Estimation of Transport Parameters of RO Membranes for Seawater Desalination

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Membrane transport parameters from a running plant data were studied to understand their changes with time, as well as the causes of membrane fouling under various running conditions. First, the mass-transfer coefficient of a spiral-type reverse osmosis (RO) element was measured using a polyamide membrane, designated UTC-80, and an appropriate correlation equation was obtained. Then, a computer program was developed to obtain membrane transport parameters from flux and rejection data of an actual RO plant. When it became apparent that the temperature corrections should be applied, laboratory experiments were used to determine them. Thus, the time course change of both solution and salt permeabilities and the relation between them could be followed. The permeability of each ion or solute can be obtained by the same method when their analytical data are available.

Introduction

Research on the reverse osmosis (RO) process was started in the 1950s as a new seawater desalination process, and the first RO membrane developed in 1960 at UCLA was the asymmetric cellulose acetate membrane. Recently, many polyamide RO membranes have been commercialized due to their high selectivity and good durability. Toray Industries has developed a composite flat sheet membrane made of cross-linked fully aromatic polyamide, designated as UTC-80. This membrane has been applied in many actual operating seawater desalination plants, for example, in the Okinawa 40,000 m^3/d plant, which was commissioned in February 1996 and is now the largest seawater desalination plant running in Japan.

For the stable operation of such a plant, it is important to know the change in the membrane characteristics with time under various operating conditions. Usually, these characteristics have been reported in terms of flux and salt rejection, but they only give apparent membrane properties. The true ones should be given in the form of membrane transport parameters. An example of such an analysis was reported earlier by one of the present authors for the case of a hollow fiber type membrane.

In this article the mass-transfer coefficient of the Toray spiral module using UTC-80 based on the osmotic pressure method is reported. Next, data taken at a 140 m^3/day plant, which was run for about two years, is analyzed to obtain membrane transport parameters using the mass-transfer coefficient obtained. It was also found that an appropriate temperature correction was necessary for each transport parameter besides the temperature correction of the diffusion coefficient and viscosity. Finally, it is demonstrated that the permeability of each ion can be obtained using the above method when the concentration data of each ion in the feed and the permeate are available.

Theoretical Studies

Basic transport equation

First, the salt concentration (value expressed by total dissolved solid) at the membrane surface C_M is given by the next equation (Kimura, 1995)

$$\frac{C_M - C_P}{C_B - C_P} = \exp\left(\frac{J_V}{k}\right) \tag{1}$$

where k is a mass-transfer coefficient (m/s).

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Next, a volume flux and a salt flux are given by the next equations (Kachalsky and Curran, 1965; Kimura, 1995; Fukunaga et al., 1997; Ikeda et al., 1998).

$$J_V = L_P[\Delta P - \sigma \cdot \{\pi(C_M) - \pi(C_P)\}] \tag{2}$$

$$J_S = P(C_M - C_P) + (1-\sigma)\overline{C}_S \cdot J_V \tag{3}$$

This equation was transformed to eliminate the average concentration (Spiegler and Kedem, 1966) $\overline{C}_S$ and to give the salt rejection R as follows

$$R \equiv \frac{C_M - C_P}{C_M} = \frac{\sigma(1-F)}{(1-\sigma F)} \tag{4}$$

where F is given as

$$F = \exp\left[-\frac{J_V(1-\sigma)}{P}\right] \tag{5}$$

When σ is very close to 1, a salt flux is given by the next equation

$$J_S = P(C_M - C_P) \tag{6}$$

C_P is also given by the next equation.

