBR

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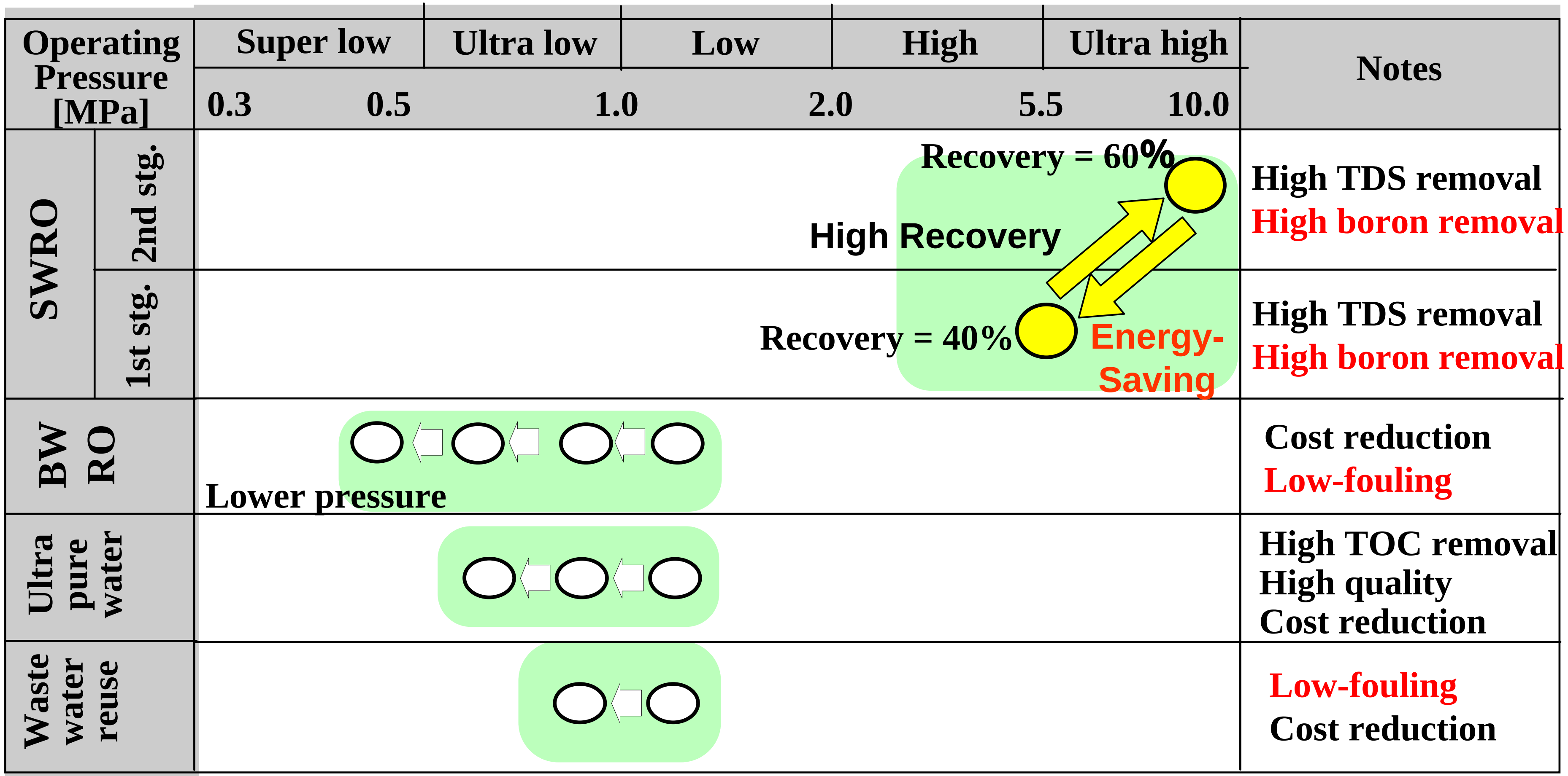
Technical Trends of RO Membranes

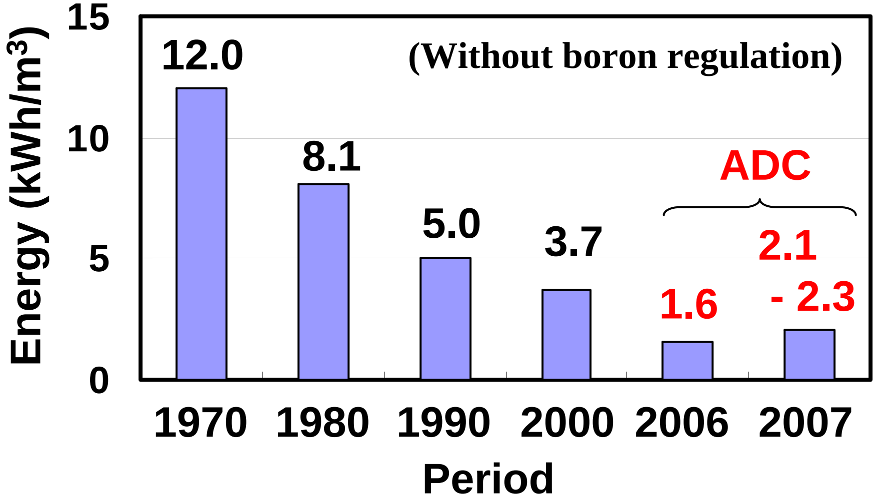


Energy saving membrane with retaining conventional performance will be expected.

Technical Trends on SWRO Membrane

Two technical requirements for SWRO membrane

I. Energy saving



Requirement for further improvement

- High flux membrane at low operating pressure
- More effective energy recovery device

II. Changes in the required water quality

1) At the time of initial stage in SWRO

SWRO = Salt rejection was the most important factor.

