Desalination and Water Treatment
www.deswater.com

14 (2010) 174–178
February

1944-3994/1944-3986 © 2010 Desalination Publications. All rights reserved
doi: 10.5004/dwt.2010.1024

Mathematical model of mass transfer in an electrodialyzer with net-like spacers

David Tvrzník[a*], Lubomír Machuča[a], Aleš Černín[b]

[a]*MemBrain s.r.o., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic*
[b]*MEGA a.s., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic*
Tel.: +420 487 888 305; email: David.Tvrznik@membrain.cz

Received 20 July 2009; accepted 26 August 2009

ABSTRACT

Data on DC current have been recorded for EDR-III/200-0.8 electrodialysis stack available from MEGA a.s., Czech Republic, as a function of feed electrolyte (NaCl) concentration and applied voltage. The flow rates and temperature have been fixed during the tests. Spacers used between the ion-exchange membranes in the stack are of net-like type. Different approaches to the mathematical modeling of mass transfer in an electrodialyzer have been verified to select one that best fits experimental data obtained for the stack. The ''turbulent flow'' model has been evaluated to be the most suitable for this purpose. The model assumes uniform distribution of linear velocities, ideal cross mixing of the liquid in the flow phase and presence of the stationary diffusion layer. In addition, a correlation coefficient has been introduced into the model to take the effect of a turbulence promoter on electrical field shielding into account.

Keywords: Electrodialysis, mass transfer modeling

---

1. Introduction

Electrodialysis (ED) or electrodialysis polarity reversal (EDR) is a known membrane separation process used to remove electrolytes from solutions. The process principle is based on the selectivity of ion-exchange membranes for either cations, or anions, while the transport of ions is affected by electrical field. A typical electrodialyzer (or ED stack) consists of number of cation-exchange and anion-exchange membranes alternating between a pair of electrodes. Each two membranes are separated by a spacer forming a flow compartment. There are two main types of flow compartments in an ED stack: the diluting compartments, where the liquid (diluate) becomes diluted during the process, and the concentrating compartments, where the electrolytes transferred from the diluting compartments through the ion-exchange membranes are collected. Two main types of spacers are common in ED: net-like spacers and tortuous path spacers. The spacers preferred in this study are of the net-like type. The nets serve as turbulence promoters, intensifying the overall mass transfer in the stack. The basic repeating element of an ED stack, a cell pair, comprises a cation-exchange membrane, a concentrating compartment, an anion-exchange membrane and a diluting compartment.

ED is used in variety of industries such as municipal and industrial wastewater treatment, whey demineralization, purification of pharmaceutical specialties, cooling tower blowdown recycling, production of supply and irrigation water etc.

---

[*] Corresponding author

Presented at the Fourth Membrane Science and Technology Conference of Visegrad Countries (PERMEA 2009), Prague, 7-11 June, 2009.

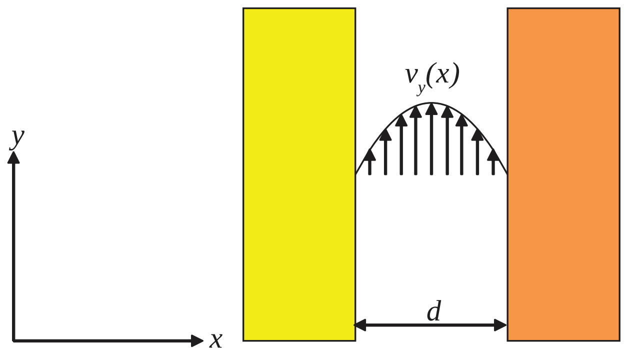

Fig. 1. Linear velocity profile for laminar flow in a smooth channel.

Most of the large installations of ED technology over the world are water treatment applications. Since the feed water composition is application specific, a potential complication for projection of the technology arises. Ideally, each case should be piloted first, but this takes too much time and increases costs. Another possibility is to provide a reliable mathematical model of mass transfer in an ED stack and to compare it with experimental data.

