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Separation of divalent ions from seawater concentrate to enhance the purity of coarse salt by electrodialysis with monovalent-selective membranes

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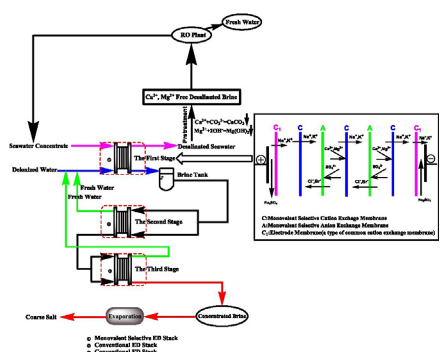
HIGHLIGHTS

- A designed electrodialysis system was used to treat seawater concentrate.
- Divalent ions removal was significantly achieved by using CIMS/ACS membranes stack as the first stage of system.
- The repeated experiments confirmed the system feasibility to enhance the purity of coarse salt.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, an electrodialysis (ED) system which was divided into three-stage operation was designed to treat seawater concentrate. The experiment was carried using a laboratory ED-cell with an effective area of 189 cm^2. Two types of monovalent selective ion-exchange membranes were investigated: CIMS/ACS and CSO/ASV. The effect of applied current density during ED process was also studied. The experimental results indicate that the separation performance for divalent ions (i.e., Ca^{2+}, Mg^{2+}) with CIMS/ACS membranes stack was superior to CSO/ASV membranes stack; furthermore, a lower current density can increase the selectivity in monovalent ions to divalent ions with either the CIMS membrane or the CSO membrane. The current efficiency and energy consumption were optimal at a current density of 4 mA/cm^2 by using CIMS/ACS membranes stack as the first stage of system in this experiment. Furthermore, the desalination rate (70%) was chosen as the experimental operation endpoint of the first-stage ED operation based on the experimental results. Moreover, the latter two-stage operation was used to concentrate brine to produce coarse salt after evaporation process. Finally, the repeated batch experiments confirmed the system feasibility for treating seawater concentrate to produce coarse salt with the purity of ~85% under continuous operation.

1. Introduction

The problem of water resources shortage becomes increasingly prominent with the rapid development of worldwide population.

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Table 1
Types of membrane and their properties[a].

Membrane type	Thickness (μm)	Burst strength (MPa)	Area resistance (Ω cm^2)	Transport number (%)	Temperature (°C)	pH
NEOSEPTA® CIMS	150	≥0.10	1.8[b]	–	≤40	0–10
NEOSEPTA® ACS	130	≥0.15	3.8[b]	–	≤40	0–8
Selemion® CSO	100	0.15	2.3[b]	>97	–	–
Selemion® ASV	120	0.2	3.7[b]	>97	–	–
NEOSEPTA® CMX	170	≥0.40	3.0[b]	>96	≤40	0–10
NEOSEPTA® AMX	140	≥0.25	2.4[b]	>96	≤40	0–8
Selemion® CMTE	220	0.9	5[b]	>94	–	–

[a] The data were collected from the product brochure provided by manufacturers.
[b] The ion-exchange membranes area resistance were measured with a 0.5 N-NaCl solution, at 25 °C.

Seawater desalination, an effective method to produce fresh water, mitigates the crisis about the water resource scarcity [1–4]. At present, for the application of seawater desalination technology, reverse osmosis (RO) as the most optimized membrane technology has been getting very popular worldwide [5]. However, the progress is still constrained by some factors, one of them is that the treatment of the RO concentrate which contains high concentration of total dissolved salt (TDS). Traditionally, the RO concentrate is discharged directly into seawater [6] or treated by evaporation. The former method is potentially harmful to marine ecosystems, and the latter is costly since the evaporation process consumes lots of conventional energy. Gonzalez et al. [7] reviewed the treatment technologies of RO concentrate in order to overcome the environmental problems associated with the direct discharge of RO concentrate. The traditional technology (solar evaporation) and emerging technologies such as electrodialysis, forward osmosis and membrane distillation all exhibit an effective processing capacity to RO concentrate. However, solar evaporation has a large requirement for land area and it is easily affected by the weather; forward osmosis and membrane distillation have some technical obstacles and they are only tested at laboratory or pilot plant scale [8,9].