2) In current years

WHO actions against the boron regulation (in addition to item 1))

- The boron regulation guideline value in drinking water (1998).
- The report for toxicity of boron in drinking water (2003).
- New boron regulation guideline will be discussed in the IDA congress (2007).

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Changes in Boron Regulation

Recent trends of boron regulation and requirement.

			1990 1993 1996 1997 1998 2000 2001 2005 2007
Boron regulation		WHO	0.3mg/l → 0.5mg/L (guidline) → 0.5mg/L (Pub.Com.) →
		×1,000m³/d	
World	Spain	42	Not required → 1.0 mg/L → 0.5 mg/L
	Trinidad	136	Not required →
	Israel	272	0.4mg/L → 0.3 mg/L
	Singapore	136	1.0mg/L →
	Abu Dhabi	227	1.0mg/L →
	California		1.5mg/L →
Japan	Okinawa	40	Not required →
	Fukuoka	50	1.5mg/L →

Boron regulation has been getting tougher especially after 2000.

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Flow Diagram of SWRO Desalination Plant with Boron Regulation & without Boron Regulation

Zone I: Single stage SWRO with boron regulation

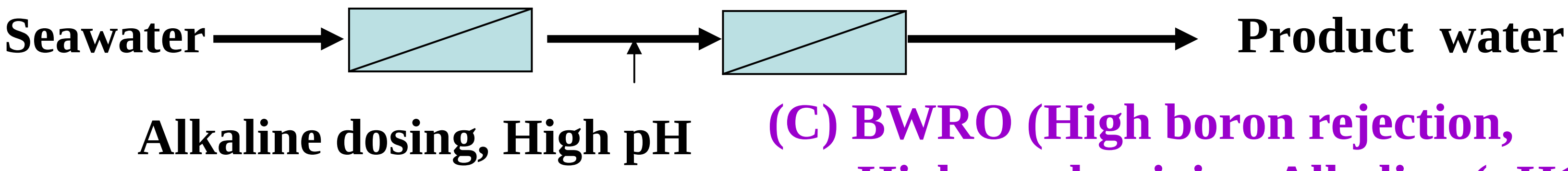
(ex. : Las Palmas III, Barcelona, Malta)

(A) SWRO membrane (High boron rejection)

Zone II: 2 to 4 stages SWRO with boron regulation

(ex. : Ashkelon, Tuas , Shuaiba III)

(B) SWRO (High boron rejection, High water productivity)



(C) BWRO (High boron rejection, High productivity, Alkaline (pH10) tolerance

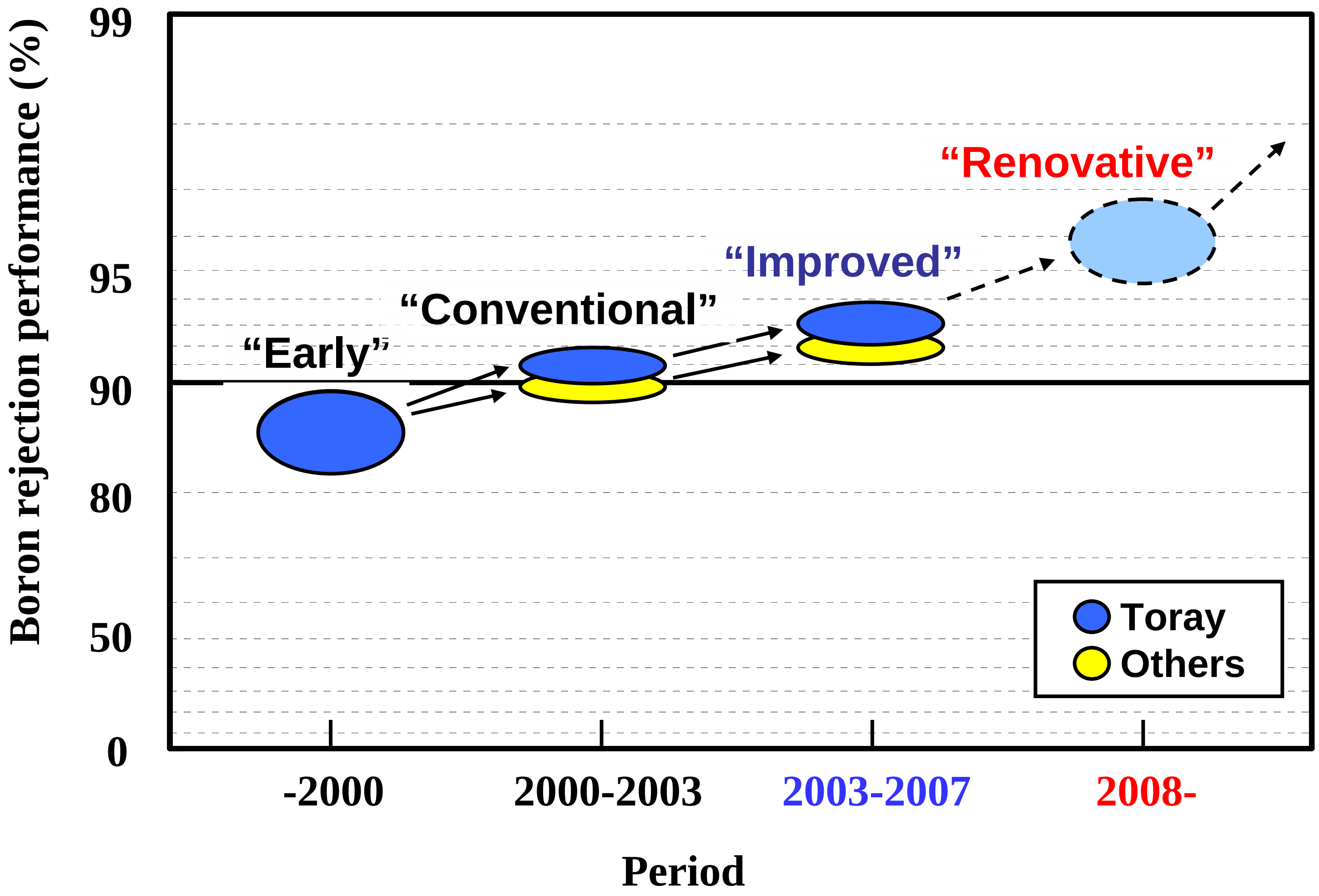
Zone III: Single stage SWRO without boron regulation

(ex. : Point Lisa, Al-Jubail, Okinawa)

(D) SWRO (High water productivity, Low energy type)

Membrane Manufacturers are competing with each other in these A - D types, respectively.

