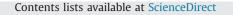
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Membrane Distillation and Reverse Electrodialysis for Near-Zero Liquid Discharge and low energy seawater desalination



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ABSTRACT

With a total capacity of 70 million cubic meters per day, seawater desalination industry represents the most affordable source of drinking water for many people living in arid areas of the world. Seawater Reverse Osmosis (SWRO) technology, driven by the impressive development in membrane materials, modules and process design, currently shows an overall energy consumption of 3-4 kW h per m³ of desalted water, substantially lower than thermal systems; however, the theoretical energy demand to produce 1 m³ of potable water from 2 m³ of seawater (50% recovery factor) is 1.1 kW h. In order to move towards this goal, the possibility to recover the energy content of discharged concentrates assumes a strategic relevance. In this work, an innovative approach combining Direct Contact Membrane Distillation (DCMD) and Reverse Electrodialysis (RE) is tested for simultaneous water and energy production from SWRO brine, thus implementing the concept of low energy and Near-Zero Liquid Discharge in seawater desalination. DCMD operated on 1 M NaCl RO retentate fed at 40-50 °C resulted in a Volume Reduction Factor (VRF) up to 83.6% with transmembrane flux in the range of 1.2–2.4 kg/m² h. The performance of RE stack fed with DCMD brine (4-5.4 M) and seawater (0.5 M) was investigated at different temperatures (10-45 °C) and flow velocities (0.7-1.1 cm/s). Experimental data show the possibility to obtain an Open Circuit Voltage (OCV) in the range of 1.5-2.3 V and a gross power density of 0.9- 2.4 W/m_{MP} (membrane pair). In general, optimization is required to find best operating conditions for the proposed system.

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1. Introduction

The huge growth in demand for water and energy is a global challenge for a sustainable industrial development. At present, about 33% of the world's population lives in water-stressed countries, and this value is expected to double by 2025 [1]. With a total capacity of 70 million cubic meters per day, desalination is the most affordable source of drinking water. Seawater Reverse Osmosis (SWRO) technology, driven by the impressive development in membrane materials, modules and process design, shows a overall energy consumption of 3–4 kW h per m³ of desalted water, substantially lower than competitor thermal systems [2]. From a thermodynamic point of view, the theoretical energy demand to produce 1 m³ of potable water from 2 m³ of seawater

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http://dx.doi.org/10.1016/j.memsci.2015.09.008 0376-7388/© 2015 Elsevier B.V. All rights reserved. (50% water recovery factor) is 1.1 kW h; in order to move towards this goal, the possibility of recovering the energy content of discharged concentrates assumes a strategic relevance. Moreover, discharged brine is one of the major environmental problems associated with the extensive practice of desalination technologies, considering that water recovery in SWRO operations generally ranges within 30–50%. Literature studies demonstrate adverse ecological and toxicological impacts of hypersaline brines on soil and groundwater [3], echinoids and ascidians [4], sediment infauna [5,6], seagrass and epifauna [7–9], planktons [10,11], fish and clam [12] etc. In addition, the net CO_2 emission associated with the generation of thermoelectric energy necessary to drive SWRO plants is about 1.4–1.8 kg/m³ [2,13,14] with the perspective of doubling it in two decades.

In this work, an innovative approach combining Membrane Distillation and Reverse Electrodialysis technologies is tested for simultaneous production of water and energy from SWRO brines, thus implementing the concept of low energy and Near-Zero Liquid Discharge in seawater desalination. In Salinity Gradient

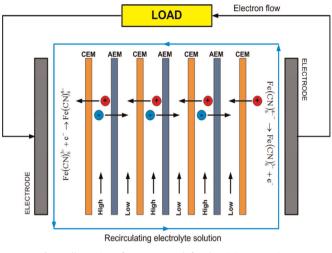


Fig. 1. Illustration of a SGP-RE stack for electricity generation.

Power-Reverse Electrodialysis (SGP-RE), anion (AEM) and cation (CEM) exchange membranes are alternatively stacked in order to build a series of adjacent compartments fed with high and low concentration solutions (High Concentration Compartment: HCC, Low Concentration Compartment: LCC) as illustrated in Fig. 1. The electrochemical potential, resulting in a voltage drop across the electrodes, is generated from the salinity gradient that drives the selective migration of cations and anions across the ion exchange membranes [15,16]. Operational principles, potentialities and current challenges of SGP-RE are discussed elsewhere [17–23].

The large part of literature studies deals with RE power generation from NaCl solutions mimicking river water (0.015 M) and seawater (0.5 M) fed to LCC and HCC, respectively. In general, results converge towards a power density of about 4 W/ m_{MP}^2 [24–28] and energy efficiency of 33–50% [29,30]. Further optimization of inter-membrane distance led to a maximum net power density of 4.4 W/ m_{MP}^2 using a spacer thickness of 60 µm [28].

