

Gypsum scaling of anion exchange membranes in electro dialysis



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ABSTRACT

Scaling of homogeneous AMV and heterogeneous MA-40 anion exchange membranes (AEM) by gypsum (CaSO₄ · 2H₂O) was investigated during electro dialysis (ED) at constant current conditions. The effects of scale development on counter-ion flux, electrical potential difference across the scaled-membrane, the overall electrical stack resistance and the extent of water splitting, were studied as a function of the current density and flow velocity of the solution in the relevant compartments.

It was found that scale grows mainly in the interior of MA-40 while for the homogeneous AMV membrane scale grows mainly on the membrane surface facing the concentrate compartment. This implies that the homogeneous membrane could be more easily cleaned and its properties almost fully retained, compared with the case of the heterogeneous membrane where the internal scale was strongly attached to the internal matrix domains. These findings have important implications for the use of ED in the treatment of highly concentrated solutions and as part of a chain of treatment towards zero liquid discharge (ZLD).

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1. Introduction

Water scarcity is becoming an increasingly serious problem due to the rapid population growth and the scarcity of fresh water supply. Reverse osmosis (RO) is steadily becoming the leading technology for sea and brackish water desalination and wastewater treatment for water reuse. However, 5–25% of the influent flow of RO treatments is in the form of concentrated brines [1], rendering concentrate disposal management a limiting factor. Traditionally, in the cases of seawater reverse osmosis (SWRO), concentrates are directly discharged into the sea, or treated by evaporation in inland facilities [2]. However, those methods fail to eliminate salts and contaminants from the water cycle, thus do not comply with the strict environmental protection regulations in developed countries and are considered unsustainable. Furthermore, in inland brackish water desalination plants, where brine disposal to the sea is not economically feasible [3,4], zero liquid discharge (ZLD) approaches become important. With ZLD, concentrates are further treated towards near or complete dryness

aiming at minimizing waste volume and increasing water recovery. A review by Pérez-González et al. [4] refers to four approaches towards ZLD. The basic scheme is a RO tandem, including primary and secondary RO. However, several studies have shown that there is a strong need for additional intermediate treatment stages to increase the recovery and avoid precipitation of sparingly soluble salts. These intermediate stages include: ion-exchange for the removal of scaling compounds (such as silica) and enhanced precipitation [5–7].

Nonetheless, post-treatment of secondary RO concentrates is required for recovering both salts and water and increasing the recovery ratio. Recently, electro dialysis (ED) was studied as an efficient method for treating RO brines and for improving the overall recovery to above 90% and reaching near ZLD [8–10]. It was demonstrated that ED is more cost-effective than conventional evaporation for minimizing waste volume due to lower energy consumption [11] and to the ability to rather easily concentrate salt from 0.2% to 2% to 12–20% [12,13]. Nevertheless, the high concentrations which develop in the brine compartment of an ED stack along with the concentration polarization at the membrane-solution interface, lead to precipitation of scaling compounds (such as CaSO₄, silica etc.), which is a major drawback in coping with continuous and smooth operation of ED. Mineral precipitation inside the ED unit has a deleterious effect on the ED performance as it causes significant, often irreversible, increase of the stack's electrical and hydraulic resistance, consequently resulting in higher energy consumption. Moreover, in severe cases, scale developed on or inside an ion-exchange membrane may clog the

Abbreviations: AEM, anion exchange membrane; BWRO, brackish water reverse osmosis; CEM, cation exchange membrane; CP, concentration polarization; ED, Electro dialysis; EDR, electro dialysis reversal; IEM, ion exchange membrane; RO, reverse osmosis; SEM, scanning electron microscope; SI, saturation index; SWRO, seawater reverse osmosis; ZLD, zero liquid discharge

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fluid flow pathways, creating stagnant regions, which results in enhanced concentration polarization (CP) that in turn, further enhances scaling.

At high current densities, especially in the over-limiting current region where water splitting occurs, this phenomenon is intensified. Rautenbach et al. [14,15] showed that scaling can be avoided even at high water recovery by using the seeding technique, whereby supersaturation is constantly kept on a low level by gypsum particles acting as nuclei for crystallization. This was done by integration of a crystallizer-clarifier into the concentrate loop of an ED unit. Korngold et al. [12,13] used a combination of ED and a precipitator to treat RO concentrates oversaturated with CaSO_4 . Gypsum seeds were used to enhance precipitation of excess CaSO_4 . In a study by Oren et al. [10], a combination of electro-dialysis reversal (EDR) and a seeding crystallizer was used for further treating of brackish water RO (BWRO) brines. A water recovery level of 97–98% was achieved. Turek et al. also studied the use of EDR for treating concentrated calcium sulfate and calcium carbonate solutions towards ZLD [16,17]. Scaling inside the EDR unit was avoided by reducing the retention time in the ED unit to values lower than the time required for nucleation of CaSO_4 . In their latest study, an algorithm for prediction of scaling during EDR was proposed, based on determining when the sum of mean residence time and square root of its variance exceeded the crystallization induction times [18]. The algorithm was found successful for analyzing the risk of calcium sulfate crystallization, but was less successful in predicting calcium carbonate precipitation. Nevertheless, the effects of factors such as membrane morphology and flow regime on the crystal nucleation and growth rate still need to be thoroughly studied in order to determine the maximum period between polarity reversals to prevent scaling.