$$C_P = \frac{J_S}{J_V} \tag{7}$$

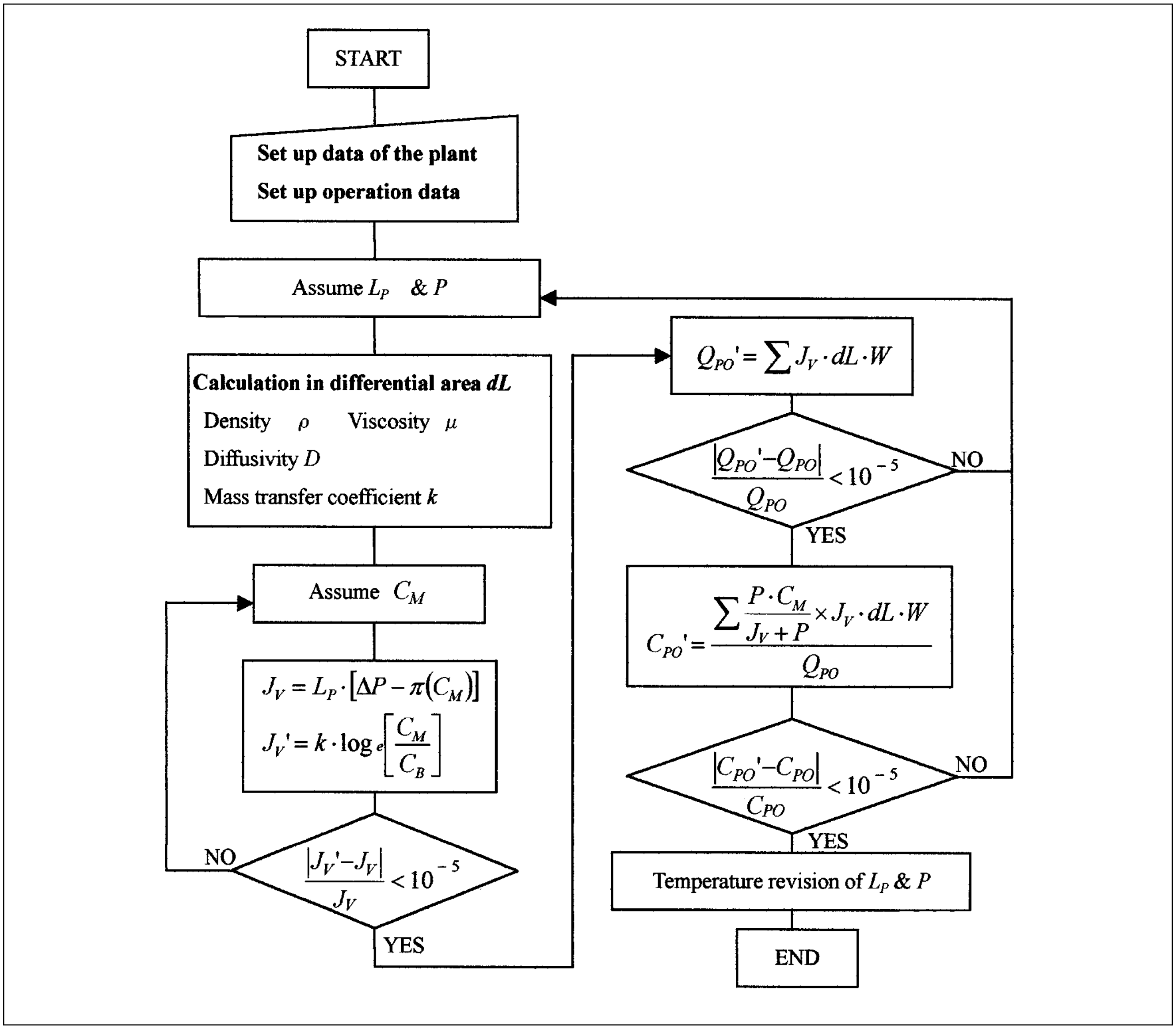

Figure 1. Computer calculation program.

Determination of mass-transfer coefficient from RO experiment

There are two methods to obtain the mass-transfer coefficient from the RO experiment. One is called the osmotic pressure method, which utilizes Eqs. 1 and 2. In this case, a high-salt-rejecting membrane should be used, whose σ is very close to 1, so that C_P may be ignored. The value of L_P is measured using pure water flux. C_M is then obtained from a measured flux using Eq. 2, and k is calculated using Eq. 1.

