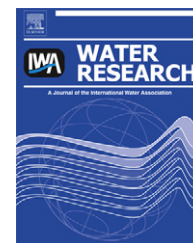


Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Competitive separation of di- vs. mono-valent cations in electro dialysis: Effects of the boundary layer properties

Younggy Kim¹, W. Shane Walker², Desmond F. Lawler*

Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX 78712, USA

ARTICLE INFO

Article history:

Received 24 September 2011

Received in revised form

6 December 2011

Accepted 7 January 2012

Available online 20 January 2012

Keywords:

Concentration polarization

Ion-exchange membranes

Limiting current density

Spacers

Hydrodynamics

Ternary electrolyte system

ABSTRACT

In electro dialysis desalination, the boundary layer near ion-exchange membranes is the limiting region for the overall rate of ionic separation due to concentration polarization over tens of micrometers in that layer. Under high current conditions, this sharp concentration gradient, creating substantial ionic diffusion, can drive a preferential separation for certain ions depending on their concentration and diffusivity in the solution. Thus, this study tested a hypothesis that the boundary layer affects the competitive transport between di- and mono-valent cations, which is known to be governed primarily by the partitioning with cation-exchange membranes. A laboratory-scale electro dialyzer was operated at steady state with a mixture of 10 mM KCl and 10 mM CaCl₂ at various flow rates. Increased flows increased the relative calcium transport. A two-dimensional model was built with analytical solutions of the Nernst–Planck equation. In the model, the boundary layer thickness was considered as a random variable defined with three statistical parameters: mean, standard deviation, and correlation coefficient between the thicknesses of the two boundary layers facing across a spacer. Model simulations with the Monte Carlo method found that a greater calcium separation was achieved with a smaller mean, greater standard deviation, or more negative correlation coefficient. The model and experimental results were compared for the cationic transport number as well as the current and potential relationship. The mean boundary layer thickness was found to decrease from 40 to less than 10 μm as the superficial water velocity increased from 1.06 to 4.24 cm/s. The standard deviation was greater than the mean thickness at slower water velocities and smaller at faster water velocities.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

For the treatment of brackish groundwater, electro dialysis or electro dialysis reversal is robust against scaling problems (Murray, 1995; Strathmann, 2004, 2010). In addition to its desalination capability, electro dialysis was proven to effectively remove disinfection byproduct precursors, such as bromide and organic matter (Valero and Arbós, 2010). These

characteristics make the technology an attractive complement of reverse osmosis to reduce the concentrate waste from an inland brackish groundwater desalination plant (Badruzzaman et al., 2009; Lawler et al., 2011). Unlike seawater desalination, brackish groundwater desalination often involves substantial hardness removal, especially for its concentrate treatment. Thus, the competitive transport between di- and mono-valent cations affects the treatment

* Corresponding author. Tel.: +1 512 471 4595; fax: +1 512 471 0592.

E-mail addresses: kimygy@gmail.com (Y. Kim), wswalker2@utep.edu (W.S. Walker), dlawler@mail.utexas.edu (D.F. Lawler).

¹ Present address: Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, PA 16802, USA.

² Present address: Department of Civil Engineering, University of Texas at El Paso, El Paso, TX 79968, USA.

Nomenclature	
<i>Abbreviations</i>	
AEM	anion-exchange membrane
CEM	cation-exchange membrane
IEM	ion-exchange membrane
<i>Symbols</i>	
$A(j)$	cross-sectional area for current in the j -th control volume (m^2)
c_i	aqueous-phase molar concentration of ionic species i (mol/L)
\bar{c}_i	membrane-phase molar concentration of ionic species i (mol/L)
D_i	aqueous-phase diffusivity of ionic species i (m^2/s)
\bar{D}_i	membrane-phase diffusivity of ionic species i (m^2/s)
F	Faraday constant (96,485 C/mol)
I	current density (A/m^2)
J_i	molar flux of ionic species i (mol/ m^2/s)
$K_{1/2}$	selectivity coefficient of species 1 to species 2 (–)
N_{CP}	number of cell pairs in electro dialyzer
Q	ion-exchange capacity of ion-exchange membrane (eq/L)
Q_{ED}	water flow rate in electro dialyzer (L/min)
R	gas constant (8.314 J/mol/K)
T	absolute temperature (K)
t_i	transport number of ionic species i (–)
\bar{t}_i	transference number of ionic species i (–)
w_{CEM}	width of cation-exchange membrane (μm)
z_i	ionic charge of ionic species i (–)
Δ	random variable for the thickness of the boundary layer
δ	boundary layer thickness (μm)
ϕ	potential (V)
Λ	ionic conductivity (S/m)
λ_i	ionic individual conductivity (S/m)
μ	mean boundary layer thickness (μm)
ρ	correlation coefficient between facing boundary layers (–)
σ	standard deviation of the boundary layer thickness (μm)
<i>Superscript</i>	
B	bulk interface or bulk solution
<i>Subscripts</i>	
1	mono-valent cation (potassium)
2	di-valent cation (calcium)
3	anion (chloride)

