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Treatment of model inland brackish groundwater reverse osmosis concentrate with electrodialysis—Part I: sensitivity to superficial velocity



DESALINATION

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- A synthetic BWRO concentrate of 7890 mg/L was successfully desalinated by electrodialysis to increase system recovery.
- At greater velocities, sulfate was separated more slowly than chloride.
- The polarization parameter was shown as a function of removal ratio, ranging from 2.0 to 3.6 A $m^{-2}\,meq^{-1}\,L.$
- At 1 V/cell-pair, the polarization parameter was slightly sensitive to Reynolds number.



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ABSTRACT

The objective of this research was to investigate the sensitivity of electrodialysis performance to variations in hydraulic flow when treating brackish water reverse osmosis (BWRO) concentrate waste. A synthetic BWRO concentrate from Arizona of 7890 mg/L total dissolved solids was prepared with poly-phosphonate antiscalants, and desalinated with a laboratory-scale electrodialyzer with 10 cell-pairs and a transfer area of 64 cm² per membrane. Flow, pressure, conductivity, temperature, and pH were measured continuously, and periodic process samples were analyzed by ion chromatography and inductively coupled plasma-optical emission spectrometry for anion and cation concentrations, respectively. The BWRO concentrate was successfully treated with a stack voltage application of 1.0 V/cell-pair and current densities less than 280 A/m² for salinity removal ratios up to 99% (without precipitation). The superficial velocities were controlled in a range of 1.2 to 4.8 cm/s, which corresponded to Reynolds numbers of 10 to 40. This paper shows the polarization parameter (ranging from 2.0 to 3.6 A/m² per meq/L) as a function of Reynolds number and removal ratio, and, at maximum sensitivity, the polarization parameter was proportional to Reynolds number raised to the 0.132 power.

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Abbreviations: AEM, anion exchange membrane; BWRO, brackish-water reverse osmosis; CEM, cation exchange membrane; ED, electrodialysis; IEM, ion exchange membrane; RO, reverse osmosis; SCADA, supervisory control and data acquisition; TDS, total dissolved solids concentration.

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1. Introduction

1.1. Goals and objectives

One of the most common membrane desalination methods is reverse osmosis (RO), but a major drawback of RO systems for inland desalination applications is limited recovery because of the scaling potential of sparingly soluble salts in the concentrate waste [1]. Typically, management of this waste in inland desalination systems is economically and environmentally expensive. The goal of this research was to improve the understanding and feasibility of high-recovery brackish water desalination. Electrodialysis (ED) is a desalination process that is robust with respect to fouling and mineral scaling; ED generally requires minimal pretreatment (e.g., 10 µm cartridge filtration) and can tolerate a feed turbidity up to 2 NTU [2]. This robustness is due to (a) the passive flow of water through the ED stack (i.e., water is not filtered through the membranes); (b) electrical polarity reversal (which alternates concentrate and diluate cells); (c) periodical clean-in-place (CIP) removal of fouling and scaling materials; and (d) the ability to disassemble the ED stack and physically scrub or rinse deposited materials from the membranes and spacers [2]. For brackish and mildly saline waters, ED can operate with a lower specific energy consumption than thermal processes such as membrane distillation, multi-effect distillation, and multi-stage flash.

This research was designed to evaluate the performance of ED treatment of brackish water reverse osmosis (BWRO) waste to increase overall system water recovery, as illustrated in Fig. 1. More specifically, the objectives of this research were to (1) experimentally quantify the efficacy and efficiency of electrodialysis separation of supersaturated synthetic BWRO concentrates, and (2) evaluate the performance sensitivities to hydraulic, electrical, and chemical variables. The purpose of these papers is to communicate a thorough evaluation of electrodialysis treatment of RO concentrate, and the first of these papers is focused on quantifying the effects of solution velocity on treatment efficacy and efficiency. (The second [3] and third [4] papers focus on electrical and chemical effects, respectively.)

