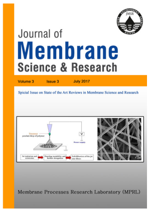
Journal of Membrane Science and Research 3 (2017) 157-173

Journal of Membrane Science & Research

journal homepage: www.msrjournal.com



Review Paper

The Pursuits of Ultimate Membrane Technology including Low Pressure Seawater Reverse Osmosis Membrane developed by “Mega-ton Water System” Project

Masaru Kurihara [1,*] and Takao Sasaki [2]

[1] *Toray Industries, Inc., 2-1-1 Nihonbashi-muromachi, Chuo-ku, Tokyo 103-8666, Japan*
[2] *Toray Industries, Inc., 3-2-1 Sonoyama, Otsu, Shiga 520-0842, Japan*

Article info

Received 2016-12-02
Revised 2017-01-23
Accepted 2017-03-11
Available online 2017-03-11

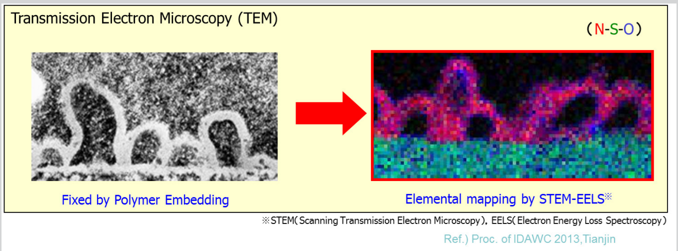
Keywords

Low-pressure SWRO
Pore size analysis
Morphology analysis
LMS
PRO

Highlights

- Notable low pressure SWRO membranes have been designed.
- They realized to create innovative large-scale desalination processes.
- These are developed in line with the progress of analytical technologies.

Graphical abstract



Abstract

Reverse osmosis (RO) technology has been widely applied to water treatment such as seawater desalination, and large RO plants are many in operation around the world. Moreover, much larger plants will be required to secure sufficient water resource in the near future because global water shortage and quality problems are still getting more serious. Mega-ton Water System project was carried out for sustainable management of water environment and for low-carbon path to develop advanced key technologies of water treatment. Low-pressure RO membrane for seawater desalination has been studied in the project as a part of the core technologies to realize mega plant that is capable of producing 1,000,000 m^3 of freshwater per day. Fundamental and scientific research for RO membranes based on fine structure analyses by means of transmission electron microscopy with a special technique was conducted, and practical tools for designing new innovative RO membrane were acquired by the structure analyses to quantify the physicochemical and chemical properties of RO membranes. As the result of studying on structural design of RO membrane, low pressure SWRO membrane was obtained to reduce energy consumption compared to conventional ones in the past of SWRO. The vision of the “Mega-ton Water System” is sustainable desalination and reclamation. The missions are: 1) energy reduction (20-30%), 2) water production cost reduction (50%), and 3) low environmental impact (fewer chemical operations). Water cycle in “Mega-ton Water System” is separated into two parts including *i) Seawater RO (SWRO)* system, and *ii) Seawater RO system with PRO* system. The main challenge of development goal is the construction of mega-ton-scale system for seawater desalination for half the current cost. Accordingly, we developed the world’s first low-pressure, multi-stage, high yield RO system, using a low-pressure seawater desalination membrane, and as a result of incorporating into it the elemental technologies gained from research in subthemes, such as highly-efficient pressure energy recovery, low-cost and highly durable plastic piping, pretreatment without the use of chemicals.

Contents

---

* Corresponding author at: Phone: +81 (3) 3245 5716; fax: +81 (3) 3245 5704
E-mail address: Masaru_Kurihara@nts.toray.co.jp (M. Kurihara)

DOI: 10.22079/jmsr.2017.53773.1119

1. History of water treatment and membrane research

Increase of world population and development of water treatment technologies are shown in Figure 1 by Tambo [1]. From this figure, evaporation (Distillation) and membrane treatment is newest technology in comparison with other conventional technology on the very long range of time schedule. In 21st century, membrane treatment technology should be considered as the important countermeasures to water shortage.

Distillation (MSF and MED) and Reverse Osmosis (RO) methods appeared nearly same time as new water treatment techniques at early 1960’s. Distillation advanced in the market at first, but since 2000, RO became the major technology with high growth rate as shown in Figure 2.

Figure 2 also classified the history of water treatment technologies into three generations. 1960-1970 is the 1st generation, 1970-2000 is the 2nd generation, after 2000, author designated the 3rd generation as shown in Table 1.

The stage of RO technology in first generation is mainly in *R&D* level, leaded by the USA and Germany. In the second generation, many changes happened in the membrane technologies itself and market diversification. Many countries such as Japan, China and Korea are going to catch up the front technologies.

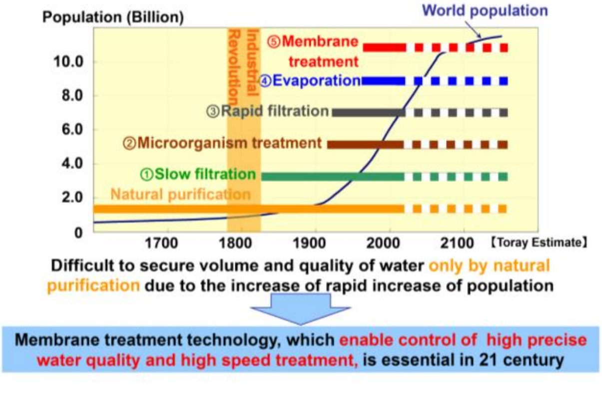


Fig. 1. Increase of wolrd population and development of water treatment technologies [1].

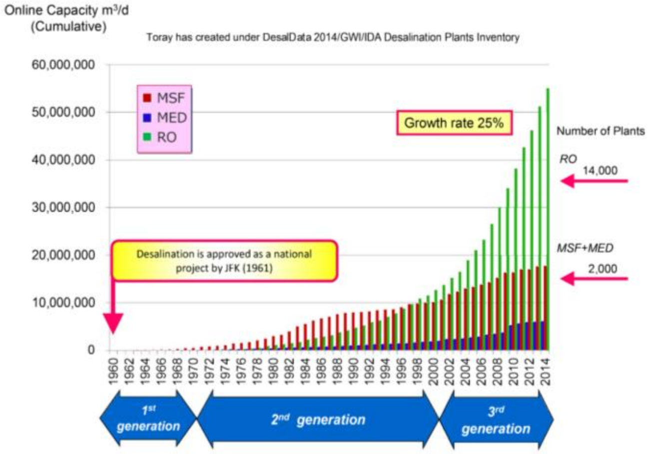


Fig. 2. History of desalination plant shifting from distillation to reverse osmosis.

In the 3rd generation, research strategy is divided into largely two groups 1) Pursuit of Existing Ultimate Membrane Technology, 2) Pursuit of Future Essential Technology. In the third generation of RO technologies, target of membranes research has been very clear, to the reduction of energy, environmental load and water production cost. As the pursuit of future essential technology, 5 different new innovative membranes and membrane processes are listed in Table 1 as 3rd generation. Especially three typical technologies are shown in Figure 3 from National Geographic, April 2010 [2]. These three technologies promised to reduce the energy requirement of desalination up to 30% and will be on the market 2010~2015. This news did much impetus to the academic researchers as the future essential technology.

2. Membrane research at 1st generation-asymmetric membrane

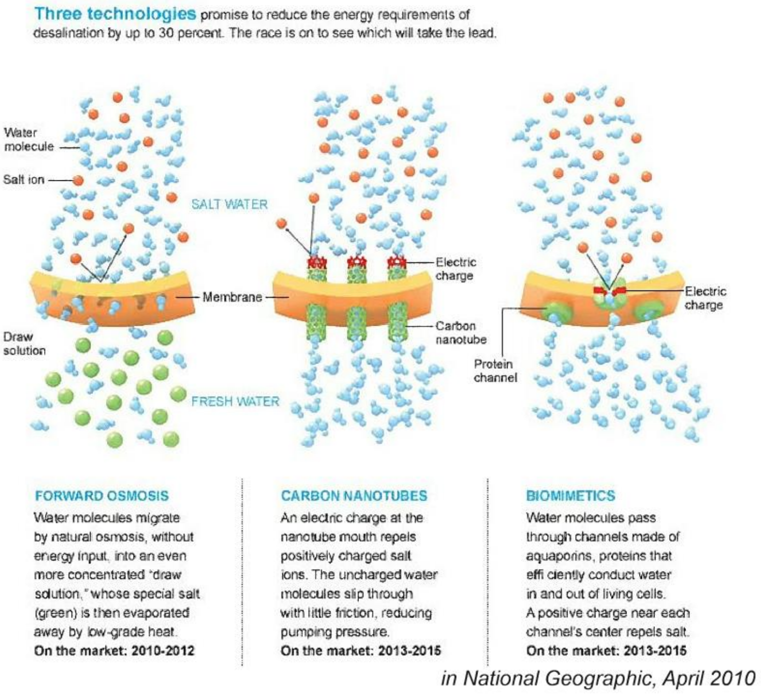
The membrane technologies have made great progress and their key technologies are as follows [3]:

1) *Materials*: Molecular design of high performance materials suitable for each separation mode
2) *Morphology*: Morphological design of high performance membrane
3) *Element/Module*: Element and module design to maintain high performance of membrane
4) *Membrane Process*: Plant design and operation technology

In the 1st generation membranes, the first commercial CA membrane was spiral-wound element by General Atomic Co. and first commercial polyamide membrane was linear aromatic polyamide hollow fiber membrane by DuPont during 1960-1970 as follows.

2.1. Cellulose acetate membrane

The first membrane which was industrially available in actual water production plants was made of cellulose acetate membrane invented by Loeb and Sourirajan in 1960 [4]. This membrane had a cross-sectional structure called "asymmetric" or "anisotropic" with a very thin separating functional layer on a coarse supporting layer. The material of this membrane was a sole polymer such as cellulose acetate, and the non-solvent induced phase separation method was used for the formation of membrane. After the invention by Loeb and Sourirajan, several companies developed and manufactured spiral-wounded elements in the United States and Japan, using the flat sheet type of asymmetric cellulose acetate membranes. RO technologies had come to the market from around 1964 [5]. Asymmetric cellulose acetate membranes were widely used from 1960's through 1980's mainly for pure water for industrial processes and ultra-pure water for semi-conductor industries, and some of them are still used even today with advantage of high chlorine resistance.



Three technologies promise to reduce the energy requirements of desalination by up to 30 percent. The race is on to see which will take the lead.

FORWARD OSMOSIS
Water molecules migrate by natural osmosis, without energy input, into an even more concentrated "draw solution," whose special salt (green) is then evaporated away by low-grade heat.
On the market: 2010-2012

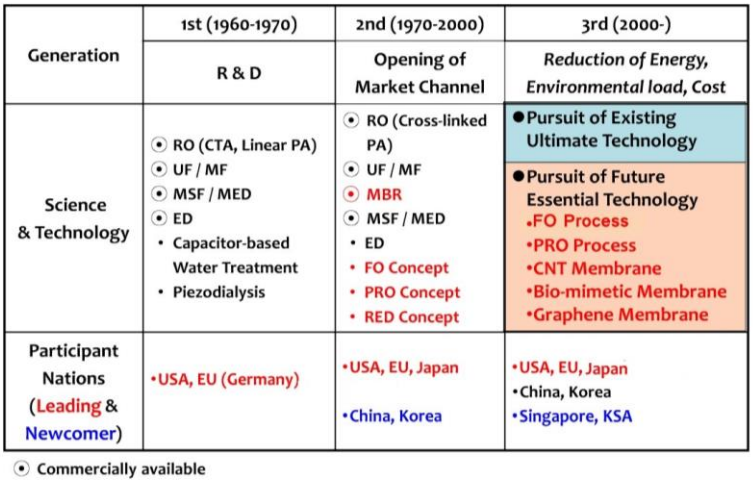
CARBON NANOTUBES
An electric charge at the nanotube mouth repels positively charged salt ions. The uncharged water molecules slip through with little friction, reducing pumping pressure.
On the market: 2013-2015

BIOMIMETICS
Water molecules pass through channels made of aquaporins, proteins that efficiently conduct water in and out of living cells. A positive charge near each channel's center repels salt.
On the market: 2013-2015

in National Geographic, April 2010

Fig. 3. The progress o future essential membrane technology [2].