The other one is called the velocity variation method (Nakao and Kimura, 1981), which utilizes the transformed style of Eq. 1 given as follows

$$\ln\left(\frac{1-R_{\text{obs}}}{R_{\text{obs}}}\right)=\ln\left(\frac{1-R}{R}\right)+\frac{J_V}{k} \tag{8}$$

where R_{obs} is defined as

$$R_{\text{obs}}=\frac{C_B-C_P}{C_B} \tag{9}$$

In this work the former method was used. In the measurement, when the feed flow rate is changed to see an effect of Reynolds Number (Re) on k, the recovery ratio of the feed through an element changes, which results in the change of the bulk concentration leaving the element. To correct this effect, we first used an average concentration of the feed and the outlet as C_B, since the maximum recovery ratio was not greater than 16%. However, to check this effect, we used a computer program, which was developed for the estimation of membrane transport parameters and is explained in the next section. The solute used in the measurement was NaCl.

Estimation of membrane transport parameters from an RO plant data

Once the mass-transfer coefficient is determined, membrane transport parameters can be calculated from flux and rejection data taken at a running RO plant, and, thus, we can trace the change in parameters with time. For this purpose, a computer program was developed and explained as follows.

A membrane element is divided into N sections along the feed flow direction. Mass balance equations at each section ($\Delta L = L/N$) are given as

$$\Delta Q_{Pi}=J_{Vi}\cdot\Delta L\cdot W_e \tag{10}$$

$$C_{Pi}=\frac{J_{Si}}{J_{Vi}} \tag{11}$$

$$Q_{PO}=\sum_{i=1}^{N}\Delta Q_{Pi}=\sum_{i=1}^{N}J_{Vi}\cdot\Delta L\cdot W_e \tag{12}$$

$$C_{PO}=\frac{\sum_{i=1}^{N}C_{Pi}\cdot\Delta Q_{Pi}}{Q_{PO}} \tag{13}$$

Assuming σ is close to 1 and neglecting C_P, Eqs. 1 and 2 are modified as follows

$$J_V=k\cdot\ln\left(\frac{C_M}{C_B}\right) \tag{14}$$

$$J_V=L_P[\Delta P-\pi(C_M)] \tag{15}$$

Using these equations, we can estimate L_P and P from Q_{PO} and C_{PO} as follows.

The computer calculation program is shown in Figure 1.

(1) Assume L_P and P; (2) Assume C_M; (3) Calculate J_V using Eqs. 14 and 15. Assume C_M until both J_V become equal; (4) Calculate J_S using Eq. 6 (C_P is neglected); (5) Then calculate C_P using Eq. 7; (6) Calculate C_{PO} and Q_{PO} using Eqs. 12 and 13. Assume L_P and P until calculated values coincide with plant data.

In the procedure previously explained, when L_P is known instead of k, we can calculate k and P by the same procedure. We used this procedure as the second osmotic pressure method to obtain k values to eliminate the effect of the bulk concentration change, explained in the previous paragraph.

Necessary Data

For the analysis of seawater desalination results, the properties of the seawater are necessary and the following data are used: For the osmotic pressure of seawater, we used Miyake's estimation (Miyake, 1939), which is given below. Although there is another data given by Stoughton (Stoughton and Lietzke, 1967), there is not much difference between them over the concentration range used (35,000–60,000 mg/L)

$$\pi(c,T)=(0.6955+0.0025\cdot T)\times 10^8\cdot\frac{c}{\rho} \tag{16}$$

For the density of seawater (Sekino, 1991)

$$\rho=498.4\cdot m+\sqrt{248{,}400\,m^2+752.4\,mc} \tag{17}$$

where

$$m=1.0069-2.757\times 10^{-4}T \tag{18}$$

For the viscosity of seawater (Sekino, 1991)

$$\eta=1.234\times 10^{-6}\exp\left(0.00212\cdot c+\frac{1{,}965}{273.15+T}\right) \tag{19}$$

For the diffusivity (Sekino, 1991)

$$D=6.725\times 10^{-6}\cdot\exp\left(0.1546\times 10^{-3}\cdot c-\frac{2{,}513}{273.15+T}\right) \tag{20}$$

