Advanced RO Membrane Technology Based on Scientific Research for Seawater and Brackish water Desalination

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ABSTRACT

Global climate change and water shortage are serious issues we face. Sea Water RO (SWRO) membrane is one of the most powerful tools for solving the global water shortage, because seawater is the hugest water resource in the world. High energy saving and high water quality have been required in SWRO membrane desalination. From the viewpoint of energy saving, SWRO membrane with high water permeability is more preferable since lower pressure operation becomes to be possible. As for the water quality, boron removal is one of the most important issues, because it is known that reproductive toxicity was shown in per oral administration to laboratory animals, furthermore, boron is a typical substance which is difficult to be removed by RO membrane. Since there is a trade-off relation (Figure.1) 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.

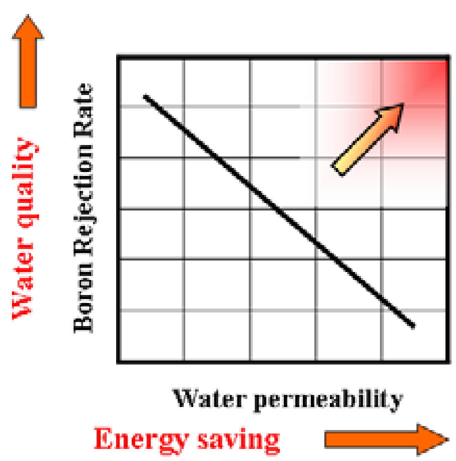


Fig1.Performance improvement of membrane

RO membrane technologies have made great progress in last 50 years. In seawater and brackish water desalination field, both energy saving and water quality improvement have been two major subjects. Today, the energy consumption in RO membrane seawater desalination process becomes less than one tenth, compared to those of 1970's, by progress of membrane and process technologies. However, advanced membranes and processes are still demanded to achieve lower cost, lower energy consumption and higher water quality.

In order to obtain further excellent performance, we have been executing fundamental research for RO membranes on investigating physical and chemical properties through PALS(Positron annihilation lifetime spectroscopy) study, Computer chemistry and TEM (Transmission electron microscopy) analysis, which has resulted in the advanced RO membranes with high flux, high rejection, excellent chemical durability and so on.

Keywords: reverse osmosis; seawater desalination; brackish water desalination

1 FUNDAMENTAL RESEARCH FOR RO MEMBRANE

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 [1]. 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 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 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 3.

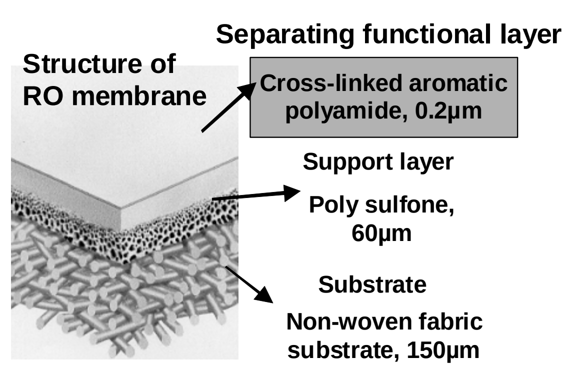


Figure2. Structure of RO membrane

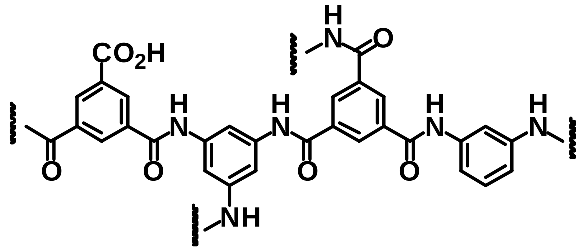


Figure3. Presumptive chemical structure of polymamide

Pore size analyses for separating functional layer in composite SWRO membranes were conducted with PALS study[2]-[4], and membranes showed pore sizes in the range of 5.6 - 7.0 Å (Figure 4). 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 5. 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[3][4][5].

