



# Study of polyethyleneimine coating on membrane permselectivity and desalination performance during pilot-scale electro dialysis of reverse osmosis concentrate

Xuesong Xu<sup>a</sup>, Lu Lin<sup>a</sup>, Guanyu Ma<sup>a</sup>, Huiyao Wang<sup>b</sup>, Wenbin Jiang<sup>a</sup>, Qun He<sup>c</sup>, Nagamany Nirmalakhandan<sup>a</sup>, Pei Xu<sup>a,\*</sup>

<sup>a</sup> Department of Civil Engineering, New Mexico State University, Las Cruces, NM 88003, United States

<sup>b</sup> Core University Research Resources Laboratory, New Mexico State University, Las Cruces, NM 88003, United States

<sup>c</sup> Carollo Engineers, City of Phoenix, AZ 85034, United States

## ARTICLE INFO

### Keywords:

Electrodialysis  
Membrane modification  
Ion permselectivity  
Concentrate treatment  
Ion-exchange membranes  
Desalination

## ABSTRACT

A two-electrical stage and four-hydraulic stage pilot-scale electro dialysis system was used to investigate desalination performance and ion permselectivity of Ionics monovalent permselective membranes (CR671/AR112B) and normal grade membranes (CR67/AR204) (Suez Water Technologies & Solutions) to treat reverse osmosis (RO) concentrate in a brackish groundwater desalination plant. Monovalent permselective cation-exchange membrane CR671 was manufactured by surface modification of standard normal grade membrane CR67 with highly-branched polyethyleneimine coating. The covalently bonded polyethyleneimine layer on membrane surface was characterized by methylene blue dye test, Fourier transform infrared spectroscopy with attenuated total reflection (ATR-FTIR), and electrochemical impedance spectroscopy (EIS). The pilot-scale testing demonstrated the monovalent permselective membranes achieved the same desalting efficiency as the normal grade membranes under the same current density. The energy efficiency in terms of normalized salt removal decreased with the increasing current density (i.e., desalination level) but increased with feed water salt concentration. Polyethyleneimine coating on the CR671 membrane enhanced the selective transport of monovalent cations over divalent cations while having negligible impact on the membrane electrical resistance. The total stack resistance of electro dialysis was insensitive to concentration changes in the diluate and concentrate chambers during desalination of RO concentrate. The electro dialysis system achieved additional 55% of water recovery by treating RO concentrate, enhancing the overall water recovery from 82.5% of the primary RO to 92.1%. Scaling on the ion-exchange membranes and electrodes was effectively mitigated by addition of antiscalant and pH adjustment in concentrate and electrode rinsing streams. Electro dialysis was demonstrated a viable technology to modify product water quality and improve water recovery for desalination concentrate treatment.

## 1. Introduction

Use of unconventional water sources such as brackish water, seawater, municipal and industrial wastewater is an attractive solution to augmenting limited fresh water resources and improving food and water security [1]. Although desalination technologies have been increasingly utilized for treating alternative waters, desalination processes are often costly and energy intensive [2,3]. Concentrate management remains a major challenge and has hindered the broad implementation of desalination technologies, particularly for inland facilities where concentrate disposal options are limited [4–7]. Depending on the volume of concentrate and disposal method,

concentrate management may account for a significant portion of the total project costs [8].

Disposal of large volumes of desalination concentrate, typically 10–50% of the feed flow, is a loss of water resource and energy [7]. Treatment of desalination concentrate can reduce concentrate volume for disposal, increase water recovery, minimize environmental impact, and convert concentrate from a waste to a resource. Substantial research has been conducted to investigate a variety of technologies for concentrate management, such as enhanced evaporation [9,10], adsorption [11–13], membrane distillation [14–18], forward osmosis [14,19–22], electro dialysis [23,24], and various intermediate precipitation followed by secondary reverse osmosis (RO) processes

\* Corresponding author at: Department of Civil Engineering, New Mexico State University 3035 S Espina Street, NM 88003, United States.  
E-mail address: [pxu@nmsu.edu](mailto:pxu@nmsu.edu) (P. Xu).

[25–28].

Electrodialysis is a membrane-based electrochemical process for separation of salts from aqueous solutions. Electrodialysis is a mature technology, primarily used in brackish water desalination [29,30], NaCl production from seawater [31], and demineralization of food products [32,33]. Compared to RO membranes, ion-exchange membranes (IEMs) installed in electrodialysis require less pretreatment and are more robust when it comes to treating waters with higher concentrations of particulate matter, silica, hardness, and organic substances [34,35]. Fouling and scaling in electrodialysis can be mitigated more easily than RO, because the IEM fouling layers are not compacted by high hydraulic pressure and the IEMs are more chemically resistant than RO membranes [36].

In addition, electrodialysis with selective IEMs provides a cost-effective process to treat desalination concentrate by partially reducing salinity and selectively removing specific contaminants to meet water quality requirements of target applications. Monovalent permselective IEMs are unique membranes for electrodialysis that preferentially separate monovalent ions (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ ) over multivalent ions (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ ) [37–39]. This makes it possible to modify ion composition in product water for different applications, such as sodium reduction to suitable level for irrigation, and removal of chloride and nitrate for in-stream flow augmentation. In monovalent anion-permselective membranes (e.g., Neosepta ACS, ASTOM Corp., Japan), the permselective layer is made of a highly cross-linked resin, whereas in monovalent cation-permselective membranes (e.g., Neosepta CMX-S) the permselective thin layer on membrane surface is positively charged. These IEMs selectively separate monovalent ions from multivalent ions via either steric exclusion (e.g., ACS membranes) or electric repulsion (e.g., CMX-S membranes) between the membranes and the ionic species [40]. Xu et al. used NEOSEPTA ACS and CMX-S to treat brackish groundwater RO concentrate [7]. The ACS exhibited high permselectivity of removing monovalent anions over di- and multi-valent anions. The transport of sulfate and phosphate through the ACS was negligible over a broad range of imposed electrical current density, while the transport of divalent cations through the CMX-S increased with increasing current density. However, these permselective membranes are challenged and susceptible to deterioration during treatment of desalination concentrate with high fouling and scaling potential in pilot- and full-scale applications. There is a need to develop robust monovalent permselective IEMs for desalination and concentrate treatment.