History and Prospect of Boron Rejection Performance



Toray has been investigating SWRO membranes with focusing on boron rejection.

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2. Scientific Research on Boron Removal Mechanism by RO Membrane

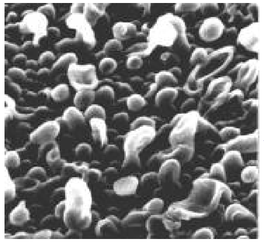
1) Positron Annihilation Lifetime Spectroscopy

2) Solid-state ^{13}C NMR Spectroscopy

3) Molecular Dynamics Simulations

Purpose

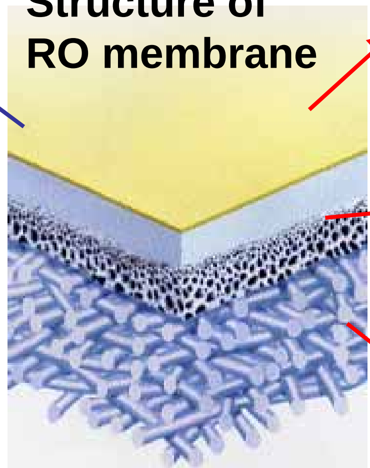
Conventional RO membrane structural analyses



Membrane Surface

How large is the pore?

Structure of RO membrane



Separating functional layer

Cross-linked aromatic polyamide, 0.2µm

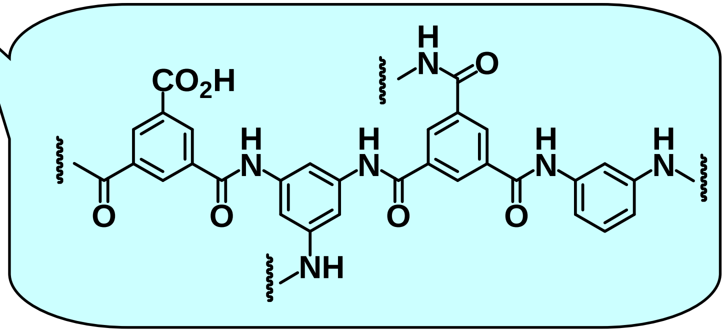
Support layer

Poly sulfone, 60µm

Substrate

Non-woven fabric substrate, 150µm

Imaginative chemical structure

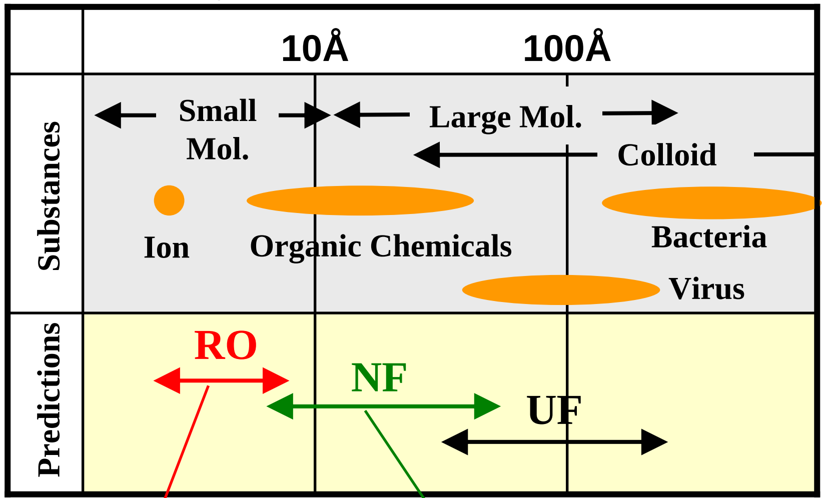


Insoluble to any solvent

⇩

Poor information

Predicted pore size distributions by removable substances



roughly 5Å

roughly 50Å

Purpose in this work:

1. To establish a certain pore size analysis method
2. To acquire some basic physicochemical information for MD simulations

