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A computer simulation of ion exchange membrane electrodialysis for concentration of seawater

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Abstract. The performance of an electrodialyzer for concentrating seawater is predicted by means of a computer simulation, which includes the following five steps; Step 1 mass transport; Step 2 current density distribution; Step 3 cell voltage; Step 4 NaCl concentration in a concentrated solution and energy consumption; Step 5 limiting current density. The program is developed on the basis of the following assumption; (1) Solution leakage and electric current leakage in an electrodialyzer are negligible. (2) Direct current electric resistance of a membrane includes the electric resistance of a boundary layer formed on the desalting surface of the membrane due to concentration polarization. (3) Frequency distribution of solution velocity ratio in desalting cells is equated by the normal distribution. (4) Current density i at x distant from the inlets of desalting cells is approximated by the quadratic equation. (5) Voltage difference between the electrodes at the entrance of desalting cells is equal to the value at the exits. (6) Limiting current density of an electrodialyzer is defined as average current density applied to an electrodialyzer when current density reaches the limit of an ion exchange membrane at the outlet of a desalting cell in which linear velocity and electrolyte concentration are the least. (7) Concentrated solutions are extracted from concentrating cells to the outside of the process. The validity of the computer simulation model is demonstrated by comparing the computed results with the performance of electrodialyzers operating in salt-manufacturing plants. The model makes it possible to discuss optimum specifications and operating conditions of a practical-scale electrodialyzer.

Keywords: ion exchange membrane; electrodialysis; seawater concentration; energy consumption; salt production.

1. Introduction

In Japan, there are no rock salt deposit and because of its climate is not suited to manufacture of bay salt, salt requirements have been largely met by imported salt. Only table salt has been produced by a method in which seawater is introduced into a salt field and then thickened by solar energy. This method, however, requires a wide area of land and much labor. In addition, such weather conditions as wind, rain, and length of the dry season raise the cost to rather higher level as compared with the price of imported salt (Tsunoda 1965). With the circumstances described above, research on sea water concentration by means of ion exchange membranes has been progressed. In 1971, all salt field methods are converted into ion exchange membrane methods, which enable the production of nearly 1,000,000 ton/year of edible salt at present. The largest problem in ion exchange membrane methods is that the price is still higher as compared with that of imported salt.

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This problem has become more acute recently because of energy price rising. So, the cost reduction is the most important target in ion exchange membrane technology. In this manuscript, we discuss the performance of an electrodialyzer for concentrating seawater.

In an ion exchange membrane electrodialysis process, cation exchange membranes, anion exchange membranes, desalting cells and concentrating cells are arranged alternately. Seawater is supplied to the cells and an electric current is passed across the membranes. Electrodialysis is a technique based on the transport of ions through selective membranes under an influence of an electric field. Ion transfer is caused by the diffusion and electro-migration, while solution transfer is caused by the electro-osmosis and concentration-osmosis (Helfferich 1962). Energy consumption is caused by electric cell resistance including solution resistance, membrane resistance and membrane potential (Shaffer and Mintz 1966). In order to improve the performance of an electrodialyzer, a lot of investigations are performed as exemplified below.

Homogeneous ion exchange membranes having excellent electrochemical properties are synthesized for increasing brine concentration and decreasing energy consumption. Mechanical strength of the membranes is increased by cross-linking and reinforcements (Mizutani, et al. 1964, Mineki, et al. 1972, Misumi, et al. 1974). Ion transferring across the membrane are supplied from a feeding solution, and the performance of an electrodialyzer is influenced by the solution flow in desalting cells. For accelerating the ionic transport from the solution toward the membrane, theoretical and experimental study of solution flow is carried out (Sonin and Probstein 1968, Belfolt and Guter 1972, Feron and Solot 1991, Shaposhnik, et al. 1997). The space between the membranes is filled with a "spacer". The influence of a spacer on solution flow is investigated theoretically (Pnueli and Grossman 1969, Solan, et al. 1971, Miyoshi, et al. 1982, Shaposhnik, et al. 1998) and experimentally (Hanzawa, et al. 1965, Berfort and Gutter 1972, Kuroda 1993). Limiting current density is caused by concentration polarization in a boundary layer formed on a desalting surface of the membrane. This parameter is usually measured from current density - voltage curves (Berragan and Ruiz-Bauza 1998, Valerdi-Perez and Ibaez-Mengual 2001, Lee, et al. 2006). The mechanism of the limiting current density is analyzed based on the mass transport in a desalting cell by means of chemical engineering techniques (Kitamoto and Takashima 1968, Miyoshi, et al. 1988, Huang and Yu 1988). At over limiting current density, water dissociation occurs and it decreases current efficiency and gives rise to scale trouble which must be prevented (Oda and Yawataya 1968, Tanaka, et al. 1982, Zabolotsky, et al. 1988, Tanaka 2007). In an electrodialysis process for concentrating seawater, divalent ion permeability across the membranes is strongly suppressed for preventing CaSO₄ scale precipitation in concentrating cells (Minzutani, et al. 1971, Mihara, et al. 1970, Mihara, et al. 1972, Hani, et al. 1961). In order to prevent $CaCO_3$ scale precipitation, a hydrochloric acid is added into circulating brine (Watanabe, et al. 1972). Surface fouling is caused by deposits of macromolecules or colloidal matter from the feed solution and its mechanism is discussed (Grossman and Sonin 1973). Small particles suspended in a feeding solution are removed usually using sand filtration (Tsunoda 1993). However, extremely small particles pass through the filter, enter into an electrodialyzer and microorganisms breed at the membrane surface (Nagatsuka, et al. 1987, Ohwada, et al. 1981). The deposits on the membrane are removed by stack disassembling or washing with a chemical reagent (Yamashita 1976, Ueno, et al. 1980, Urabe and Doi 1987).

Simulation of electrodialysis process is performed by following several researchers. Lee, *et al.* (2002) developed a computer simulation program for describing a continuous flow process and estimated investment and operation costs. Further, an electrodialysis plant was designed and optimized in terms of overall costs and different parameters. Moon, *et al.* (2004) investigated ionic

transport across the membrane based on one- and two-dimensional continuous electrodialysis modeling using the principles of electrochemistry, transport phenomena and thermodynamics. Fidaleo and Moresi (2005) simulated mass transfer, mass balance and potential drop and limiting current density in a continuous operation based on the Nernst-Planck equation. Sadzadeh, *et al.* (2007) modeled an one-pass flow process starting from a differential equation of steady-state mass balance and gave concentration in a dilute compartment or separation percent for various voltage, flow rates and feed concentrations.

In this investigation, the performance of an electrodialyzer is discussed by means of a computer simulation. The program is developed on the basis of the following experimental measurement; (1) Membrane characteristics $(\lambda, \mu, \phi, \rho)$, (2) Alternating and direct current electric resistance of the membranes, (3) Solution velocity distribution between desalting cells and current density distribution in an electrodialyzer, (4) Voltage difference between electrodes at the inlets and outlets of desalting cells in an electrodialyzer, (5) Physical properties of desalted and concentrated seawater, (6) Limiting current of ion exchange membranes, (7) Solution leakage in an electrodialyzer. Further, we discuss the direction of research and development for reducing salt manufacturing cost.