Membrane surface modification has been proven to be one of the most effective methods to tune the permselectivity among different cations [41]. In this study, polyethyleneimine was coated on the Ionics standard normal grade membrane CR67 to produce the monovalent permselective membrane CR671. The CR67 contains sulfonic functional groups, which allows the cations to pass through [42]. A thin layer of conductive cationic polymer, polyethyleneimine, induces stronger electric repulsion at the membrane surface to multivalent cations (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) than to the monovalent cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ), resulting

in relatively higher permselectivity of monovalent cations in the CR671. Meanwhile, the structure of polyethyleneimine is highly branched with most of its amino groups remain on the CR671 membrane surface [43], thereby minimizing the decrease of ion-exchange capacity (IEC) caused by inactivation of sulfonic functional groups with the amino groups inside the membrane matrix. To increase the stability of the polyethyleneimine coating on the CR671 surface during long-term operation, the reactive epoxy groups were doped on the membrane surface to react with the amino groups of polyethyleneimine, forming a relatively stable acid-amide chemical bond.

The objectives of this study are to (1) manufacture and characterize the selective cation-exchange membranes, and (2) evaluate the impact of polyethyleneimine coating on desalination performance and permselectivity of the CR67 and CR671 during treatment of brackish groundwater RO concentrate. The effectiveness of polyethyleneimine membrane coating was characterized by dye test, hydrophobicity measurement, electrochemical impedance spectroscopy (EIS), and Fourier transform infrared spectroscopy with attenuated total reflection (ATR-FTIR). A pilot-scale electrodialysis system with 2-electrical stage and 4-hydraulic stage was used to compare the overall desalination efficiency, energy demand, and ion transport of the selective membrane CR671 and the normal grade membrane CR67.

## 2. Materials and methods

### 2.1. Pilot-scale electrodialysis system

In this study the electrodialysis performance of the monovalent permselective membranes (CR671 and AR112B) was compared with the standard normal grade membranes (CR67 and AR204) during the pilot-scale testing. The pilot-scale electrodialysis system AQ3-1-4 manufactured by General Electric Water & Process Technologies (now Suez Water Technologies & Solutions), was configured having 2-electrical stage (//) and 4-hydraulic stage (/) with 186 cell pairs of cation-exchange membranes (CEMs, CR67 or CR671) and anion-exchange membranes (AEMs, AR204 or AR112B). The membrane pairs were arranged in //53/53//40/40// for four hydraulic stages, i.e., 106 pairs of membranes for the 1<sup>st</sup>-electrical stage (53 and 53 pairs for the 1<sup>st</sup>- and 2<sup>nd</sup>-hydraulic stage, respectively) and 80 pairs of membranes for the 2<sup>nd</sup>-electrical stage (40 and 40 pairs for the 3<sup>rd</sup>- and 4<sup>th</sup>-hydraulic stage, respectively). The effective surface area of each membrane was 3200 cm<sup>2</sup> (3.44 ft<sup>2</sup>). Each electrical stage allowed the use of an independently controlled current to the cell pairs within that electrical stage. Before electrodialysis experiments, new membranes were equilibrated with feed water for at least 24 h by recirculating the RO concentrate in the system without applying electrical voltage. All the experiments were conducted under the mode of constant current condition, and 30 ~ 60 min flushing with power off was of necessity to eliminate the visible air bubbles trapped in the electrodialysis system (in both pipelines and electrodialysis stack), to avoid the negative impact on increased total stack resistance and induced membrane damage

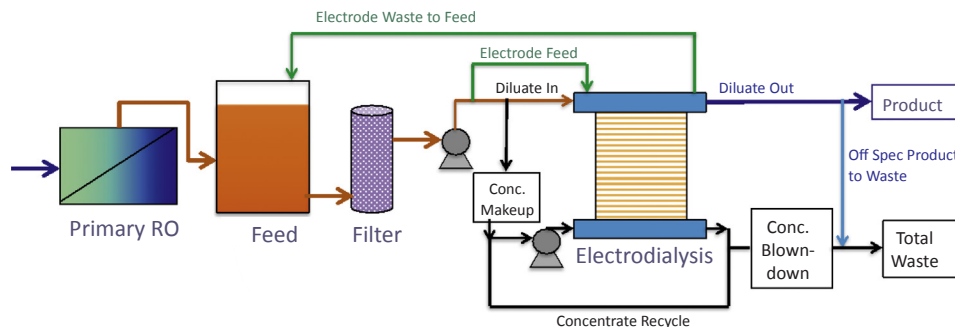


Fig. 1. Schematic diagram of the pilot-scale electrodialysis system.

Download English Version:

<https://daneshyari.com/en/article/7043552>

Download Persian Version:

<https://daneshyari.com/article/7043552>

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