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Simulation of an ion exchange membrane electrodialysis process for continuous saline water desalination

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ABSTRACT

A computer program is developed and a continuous ion exchange membrane process is simulated applying a constant voltage between electrodes. Inputting membrane characteristics, electrodialyzer specifications and electrodialysic conditions into the program, the performance of an electrodialyzer is predicted. Salt concentration in a desalted solution, current efficiency, desalting ratio, water recovery, energy consumption, current density distribution, current density non-uniformity coefficient, limiting current density are evaluated. Influence of cell voltage and salt concentration in a feeding solution on (1) the transport of ions (migration and diffusion) and solutions (electro-osmosis and hydro-osmosis) across a membrane pair, (2) ohmic and membrane voltage in a membrane pair and (3) electric resistance of membranes, desalting cells and concentrating cells in a stack are discussed at the inlets and outlets of desalting cells. Electro-osmosis, ohmic voltage and electric resistance of membranes are increased with the increase of cell voltage and salt concentration of a feeding solution. Hydro-osmosis and membrane voltage are remarkable at lower cell voltage and lower feeding solution concentration and this phenomenon contributes to energy-saving in brackish water desalination. However, in this circumstance, electric resistance of desalting cells is relatively high.

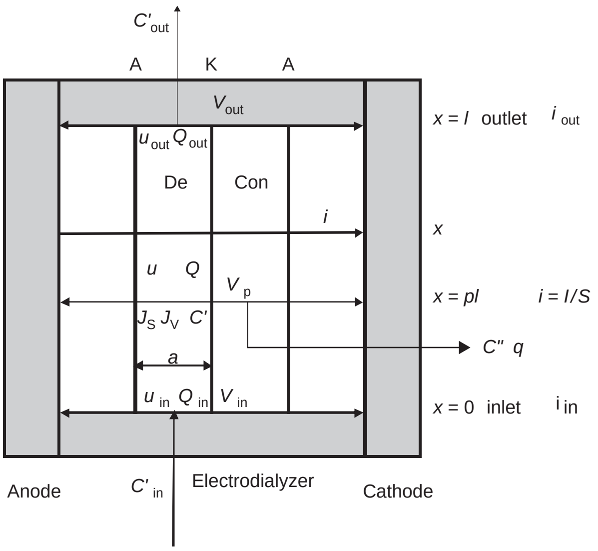
Keywords: Ion exchange membrane; Electrodialyzer; Continuous electrodialysis; Saline water desalination; Limiting current density

1. Introduction

In an ion exchange membrane electrodialysis process, cation exchange membranes, anion exchange membranes, desalting cells and concentrating cells are arranged alternately. Salt solutions are 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 electrical field. Ion transfer is caused by the diffusion, and electro-migration, while solution transfer is caused by the electro-osmosis and hydro-osmosis. Energy consumption is caused by electric cell-pair resistance including solution resistance, membrane resistance and membrane potential. An ion exchange membrane electrodialysis system is classified to a continuous (one-pass flow), batch and feed-and-bleed process [1–4], and the performance of these processes was discussed with computer simulation in the previous investigation [5–7]. Among these processes, the continuous process is the most fundamental one and it was investigated so far as follows. Belfort and Daly [8] constructed optimization routine for a continuous electrodialysis plant. The algorithm was applied to the Office of Saline Water test bed plant at Webstar, South Dakota and compared the actual cost and operation conditions. Aviriel and Zelighter [9] developed a mathematical model for preliminary engineering design and economical evaluation of a continuous electrodialysis plant. Detailed cost computations were performed resulting in capital investment and annual operating costs. Lee et al. [10] developed a computer simulation program for describing a continuous flow process and estimated investment and operation costs. Further, electrodialysis plant was designed and optimized in terms of overall costs and the different parameters. Moon et al. [11] investigated ionic transport across membranes based on one- and two-dimensional continuous electrodialysis modeling using the principles of electrochemistry, transport phenomena and thermodynamics. Fidaleo and Moresi [12] simulated mass transfer, mass balance, potential drop and limiting current density in a continuous operation based on the Nernst-Planck equation. Sadrzadeh et al. [13] modeled continuous flow desalination starting from a differential equation of steady-state mass balance and gives concentration of dilute compartment or separation percent for various voltage, flow rates and feed concentrations. Nikonenko et al. [14] described electrodialysis or electrodialysis reversal characteristics (the mass transfer coefficient, the Sherwood number, the degree of desalination and others) as functions of four parameters (the inlet concentration, the solution flow rate, the potential drop over a cell pair, length of desalination channel). The reasonability of the functions was discussed with experimental measurements. Brauns et al. [15] developed simulation model through solver software. Experimental verification of the software was performed using industrial type pilot plant. Limiting current density was theoretically evaluated in the model calculations for design purpose and corrected with the experimental results. In the previous investigation [5], we discussed the continuous process operated applying a constant electric current. Further the validity of the model for a continuous constant mode was discussed by computing with the performance (NaCl concentration in concentrated solutions, energy consumption to obtain 1 ton of NaCl) of continuous electrodialyzers operated during 1 y in 7 salt-manufacturing plants (output; 200,000 ton/y for each plant)[16]. The differences of data between the computations and the operations are assumed to be due to solution leakages and electric current leakages generated in the electrodialyzers, which are not taken into account in the model. From the above discussion, the validity of the computer simulation model was assumed to be supported by the plant operations [16]. However, the process is so often operated applying constant voltage, which is discussed in this investigation.

2. Continuous electrodialysis process operated applying constant voltage

In Fig. 1, an electrodialyzer (effective membrane area: S, number of desalting cells: N) is operated with constant applied voltage V, and a salt solution (concentration; C'_{in}) is supplied to the inlets of desalting cells at average linear velocity u_{in}. Ions and solutions transfer from desalting cells to concentrating cells and their fluxes through a membrane pair are given as J_S and J_V respectively. In desalting cells, salt concentration is decreased from C'_{in} at the inlets to C'_{out} at the outlets. Salt 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. 1 shows the current density becomes I and I/S respectively at x and pl distant from the inlets of desalting cells. Further, the figure shows that J_S, J_V and average salt concentration C' and $C'' = J_S/J_V$ are the values at pl distant from the inlets of desalting cells. Here, l is flow-pass length of a desalting cell and p is the 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. $u = (u_{in} + u_{out})/2$ is average median velocity in desalting cells. Salt solution in the concentrating cells are extracted at pl and discharged to the outside of the electrodialyzer. Ionic constituent ratio in the solution supplied is assumed to the same to that of



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 $x = pl$
C', C'': Electrolyte concentration in desalting and concentrating cells at $x = pl$
$u = (u_{in}+u_{out})/2$ $Q = (Q_{in}+Q_{out})/2$

Fig. 1. Continuous electrodialysis process.

seawater. The electrodialyzer in Fig. 1 is operated applying constant voltage $V_{in} = V_p = V_{out}$ between electrodes.

3. Computer simulation program for electrodialysis (ED program)

The algorism consists of the principle of mass transport (Step 1), current density distribution (Step 2), energy consumption (Step 3) and limiting current density (Step 4). The process is exhibited in Fig. 2 (Steps 1–3) and Fig. 3 (Step 4). The program is developed on the following assumptions.