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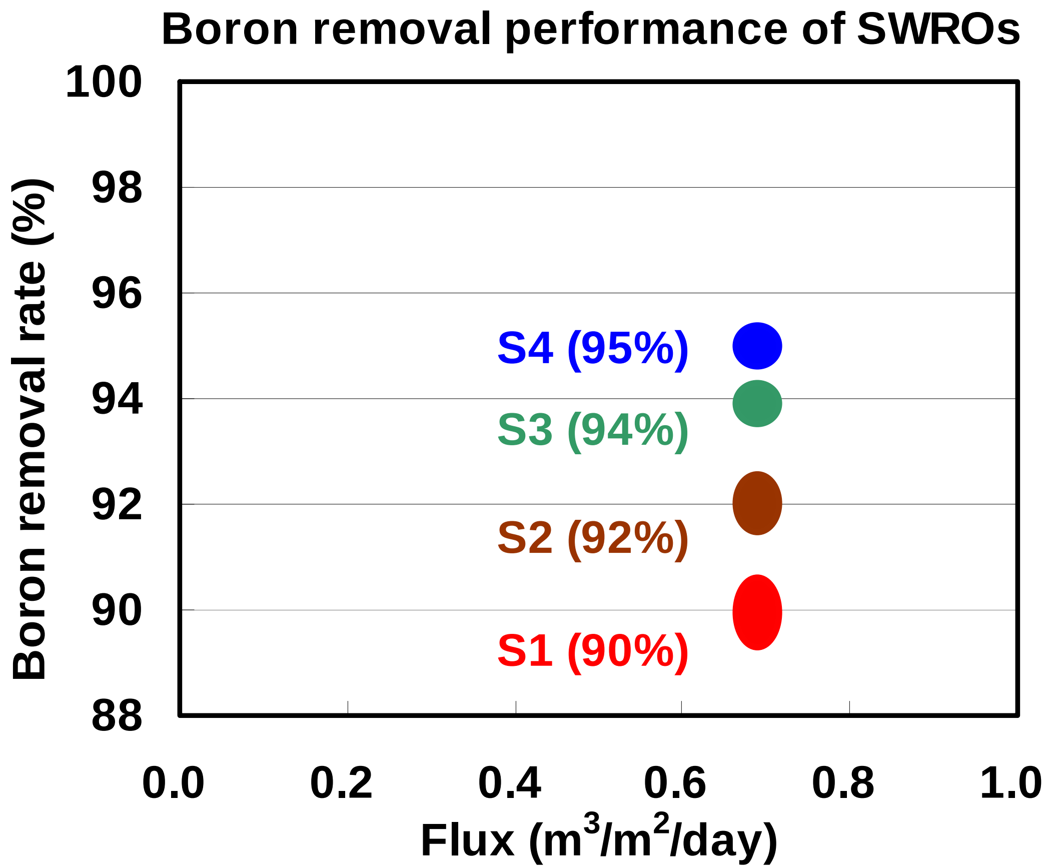
Candidate Membranes for Analyses

The SWRO membranes with different boron removal rate were prepared, even though SWRO membranes had same NaCl rejection and water flux.



Test condition: feed solution; TDS 35000 mg/l, temperature; 25 degree C., pH; 6.5, operating pressure; 800 psig (5.5 MPa), flow rate; 3.5 L/min.

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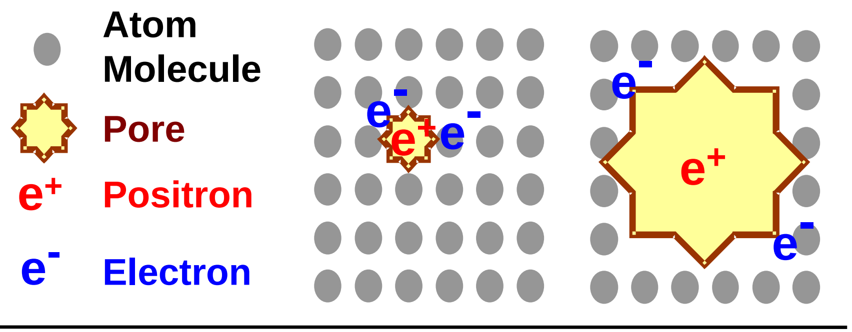
Analysis of RO Membrane Pore Size by Positron Annihilation Lifetime Spectroscopy (PALS)



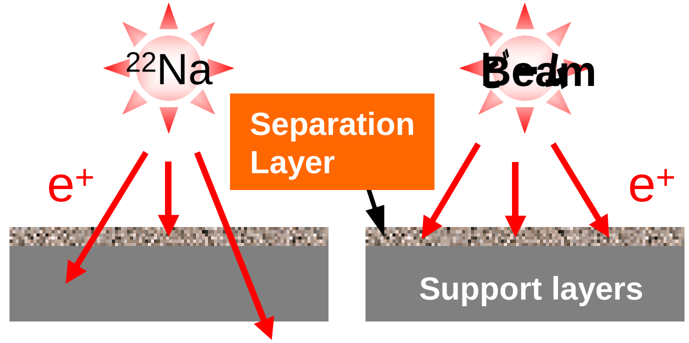
Pore size	Small	Large
Positron Annihilation Lifetime	Short	Long

