Concentration distribution along the electrodialyzer

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HIGHLIGHTS

- A simple model describing counter-current single-pass electrodialysis is established.
- Concentration distribution along the membrane is calculated.
- Influence of concentration distribution on scaling risk is discussed.

GRAPHICAL ABSTRACT
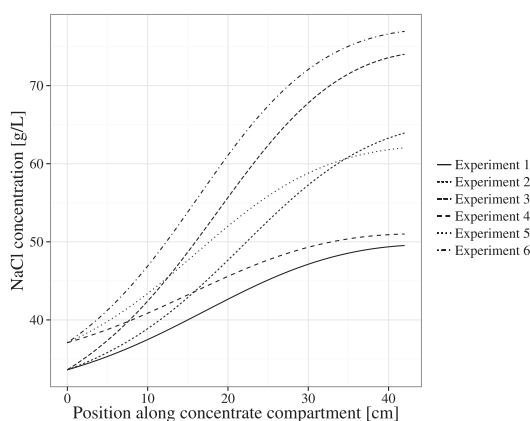
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ABSTRACT

Electrodialyzer equipped with a segmented electrode was used for a desalination of a model sodium chloride solution in the diluate linear flow velocity range of 2.11–3.37 cm/s, concentrate linear flow velocity range of 0.38–0.70 cm/s and current density of up to 722 A/m^2. The observed current density distribution, concentration and velocity changes allowed for the establishment of the concentration and linear flow velocity distributions along the concentrate and diluate compartments, taking into account the solute diffusion and electromigration, the solvent osmotic and electroosmotic flux and the solvent–solute interactions. The influence of concentration distribution and concentration polarization on the gypsum scaling risk was discussed.

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1. Introduction

Electrodialysis (ED) and electrodialysis reversal (EDR) are known to be competitive with other desalination methods as in the case of brackish water; however, a possibility of ED or EDR application for the desalination of more concentrated feeds is being investigated. Electrodialysis can be applied in the preconcentration of reverse osmosis brines for a further production of evaporative salt [1–3] or saturated brine [4–7]. Electrodialysis had also been applied in the salt production from seawater [8–11] — in Japan, the ED plants with capacity of up to 230 000 t of salt per year are in operation [8]. Another possible application of electrodialysis may be coal-mine water treatment [12], however the crystallization of sparingly soluble salts on the membrane surface (scaling) can be a major problem here. For instance, when applying ED for a dual-stage seawater desalination [11], the concentrate Ca^{2+}, Mg^{2+} and SO_4^{2-} content in the second stage concentrate, according to

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calculations, could reach 3.34, 12.16 and 26.18 g/L, respectively, at TDS 99 g/L, which means a gypsum saturation level would be extremely high. CaSO$_4$ scaling has been recognized as a real problem in seawater desalination [2,13]. The inorganic deposits increase the stack resistance, leading to increased energy consumption, hinder the mass transfer, and could even lead to membrane deterioration. In the previous works [14, 15], a method for scaling risk assessment in the single-pass electrodialysis was established by binding crystallization kinetics with the module hydrodynamics. As the concentration of sparingly soluble salts increases along the concentrate compartment, the crystallization induction time (time passing between the reaching of saturation and the appearance of observable crystals) drops. Simultaneously, as the sparingly soluble salt solution flows through the concentrate compartment, the time required for the majority of growing crystal clusters drops. Thus, in order to assess the scaling risk, both crystallization induction time and residence time can be formulated as the functions of position along the electrodialyzer, as depicted in previous paper (see Figs. 5–7 and 9 in [15]). If those two curves enclose an area, then the crystallization would occur, as there is a place inside the electrodialyzer in which the solution stays long enough for the crystallization to occur. The method, however, requires the knowledge of the concentration distribution along the electrodialyzer, which is the focus of the presented paper.