Nevertheless, despite the numerous studies in the field, our understanding of the mechanisms involved in scale formation in ED is yet limited. In our previous study [19], gypsum scaling was studied with two types of anion exchange membranes (AEM), applying Donnan exchange. It was clearly shown that the location of precipitation sites depends explicitly on the membrane structure, significantly affecting ion flux and membrane potential difference. Precipitation associated with the homogeneous membrane, AMV was mainly on its surface, while the heterogeneous MA-40 was mainly scaled inside the membrane matrix. We showed that internal scaling, predominantly caused by low permselectivity of the heterogeneous membrane, strongly reduced the counter-ions (sulfate) flux in comparison to surface precipitation. The Donnan exchange studies allowed isolating the effect of membrane type and structure on scaling characteristics and extent. However, at ED operation, interfacial phenomena such as water splitting and local current density distribution [20,21] must be taken into account, as they might affect and be affected by scale precipitation inside the ED unit. Moreover, since under ED conditions the mass transport in the boundary layer is a complex process comprised of diffusion, migration and convection [22], the effect of the flow regime on scaling extent may be more pronounced under ED conditions in comparison to Donnan exchange. Above the limiting current density where water splitting occurs, the issue of co-precipitation in the concentrate compartments must be considered. Fig. 1 illustrates the concentration profiles of a salt in the boundary layer on both sides of an AEM and the fluxes of ions in the boundary layer and in the membrane. The generation of hydroxyl ions (OH^-) and protons (H^+) in the water dissociation layer located between the ion-exchange membrane (IEM) and the boundary layer due to water splitting in the diluate compartment is also indicated. The hydroxyl ions migrate across the anion exchange membrane towards the anode, causing a pH increase next to the membrane on the concentrate side [23]. This may result in precipitation of calcium carbonate and hydroxide salts such as Ca

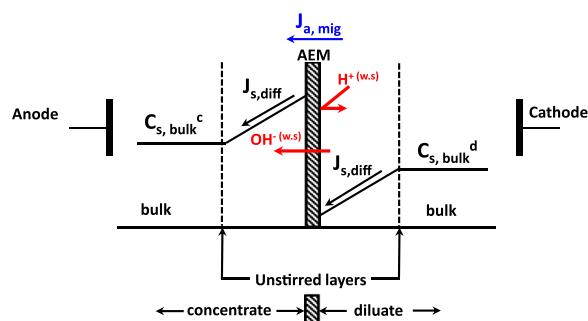


Fig. 1. Schematic illustration of concentration profiles of a salt in the boundary layer on both sides of an anion-exchange membrane and the fluxes of ions in the boundary layer, and in the membrane; AEM – anion-exchange membrane, J – ion fluxes; the subscripts a , s , mig , $diff$ refer to anions, salt, migration and diffusion, respectively; the superscripts c , d , and $w.s.$ refer to concentrate, diluate and water splitting, respectively.

$(\text{OH})_2$ at the concentrate side which must be taken into account while investigating the scaling phenomenon.

The present study focuses on gypsum scaling in a heterogeneous and homogeneous AEM during ED. The impact of current density and linear velocity on the scaling of the ED stack, and the influence of scaling inside the ED unit on its performance were investigated. The effects on performance were expressed in terms of changes to stack electrical resistance and changes to membrane potential difference as well as the extent of water splitting.

2. Experimental

2.1. Experimental setup

A schematic representation of the ED setup is shown in Fig. 2. The Plexiglas ED stack consists of five 175 mm long, 25 mm wide compartments, separated by four ion-selective membranes with an active area of 43.8 cm^2 . All compartments are 4 mm thick, except the anode compartment (compartment 1), which is 3 mm thick. Platinum-coated titanium electrodes $[\text{Ti}(\text{Pt})]$ were used as anode and cathode, and constant current or voltage were applied by a MOTTECH DC power supplier (PPS-1200 series). The arrangement of the ion-exchange membranes (IEM's) inside the ED stack is presented in Fig. 3. The studied AEM was placed between compartments 1 and 2. Two types of AEM's were studied: MA-40, a heterogeneous membrane (Shchekinoazot, Russia), and AMV, a homogeneous membrane (Asahi Glass, Japan). The MK-40 heterogeneous cation exchange membrane (CEM, Shchekinoazot) was also used for separating between the other compartments (3–5) in the stack. Key properties of the above membranes are provided in Table 1. Plastic net spacers were placed in all compartments excluding the studied compartment (1). Feed solutions were circulated through stirred 2 L vessels by five centrifugal pumps (NEMP 20/18 in compartment 1 and NDP 14/2 in compartments 2–5, Totton, ITT Corporation, UK). Flow rates were monitored at the outlet of the stack using variable area flow-meters (DFM 10–100 L/h, Stubbe, Germany). The pH in the electrode compartments (1 and 5) was kept constant at ~ 7 by an on-line dual pH-stat. Solution conductivity (comp. 1) was monitored using an alpha 190 conductivity-meter, by Thermo. All experiments were performed at $22 \pm 1 \text{ }^\circ\text{C}$, controlled by a refrigerating/heating circulator (BL 30, MRC, IL). Data were collected on-line via Advantech ADAMView[®] data software (version 4.25).

2.2. Scaling and non-scaling studies

Scaling and non-scaling studies were carried out with constant current densities; 3, 6 and 12 mA/cm^2 . Prior to each ED run, the

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