2. Electrodialysis process

The seawater concentrating process and compositions of an electrodialyzer are illustrated in Figs. 1 and 2 (Tomita). In the seawater concentrating process, seawater pumped up from sea is filtered and supplied to the electrodialyzer via the filtered solution tank. Concentrated seawater is circulated between the concentrated seawater tank and the electrodialyzer, and its gain is supplied to an evaporating process to obtain salt crystal. CaCO₃ scale precipitation in concentrating cells is prevented by adding hydrochloric acid to the concentrated seawater to decompose HCO_3^- and CO_3^{2-}



Fig. 1 Electrodialytic seawater concentrating process (Tomita)

1: Diluted seawater tank, 2: Cathode solution tank, 3: Concentrated seawater tank, 4: Washing solution tank, 5: HCl tank, 6: Filtrated seawater, 7: Concentrated seawater output, 8: HCl, 9: Electrodialyzer, 10: Anode solution



Fig. 2 Composition of an electrodialyzer (Tomita)

1: Cathode chamber, 2: Anode chamber, 3: Cathode plate, 4: Anode plate, 5: Intermediate frame, 6: Desalting cell, 7: Concentrating cell, 8: Cation exchange membrane, 9: Anion exchange membrane, 10: Packing cell frame, 11: Intermediate packing, 12: Blind cell frame

ions (Watanabe, *et al.* 1972). A part of filtered seawater is supplied to anode chambers. Titanium is adopted as the anode material. In order to avoid membrane destruction due to Cl_2 and HClO generated by an anode reaction, a perfluorinated ion exchange membrane is integrated between the cathode chamber and the adjacent stack. The washed solution from the anode chamber is mixed with the filtered seawater to suppress the growth of microorganisms in seawater. Cathode material is plated with Pt. An HCl solution is supplied to the cathode chamber to neutralize OH^- ions generated by the cathode reaction. A washing system is provided for washing the inside of desalting cells by acid or chemical reagents and dissolving adhered substances (Yamashita 1976, Ueno, *et al.* 1980, Urabe and Doi 1987).

When the turbidity of raw seawater exceeds about 2 ppm, it is decreased to about 0.05 ppm by filtering through two-stage sand filters (Tsundoa 1993). In spite of such filtration, fine particles pass through the filter and invade into the electrodialyzer and precipitate on the membrane surfaces (Nagatsuka, *et al.* 1987). Fe(OH)₃ components precipitated on the membrane possibly give rise to water dissociation (Tanaka 2007). Sometimes, fine organisms pass through the filter and breed in the electrodialyzer (Ohwada, *et al.* 1981). These troubles are avoided by disassembling and washing the electrodialyzer at the interval of 4-6 month. In order to increase current efficiency and avoid CaSO₄ scale precipitation, membrane surfaces are treated to give monovalent ion permselectivity (Minzutani, *et al.* 1971, Mihara, *et al.* 1970, 1972, Hani, *et al.* 1961).

Energy consumption in a salt manufacturing process is supplied by a simultaneous heat-generating electric power unit consisting of a boiler and back-pressure turbine (Tanaka, *et al.* 2003). Boiler steam is introduced to a turbine and generates electricity, which is distributed to electrodialyzers etc. The back-pressure steam of a back-pressure turbine is supplied to a heater in a No. 1 evaporator in

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Current density	A/dm ²	2.66
Temperature	°C	23.5
Cl current efficiency	%	86.5
Na current efficiency	%	78.4
Energy consumption	kWh/tNaCl	164.6
Concentrated solution purity*	%	90.64
Constituent of concentrated solution NaCl	g/dm ³	173.6
Cl current efficiency	eq/dm ³	3.273
SO_4	eq/dm ³	0.007
Ca	eq/dm ³	0.062
Mg	eq/dm ³	0.160
Κ	eq/dm ³	0.088
Na	eq/dm ³	2.970

Table 1 Performance of an electrodialyzer for concentrating seawater (Salt Industry Center 1998)

*NaCl(g)/Totaleletrolyte (g)

multiple-effect evaporators. Evaporated steam in a No.1 evaporator is supplied in turn to the following evaporator. The number of evaporators is kept to minimum, but the electric power generation does not exceed the electric power consumption in the salt manufacturing plant. An electric power shortfall is made up by purchased electric power. In order to minimize the energy consumption in the salt manufacturing process described above, it is necessary to keep balance between electric power generation capacity and back-pressure steam quantity.

Typical performance of an electrodialyzer is exemplified in Table 1 (Salt Industry Center 1998)

3. Electrodialyzer

3.1. Structure of an electrodialyzer

The basic structure of an electrodialyzer consists of stacks in which cation exchange membranes, anion exchange membranes, gaskets (desalting cells and concentrating cells) are arranged alternately (Fig. 3 (Azechi 1980)). Fastening frames are put on both outsides of the stack which is fastened up together through crossbars setting in the figure. The deformation of the membranes is prevented by regulating hydrostatic pressure in the fastening frames. Inlet manifold slots and outlet manifold slots are prepared at the bottoms and heads of the gaskets, respectively. Spacers are incorporated with the gaskets to prevent the contact of cation exchange membranes with anion exchange membranes and to mix the solution. Many stacks are arranged through the fastening frames and electrode cells are put on both ends of the electrodialyzer, which are fastened by a press putting on the outsides of electrode cells.

Seawater is supplied from solution feeding frames to entrance manifolds, flows through entrance slots, current passing portions and exit slots, and discharged from exit manifolds to the outside of the stack (Fig. 3 (Azechi 1980)). Concentrated brine is supplied to concentrating cells in a circulating flow system, and extracted to the outside of the stack through overflow extracting system.

Effective membrane area is in the range from less than 1 m^2 to about maximum 2 m^2 . In order to



Fig. 3 Structure of a stack (Azechi 1980)

a: desalting cell, b: concentrating cell, c: manifold, d: slot, e: fastening frame, f: feeding frame, g: cation exchange membrane, h: anion exchange membrane, i: spacer, j: feeding solution, k: desalted solution, l: concentrated solution

reduce energy consumption, it is desirable to decrease the electric resistance of the membrane and gasket thickness. A gasket material is selected from synthesized rubber, polyethylene, polypropylene, polyvinyl chloride and ethylene-vinyl acetate copolymer etc. The spacer is usually incorporated with the gasket and a solution flows dispersing along the spacer net.

3.2. Requirement for improving the performance of an electrodialyzer

In order to improve the performance of an electrodialyzer, membrane characteristics should be naturally improved. At the same time, the circumstances in an electrodialyzer in which the membranes work should be better. Here, we describe the definite problems lowering the circumstances in an electrodialyzer and requirement for improving the circumstances and performance of an electrodialyzer (Urabe and Doi 1978).

3.2.1. Solution velocity distribution between desalting cells

In an electrodialyzer, ion exchange membranes, desalting cells and concentrating cells are arranged alternately and a solution is supplied into desalting cells. In this flow system, the solution velocity distribution in desalting cells does not become uniform. This phenomenon causes the concentration distribution, electric resistance distribution and current density distribution in the electrodialyzer, and gives rise to the decrease of the limiting current density. In order to operate the electrodialyzer stably, it becomes necessary to make the solution velocities between the desalting cells uniform.

3.2.2. Solution leakage in an electrodialyzer

The dimensions of all parts of an electrodialyzer are not always consistent with the figures in the

specifications. Small pinholes can open in an electrodialyzer because the mechanical strength of ion exchange membranes is relatively low. Gaps may occur between the materials composing the electrodialyzer in the assembly work of an electrodialyzer. If a pressure difference between the desalting cells and concentrating cells exists in these circumstances, solutions leak through membranes and lower the performance of the electrodialyzer. In order to avoid these troubles, we have to remove the pinholes and gaps in the electrodialyzer and control the pressure difference between desalting cells and concentrating cells.