Table 1
History of water treatment research.



Generation	1st (1960-1970)	2nd (1970-2000)	3rd (2000-)
	R & D	Opening of Market Channel	*Reduction of Energy, Environmental load, Cost*
Science & Technology	⊙ RO (CTA, Linear PA) ⊙ UF / MF ⊙ MSF / MED ⊙ ED • Capacitor-based Water Treatment • Piezodialysis	⊙ RO (Cross-linked PA) ⊙ UF / MF ⊙ MBR ⊙ MSF / MED • ED • FO Concept • PRO Concept • RED Concept	● Pursuit of Existing Ultimate Technology ● Pursuit of Future Essential Technology •FO Process •PRO Process •CNT Membrane •Bio-mimetic Membrane •Graphene Membrane
Participant Nations (Leading & Newcomer)	•USA, EU (Germany)	•USA, EU, Japan •China, Korea	•USA, EU, Japan •China, Korea •Singapore, KSA

⊙ Commercially available

2.2. Liner aromatic polyamide hollow fiber membrane

Many intensive and continuous research and development efforts were made mainly in the United States and Japan to meet the demands from markets, and many inventions and breakthroughs in membrane materials and configurations had been also suggested to improve the membrane performances higher and higher.

To overcome the problems of cellulose acetate membranes, which were comparatively low water permeability and substance removal performance, many synthetic polymeric materials for reverse osmosis were proposed. However, all of them were unsuccessful except for linear aromatic polyamides with pendant sulfonic acid groups. This material was invented by DuPont Company, which was fabricated into very fine hollow fiber membrane, and the modules of this membrane were designated “B-9” and “B-10” [6]. They showed high rejection performance, which could be used for single stage seawater desalination with low water recovery, and were widely used for seawater or brackish water desalination and recovery of valuable materials, such as electric deposition paints, until DuPont withdrew from market in 2001.

3. Membrane research at 2nd generation – composite membrane

3.1. Cellulose acetate membrane

Other approaches to obtain a high performance reverse osmosis membrane had been taken by some institutes and companies from 1970’s [3]. Many methods to prepare composite membranes had been proposed. In the early stage, very thin film of cellulose acetate polymer coating on a substrate such as a porous substrate of cellulose nitrate was tried, but in spite of their efforts, only Riley group of Gulf General Atomics (Koch Membrane Systems at present) industrially has succeeded in manufacturing.

3.2. Cross-linked aromatic polyamide membrane

Next approach was using the interfacial condensation reaction to form a very thin polymeric layer onto a substrate. Morgan firstly proposed this method [7] and then Scala and Van Hauben actually applied it to obtain a reverse osmosis membrane [8]. Cadotte invented a high performance membrane using an *in-situ* interfacial condensation method [9]. In his method, the interfacial condensation reaction between polymeric polyamine and monomeric poly functional acid halides or isocyanates was carried out on a substrate material to deposit a thin film barrier layer.

Then, many companies succeeded in developments of composite membranes using this method, and the membrane performance has been drastically improved up to now. Composite membrane of cross-linked fully aromatic polyamide is already regarded as the most popular and reliable material of RO membrane [5, 10].

Typical aromatic polyamide composite membrane is shown in Figure 4. Thickness of cross-linked aromatic polyamide should be 0.2 μm and membrane surface has protuberance structure. In this membrane formation by interfacial polycondensation, amine reacts with acid halide in the organic phase by diffusion. This diffusion of the amine in aqueous phase is very important [10].

3.3. Cross-linked polyether membrane

Some of the composite membranes were succeeded in industrial fabrication by another party. Riley and co-workers developed cross-linked polyether membranes designated as PA-300 and RC-100, which showed high salt rejections and productivity [6]. The RC-100 membrane is known as the first composite RO membrane to be majorly installed in real seawater desalination plant in Saudi Arabia.

Otherwise, many methods to prepare RO membranes had been proposed. The summary of RO membrane materials including the related information of membrane morphology, module configuration and their suppliers is shown in Table 2 [3].

Most membranes developed in 1st and 2nd generations are also as listed in Table 2 [3]. It is very interesting to find only two commercially successful membranes, such as the cellulose acetate asymmetric membrane and cross-linked aromatic polyamide membrane in the market up to now.

The fabrication methods are also very important factor to get new high performance membranes as listed in Figure 5. As result, only two approaches are remained even now;

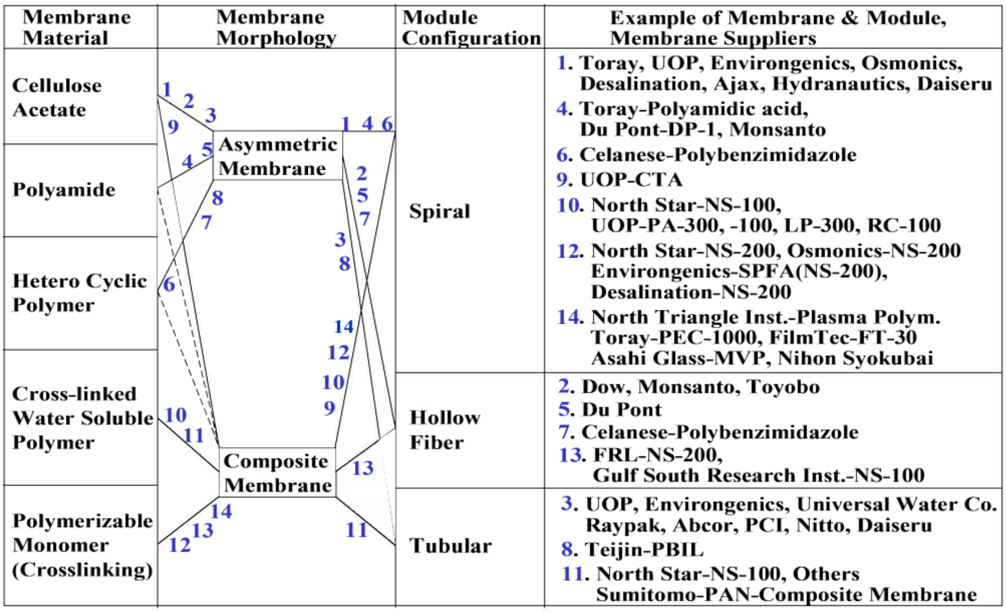
(1) Dry-Wet Coating (Phase separations) by Polymer Coating
(2) Interfacial polymerization by in situ polymerization methods

Cross-sectional structures of CA asymmetric membrane and cross-linked polyamide composite membrane (UTC-70) by Toray Ind. Inc. are shown in Figure 6 [3].

3.4. Application of RO membrane

RO membranes have been widely used for water treatment such as production of ultra-pure water and boiler pure water for industrial use, seawater and brackish water desalination for drinking water and agricultural water use, wastewater reclamation for industrial, agricultural and indirect drinking water use, etc. The expansion of RO membrane applications promoted the redesign of suitable membrane material with taking into consideration of the chemical structure, membrane configuration, chemical stability and ease of fabrication. Along with the improvements of the membranes, historically performance changes of brackish water RO membrane is shown in Figure 7.

Table 2
Primary membrane materials, morphology and configuration for RO membrane [3].



Membrane Material	Membrane Morphology	Module Configuration	Example of Membrane & Module, Membrane Suppliers
Cellulose Acetate	Asymmetric Membrane	Spiral	1. Toray, UOP, Environgenics, Osmonics, Desalination, Ajax, Hydranautics, Daiseru 4. Toray-Polyamidic acid, Du Pont-DP-1, Monsanto 6. Celanese-Polybenzimidazole 9. UOP-CTA 10. North Star-NS-100, UOP-PA-300, -100, LP-300, RC-100 12. North Star-NS-200, Osmonics-NS-200 Environgenics-SPFA(NS-200), Desalination-NS-200 14. North Triangle Inst.-Plasma Polym. Toray-PEC-1000, FilmTec-FT-30 Asahi Glass-MVP, Nihon Syokubai
Polyamide	Composite Membrane	Hollow Fiber	2. Dow, Monsanto, Toyobo 5. Du Pont 7. Celanese-Polybenzimidazole 13. FRL-NS-200, Gulf South Research Inst.-NS-100
Hetero Cyclic Polymer		Tubular	3. UOP, Environgenics, Universal Water Co. Raypak, Abcor, PCI, Nitto, Daiseru 8. Teijin-PBIL 11. North Star-NS-100, Others Sumitomo-PAN-Composite Membrane
Cross-linked Water Soluble Polymer			
Polymerizable Monomer (Crosslinking)			

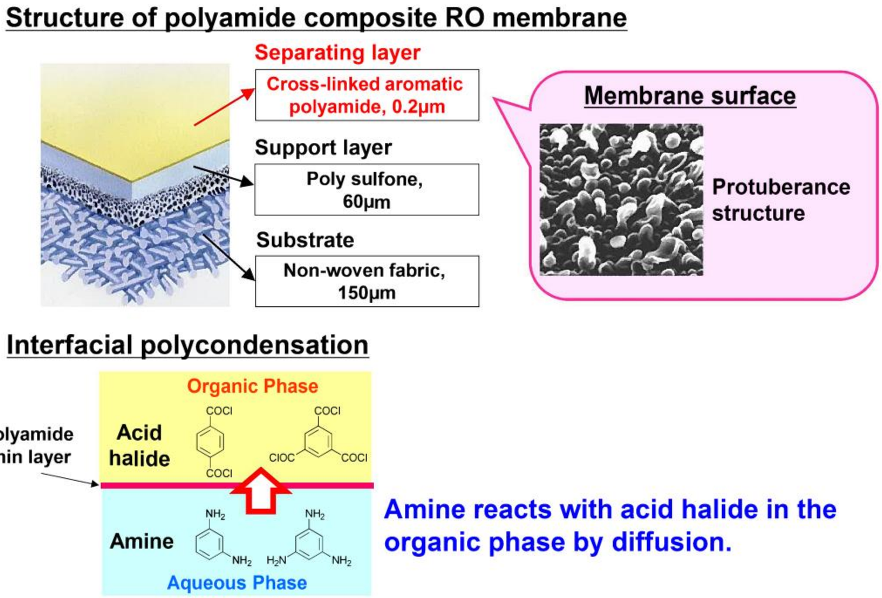


Fig. 4. Polyamide composite RO membrane [10].

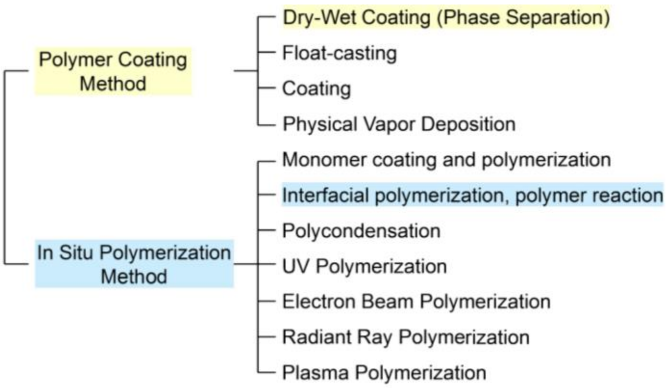


Fig. 5. Classification of thin-layer fabrication method.

