High performance RO membranes for desalination and wastewater reclamation and their operation results
M. Henmi, Y. Fusaoka, H. Tomioka and M. Kurihara

ABSTRACT

Reverse osmosis (RO) membrane is one of the most powerful tools for solving the global water crisis, and is used in a variety of water treatment scenes such as drinking water purification, waste-water treatment, boiler feed water production, ultra pure water production for semiconductor industry, etc. The desired performance of RO membrane varies according to quality of feed water being treated, and Toray has been developing RO membranes with suitable characteristic for each operating condition. RO membranes for seawater desalination and wastewater reclamation are especially regarded as most promising targets. Recently, high boron removal and energy saving RO membrane for seawater desalination and low fouling RO membrane for wastewater reclamation have been developed. In this paper, the prospect of attaining these renovative RO membrane, and furthermore, job references will be discussed.

Key words | boron removal, desalination, low fouling, reverse osmosis, seawater, wastewater

INTRODUCTION

Population explosion and human industrial activities have been causing huge consumption of water resources and water pollution, and now insuring enough quantity and quality of water is one of the most serious issues in the world. On the other hand, new technologies for water treatment have also been developed for the countermeasures to the water shortage, and the membrane technology is recently regarded as indispensable in this century since it supplies a lot of high-grade water with low cost and maintaining sustainable water resources. 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.

RENOVATIVE RO MEMBRANE

High boron removal and energy saving SWRO membrane

Background

Improvement of water quality and saving energy are two main subjects in seawater RO desalination. At the point of energy saving, the average energy consumption at seawater RO (SWRO) plants has been reduced to one fifth for these 40 years as shown in Figure 1 (MacHarg 2007). 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 required.

As for the water quality, one of the most significant problems in the SWRO desalination field is inadequate boron removal (Fukunaga et al. 1997). Boron usually exists as boric acid in natural water, and boric acid mainly shows the disorder of male reproductive tract per oral administration in laboratory animals. WHO proposed the boron concentration in drinking water to be below 0.5 mg/L as a provisional guideline value (WHO 2004). It is not so easy for SWRO desalination plants to meet the guideline value because the boron concentration in seawater is comparatively high, 4–7 mg/L. In addition, boric acid is a typical substance which is hard to be removed by RO processes for the following reasons. Firstly, the molecular size of boric acid is about 0.4 nm in diameter and so small that the removal by size exclusion is difficult. Secondly, boric acid has a pKa 9.14–9.25; it is not ionized in natural seawater.
with pH of 7–8 and dissociates at pH 9 or more (Rodriguez et al. 2001; Hyung & Kim 2006), so the boron rejection by electric repulsive force between boric acid and RO membrane cannot be expected in neutral condition.

**Needs for next SWRO membrane**

Although the conventional standard type of SWRO membrane elements have shown a little more than 90% of boron rejection rate, it is still inadequate. Therefore, SWRO desalination plants actually adopt special processes to reduce the boron concentration in the product water. The boron removal SWRO processes are roughly classified into two groups such as the single-stage RO process and the multi-stage RO process as shown in Figure 2. The single-stage RO process is characterized by simple composition without supportive processes and low operating cost. Seawater is treated by only “Type A” membrane element, and strongly high boron rejection performance is required for the Type A membrane. The multi-stage RO process consists of SWRO membrane element “Type B” and BWRO membrane element “Type C”. Seawater is first fed to the Type B membrane element, then the permeate is alkaliified and treated by the Type C membrane element by which boron is effectively removed. The quality of water produced by the multi-stage RO process is higher than that of the single-stage RO process due to the multi-stage treatment, and it is possible to use the membrane with the performance of high water production as type B membrane in the multistage RO process. For the Type C membrane, it is required not only high boron rejection and water productivity but also alkaline tolerance to treat feed water under basic condition (Table 1).

Furthermore, RO membrane with extremely high water permeability will be required for the effective energy saving operation. In addition, this membrane must have an adequate performance for the removal of salt and other harmful compounds. Consequently, there are three courses for the development of seawater RO membranes as follows:

1. Pursuit of highest boron removal performance
2. High water permeability with high boron removal performance
3. Extremely high water permeability

In order to obtain further excellent performances, scientific researches with a point on the solute transport mechanism in RO membrane are necessary.

**Result and discussion**

Toray have been making basic research on physical and chemical properties of high boron removal RO membrane for the purpose of finding out parameters which influence its performance. In this work, actual pore size analyses in polyamide separating functional layer were studied by means of positronium annihilation lifetime spectroscopy (PALS) analyses (Kurihara et al. 2006a,b; Tomioka et al. 2006). PALS is a technique in which the period from the incidence of a positron in a sample to the annihilation is measured and information such as the size of the pores in the range of 0.1 to 10 nm, number density and size distribution is nondestructively evaluated based on the

<table>
<thead>
<tr>
<th>Energy (kWh/m³)</th>
<th>12.0</th>
<th>8.1</th>
<th>5.0</th>
<th>3.7</th>
<th>1.6</th>
<th>2.1–2.3</th>
</tr>
</thead>
</table>

