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Membrane technology in seawater desalination: History, recent developments and future prospects

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ABSTRACT

RO membrane technologies have achieved great progress in last 50 years. In seawater RO desalination field, energy saving and water quality improvement have always been two major subjects. Today, the energy consumption of RO membrane treatment process is one fifth and the operation cost is less than one tenth, compared to those of 1970's. However, innovative membranes are still demanded to achieve lower cost, lower energy consumption and lower impact to the global environment such as brine discharge, disposal of chemicals using in pretreatment processes and so on. In order to obtain further excellent performance, Toray has been executing basic research for RO membranes on focusing physical and chemical properties through PALS (Positron annihilation lifetime spectroscopy) study, TEM (transmission electron microscopy) analysis, etc. Accordingly, many innovative high performance RO membranes have been produced, and TM820R, which has achieved coexistence of high solute removal and high water permeability, has recently been released. Further study for effective use of high performance RO membranes which will be obtained near future to apply to the various temperature and salinity of feed water was also conducted. With considering recommended flux to avoid fouling, it was estimated that high flux membrane was suitable for low temperature and low salinity, and high rejection membrane was suitable for high temperature and high salinity. In this presentation, the prospects of attaining novel RO membranes including their histories and recent topics of desalination technologies will be introduced.

Keywords: Desalination; Energy saving; Reverse osmosis; Seawater; Water quality

1. Introduction

1.1. Requirement for energy-saving and water quality improvement

Population explosion and human industrial activities have been causing huge consumption of water resources and water pollution. Membrane technologies are regarded as the most powerful tools to solve these problems, since they make it possible to supply high-grade water with low cost and low energy consumption. Especially in desalination fields, RO membranes have been widely applied to not only seawater desalination but also brackish water desalination including industrial and wastewater reclamation. Today, their commercial markets are spreading rapidly and world widely.

Seawater is one of the most important water resources due to its availability. Many large seawater RO (SWRO) desalination plants have already been running in the world. Energy saving and improvement of water quality have always been two major subjects in SWRO desalination. At the point of energy saving, the average energy

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consumption in SWRO plants has been reduced to one fifth for these 40 years [1]. This has arisen from the remarkable technical advancements on membrane, pump and power recovery device. However further technical progress to reduce more energy consumption is still required. As for water quality, the regulation of boron concentration has recently been regarded [2–5] because it is known that reproductive toxicity was shown in per oral administration to laboratory animals [6]. 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 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 [7,8], 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 between the increase of water permeability and the decrease of solute rejection rate as shown in Fig. 1. 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, and water permeability depends on the quantity of pore. 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.

1.2. Structure analyses of RO membrane

Cross-linked aromatic polyamides are most popular materials for a separating functional layer in a composite RO membrane since they show excellent substance removal performance and durability under operation [9]. 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 Fig. 2. 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 separating functional layer against operating pressure, but no RO functions appear. Therefore, the function of

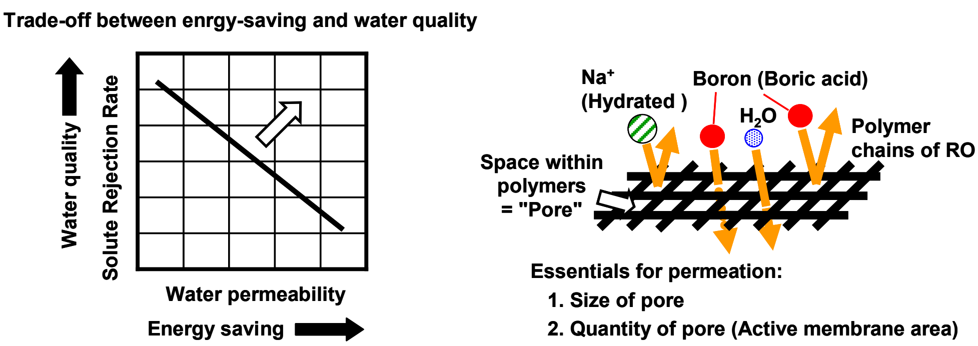

Fig. 1. Concept of RO membrane performance improvement.