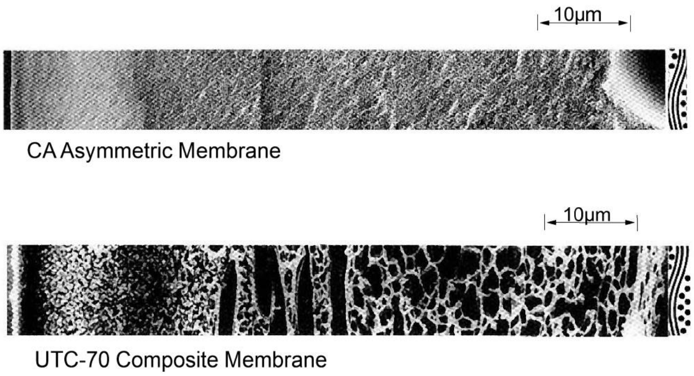


Fig. 6. Cross-sectional structures of CA asymmetric membrane and cross-linked polyamide composite membrane by Toray Industries Inc. [3].

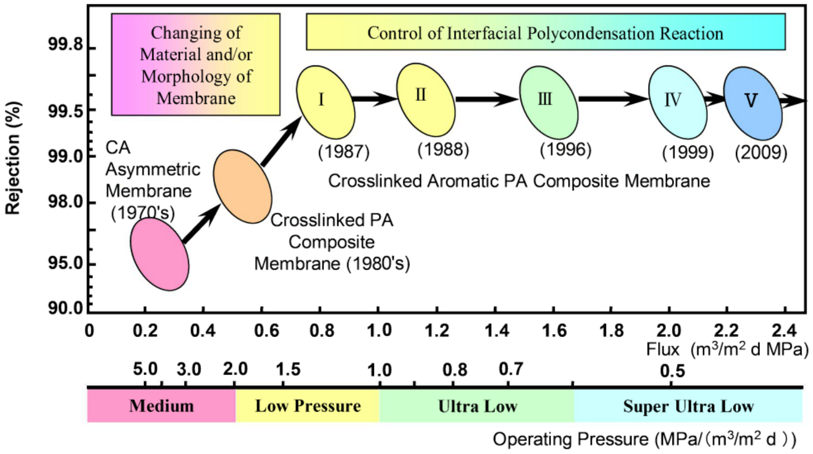


Fig. 7. Performance changes in brackish water RO membrane.

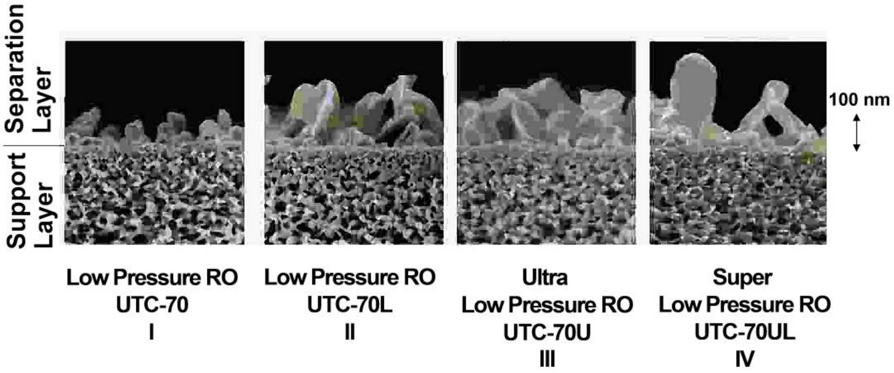


Fig. 8. Micro-structure of brackish RO membranes [3].

Figure 7 shows the progress of low-pressure membrane performance in brackish water desalination in these four decades, including industrial water treatment such as ultra-pure water production. At the first decade from 1970 many efforts was devoted for developing high performance membrane materials and improving the membrane performance, and as a result of that membrane performance was well improved with a new developed material of cross-linked aromatic polyamide by appropriate modification of membrane morphology and fabrication technology. The membrane developed at 1987, which is depicted as I in Figure 8, with 4 or 5 times larger water productivity and 5 times lower salt passage (100-rejection (%)) than those of cellulose acetate membranes [5]. After 1987, based on the adoption of cross-linked fully aromatic polyamide composite membrane, the performance of brackish water RO membrane has been rapidly improved [10]. Typical change of microstructure of brackish RO membrane is shown in Figure 8 [3]. As could be observed, higher performance membranes (IV) in Figure 8 have thicker separation layer.

4. Pursuit of ultimate membrane technology

4.1. Structural analysis of RO membrane

As for water quality, the regulation of boron concentration has recently been regarded [10–13] because it is known that reproductive toxicity was shown in per oral administration to laboratory animals [14]. Boron exists as boric acid in seawater, and its concentration is 4–7 mg/L which is 20 times or higher than that of surface water. And it is difficult for RO membrane to remove the boric acid in water by following reasons. Firstly, the molecular size of boric acid is so small that it is difficult to remove by size exclusion. Secondly, since boric acid has pKa of 9.14–9.25; it is not ionized in the natural seawater with pH of 7–8 and dissociates at pH 9 or more [15, 16], the boron rejection by the electric repulsive force between boric acid and the membrane cannot be expected in neutral condition. WHO proposed the boron regulation to be below 2.4 mg/L at the end of 2008, however, the required boron concentration value in product water of each plant actually depends on the system design of plant, the usage of water, the policy of country, and so on.

Although the ideal SWRO membrane should have both high water permeability and high solute removal performance, there is usually a trade-off potential between the increase of water permeability and the decrease of solute rejection rate (equal to salt permeability). However, when a pore in RO membrane, which is a space within polymers, is assumed, the performance of RO membrane must be controlled by its size and quantity. Namely, solutes in water are excluded by the size of pore (to reduce salt permeability), and water permeability depends on the quantity of pore (to increase water permeability). In order to obtain further excellent performance, scientific researches with a point on the molecular structure and solute transport mechanism in RO membrane are necessary. Thus, we need more scientific research on membrane itself.

Since there is a trade-off relation between the water permeability and the boron removal, the developments of seawater RO membranes are executed according to three courses: *i*) Extremely high boron removal performance, *ii*) High water permeability with high boron removal performance and *iii*) Extremely high water permeability. In order to obtain further excellent performances which are suitable for respective courses, scientific researches with a point on the solute transport mechanism in RO membrane are needed.

4.2. Overview of “mega-ton water system” project

As stated above, RO technology is widely used all over the world to secure sustainable water source and to solve the water issues. It is interesting to note that the size of water treatment plants with RO technology shows a certain trend. Figure 9 shows the productivity of top 20 RO plants constructed in each year. According to the advancement of technologies, plant scale has been getting larger for a few decades, and huge water treatment plants capable of producing more than 100,000 m^3 of freshwater per day (equivalent to the daily supply for around 400,000 people) have been built after the 2000s. However, water problems continue to worsen and even larger plants with producing capacity of 1,000,000 m^3/day will be required in the foreseeable future. This has led to urgent needs of developing innovative water treatment systems which address the problems caused by the construction of mega plants, such as massive energy consumption and environmental destruction [17-19]. Compared to small plants, it is possible to design an optimum layout through effective accumulation of components in the mega plants. This layout can decrease total foot print of the plants, increase energy efficiency and decrease environmental impact. Therefore, technological developments for mega plants were required. In 2010, FIRST (Funding program for world-leading innovative R&D on science and technology) program “mega-ton water system” started. "Mega-ton water system” project, which was a cutting-edge research and development project in Japan, was carried out to develop 21st century key technologies on water treatment for sustainable management of water environment and for low-carbon path [17-19]. The project aimed at developing innovative water treatment technologies, which are necessary for realizing mega plants such as bio friendly pretreatment, low-pressure multi-stage RO system, low pressure

SWRO membrane, highly efficient energy recovery device, high pressure resin pipes, etc., and proposing a system for mega plant.

5. Research target

5.1. Progress of RO membrane analysis

The membrane technologies have made great progress and their key technologies are as follows;

1) *Materials*: Molecular design of high performance materials suitable for each separation mode
2) *Morphology*: Morphological design of high performance membranes
3) *Element/Module*: Element and module design to maintain high performance of membrane
4) *Membrane Process*: Plant design and operation technology

It is reported that cross-linked aromatic polyamides are most popular materials for RO membrane since they show excellent substance removal performance and durability under operation. A composite RO membrane is usually composed of three layers, namely a separating functional layer, a polysulfone porous support layer and a polyester non-woven fabric substrate as shown in Figure 4. In the separating functional layer, the semipermeable membrane with RO function is formed by cross-linked aromatic polyamide. The other two layers play a role of supporting the structure of the separating functional layer against operating pressure. Therefore the function of RO membrane depends upon the physicochemical and chemical property of the cross-linked aromatic polyamide as shown in Figure 10.

Should be the unsolved issues in RO membrane fine structure;

1) Membrane pore will be present or not. If the pore is present, what is the pore size?
2) Fine membrane morphology such as membrane inside structure, membrane thickness is not clear at the time of 1970-1980.

These issues had remained until 2000's due to lack of appropriate analytical method as shown in Figure 11. Following new advancements based on basic and scientific approach afforded the solution to the problems in Figure 11, author continued to focus on pore size estimation for RO membranes.

5.2. Structure analyses of RO membrane surface

Pore size analysis method of polymeric membrane is compared with the others in Figure 12. Only positronium annihilation lifetime spectroscopy (PALS) can be useful to detect the real pore size of the cross-linked aromatic polyamide membranes.

Pore size analyses for separating functional layer in composite SWRO membranes were conducted with PALS study [20], and membranes showed pore sizes in the range of 5.6-7.0 Å (see Figure 13). It was considered that this range of pore in the separating functional layer would characterize the membrane property. Furthermore, the correlation between pore size of RO membrane and boron permeability was revealed as shown in Figure 14. It was suggested that the pore size in separating functional layer was regarded as one of the major factors to control solute removal performance of RO membranes [21]. In addition, the molecular dynamics simulations based on the chemical structures established by 13C NMR study were performed. Optimized models were calculated from the initial structures, which contained the estimated amount of water, as shown in Figure 15. In order to determine pore sizes in the polymer models, the Connolly surface calculations were performed to water-deleted optimized polymer models. The calculation results showed that the pore sizes were estimated as 6-8 Å, which were well agreed with those of measured from PALS analyses (see Figure 16). Thus, it was confirmed that the reliability of these polymer models.

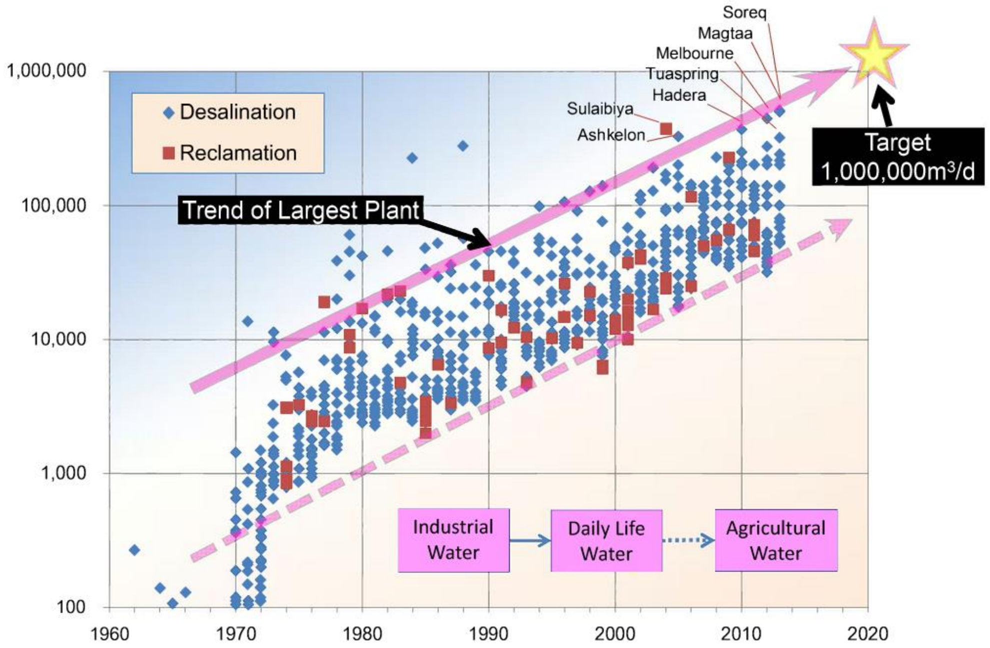


Fig. 9. Change in size of SWRO plant and WW reclamation RO plant.