Experimental Results

Correlation of mass-transfer coefficient for the Spiral-Type Element

In many cases, the correlation of the mass-transfer equation is described by the following equation

$$Sh=b\cdot Re^{a}\cdot Sc^{0.25} \tag{21}$$

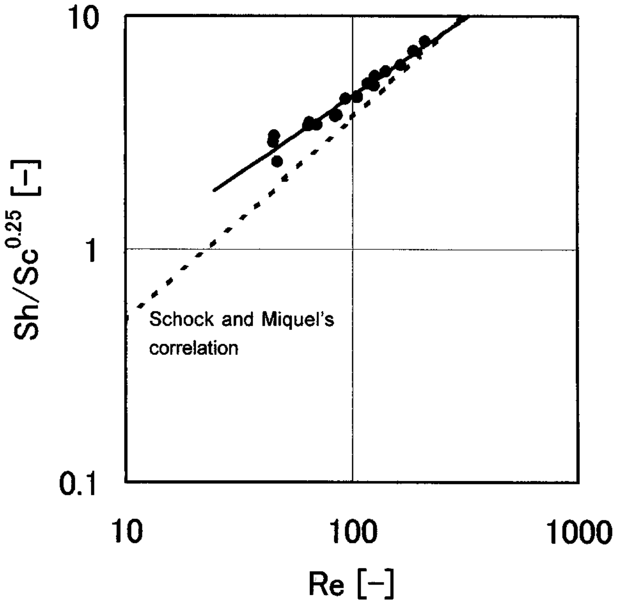

Figure 2. Correlation between $Sh/Sc^{0.25}$ vs. Re.

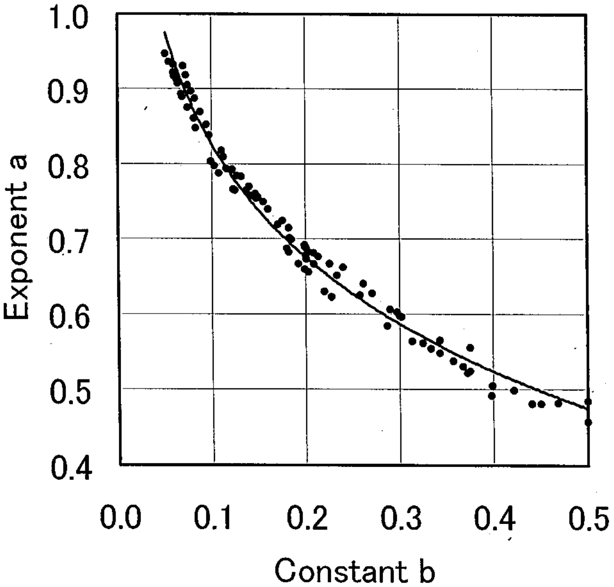

Figure 3. Relationship between exponent *a* and constant *b*.

Schock and Miquel (1987) obtained the following correlation for the spacer-filled flat channel using the effective hydraulic diameter depending on the types of spacers used

$$Sh = 0.065 \cdot Re^{0.875} \cdot Sc^{0.25} \tag{22}$$

Mass-transfer coefficients obtained in this study using the first osmotic pressure method are shown in Figure 2, where Eq. 22 is also shown. The present results are finally correlated to the next equation

$$Sh = 0.210 \cdot Re^{0.667} \cdot Sc^{0.25} \tag{23}$$

There is a slight difference between two equations, and this may be due to different structures and types of spacers used in different commercial spiral-type elements.

Using the second osmotic pressure method, k can be obtained from a set of J_V and C_P data taken at a fixed Re. An exponent a and a coefficient b in Eq. 21 are then obtained from two sets of k values determined at different Re using the next equation

$$a = \frac{1}{\ln Re}\left[-\ln(b) + \ln\left(\frac{kd}{D \cdot Sc^{0.25}}\right)\right] \tag{24}$$

From a different set of k and Re, we obtained a different set of a and b. The obtained results can be expressed as follows and are shown in Figure 3.