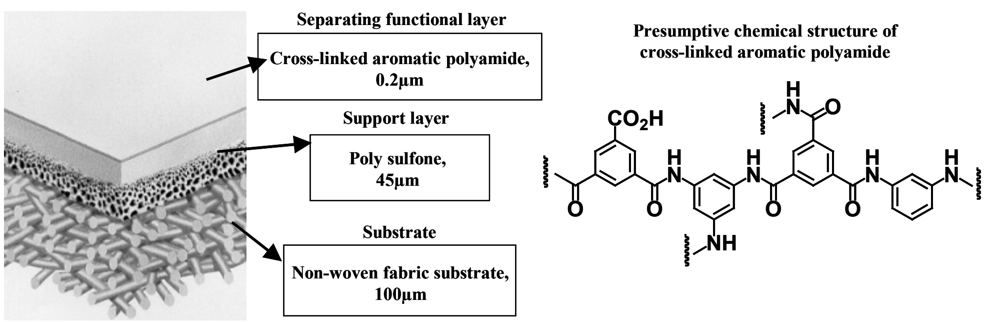

Fig. 2. Structure of composite RO membrane and chemical structure of cross-linked polyamide.

RO membrane depends upon the physical and chemical property of the cross-linked aromatic polyamide.

Recently, pore size analyses for separating functional layer in composite SWRO membranes were conducted with PALS study, and every membrane showed pore sizes in the range of 5.6–7.0 Å. It was considered that this range of pore in the separating functional layer would characterize the property as RO membrane. Furthermore, the correlation between pore size of RO membrane and boron permeability was revealed. Obviously, the boron permeability increases according to the pore size. 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 [10–12].

Then, the molecular dynamics simulations based on the established chemical structures by ^{13}C NMR study were performed. Optimized models were calculated from the initial structures, which contained the estimated amount of water. In order to know 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 by PALS analyses. Thus, it was confirmed that the reliability of these polymer models. 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 Fig. 3. 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 boron permeability 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.

1.3. 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 Fig. 4 (left-hand). 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.

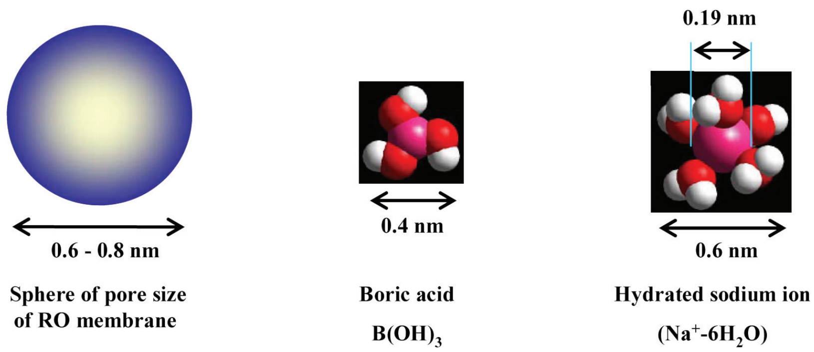

Fig. 3. Comparison between pore size of RO membrane and typical removal substances.

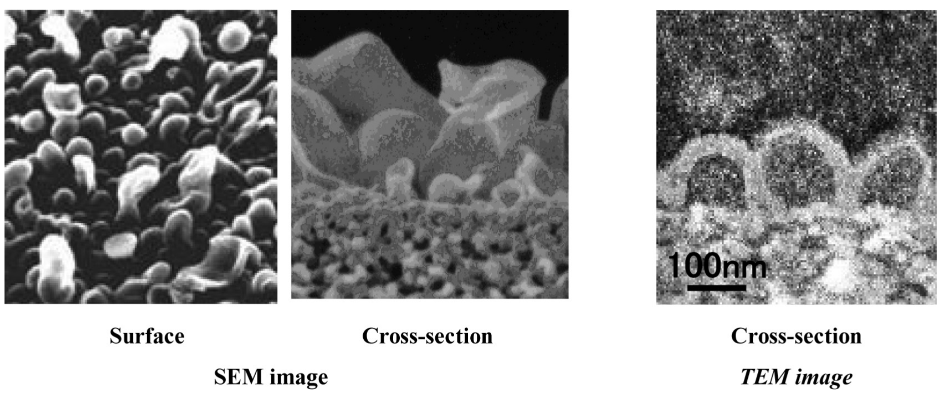

Fig. 4. Examples of protuberance image by conventional SEM and TEM with a special treatment.