1. In membrane characteristics appeared in the overall mass transport equation (Eqs. ((1) and (2)), the overall transport number λ, overall solute permeability μ, overall electro-osmotic permeability ϕ and alternating electric resistance r_{alter} are expressed by the empirical functions of overall hydraulic permeability ρ (Eqs. (3) – (6)).
2. Influence of temperature T on the performance of an electrodialyzer is evaluated from the relationship between T and ρ
3. Solution leakage and electric current leakage in an electrodialyzer are negligible.
4. 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.
5. Frequency distribution of solution velocity ratio in desalting cells is equated by the normal distribution.
6. Current density i at x distant from the inlets of desalting cells is approximated by the quadratic equation (Eq. (15)).
7. Voltage difference between the electrodes at the entrance of desalting cells is equal to the value at the exits (Eq. (16)).
8. Limiting current density of an electrodialyzer is defined as average current densit I/S 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.
9. Salt concentrations in concentrating cells are uniform in the cells and the concentrated solutions are extracted from concentrating cells to the outside of the process.

The program aims at determining the relationship between the parameters in the figure and the principles were already explained in detail in the previous investigation [5], so we describe here the steps briefly.

3.1. Step 1: Mass transport (Fig. 2)

Ion exchange membrane electrodialysis is a process for transporting ionic species across the membranes. When a salt 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 fluxes of ions J_S and a solution J_V are expressed by the following overall mass transport equation [17,18].

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

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

in which, i is current density, η current efficiency, F the Faraday constant, C' and C'' salt 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.

On the basis of many saline water electrodialysis operations incorporated with commercially available ion exchange membranes and spacers, λ (eqC^{-1}), μ (cm s^{-1}) and ϕ (cm^{3}C^{-1}) are known to be presented by the following empirical functions of ρ (cm^{4}eq^{-1}s^{-1}).

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

$$\mu = 2.005 \times 10–5\rho \tag{4}$$

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

The relationship between membrane pair alternating electric resistance $2r_{alter}$ (= $r_{alter,K} + r_{alter,A}$, Ω cm^2) and ρ is expressed by the following equation.

$$2r_{alter} = 5.107 \times 10^{-2}\rho^{-1} \tag{6}$$

Direct current electric resistance of an ion exchange membrane r_{dire} (r_K for a cation exchange membrane and r_A for an anion exchange membrane) are estimated from r_{alter} based on the electrodialysis experiments (Appendix A), and the following membrane pair direct current electric resistance r_{memb} is computed (subscript dire is deleted in Eq. (7)).

$$r_{memb} = r_K + r_A \tag{7}$$

r_{memb} includes the electric resistance of a boundary layer formed on the desalting surface of the membrane due to the concentration polarization.

Salt concentration at the outlets of desalting cells C'_{out} and that in concentrating cells are introduced by the following equations.

$$C'_{out} = C'_{in} - \left(\frac{\eta l}{aF}\right)\left(\frac{1}{u}\right)\left(\frac{I}{S}\right) \tag{8}$$

$$C'' = \frac{\sqrt{A^2 + 4\rho B} - A}{2\rho} \tag{9}$$

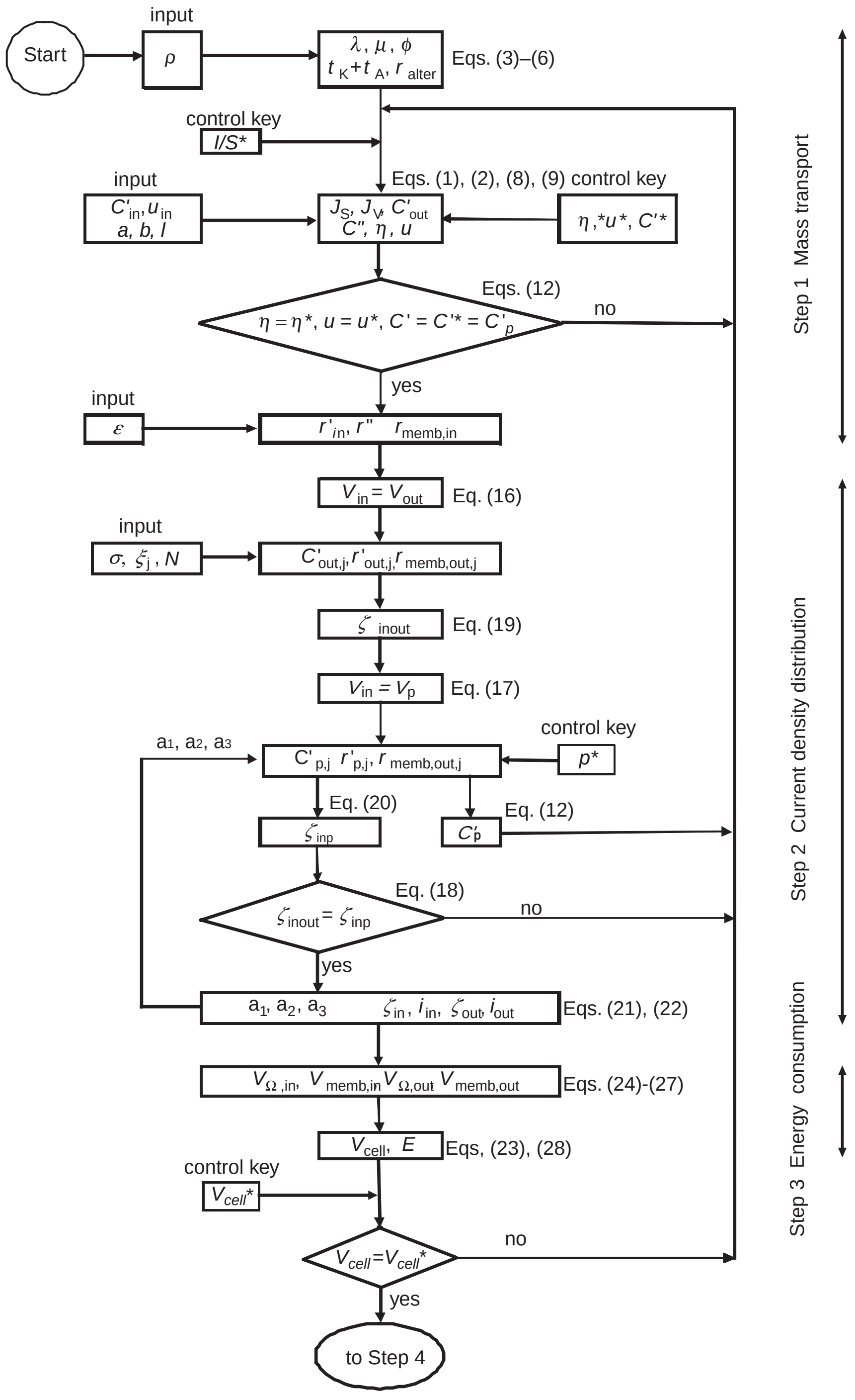


Fig. 2. Simulation of mass transport, current density distribution and energy consumption.

$$\mathrm{A} = \phi(I/S) + \mu - \rho C' \tag{10}$$

$$\mathrm{B} = \lambda(I/S) + \mu C' \tag{11}$$

in which C' is salt concentration at $x = pl$ in desalting cells C'_p and it is given by the following equation.

$$C' = C'_p = \frac{1}{N}\sum_{j=1}^{j\,\max} Y_j C'_{p,j} \tag{12}$$

j in Eq. (12) denotes group j in the normal distribution of solution velocity ratio ξ (Eq. (14)). Y_j is number of desalting cells in group j.

