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Cesium (Cs) and strontium (Sr) removal as model materials in radioactive water by advanced reverse osmosis membrane

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ABSTRACT

Reverse osmosis (RO) membrane is among the most powerful tools for solving the global water crisis, and Toray has developed high-performance RO membranes for seawater desalination, brackish water desalination, and wastewater reclamation by molecular design in the preparation of cross-linked aromatic polyamide membrane, which produces more appropriate water quality and quantity as compared with conventional ones. Several previous papers provided the removal performances of radioactive substances by RO membranes, but accurate data have not been reported about the advanced RO membranes. It is more recently desired to demonstrate Cesium (Cs) and Strontium (Sr) removal performance in radioactive water by RO membrane because of the considerable concern of the water quality control for nuclear power stations. In this study, removal performance of Cs, Sr, and Iodine was examined to use model compounds adding nonradioactive chemicals to seawater and analyzed by inductively coupled plasma mass spectrometry for ultra-trace detection. Consequently, Toray advanced seawater reverse osmosis membrane UTC-80R has high removal performance to reduce the concentration of Cs, Sr, and Iodine by less than one hundredth in high salinity water.

Keywords: Radioactive water; Reverse osmosis; Membrane; Cesium removal; Strontium removal; Iodine removal; Seawater desalination; ICP-MS

1. Introduction

1.1. Advanced reverse osmosis membrane technology for seawater desalination

1.1.1. Structure analyses of RO membrane

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, reverse osmosis 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. 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 [1]. A compos-

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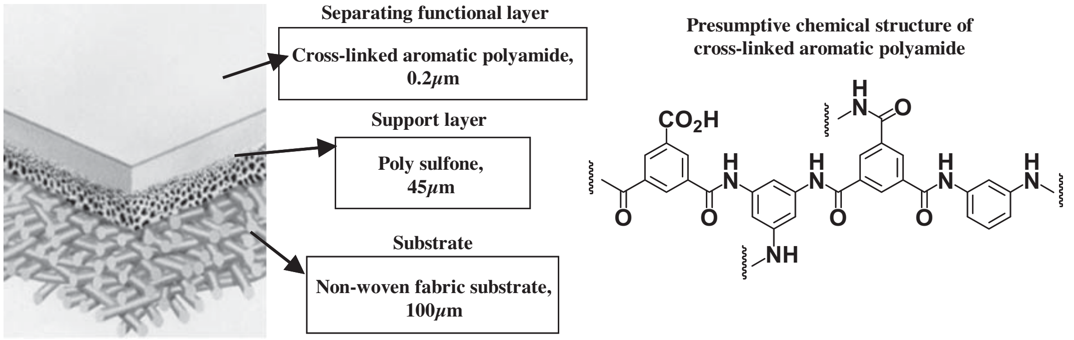


Fig. 1. Structure of composite RO membrane and chemical structure of cross-linked polyamide.

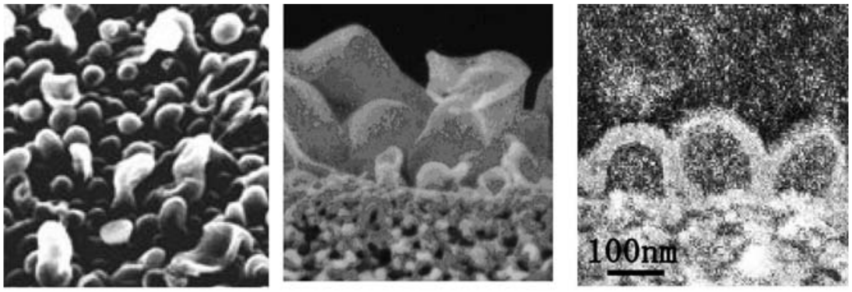
ite RO membrane is usually composed of three layers, namely a separating functional layer, a polysulfone porous support layer, and a polyester non-woven fabric substrate, as shown in Fig. 1. In the separating functional layer, the semipermeable membrane with RO function is formed by cross-linked aromatic 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 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 seawater reverse osmosis (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 [2].