Electrodialysis as a mature technology has been widely used in water treatment due to some significant advantages [10–12], such as cost-effective, convenient operation, environment-friendly, etc. Therefore, ED has been considered as a good option to treat RO brines. Yang et al. [13] have given an innovative view to treat seawater concentrate for producing mixed acid and sodium hydroxide by electrodialysis with bipolar membranes. Tanaka et al. [14] have made a careful research toward current density and energy consumption for treating RO brines to produce salt by electrodialysis, and Reig et al. [15] have achieved higher concentration of NaCl from RO brines which can be used for raw materials for chlor-alkali industry by electrodialysis. Furthermore, Reig et al. [16] have valorized the seawater desalination reverse osmosis (SWD-RO) brine to obtain strong acid and base (up to 2 M) by integration of monopolar and bipolar membrane electrodialysis in 2016. Jiang et al. [17] have also investigated the usability of ED process to produce coarse salt and freshwater from RO effluent simultaneously. Zhang et al. [18,19] have taken the techno-economic analysis into consideration for reducing operational cost and have investigated the feasibility to improve the water recovery with the treatment of RO concentrate through ED process. Although these studies demonstrate the feasibility of ED technology effectively to treat RO concentrate, further investigation on the separation of monovalent/multivalent ions from RO concentrate should be taken into account since membrane fouling and scaling processes can be unavoidable. On the other hand, the coarse salt extracted from RO concentrate is difficult to be used broadly due to the high content of multivalent ions.

Korngold et al. [20,21] investigated the treatment of brine solutions from an RO plant through a separate $CaSO_4$ precipitator containing gypsum seeds to remove divalent ions (i.e. Ca^{2+}, Mg^{2+}) for reducing the scaling problem in ED. Moreover, Tran et al. [22] investigated the feasibility of a hybrid system consisting of a pellet reactor and electro- dialysis (ED) to treat RO concentrate in which the pellet reactor was used to remove the scaling potential before ED treatment. The results indicated that 80% calcium in RO concentrate in the pellet reactor can be removed and the ED system can be operated in a stable way without scaling. Furthermore, Zhang et al. [23] investigated the separation efficiency of monovalent/multivalent anions from RO concentrate by using standard membrane (a nonselective membrane) and monovalent selective anion membrane in ED. In addition, many other researchers have made efforts to investigate the possibilities of separating monovalent and divalent ions from simulated brines during ED process [24,25].

Although ED that shows remarkable advantages technically and economically on the separation of divalent ions from RO concentrate has been done, further study about how to separate divalent ions from RO concentrate efficiently by using monovalent selective cation-exchange membranes and monovalent selective anion-exchange membranes in ED was needed. In this work, the application of ED stack equipped with monovalent selective ion-exchange membranes with three separated compartments (i.e., electrode compartment, concentrate compartment, diluate compartment) was studied. In particular, each compartment has been continued an internal circulation in the ED stack by adopting batch mode. The feasibility of treating seawater concentrate to enhance the purity of coarse salt in ED process has been investigated in this study. The operational parameters such as current density, type of membranes were also investigated. Furthermore, this study provides a good reference for producing table salt on a large scale in the future by treating RO concentrate used in ED.

Table 2
Properties of seawater concentrate supplied by Zhejiang Liuheng Seawater Desalination Plant, Zhoushan City, Zhejiang Province, China in this study.

Item	Characteristics
Conductivity (ms/cm)	60
pH	7.53
Sodium (mg/L)	15,117
Potassium (mg/L)	392
Bromide (mg/L)	89
Calcium (mg/L)	665
Magnesium (mg/L)	1546
Chloride (mg/L)	23,525
Sulfate (mg/L)	3041
TOC (mg/L)	142

2. Materials and methods

2.1. Materials

The reagents were of analytical grade, and deionized water was used throughout. The different types of monovalent selective ion-exchange membranes were used: NEOSEPTA® CIMS (monovalent selective cation-exchange membranes, from ASTOM Co., Japan), NEOSEPTA® ACS (monovalent selective anion-exchange membranes, from ASTOM Co., Japan), Selemion® CSO (monovalent selective cation-exchange membranes, from ASAHI GLASS CO., LTD., Japan), and Selemion® ASV (monovalent selective anion-exchange membranes, from ASAHI GLASS CO., LTD., Japan). The ordinary ion-exchange membranes