

Advances in Electrodialytic Membrane Process Technology for Table Salt Production

Masato Hamada, Isamu Azuma, Norio Imai and Hiroshi Ono

Ion Exchange Membrane Administration, Asahi Chemical Industry Co., Ltd., Kanagawa, Japan

ABSTRACT

In the commercial utilization of the electrodialytic process for table salt production, essential requirements for increasing productivity through improvement of the membrane performance include increasing its counterion permselectivity, decreasing its electric resistance, and increasing its electro-osmosis concentration. Two basic indicators of electrodialytic process efficiency are its power consumption and its product brine concentration. The two are inversely related. Continuing improvements have nevertheless reduced the power consumption to 150 kWh/T-NaCl, which is about half that of the 1970s and approaches the practicable minimum, and increased the product brine concentration to 200 g/l, by increasing the fixed ion concentration and uniformity and decreasing the membrane pore size, as well as optimizing the membrane and reinforcement design, while reducing its overall electric resistance.

Long-term process stability requires high co-ion permselectivity and prevention of hydrolysis, as well as high mechanical strength. It has been increased by an optimal combination of polymer cross-linking and polyionic surface layer, together with improved cell and internal porting design, to prevent scaling due to transport of Ca^{2+} and Mg^{2+} and formation of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ due to hydrolysis and transport of OH^- . These improvements are now being incorporated into commercial plants using the Asahi Chemical process and technology in Japan and abroad.

INTRODUCTION

Research and development in ion-exchange membranes at Asahi Chemical since 1951 has led to membranes and membrane-based industrial processes for production of table salt from seawater and potable water from brine (Azuma et al., 1991), desalination of whey (Tomita and Okonogi, 1979a,b), electroreductive dimerization of adiponitrile (Seko et al., 1983), and production of caustic soda and chlorine by salt electrolysis (Shiroki et al., 1992).

The production of table salt from seawater is the oldest commercial application. The world's first table-salt plant utilizing the ion-exchange membrane has been in operation since 1961. The main steps in the production process are seawater intake and filtration, membrane electrodialysis, and multiple-effect evaporating crystallization.

Since the 1970s, improvements in membrane performance and in other electrodialytic components have reduced the unit electrodialytic power consumption by about one-half, to a level approaching the practicable minimum.

Here, we describe the most recent advances in membrane performance, which are being incorporated in plants of table-salt manufacturers utilizing the Asahi Chemical process and technology, which produce 630,000 T-NaCl/year in Japan or about 45% of Japan's total production and 260,000 T-NaCl/year overseas.

ION-EXCHANGE MEMBRANE REQUIREMENTS AND PERFORMANCE

The three major requirements of an ion-exchange membrane, in respect to electrodialytic efficiency in the production of table salt from seawater, are low electric resistance, high current efficiency and electro-osmosis concentration, and high permselectivity for counterions. All three requirements are related to the overall efficiency of the salt production process, and are essential for volume production with low power consumption. A succession of improvements in all three, in the membrane series HM-I, HM-II, and HM-III, has increased the product brine concentration by nearly 20% and decreased the

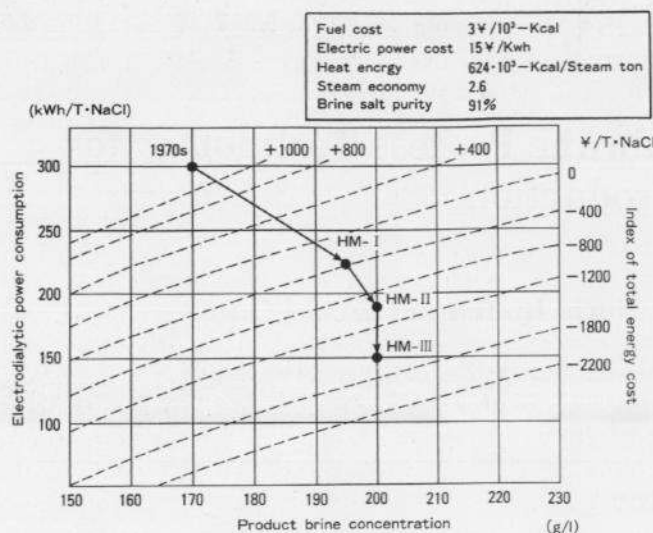


Fig. 1. Reduction in total energy cost of table-salt production by membrane improvement.

table-salt production cost by nearly 3,000 yen per ton, as shown in Fig. 1 by the plot of electrolysytic power consumption and product brine concentration on energy cost isoclines.