Pore size is estimated from Positron Annihilation Lifetime

For measurement of separation layer alone, positron beam method is applied

^{22}Na method | **Beam method**

Controllable positron energy



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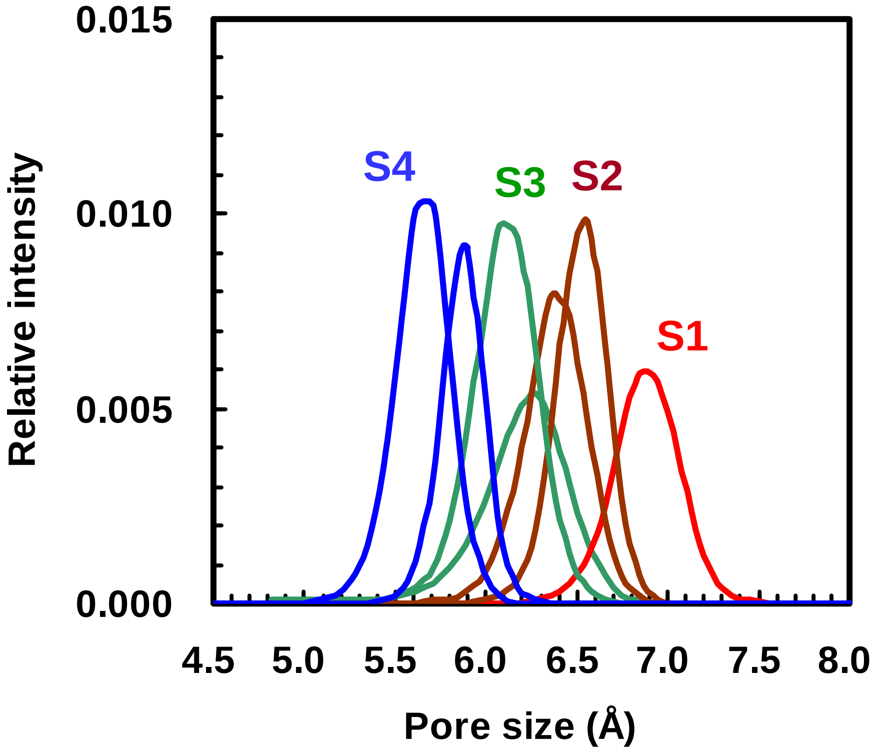
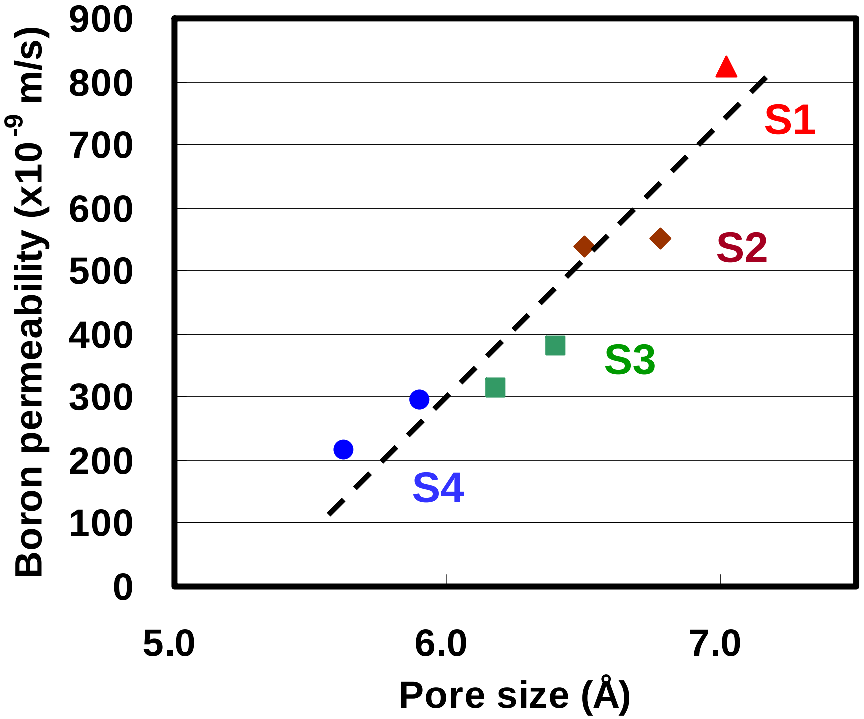
Comparison of Pore Size between SWROs

Pore size distribution[2a)]



Correlation between pore size[2b)] and boron permeability in SWROs



2) a) MELT: A. Shukla, L. Hoffmann, A. A. Manuel, M. Peter, Materials Science Forum, 255-257, 233-237 (1997).
b) POSITRONFIT: P. Kirkegaard and M. Eldrup, Computer Physics Communications, 3, 240 (1972).

1. Any SWRO has 5.6-7.0 Å of pore.
2. Pore sizes in SWROs show clear correlation with those of boron removal performance.

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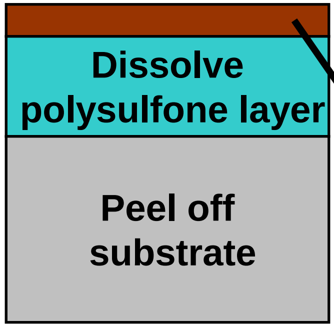
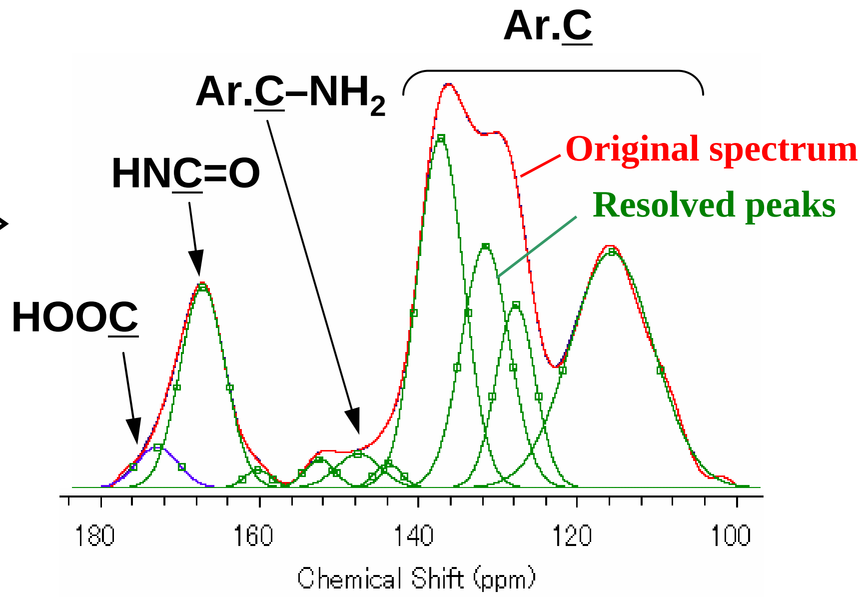
Estimation of Chemical Structure by Solid-State ^{13}C NMR

Remaining functional layer = Cross-linked aromatic polyamide





DD/MAS ^{13}C NMR spectrum of Membrane S1 (90% boron removal)

Prospective chemical shift[3)]

Type of carbon	δ (ppm)
Aromatic C (except for ArC-NH_2)	107-139
ArC-NH_2	147
HNC=O	165
HOOC	172