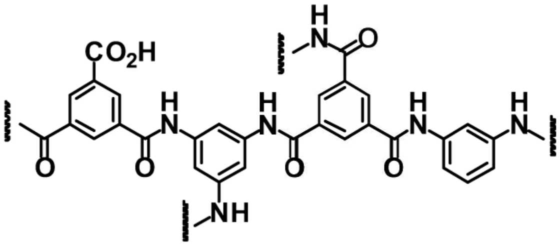
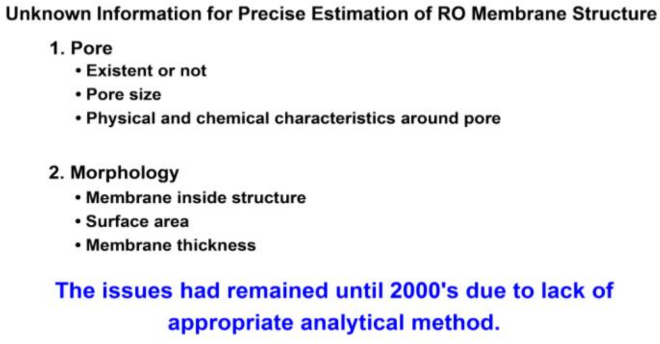


Fig. 10. Presumptive chemical structure of polyamide.


Unknown Information for Precise Estimation of RO Membrane Structure

1. Pore
   - Existent or not
   - Pore size
   - Physical and chemical characteristics around pore

2. Morphology
   - Membrane inside structure
   - Surface area
   - Membrane thickness

The issues had remained until 2000's due to lack of appropriate analytical method.

Fig. 11. Unsolved issues in RO membrane structure in 1970's.

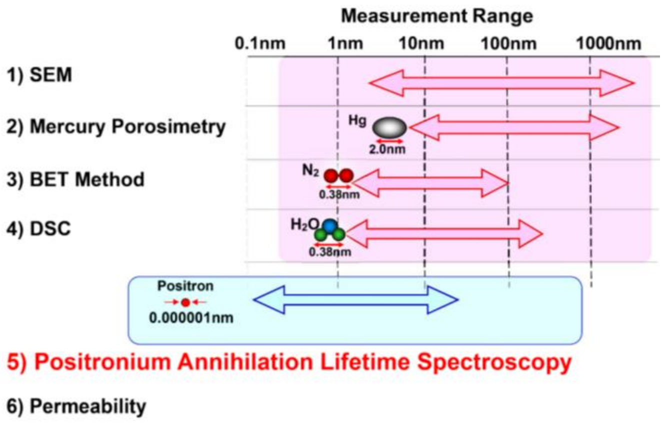


Fig. 12. Pore size analysis method of polymeric membranes.

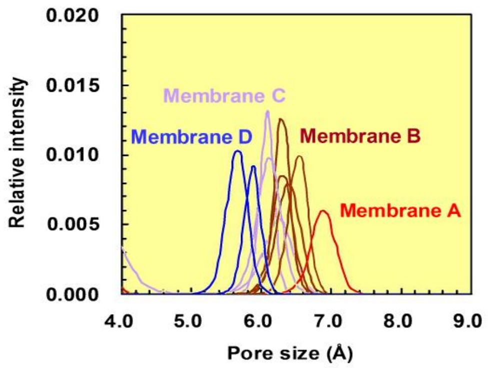


Fig. 13. Pore size distribution.

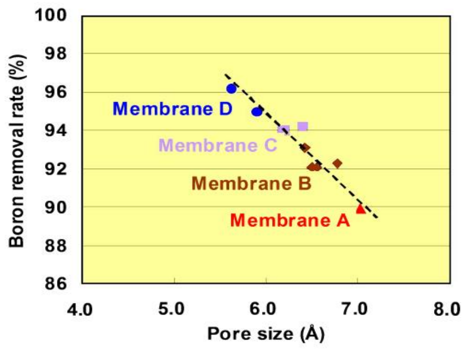
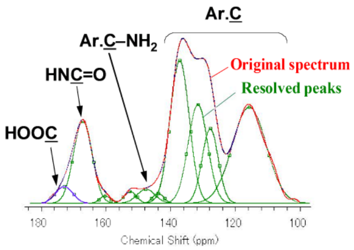


Fig. 14. Pore size and Boron permeability.



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

Fig. 15. DD/MAS 13C NMR spectrum of RO membrane and mol ratio of each moiety.

The comparison between pore size of RO membrane and typical removal substances, such as boric acid and sodium ion, were conducted by calculation with considering their hydrated state as shown in Figure 17. Sodium ion was strongly hydrated, however, boric acid was hardly hydrated in neutral pH region. Consequently, the pore size of RO membrane was almost same as a hydrated sodium ion, but was a little larger than a non-hydrated boric acid. It was considered that it's reason why permeability of boron is larger than that of NaCl. Only a little difference in the size between pore and substances, including the difference between hydrated states, must dominate the removal performance.

5.3. Morphology analysis of RO membrane surface

According to the past studies for membrane surface morphology, it is well known that RO membrane surface of which the material of separating functional layer is cross-linked aromatic polyamide is covered with protuberance structure. And it was hypothesized that this structure would largely contribute to water permeability of the RO membrane. However, analyses by conventional SEM methods gave only information from an appearance as shown in Figure 18. It was not completely clear how this structure takes part in the performance of membrane. In order to obtain reliable information, more precise estimation of the protuberance structure was needed.

The analysis with TEM through a special treatment of membrane for preserving the structure gave clear image of cross section of protuberance, and it enabled a quantification of surface morphology. According to the image, since the inside of protuberance was proved as a cave-like, the contribution of this structure to water permeability was agreeable. Through this analysis, new parameters for the estimation of the inside structure, membrane surface area which was represented by the ridgeline length of protuberance, and membrane thickness were obtained. With the comparison between membranes having different water permeability, larger membrane surface area or thinner membrane thickness showed higher water permeability. Consequently, the correlation between the morphology of protuberance and water permeability of membrane was revealed.

Thus, the structural study relating to the RO membrane performance of solute removal and water permeability has been greatly progressed by the pore size and the morphology analyses.

The structural analysis with TEM through a special treatment of membrane for preserving the structure gave precise image of cross section of protuberance, and it enabled a quantification of surface morphology compared with SEM image.

According to the precise image, since the inside of protuberance was proved as a cave-like structure, the contribution of this structure to water permeability was agreeable. With the comparison between membranes having different water permeability, larger membrane surface area or thinner membrane thickness showed higher water permeability. This result opens the door of new transport mechanism of water through the protuberance. Consequently, the correlation between the morphology of protuberance and water permeability of membrane was revealed. Thus, the total structural study relating to the RO membrane performance of solute removal and water permeability has been greatly progressed by the pore size and the morphology analyses.

5.4. Progress of RO membrane performance

On the basis of this knowledge, Toray has developed new RO membrane elements with high solute rejection performance for SWRO processes [22]. The lineup of RO membrane elements for SWRO processes is shown in Table 3.

TM820C shows 93% of boron rejection rate with high TDS rejection rate. TM820E and TM820M have both high boron rejection rate and high water productivity. TM720C is utilized for second stage in multi-stage process due to the tolerance of alkaline agent. And most recently, TM820R, which has achieved coexistence of high TDS and boron rejection rate and high water productivity, has been released. TM820R has already been run with high performance and stable operation. Additionally, extremely high rejection membrane TM820K and further energy-saving membrane TM820L are shown as new lineup products.

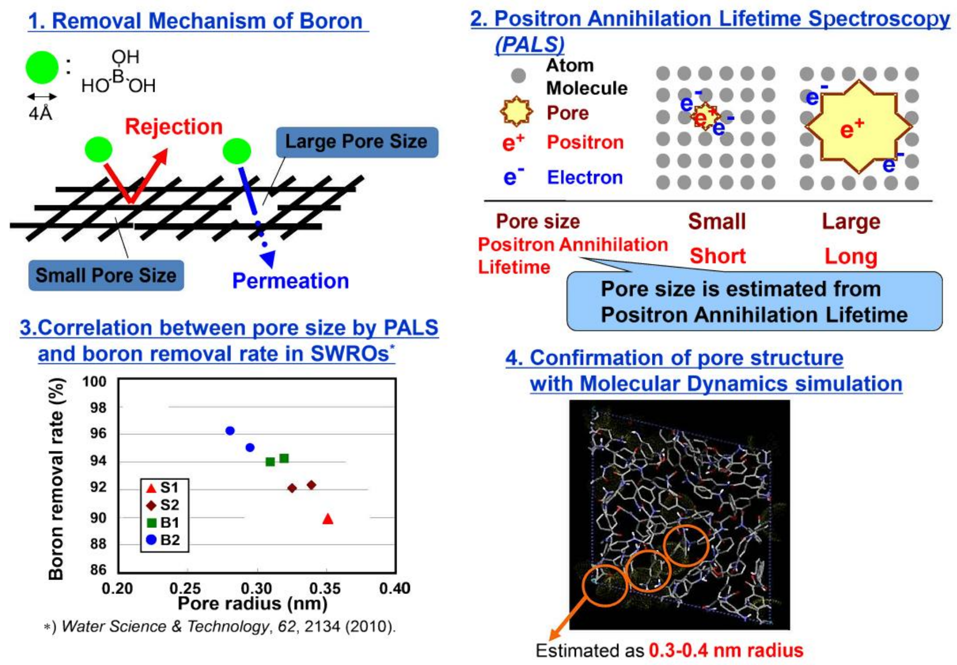


Fig. 16. Pore size estimation for RO membranes.

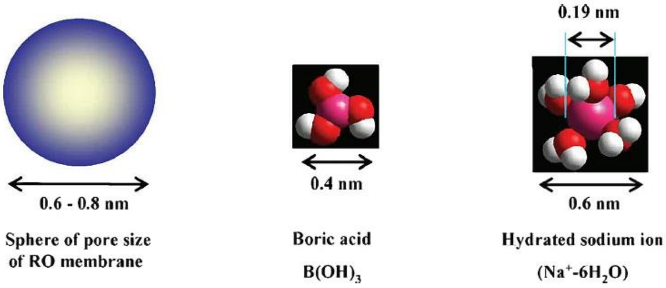


Fig. 17. Comparison between pore size of RO membrane and typical removal substances.

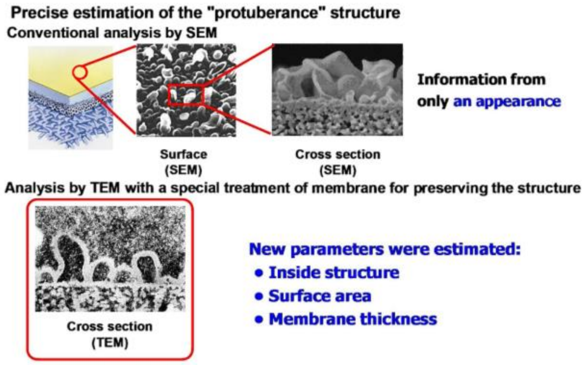


Fig. 18. Morphology analysis by TEM.