Several factors influence the concentration distribution along the membrane. The amount of transported salt depends on the mass transfer driving forces across the membranes: diffusion driven by the concentration gradient, electromigration driven by potential gradient and convective mass transfer driven by solvent–solute interactions [16]. The commonly-applied model for the mass transfer during electrodialytic desalination is the Nernst–Planck equation, which in its extended form can be written as [17]:

$$J_i = -D_i\left(\nabla C + \frac{z_i F}{RT} C_i \nabla \psi\right) + C_i \sum_{j=1}^{n} \nu_j J_j. \tag{1}$$

The inevitable, in the case of the electrodialysis, water flux across the membranes depends on the differences in the osmotic pressure between the diluate and concentrate and the applied current causing the electroosmotic flow [18,19]:

$$J_w = P_w^* \Delta c + t_w^* \frac{i}{F}. \tag{2}$$

Evangelista [20] proposed a method for evaluating the co-current and counter-current electrodialysis by calculating either required membrane area or outlet concentrations. The method was based on mass and volume balance of the elementary units of the electrodialyzer, but the solvent flux across the membrane was neglected. Tanaka [21] modeled the concentration distribution in the direction of electric field, i.e. perpendicular to the diluate and concentrate flow, during the co-current electrodialysis. He observed a quadratic current density distribution along the electrodialyzer. The quadratic current distribution has also been observed in our previous work [22] during the counter-current

electrodialysis, although in our case there was a maximum in the middle of the electrodialyzer. A non-linear, sigmoidal-like concentration distribution along the electrodialyzer was also observed (see Table. 4 in [21]). Later, Tanaka presented a simulation of electrodialytic desalination based on an ED plant and investigated the influence of overall applied current on current density distribution [13,23]. It was observed that the non-linearity of current density distribution is very clear at high overall current density. A diluate concentration distribution along the electrodialyzer was also studied [23]. Shaposhnik et al. [24,25] also observed the quadratic current density distribution in a co-current electrodialysis, and applied laser interferometry to obtain a concentration profile in a layer adjacent to the membrane surface. They provided the diffusion boundary layer thickness distribution along the electrodialyzer [26–28]; however they were more interested in changes of the boundary layer dimensionless concentration (i.e. concentration divided by bulk concentration at given position along the membrane).

2. Experimental

An electrodialyzer consisting of four pairs of Neosepta CMS/ACS membranes and 0.26 mm thick intermembrane spacers was applied for the desalination of sodium chloride solution. The effective length of membrane was 42 cm, channel width was 2 cm. Electrodialysis was performed in a single-pass, counter-current mode with respect to diluate and concentrate, with no recirculation. A segmented electrode, made of platinum-coated titanium, allowed the observation of current density distribution along the membrane. Anolyte and catholyte – 0.5 M sodium sulfate solution – were circulated and allowed to mix in an open tank. The concentrations and linear flow velocities are presented in Table 1. The concentration range and applied current densities were chosen to simulate electrodialytic seawater desalination.

2.1. Electrodialysis modeling

Following assumptions have been made:

- Electrodialyzer consists of 841 elementary units, each having length of $\Delta l = 0.05$ cm, width of 2 cm and consisting of four membrane pairs of intermembrane distance $s = 0.026$ mm. Increasing the number of elementary units to 8401 – each having one order of magnitude with smaller length, 0.005 cm – did not produced better fit of calculated values to experimental data — the errors, as presented in Table 4, differed by less than 0.1%,
- Elementary units are treated as CSTR tanks connected in series (see Fig. 1),
- membrane stack is treated as 841 parallelly-connected resistors, each subjected to current calculated based on the experimentally observed current distribution,
- sodium cation molar flux is equal to chloride anion molar flux,
- electromigration flux of ions is directly proportional to applied current,
- membranes are completely selective and do not pass co-ions.

Table 1
Experimental conditions.

Experiment		1	2	3	4	5	6
Current density [A/m^2]		243	491	720	248	491	722
Concentration	Diluate inlet	33.6	33.6	33.6	37.1	37.1	37.1
[g/L]	Diluate outlet	31.7	28.8	22.6	34.1	30.7	26.4
	Concentrate inlet	33.6	33.6	33.6	37.1	37.1	37.1
	Concentrate outlet	49.9	64.8	72.0	50.9	61.9	77.3
Linear flow velocity	Diluate inlet	3.37	3.37	3.37	2.31	2.31	2.31
[cm/s]	Diluate outlet	3.31	3.27	3.22	2.25	2.16	2.11
	Concentrate inlet	0.561	0.561	0.561	0.385	0.385	0.385
	Concentrate outlet	0.617	0.657	0.705	0.441	0.537	0.585