3) by ChemDraw Ultra 7.0.1

Mol ratio of each moiety

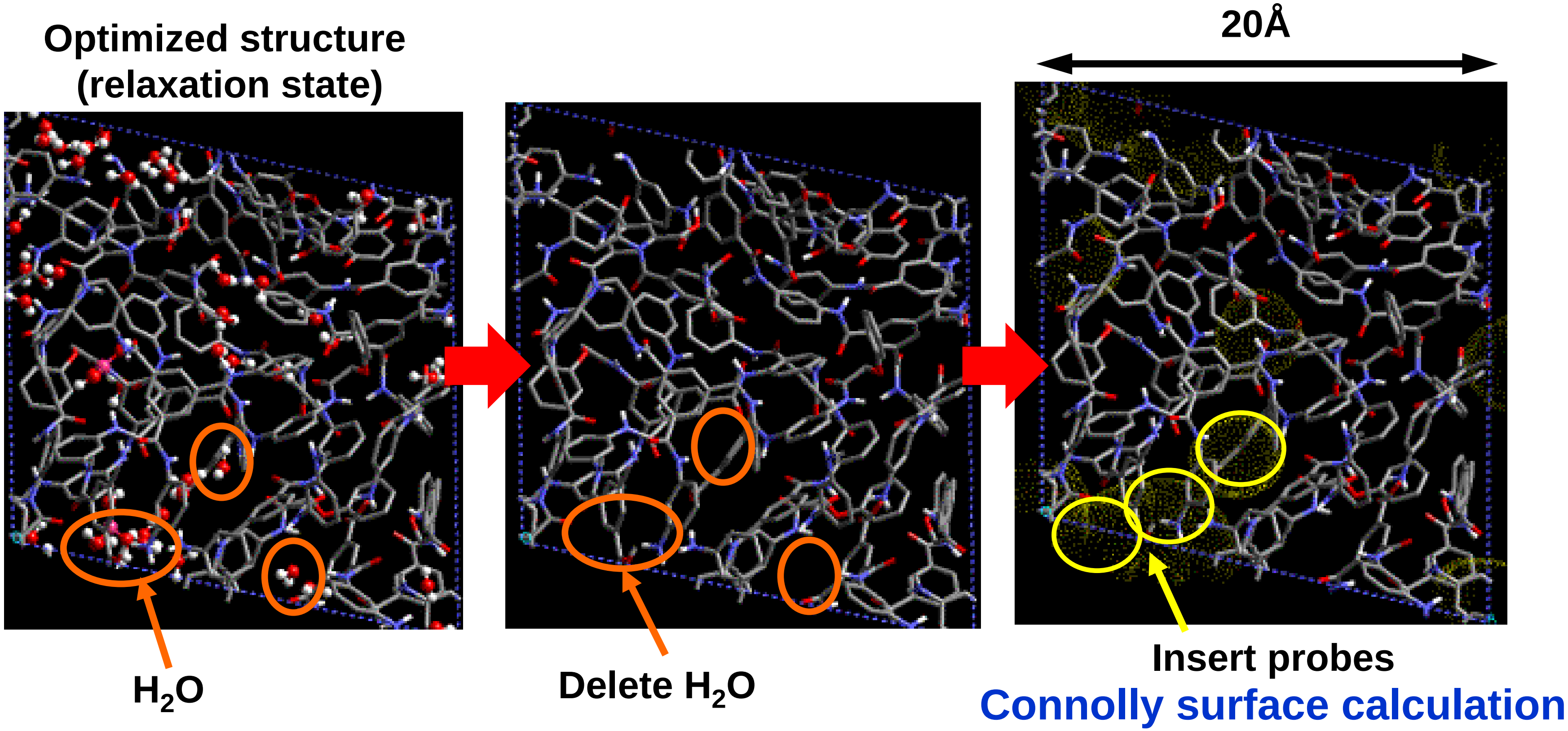
Moiety	Aromatic amine	Aromatic acid halide
Ratio (mol)	1.2	1

⇨ **Estimating presumable chemical structure**

1. All of peaks characteristic to each moiety are observed.
2. A chemical structural model unit of polyamide is estimated by the ratio of moiety.

Investigation of RO Membrane Pore via MD Simulations Analyses

MD simulations were performed with initial structure (determined by ^{13}C NMR).



Larger probes than pore size cannot be inserted.

The probe diameter when the Connolly surface reached zero should be pore size.

The calculated pore size was 6 - 8 Å.

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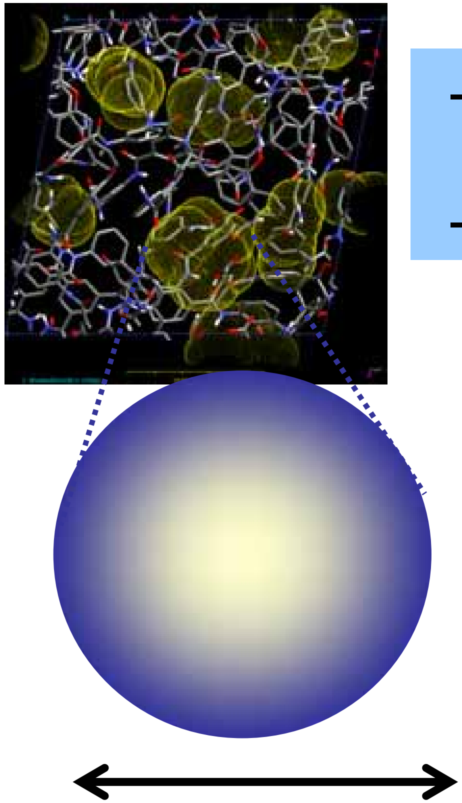
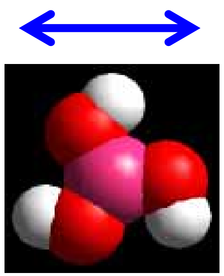
Comparison between Pore Size and Referential Substances

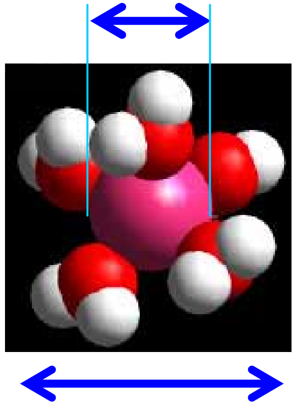
- Hydrated state of boric acid and sodium ion were calculated as referential substances for pore size.
- Boric acid is hardly hydrated in neutral pH region.