$$a = -0.219 \cdot \ln(b) + 0.323 \tag{25}$$

A set of a and b in Eq. 23 is on this line and shows the coincidence of the two osmotic pressure methods. When a is taken as 0.875 as in Eq. 22, we get the next equation, in which b is 0.080 and the experimental error is approximately ±0.010. This gives slightly larger k at a smaller Reynolds Number than Eq. 22

$$Sh = 0.080 \cdot Re^{0.875} \cdot Sc^{0.25} \tag{26}$$

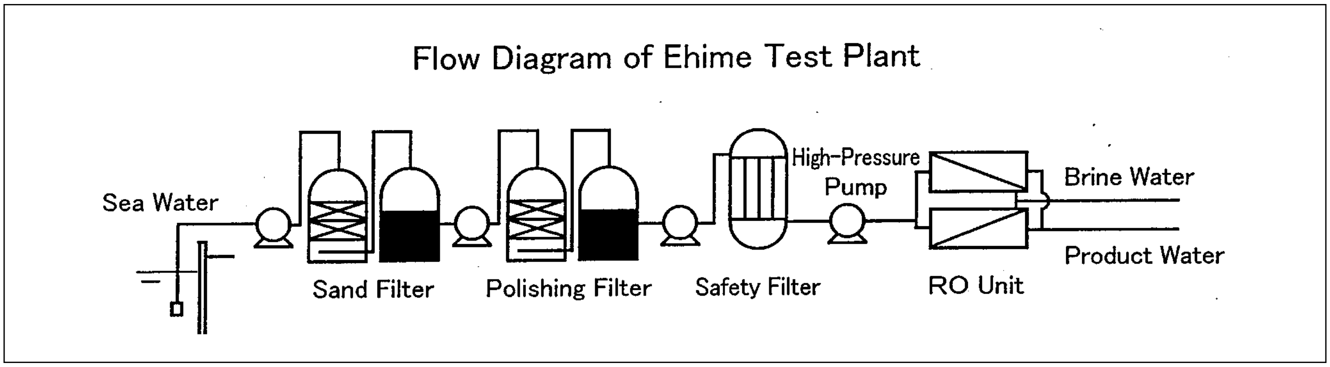

Figure 4. Ehime test plant.

Table 1. Standard Operating Conditions of RO Plant

Feed Seawater	Flow Rate	350 (m^3/d)
	TDS Concentration	35,000 (mg/L)
Permeated Water	Flow Rate	140 (m^3/d)
	TDS Concentration	100 (mg/L)
Operating Pressure		6.5 (MPa)
TDS Rejection		99.8 (%)
Recovery Ratio		40 (%)
Membrane Module		SU-820×6
Number of Modules		2

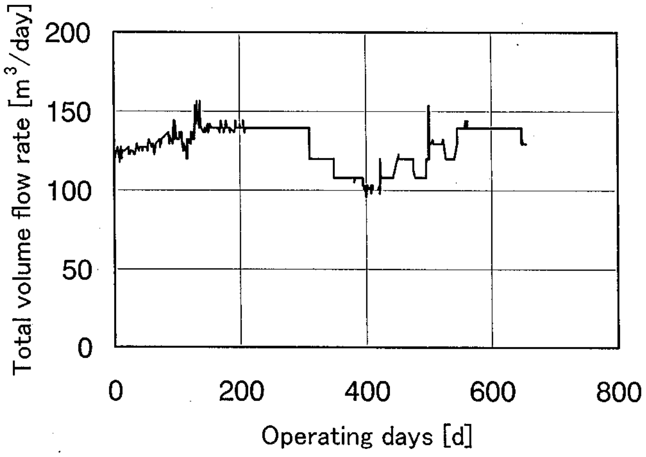

Figure 5. Total volume flow rate vs. time.

Analysis of a long-run RO plant data

In the Ehime factory, Toray Industries established a 140 m^3/day RO seawater desalination plant using SU-820 spiral wound elements and ran beginning in February 1995 for about two years. The test plant is shown in Figure 4, and its operating conditions are listed in Table 1. Data taken there were analyzed to obtain L_P and P using the program previously explained, and to investigate the time change of these values. Figures 5 to 9, respectively, show the raw data of flux, operating pressure, permeate concentration measured as TDS, salt rejection based on TDS unit, and permeate temperature. From Figure 9, it is clearly seen that there exists a seawater temperature effect, which should be corrected by an appropriate method.