3.2.3. Electric current leakage

A part of an electric current flows through slots and manifolds causing ineffective current leakage. Current leakage is increased by the increases of the numbers of cell pairs integrated in a stack and the increase of sectional area of slots and manifolds. These events, however, relate with the solution velocity distribution between the cells described in Section 3.2.1.

3.2.4. Distance between the membranes

Decrease of the distance between the membranes brings about the decrease of electric resistance and energy consumption. On the other hand, it brings about the increase of friction loss of solution flow, blocking of the materials suspended in a feeding solution and the increase of pumping motive power. Accordingly, it becomes necessary to realize the optimum distance between the membranes. The optimum distance is decided further taking account of electric resistance of an ion exchange membrane and that of electrolyte solutions in desalting and concentrating cells.

3.2.5. Spacer

Main functions of a spacer are to create space between a cation and an anion exchange membrane in a desalting and concentrating cell. When solution velocity and the Reynolds number are decreased, hydrodynamic pattern exhibits laminar flow, which decreases limiting current density. In order to increase the limiting current density, turbulent flow should be induced by incorporating the spacer into desalting cells.

3.2.6. Simplicity of structure of an electrodialyzer

Disassembling and assembling work is peculiar features in operating an electrodialyzer. Excellent durability of ion exchange membranes is owing to careful handling in this work.

4. Computer simulation of ion exchange membrane electrodialysis for seawater concentration

4.1. Assumptions

In order to enhance the performance of electrodialyzers, it is expected to increases NaCl concentration in a concentrated solution C_{NaCl}'' (NaCl g/l) and decrease energy consumption to obtain one ton of NaCl E_{NaCl} (kWh/t NaCl). Technical targets in operating electrodialyzers are C_{NaCl} >200 NaCl g/l and $E_{NaCl} < 120$ kWh/t NaCl at present (Fujita 2009). We develop the electrodialysis (ED) program to calculate the performance of an electrodialyzer taking the target into account on the basis of the following assumptions.

(1) Solution leakage and electric current leakage in an electrodialyzer are negligible.

- (2) Direct current electric resistance of a membrane includes the electric resistance of a boundary layer formed on the desalting surface of the membrane due to concentration polarization.
- (3) Frequency distribution of solution velocity ratio in desalting cells is equated by the normal distribution.
- (4) Current density i at x distant from the inlets of desalting cells is approximated by the quadratic equation.
- (5) Voltage difference between the electrodes at the entrance of desalting cells is equal to the value at the exits.
- (6) Limiting current density of an electrodialyzer is defined as average current density applied to an electrodialyzer when current density reaches the limit of an ion exchange membrane at the outlet of a desalting cell in which linear velocity and electrolyte concentration are the least.
- (7) Concentrated solutions are extracted from concentrating cells to the outside of the process.

4.2. Electrodialysis (ED) program

In the previous investigation (Tanaka), the performance of a saline water desalination process was computed using the electrodialysis program. In this investigation, the program is developed for predicting concentrating performance of seawater. In a practical-scale electrodialyzer, electrolyte concentration in desalting cells is decreased along a flow-pass and it gives rise to electrolyte



De: Desalting cell, Con: Concentrating cell K: Cation exchage membrane, A: Anion exchange membrane J_S, J_V : Fluxes of ions and solutions across membrane pairs at x = plC', C'': Electrolyte concentration in desalting and concentrating cells at x = pl $u = (u_{in}+u_{out})/2$ $Q = (Q_{in}+Q_{out})/2$

Fig. 4 Electrodialysis process (Tanaka)

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concentration distribution. It causes electric resistance distribution and current density distribution. In this simulation, these distributions are taken into account and the relationship between the concentration of a concentrated solution and energy consumption in a concentrating process is discussed.

An electrodialyzer (effective membrane area: *S*, number of desalting cells: *N*) is operated with a constant electric current *I* as illustrated in Fig. 4, and an electrolyte solution (Concentration: C'_{in}) is supplied to the inlets of desalting cells at average linear velocity u_{in} . Electrolytes and solutions transfer from desalting cells to concentrating cells. In desalting cells, electrolyte concentration is decreased from C'_{in} under applied average current density *I/S* and reaches average electrolyte concentration C'_{out} at the outlets of desalting cells. Electrolyte concentration change in desalting cells causes current density change along the flow-pass from i_{in} at the inlets to i_{out} at the outlets. Fig. 4 shows that current density becomes respectively *i* and *I/S* at *x* and *pl* distant from the inlets of desalting cells. Further, the figure shows that J_S , J_V and average electrolyte concentration *C'* and *C''* = J_S/J_V are the values at *pl* distant from the inlets of desalting cells. u_{out} is average linear velocity at the outlets of desalting cells is extracted at x=pl and discharged to the outside of the electrolyte.

The performance of an electrodialyzer is computed by the simplified program in Fig. 5 which



Fig. 5 Electrodialysis (ED) program

consists of the following five steps and principles: Step 1 Mass transport, Step 2 Current density distribution, Step 3 Cell voltage, Step 4 NaCl concentration in a concentrated solution and energy consumption and Step 5 Limiting current density. The details of these principles are described below.

Step 1 Mass transport (Tanaka 2006, 2007)

Ion exchange membrane electrodialysis is a process for transporting ionic species across the membrane. When an electrolyte solution is supplied to an electrodialyzer and an electric current is passed through it, ions and a solution in a desalting cell are transported to a concentrating cell across a cation and an anion exchange membrane. The quantity of ions J_S and a solution J_V transported across a pair of membranes per unit area and per unit time at current density *i* are expressed by the following overall mass transport equation, Eqs. (1) and (2).

$$J_S = \eta(i/F) = C''J_V = \lambda i - \mu(C'' - C') = \lambda i - \mu\Delta C$$
⁽¹⁾

$$J_V = \phi i + \rho (C'' - C') = \phi i + \rho \Delta C \tag{2}$$

 η is current efficiency, F the Faraday constant, C' and C" electrolyte concentration in a desalting and a concentrating cell, respectively, λ the overall transport number, μ the overall solute permeability, ϕ the overall electro-osmotic permeability and ρ the overall hydraulic permeability, and these parameters are termed the overall membrane pair characteristics altogether. The term "overall" means that the parameters are the sum of the contributions of a cation and an anion exchange membrane. It also means that the parameters are the sum of the contributions of many kinds of ions dissolving in an electrolyte solution. Parameters λi and $\mu\Delta C$ in Eq. (1) stand for the electro-migration and solute diffusion, respectively. Parameters ϕi and $\rho\Delta C$ in Eq. (2) correspond to



Fig. 6 J_S/i vs. $\Delta C/i$ plot and J_V/i vs. $\Delta C/i$ plot. Selemion CMR. ASR



Fig. 7 ρ versus λ , μ and ϕ (Tanaka 2006). Seawater electrodialysis Aciplex: \bigcirc CK-2/CA-3, \bigcirc K-172/A-172, Selemion: \triangle CSV-2/AST, \blacktriangle CMR/ASR, Neocepta \square CL-2.5T/AVS-4T, \blacksquare CIMS/ACS-3, 0.5 M NaCl sol. electrodialysis, \Rightarrow : Aciplex K-172/A-172

the electro-osmosis and concentration-osmosis. J_S/i and J_V/i against $\Delta C/i$ yield straight lines, so that λ , μ , ϕ and ρ are obtained from the intercepts and the gradients of the lines based on the electrodialysis experiment.