The analysis with TEM through a special treatment of membrane for preserving the structure gave clear image of cross section of protuberance as shown in Fig. 4 (right-hand), 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 [13]. 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. In this paper, new energy-saving and high rejection membranes utilizing these studies and its utility study will be discussed.

2. Results and discussion

2.1 Energy-saving and high rejection SWRO membranes

Through the above-mentioned studies, a special molecular design, which controls physical and chemical property of RO membranes, is found to be necessary to develop further renovative membranes. On the basis of this knowledge, Toray has developed new RO membrane elements with high solute rejection performance for SWRO processes. The lineup of RO membrane elements for SWRO processes is shown in Table 1. TM820A shows 93% of boron rejection rate with high TDS rejection rate. TM820C, TM820E and TM820S 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 solute 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 TM820X are our interest as the next targets in the near future. In the following section, the utility study of these membranes will be discussed.

2.2. Utility study of high performance SWRO membranes

The recent progress and future prospect of Toray's SWRO membrane elements are depicted as shown in Fig. 5. The innovative improvements, which have made high water productivity and high solute rejection coexist, have been accomplished through utilizing the results of basic researches. Subsequently, the study for effective use of high flux membrane and high rejection membrane to apply to various temperature and salinity of feed water was conducted with calculations designed as Table 2. In SWRO operation, since too rapid flux causes fouling phenomena, a certain value of recommended flux is usually set to keep stable operation. In this case, the maximum flux to avoid fouling at lead element in a vessel was considered as under 30 LMH. Within this boundary condition, the element must be fully working with suitable operation pressure. As a result of the calculation, the suitable type of SWRO according to the quality of feed water is depicted as Fig. 6. The blue line represents the

Table 1
Products lineup of Toray's SWRO

Period	Product	Specifications*			Character
		TDS rej. (%)	Water productivity GPD, (m^3/d)	Boron rej. (%)	
Present	TM820A	99.75	6,000 (22.7)	93	High boron rejection
	TM820C	99.75	6,500 (24.6)	93	Energy saving High boron rejection
	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	Alkaline tolerance (pH10)
Near future	TM820K	99.87	6,000 (22.7)	96	Extremely high rejection
	TM820X	99.80	12,000 (45.4)	92	Further energy saving

*Test condition: except TM720C: feed water; NaCl 32,000 mg/L, boron 5 mg/L, temperature 25°C, pH 6.5, operating pressure 5.52 MPa, flow rate; 80 L/min, recovery rate 8%; TM720C: NaCl 1,500 mg/L, boron 5 mg/L, temperature 25°C, pH 10, operating pressure 1.03 MPa, flow rate; 80 L/min, recovery rate 15%.

Table 2
Calculation conditions and specifications of target elements

Designed condition	
Recovery (%)	40
Element number per vessel	7
Average flux (LMH)	16
Boundary condition	
Max. flux at lead (LMH)	<30

Target elements	NaCl Rej. (%) –flux (GPD)
TM820X (high flux)	99.80–12,000
TM820S (standard)	99.75–9,000
TM820K (high rejection)	99.87–6,000

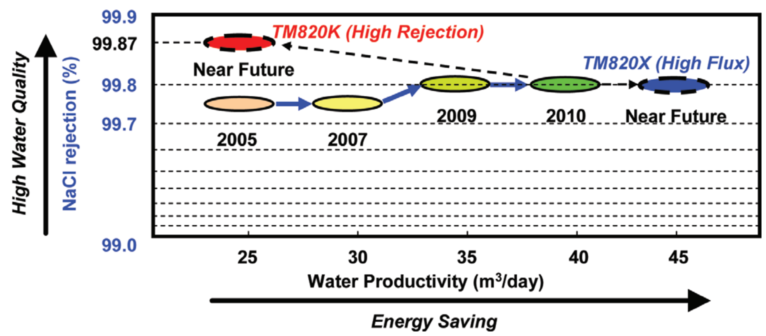

Fig. 5. Recent progress and future prospect of SWRO membrane performance.