2. Theory

2.1. Cell pair voltage drop

The DC current passing through an ED stack can be expressed as

$$I = w\int_{0}^{L} j_x \mathrm{d}y. \tag{1}$$

Suppose we are able to calculate the cell pair voltage drop $\Delta\phi_{\mathrm{CP}}$ as a function of j_x for a binary electrolyte solution and the real cell pair voltage drop $\Delta\varphi_R$ is known. Under this condition, j_x can be calculated by solving a non-linear equation

$$\Delta\phi_{\mathrm{CP}}(j_x) - \Delta\phi_R = 0. \tag{2}$$

$\Delta\phi_{\mathrm{CP}}$ is a sum of contributions of respective elements of the cell pair, ie.

$$\Delta\phi_{\mathrm{CP}}(j_x) = \Delta\phi_D(j_x) + \Delta\phi_{\mathrm{CM}}(j_x) + \Delta\phi_{\mathrm{C}}(j_x) + \Delta\phi_{\mathrm{AM}}(j_x). \tag{3}$$

The respective voltage drops can be calculated from the following equations

$$\Delta\phi_D = -\alpha j_x \int_{x=0}^{x=d_D} \frac{\mathrm{d}x}{\kappa_D(x)} - \frac{\mathrm{RT}}{F}\left[\frac{t_C^S}{z_C} + \frac{(1-t_C^S)}{z_A}\right] \ln\frac{c_S^D(d_D, y)}{c_S^D(0, y)}, \tag{4}$$

$$\Delta\phi_C = -\alpha j_x \int_{x=0}^{x=d_K} \frac{\mathrm{d}x}{\kappa_C(x)} - \frac{\mathrm{RT}}{F}\left[\frac{t_C^S}{z_C} + \frac{(1-t_C^S)}{z_A}\right] \ln\frac{c_S^C(d_C, y)}{c_S^C(0, y)}, \tag{5}$$

$$\Delta\phi_{\mathrm{CM}} = -\alpha R_{A,\mathrm{CM}} j_x - \frac{\mathrm{RT}}{z_A F}\left(t_C^{\mathrm{CM}}\frac{z_A - z_C}{z_C} + 1\right) \ln\frac{c_S^C(0, y)}{c_S^D(d_D, y)}, \tag{6}$$

$$\Delta\phi_{\mathrm{AM}} = -\alpha R_{A,\mathrm{AM}} j_x - \frac{\mathrm{RT}}{z_A F}\left(t_C^{\mathrm{AM}}\frac{z_A - z_C}{z_C} + 1\right) \ln\frac{c_S^D(0, y)}{c_S^C(d_C, y)}. \tag{7}$$

α in Eqs. (4) to (7) is a correlation coefficient taking into account the shielding effect of the turbulence promoters on electrical field in the ED stack.

2.2. Convective-diffusion model

This model is well described in literature [0–0]. The model assumes that the flow channels are smooth and flow of the liquid is laminar (Fig. 1.). In such case, the well known equation for calculation of linear velocity profile in the flow compartments can be used

$$v_y(x) = 6\bar{v}_y\left[\frac{x}{d} - \left(\frac{x}{d}\right)^2\right]. \tag{8}$$

The concentration field in the compartment can be calculated from the mass balance of the volume element of the liquid phase resulting in equation

$$\frac{\mathrm{d}c_S}{\mathrm{d}y} = \frac{D_S}{v_y(x)}\frac{\mathrm{d}^2 c_S}{\mathrm{d}x^2}, \tag{9}$$

that is valid in the range $x \in (0, d)$. Concentration gradient, and thus the electrolyte concentration at the liquid/membrane interface ($x = 0, d$) is calculated from equation

$$\frac{\mathrm{d}c_S}{\mathrm{d}x} = -\frac{(t_C^M - t_C^S)j_x}{\nu_C z_C F D_S}. \tag{10}$$

j_x can be calculated by solving Eq. (2) and setting $\alpha = 1$ (absence of turbulence promoter). An initial condition for calculation the concentration field is

$$c_S(x, 0) = c_S^0. \tag{11}$$

2.3. "Turbulent flow" model

Most commercial ED stacks use net-like spacers (Fig. 2) to promote liquid flow turbulence and mass transfer. To calculate the linear velocity field, Navier-Stokes equation should generally be solved instead of simple calculation using Eq. (8). However, this is too