 J_S/i and J_V/i vs. $\Delta C/i$ plots are obtained by repeating the electrodialysis by changing current density. The plots are not influenced by the concentration polarization and are obtained by the electrodialysis of seawater as shown in Fig. 6. On the basis of many electrodialysis experiments of seawater described above, the regularity in ion exchange membrane characteristics is found from the plot of λ (eq C⁻¹), μ (cm s⁻¹) and ϕ (cm³ C⁻¹) against ρ (cm⁴ eq⁻¹ s⁻¹) as shown in Fig. 7. The plots for a 0.5M NaCl solution electrodialysis are marked by asterisks in Fig. 7, indicating that the plotting is done on the same lines for seawater electrodialysis. ρ vs. membrane pair electric resistance R (= R_K + R_A , Ω cm²) is indicated in Fig. 8. Further, the plots in Figs. 7 and 8 are expressed by the following empirical equations.

$$\lambda = 9.208 \times 10^{-6} + 1.914 \times 10^{-5} \,\rho \tag{3}$$

$$\mu = 2.005 \times 10^{-4} \rho \tag{4}$$

$$\phi = 3.768 \times 10^{-3} \,\rho^{0.2} - 1.019 \times 10^{-2} \,\rho \tag{5}$$

$$R = 5.107 \times 10^{-2} \,\rho^{-1} \tag{6}$$

Phenomenological meanings of the overall membrane pair characteristics are given by the following equations.

$$\lambda = \frac{t_K + t_A - 1}{F} \tag{7}$$



Fig. 8 ρ versus *R* (Tanaka 2006).

○ Aciplex K102/A102, ○ Aciplex K172/A172, $\triangle \blacktriangle$ Selemion CMV/AST, □ ■ Neocepta CH45T/AFS4T, \Rightarrow JTS K/JTSA, Filled are the membranes integrated in an electrodialyzer operating for electrodialyzing seawater.

$$\mu = RT(\omega_K + \omega_A) \tag{8}$$

$$\phi = \beta_K + \beta_A \tag{9}$$

$$\rho = RT(L_{P,K} + L_{P,A}) \tag{10}$$

where t is the transport number, ω is the solute permeability, β is the electroosmotic permeability and L_p is the hydraulic permeability. The subscripts K and A denote a cation and an anion exchange membrane, respectively.

The electrolyte concentration in a concentrating cell C'' is introduced from Eqs. (1) and (2) as follows:

$$C'' = \frac{1}{2\rho} (\sqrt{A^2 + 4\rho B} - A)$$
(11)

$$A = \phi i + \mu - \rho C' \tag{12}$$

$$B = \lambda i + \mu C' \tag{13}$$

Eqs. (3)-(6) indicate that ρ is a leading parameter and represent all of the overall membrane pair characteristics. λ , μ , ϕ and R are computed by substituting ρ in Eqs. (3)-(6). C'' is computed by substituting *i* and *C*' in Eqs. (11)-(13). Accordingly, the electro-migration λi , the solute-diffusion $\mu\Delta C$, the electro-osmosis ϕi and concentration-osmosis $\rho\Delta C$ are determined using Eqs. (1)-(5) and (11)-(13) by setting ρ , *i* and *C*' as parameters.

In Figs 7 and 8, it should be noticed that μ , ϕ and 1/R decreases with ρ and they approach zero at $\rho = 0$ as be seen in the following equation.

$$\lim_{\rho \to 0} \mu = \lim_{\rho \to 0} \phi = \lim_{\rho \to 0} \left(\frac{1}{R}\right) = 0 \tag{14}$$

Physical meaning of Eq. (14) is understandable from the following equation including porosity ε of the membrane.

$$\lim_{\varepsilon \to 0} \rho = \lim_{\varepsilon \to 0} \mu = \lim_{\varepsilon \to 0} \phi = \lim_{\varepsilon \to 0} \left(\frac{1}{R}\right) = 0$$
(15)

which means that ρ , μ , ϕ and 1/R decrease with the porosity and become zero (*R* becomes infinite) at $\varepsilon = 0$ which corresponds to an insulator. Eqs. (14) and (15) show that ρ reflects the porosity of the membrane, and these equations show that for a fine porous (dense structural) membrane, ρ , μ and ϕ are decreased and *R* is increased.

Steps 2 Current density distribution (Tanaka 2000, 2005, 2007)

We assume that current density i at x distant from the inlet of a desalting cell is approximated by the following current density distribution equation.

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$$i = a_1 + a_2 \left(\frac{x}{l}\right) + a_3 \left(\frac{x}{l}\right)^2 \tag{16}$$

in which *l* is the flow-pass length in a desalting cell.

To determine a_1 , a_2 and a_3 in Eq. (16), following three-simultaneous equations are set up.

$$V_{\rm in} = V_{\rm out} \tag{17}$$

$$V_{\rm in} = V_{\rm p} \tag{18}$$

$$\zeta_{\text{inout}} = \zeta_{\text{inp}} \tag{19}$$

 ζ_{inout} is introduced from Eq. (17) and expressed by Eq. (20). It equals to the outlet current density non-uniformity coefficient ζ_{out} as follows.

$$\zeta_{inout} = \frac{\alpha_1 + \alpha_2 p + \alpha_3 p^2}{\beta_1 + \beta_2 p + \beta_3 p^2} = \zeta_{out} = \frac{i_{out}}{I/S}$$
(20)

 ζ_{inp} is introduced from Eq. (18) and expressed by Eq. (21). It also equals to ζ_{out} as follows.

$$\zeta_{inp} = \frac{\gamma_1 + \gamma_2 p + \gamma_3 p^2}{(2p - 3p^2)(I/S)} = \zeta_{out}$$
(21)

We determine a_1 , a_2 , a_3 with the inlet electric current non-uniformity coefficient ζ_{in} , outlet electric current non-uniformity coefficient ζ_{out} , inlet electric current density i_{in} and outlet current density i_{out} .

$$\zeta_{in} = \frac{i_{in}}{I/S} = \frac{a_1}{I/S} \tag{22}$$

$$\zeta_{out} = \frac{i_{out}}{I/S} = \frac{a_1 + a_2 + a_3}{I/S}$$
(23)

Step 3 Cell voltage

Cell voltage is given by the following equation.

$$V_{\text{cell}} = V_{\Omega, in} + V_{memb, in} = V_{\Omega, out} + V_{memb.out}$$
(24)

Ohmic potential $V_{\Omega, in}$ and membrane potential $V_{memb,in}$ at the inlets of desalting cells in Eq. (24) are given as;

$$V_{\Omega,in} = (r'_{in} + V_{\text{mem,in}} + r'')i_{in}$$
(25)

$$V_{memb,in} = 2(t_K + t_A - 1) \times \left(\frac{RT}{F}\right) \ln \frac{\gamma''C''}{\gamma'_{in}C_{in}'}$$
(26)

in which, r'_{in} and $r_{memb,in}$ are respectively electric resistance of a solution and a membrane at the inlet of a desalting cell. r'' is electric resistance of a solution in a concentrating cell. $t_{\rm K}$ and $t_{\rm A}$ are

the transport number of a cation and anion exchange membrane respectively. γ'_{in} is the activity coefficient of ions dissolving in a solution at the inlet of desalting cell. γ'' is the activity coefficient of ions dissolving in a concentrating cell.

Solution velocities in desalting cells vary between the cells, and give rise to solution velocity distribution. We assume here that the frequency Y_j of solution velocity ratio ξ of group j defined in Eq. (27) is approximated by the normal distribution.

$$\xi = \frac{u^b - u}{u} \tag{27}$$

where u is the average linear velocity in every desalting cell and u^{b} (u flat) is the linear velocity in each desalting cell.