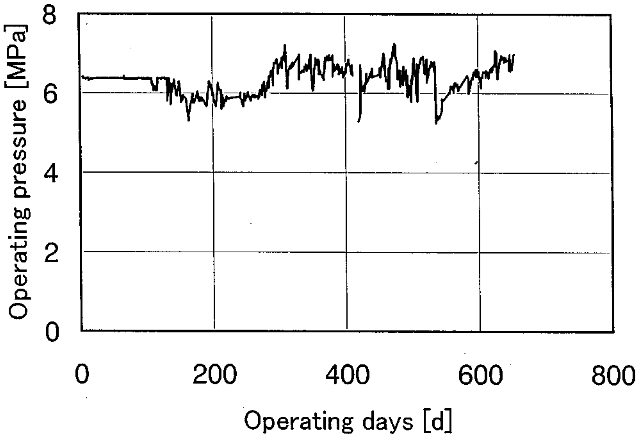

Figure 6. Operating pressure vs. time.

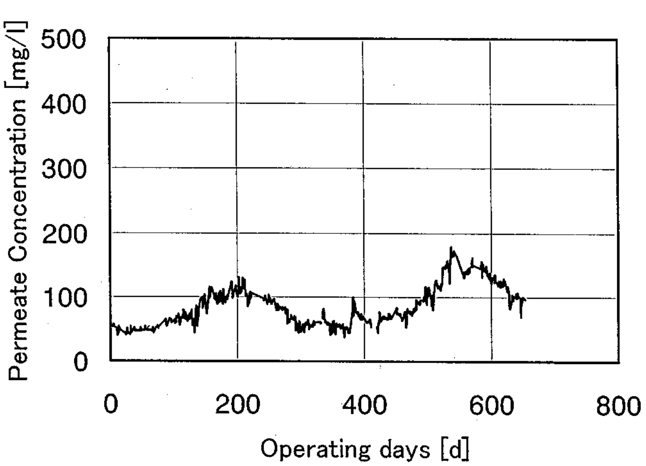

Figure 7. Permeate concentration vs. time.

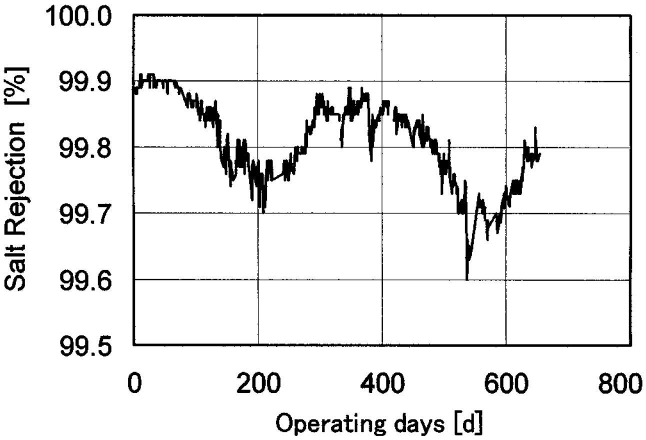

Figure 8. Salt rejection vs. time.

First, we tried to adopt the temperature effect of salt diffusivity and water viscosity taking the standard at 25°C using

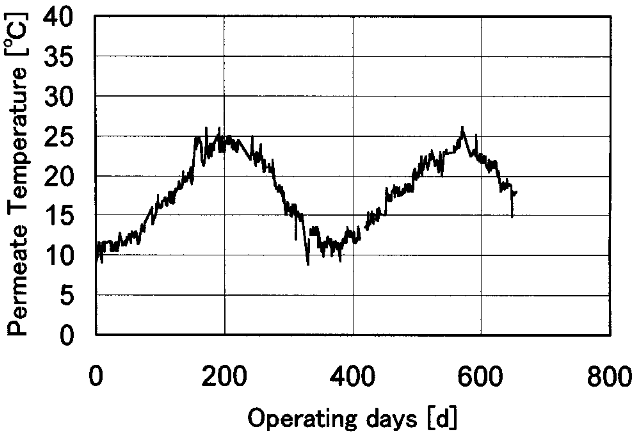

Figure 9. Permeate temperature vs. time.