**Figure 1** Trend of energy consumption for SWRO desalination process.

**Table 1** Required performance for SWRO membrane elements

<table>
<thead>
<tr>
<th>RO element type</th>
<th>Demanded performance</th>
</tr>
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<tbody>
<tr>
<td>Type A</td>
<td>Extremely high boron rejection</td>
</tr>
<tr>
<td>Type B</td>
<td>High boron rejection, high water production</td>
</tr>
<tr>
<td>Type C</td>
<td>High boron rejection, high water production, alkaline tolerance (pH10)</td>
</tr>
</tbody>
</table>

**Figure 2** Flow diagrams of SWRO desalination plant with boron regulation.
annihilation lifetime. PALS is classified into two types depending on the kind of the positron beam source. One is \(^{22}\text{Na}\) method uses a radioactive isotope \(^{22}\text{Na}\), and this method is suitable for pore evaluation of resin, powder, fibre, fluid, etc. Another is a positron beam method using positron beam emitted from an electron beam-type accelerator as the positron beam source, and is useful for pore evaluation for thin films with a thickness of about several hundred nanometres formed on various substrates. In this study, the positron beam method was adopted for the pore analysis of RO membranes.

Four kinds of polyamide composite RO membranes for seawater desalination (S1, S2, B1 and B2) were prepared for this study. Detailed specifications of these membranes and test conditions are summarized in Table 2. S1 and S2 are standard type SWRO membranes, while B1 and B2 stand for SWRO membranes for high boron removal. Especially, membrane B2, the improved high boron removal RO membrane that is now under development, shows around 96% of boron rejection rate. Each membrane shows different boron removal performance but almost same TDS rejection rate.

As the results of PALS measurement, the annihilation lifetime-positron count curve gave each parameter related to pore size by POSITRONFIT analyses (Kirkegaard \& Eldrup 1972; Nakanishi \textit{et al.} 1989), as shown in Table 3, and the pore size distributions by MELT analyses (Shukla \textit{et al.} 1997), as shown in Figure 3. According to Table 3, every membrane shows 2–3 ns of annihilation lifetime, and obtained pore sizes are in the range of 5.6–7.0 Å. It is considered that this range of pore in the separating functional layer would characterize the property as RO membrane. The correlations between the measured pore size and boron rejection rate in seawater RO membranes are described as shown in Figure 4. Obviously, boron rejection rate decreases according to increase of pore size. The fact suggests that the pore size in polyamide separating functional layer is one of the major factors to control boron removal performance of RO membrane.
In order to obtain novel RO membrane with high boron rejection rate, we found that it is important to control pore size by sub-nanometre level. On the basis of this knowledge, new RO membrane elements with high boron removal performance for SWRO processes were developed. The line-up of RO membrane elements for SWRO processes is shown in Table 4. TM820A which was developed as a Type A element for the single-stage RO process shows 93% of boron rejection rate with high TDS rejection rate and high water productivity. TM820C, TM820E and TM820S have both high boron rejection rate and high water productivity, and are suitable for Type B element. TM720C is utilized as a Type C element for second stage of 2-pass process due to the tolerance of alkaline reagent. Further study on other parameters for controlling membrane performance is continued, which helps us to understand the solute transport mechanism through RO membranes and makes it possible preparing the advanced membrane with desired performance.

### Low fouling RO membrane

#### Background

With increase of demands for sustainable water resources preservation, the number of wastewater reclamation plant construction has been increasing every year. The operating pressure of wastewater desalination is much lower than that of seawater desalination. Therefore, utilizing wastewater is useful for saving energy. In the wastewater reclamation plant, the wastewater is firstly treated with biological technology, such as activated sludge method and membrane bio-reactor (MBR), and the biologically treated water is further treated with RO membrane. In RO membrane process, stable operation is one of the most important matters. Many operational troubles have been reported, especially, problems of membrane fouling occupy 80 percent of them. In order to avoid membrane fouling, it is significant to consider of following items: (1) RO membrane with low fouling property; (2) adequate pretreatment before RO membrane treatment; (3) suitable cleaning operation of RO membrane (Kurihara et al. 2003).

Membrane fouling phenomena are categorized into chemical fouling and biological fouling. Chemical fouling is caused by the adsorption of organic matters such as humic substances and surfactants in the feed water onto membrane surface. Humic substances and surfactants have various chemical structures depending on the water origin, however, they unexceptionally have both hydrophobic groups and ionic groups. Since RO membrane material is generally polyamide which also has properties of both hydrophobic and ionic, it strongly interacts with humic substances and surfactants. In case of biological fouling, following estimations are reported: (1) microbe adsorption by hydrophobic or electrostatic interaction; (2) propagation of microbe with nutrition in the feed water; (3) deposition of exhaust material of biological metabolism. (1) is reversible process, however, (2) and (3) are irreversible, which are impossible to be removed by chemical cleaning. Therefore it is very important for protecting RO membrane from fouling to control (1). And it is necessary to develop low fouling RO membrane in this field.