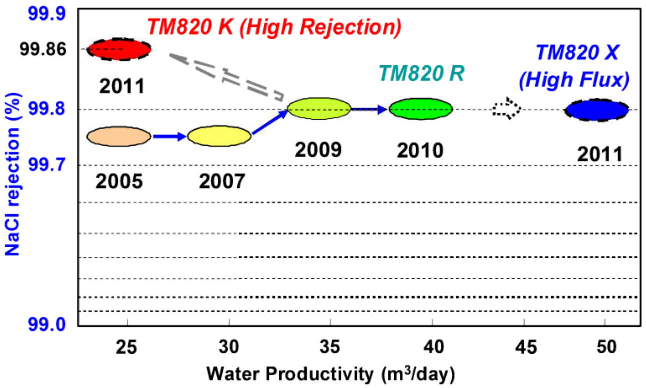


Fig. 19. Recent progress and future prospect of SWRO membrane performance [18].

These scientific approaches afford the tremendous progress of Seawater RO membrane performance measured at 6.0MPa. As shown in Figure 19. The innovative improvements, which have made high water productivity and high solute rejection coexist, have been accomplished through utilizing the results of fundamental researches. Boron rejection has been increased from 90% to 93%, on the other hand, water permeability (flux) has been drastically improved with keeping high TDS Rej (>99.75%) over 5 years. Progress of seawater RO membrane performance contributes to the many large SWRO plants by the water production cost down and less energy consumption.

Table 3
Products lineup of Toray's SWRO

Product	Specifications		
	TDS rej. (%)	Water Productivity (GPD, (m^3/d))	Boron rej. (%)
TM820A	**99.75**	**6,000 (22.7)**	**93**
TM820C	**99.75**	**6,500 (24.6)**	**93**
TM820E	**99.75**	**7,500 (28.0)**	**91**
TM820S	**99.75**	**9,000 (34.1)**	**90**
TM820R	**99.80**	**9,400 (35.6)**	**95**
TM720C	**99.2**	**8,800 (33.3)**	**94**
TM820K	***99.86***	***6,400 (24.2)***	***96***

6. Pursuit of ultimate performance by advanced membrane technology

6.1. Membrane research at "mega-ton water system" project–innovative low pressure SWRO membrane

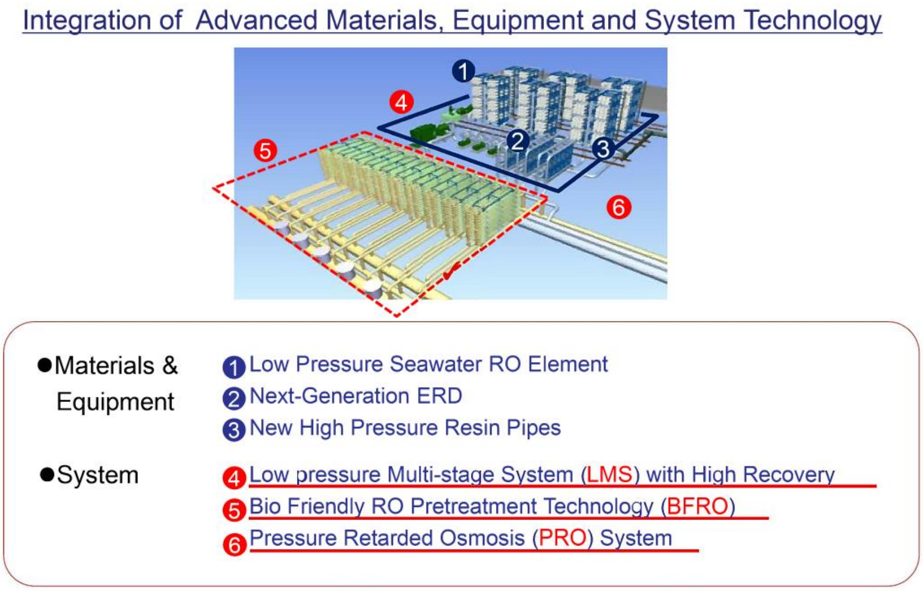
"Mega-ton water system" project, which was a cutting-edge research and development project in Japan, was carried out to develop 21st century key technologies on water treatment for sustainable management of water environment and for low-carbon path [17-19, 23, 24]. The project aimed at developing innovative water treatment technologies, which are necessary for realizing mega plants such as bio friendly pretreatment, low-pressure multi-stage RO system, low pressure SWRO membrane, highly efficient energy recovery device, high pressure resin pipes, etc., and proposing a system for mega plant. The summary and noteworthy outcome of this project were as shown in Figure 20 and 21 [18].

6.2. Low pressure SWRO membrane technology

In order to develop innovative low pressure seawater RO membrane, fine structural analyses of functional layer of RO membrane is inevitable. Regarding the surface morphology of SWRO membranes, it was hypothesized that protuberance structure on the membrane surface would largely contribute to water permeability of the membranes as shown in Figure 22 [18].

However, the conventional SEM analysis methods had provided limited information from an appearance as shown in Figure 23.1 (left-hand) [18]. It was not completely clear how the protuberance structure took part in the performance of SWRO membranes. In order to obtain reliable information, more precise estimation of the protuberance structure was needed. In this study, a modified treatment procedure that enabled to detect the fine protuberance structure as measuring in wet condition was developed. It seemed that the shape of the protuberances treated by the modified method was well kept even in a high vacuum environment for microscopic analyses as shown in Figure 23.1 (right-hand) while a change of shape in the case of the conventional method was found [18].

Transmission electron microscope (TEM) was used to analyze the cross-section structure of RO membranes. Membrane samples for the observation were prepared with a special technique to preserve the shape of the protuberances. Analyses by TEM gave clear images as shown in Figure 23.2 (left-hand) [18]. TEM images indicated that the protuberances had a cave-like inside structure and enabled to quantitatively analyze the surface morphology of RO membranes. Surface area of RO membrane was estimated from the ridgeline length of the protuberances and thickness of the polyamide layer was estimated as thickness of the protuberance skin. Additional analyses by a scanning transmission electron microscope with electron energy loss spectroscopy (STEM-EELS) provided an elemental mapping image as shown in Figure 23.2 (right-hand) [18], which enabled to confirm that polyamide does not exist inside of the protuberances. It was found that the skin part of the protuberances is a real polyamide layer which is about 200 nm in height and 20 nm in thickness.



Integration of Advanced Materials, Equipment and System Technology

- Materials & Equipment
  ① Low Pressure Seawater RO Element
  ② Next-Generation ERD
  ③ New High Pressure Resin Pipes
- System
  ④ Low pressure Multi-stage System (LMS) with High Recovery
  ⑤ Bio Friendly RO Pretreatment Technology (BFRO)
  ⑥ Pressure Retarded Osmosis (PRO) System

Fig. 20. "Mega-ton water system" technology [18].

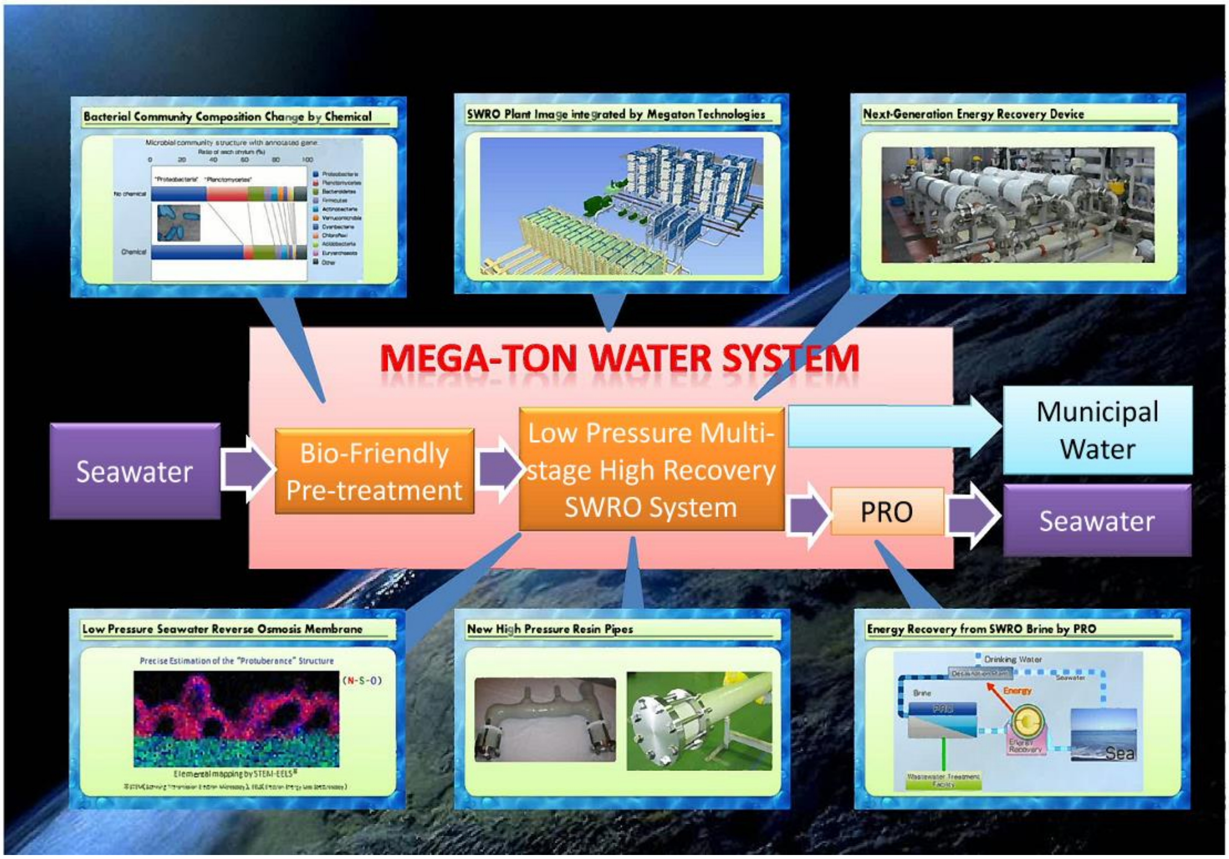
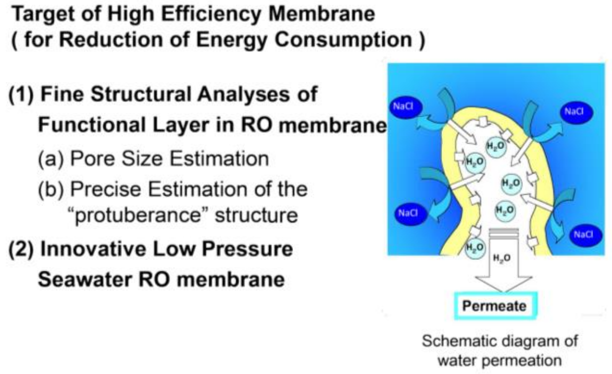


Fig. 21. Indispensable ket technology of "Mega-ton water system" for 21st century.



Target of High Efficiency Membrane
(for Reduction of Energy Consumption)

(1) Fine Structural Analyses of Functional Layer in RO membrane
- (a) Pore Size Estimation
- (b) Precise Estimation of the "protuberance" structure

(2) Innovative Low Pressure Seawater RO membrane

Fig. 22. RO membrane separation mechanism [18].