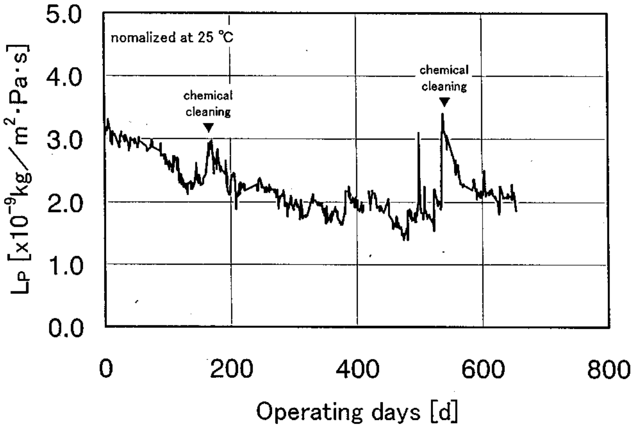

Figure 10. L_P values obtained after temperature correction.

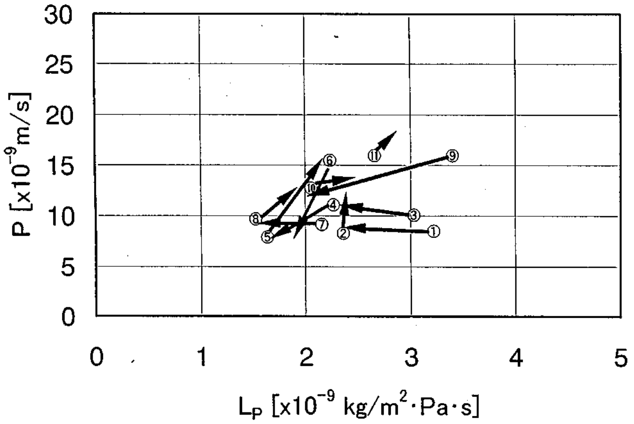

Figure 12. Relative variation of L_P and P with time.

the following relationships

$$L_P = L_{P25} \cdot \frac{\eta_{25}}{\eta} \tag{27}$$

$$P = P_{25} \cdot \frac{\eta_{25}}{\eta} \cdot \frac{273.15 + T}{273.15} \tag{28}$$

Results thus obtained still showed the temperature effect. These effects were estimated from the laboratory experimental data taken using membrane pieces as follows

$$\frac{L_{PT}}{L_{P25}} = \exp\left[0.0114(T - 25)\right] \tag{29}$$

$$\frac{P_T}{P_{25}} = \exp\left[0.0299(T - 25)\right] \tag{30}$$

The final data thus corrected are shown in Figures 10 and 11, which show the reasonable trend of the membrane property changes. It is also very interesting to know the relationship between the time changes of L_P and P, which may give the causes of membrane fouling and is shown in Figure 12. Numbers in the figure show the time course of the runs and the position where the operation was stopped for short intervals and then resumed. At positions 3 and 9, the membranes were chemically cleaned, which may cause an increase in P, and, at other points, L_P tends to decrease due to compaction, but P does not change very much. These facts may show that we must adopt milder chemical cleaning solutions.

Permeability of various ions

When the concentrations of various ions and components in the feed and the permeated water are obtained, we can calculate the permeability for each ion and component by the same method as that explained in the subsection on estimation of membrane transport parameters from an RO plant data. The necessary diffusivity data can be obtained from the literature (Wilke and Chang, 1955; Mills and Lobe, 1989) and used to obtain each mass-transfer coefficient. Results thus obtained are shown in Figure 13, where P values of various ions and one, based on TDS values and measured at different dates, are plotted against the diffusivity. The results first