An underlying indicator of a membrane's performance is its fixed ion concentration (C_R). It is related to the membrane's Donnan salt adsorption, and closely associated with its permselectivity and electric conductivity. In general, it may be expressed as

$$C_R(\text{meq/g}) = \frac{\text{Exchange capacity (meq/g-membr)}}{\text{Water content (g/g-membr)}}$$

The relation between the fixed ion concentration (C_R) and the concentration of Na^+ (\bar{C}_{Na}) and Cl^+ (\bar{C}_{Cl}) in a cation-exchange membrane, and the concentra-

tion of either Na^+ or Cl^+ (C) outside the membrane, may be expressed as

$$\bar{C}_{\text{Na}} = \frac{\sqrt{C_R^2 + 4C^2} + C_R}{2}, \quad \bar{C}_{\text{Cl}} = \frac{\sqrt{C_R^2 + 4C^2} - C_R}{2}$$

The relation for an anion-exchange membrane may similarly be expressed as

$$\bar{C}'_{\text{Cl}} = \frac{\sqrt{C_R^2 + 4C^2} + C_R}{2}, \quad \bar{C}'_{\text{Na}} = \frac{\sqrt{C_R^2 + 4C^2} - C_R}{2}$$

It is evident from these equations that the membrane selectivity for counterions increases with increasing fixed ion concentration. As shown in Table 1, the fixed ion concentration has been increased by 0.5 meq/g- H_2O to 7.8 meq/g- H_2O in the cation-exchange membrane and by 1.8 meq/g- H_2O to 8.5 meq/g- H_2O in the anion-exchange membrane, during the past ten years.

On the other hand, the electro-osmosis concentration (NOS) and current efficiency (η) of the membrane, in terms of the material transfer through the membrane as shown in Fig. 2, may be derived from the Nernst-Planck equation (Azuma et al., 1987) and expressed as follows.

$$\text{NOS (N)} = \frac{(t_{\text{Na}} + t_{\text{Cl}} - 1) I/F - K_s \Delta C/d}{\beta I + K_w \Delta C/d}$$

$$\eta = (t_{\text{Na}} + t_{\text{Cl}} - 1) - K_s (\Delta C/d) (F/I)$$

where t_{Na} and t_{Cl} represent the transfer numbers of the ions through the membrane, I is the current density (A/m^2), d is the membrane thickness (m), ΔC

TABLE 1

Membrane characteristics

	Electric resistance* $\Omega \cdot \text{cm}^2$	Thickness μ	Ion-exchange capacity meq/g-dry memb.	Water content g- H_2O /g-dry memb.	Fixed ion concentration meq/g- H_2O
Cation-exchange membrane					
HM-I	4.4	170	1.75	0.24	7.3
HM-II	4.1	120	1.55	0.21	7.4
HM-III	3.6	90	1.40	0.18	7.8
Anion-exchange membrane					
HM-I	2.3	170	1.80	0.27	6.7
HM-II	1.8	140	1.85	0.25	7.4
HM-III	1.6	100	1.95	0.23	8.5

*In seawater at 25°C.

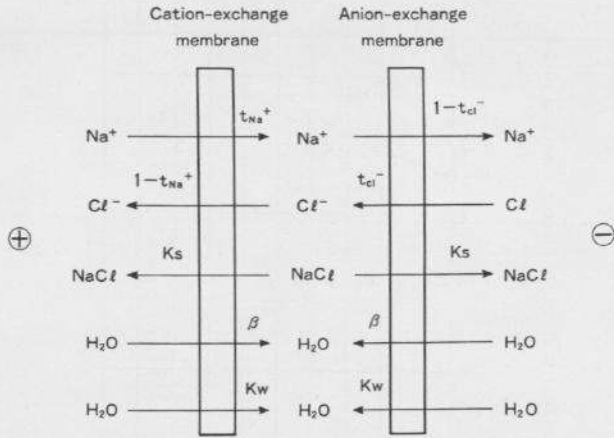


Fig. 2. Material transfer in electro dialysis.

during the past ten years. This decrease has been accompanied by a decrease in the electric conductivity of the membrane material, but this has been more than offset by reduction in the membrane thickness.

These improvements have been gained mainly by increasing the density and uniformity of the fixed ion distribution in the membrane and decreasing the membrane's pore size, and by optimizing the membrane and membrane reinforcement design.

