



Residence time distribution of the electro dialyzer under electric field conditions



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HIGHLIGHTS

- A method of measuring residence time of working electro dialyzer is proposed.
- Mean residence time and its variance decrease as applied current density increase.
- Hydrodynamics of the electro dialyzer is discussed.

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ABSTRACT

To avoid the membrane scaling during electro dialytic desalination of sparingly soluble salt solutions, the electro dialysis should be performed in a way that the vast majority of growing clusters is washed out from the module before the crystallization occurs (the residence time is lower than nucleation induction time). Such method requires the determination of residence time distribution (RTD) of the electro dialyzer. While available literature presents only RTD measured at no current conditions, with only water passing through the module, this study presents a method of measuring the RTD on the working electro dialyzer, when the applied current causes ion migration and electroosmotic water flux. The change in concentrate compartment RTD was confirmed for the linear flow velocity range of 0.38–0.84 cm/s and current density range of 0–673 A/m². The hydrodynamic conditions inside the module were described using an open–open vessel dispersion model and it was shown that significant longitudinal dispersion is observed (on average $D/uL = 0.08$). The current density distribution along the electro dialyzer was observed and quantified and the question of velocity distribution along the electro dialyzer was tackled.

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1. Introduction

Brackish water desalination can be achieved with the electro dialysis (ED) or electro dialysis reversal (EDR)—an ED performed with periodic reversal of electrodes' polarity. To increase the efficiency and decrease the environmental impact of desalination, the concentrate produced during the desalination should have as small volume as possible. Simultaneously, to allow the further reuse of ED concentrate for the production of evaporated salt or as a sodium chloride source for membrane electrolysis [1], the brine concentration should be as high as possible. Because of these two reasons, high water recovery is desired in the electro dialytic desalination. However, high salinity of the concentrate may increase the risk of sparingly soluble salt crystallization on the membrane surface (scaling). Several methods of reduction of scaling risk were proposed. Korngold et al. [2,3] presented the idea of reducing EDR scaling probability by controlled precipitation of recirculated (to achieve high recovery ratio) concentrate, oversaturated with calcium sulfate. The relative supersaturation in recirculated brine after the

precipitator was less than 10% and no gypsum crystallization inside the ED stack was observed. Higher concentration of brine stream probably would not be possible, because of the excess turbidity of precipitator effluent. Korngold et al. pointed that this indicates the presence of small, difficult to remove crystals, which accelerate the gypsum precipitation. The idea was applied in a pilot-scale desalination plant [4], which showed the possibility of stable work with brine gypsum oversaturation at EDR stack exit reaching 35%. Korngold et al. and Oren et al. [2–4] fed antiscalants to a BWRO node and used the RO retentate as the feed for the diluate compartment of the ED node. In their case, antiscalants would not be transported into the concentrate stream and would not be problematic if the concentrate was to be used in the controlled crystallization step. If, however, the BWRO retentate stream was to be used as a concentrate in the EDR unit to the crystallizer [5], there should be no antiscalants in the system. Authors' earlier research [5–9] showed that the high recovery ratio may be achieved not by concentrate recycle, but by the application of thin spacer (intermembrane distance 0.16–0.25 mm) having densely distributed membrane abutments. Such spacers allow different linear velocities of diluate and concentrate streams without membrane bulging. A single-pass EDR can be performed with relative CaSO₄ saturation of factor 5.2 and LSI

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of +2.3 [9]. To determine the maximal saturation conditions in the ED process, the appearance of self-growing crystal nuclei was assumed to be a limiting point of the process. The ED should be performed in a manner prohibiting the creation of such crystal nuclei inside the ED module, meaning that the residence time of majority of the particles should be smaller than the nucleation induction time. In order to calculate how long exactly the particles spent inside the electro dialyzer, the residence time distribution (RTD) [10] has to be determined.

The experimentally measured tracer concentration is not a residence time of particles leaving sole reactor, but a RTD of the whole detection system, including tracer injector, reactor and tracer detector. Usually, if the detector and injector residence times are very short compared to reactor residence time, the influence of detector can be neglected. This however is not the case in some of the experimental set-ups with relatively small mean residence time of the membrane modules. From the mathematical point of view, a measured RTD signal is a convolution of a reactor RTD and RTD of all other parts of the system, so the measured signals should be deconvoluted first. For instance, Miskiewicz et al. [11] have used radioactive tracers and fluorescein to investigate hydrodynamic conditions inside ultrafiltration modules, but scintillation probes placed along the membrane were used as the detector, and the measured RTD could be assumed to be identical with RTD of the membrane module. This was not the case for Dydo et al. [12], who used ion-selective electrode immersed in the outlet stream, so the module RTD had to be recalculated with a Kalman filter algorithm. Roth et al. [13–15] have investigated the RTD of reverse osmosis (RO) module. They have used the RTD experiments to determine which tracer was inert to the membrane surface and used the Kalman filter method for the deconvolution of RTD signals. Later they investigated the influence of membrane fouling on RTD. Yang et al. [16] and Hasson et al. [17] have used the RTD experiments for fouling detection in reverse osmosis and showed that new dead zones may be created by wearing out of the membrane, a phenomenon which was also observed in electrodialysis [18].