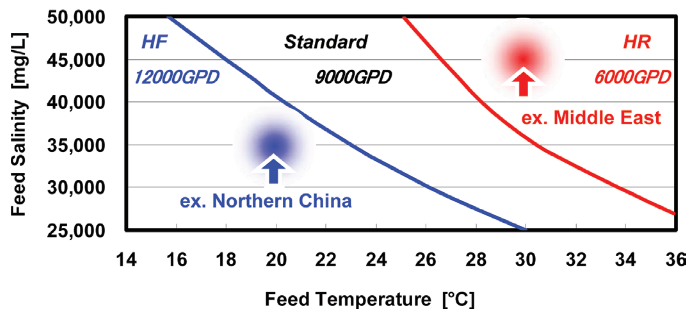

Fig. 6. Suitable type of SWRO for various temperatures and salinities of feed water.

borderline of high flux type membrane, and the red line represents that of standard type membrane.

Thus, it is shown that high flux membrane is suitable for low temperature and low salinity, and high rejection membrane is suitable for high temperature and high salinity. Furthermore, with postulating two sea areas, which were northern China and the Middle East, the projections of operation were estimated as shown in Table 3. In the case of northern China sea, high flux membrane exhibits lower operation pressure with higher flux than those of standard membrane. And in the sea of Middle East, high rejection membrane exhibits excellent product water salinity with appropriate flux, while standard membrane exceeds the borderline in the lead element flux. Consequently, it is suggested that both type of SWRO is useful to correspond to various feed water.

2.3. Recent topics of desalination technologies

Further studies on more innovative RO membranes has been still conducted, some of which are to understand the transport mechanism through RO membranes and to control membrane characteristics. It will be realized in the near future to produce the advanced membranes with desired performance.

In addition, new challenges for next generation of RO membranes have been started utilizing aquaporins and carbon nanotubes, which are expected as the basic materials of innovative RO membranes with advanced performance. And forward osmosis (FO) is gathering many interest as one of the strong candidates to resolve the energy consumption. However, since these studies are still in early stage, much time, effort, and a big break-

Table 3
Estimated projection in postulated sea areas

Feed water	Northern China (20°C, 35,000 mg/L)		Middle East (30°C, 45,000 mg/L)	
Type of SWRO	TM820X (high flux)	Standard	TM820K (high rejection)	Standard
Lead element flux (LMH)	28.6	25.5	25.5	31.5
Operation pressure (bar)	47	50	66	59
Product water salinity (mg/L)	180	130	200	338

through will be probably needed. RO membrane is going to be one of the most important technologies of water treatment for the time being, and the further research will be continued.

3. Conclusion

In SWRO desalination, energy saving and solute removal are always most significant matters, however, the coexistence of them is hard due to the correlation of trade-off. Structure analyses of polyamide composite RO membranes have been conducted in order to obtain the prospect for development of new membranes with further excellent performance. This 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. Consequently, the effective tools for estimating the physical and chemical property of RO membrane were acquired.

With utilizing these knowledge, a novel energy saving and high rejection membrane TM820R, which achieved coexistence of high solute rejection rate and high water productivity, was developed. TM820R has already been run with high performance and stable operation.

Additionally, the utility study for membranes of our next targets, which were extremely high rejection membrane TM820K and further energy-saving membrane TM820X, was conducted. With considering recommended flux to avoid fouling, it was estimated that high flux membrane was suitable for low temperature and low salinity, and high rejection membrane was suitable for high temperature and high salinity.

RO membrane will surely continue to be regarded as one of the most important technology of water treatment. Toray has a belief of contributing to solve the water problems through membrane technology, and will continue the further research.

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