Then ohmic potential $V_{\Omega out}$ and membrane potential $V_{memb,out}$ at the outlets of desalting cells in Eq. (24) are given by averaging the values for N cells integrated in an electrodialyzer (Tanaka 2000, 2005, 2007);

$$V_{\Omega,out} = \left(\sum_{1}^{N} Y_{j} r'_{out,j} + \sum_{1}^{N} Y_{j} r_{memb,out,j} + r'' N\right) \times i_{out} \left(\frac{1}{N}\right)$$
(28)

$$V_{mem,out} = 2(t_K + t_A - 1) \times \left(\frac{RT}{F}\right) \sum_{1}^{N} \ln \frac{\gamma''C''}{\gamma'_{out,j}C'_{out,j}} \times \left(\frac{1}{N}\right)$$
(29)

Step 4 NaCl concentration in a concentrated solution and energy consumption

In the seawater electrodialysis process, it is strongly expected to decrease the transport of

divalent ions for preventing scale (CaSO₄) formation in concentrating cells. In order to accomplish this purpose, many attempts on the membrane treatment had been made (Mizutani, *et al.* 1971, Mihara, *et al.* 1970, 1972, Hani, *et al.* 1961). The representative concentration ratio of ion *i*, r_i to total ions (equiv. of ion *i*/equiv. of total ions) in a concentrated solution in seawater electrodialysis incorporated with divalent ion low-permeable membranes are given by the following functions of average current density *I/S* (A/dm²) (Tanaka 2003).

$$r_{Na} = 0.8220 + 0.7286 (I/S)^{-0.5} - 1.644(I/S)^{-1} + 1.308(I/S)^{-1.5} - 0.3573(I/S)^{-2}$$
(30)

$$r_{Cl} = 0.9911 + 0.02249(I/S)^{-0.5} - 0.03424(I/S)^{-1} + 0.02328(I/S)^{-1.5} - 0.005919(I/S)^{-2}$$
(31)

$$r_K = 0.00585 + 0.02268r_{Na} \tag{32}$$

$$r_{Mg} = 0.7736 - 0.7958r_{Na} \tag{33}$$

$$r_{Ca} = 0.1925 - 0.1910r_{Na} \tag{34}$$

$$r_{SO4} = 1 - r_{Cl} \tag{35}$$

The concentration of ion *i*, C_i'' (eq/cm³) in a concentrated solution is expressed by Eq. (36).

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$$C_i'' = r_i \times C'' \tag{36}$$

The concentration of NaCl, C''_{NaCl} , and concentration of electrolytes, C'', in a concentrated solution; the NaCl purity p of the concentrated solution; and electrolyte output P and NaCl output P_{NaCl} are presented by Eqs. (37)-(41).

$$C''_{NaCl}$$
 (g/cm³) = 58.443 C''_{Na} (eq/cm³) (37)

$$C''(g/cm^3) = 57.87C''(eq/cm^3)$$
 (38)

$$p = C''_{NaCl}(g/cm^{3})/C''(g/cm^{3})$$
(39)

$$P(kg/m^{2}h) = C''(kg/m^{3})J_{\nu}(m/h)$$
(40)

$$P_{NaCl}(kg/m^2h) = J_{S}(kg/m^2h)p$$
(41)

Finally, energy consumption to obtain one ton of NaCl E_{NaCl} is expressed using V_{cell} by the following equations.

$$E_{NaCl} = \frac{V_{cell}I}{P_{NaCl}} \tag{42}$$

Step 5 Limiting current density (Tanaka 2000, 2005, 2007)

Limiting current density of a cation exchange membrane is less than that of an anion exchange membrane, because the mobility of counter ions in a solution for a cation exchange membrane is less than that for an anion exchange membrane. So the limiting current density of an ion exchange membrane integrated in an electrodialyzer; i_{lim} is given by the following empirical equation established for a cation exchange membrane.

$$i_{\rm lim} = (m_1 + m_2 u_{out}) C'_{out}^{n_1 + n_2 u_{out}}$$
(43)

When current density reaches the limit of a cation exchange membrane i_{lim} at the outlet of a desalting cell in which linear velocity becomes the least among u_{out} ; u_{out}^{*} (u_{out} sharp), the average current density applied to an electrodialyzer is defined as its limiting current density (I/S)_{lim} which is expressed by Eq. (44) introduced from Eqs. (23) and (43).

$$\left(\frac{I}{S}\right)_{\lim} = \frac{i_{\lim}}{\zeta_{out}} = \frac{(m_1 + m_2 u_{out}^{\#})}{\zeta_{out}} (C'_{out}^{\#})^{n_1 + n_2 u_{in}^{\#}}$$
(44)

in which $C'_{out}^{\#}$ (C'_{out} sharp) is C'_{out} at $u = u_{out}^{\#}$. In Eq. (44), $u_{out}^{\#}$ is nearly equal to $u_{in}^{\#}$ for commercially available membranes. Substituting $u_{in}^{\#} = u_{out}^{\#}$ in Eq. (44) leads to:

$$\left(\frac{I}{S}\right)_{\lim} = \frac{m_1 + m_2 u_{in}^{\#}}{\zeta_{out}} \left(C_{out}^{\#}\right)^{n_1 + n_2 u_{in}^{\#}}$$
(45)

in which $C'_{in}^{\#}$ is C'_{in} at $u = u_{in}^{\#}$ which is given by;

$$u_{in}^{\#} = u_{in}(1-3\sigma)$$
 (46)

On the other hand, the relationship between $(I/S)_{lim}$ and $C_{out}^{\#}$ is also introduced for commercially available membranes as follows

$$\left(\frac{I}{S}\right)_{\lim} = \left(\frac{a}{\lambda l}\right) u_{in}^{\#} (C_{in}' - C_{out}'^{\#})$$
(47)

Putting Eq. (45) = Eq. (47):

$$Z_{1} = \frac{(C'_{out})^{n_{1}+n_{2}u_{in}^{*}}}{C'_{in} - C'_{out}^{\#}}$$
(48)

$$Z_2 = \left(\frac{a\zeta_{out}}{\lambda l}\right) \left(\frac{u_{in}^{\#}}{m_1 + m_2 u_{in}^{\#}}\right)$$
(49)

$$Z_1 = Z_2 \tag{50}$$

Limiting current density of an electrodialyzer $(I/S)_{\text{lim}}$ is computed using trial and error calculation by substituting control key $C'_{out}^{\#}$ for $C'_{out}^{\#}$ in Eq. (48) to realize $Z_1=Z_2$ (Eq. (50)) for determining $C'_{out}^{\#}$. $(I/S)_{\text{lim}}$ is calculated by substituting $C'_{out}^{\#}$ into Eq. (45).

4.3. Computation

4.3.1. Influence of current density I/S and overall hydraulic permeability of a membrane pair ρ on the performance of an electrodialyzer

The following basic values are inputted to the program.

Current density I/S = 0.5-7 A/dm²; varied

Overall hydraulic permeability of a membrane pair $\rho = 0.005 \cdot 0.025 \text{ cm}^4/\text{eq}$ s; varied Electrolyte concentration at the inlets of desalting cells $C'_{in} = 0.6 \text{ eq/dm}^3$

Linear velocity at the inlets of desalting cells $u_{in} = 5$ cm/s

Standard deviation of normal distribution of solution velocity ratio $\sigma = 0.1$

Flow-pass thickness in a desalting cell a = 0.05 cm

Flow-pass width in a desalting cell b = 100 cm

Flow-pass length in a desalting cell l = 100 cm

Current screening ratio of a spacer $\varepsilon = 0.15$

Number of desalting cells integrated in an electrodialyzer N = 300 cells

4.3.2. Influence of standard deviation of normal distribution of solution velocity ratio σ on the performance of an electrodialyzer

The following basic values are inputted to the program.