For long-term membrane stability, co-ion permselectivity is particularly important. Without monovalent ion permselectivity, Ca^{2+} , Mg^{2+} , SO_4^{2-} , and other bivalent ions in the seawater will be transported through the membranes to the concentration compartment, where they will form $CaSO_4$ and $MgSO_4$ scaling on the membrane surfaces, and thus block the flow of current through the membrane.

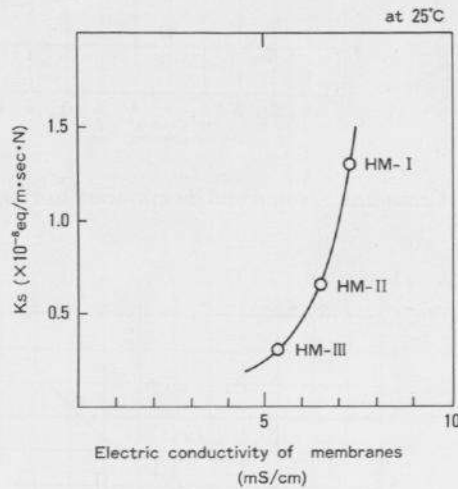


Fig. 3. Coefficient of NaCl diffusion through membrane.

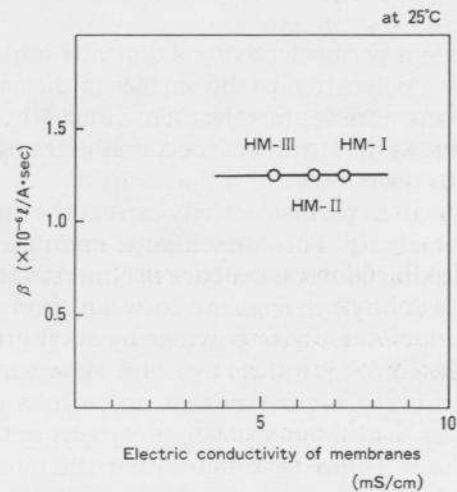


Fig. 4. Coefficient of H_2O electro-osmosis through membrane.

is the difference in concentration between the two membrane surfaces (N), F is Faraday's constant, β is the electro-osmotic coefficient of water (l/A·s) in the membrane, K_w is the osmotic coefficient of water in the membrane (l/m·s·N) and thus represents the migration of water through the membrane due to osmotic pressure difference between its two surfaces, and K_s is the diffusion coefficient of salt in the membrane (eq/m·s·N) and thus represents the salt diffusion through the membrane due to the concentration difference between its two surfaces.

These two equations show the desirability of a membrane with low coefficients of salt diffusion, water electro-osmosis, and water osmosis, for high salt electro-osmosis concentration and high current efficiency. Figures 3-5 show the decrease in water osmosis and salt diffusion coefficients with no increase in water electro-osmosis coefficient, which has been achieved by membrane development

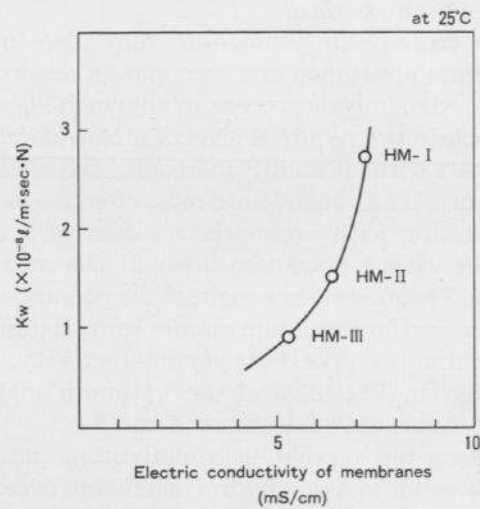


Fig. 5. Coefficient of H_2O osmosis through membrane.

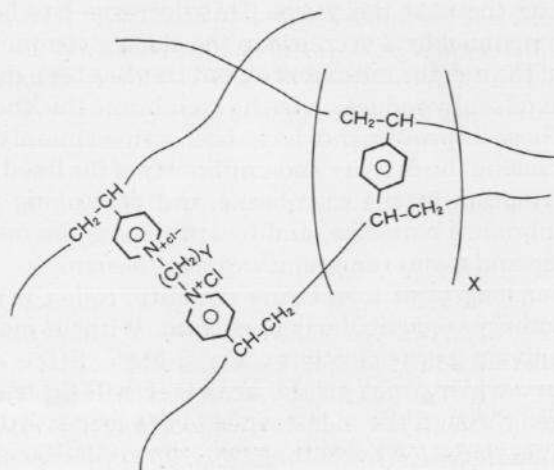


Fig. 6. Polymeric cross-linking of anion-exchange membrane.