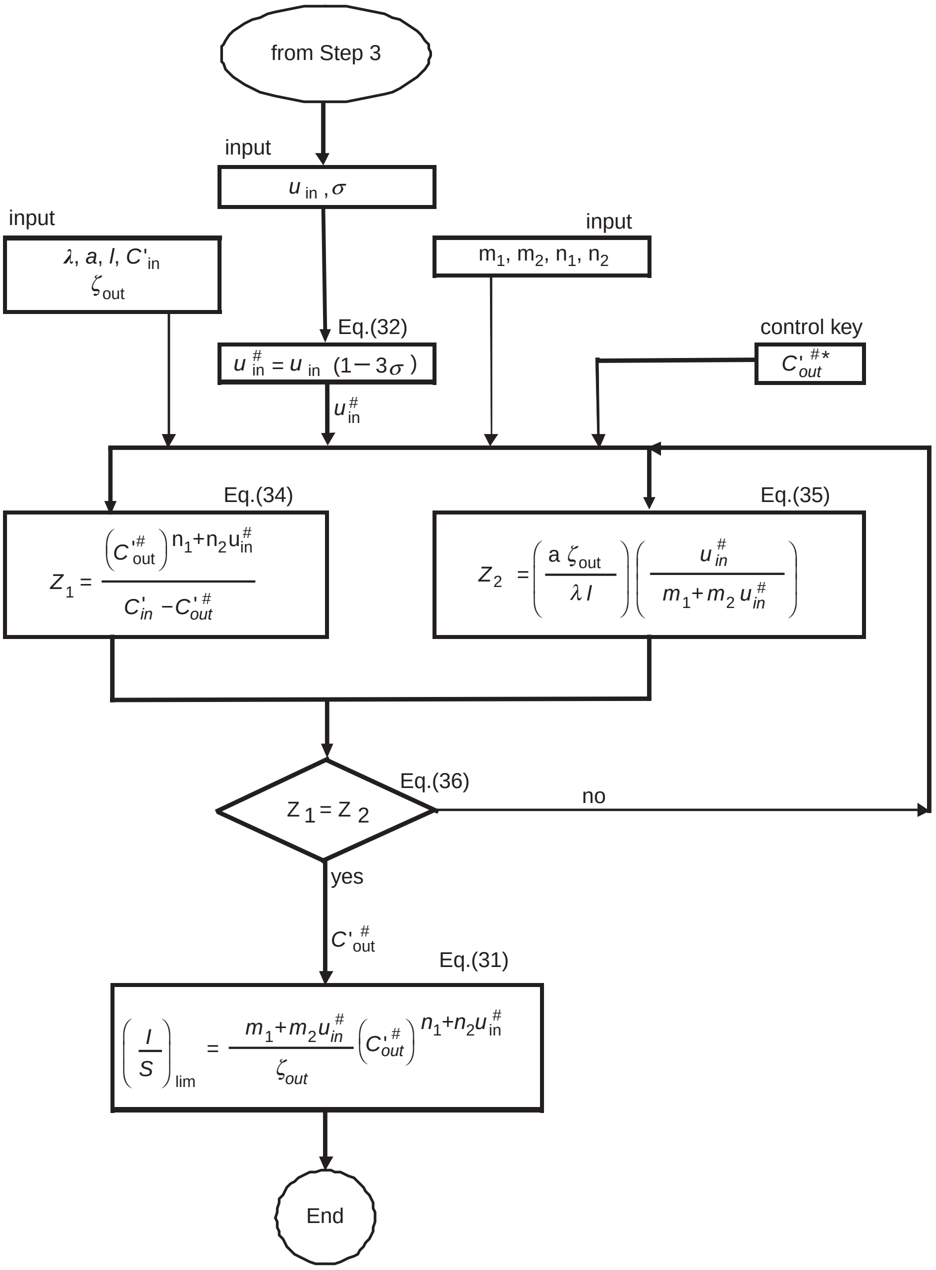


Fig. 3. Simulation of limiting current density.

Output of a desalted solution of an electrodialyzer Q_{out} is

$$Q_{out} = (au_{in} - J_V)bN \tag{13}$$

3.2. Step 2: Current density distribution (Fig. 2)

In a practical-scale electrodialyzer, solution velocities in desalting cells vary between the cells. In this program, we assume that the frequency distribution of the solution velocity ratio ξ (Eq. (14)) is equated by the normal distribution.

$$\xi = \frac{u - \bar{u}}{\bar{u}} \tag{14}$$

Salt concentrations in desalting cells are decreased along flow-passes and give rise to salt concentration distribution. It causes electric resistance distribution and current density distribution. In order to determine current density distribution in an electrodialyzer, 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.

$$i = a_1 + a_2\left(\frac{x}{l}\right) + a_3\left(\frac{x}{l}\right)^2 \tag{15}$$

To determine a_1, a_2 and a_3 in Eq. (15), the following three-simultaneous equations are set up [18-20] (Appendix B).

$$V_{in} = V_{out} \tag{16}$$

$$V_{in} = V_p \tag{17}$$

$$\zeta_{inout} = \zeta_{inp} \tag{18}$$

ζ_{inout} is introduced from Eq. (16) and expressed by Eq. (19). It equals to the outlet current density non-uniformity coefficient ζ_{out}.

$$\zeta_{inout} = \frac{\alpha_1 + \alpha_2 p + \alpha_3 p^2}{\beta_1 + \beta_2 p + \beta_3 p^2} = \zeta_{out} = \frac{i_{out}}{I / S} \tag{19}$$

ζ_{inp} is introduced from Eq. (17) and expressed by Eq. (20), which equals to ζ_{out}.

$$\zeta_{inp} = \frac{\Upsilon_1 + \Upsilon_2 p + \Upsilon_3 p^2}{\left(2\rho - 3\rho^2\right)\left(I / S\right)} = \zeta_{out} \tag{20}$$

We determine a_1, a_2, a_3 with $\zeta_{in} = i_{in}/(I/S)$ (inlet electric current non-uniformity coefficient), ζ_{out}, i_{in} and i_{out};

$$\zeta_{in} = \frac{i_{in}}{I / S} = \frac{a_1}{I / S} \tag{21}$$

$$\zeta_{out} = \frac{i_{out}}{I / S} = \frac{a_1 + a_2 + a_3}{I / S} \tag{22}$$

3.3. Step 3: Energy consumption [18,21] (Fig. 2)

Cell voltage is given by the following equation.

$$V_{cell} = V_{\Omega,in} + V_{memb,in} = V_{\Omega,out} + V_{memb,out} \tag{23}$$

Ohmic voltage $V_{\Omega,in}$ and membrane voltage $V_{memb,in}$ at the inlets of desalting cells in Eq. (23) are given as;

$$V_{\Omega,in} = (r'_{in} + r_{memb,in} + r'')i_{in} \tag{24}$$

$$V_{memb,in} = 2\left(t_K + t_A - 1\right)\left(\frac{RT}{F}\right)\ln\frac{\Upsilon''C''}{\Upsilon'_{in}C'_{in}} \tag{25}$$

in which, r'_{in} and $r_{memb,in}$ are respectively electric resistance of a solution and a membrane at the inlet of desalting cell. r'' is electric resistance of a solution in a concentrating cell. r' and r'' include the influence of the electric current screening ratio of a spacer ε = (electric current screening area of a spacer/membrane area). t_K and t_A are the transport number of a cation and an anion exchange membrane respectively. γ'_{in} is the activity coefficient of ions dissolving in a solution at the inlets of a desalting cell. γ'' is the activity coefficient of ions dissolving in a concentrating cell.