1.1.2. 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 RO membrane. However, analyses by conventional SEM methods gave only information from an appearance as shown in Fig. 2 (left-hand, surface, and cross-section). 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 as shown in Fig. 2 (right-hand), and it enabled a quantification of



Surface Cross-section Cross-section

SEM image *TEM image*

Fig. 2. Examples of protuberance image by conventional SEM and TEM with a special treatment.

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 [3]. 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.

1.1.3. Radioactive substances removal by conventional RO membranes

Membrane technology has been used for removal of radio nuclides from low level liquid wastes such as waste streams at nuclear power plants. Because reverse osmosis membrane rejects nearly all contaminants from a solution with dissolved gases and tritium exceptions, the high purity product water may be recycled within the power plant. The purified water is usually of such low activity (sometimes after ion exchange polishing) that it might be suitable for discharge to the environment. In recent years, reverse osmosis systems have been used to replace or increase existing evaporation and/or ion exchange technology. Reverse osmosis systems in the nuclear industry are also usually a part of an overall liquid waste treatment system.

Most of the detailed information on performance of a reverse osmosis system applied for cleaning liquid radioactive effluents has been previously reported [4–8]. Development of a membrane installation for cleaning LRW at AECL Research Laboratories at Chalk River, Canada, began in the 1970s [7]. The objective was development and acquisition of a two stage reverse osmosis system. The LRWs at the AECL nuclear research centre are characterized by a salinity of up to 5 g/L and specific radioactivity of up to 2×10^5 Bq/L (^{50}Mn, ^{51}Cr, ^{60}Co, ^{95}Zr, ^{103}Ru, ^{144}Ce). Research and exploratory work was conducted in the 1980s, which enabled design of a full scale system consisting of cross-flow microfiltration, spirally wound reverse osmosis (first stage), and tubular reverse osmosis (second stage) [7]. According to these studies for removal performance of radioactive cesium ^{137}Cs, the rejection is 96% in spirally wound polyamide RO elements [8].

1.2. Progress in multielement ultra-trace analysis

Spectrometric studies on sunlight after the middle of seventeenth century have brought discoveries including emission spectrum. Bunsen and Kirchhoff [9] discovered new elements in the 1860s with the use of atomic spectrometry, which opened spectrochemistry. In the 1960s, Fassel [10] and Greenfield [11] developed inductively coupled plasma atomic emission spectrometry (ICP-AES). This technology has come to be used in the study of many fields with the achievement of significant improvement in sensitivity and with the development of simultaneous multi-element analysis. Houk et al. [12,13] developed inductively coupled plasma mass spectrometry (ICP-MS) in the 1980s using this ICP plasma as ion source due to its excellent properties. Mass spectrometry has theoretically higher sensitivity than spectrometry, because each ion can be detected. Recent ICP-MS instruments achieved the detection limit of parts per trillion level through the instrumental improvement. It has become popular as most sensitive technique in elemental analysis.

In order to obtain reliable data using such an instrument with high sensitivity, great care has to be paid in the whole analytical procedure from sample pretreatment to measurement. In the measurement of parts per trillion level, it is required to control the blank values originated from apparatus, environment, and reagents to parts per trillion level.

2. Results and discussion

2.1. Advanced 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 TM820L have been released as the next targets.

Table 1
Products lineup of Toray's SWRO

Period	Product	Specifications[a]			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	
	TM720C	99.2	8,800 (33.3)	94	Alkaline tolerance (pH 10)
New lineup	TM820K	99.86	6,400 (24.2)	96	Extremely high rejection
	TM820R	99.80	9,400 (35.6)	95	Standard
	TM820L	99.80	13,500 (51.1)	92	Further energy saving

[a] Test conditions: Except TM720C: feed water; NaCl 32,000 mg/L, boron 5 mg/L, temperature 25℃, 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℃, pH 10, operating pressure 1.03 MPa, flow rate; 80 L/min, recovery rate 15%.

In the following section, the utility study of these membranes will be discussed.