Pore size sphere



Boric acid
$B(OH)_3$



Hydrated sodium ion
(Na^+-$6H_2O$)

Only a little difference in the size between pore and substances, including the difference between hydrated states, must dominate the removal performance.

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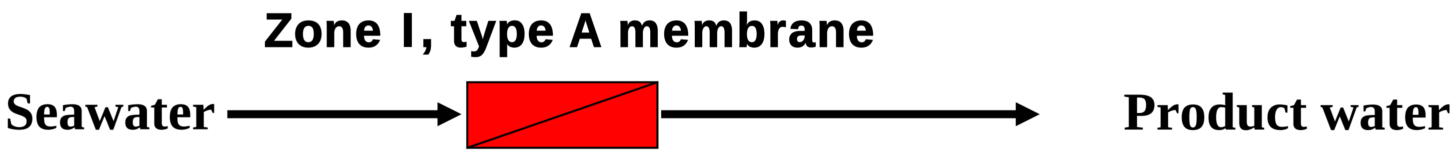
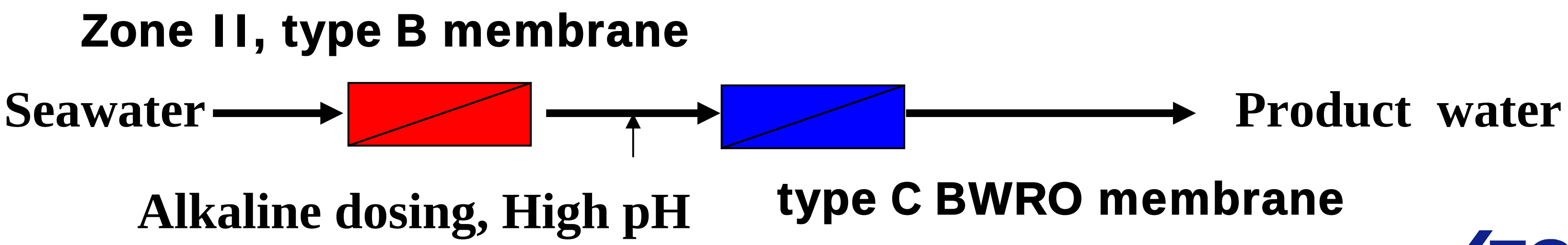
New High Boron Removal SWROs

New High Boron Removal SWRO membranes were developed by special molecular design controlling the pore size of membrane in sub-nanometer level.

1. **From the viewpoint of *water quality*, a high boron removal type (for Zone Ⅰ, type A), *TM800A*, was commercialized.**



2. **From the viewpoint of *energy saving*, a high productivity with high boron removal type (for Zone ⅠⅠ, type B), *TM800C and TM800E*, and a high boron removal BWRO (for type C), *TM700C*, were also commercialized.**



Water Treatment Plants in the World using Toray RO Membrane "ROMEMBRA"

as of January 2008

Israel
92,960 m^3/d

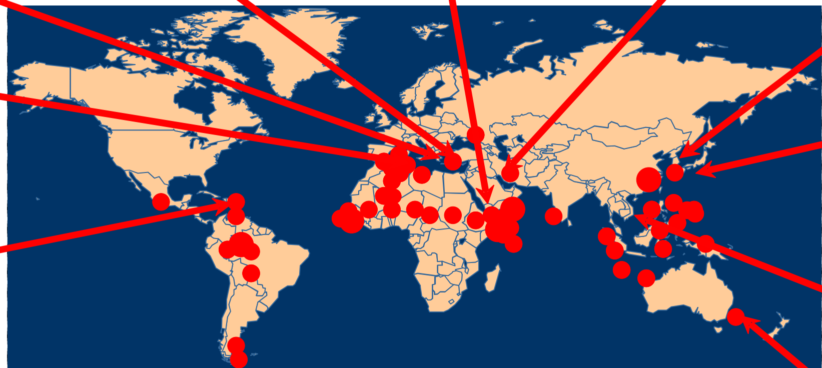
Kuwait
320,000 m^3/d

Saudi Arabia
150,000 m^3/d

Saudi Arabia
91,000 m^3/d*

Korea
84,000 m^3/d

Algeria
200,000 m^3/d



Okinawa
40,000 m^3/d*

Trinidad and Tobago
136,000 m^3/d

Singapore
136,000 m^3/d

*** Joint delivery with other companies**

Australia
66,000 m^3/d

Seawater Desalination | **Brackish Water Desalination** | **Waste Water Reuse**

Cumulative installation: about 11,750,000 m^3/day
(as of seawater desalination: over 2,300,000 m^3/day)

- **Equivalent to water for daily use of about 50,000,000 people**

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Large Scale Desalination Plants in the World with Toray "ROMEMBRA" Elements