The problem with determination of RTD of membrane module is the change of linear flow velocity along the membrane caused by the water transport across membranes. In case of pressure-driven membrane processes, the collection of permeate causes the retentate solution to slow down. In case of electrodialysis, the main reason for the water transport is the electroosmotic flow—ions are transported with their solvation water. Osmosis and hydraulic pumping can also influence the linear flow velocity. As the current density increases, the electroosmotic transport also increases, causing the increase in linear flow velocity in the concentrate and decrease in the diluate. In many cases the flow changes can be, and are, neglected. If the linear flow velocity changes are negligible, then RTD experiments can be performed in a non-working condition, when only water is flowing through the electro dialyzer and no current is applied. However, if a high water recovery is to be achieved, it is necessary to apply thin intermembrane

spacers and low concentrate velocity. In such conditions, the concentrate linear flow velocity at the end of the concentrate compartment (later called “the terminal velocity”) can be up to 50% higher than the concentrate linear flow velocity at the beginning of the concentrate compartment (“initial velocity”) [9], making RTD experiments performed in a non-working condition unreliable. In this paper the RTD of the electro dialyzer was investigated in working conditions.

2. Experimental

The measurement setup consisted of feed tank, pumps, injector – a six-way valve with 12 cm sample loop of 1 mL volume, electro dialyzer, reactor and detector – see Fig. 1.

The electro dialyzer consisted of four pairs of alternately placed Neosepta ACS and CMS ion-exchange membranes (see Fig. 2). Concentrate and diluate compartment spacers were made of 0.26 mm thick net sealed with silicone caulk. The effective membrane length was 42 cm, channel width was 2 cm. Diluate and concentrate entrances were 2.5 cm long and 5 mm wide. Electrolytic compartment spacer was 0.5 cm thick cored Plexiglas, perforated in order to both allow electric current flow, and to support the membrane. The segmented electrodes were made of platinum-coated titanium and the applied current was measured on each of the five electrode’s segments, allowing the observation of a current density distribution. Each of the electrode’s segments was 8 cm long, with 0.5 cm non-conducting space between them. The central points of the electrodes, used for current distribution calculations in Section 3.2, were located 4, 12.5, 21, 29.5 and 38 cm from the beginning of effective membrane length. Linear flow velocities in the concentrate compartment varied from 0.38 to 0.84 cm/s (see Appendix B) and were relatively low, but probably similar changes in residence time could be observed with higher velocities on longer, industrial-scale electro dialyzers. Diluate initial velocity (that is the linear flow velocity and the beginning of the compartment) was 6 times higher than concentrate initial velocity to ensure the conditions allowing high supersaturation of the concentrate. The electro dialyzer was operated in a single pass, counter-current mode with respect to diluate and concentrate, while the electrode rinsing solution was circulated. Anolyte and catholyte were allowed to mix in an open tank.

The experimentally determined residence time distribution (RTD) of the whole system, E_{EXP} , is a convolution of the electro dialyzer RTD, E_{ED} , and the RTD of every other part of the system, E_{DET} [13,14,19] or in other words, the RTD of the system in which the electro dialyzer has been bypassed:

$$E_{EXP}(t) = (E_{ED} * E_{DET})(t). \quad (1)$$

Both the RTD of the whole system and the RTD of the system with bypassed electro dialyzer were determined experimentally. The functions describing the behavior of E_{DET} at varying outlet flow rates

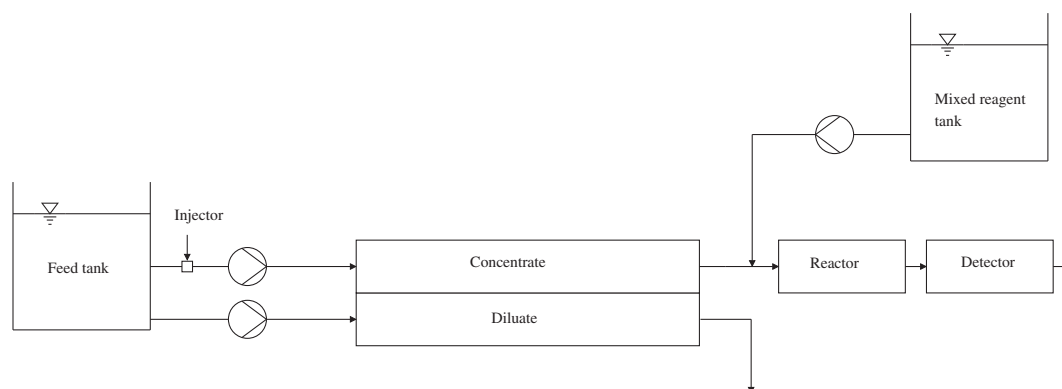


Fig. 1. Experimental set-up with the working electro dialyzer.

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