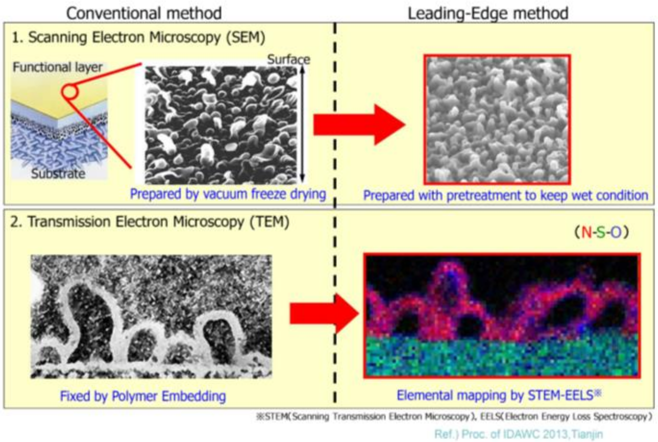


Fig. 23. Technologies for precise estimation of "Protuberant structure" [18].

Through the TEM analyses, two structural parameters i.e. surface area and thickness which contribute to RO membrane performance were obtained [17, 18]. With the comparison of morphologies between RO membranes having different water permeability, membrane with a larger surface area or smaller thickness showed higher water permeability. Furthermore, the number of the protuberances also affected the surface area and water permeability. Thus, the correlation between the morphology of protuberance structures and water permeability of RO membrane was revealed. Utilizing the relationships, the ultimate membrane microstructure which maximized not only water permeation but also salt rejection was pursued in this project [18].

The pore structure with an appropriate size and number for effective salt removal and the protuberance structure with a larger surface area and smaller thickness for higher water productivity were desired. Membrane fabrication process, particularly the step of interfacial polycondensation reaction to form polyamide layer, was studied for realizing the desired structure. The interfacial polycondensation reaction was affected by various conditional factors such as monomers, solvent, additives, temperature, pH, and support layer. A fine polycondensation technique had been successfully established by precisely controlling the conditional factors, and an innovative low pressure SWRO membrane was prepared in this project.

With the abovementioned knowledge based on the fundamental analytical researches, the structure of the polyamide layer for further excellent performance was designed. Energy saving effect of the new membrane was estimated in comparison with Toray's standard SWRO membrane as shown in

Figure 24 [18]. The standard SWRO membrane was manufactured by the conventional fabrication method and it was commercially available. The performance of each SWRO membrane itself was measured without energy recovery in the laboratory test. The conventional SWRO membrane needs more than 6.0 MPa as an operating pressure to show the membrane performance of 99.85% salt rejection and 1.0 $m^3/m^2/d$ water permeability for desalination of 3.5% seawater. On the other hand, new innovative low pressure SWRO membrane shows the similar excellent performance at the feed pressure lower than 5.0 MPa, and the result indicates that the new SWRO membrane will contribute to significant energy reduction in seawater desalination process. [18, 19].

In the schematic view of structure of polyamide composite RO membrane, membrane thickness of crosslinked aromatic polyamide should be 200nm (0.2 μm) at the time of 80's, and membrane surface have the protuberance after the "Mega-ton Water System" project, we learn that the real membrane thickness is 20 nm (0.02 μm). And precise consideration for the interfacial condensation is very important to discuss the real membrane formation and its structure.

Energy saving effect of the new membrane was estimated in comparison with Toray's standard SWRO membrane as shown in Figure 24. The standard SWRO membrane was manufactured by the conventional fabrication method and it was commercially available. The performance of each SWRO membrane itself was measured without energy recovery in the laboratory test.

7. "Mega-ton water system"

7.1. Research objective

"Mega-ton Water System" Project is aiming to develop 21st century key technology for water treatment with Japanese initiative and contribute to global water problem solutions.

The vision of the "Mega-ton water system" is sustainable desalination and reclamation [17-19].

The missions are 1) energy reduction (20-30%); 2) water production cost reduction (50%).

Water cycle in "Mega-ton Water System" is shown in Figure 25 and separated into two parts:

1. Seawater RO(SWRO)system
2. Seawater RO system with PRO system

7.1.1. Seawater RO (SWRO) system

Research objectives of Seawater (SWRO) system are the same as the missions of "mega-ton water system".

7.1.2. Seawater RO system with PRO system

SWRO is one of the promising processes to solve the water shortage problem, because it claims lower cost and less energy. However, there are still several concerns like concentrated brine released from SWRO plant, sometimes causing environmental problems. And SWRO plants with more cost effective and less energy consumption are demanded, especially on the mega scale SWRO plant. In the "Mega-ton water system", PRO was focused on as a process that could recover energy from the salinity difference between the concentrated brine and fresh water and, simultaneously, as a candidate to solve the environmental problem caused by the SWRO brine released back into the sea. PRO was proposed by Loeb.et al. 40 years ago [25-28]. They conducted experiments of the PRO process at the Dead Sea in [28] and the Great Salt Lake in the USA [29], where both concentrated saline and fresh water were available. Their results were not so good because these experiments employed semi-permeable membranes that were not for forward osmosis, but for SWRO. Dr. Takeo Honda of National Institute of Advanced Industrial Science and Technology (AIST) showed that net output power from PRO, generated power minus consumed power, would be positive if membrane module is properly modified [30]. Recently, some research teams, especially from Europe, are studying the process to recover salinity gradient power like WETSUS in the Netherlands [31]. In Japan, Kyowakiden Industry Co., Ltd., since 2002, has conducted fundamental and operational research with the cooperation of Kyushu University, Nagasaki University and Tokyo Institute of Technology. In 2002, a PRO bench scale plant using membrane modules was constructed near Fukuoka SWRO Facility. From 2007 to 2009, PRO possibilities were investigated and the first prototype plant of PRO using commercial type membrane module was constructed under the support of NEDO, New Energy and Industrial Technology Development Organization. In 2010, the prototype PRO plant joined the "Mega-ton Water System" project [32].

- Target of PRO

The recent reports and discussions related PRO are very confusing. Thus, the target of PRO in "Mega-ton Water System" project is clearly limited to the energy recovery from the SWRO brine [32]. PRO energy recovery system & process flow diagram is shown in Figure 26.

7.2. Research conducted

7.2.1. Seawater RO (SWRO) system

Major innovative technologies of "mega-ton water system" are composed of six technologies as follows [17-19] (see Figure 20):

- Materials & equipment

① Low-pressure seawater RO element
② Next-generation energy recovery device (ERD)
③ New high-pressure resin pipes

- System

④ Low-pressure multi-stage system (LMS) with high rec
⑤ Bio-friendly RO pretreatment technology (BFRO)
⑥ Pressure-retarded osmosis (PRO) system

By integration of advanced devices and system technology, indispensable key technology of the "Mega-ton Water System" for the 21st century is composed (see Figure 21).

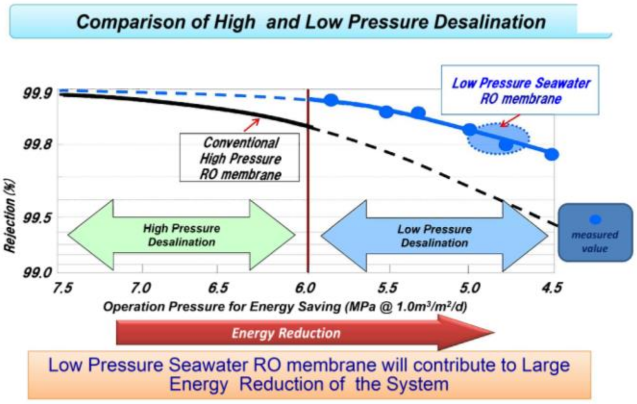


Fig. 24. Innovative low pressure seawater RO membrane.

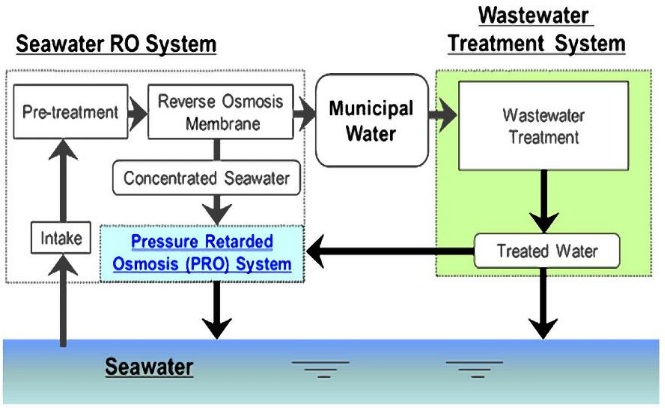


Fig. 25. Water cycle in "Mega-ton water system".

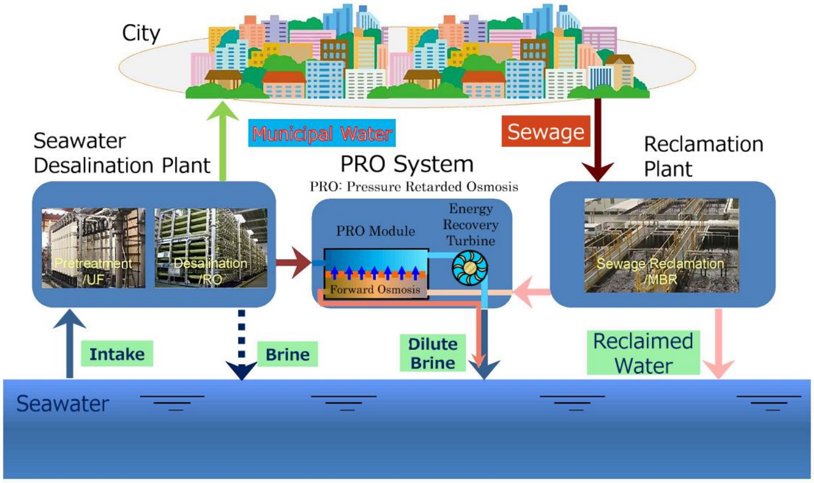


Fig. 26. Pressure retarded osmosis (PRO) system.

7.2.2. Seawater RO system with PRO system

Outline of PRO energy recovery system flow is shown in Figure 27. The PRO plant can be constructed near or in urban area.

1) Prototype PRO Plant

Prototype PRO plant was constructed and operated using 8 pieces of 10-inch PRO module (Toyobo CTA Hollow Fiber) as shown in Figure 27. Brine from the SWRO facility was used as draw solutions (DS: 460 m^3/day) and low salinity water from the regional wastewater treatment facility, was used as feed solution (FS: 420 m^3/day) after removing any potential foulants of the membranes using UF unit and chemical, before introducing into PRO units.

The prototype plant has achieved 13.5 W/m^2 of the maximum membrane power density per surface area using 10 inch membrane modules. On the other hand, lab-scale plant showed 17.1 W/m^2 with 5 inch module as shown in Figure 28 [32].

2) Long term operations at PRO prototype plant

Long term test operations at the PRO prototype plant was carried out over one year as shown in Figure 29. The osmotic flow rate through membrane was found to depend on the temperature, which seasonally varied as traditional membranes. Also found was little decline in osmosis flow rate between the beginning and one year after the test launch, even though continuing the same membrane modules. This means that we have successfully produced fresh water from the treated waste water of enough quality for the PRO system, employing some traditional pre-treatment method and that commercial scale operation would be possible for long period. [32]. In case of PRO field test (450m^3/day) is confirmed over 1 year (see Figure 29).

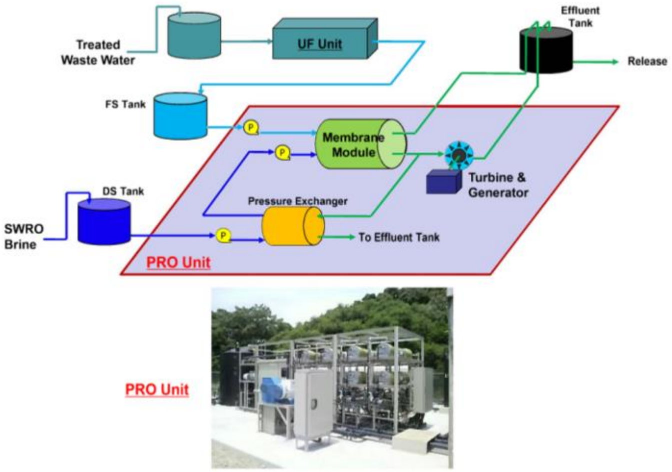


Fig. 27. PRO system flow.