Standard deviation of normal distribution of solution velocity ratio $\sigma = 0.01$. 0.05, 0.10, 0.15, 0.20, 0.25

Current density $I/S = 3 \text{ A/dm}^2$

Overall hydraulic permeability of a membrane pair $\rho = 0.01$ cm⁴/eq s

Electrolyte concentration at the inlets of desalting cells $C'_{in} = 0.6 \text{ eq/dm}^3$

Linear velocity at the inlets of desalting cells $u_{in} = 5$ cm/s

Flow-pass thickness in a desalting cell a = 0.05 cm

Flow-pass width in a desalting cell b = 100 cm

Flow-pass length in a desalting cell l = 100 cm

Current screening ratio of a spacer $\varepsilon = 0.15$

Number of desalting cells integrated in an electrodialyzer N = 300 cells

4.4. Results and discussion

4.4.1. Influence of current density I/S and overall hydraulic permeability of a membrane pair ρ on the performance of an electrodialyzer

Figs. 9, 10 and 11 show the relationship between current density I/S and ion flux J_S , solution flux J_V and current efficiency η taking the overall hydraulic permeability of a membrane pair ρ as a parameter. They are increased with I/S and ρ , but J_S is not influenced by ρ . Cell voltage V_{cell} and membrane potential V_{memb} are plotted against I/S in Fig. 12. The difference of V_{cell} and V_{memb} is equivalent to ohmic potential V_{ohm} . Figs. 13 and 14 present the influence of I/S on NaCl concentration in a concentrated solution C''_{NaCl} and energy consumption to obtain one ton of NaCl E_{NaCl} . They are increased with increasing I/S and decreasing ρ . Fig. 15 gives the relationship between I/S and limiting current density of an electrodialyzer $(I/S)_{lim}$ showing considerably larger values.



Fig. 9 Relationship between current density and ion flux across a membrane pair $\rho = 0.005(\bigcirc), 0.01(\triangle), 0.015(\square), 0.02(\bullet), 0.025(\blacktriangle), \text{cm}^4\text{eq}^{-1}\text{s}^{-1}$



Fig. 10 Relationship between current density and solution flux across a membrane pair $\rho = 0.005(\bigcirc), 0.01(\triangle), 0.015(\square), 0.02(\bullet), 0.025(\blacktriangle), \text{cm}^4\text{eq}^{-1}\text{s}^{-1}$



Fig. 11 Relationship between current density and current efficiency

 ρ = 0.005(○), 0.01(△), 0.015(□), 0.02(●), 0.025(▲), cm⁴eq⁻¹s⁻¹



Fig. 13 Relationship between current density and NaCl concentration in a concentrated solution $\rho = 0.005(\bigcirc), 0.01(\triangle), 0.015(\Box), 0.02(\bullet), 0.025$ (**A**), cm⁴eq⁻¹s⁻¹



Fig. 12 Relationship between current density and cell voltage and membrane poteitional $\rho = 0.005(\bigcirc), 0.01(\triangle), 0.015(\square), 0.02(\bullet), 0.025(\blacktriangle),$

 $\rho = 0.005(\bigcirc), 0.01(\triangle), 0.015(\bigcirc), 0.02(\bigcirc), 0.025(\blacktriangle), cm^4 eq^{-1} s^{-1}$



Fig. 14 Relationship between current density and energy consumption to obtain one ton of NaCl. $\rho = 0.005(\bigcirc), 0.01(\triangle), 0.015(\square), 0.02(\bullet), 0.025(\blacktriangle), \text{cm}^4\text{eq}^{-1}\text{s}^{-1}$

4.4.2. Influence of standard deviation of normal distribution of solution velocity ratio σ on the performance of an electrodialyzer

 σ is influenced extremely by precision of part dimensions of a stack and skill of stack assembling work of an electrodialyzer, so we can not decide reasonable σ value before hand. $\sigma = 0.1$ inputted in Fig. 15 is decided in a rough-and-ready manner referring to the experimental observation. (*I/S*)_{lim}



Fig. 15 Relationship between current density and limiting current density. $\rho = 0.005(\bigcirc), 0.01(\bigtriangleup), 0.015(\Box), 0.02(\bigcirc), 0.025(\blacktriangle), \text{cm}^4\text{eq}^{-1}\text{s}^{-1}$



Fig. 16 Relationship between standard deviation of normal distribution and limiting current density $I/S = 3 \text{ A/dm}^2$, $\rho = 0.1$

Fig. 17 Relationship between standard deviation of normal distribution and ion flux, solution flux and cell voltage $I/S = 3 A/dm^2$, $\rho = 0.1$

is strongly influenced by σ as shown in Fig. 16 and it is decreased by the increase of σ . Current density in this electrodialyzer is adjusted to 3 A/dm² in the calculation (Section 4.3.2), so that limiting standard deviation σ_{lim} is estimated to be $\sigma_{\text{lim}} = 0.268$ as shown in the figure. On the other hand, Fig. 17 shows that J_S , J_V and V_{cell} are not influenced at all by σ . In conclusion, excepting the limiting current density, we are permitted to assume that the performance of an electrodialtzer is hardly influenced by σ , even though σ is inputted in a rough-and-ready manner.

4.4.3. NaCl concentration in concentrating cells $C_{NaCl}^{"}$ and energy consumption to obtain one ton of NaCl E_{NaCl}

The relationship between E_{NaCl} and C''_{NaCl} with the performance of electrodialyzers operating in salt-manufacturing plants (Salt Industry Center 1998) and the target; $C''_{NaCl} > 200 \text{ NaClg/l}$ and $E_{NaCl} < 120 \text{ kWh/tNaCl}$ (cf. Section 4.1) is presented in Fig. 18, showing that both computation and operation are inferior to the target. On the other hand, experimental-scale electrodialysis experiment performed in another investigation shows that ρ values for commercially available membranes integrated in the plants in Fig. 18 are estimated to be in the range of $\rho = 1.12-1.25 \times 10^{-2} \text{ cm}^4/\text{eq} \text{ s at } 25^{\circ}\text{C}$. Accordingly, the data of the operation in Fig. 18 are inferior to the computed data as follows:

$$C_{NaCl}'' \text{ (operation)} < C_{NaCl}'' \text{ (computation)}$$

$$E_{NaCl} \text{ (operation)} > E_{NaCl} \text{ (computation)}$$
(51)

Fig. 18 shows that it is very difficult to hit the target, however it is estimated to be possible to approach the target by promoting the following research and development.

- (1) It is assumed from Fig. 18 that integration of fine porous membranes (having low ρ values) into an electrodialyzer is desirable when the electrodialyzer is operated at rather lower electric current density. However, it induces the increase of capital cost.
- (2) Development of fine porous membranes (having dense structure) is desirable if it does not causes notable increases of electric resistance. Otherwise, for example, ① formation of a double layered membrane consisting from a fine porous thinner functional layer and porous reinforcement layer, or ② increasing of desalting surface membrane area by forming microfolds, might decrease electric resistance of the membrane and enhance the performance toward the target.
- (3) The inequality in Eq. (51) is estimated to be due to the leakage of solutions and an electric



Fig. 18 Relationship between NaCl concentration in a concentrated solution and energy consumption to obtain one ton of NaCl

 $\rho = 0.005(\bigcirc), 0.01(\bigtriangleup), 0.015(\Box), 0.02(\bigcirc), 0.025(\blacktriangle), cm^4 eq^{-1}s^{-1}, \Leftrightarrow$: Electrodialyzers operating in salt-manufacturing plants (Salt Industry Center 1998)

current generated in practical-scale electrodialyzers, because the computation is carried out with neglecting (cf. Section 4.1) the solution leakage (cf. Section 3.2.2) (Tanaka 2004, 2005) and current leakage (cf. Section 3.2.3) (Wilson 1960, Mandersloot and Hicks 1966). So, it is desirable to reduce both leakages.