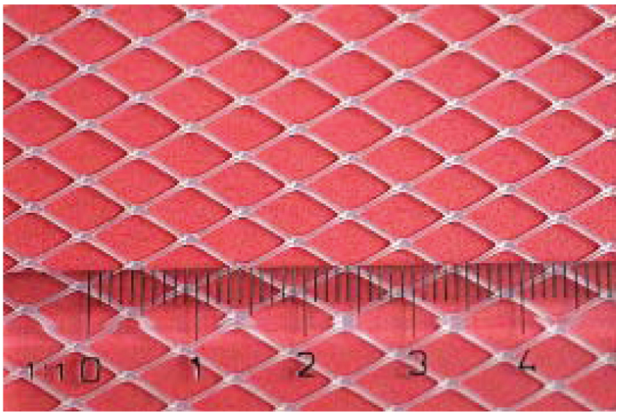

Fig. 2. Detail of the flow turbulence promoter.

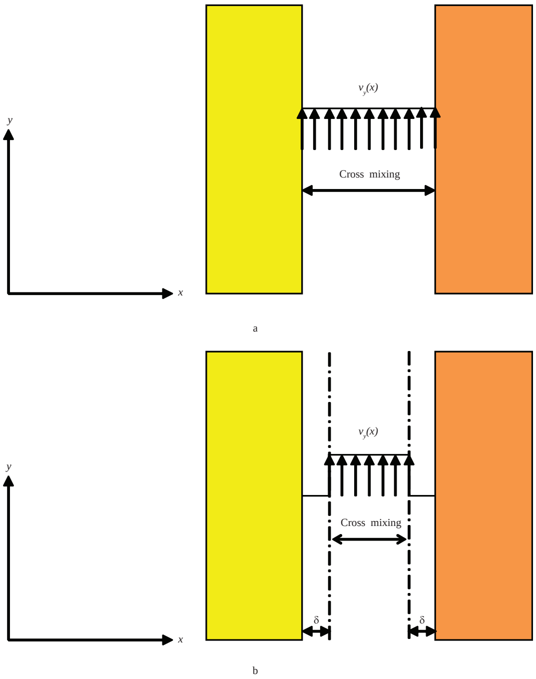

Fig. 3. Linear velocity profile assumed by the "turbulent flow" model; a without diffusion layer, b with diffusion layer.

difficult in most cases. To eliminate the complexity of the solution, "turbulent flow" model is introduced (Fig. 3).

Since the case with the absence of the diffusion layer is only an extreme of the case with the presence of the diffusion layer ($\delta = 0$ m), the linear velocity and concentration fields can be expressed in both cases as

$$v_y(x) = \bar{v}_y, \tag{12}$$

$$\frac{\mathrm{d}c_S}{\mathrm{d}y} = \pm\frac{w}{\dot{V}}J_{S,x} = \pm\frac{w}{\dot{V}}\frac{\left(t_C^{\mathrm{CM}} - t_C^{\mathrm{AM}}\right)j_x}{\nu_C z_C F} \tag{13}$$

in the range $x \in \langle \delta, d - \delta \rangle$, and

$$v_y(x) = 0, \tag{14}$$

and using equation (10) to calculate the concentration profile in the range $x \in \langle 0, \delta) \wedge (d - \delta, d \rangle$. The sign in expression (13) depends on weather the diluting (–) or concentrating (+) compartment is balanced.

3. Experimental

The experimental setup consisted of one EDR-III/200-0.8 electrodialysis stack, 2 m^3 storage tank for NaCl feed solution, diluate and concentrate pumps, piping, fittings and switchgear provided with DC power supply for the ED stack. ED-II 4/2 Type 99 net-like spacers with a thickness of 0.8 mm and RALEX® CM-PES and AMH-PES membranes are used in the stack.

Diluate, concentrate and electrode compartments of the stack were all fed in parallel with the same solution from the storage tank. After a single pass of the streams through the stack, all liquids were returned back to the storage tank to maintain the concentration of the feed solution. DC voltage from the power supply was applied on the ED stack.

The operating conditions were fixed for all hydraulic streams, ie. diluate and concentrate at 16 m^3 h^{-1} and electrode feed at 2 × 1,000 L h^{-1}, and for temperature at 25°C. The concentration of NaCl in the feed solution was varied from 1 to 5 g L^{-1} and voltage was varied from 0 to 400 V (0–2 V/cell pair). Samples of inlet and outlet solutions were taken to measure conductivity and pH and DC current passing through the stack was recorded.