7.3. Results

7.3.1. Seawater RO (SWRO) system

7.3.1.1. Low pressure seawater RO membrane

By using the results of precise estimations of “protuberance structure,” the innovative low-pressure seawater RO membrane is developed. This membrane can be operated below 4.5 MPa compared to 6.5 MPa operation of conventional membranes under the conditions of same membrane performance. The low-pressure seawater membrane will greatly contribute to large energy reductions of the system (see Figure 30) [17-19].

7.3.1.2. The low-pressure multi-stage high-recovery seawater RO system (LMS)

The low-pressure multi-stage high-recovery seawater RO system (LMS) (see Figure 20) [19] is also developed by using a low-pressure seawater membrane. This system allows 20% energy reduction due to low-pressure operation (see Figure 31). Water production cost is reduced by 50% due to high-recovery operation up to 60%.

7.3.2. Energy reduction by “mega-ton water system” without PRO system

Mega-ton water technology system without PR system established 20% energy reduction with Mega-ton size plant as shown in Figure 32 [17, 18].

7.3.3. Seawater RO system with PRO system: Energy reduction by “Mega-ton water system” with PRO system

Specific energy consumption rates in case of 3.5% seawater as total dissolved salts concentration are compared in the process (1) conventional process, (2) “Mega-ton Water System” without PRO and (3) “Mega-ton Water System” including PRO as shown in Figure 27. 20% energy reduction is established in (2) and 30% energy reduction in (3) compared to (1) as shown in Figure 32.

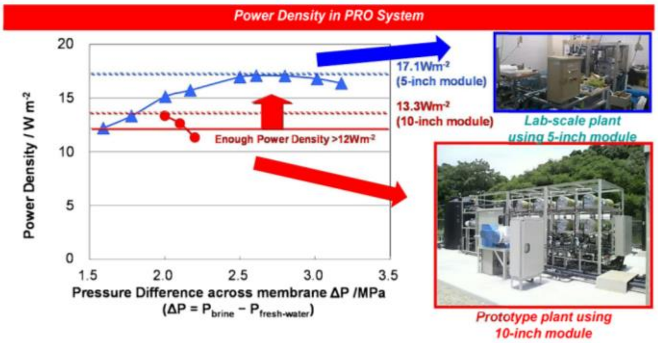


Fig. 28. Achieved power density at prototype plant and lab-scale plant.

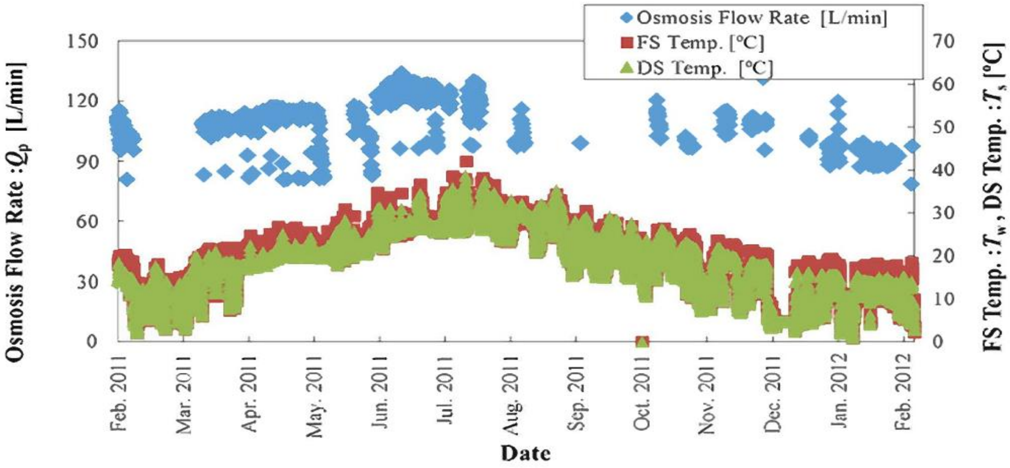
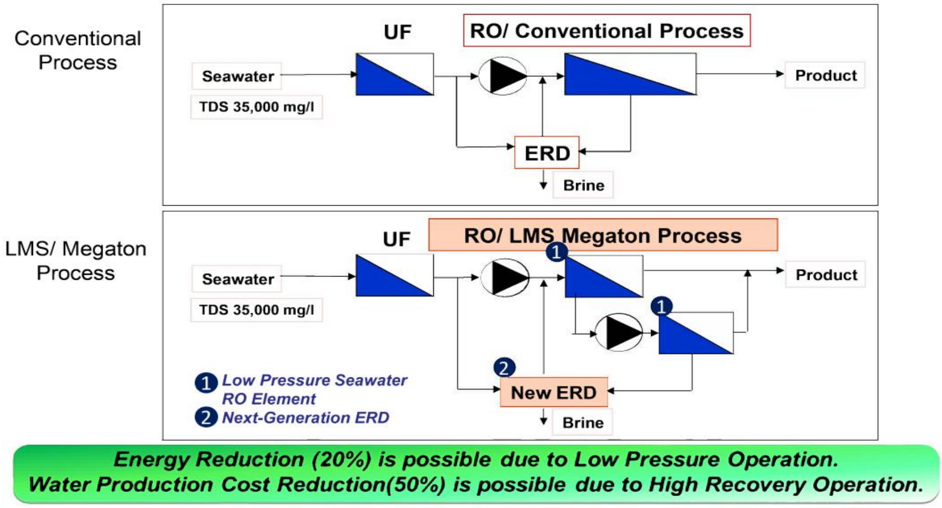
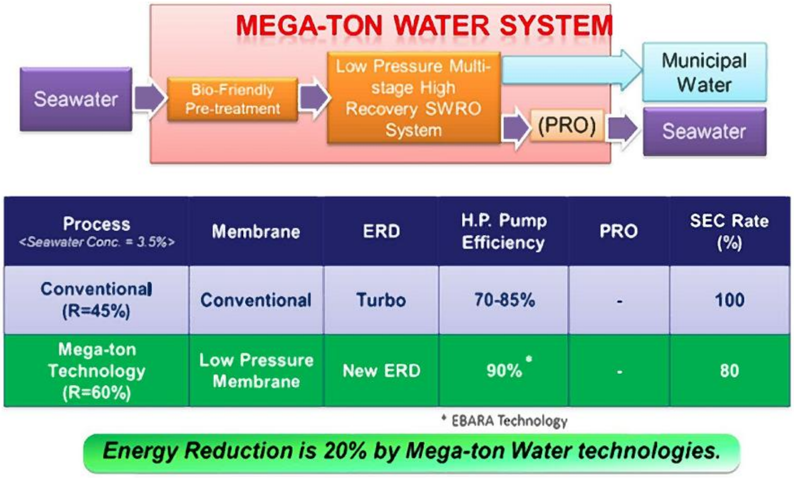


Fig. 29. Long term prototype PRO plant operation over 1 year.



Energy Reduction (20%) is possible due to Low Pressure Operation.
Water Production Cost Reduction(50%) is possible due to High Recovery Operation.

Fig. 30. Comparison of flow diagrams of conventional process and LMS process.

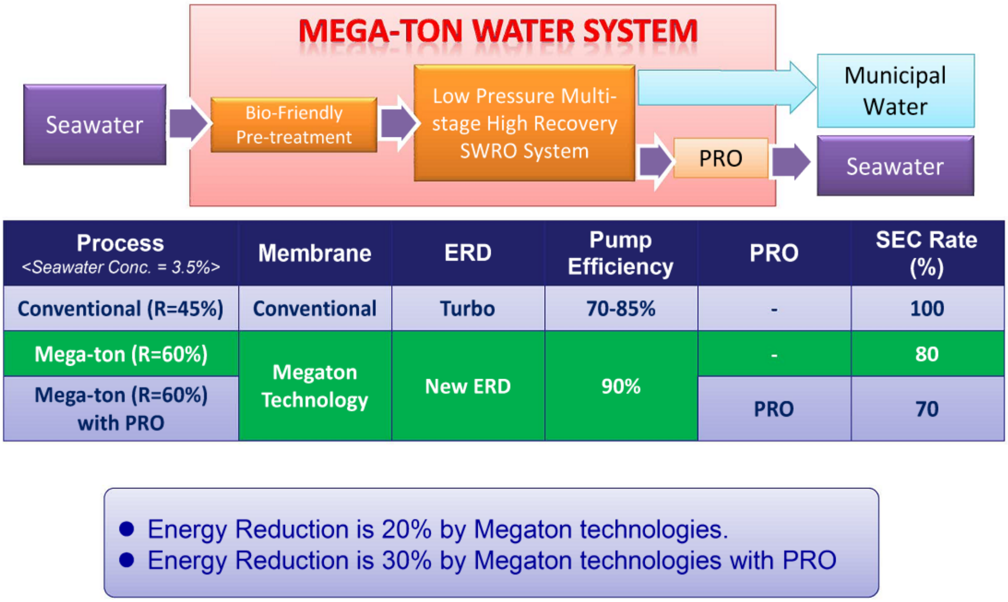


Process <Seawater Conc. = 3.5%>	Membrane	ERD	H.P. Pump Efficiency	PRO	SEC Rate (%)
Conventional (R=45%)	Conventional	Turbo	70-85%	-	100
Mega-ton Technology (R=60%)	Low Pressure Membrane	New ERD	90%*	-	80

* EBARA Technology

Energy Reduction is 20% by Mega-ton Water technologies.

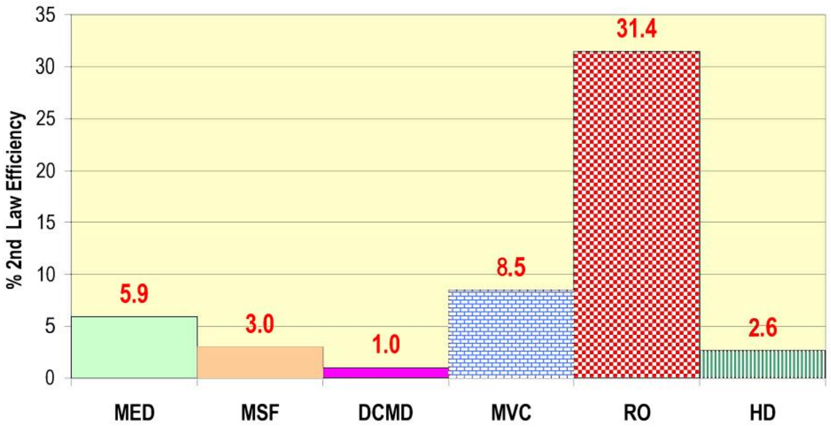
Fig. 31. Energy reduction by Mega-ton water technology without PRO system.



Process <Seawater Conc. = 3.5%>	Membrane	ERD	Pump Efficiency	PRO	SEC Rate (%)
Conventional (R=45%)	Conventional	Turbo	70-85%	-	100
Mega-ton (R=60%)	Megaton Technology	New ERD	90%	-	80
Mega-ton (R=60%) with PRO				PRO	70

- Energy Reduction is 20% by Megaton technologies.
- Energy Reduction is 30% by Megaton technologies with PRO

Fig. 32. Energy reduction by Mega-ton water technology with PRO system.



MED, Multi-Effect Distillation
MSF, Multi-Stage Flush
DCMD, Direct Contact Membrane Distillation
RO, Conventional SWRO with ERD
HD, Humidification/dehumidification
MVC, Mechanical Vapor Compression

Showing: RO is the method of lowest irreversibility & highest Entropic Efficiency

* Mistry, McGovern, Theil, Summsers, Zubair & Lienhard. Entropy **13**(2011)1829-1864

Fig. 33. Thermodynamic evaluation of seawater desalination methods.