Monovalent permselectivity is typically imparted by bonding a polycation to the surface of the cation-exchange membrane, to reject Ca^{2+} and Mg^{2+} , and a polyanion to the surface of the anion-exchange membrane, to reject SO_4^{2-} .

Monovalent permselectivity can also be increased, particularly in anion-exchange membranes, by cross-linking between the base polymers of the membrane by divinylbenzene and between vinyl pyridine side chains of the base polymer by alkyl groups, as illustrated in Fig. 6 (Kamaya and Miyauchi, 1983). The number of divinylbenzene cross-links is represented as X , and the number of carbons in the alkyl group as Y . It has been found that the monovalent permselectivity increases with increasing X , as shown in Fig. 7, and Y , as shown in Fig. 8. The cross-linking can also reduce the effective pore size of the membrane, and increase the hydrophobicity of the membrane surface.

This cross-linking, however, may also increase membrane resistance and thus power consumption in the electrodialysis process, as shown in Figs. 7 and 8. To obtain the required level of monovalent permselectivity without unduly increasing the membrane resistance, it has been found most effective to utilize cross-linking with appropriate values of X and Y , together with a polyanion layer at the membrane surface. The molecular weight of the polyanion must be optimized for minimum membrane resistance and maximum monovalent permselectivity, as illustrated in Fig. 9, and the optimum molecular weight varies with the values X and Y .

For long-term stable electrodialytic operation, it is also essential to avoid hydrolysis due to excessively high current density and membrane fouling due to microorganisms in the feed seawater. Hydrolysis oc-

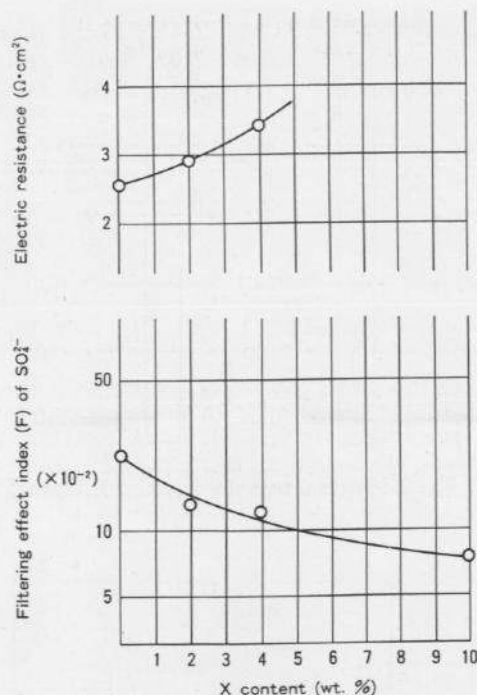


Fig. 7. Cross-link X value and membrane filtering effect.

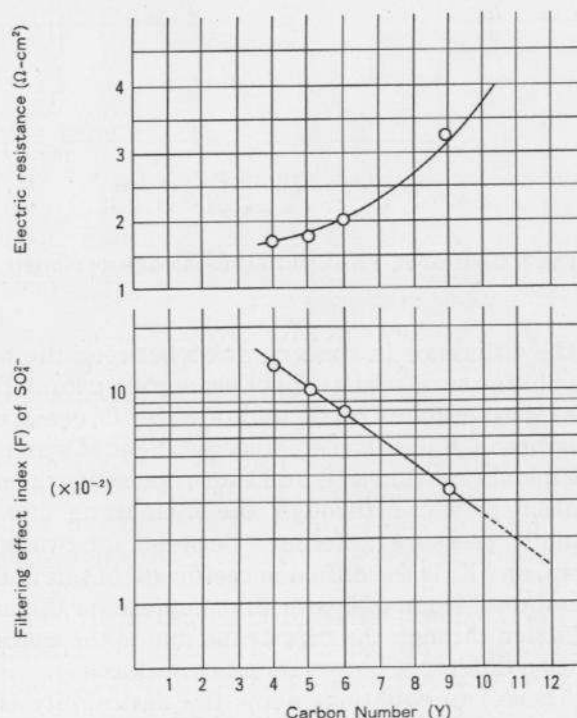


Fig. 8. Cross-link Y value and membrane filtering effect.

curs if the rate of ion supply from the ion-depleted boundary layer at the membrane surface becomes lower than the rate of ion transport through the membrane. The limiting current density (I_0), beyond