It is suggested from the discussion mentioned above, that the validity of the computer simulation model is demonstrated by comparing the computed results with the performance of electrodialyzers operating in salt-manufacturing plants. The model makes it possible to discuss optimum specifications and operating conditions of a practical-scale electrodialyzer.

5. Conclusion

The following parameters or phenomena influencing to the performance of an electrodialyzer are discussed with computer simulation; (1) Current density and overall hydraulic permeability of a membrane pair. (2) Standard deviation of normal distribution of solution velocity ratio in desalting cells. (3) NaCl concentration in concentrating cells and energy consumption to obtain one ton of NaCl. Excepting limiting current density, the performance of an electrodialtzer is hardly influenced by standard deviation of normal distribution of solution velocity ratio in desalting cells. In order to reduce salt manufacturing cost, it is desirable to promote the following research and development: (1) Integration of fine porous membranes having dense structure into an electrodialyzer being operated at rather lower electric current density. (2) Development of fine porous membranes without notable increase of electric resistance. (3) Decrease of solution leakage and electric current leakage in an electrodialyzer.

References

Azechi, S. (1980), "Electrodialyzer", Bull. Soc. Sea Water Sci., Jpn., 34, 77-83.

- Belfolt, G. and Guter, G.A. (1972), "An experimental study of electrodialysis hydrodynamics", *Desalination*, **10**, 221-262.
- Berfort, G and Gutter, G.A. (1972), "An experimental study of electrodialysis hydrodynamics", *Desalination*, **10**, 221-262.
- Berragan, V.M. and Ruiz-Bauza, C. (1998), "Current-voltage curves for ion-exchange membranes: A method for determining the limiting current density", J. Colloid Inter. Sci., 205, 365-373.
- Feron, P. and Slot, G.S. (1991), "The influence of separators on hydrodynamics and mass transfer in narrow cells: Flow visualization", *Desalination*, **84**, 137-152.
- Fidaleo, M. and Moresi, M. (2005), "Optimal strategy to model the electrodialytic recovery of a strong electrolyte", J. Membr. Sci., 260, 90-111.
- Fujita, T. (2009), "Current challenges of salt production technology", Bull. Soc. Sea Water Sci., Jpn., 63, 15-20.
- Grossman, G. and Sonin, A.A. (1973), "Membrane fouling in electrodialysis: A model and experiments", *Desalination*, **12**, 107-125.
- Hani, H., Nishihara, H. and Oda, Y. (1961), Anion-exchange membrane having permselectivity between anions, JP Patent, S36-15258.
- Hanzawa, N., Azechi, S., Fujimoto, Y. and Nagatsuka, S. (1965), Studies on electrodialytic equipment with ion exchange membrane X, Comparison of spacer used for electrodialytic equipment, Scientific Papers of The Odawara Salt Experiment Station, 10, pp. 16-25.

Helfferich, F. (1962), Ion-Exchange, McGraw-Hill Book., New York, pp 397-408.

Huang, T.C. and Yu, I.Y. (1988), "Correlation of ionic transfer rate in electrodialysis under limiting current

density conditions", J. Membr. Sci., 35, 193-206.

- Kitamoto, A. and Takashima, Y. (1968), "Studies on electroosmosis, maximum attainable concentration, limiting current density and energy efficiency in electrodialysis using ion-exchange membranes", J. Chem. Eng. Jpn., 32, 74-82.
- Kuroda, O. (1993), "Study for improvement of efficiency in electrodialyzer", Bull. Soc. Sea Water Sci., Jpn., 47, 248-258.
- Lee, H.J., Strathmann, H. and Moon, S.H. (2006), "Determination of the limiting current density in electrodialysis desalination as an empirical function of linear velocity", *Desalination*, **190**, 43-50.
- Lee, H.J., Sarfert, F., Strathmann, H. and Moon, S.H. (2002), "Designing of an electrodialysis desalination plant", *Desalination*, 142, 267-286.
- Mandersloot, W.G.B. and Hicks, R.E. (1966), "Leakage current in electrodialytic desalting and brine production", *Desalination*, **1**, 178-193.
- Mihara, K., Misumi, T., Yamauchi, H. and Ishida, Y. (1970), *Anion-exchange membrane having excellent specific permselectivity between anions*, JP Patent, S45-19980, S45-30693.
- Mihara, K., Misumi, T., Yamauchi, H. and Ishida, Y. (1972), *Production of a cation-exchange membrane having* excellent specific permselectivity between cations, JP Patent, S47-3081.
- Mineki, Y., Gunzima, T. and Arai, S. (1972), Production of an ion exchange membrane, JP Patent, S47-40868.
- Misumi, T., Kawashima, Y., Takeda, K. and Kamaya, M. (1974), Production of an ion exchange membrane structure and an apparatus, JP Patent, S49-34476.
- Miyoshi, H., Fukumoto, T. and Kataoka, T. (1982), "A consideration on flowdistribution in an ion exchange compartment with spacer", *Desalination*, **42**, 47-55.
- Miyoshi, H., Fukumoto, T. and Kataoka, T.A. (1988), "Method for estimating the limiting current density in electrodialysis", Sep. Sci. Technol., 23, 585-600.
- Mizutani, Y., Yamane, R. and Kimura, K. (1964), Production of ion exchange membrane, JP Patent, S39-27861.
- Mizutani, Y., Yamane, R., Sata, T. and Izuo, T. (1971), *Permselectivity treatment of a cation-exchange membrane*, JP Patent, S5642083.
- Moon, P., Sandi, G., Stevens, D. and Kizilel, R. (2004), "Computational medeling of ionic transport in continuous and batch electrodialysis", *Sep. Sci. Technol.*, **39**, 2531-2555.
- Nagatsuka, S., Kagiwada, K., Soga, K. and Sugita, S. (1987), "The influence of the sea water quality on the adhered matter of membrane", *Bull. Soc. Sea Water Sci.*, Jpn., 40, 356-362.
- Oda, Y. and Yawataya, T. (1968), "Neutrality-disturbance phenomenon of membrane-solution system", *Desalination*, **5**, 129-138.
- Ohwada, K., Shimizu, U. and Taga, N. (1981), "Microorganism and organic matter deposited on the ion exchange membrane", *Bull. Sea Water Sci.*, Jpn., 34, 367-372.
- Pnueli, D. and Grossman, G.A. (1969), "Mathematical model for the flow in an electrodialysics cell", *Desalination*, **6**, 303-308.
- Sadrzadeh, M., Kaviani, A. and Mohammadi, T. (2007), "Mathematical modeling of desalination by electrodialysis", *Desalination*, **206**, 538-546.
- Salt Industry Center (1998), Jpn., Salt Production Technical Report.
- Shaffer, L.H. and Mintz, M.S. (1966), *Electrodialysis*, In K.S. Spiegler (Ed.), Principles of Desalination, Academic Press, New York, London, pp. 200-289.
- Shaposhnik, V.A., Grigorchuk, O.V., Korzhov, E.N., Vasil'eva, V.I. and Klimov, Y.V. (1998), "The effect of ionconducting spacers on mass transfer - numerical analysis and concentration field visualization by means of laser interferometry", J. Membrane Sci., 139, 85-96.
- Shaposhnik, V.A., Kuzminykh, V.A., Drigorchuk, O.V. and Vasil'eva, V.I. (1997), "Analytical model of laminar flow electrodialysis with ion-exchange membranes", J. Membrane Sci., 133, 27-37.
- Solan, A., Winograd, Y. and Katz, U. (1971), "An analytical model for mass transfer in an electrodialysis cell with spacer of finite mesh", *Desalination*, **9**, 89-95.
- Sonin, A.A. and Probstein, R.F. (1968), "A hydrodynamic theory of desalination by electrodialysis", *Desalination*, **5**, 293-329.
- Tanaka, Y. (2000), "Current density distribution and limiting current density in ion-exchange membrane electrodialysis", J. Membrane Sci., 73, 179-190.