Ohmic voltage $V_{\Omega,out}$ and membrane voltage $V_{memb,out}$ at the outlets of desalting cells in Eq. (23) are given by averaging the values for N cells integrated in an electrodialyzer.

$$V_{\Omega,out} = \left(\sum_{j=1}^{J\max} \Upsilon_j r'_{out,j} + \sum_{j=1}^{j\max} \Upsilon_j r_{memb,out,j} + r''N\right) \times i_{out}\left(\frac{1}{N}\right) \tag{26}$$

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

Energy consumption E is expressed as follows.

$$E = \frac{V_{cell}I}{Q_{out}} \tag{28}$$

3.4. Step 4: Limiting current density (Fig. 3)

Limiting current density of a cation exchange membrane is less than that of an anion exchange membrane, because the mobility (transport number) of counter ions in a solution for a cation exchange membrane is less than that for an anion exchange membrane[1]. 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.

$$i_{\lim} = \left(m_1 + m_2 u_{out}\right) C'^{\,n_1 + n_2 u_{out}}_{out} \tag{29}$$

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. (30) introduced from Eqs. (22) and (29) [18,22].

$$\left(\frac{I}{S}\right)_{\lim} = \frac{i_{\lim}}{\zeta_{out}} = \frac{\left(m_1 + m_2 u^{\#}_{out}\right)}{\zeta_{out}} \left(C'^{\#}_{out}\right)^{n_1+n_2u^{\#}_{out}} \tag{30}$$

in which $C'^{\#}_{out}$ (C'_{out} sharp) is C'_{out} at $u = u^{\#}_{out}$.

In Eq. (30), $u^{\#}_{out}$ is nearly equal to $u^{\#}_{in}$ for commercially available membranes. Substituting $u^{\#}_{out} = u^{\#}_{in}$ in Eq. (30) leads to:

$$\left(\frac{I}{S}\right)_{\lim} = \frac{m_1 + m_2 u^{\#}_{in}}{\zeta_{out}} \left(C'^{\#}_{out}\right)^{n_1+n_2u^{\#}_{in}} \tag{31}$$

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

$$u^{\#}_{in} = u_{in}(1 - 3\sigma) \tag{32}$$

in which σ is the standard deviation of the normal distribution of the solution velocity ratio ξ (Eq. (14)).

On the other hand, from the material balance in the desalting cell in which linear velocity becomes the least, the relationship between $(I/S)_{\lim}$ and $C^{\#}_{out}$ is given as follows:

$$\left(\frac{I}{S}\right)_{\lim} = \left(\frac{a}{\lambda l}\right) u^{\#}_{in} \left(C'_{in} - C^{\#}_{out}\right) \tag{33}$$

Putting Eq. (31) = Eq. (33) and collecting $C'_{out}{}^{\#}$ into Z_1:

$$Z_1 = \frac{\left(C'^{\#}_{out}\right)^{n_1+n_2u^{\#}_{in}}}{C'_{in} - C'^{\#}_{out}} \tag{34}$$

$$Z_2 = \left(\frac{a\zeta_{out}}{\ddot{e}l}\right)\left(\frac{u^{\#}_{in}}{m_1 + m_2 u^{\#}_{in}}\right) \tag{35}$$

$$Z_1 = Z_2 \tag{36}$$

Foot note 1: Transport numbers t_A of counter ions A for example in a 25 °C 0.1 eq/dm^3 chloride solution are less than those of Cl$^-$ ions $1 - t_A$ for a cation exchange membrane as follows; $t_{Na} = 0.3854$ for NaCl, $t_K = 0.4898$ for KCl, $t_{Mg} = 0.375$ for MgCl$_2$, $t_{Ca} = 0.4070$ for CaCl$_2$, $t_{Li} = 0.3168$ for LiCl, $t_{Ba} = 0.406$ for BaCl$_2$, $t_H = 0.8314$ for HCl [23]. These phenomena are due to smaller mobility of cations in the solution.

4. Computation procedures

Computation is carried out using the following trial and error calculation by adjusting control keys; I/S^*, V^*_{cell}, C'^*, η^*, u^*, p^* and C'^*_{out}.

4.1. Step 1 – Step 3 (Fig. 2)

- I/S^* is adjusted to realize

$$V_{cell} = V^*_{cell} \tag{37}$$

- C′* is adjusted to realize

$$C' = C'_p = \frac{1}{N}\sum_{j=1}^{j\max} Y_j C'_j = C'^* \tag{38}$$

- η^* is adjusted to realize
- $\eta = FJ_S/(I/F) = \eta^*$ (39)
- u is adjusted to realize
- $u = (u_{in} + u_{out})/2 = u^*$ (40)
- p^* is adjusted to realize

$$\zeta_{inout} = \zeta_{inp} \tag{41}$$

4.2. Step 4 (Fig. 3)

C'^*_{out} is adjusted to realize

$$Z_1 = Z_2 \tag{42}$$

In the above computation, if an algorithm reaches a decision point (diamond symbol), it is adjusted by changing control keys to realize the equations; Eqs. (37)–(42) given in the decision points. Then it loops back to an earlier portion in the algorithm. The trial-and-error calculation is repeated until all equations are satisfied. The computation is finished within 10 minutes to obtain one group of plots in the figures shown in this article.

5. Computation

5.1. Input data

A continuous process is assumed to be operated applying constant voltage between electrodes. We assume the following specifications of an electrodialyzer operating with changing the level of C'_{in} and V_{cell}.

Salt concentration in a feeding solution (at the inlets of desalting cells) C'_{in} = 0.03 eq/dm^3 (brackish water TDS 1,736 mg/*l*), 0.2 eq/dm^3 (11,574 mg/*l*), 0.4 eq/dm^3 (23,148 mg/*l*), 0.6 eq/dm^3 (seawater 34,722 mg/*l*).

Cell voltage V_{cell} = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 V/pair

Linear velocity at the inlets of desalting cells u_{in} = 10 cm/s

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

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

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

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

Membrane area $S = bl = 10^4$ cm^2 = 1 m^2

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

Overall hydraulic conductivity of a membrane pair $\rho = 1 \times 10^{-2}$ cm^4/eq s

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

σ is influenced extremely by precision of part dimensions of a stack and skill of stack assembling work of an electrodialyzer and it is desirable to keep σ value as low as possible. An electrodialyzer is operated stably at $\sigma < 0.1$ because the limiting current density $(I/S)_{\lim}$ is high. However, electrodialyzer operation becomes unstable at $\sigma > 0.2$ because $(I/S)_{\lim}$ is lowered. $\sigma = 0.1$ inputted above is decided in rough-and-ready manner referring to the experimentally observed data. ρ values of commercially available ion exchange membranes vary to some extent. $\rho = 1\ 10^{-2}$ cm^4/eq s inputted above is estimated to be a reasonable and convenient value which was decided based on the observed data.