2.2. Quantitative determination of Sr, Cs, and iodine in RO flat-sheet membrane test

Concentration of Cs, Sr, and iodine elements in feed seawater was measured by ICP-MS. In RO flat-sheet membrane test, determination of permeates and membrane performances is also shown in Table 2. Natural seawater contained the proportions of trace elements, 5.8 μg/mL Sr, 40 ng/mL Cs, and 0.2 ng/mL iodine, which is well accorded with the literature data. In the flat-sheet membrane test by natural seawater, the concentration of permeates in Cs and iodine reached below to LOQ, accurate rejection performance could not be estimated. In prepared seawater (added 0.50 mg/L cesium iodide), the removal performance of trace elements shows high rate rejection corresponding to the rejection of total dissolved solids (TDS) with accuracy. Especially UTC-80R membrane has the highest rejection in four membranes and higher water flux than UTC-80C and 80 M. These performances are corresponding to the density of functional layer in RO membranes, which affects size exclusion. Trace elements in saline water are also rejected by hydrated molecular size.

In previous paper [17], precise membrane performance in radioactive water was not sufficient because of organic fouling substances or restricted environments in the real operation. This study displays accurate membrane performance in radioactive water is predictable by model experiments. Recent advanced polyamide RO membranes have high rejection and high water productivity compared to cellulose acetate RO membranes at that point of Three Mile Island (nuclear power plant) accident. The additional comparison is shown in Fig. 3 between previous data from AECL nuclear research centre and estimation from fundamental RO membrane experiments in 1978.

2.3. Quantitative determination of Cs, Sr, and iodine in 4-inch membrane element filtration test

As described above, high removal performance of advanced RO membrane was indicated by flat-sheet membrane performance test. Cs, Sr, and iodine removal performance was evaluated by using 4-inch size element in the performance demonstration. Cs and iodine concentration were varied from 100 to 5,000 ng/L. Concentration of trace elements in water samples and membrane element performances are shown in Table 3.

TM-810C element including UTC-80C as RO membrane has high removal performance in variable concentrate region (100–5,000 ng/mL Cs and iodine). Removal rate is higher than 99.7%, and the amount of trace elements can be reduced ranging from a part per three hundreds to fifteen thousands. The difference of removal performance between TM-810C and UTC-80C arises from the difference of membrane surface condensation of solutes in the operation condition.

Table 2
Sr, Cs, and iodine removal by flat-sheet membrane performance test. Prepared seawater test (added 1.0 mg/L CsI (cesium iodide) in natural seawater)

	Concentration			Rejection			General performance	
	Sr (ng/mL)	Cs (ng/mL)	I (ng/mL)	Sr rej. (%)	Cs rej. (%)	I rej. (%)	TDS rej. (%)	Flux ($m^3/m^2/d$)
Natural seawater	5,700	500	470					
UTC-80C permeate	1.0	0.7	0.71	99.98	99.86	99.85	99.85	0.78
UTC-80S permeate	0.99	1.0	1.1	99.98	99.80	99.77	99.75	1.00
UTC-80R permeate	0.46	0.4	0.44	99.99	99.92	99.91	99.91	0.89
UTC-80 M permeate	1.7	0.6	0.84	99.97	99.88	99.82	99.87	0.77

Operation pressure: 5.5 MPa, pH 8.0, temp. 25°C, feed water: Ehime seawater.

Table 3
Results of 4-inch RO element (TM-810C) performance test

Addition	Feed water concentration			Permeate water concentration			Rejection			General performance	
CsI (mg/L)	Sr (ng/mL)	Cs (ng/mL)	I (ng/mL)	Sr (ng/mL)	Cs (ng/mL)	I (ng/mL)	Sr Rej. (%)	Cs rej. (%)	I rej. (%)	TDS rej. (%)	Flux (m^3/d)
0.1	7,400	96	140.0	5	0.27	0.3	99.93	99.72	99.79	99.83	4.3
1.0	7,600	540	600	5.1	1.6	1.4	99.93	99.70	99.77	99.85	4.1
10	8,000	5,300	4,800	5.1	14	12	99.94	99.74	99.75	99.84	4.1

Operation pressure: 5.5 MPa, pH 7.6, temp. 25°C, recovery 13%.