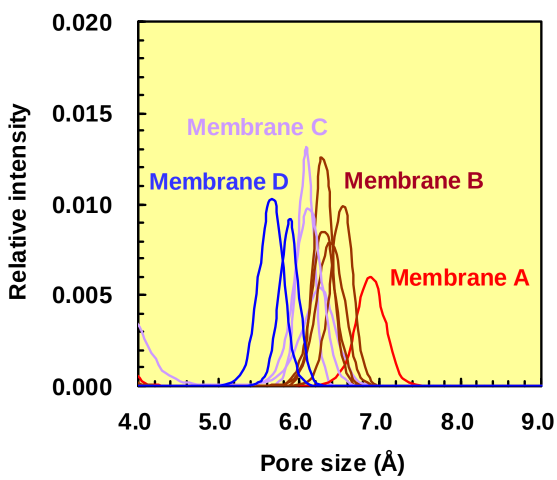


Figure 4. Pore size distribution

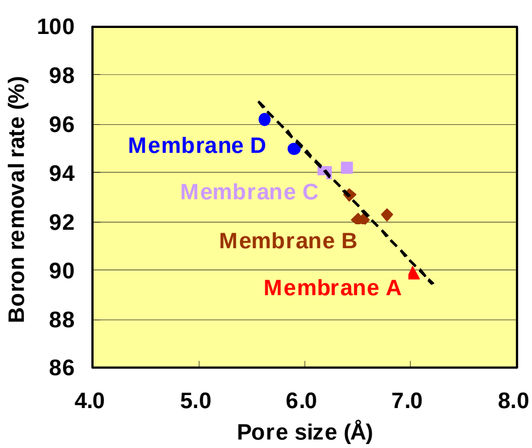
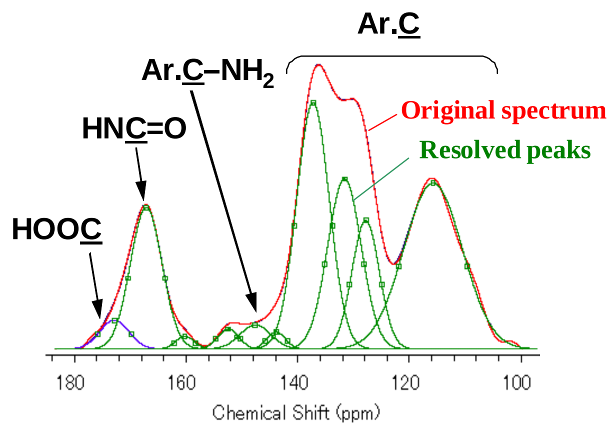


Figure 5. Pore size and Boron permeability

In addition, The molecular dynamics simulations, based on the chemical structures established by 13C NMR study and the estimated amount of water, were performed as shown in Figure 6[3][4]. 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. 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. 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.



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

Figure 6. DD/MAS 13C NMR spectrum of RO Membrane and mol ratio of each moiety

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(Figure 7), compared with SEM image(Figure 8).

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. Consequently, the correlation between

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the morphology of protuberance and water permeability of membrane was revealed.

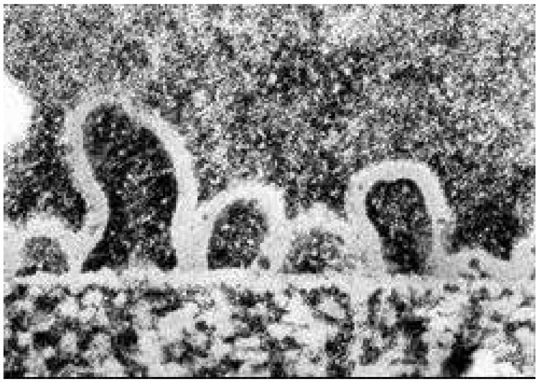

Figure 7. Cross section of RO membrane (TEM image)

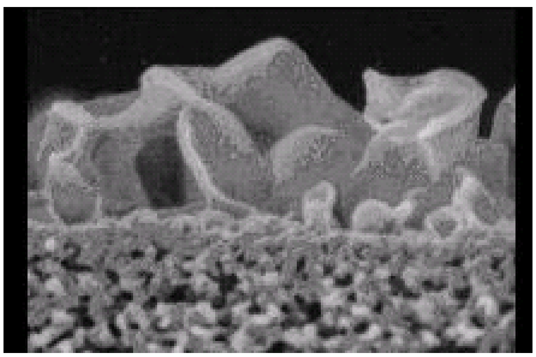

Figure 8. Surface image of RO membrane (SEM image)

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. In this presentation, new energy-saving and high rejection membranes utilizing these studies and its utility study will be introduced.

2 RESULTS:ADVANCED RO MEMBRANE

Through the abovementioned studies, a special molecular design, which controls physical and chemical property of RO membranes, is found to be necessary to develop further renovative membranes for seawater and brackish water desalination.