- Tanaka, Y. (2003), "Mass transport and energy consumption in ion-exchange membrane electrodialysis of seawater", J. Membane Sci., 215, 265-279.
- Tanaka, Y. (2004), "Pressure distribution, hydrodynamics, mass transport and solution leakage in an ion exchange membrane electrodialyzer", J. Membrane Sci., 234, 23-39.
- Tanaka, Y. (2005), "Limiting current density of an ion-exchangemembrane and of an electrodialyzer", J. Membrane Sci., 266, 6-17.
- Tanaka, Y. (2005), "Overall mass transport and solution leakage in an ion exchange membrane electrodialyzer", J. Membrane Sci., 235, 15-24.
- Tanaka, Y. (2006), "Irreversible thermodynamics and overall mass transport in ion exchange membrane electrodialysis", *J. Membrane Sci.*, **281**, 517-531.
- Tanaka, Y. (2007), "Acceleration of water dissociation generated in an ion exchange membrane", J. Membrane Sci., 303, 234-243.
- Tanaka, Y. (2007), *Ion Exchange Membranes: Fundamentals and Applications*, Membrane Technology Series 12, Elsevier, Amsterdam.
- Tanaka, Y.A., "Computer simulation of continuous ion exchange membrane electrodialysis for desalination of saline water", *Desalination*, The article to be published.
- Tanaka, Y., Ehara, R., Itoi, S. and Goto, T. (2003), "Ion-exchange membrane electrodialytic salt production using brine discharged from a reverse osmosis seawater desalination plant", J. Membrane Sci., 222, 71-86.
- Tanaka, Y., Matsuda, S., Sato, Y. and Seno, M. (1982), "Concentration polarization and dissociation of water in ion exchange membrane electrodialysis III. The effects of electrolytes on the dissociation of water", J. Electrochem. Soc., Jpn, 50, 667-672.
- Tomita, A. *Electrodialyzer*, In. N. Ogata (Ed.), Engineering in Salt Manufacturing, vol. 2, Electrodialysis, Japan Salt Industry Foundation, Tokyo, pp. 85-101.
- Tsunoda, S. (1993), "Present status and latest trends of deep bed filtration", Bull. Soc. Sea Water Sci., Jpn., 48, 27-37.
- Tsunoda, Y. (1965), "Electrodialysis for producing brine concentrates from sea water", *Proc. of the First Int. Symp. on Water Desalination*, **99**, 325-339, Washington D.C.
- Ueno, K., Ozawa, T., Ooki, H., Ishida, T. and Sudo, T. (1980), *Washing method of ion-exchange membranes*, JP Patent, S55-33662.
- Urabe, S. and Doi, K. (1978), "Electrodialyzer", Ind. Water, 239, 24-28.
- Urabe, S. and Doi, K. (1987), Washing method of ion-exchange membranes, JP Patent, S62-52624.
- Valerdi-Perez, R. and Ibaez-Mengual, J. (2001), "Current-voltage curves for an electridialysis reversal pilot plant: Determination of limiting currents", *Desalination*, **141**, 23-37.
- Watanabe, T., Yamamoto, H., Akiyama, M. and Yugi, N. (1972), "Prevention of calcium-carbonate deposition by acid-adding method", *Bull. Soc. Sea Water Sci.*, Jpn., 26, 83-90.
- Wilson, J.R. (1960), Demineralization by Electrodialysis, Buther-worth Scientific Publication, London, p. 256.
- Yamashita, I. (1976), Removing method of fouling substances in an electrodialyzer, JP Patent, S51-131477.
- Zabolotsky, V.I., Shel'deshov, N.V. and Gnusin, N.P. (1988), "Dissociation of water molecules in systems with ion-exchange membranes", *Rus. Chem. Rev.*, 57, 801-808.

CC

Nomenclature

- *a* flow-pass thickness in a desalting cell (cm)
- *b* flow-pass width in a desalting cell (cm)
- C electrolyte concentration (eq cm⁻³)
- *E* energy consumption (kWh t^{-1} NaCl)
- *F* Faraday constant (A s eq^{-1})
- *i* current density (A cm⁻²)

- *I* electric current (A)
- I/S average current density (A cm⁻²)
- $J_{\rm S}$ flux of ions across a membrane pair (eq cm⁻² s⁻¹)
- $J_{\rm V}$ flux of a solution across a membrane pair (cm³ cm⁻² s⁻¹)
- *l* flow-pass length in a desalting cell (cm)
- L_P hydraulic conductivity (mol cm⁴ equiv⁻¹ J⁻¹ s⁻¹)
- *N* number of desalting cells in an electrodialyzer
- p dimensionless distance from the inlet of a desalting cell at which current density is equal to the average current density I/S of an electrodialyzer; NaCl purity (g NaCl g⁻¹ concentrated solution)
- P_{NaCl} NaCl output (kg m⁻² h⁻¹)
- *r* electric resistance (Ω cm²); concentration ratio of ion *i* to total ions in a concentrated solution (equiv equiv⁻¹)
- *R* gas constant (J K⁻¹ mol⁻¹); electric resistance of a membrane pair (Ω cm²)
- S ion exchange membrane area (cm^2)
- t transport number of ions in a membrane
- *T* absolute temperature (K)
- *u* linear velocity in desalting cells (cm s⁻¹)
- V voltage (V)
- V_{cell} cell voltage (V pair⁻¹)
- $V_{\rm memb}$ membrane potential (V pair⁻¹)
- V_{Ω} Ohmic potential (V pair⁻¹)
- *x* distance from the inlet of a desalting cell (cm)
- Y_j number of desalting cells in group j

Greek letters

- β electro-osmotic permeability (cm² C⁻¹)
- γ activity coefficient of electrolytes
- ε electric current screening ratio of a spacer; porosity
- ζ current density non-uniformity coefficient
- η current efficiency
- $\dot{\lambda}$ overall transport number of a membrane pair (eq A⁻¹ s⁻¹)
- μ overall solute permeability of a membrane pair (cm s⁻¹)
- ξ linear velocity ratio of solutions in desalting cells
- $\Delta C \qquad C'' C'$
- $\Delta \xi$ half of ξ value range of desalting cells
- ρ overall hydraulic conductivity of a membrane pair (cm⁴ eq⁻¹ s⁻¹)
- σ standard deviation of normal distribution of linear velocity ratio ξ
- ϕ overall electro-osmotic permeability of a membrane pair (cm³ A⁻¹ s⁻¹)
- ω solute permeability (mol cm J⁻¹ s⁻¹)

Subscript

- A anion exchange membrane
- in inlet of a desalting cell
- j group j in the normal distribution within the range of $\xi_j \Delta \xi_j < \xi < \xi_j + \Delta \xi_j$

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- K cation exchange membrane
- lim limiting current density
- out outlet of a desalting cell
- p point x = pl distant from the inlet of a desalting cell

Superscript

- ' desalting cell
- " concentrating cell
- * control key
- # desalting cell in which solution velocity becomes the least
- b each desalting cell