5.2. *Influence of cell voltage V_{cell} and salt concentration in a feeding solution C'_{in} on the performance of an electrodialyzer*

Salt concentration at the outlets of desalting cell C'_{out} is decreased with the increase of V_{cell} and the decrease of C'_{in} (Fig. 4). Current efficiency η is increased with the increase of V_{cell} and C'_{in} (Fig. 5). Desalting ratio α is increased with the increase of V_{cell} and the decrease of C'_{in} (Fig. 6). Water recovery Re is higher than 0.95, and it is decreased with the increase of V_{cell} and C'_{in} (Fig. 7). Energy consumption E is increased with the increase of V_{cell} and C'_{in} (Fig. 8). Inlet current density non-uniformity coefficient ζ_{in} and outlet current density non-uniformity coefficient ζ_{out} coverage 1 at lower V_{cell}. ζ_{in} is increased and ζ_{out} is decreased with the increase of V_{cell} and decrease of C'_{in} (Fig. 9). Limiting current density $(I/S)_{\lim}$ is plotted against current density I/S taking V_{cell} as a parameter (Fig. 10). Intersections between the plot and

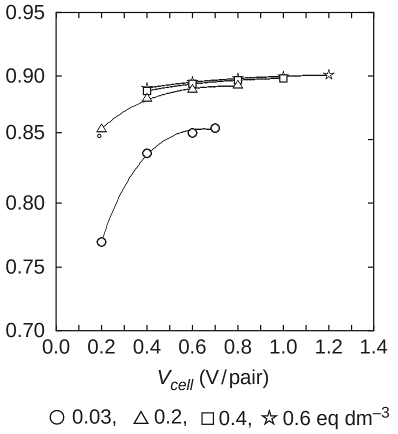


Fig. 5. Cell voltage and current efficiency.

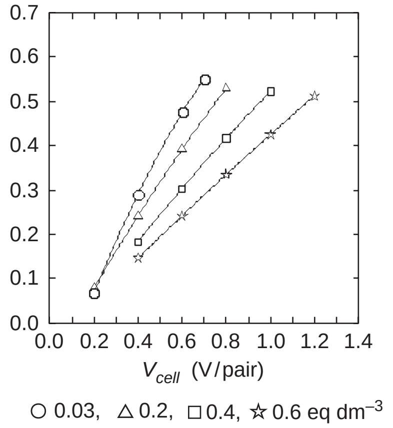


Fig. 6. Desalting ratio.

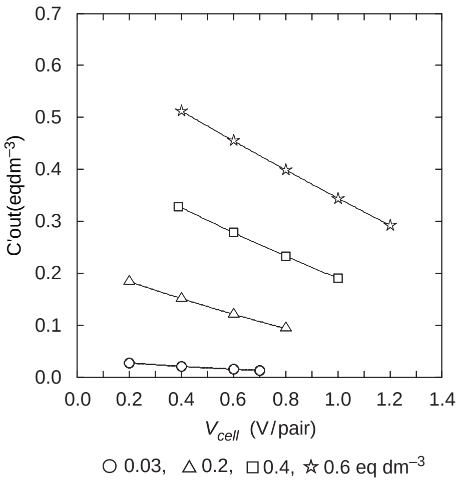


Fig. 4. Salt concentration in a desalted solution.

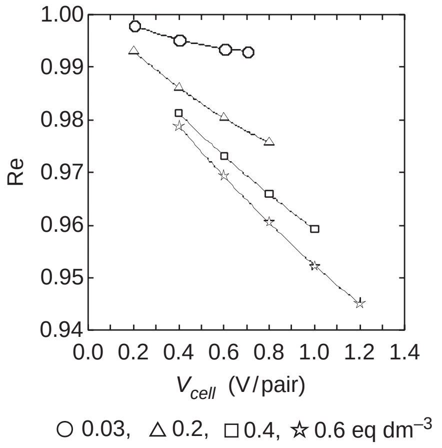


Fig. 7. Water recovery.

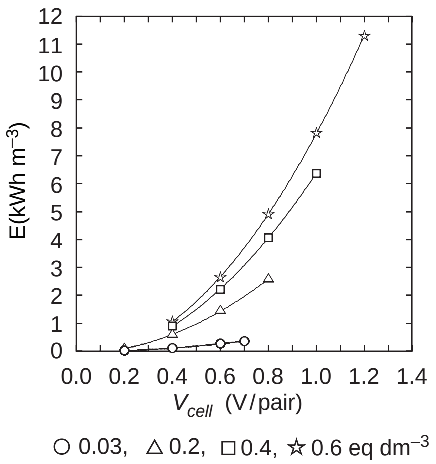


Fig. 8. Energy consumption.

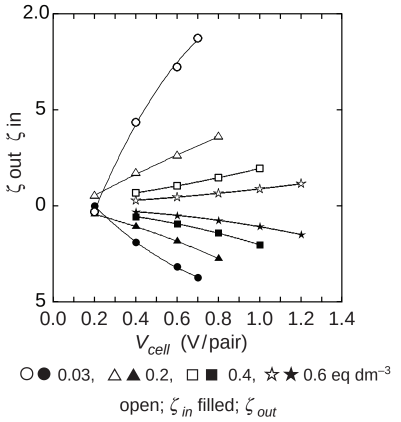


Fig. 9. Current density non-uniformity coefficient.

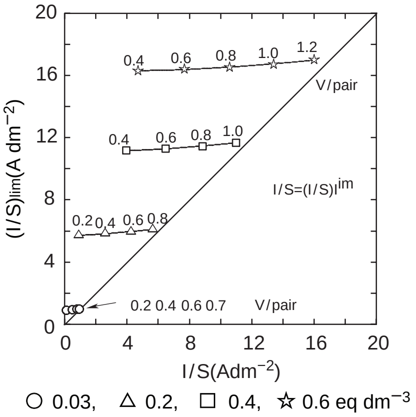


Fig. 10. Limiting current density.

a $I/S = (I/S)_{\text{lim}}$ line show the real limiting current density of the electrodialyzer $(I/S)_{\text{lim}}$ operating in this investigation. $(I/S)_{\text{lim}}$ appears at over 0.7 V/pair (C'_{in} = 0.03 eq dm^{-3}), 0.8 V/pair (0.2 eq dm^{-3}), 1.0 V/pair (0.4 eq dm^{-3}) and 1.2 V/pair (0.6 eq dm^{-3}).

5.3. Influence of cell voltage V_{cell} and salt concentration in a feeding solution C'_{in} on current density distribution, the transport of ions and solutions across a membrane pair, ohmic and membrane voltage in a membrane pair and electric resistance in a stack

Current density i is plotted against dimension-less flow-pass in desalting cells x/l in Fig. 11 which shows i to be decreased with increasing x/l. This phenomenon is remarkable at lower C'_{in}, and at higher V_{cell}. Hence, it is assumed that current density distribution contributes to the stable operation of the electrodialyzer.

Flux of ions J_S in Eq. (1) is separated into migration J_{migr} and diffusion J_{diff} as follow:

$$J_S = J_{migr} + J_{diff} \tag{43}$$

$$J_{migr} = \lambda i \tag{44}$$

$$J_{diff} = -\mu\Delta C \tag{45}$$

J_{migr} and J_{diff} are computed at the inlets and outlets of desalting cells. They are plotted against V_{cell} putting C'_{in} = 0.03, 0.2, 0.4 and 0.6 eq/dm^3 in Fig. 12. J_{diff} takes minus values and it is very small because of small μ values. J_{migr} increases with V_{cell} and C'_{in}, and further J_{migr} at the inlets of desalting cells are larger than that at the

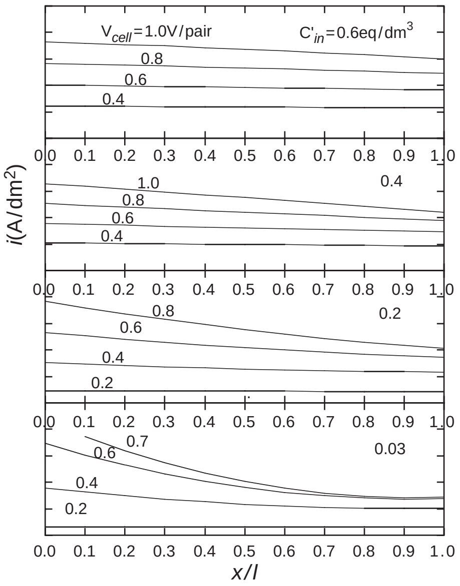


Fig. 11. Current density distribution.

outlets. This phenomenon is caused by the electric current increase at the inlets of desalting cells (Fig. 11).