When feeding LCC with NaCl solutions at salinity higher than river water, the consequential depletion in power density can be partially mitigated by using high-concentrated brine in HCC, thus reducing the extent of Ohmic resistances. Theoretical and experimental investigations of Tedesco et al. showed the possibility to obtain a maximum power density of 2.4 W/m²_{MP} when feeding LCC and HCC with seawater and 5.4 M NaCl brine from solar pond, respectively [31]. Tufa et al. achieved a power density up to 3 W/m²_{MP} using a cross flow RE stack fed with 0.1 M/5 M NaCl solutions [17]. The technical and economical feasibility of SGP-RE operated with brine was assessed in [32–34].

In the present work, with the aim to obtain highly concentrated NaCl brines (from 4 to 5.4 M) as inlet stream to HCC of a SGP-RE unit, Direct Contact Membrane Distillation (DCMD) was operated on the retentate stream of a typical SWRO desalination unit (1 M NaCl) working at 50% recovery factor. In DCMD, a microporous hydrophobic membrane is in contact with a heated solution on the feed side and with pure cold water on the opposite side ("distillate"). The hydro-repellent nature of the membrane avoids the permeation of the liquid phase while sustaining a vapor-liquid interface at the entrance of each pore. Driven by a partial pressure gradient, water evaporates from the warm side, diffuses across the membrane, and condenses into the distillate stream. In Membrane Distillation, a modest temperature difference (30–50 °C) is generally sufficient to establish a quite satisfactory transmembrane flux $(1-10 \text{ kg/m}^2 \text{ h})$, permitting an efficient recycling of low-grade or waste heat streams or the use of alternative renewable sources [35,36]. The most interesting advantage of Membrane Distillation is its small sensitivity to concentration polarization; therefore, integrated RO–DCMD systems have the potential to reduce the volume of disposed brine (by about 90%), thereby increasing significantly the overall water recovery factor. Permeate fluxes in the range of 2.5–12.5 L m⁻² h⁻¹ were obtained when feeding Accurel PP S6/2 capillary membranes with a 35 g/L NaCl solution in a temperature range of 40–70 °C and keeping the distillate at 15 °C [37]. Godino et al. showed a 100% increase in transmembrane flux when shifting feed temperature from 30 to 50 °C, while a 20% flux reduction was observed when feed concentration increased from 0.5 to 2.0 M NaCl [38]. A flux of about 30 L m⁻² h⁻¹ was achieved when operating with 0.5 M NaCl solution at 85 °C, distillate at 20 °C and feed flow rate of 0.7 m/s [39].

Combination of SGP technologies with solar-driven desalination for effective conversion of osmotic energy into electrical power with simultaneous production of pure water was envisaged by Brauns [40,41]. An integrated RO–RE system was proposed by Li et al. in order to reduce the high-pressure pump energy at RO stage [42]. Use of RO brine in Pressure Retarded Osmosis (PRO) was found to reduce by 40% the net specific energy consumption of a seawater RO system with respect to state-of-art values [43]. Feinberg et al. showed that the integration of osmotic energy recovery systems (including RE and PRO) in conventional SWRO plant could offset the total capital cost by 42% [44].

The present work experimentally proves the feasibility of simultaneous production of energy and desalted water by exploiting the synergistic combination of DCMD and RE units operated on the retentate stream of a SWRO desalination plant. Starting from separate lab-scale experiments for DCMD and RE, Fig. 2 conceptually translates the proposed strategy to a continuous process: the brine rejected from the RO stage is further concentrated by DCMD and used to feed the HCC of the SGP-RE stack for electrochemical energy generation, while seawater is fed to LCC of the SGP-RE stack. Reverse Electrodialysis allows to recover the Gibbs free energy of mixing from low and high concentration solutions: therefore, the composition of the outlet stream leaving the SGP-RE unit (having sufficient membrane area to fully accomplish the operation) is theoretically given by the average of LCC and HCC compositions weighted by the respective volumetric flowrates. On this basis, the outlet stream can be partially recycled back to DCMD unit.

The performance of the integrated system is investigated in terms of DCMD flux and RE power density as a function of the most significant operational parameters.

2. Theoretical background

2.1. Direct Contact Membrane Distillation

According to the Dusty Gas Model theory, the flux of *i*-th volatile component (J_i) through a porous medium driven by a partial

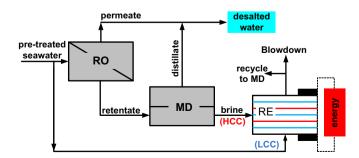


Fig. 2. Integrated membrane system for simultaneous production of water and renewable energy (RO: Reverse Osmosis; MD: Membrane Distillation; RE: Reverse Electrodialysis; HCC: High Concentration Compartment; LCC: Low Concentration Compartment).

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