4. Results and discussion

Current efficiencies were high in all cases (above 98%). Thus, it was possible to neglect the effect of back diffusion and side currents on mass transfer.

The comparison between experimental and calculated data using convective diffusion model with $\alpha = 1$ is shown in Fig. 4a. It is obvious that the convective-diffusion model cannot explain the real performance of an ED stack in a satisfactory manner. The convective diffusion model explains the real data at low voltages (low current densities) only due to small changes in concentration field. At higher voltages, however, the experimentally observed currents are much higher than those calculated with the model.

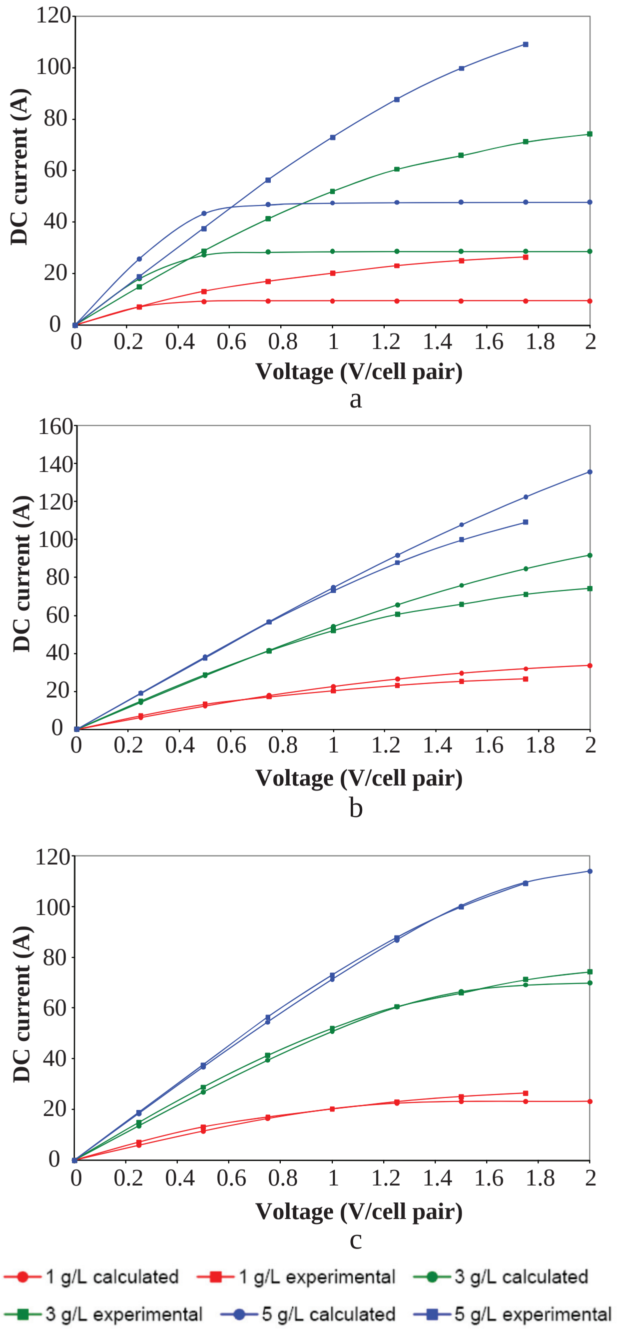

Fig. 4. Calculated versus experimental data for EDR-III/200-0.8 electrodialysis stack; a using convective-diffusion model, b using ''turbulent flow'' model with $\alpha = 1.66$ and $\delta = 0$ m, c using ''turbulent flow'' model with $\alpha = 1.66$ and $\delta = 5.10^{-5}$ m.

This is due to the effect of turbulence promoter on liquid cross mixing.

The effect of turbulence promoters must be taken into account using ''turbulent flow'' model. When setting $\alpha = 1.66$ and $\delta = 0\ m$, the ''turbulent flow'' model fits the experimental data quite well for all feed concentrations at low voltages while there is a significant difference between the data at higher voltages, see Fig. 4b. This is because, that no limiting current density (and current) is defined, if $\delta = 0\ m$. However, the limiting currents are usually observed when operating ED stacks.