Flux of a solution J_V in Eq. (2) is separated into electro-osmosis J_{elosmo} and hydro-osmosis $J_{hydrosmo}$ as follows.

$$J_V = J_{elosmo} + J_{hydrosmo} \tag{46}$$

$$J_{elosmo} = \phi i \tag{47}$$

$$J_{hydrosmo} = \rho \Delta C \tag{48}$$

J_{elosmo} and $J_{hydrosmo}$ are computed at the inlets and outlets of desalting cells and indicated in Fig. 13. It is found that the ratio of $J_{hydrosmo}$ is remarkable at lower V_{cell} and C'_{in}. J_{elosmo} is increased notably with V_{cell} and C'_{in} and its values at the inlets are larger than those at the outlets.

Fig. 14 shows V_{cell} versus ohmic voltage V_Ω ($V_{\Omega,in}$; (Eq. (24), $V_{\Omega,out}$; Eq. (26)) and membrane voltage V_{memb} ($V_{memb,in}$; Eq. (25), $V_{memb,out}$; Eq. (27)). The figure reveals Eq. (23) to hold. V_Ω is generally larger than V_{memb}, increased with C'_{in} and V_{cell} and it causes the increase of energy consumption as shown in Fig. 8. At lower C'_{in} and V_{cell}, however, V_Ω is decreased while V_{memb} is relatively increased. Inspecting Figs. 8, 13 and 14, it is understandable that energy consumption decrease at lower V_{cell} and C'_{in} is due to relative increase of $J_{hydrosmo}$ and V_{memb} which is generated by concentration (chemical potential) difference between concentrating cells and desalting cells and does not accompany energy consumption. A low V_{cell} operation is reasonable in brackish water desalination also from the stand point of a stable operation (cf. limiting current density (Fig. 10)), however we have to pay attention to that it causes capital cost increase.

Electric resistance of membranes R_m, desalting cells R' and concentrating cells R'' integrated in a stack including 300 pairs of cells (N = 300 pairs) are computed and shown in Fig. 15. R'' is very small

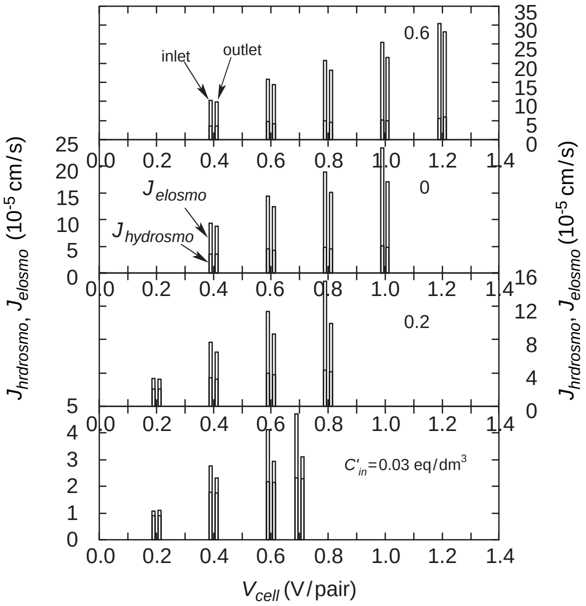


Fig. 13. Electro-osmosis J_{elosmo} and hydro-osmosis $J_{hydrosmo}$.

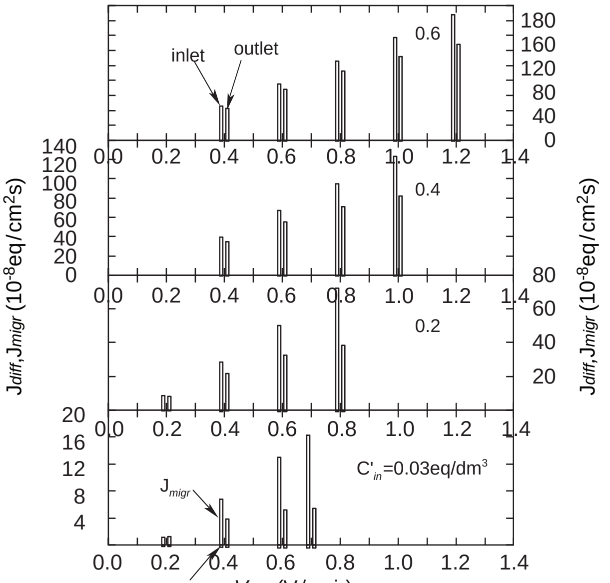


Fig. 12. Migration J_{migr} and diffusion J_{diff}.

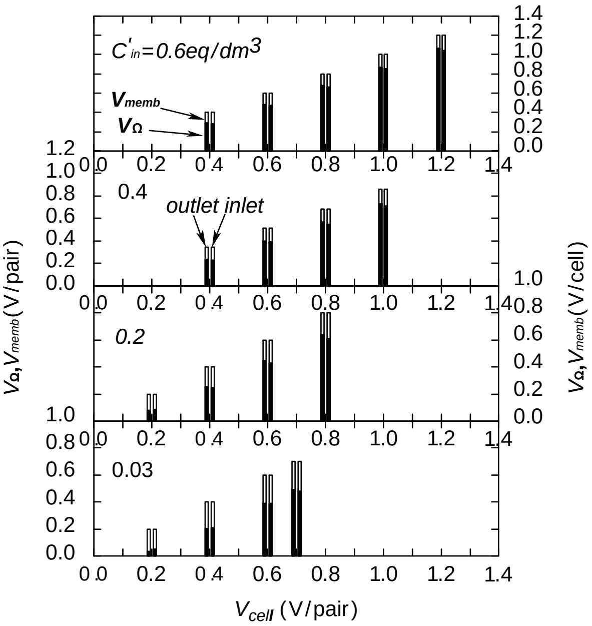


Fig. 14. Ohmic voltage V_Ω and membrane voltage V_{memb}.

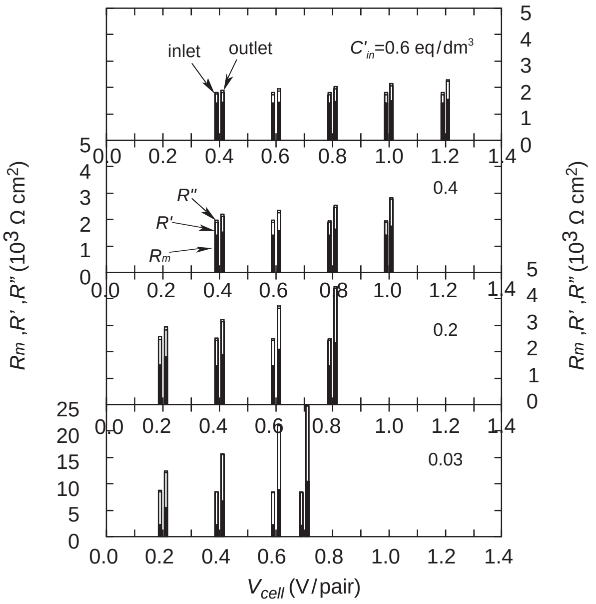


Fig. 15. Electric resistance of membranes R_m, desalting cells R' and concentrating cells R'' in a stack.