### Table 4 | RO line-up for SWRO processes corresponding to various coverage

<table>
<thead>
<tr>
<th>Type</th>
<th>Element name</th>
<th>Specification†</th>
<th>TDS rejection, %</th>
<th>Water productivity, GPD (m³/d)</th>
<th>Boron rejection, %</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TM820A-400</td>
<td></td>
<td>99.75</td>
<td>6,000 (22.7)</td>
<td>93</td>
<td>High boron rejection</td>
</tr>
<tr>
<td></td>
<td>TM820C-400</td>
<td></td>
<td>99.75</td>
<td>6,500 (24.6)</td>
<td>93</td>
<td>High water productivity</td>
</tr>
<tr>
<td>B</td>
<td>TM820E-400</td>
<td></td>
<td>99.75</td>
<td>7,500 (28.3)</td>
<td>91</td>
<td>High boron rejection</td>
</tr>
<tr>
<td></td>
<td>TM820S-400</td>
<td></td>
<td>99.75</td>
<td>9,000 (34.1)</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>TM720C-400</td>
<td></td>
<td>99.2</td>
<td>8,800 (33.3)</td>
<td>94</td>
<td>2nd stage of 2-pass High boron rejection</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkaline tolerance</td>
</tr>
</tbody>
</table>

†Test Condition: Type A and B: 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%; Type C: 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%.
Result and discussion

A low fouling RO membrane TML for wastewater reclamation was developed by focusing on adding hydrophilic property on membrane surface. TML has the same level of pure water permeability as conventional RO membranes, and also has low fouling property with keeping water permeability against chemical and biological fouling during the operation (Yamamura 2002).

Low fouling properties of RO membranes were evaluated with a nonionic surfactant aqueous solution as shown in Figure 5. Test result shows that TML has relatively small permeability declination rate of 27%, compared with initial pure water permeability, and shows stable operation. On the other hand, conventional fully aromatic polyamide membranes, TM700, which is standard RO membrane for brackish water use, and TMG, which has high water permeability available for ultra low pressure operation, show 36 to 47% declination rate, respectively. And as for the chemical cleaning properties, permeability of TML shows 95% of initial value after chemical cleaning. However, TM700 and TMG show 82 to 77% of that. This result shows TML enables stable operation in chemical fouling condition.

In order to evaluate the fouling property against microbe, adhesion property was measured by membrane biofouling potential (MBP) assays (Knoell et al. 1999) as shown in Figure 6. In the MBP assay, two standard bacterial strains which include Mycobacterium strain BT12-100 and Flavobacterium strain PA-6 were used. These strains were isolated from actually biofouled RO membranes. Namely, MBPs were estimated from the attachment behavior of known membrane fouling bacteria. The Mycobacterium strain exhibits a hydrophobic cell surface, whereas the Flavobacterium strain is hydrophilic. By employing biofouling bacteria whose surfaces correspond to opposite poles, the MBP assay more accurately simulates the range of microbial types to be suspected in feed waters. The amount of MBP is generally expressed as the ratio of the number of membrane bound bacteria (B) to the number of free bacteria (F). As the results of the MBP assays, the hydrophobic microbe is severely adhered to conventional RO membrane and will cause biological fouling of RO membrane. In case of TML, the adhesion property of the hydrophobic microbe is quite low which is less than one tenth of conventional RO membrane.

![Figure 5](image-url) | Low fouling properties of TML compared with conventional RO.

![Figure 7](image-url) | Water productivity of TML compared with TMG.

![Figure 6](image-url) | Evaluation of anti-fouling activity by MBP assay.

![Figure 8](image-url) | Autopsied TMG membrane after pilot test: a) Membrane surface; b) Gathered foulant.
Plant data of low fouling membrane

A field test of wastewater reclamation using TML and TMG has been carried out in a wastewater treatment facility in Japan as shown in Figure 7. In this test, secondary effluent was directly filtered by UF membrane and permeate was fed to both of RO membranes. In case of TMG membrane, water permeability was dropped to 60% of initial permeability in a day due to biological fouling as shown in Figure 8, however, the permeability drop of TML was smaller than that of TMG and the stable operation has been performed.

Low fouling RO membrane is strongly required from market for the purpose of stable operation of wastewater reclamation plant. And the newly developed low fouling RO membrane TML has already been adopted in large plants as shown in Table 5 (Kurihara et al. 2008). For example TML elements having low fouling were running with stable for 8 months at Luggage Point advanced water treatment plant (Pilot Plant) in Australia as shown in Figure 9. As a result, TML was installed to this plant in September 2008 and RO operation was started.

**CONCLUSION**

Pore size analyses in polyamide separating functional layer were studied by means of the PALS using positron beam method in order to find the prospect for development of novel membranes with further excellent performance, especially boron removal. Through these studies, the importance of controlling pore size in separating functional
layer of RO membrane by sub-nanometer level to obtain high boron removal RO membrane was revealed. On the basis of this knowledge, Toray has developed novel RO membrane elements with high boron removal performance for SWRO processes.

As for wastewater treatment, low fouling RO membrane element TML was developed by a modification of membrane surface. TML showed both of excellent anti-chemical and anti-bio fouling property, and has already been running in several wastewater plants with long term stable operation.

RO membrane technologies 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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