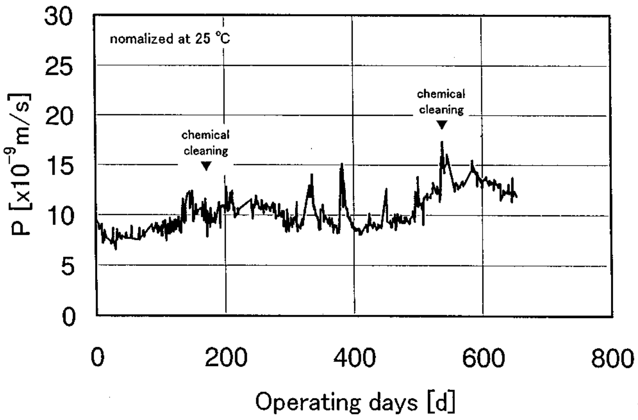

Figure 11. P values obtained after temperature correction.

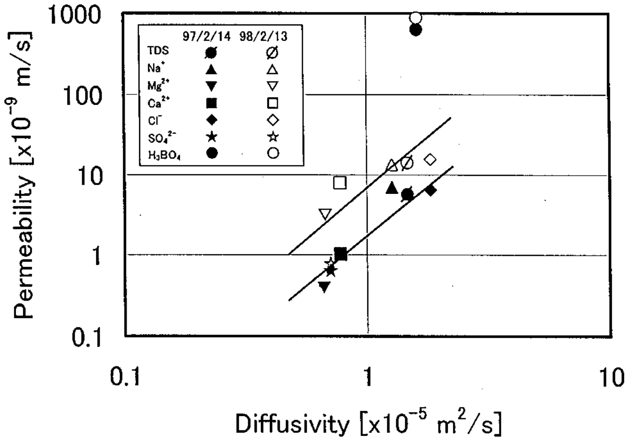

Figure 13. Relationship between ion and solute permeability and diffusivity in water.

show that the permeability of each ion may depend on the diffusivity in water except boron. They then show that the permeability increases after the operation for one year, but there are slight differences of the degree of increase depending on ions. We make no attempt to discuss here the transport mechanism of ions through a polyamide membrane; we try to show that we can estimate the permeate water quality and its change with time using the results obtained.

Conclusions

First, the mass-transfer coefficient k of a spiral-type RO element, designated SU-820, is measured by the osmotic pressure method and correlated to a form, similar to the previously obtained one.

Next, a computer program is developed, which can take into consideration of a bulk concentration increase with an increase of water recovery ratio. Using this program, we calculate L_P and P from measured data of a flux and a permeate concentration, when k is known. It also can be used to obtain k, when L_P and P are known. This latter fact is used to check the effect of a recovery ratio change with the variation of the feed flow rate.

In applying this method to data taken at a 140 m^3/d plant, it becomes clear that a temperature correction of both L_P and P are necessary and they are determined using laboratory test cells. It becomes then possible to know a general trend of a time change of L_P and P.

Finally, it is shown that P values of each ion can be determined, when each ion concentration in the feed and the permeate are measured, instead of TDS values used so far.

Notation

a = exponent of Reynolds Number
b = constant in correlation
c = concentration, kg/m^3
C = concentration, mg/L or mol/m^3
d = hydraulic diameter, m
D = diffusivity, m^2/s
J_S = salt or ion flux, $mg/m^2 \cdot s$ or $mol/m^2 \cdot s$
J_V = solution flux, $kg/m^2 \cdot s$
L = length of element or module
L_P = solution permeability, $kg/m^2 \cdot Pa \cdot s$
m = constant
N = total number of sections
P = solute or ion permeability, m/s
Q = volume flow rate, m^3/s
R = salt or ion rejection
Sc = Schmidt Number
Sh = Sherwood Number
T = temperature, °C
W = width of membrane, m
ΔL = length of a section, m
ΔP = applied pressure, Pa
ΔQ = volume flow from a section, m^3/s
η = viscosity, $Pa \cdot s$
π = osmotic pressure, Pa
ρ = density, kg/m^3
σ = reflection coefficient

Subscripts

B = bulk
i = ith section
M = membrane surface
O = overall
P = permeate
25 = 25°C

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