8. Pursuit of future essential technology

The researches on these subjects are really reminded the time of research at 1970-1980 for the research activities, but much difference in these days, many research are handled by the academic groups [33].

The current status of future essential technology summarized in Table 4 at the time of March 15, 2016. From Table 4, FO is no more RO technology alternative, FO is used as pretreatment of SWRO or posttreatment of SWRO. And actual state of innovative membrane material is shown in Table 5. From Table 5, we have to take care those innovative membrane materials from FO, PRO, Biomimetic (Aquaporin), CNT are all hybrid (embedded) of polyamide.

Thus, it is very important to clarify the effect of embedded material to the performance. We have to learn from the history of the membrane performance and also patent situation listed in Table 6. Recent hybrid (embedded) of polyamide look to belong to others of Table 6. The additives of Table 6 are really included or not included to the protulance layer of polyamide as shown in Fig. 23.2 (Right side).

Another comparison from the point view of thermodynamic evaluation shown in Figure 33, it is very clear that RO is most efficient to the other seawater desalination method.

Best way for FO, Bio-mimetic, CNT and graphene are looking for the new niche market in which reverse osmosis is not applied.

9. Conclusions

1. Long history of water treatment and membrane research over 50 years, Reverse osmosis membrane process has been remained and continued to be main desalinations technology.
2. Although reverse osmosis membranes have been changed according to the generation of research, cellulose acetate asymmetric membrane and

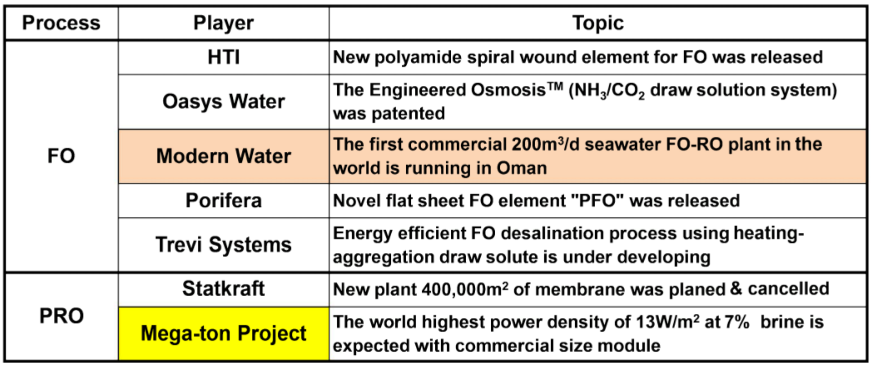
cross-linked aromatic polyamide composite membranes are commercially used in the real market even now.
The latter polyamide should be major membrane in many applications of RO membranes.

3. As Pursuit of Ultimate Membrane Technologies, undissolved problems in 1970-1980 are solved by the progress of analytical method such as “PALS” and Scanning Transmission Election Microscope: Election Energy Loss Spectroscopy (SEM-EELS).
From these scientific researches, new innovative low pressure SWRO membrane is designed and realized.
4. As Pursuit of Future Essential Technology, FO, PRO, CNT. Biomimetic membrane should be studied aggressively but so far only PRO done by “Mega-ton Water System” project should be very cross to commercial phase to recover energy from the SWRO brine but the others are not mainstream for reverse osmosis alternative.

Acknowledgment

The part of “Mega-ton Water System” research in this report is granted by Japanese Society for the Promotion of Science(JSPS) through the “Funding Program for World-Leading Innovative *R&D* on Science and Technology (FIRST Program)” initiated by the council for Science and Technology Policy (CSTP). The author’s deep appreciation goes to NEDO that supports “Mega-ton Water System” project

Table 4
The current status of the progress of future essential technology



Process	Player	Topic
FO	HTI	New polyamide spiral wound element for FO was released
	Oasys Water	The Engineered Osmosis™ (NH_3/CO_2 draw solution system) was patented
	Modern Water	The first commercial 200m³/d seawater FO-RO plant in the world is running in Oman
	Porifera	Novel flat sheet FO element "PFO" was released
	Trevi Systems	Energy efficient FO desalination process using heating-aggregation draw solute is under developing
PRO	Statkraft	New plant 400,000m² of membrane was planed & cancelled
	Mega-ton Project	The world highest power density of 13W/m² at 7% brine is expected with commercial size module

Table 5
The actual state of innovative membrane material

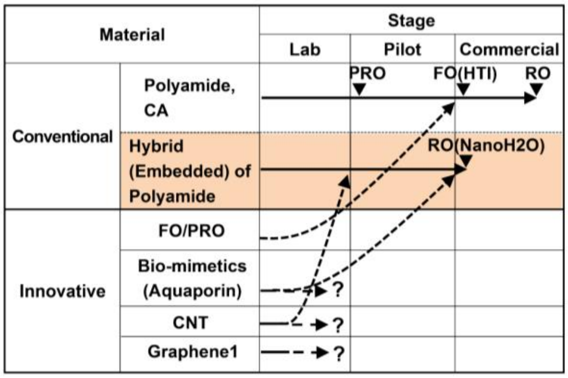
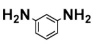
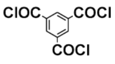
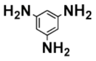
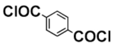


Table 6
Improvement of polyamide by interfacial polycondensation

Player	Amine	Acid halide	Additive
FilmTec (Dow)	 MPDA	 TMC	-
Toray	MPDA  TAB	TMC  TPC	-
Hydranautics (Nitto Denko)	MPDA	TMC	Surfactant or PVA
Others	MPDA	TMC	Zeolite CNT Aquaporin etc

References

[1] N. Tambo, Infrastructure Development under Decreasing Population - A Design from Expansion to Shrink -, Japan Society of Civil Engineers, Tokyo, 2002 (Japanese).

[2] K. E. Lange, The Big Idea Get The Salt Out, in National Geographic. A Special issue. Water – Our Thirsty World, April 2010. pp. 32-36.

[3] M. Kurihara, H. Tomioka, Preparation of Industrial RO, NF Membranes and Their Membrane Modules and Applications, in: E. Drioli, L. Giorno (Eds.), Comprehensive Membrane Science and Engineering vol. 2, Elsevier: Oxford, U.K., 2010, pp. 23-34 .

[4] S. Loeb, S. Sourirajan, Sea water demineralization by means of an osmotic membrane, Adv. Chem. Ser. 38 (1963) 117-132.

[5] M. Kurihara, Y. Himeshima, T. Uemura, Crosslinked Aromatic Polyamide Ultra-thin Composite Membrane from 1,3,5-Triaminobenzene, Proceedings of ICOM '87, Tokyo, 1987, pp.428.

[6] R. J. Petersen, Composite reverse osmosis and nanofiltration membranes, J. Membr. Sci. 83 (1993) 81-150.

[7] P. W. Morgan, Condensation Polymers: By Interfacial and Solution Methods, in Polymer Reviews Vol. 10, Wiley, New York, 1965, 561 pp.

[8] R. C. Scala, D. F. Berg, D. Ciliberti, Interface condensation desalination membrane. U. S. Patent 3,744,642. July 10 1973.

[9] J. E. Cadotte, Interfacially synthesized reverse osmosis membrane, U. S. Patent 4,277,344, July 7 1981.

[10] M. Kurihara, T. Uemura, Y. Himeshima, K. Ueno, Y. Bairinji, Development of Crosslinked Aromatic Polyamide Composite Reverse Osmosis Membrane, J. Chem. Soc. Japan. 1994 (1994) 97-107.

[11] M. Taniguchi, M. Kurihara, S. Kimura, Boron reduction performance of reverse osmosis seawater desalination process, J. Membr. Sci. 183 (2001) 249–267.

[12] M. Taniguchi, Y. Fusaoka, T. Nishikawa, M. Kurihara, Boron removal in RO seawater desalination, Desalination 167 (2004) 419–426.

[13] K. Fukunaga, M. Matsukata, K. Ueyama, S. Kimura, Reduction of boron concentration in water produced by a reverse osmosis sea water desalination unit, Membrane 22 (1997) 211–216.

[14] WHO, Guidelines for Drinking Water Quality, 3rd ed., 2004: http://www.who.int/water_sanitation_health/dwq/GDWQ2004web.pdf.

[15] M. Rodriguez, A.F. Ruiz, M.F. Chilon, D.P. Rico, Influence of pH in the elimination of boron by means of reverse osmosis, Desalination 140 (2001) 145–152.

[16] H. Hyung, J.-H. Kim, A mechanistic study on boron rejection by sea water reverse osmosis membranes, J. Membr. Sci. 286 (2006) 269–278.

[17] M. Kurihara, M. Hanakawa, Mega-ton Water System: Japanese national research and development project on seawater desalination and wastewater reclamation, Desalination 308 (2013) 131-137.

[18] M. Kurihara, T. Sasaki, K. Nakatsuji, M. Kimura, M. Henmi, Low pressure SWRO membrane for desalination in the Mega-ton Water System, Desalination 368 (2015) 135-139.

[19] N. Kishizawa, K. Tsuzuki, M. Hayatsu, Low pressure multi-stage RO system developed in Mega-ton Water System for large-scaled SWRO plant, Desalination 368 (2015) 81-88.

[20] D. Dutta, B. N. Granguly, D. Gangopadhyay, T. Mukherjee, B. Dutta-Roy, General trends of positron pick-off annihilation in molecular substances, J. Phys. Condens. Matter 14 (2002) 7539.

[21] M. Henmi, Y. Fusaoka, H. Tomioka, M. Kurihara, High performance RO membranes for desalination and wastewater reclamation and their operation results, Water Sci. Technol. 62 (2010) 2134-2140.

[22] T. Uemura, K. Kotera, M. Henmi, H. Tomioka, Membrane technology in seawater desalination: History, recent developments and future prospects, Desalin. Water Treat. 33 (2011) 283-288.

[23] M. Kurihara, H. Takeuchi, FIRST Program "Mega-ton Water System" Development of Large-scale Water Treatment Systems for 21st Century, J. Japan Soc. Water Environ. 36 (2013) 11-14.

[24] B. McCann, T. Asano, Water21-Magazine of the International Water Association December 2011 (2011) 59.

[25] J. Bartram, Improving on haves and have-nots, Nature 452 (2008) 283–284.

[26] S. Loeb, Production of energy from concentrated brines by pressure-retarded osmosis: I. Preliminary technical and economic correlations, J. Membr. Sci. 1 (1976) 49–63.

[27] S. Loeb et al., Production of energy from concentrated brines by pressure-retarded osmosis: II. Experimental results and projected energy costs, J. Membr. Sci. 1 (1976) 249–269.

[28] S. Loeb, Energy production at the Dead Sea by pressure retarded osmosis: challenge or chimera? Desalination 120 (1998) 247–262.

[29] S. Loeb, One hundred and thirty benign and renewable megawatts from Great Salt Lake? The possibilities of hydroelectric power by pressure-retarded osmosis, Desalination 141 (2001) 85–91.

[30] T. Honda, F. Barclay, “The Osmotic Engine”, The Membrane Alternative, The Watt Committee on Energy, Report Number 21, 13 (1990) 105-129.

[31] S.E. Skilhagen, Osmotic power — a new, renewable energy source, Desalin. Water Treat. 15 (2010) 271–278.

[32] K. Saito, Power generation with salinity gradient by pressure retarded osmosis using concentrated brine from SWRO system and treated sewage as pure water, Desalin. Water Treat. 41 (2012) 114-121.

[33] H. F. Ridgeway, J. Orbell, S. Gray, Molecular simulations of polyamide membrane materials used in desalination and water reuse applications: Recent developments and future prospects, J. Membr. Sci. 524 (2017) 436-448.