1.2. Theoretical background

Consider a single concentrate and diluate cell-pair, from one cation exchange membrane (CEM) to the next CEM in an ED stack, as illustrated in Fig. 2 (inter-membrane spacers not shown). The hydraulic behavior is often approximated as one-dimensional, with velocity variations along the *x*-dimension. The hydraulic effect of the spacer may be approximated as a well-mixed bulk flow with a no-slip boundary condition at the membrane surfaces, which causes diffusion boundary layers, of thickness δ , with negligible mixing.

Application of an electric field $(E = -\frac{d\phi}{dx})$ creates a gradient in electrochemical potential, which drives ion flux (*J*), approximated by the Nernst–Planck equation [5]:

$$J_i = J_{i,D} + J_{i,\psi} = -D_i \frac{dc_i}{dx} - \frac{F}{R_g T} D_i z_i c_i \frac{d\phi}{dx}$$
(1)

lons are driven by electromigration (anions toward the anode on the left and cations toward the cathode on the right). Anion exchange



Fig. 1. Process schematic for recovery of RO concentrate by ED.

membranes (AEMs) selectively allow the passage of anions, and CEMs selectively allow the passage of cations. Under steady-state operation, electroneutrality establishes a concentration gradient (and consequential diffusive flux) in the diffusion boundary layer (illustrated in Fig. 2), which supplements the electromigration of selected ions toward the membranes and counteracts the electromigration of rejected ions away from the membrane. Thus, in the diluate cells, the salt concentration decreases from the diluate bulk to the membrane surfaces, and conversely, in the concentrate cells, the salt concentration increases from the bulk to the membrane surfaces. The concentration profile in the x-dimension is often idealized (approximated) as a constant concentration within the (well-mixed) bulk regions, and linear concentration gradients in the (stagnant) diffusion boundary layers [6, §4.2]. This gradient in concentration near the membrane surface (dc/dx) is known as concentration polarization [6-8], and the resulting difference in concentration across the boundary layer (Δc_{dbl}) is approximately proportional to the current density [9]:

$$\frac{\Delta c_{dbl}}{\delta} \propto i$$
 (2)

As illustrated in Fig. 2, in the diluate cell, the concentration of ions at the membrane surface is lower than the bulk concentration, whereas in the concentrate cell, the concentration of ions at the membrane surface is higher than the bulk concentration. Both cases are problematic. First, low ion concentrations at the diluate membrane surfaces can limit the current density and the rate of desalination within the electrodialyzer. If the applied voltage (per cell-pair) is sufficiently high, then the concentration of ions at the diluate membrane surfaces may become too low, and the splitting of water into hydrogen and hydroxide ions may be induced at diluate membrane surfaces. Second, high ion concentrations at the concentrate membrane surfaces may exceed the solubility limits of sparingly soluble salts (such as salts of divalent cations and divalent anions). Precipitation of salts may scale the membrane surface and limit ionic transport or may accumulate in the spacer and block flow through the electrodialyzer.

The rate of separation through the boundary layers is the net flux of electrical charge through each boundary layer, which is equal to the current density, and at steady state, the current density through each boundary layer is equal. Thus, the overall mass transfer coefficient (K) is correlated with the electrical current density [9] (assuming a stable Coulombic efficiency):

$$K \propto i$$
 (3)

A dimensionless mass-transfer coefficient (*i.e.*, the Sherwood number, *Sh*) can be defined as [10,11]:

$$Sh = \frac{K \ L_{char}}{D} \tag{4}$$

where L_{char} is a characteristic length scale, and D is the diffusivity. Thus, the Sherwood number is a dimensionless representation of the concentration gradient at the membrane surface [11], which is proportional to the current density:

$$Sh \propto i$$
 (5)

The Sherwood number has been shown to be related to hydraulic and chemical conditions, characterized by the Reynolds (Re) and Schmidt (Sc) numbers in the form:

$$Sh = \alpha_0 R e^{\alpha_1} S c^{\alpha_2} \propto v^{\alpha_1} \tag{6}$$

where α_0 , α_1 , and α_2 are fitting parameters that may be theoretically approximated and empirically validated; α_0 is typically in the range of 0.6–1.2, and α_1 and α_2 are approximately 0.3–0.5, depending on

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