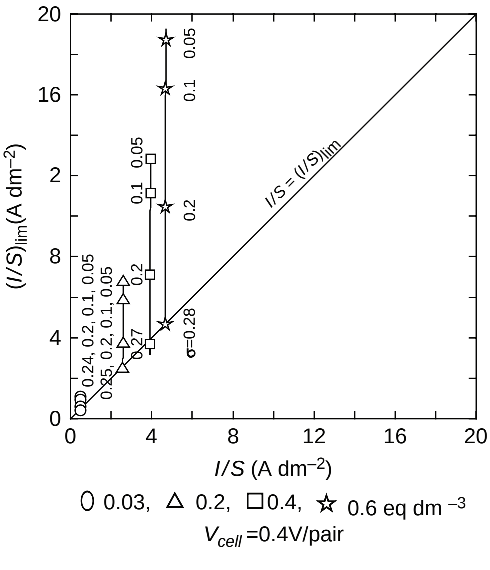


Fig. 16. Influence of standard deviation of normal distribution of solution velocity ratio on limiting current density.

and negligible in all circumstances. The ratio of R_m is increased with C'_{in} and it is predominant at seawater electrodialysis (C'_{in} = 0.6 eq/dm^3). R' is increased at lower C'_{in} and it is remarkable at brackish water electrodialysis (C'_{in} = 0.03 eq/dm^3). From Fig. 15, we understand that it is necessary to reduce electric resistance of ion exchange membranes for decreasing energy consumption in seawater electrodialysis. For decreasing energy consumption in brackish water electrodialysis, it is presumably necessary to reduce R' by incorporating with ion conducting spacers [24–27].

5.4. Influence of standard deviation of normal distribution of solution velocity ratio in desalting cells σ

Changing the level of σ as 0.05, 0.1, 0.2, 0.24, 0.25 and 0.28 and setting V_{cell} = 0.4 V/pair and keeping other parameters to the values described in Section 5.1, $(I/S)_{\text{lim}}$ is computed and shown in Fig. 16. $(I/S)_{\text{lim}}$ is found at σ = 0.24 (C'_{in} = 0.03 eq dm^{-3}), 0.25 (0.2 eq dm^{-3}), 0.27 (0.4 eq dm^{-3}) and 0.28 (0.6 eq dm^{-3}). Excepting limiting current density, the performance of an electrodialyzer is not influenced by σ [5–7].

6. Conclusion

Energy consumption in brackish water desalination is decreased when it is operated under lower cell voltage. This is because the process is operated with increased hydro-osmosis and membrane voltage which does not accompany energy consumption. For decreasing energy consumption further in brackish water desalination, it is necessary to reduce electric resistance of desalting cells presumably by incorporating ion conducting spacers. For decreasing energy consumption in seawater desalination, it is necessary to reduce electric resistance of ion exchange membranes. The process described in this investigation is a single stage. We have to develop hereafter the computer simulation of a multiple stage saline water desalination process. Further we have to investigate a feeding solution adding operation into concentrating cells for preventing $CaSO_4$ scale precipitation and decreasing electric current leakage. The computing method described in this investigation provides the technique to evaluate the performance of a batch process and a feed-and-bleed process. The model makes it possible to discuss optimum specifications and operating conditions of a practical-scale electrodialyzer.

Appendix A

Alternating current electric resistance and direct current electric resistance of an ion exchange membrane

The electric resistance of an ion exchange membrane is measured usually under an alternating current. It is a property of the membrane only and referred here as the alternating current electric resistance r_{alter}. In an electrodialysis process, a direct current is passed across the membrane, so we have to evaluate the direct current r_{dire} for discussing electrodialysis phenomena. r_{alter} is estimated from r_{alter} as follows [21].

1. The membrane is integrated in a 2 cell apparatus and low-concentration NaCl solutions (specific conductivity, κ_{low} (mScm^{-1})) are supplied into the compartments. Electric resistance of the membrane (r'_{dire} (Ωcm^2)) is measured passing a direct current. Eq. (A1) is the empirical relationship between κ_{low} and r'_{dire}/r_{alter}.

$$\log\left(\frac{r'_{dire}}{r_{alter}}\right) = a_1 + a_2 \log \kappa_{low} + a_3 \left(\log \kappa_{low}\right)^2 \qquad \text{(A1)}$$

2. A low-concentration NaCl solution (specific conductivity, κ_{low}) and a high-concentration NaCl solution (specific conductivity, κ_{high}) are supplied respectively to the desalting side and the concentrating side of the apparatus. The electric resistance of the membrane r_{dire} is measured passing a direct current and subtracting the influence of membrane potential. Eq. (B2) gives the empirical relationship between $\kappa_{high}/\kappa_{low}$ and r_{dire}/r'_{dire}:

$$\frac{r_{dire}}{r'_{dire}} = 1.00 + b\left(\frac{\kappa_{high}}{\kappa_{low}}\right) \qquad \text{(A2)}$$

3. r_{dire} is calculated by multiplying Eq. (A1) by Eq. (A2) and substituting r_{alter} measured by an usual manner. r_{dire} includes the electric resistance of a boundary layer formed on the desalting surface of the membrane due to the concentration polarization.

Appendix B

Current density distribution in an electrodialyzer

Current density distribution is presented by a quadratic equation as Eq. (B1).

$$i = \mathrm{k}_1 + \mathrm{k}_2 x + \mathrm{k}_3 x^2 \qquad \text{(B1)}$$

To determine k_1, k_2 and k_3 in Eq. (B1), the three-dimensional simultaneous equation are set up as follows [19,21].

With a large number of membrane pairs integrated in an electrodialyzer, the first three-dimensional simultaneous equation, Eq. (B2) is realized.

$$V_{in} = V_{out} \qquad \text{(B2)}$$

$$V_{in} = \mathrm{A}_1 i_{in} + \mathrm{A}_2 \qquad \text{(B3)}$$

$$V_{out} = \mathrm{B}_1 i_{out} + B_2 \qquad \text{(B4)}$$

$$\mathrm{A}_1 = (r'_{in} + r_{in,K} + r_{in,A} + r'')N \qquad \text{(B5) (Eq. (24))}$$

$$A_2 = 2\left(t_K + t_A - 1\right)\left(\frac{RT}{F}\right) N\, \mathrm{In}\left(\frac{\gamma'' C''}{\gamma''_{in} C''_{in}}\right) \qquad \text{(B6) (Eq. (25))}$$

$$B_1 = \sum_1^N Y_j r'_{out,j} + \sum_1^N Y_j r_{out,K,j} + \sum_1^N \Upsilon_j r_{out,A,j} + r'' N \qquad \text{(B7) (Eq. (26))}$$

$$B_2 = 2\left(t_K + t_A + 1\right)\left(\frac{RT}{F}\right) \sum_1^n Y_j\, \mathrm{In}\left(\frac{\gamma'' C''}{\gamma''_{out} C'_{out,j}}\right) \qquad \text{(B8) (Eq. (27))}$$

r' (r'_{in}, r'_{out}) and r'' in Eqs. (B5) and (B7) are electric resistance (Ωcm^2) of a desalting and a concentrating cell, respectively, given by the following definitions.

$$r' = \frac{a \times 10^{-3}}{\left(1-\varepsilon\right)\kappa} \qquad \text{(B9)}$$

$$r'' = \frac{a \times 10^{-3}}{\left(1-\varepsilon\right)\kappa} \qquad \text{(B10)}$$

ε the current screening ratio of a spacer. The electric resistance of the concentrated solution r'' is assumed to be invariable in the system.

r_K ($r_{in,K}$, $r_{out,K}$) and r_A ($r_{in,A}$, $r_{out,A}$) in Eqs. (B5) and (B7) are electric resistance (Ωcm^2) of a cation and an anion exchange membrane, respectively, evaluated at a direct electric current (Appendix A).