2.1 ADVANCED RO MEMBRANE FOR SEAWATER DESALINATION

On the basis of this knowledge, Toray has developed new RO membrane elements with high solute rejection performance for SWRO processes[6]. The lineup of RO membrane elements for SWRO processes is shown in Table 1.

Table 1. 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***
TM820L	***99.80***	***13,500 (51.1)***	***92***

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 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.

The recent progress and future prospect of Toray's advanced SWRO membrane elements are depicted as shown in Figure 9. The innovative improvements, which have made high water productivity and high solute rejection coexist, have been accomplished through utilizing the results of fundamental researches.

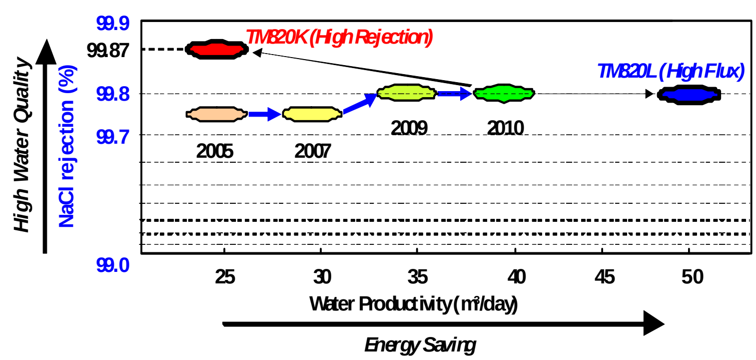

Figure 9. Recent progress and future prospect of SWRO membrane performance

2.2 ADVANCED RO MEMBRANE FOR BRACKISH WATER DESALINATION

Toray has developed new RO membrane elements with high solute rejection performance for BWRO process[7]. The lineup of RO membrane elements for BWRO processes is shown in Table 2. TM720 shows high TDS rejection rate. TMG20 and TMH20 for energy saving can be operated under low pressure. TML20 shows eminent low fouling performance. TMD720D has superior chemical tolerance with both high TDS rejection rate and high water productivity.

Table 2. Products lineup of Toray's BWRO

Product	Specification		Test Condition*	
	TDS rej. (%)	Water Productivity (GPD, (m^3/d))	Feed Water NaCl (mg/L)	Pressure (MPa)
TM720-440	99.7	11,300 (42.6)	2,000	1.55
TM720L-430	99.5	9,200 (34.8)	2,000	1.03
TMG20-430	99.5	11,000 (41.6)	500	0.76
TMH20A-430	99.3	11,800 (44.7)	500	0.69
TML20-400	99.7	10,200 (38.6)	2,000	1.55
TM720D-440	99.8	12,100 (45.8)	2,000	1.55

Toray advanced BWRO membrane elements have been made in progress as shown in Figure 10.

In this presentation, new membranes with high water productivity, high solute rejection and high chemical durability utilizing fundamental studies will be introduced.

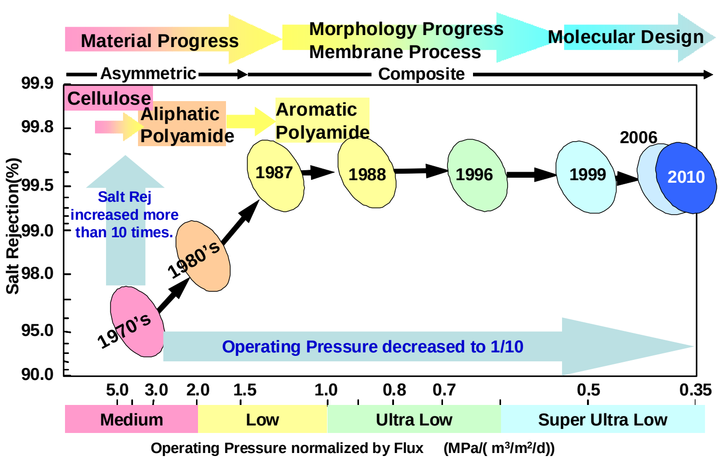

Figure 10. Recent progress of BWRO membrane performance

3. Conclusion

Advanced RO membrane technology based on scientific research for seawater and brackishwater desalination has made in progress[8]. Recently, advanced RO membrane with fine pore structure development and industrialization was reported [9]. We will continue to develop advanced RO membrane based on scientific research works.

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