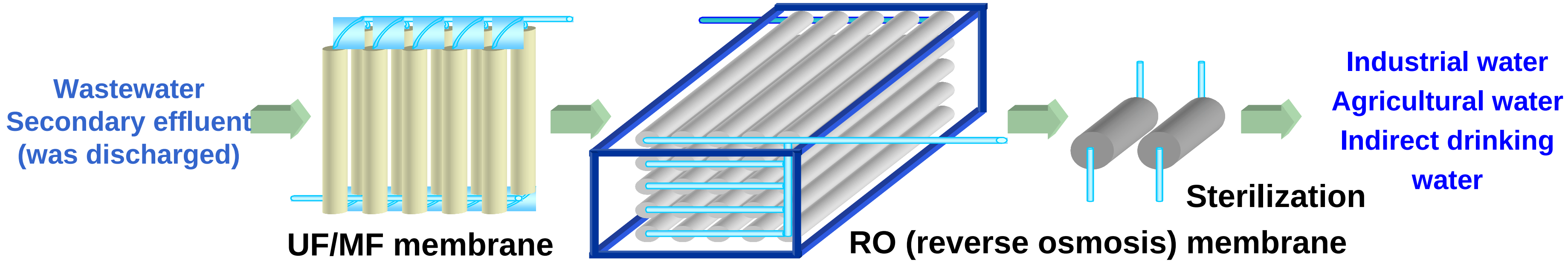
as of January 2008

No.	Country	Location	Capacity *1 m^3/d	Purpose	Operation Year *2	Notes
1	Algeria	Hamma	200,000	Seawater Desalination	(2008)	
2	Saudi Arabia	Shuaibah	150,000	Seawater Desalination	(2009)	
3	Trinidad & Tobago	Point Lisas	136,000	Seawater Desalination	2002	
3	Singapore	Tuas	136,000	Seawater Desalination	2005	
5	Iran	Fajr	100,000	Process Water	2001	
6	Israel	Palmachim	92,250	Seawater Desalination	2007	
7	Saudi Arabia	Al Jubail-III	90,909	Seawater Desalination	2000	*3 : 24,240 m^3/d
8	Korea	Daesan/HPC	84,000	Process Water	1997	
9	Korea	Daesan	80,000	Process Water	2001	
10	Spain	Mallorca	69,300	Seawater Desalination	2001	*3 : 23,100 m^3/d
11	Spain	Alicante	65,000	Seawater Desalination	2002	expansion: 15,000m^3/d (2006)
12	Korea	Suwon	60,000	Process Water	2001	
13	Malta	Ghar Lapsi, etc.	53,500	Seawater Desalination	2007	replacement for three places
14	United States	Collier	45,000	Drinking & Process Water	2006	
15	Japan	Okinawa	40,000	Seawater Desalination	1997	*3 : 30,000 m^3/d
16	Saudi Arabia	Al Rass	36,000	Drinking & Process Water	1989	
16	Saudi Arabia	Al Bukariyah	36,000	Drinking & Process Water	1989	

10,000m^3/d of water is equivalent to daily life water of 40,000 people

(Notes)
*1 Total output of all units
*2 The year in which the plant was commissioned, ( ) shows a project
*3 Toray's initial installation

Advanced Wastewater Treatment & Reclamation Plant in the World with Toray "ROMEMBRA", "TORAYFIL" and "MEMBRAY"



No	Country	Location	Capacity *1 m³/d	Membrane Brand Name *3	Purpose	Operation Year *2	Notes
1	Kuwait	Sulaibiya	320,000	ROMEMBRA	Municipal	2005	
2	Australia	Luggage Point	66,000	ROMEMBRA	Wastewater Reuse	(2008)	
3	China	Tianjin	30,000	ROMEMBRA	Wastewater Reuse	2006	
3	China	Tianjin	30,000	ROMEMBRA	Municipal	2006	
5	China	Dongguan	25,000	ROMEMBRA	Industrial	2005	For Paper Industry
6	Singapore	Seletar	24,000	ROMEMBRA	Wastewater Reuse	2004	
6	Singapore	Seletar	24,000	ROMEMBRA	Municipal	2004	
8	UAE	---	15,000	MEMBRAY	Municipal	(2008)	
9	India	---	11,200	MEMBRAY	Industrial	(2008)	For Textile Industry
10	Canada	---	2,500	MEMBRAY	Municipal	(2008)	
11	Bahrain	---	2,400	MEMBRAY	Municipal	(2008)	
12	Netherlands	---	2,400	MEMBRAY	Municipal	2006	
13	China	Beijin	2,160	TORAYFIL	Industrial	2006	
13	Philippines	---	2,160	TORAYFIL	Industrial	2006	
15	UK	---	1,975	MEMBRAY	Municipal	2006	

(Notes) *1 Total output of all units
*2 The year in which the plant was commissioned, ( ) shows a project
*3 ROMEMBRA(RO/NF), TORAYFIL(UF/MF), MEMBRAY(MBR)

Conclusion

1. **With the Pore size analyses studies,**
   a. **The nondestructive method of measuring pore size in RO membrane was established, and reliable values, 5.6-7.0Å, almost agreeing with predictions, were respectively acquired.**
   b. **The clear correlation between pore size and boron removal performance of SWRO membrane was revealed.**

2. **Back to basic, the scientific knowledge on RO membrane was accumulated. Based on these new knowledge, the new high boron removal membranes were obtained.**

SWRO Membrane Lineup of Typical Membrane Manufacturer

SWRO products lineup corresponding to various coverage released from each company*.

	Coverage \ Manufacturer	Toray	Dow	Hydranautics
Energy Saving ↑	Ultra Low Energy	TM800L (2001)	SW30XLE	SWC5
	Low Energy	TM800E (2007)	SW30HRLE	
	Standard	TM800 (2001)	SW30HR	SWC3+
Water Quality ↓	High Salinity, High Temperature	TM800H (2001)	-	SWC4+
	Ultra High Salinity	SU-800BCM (1997)	-	-
	High Boron rejection	TM800A (2007) TM800C (2007)	SW30XHR (2007)	SWC4+ SWC5

*( ): Year in which the product is launched.

Many types of SWROs for energy saving & water quality have been announced.