Using Eq. (B2), the current density distribution equation is introduced as:

$$i = a_1 + a_2\left(\frac{x}{l}\right) + a_3\left(\frac{x}{l}\right)^2 \qquad \text{(B11) (Eq. (15))}$$

$$a_1 = \left(Z_1 \zeta_{out}\right)\left(\frac{I}{S}\right) + Z_2 \qquad \text{(B12)}$$

$$a_2 = 2\left[\left\{3 - \left(2Z_1 + 1\right)\zeta_{out}\right\}\left(\frac{I}{S}\right) - 2Z_2\right] \qquad \text{(B13)}$$

$$a_3 = -3\left[\left\{2 - \left(Z_1 + 1\right)\zeta_{out}\right\}\left(\frac{I}{S}\right) - Z_2\right] \qquad \text{(B14)}$$

$$Z_1 = \frac{B_1}{A_1} \qquad \text{(B15)}$$

$$Z_2 = -\frac{A_2 - B_2}{A_1} \qquad \text{(B16)}$$

ζ_{out} is the outlet current density non-uniformity coefficient defined by:

$$\zeta_{out} = \frac{i_{out}}{I / S} \qquad \text{(B17) (Eq. (22))}$$

Under the situation in which Eq. (B2) is realized, ζ_{out} is expressed by ζ_{inout}:

$$\zeta_{out} = \zeta_{inout} = \frac{\alpha_1 + \alpha_2 p + \alpha_3 p^2}{\beta_1 + \beta_2 p + \beta_3 p^2} \qquad \text{(B18) (Eq. (19))}$$

$$\alpha_1 = \left(\frac{I}{S}\right) - Z_2 \qquad \text{(B19)}$$

$$\alpha_2 = -2\left\{3\left(\frac{I}{S}\right) - 2Z_2\right\} \qquad \text{(B20)}$$

$$\alpha_3 = 3\left\{2\left(\frac{I}{S}\right) - Z_2\right\} \qquad \text{(B21)}$$

$$\beta_1 = Z_1\left(\frac{I}{S}\right) \qquad \text{(B22)}$$

$$\beta_2 = -2\left(2Z_1 + 1\right)\left(\frac{I}{S}\right) \qquad \text{(B23)}$$

$$\beta_3 = 3\left(Z_1 + 1\right)\left(\frac{I}{S}\right) \qquad \text{(B24)}$$

where p is the non-dimensional distance x/l at which $i = I/S$ is satisfied. Next, the voltage difference between electrodes at inlets V_{in} is equal to V_p at the point $x = pl$ distant from the inlets of desalting cells.

$$V_{in} = V_p \qquad \text{(B25)(Eq. (17))}$$

Equation (B25) is the second three-dimensional simultaneous equation, and V_p is expressed as:

$$V_p = C_1\left(\frac{I}{S}\right) + C_2 \qquad \text{(B26)}$$

$$C_1 = \sum_1^N Y_j r'_{p,j} + \sum_1^N Y_j r_{p,K,j} + \sum_1^N Y_j r_{p,A,j} + r''N \qquad \text{(B27)}$$

$$C_2 = 2\left(t_k + t_A + 1\right)\left(\frac{RT}{F}\right)\sum_1^N Y_j\left(\frac{\gamma''C''}{\gamma'_{p,j}C'_{p,j}}\right) \qquad \text{(B28)}$$

Under the situation in which Eq. (B25) holds, ζ_{out} is expressed by ζ_{inp}:

$$\zeta_{out} = \zeta_{inp} = \frac{\gamma_1 + \gamma_2 p + \gamma_3 p^2}{\left(2p - 3p^2\right)\left(I / S\right)} \qquad \text{(B29) (Eq. (20))}$$

$$\gamma_1 = \left(Z_3 - 1\right)\left(\frac{I}{S}\right) + Z_4 \qquad \text{(B30)}$$

$$\gamma_2 = 2\left\{\left(3 - 2Z_3\right)\left(\frac{I}{S}\right) - 2Z_4\right\} \qquad \text{(B31)}$$

$$\gamma_3 = 3\left\{\left(Z_3 - 2\right)\left(\frac{I}{S}\right) + Z_4\right\} \qquad \text{(B32)}$$

$$Z_3 = \frac{C_1}{A_1} \qquad \text{(B33)}$$

$$Z_4 = -\frac{A_2 - C_2}{A_1} \qquad \text{(B34)}$$

Finally, the third three-dimensional simultaneous equation is obtained from Eqs. (B18) and (B29) as follows:

$$\zeta_{inout} = \zeta_{inp} \qquad \text{(B35) (Eq. (18))}$$

Using the equations described above, we obtain ζ_{in}, ζ_{out}, p, a_1, a_2 and a_3. ζ_{in} is the inlet current density non-uniformity coefficient defined by:

$$\zeta_{in} = \frac{i_{in}}{I / S} \qquad \text{(B36) (Eq. (21))}$$

ζ_{in} and ζ_{out} are related to a_1, a_2 and a_3 as follows:

$$\zeta_{in} = \frac{a_1}{I / S} \qquad \text{(B37) (Eq. (21))}$$

$$\zeta_{out} = \frac{a_1 + a_2 + a_3}{I / S} \qquad \text{(B38) (Eq. (22))}$$

Symbols

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 m^{-3})
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_{diff} — diffusion (eq cm^{-2}s^{-1})
J_{elosmo} — electro-osmosis (cm^{3}cm^{-2}s^{-1})
$J_{hydrosmo}$ — hydraulic osmosis (cm^{3}cm^{-2}s^{-1})
J_{migr} — migration (eq cm^{-2}s^{-1})
J_S — flux of ions across a membrane pair (eq cm^{-2} s^{-1})
J_V — flux of a solution across a membrane pair (cm^3 cm^{-2} s^{-1})

l — flow-pass length in a desalting cell (cm)
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
Q — solution volumetric floe rate ($cm^3\ s^{-1}$)
r — electric resistance ($\Omega\ cm^2$)
r_{alter} — altering current electric resistance ($\Omega\ cm^2$)
r_{dire} — direct current electric resistance ($\Omega\ cm^2$)
R — gas constant ($J\ K^{-1}\ mol^{-1}$)
R_m — electric resistance of membranes in a stack ($\Omega\ cm^2$)
R' — electric resistance of desalting cells in a stack ($\Omega\ cm^2$)
R'' — electric resistance of concentrating cells in a stack (Ωcm^2)
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_{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

γ — activity coefficient of electrolytes
ε — electric current screening ratio of a spacer
ζ — current density non-uniformity coefficient
η — current efficiency
λ — 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
$\Delta\xi$ — half of ξ value range of desalting cells
ρ — overall hydraulic conductivity of a membrane pair ($cm^4\ eq^{-1}\ s^{-1}$)
σ — standard deviation of normal distribution of linear velocity ratio ξ
ϕ — overall electro-osmotic permeability of a membrane pair ($cm^3\ A^{-1}\ s^{-1}$)

Subscript

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

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