efficiency. The competitive transport is known to be governed primarily by the ionic partitioning with the ion-exchange membrane (IEM). In this study, however, we examined the idea that the competitive transport can also be influenced by the boundary layer near the IEM, because the individual ionic diffusivity of different ions influences the relative rate of ionic transport, and this influence is magnified with a sharp change in concentration over a few tens of micrometers. In this research, the boundary layer thickness was defined with three statistical parameters: mean, standard deviation, and correlation coefficient between two boundary layers facing across a spacer. Previously, these statistical parameters were investigated for their effects on the rate of desalination, and the magnitude of the standard deviation was found to be similar to the mean boundary layer thickness with plastic mesh spacers in a lab-scale electro dialyzer (Kim et al., 2011). However, the discussion was limited to the ionic transport in a binary system (Na^+ and Cl^-), and the parameters could only be approximated based on the current and potential relationship. Thus, the objectives of this study were (1) to explain the effects of the boundary layer thickness on the competitive separation between di- and mono-valent cations in electro dialysis desalination, (2) to refine the estimation of the statistical parameters of the boundary layer thickness in a laboratory-scale electro dialyzer based on the competitive transport and current density, and (3) to suggest design and operational guidelines for efficient electro dialysis desalination regarding both the competitive transport and current density.

An electro dialyzer consists of two electrodes (anode and cathode), anion-exchange membranes (AEMs), cation-exchange membranes (CEMs), and spacers. An AEM contains such a high concentration of cations fixed in its polymeric

textile that only anions can pass through it, and vice versa for a CEM. By alternating AEMs and CEMs in series and applying an electric potential through the resulting IEM stack, salty water in one cell (a space between two IEMs) loses ions through the adjacent IEMs while the adjacent cell on the other side of the IEM collects ions. These two cells (one losing ions and the other collecting ions) are called a cell pair of a diluate and concentrate cells, respectively, and an electro dialyzer can be considered to be a repetitive set of cell pairs.

As water flows in a cell, the spacer plays a role in mixing the aqueous solution. Since the mixing is not complete within tens of micrometers from the IEM surface, one can assume a thin boundary layer where the ionic flux by advection is negligible in the direction normal to the IEM surface. Without advection in the boundary layer, a concentration gradient develops so that the diffusion flux of rejected co-ions by the adjacent IEM cancels the migration (or electro-migration) flux caused by the applied potential. In this phenomenon called concentration polarization (Spiegler, 1971; Strathmann, 2004), the ionic concentration in the direction from the bulk solution in the cell toward the IEM increases in the concentrate cell and reduces in the diluate cell. This reduced ionic concentration in the diluate boundary layer increases the electric resistance and consumes substantial electric potential to drive the ionic transport. With increasing ionic flux, the concentration gradient in the diluate boundary layer becomes steeper until the concentration at the IEM surface approaches zero, where the rate of ionic transport is defined as the limiting current density. The limiting current density represents the maximum possible rate of ionic transport under the electro-neutral condition.

Di-valent cations usually have a higher affinity to the IEM than mono-valent cations due to valence effect (Helfferich,

Download English Version:

<https://daneshyari.com/en/article/4482908>

Download Persian Version:

<https://daneshyari.com/article/4482908>

[Daneshyari.com](https://daneshyari.com)