When setting $\alpha = 1.66$ and $\delta = 5.10^{-5}$ m, the ''turbulent flow'' model fits the experimental data well in whole range of feed concentrations and voltages, see Fig. 4c.

Generally, values of both α and δ parameters must be found for each ED stack configuration and hydraulic conditions in order to attain good correlation between the experimental and calculated data. It can be shown, that the calculated current is relatively independent on δ at very low voltages, while the limiting current (density) is independent on α. Thus, the experimental data for at least two voltages must be obtained. At least one data record should be obtained for a low voltage and at least one data record for a high voltage.

5. Conclusions

Several approaches to the mathematical modeling of mass transfer in an electrodialyzer have been used to fit the experimental data obtained for EDR-III/200-0.8 electrodialysis stack with net-like spacers. For this purpose, the ''turbulent flow'' model assuming both cross mixing of the liquid in the flow compartments and the presence of the stationary diffusion layer at the membrane/liquid interface is preferred because of the best correlation with experimental data at a wide range of operating conditions. There are two parameters (α and δ) which must be determined for each stack configuration and hydraulic condition based on experimental data, however. Since the found value of α parameter is relatively high (1.66) for used configuration of the ED stack, the turbulence promoter should be optimised to decrease this value while maintaining the level of mass transfer.

Symbols

D_S	Diffusion coefficient of a binary electrolyte ($m^2\ s^{-1}$)
F	Faraday constant ($C\ mol^{-1}$)
I	DC current (A)
L	Flow path (m)
R	Molar gas constant ($J\ mol^{-1}\ K^{-1}$)
$R_{A,AM}$	Area resistance of the anion-exchange membrane ($\Omega\ m^2$)

$R_{A,\mathrm{CM}}$	Area resistance of the cation-exchange membrane (Ω m^2)
T	Thermodynamic temperature (K)
$\dot{V}$	Flow rate (m^3 s^{-1})
c_S	Concentration of electrolyte (mol m^{-3})
c_S^0	Initial concentration of electrolyte (mol m^{-3})
c_S^C	Concentration of electrolyte in the concentrate (mol m^{-3})
c_S^D	Concentration of electrolyte in the diluate (mol m^{-3})
d	Thickness of the flow compartment (m)
d_C	Thickness of the concentration compartment (m)
d_D	Thickness of the diluting compartment (m)
j_x	Local current density (A m^{-2})
t_C^{AM}	Transference number of a cation in the anion-exchange membrane
t_C^{CM}	Transference number of a cation in the cation-exchange membrane
t_C^S	Transference number of a cation in the liquid phase
w	Effective width of the ion-exchange membrane (m)
x	Coordinate perpendicular to the surface of the ion-exchange membranes (m)
y	Coordinate parallel to the macroscopic liquid flow direction (m)
v_y	Linear velocity of the liquid (m s^{-1})
$\bar{v}_y$	Average linear velocity of the liquid (m s^{-1})
z_A	Anion charge
z_C	Cation charge
$\Delta\phi_{\mathrm{AM}}$	>Anion-exchange membrane voltage drop (V)
$\Delta\varphi_C$	Concentration compartment voltage drop (V)
$\Delta\phi_{\mathrm{CM}}$	Cation-exchange membrane voltage drop (V)
$\Delta\phi_{\mathrm{CP}}$	Calculated cell pair voltage drop (V)
$\Delta\varphi_D$	Diluting compartment voltage drop (V)
$\Delta\varphi_R$	Real cell pair voltage drop (V)
α	Correlation coefficient
κ_{C}	Concentrate conductivity (Sm^{-1})
κ_{D}	Diluate conductivity (S m^{-1})
ν_C	Stoichiometric coefficient of a cation

References

[1] V.V. Nikonenko, A.G. Istoshin and M.Kh. Urtenov, Desalination 126 (1999) 207–211.

[2] V.A. Shaposhnik and O.V. Grigorchuk, VGU, (2000) 13–19.

[3] O.V. Grigorchuk, V.I. Vasileva and V.A. Shaposhnik, Russ. J. Electrochem. 39(7), 777–783 (2003).