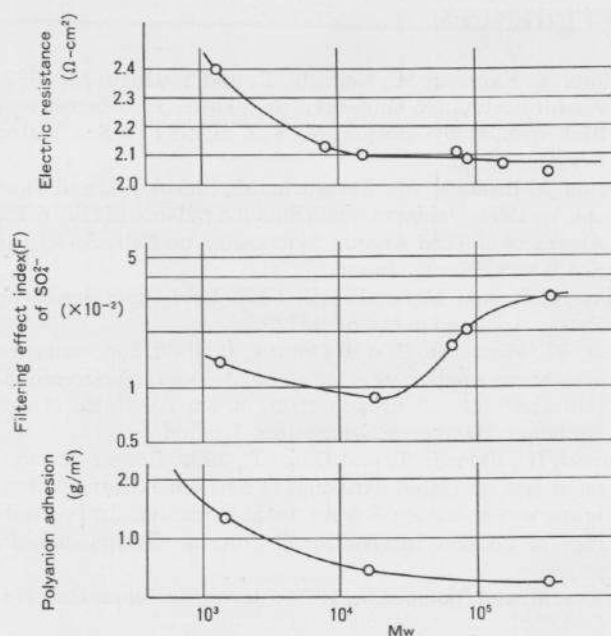


Fig. 9. Polyanion molecular weight and membrane filtering effect.

which ion supply becomes insufficient, may be expressed as

$$I_0(\text{A/dm}^2) = \frac{D}{\delta} \times \frac{C}{(\bar{\tau} - \tau)}$$

where D is the coefficient of ion dispersion in the solution, δ is the thickness of the boundary layer, C is the ion concentration outside the membrane, and $\bar{\tau}$ and τ are the transport numbers inside and outside the membrane, respectively.

If the operating current density is above I_0 , it will result in hydrolysis, transport of the resultant OH^- ions through the membrane to the concentration compartment, and formation there of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. Care is necessary to ensure operation within I_0 , particularly in the summer months when low salt concentration in the seawater means a lower value for C in the above equation and thus a lower I_0 value.

Plankton and other microorganisms in feed seawater can cause porting blockage and membrane contamination leading to an increase in δ , and thus to a lowered I_0 value and the occurrence of hydrolysis. Any porting blockage or membrane fouling due to such contamination necessitates laborious cleaning and washing to remove the deposited microorganisms. It is therefore important to remove them from the seawater prior to electrodialysis. This is generally done by two-stage sand filtration. Salt manufacturers have devised various other addi-

tional means of microorganism removal, since sand filtration may be insufficient, particularly in the presence of red tide or other high levels of microorganism content in the raw seawater.

ELECTRODIALYZER CELL AND SYSTEM

Continuing improvement in electrodialyzer cell and system design, as well as in the ion-exchange membranes, has led to a new standard in commercial electrodialysis for table salt production, as shown in Table 2. These improvements have centered on reduction of the dilution compartment thickness, optimization of porting design, new gasket materials, and increased fluid flow uniformity.

TABLE 2

New electrodialyzer specifications and performance

Configuration	
Membranes	
Grade	HM-III
Area	1.4 m ²
Cells per stack	300
Stacks	8
Total cells	2400
Standard operating conditions	
Current density	3 A/dm ²
Seawater	
Linear velocity	4 cm/s
Quantity	216 m ³ /h
Temp.	25°C
Performance	
Capacity	44 T-NaCl/day
Product brine concentration	200 g/l
Current efficiency (Cl)	89%
Power consumption	150 DC-kWh/T-NaCl

Since the electric resistance of a dilute solution is relatively high, the width of the dilution compartment should be as small as possible in order to minimize cell voltage. It must, on the other hand, be large enough to ensure a supply of seawater sufficient to avoid hydrolysis. The volume of seawater supply required is dependent on the operating current density and other operational conditions, which must therefore be considered in obtaining the optimum cell thickness and design.

The porting configuration has been optimized, to

minimize pressure loss, prevent clogging, and ensure freedom from leakage, as well as to promote uniform fluid flow. Gaskets have been designed and fabricated from new materials to ensure freedom from damage to the membrane in direct contact, as well as complete sealing and long-term durability.

CONCLUSIONS

The advances outlined here have led to the development and adoption of the HM-III membranes and electro dialyzer system, which concentrate seawater to a product brine concentration of 200 g/l at a power consumption of 150 kWh/T-NaCl in commercial operation, compared with 170 g/l at 300 kWh/T-NaCl in the 1970s. The process is thus now approaching the practicable limit of electro dialytic efficiency for brine concentration, which is estimated to be about 100 kWh/T-NaCl.

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