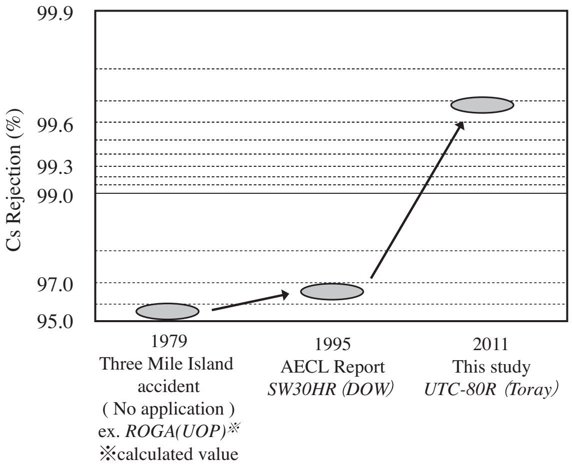


Fig. 3. Comparison of Cs rejection rate among previous reports and this study. Italic face shows the description of membrane (this work) or membrane elements.

3. Conclusions

Fundamental analysis of removal performance of trace elements was performed in this study. It is verified removal performance is higher than 99.7% rejection and the amount of trace elements can be reduced ranging from three hundredth part to fifteen thousandth part.

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References

[1] R.J. Petersen, J. Membrane Sci. 83 (1993) 81–150.
[2] M. Henmi, Y. Fusaoka, H. Tomioka, M. Kurihara, Water Science and Technology—WST 62(9) (2008) 2134–2140.
[3] M. Kurihara, M. Henmi, H. Tomioka, T. Kawakami, Advancement of RO membrane for seawater desalination and wastewater reclamation, in: Oral presentation in the ICOM 2008, Hawaii, 13–18 July, 2008.
[4] S.K. Sen Gupta, L.P. Buckley, S. Rimpelainen, A.Y. Tremblay, Liquid radwaste processing with spiral-wound reverse osmosis, in: WM'96 (Proc. Conf. Tucson, AZ, 1996), WM Symposia, Inc., Tucson, AZ, 1996.
[5] S.K. Sen Gupta, J.A. Slade, W.S. Tulk, Liquid radwaste processing with cross-flow microfiltration and spiral-wound reverse osmosis, in: WM'95 (Proc. Conf. Tucson, AZ, 1995), WM Symposia, Inc., Tucson, AZ, 1995.
[6] W.T. Bourns, L.P. Buckley, K.A. Burrill, Development of techniques for radwaste systems in CANDU power stations, On-site Management of Power Reactor Wastes (Proc. Symp. Zurich, 1979), OECD, Paris, 1979, pp. 309–330.
[7] L.P. Buckley, S.K. Sen Gupta, J.A. Slade, Treatment of low-level radioactive waste liquid by reverse osmosis, in: ICEM'95 (Proc. Conf. Berlin, 1995), American Society of Mechanical Engineers, New York, 1995, p. 1015.
[8] S.K. Sen Gupta, L.P. Buckley, Bitumen immobilization of aqueous radwaste by thin-film evaporation, in: WM'96 (Proc. Conf. Tucson, AZ, 1996), WM Symposia, Inc., Tucson, AZ, 1996.
[9] G.R. Kirchhoff, R. Bunsen, Ann. Phys. 74 (1860) 337.
[10] R.H. Wendt, V.A. Fassel, Anal. Chem. 37 (1965) 7.
[11] S. Grennfield, I.L.L. Jones, C.T. Berry, Analyst 89 (1964) 713.
[12] R.H. Houk, V.A. Fassel, G.D. Flesch, H.I. Svec, A.L. Gray, C. E. Taylor, Anal. Chem. 52 (1980) 2283.
[13] R.S. Houk, A. Montaser, V.A. Fassel, Appl. Spectrosc. 37 (1983) 425.
[14] M. Taniguchi, M. Kurihara, S. Kimura, J. Membr. Sci. 183 (2001) 249–257.
[15] M. Taniguchi, M. Kurihara, S. Kimura, J. Membr. Sci. 183 (2001) 259–267.
[16] M. Taniguchi, S. Kimura, AIChE J. 46 (2000) 1967–1973.
[17] IAEA Technical Report Series no. 431 (2004) 113.