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Seawater electrodialysis with preferential removal of divalent ions

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ABSTRACT

In this work desalination of a ternary salt mixture and artificial North Sea water is studied with a lab scale electrodialysis stack, which was used in a recycling batch mode. During desalination samples were taken and the ionic composition of the dilute stream was determined. The effect of applied current density (10–300 A/m²) on this composition was investigated.

A clear effect of applied current density was observed. A lower applied current density leads to a more complete reduction in concentration of divalent ions, in an earlier extent of desalination. This influence of the applied current density could be related to the concentration polarization effects that occur in the diffusional boundary layer and are explained with a model based on the Nernst–Planck flux equation. It was found that the lower initial ion concentration of Ca²⁺, Mg²⁺, but also of K⁺, and SO₄²⁻ compared to respectively Na⁺ and Cl⁻, leads to stronger depletion of these ions in the transport layer adjacent the membrane. These boundary layer effects are more pronounced at higher applied current densities, resulting in reduced transport of ions with a low initial concentration. High monovalent over divalent ion ratios can be found at low applied current.

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1. Introduction

When looking into the ionic composition of seawater one will find that it mainly consists of monovalent sodium and chloride ions, but significant amounts of multivalent ions like calcium, magnesium, and sulphate are present as well. When treating seawater, these ions and other multivalent ions may represent several challenges for several reasons. Firstly, undesired precipitates might be formed by calcium, magnesium and sulphate (e.g. CaSO₄) and these can irreversibly clog parts of seawater desalination modules or any other (supporting) process equipment [1]. Secondly, final drying of seawater originated salt might become more challenging and more expensive (if for instance a drying agent is needed) as these divalent ions form more hygroscopic precipitates. Together with the previous issue, this makes that for edible salt production electrodialysis, with monovalent selective membranes, is used to prevent the concentration of multivalents in the seawater brines [2,3]. Thirdly the presence of these ions, sulphate in particular, represents a challenge for the off-shore oil reservoir desalinated water injection. To increase the oil extraction one can desalinate seawater (on a platform) and inject this to the

reservoir. In order to avoid formation of hydrogen sulphide [4], the requirements for the sulphate concentration in the processed injection water are very strict. Sulphate concentrations must be lowered to levels much smaller than the chlorides. From these examples, it is clear that ions have to be selectively transported, either the monovalent ones (e.g. for desalination, for edible salt production), or the multivalent ions (e.g. for pre-desalination, for production of oil recovery injection water). For the selective transport of monovalent ions from seawater so-called monovalent selective ion exchange membranes can be used. With this type of membranes one can achieve an almost complete separation between monovalent ions and divalent ions [3,5–8]. However, in this study, the focus was not on the removal of monovalent ions but on the preferential removal of the multivalent ions from seawater using membranes that are anion or cation selective. For this process there is no obvious technique available.

There are three widely applied desalination technologies; electrodialysis (ED) [9], reverse osmosis (RO) [10], and distillation [11]. ED and RO are membrane-based processes, whilst distillation deploys heat to vaporize water. In RO, water permeates through the membrane under an applied pressure while salts are retained. In ED, the salts permeate through the membrane under the influence of an applied electrical current. By placing anion exchange membranes (AEM) and cation exchange membranes (CEM) in alternating order between an anode and a cathode an ED stack is formed. When applying a DC current, the cations start

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to migrate towards the cathode and the anions towards the anode. As a result, desalinated streams (dilute) and concentrated streams (concentrate) are created in alternating channels. RO and distillation techniques generally provide a (close to) complete separation of pure water from the concentrated feed solution. With ED, ions and small charged molecules can be removed from a solution to a chosen extent. Therefore, ED is a very suitable pre-desalination technique [12,13].

For desalination with a preferential removal of multivalent ions, distillation and RO techniques are less suitable. Techniques that might provide a selective desalination are nanofiltration (NF) and ED [14–16]. With NF membranes water and a considerable fraction of monovalent ions can permeate through the membrane, while rejection of divalent ions can be close to 100% [14]. NF is a technology that gained interest as a pretreatment technique for seawater desalination or even as seawater desalination technique [17–20]. Being a pressure driven technique, NF is limited in its water recovery by the osmotic pressure [12,17–19]. Therefore, NF is very suitable for water softening of solutions with low salinity and less suitable for pre-desalination of seawater [12] or the production of oil injection water. For ED, it was reported that although small differences in transport rates can be observed for monovalent ions and divalent ions, this does not lead to a selective desalination of practical use [15,16]. However, some operational measures may improve the selectivity of the process. Van der Bruggen et al. [15] proposed that separation efficiency with ED may also be influenced by applied voltage or current.

A selective desalination was found by Kabay et al. at decreased applied voltage [21,22]. Kim et al. investigated the properties of the boundary layers and their effect on the membrane selectivity for monovalent and divalent ions [23,24]. In the second study an indirect effect of applied potential on the membrane selectivity is reported [24]. In these studies, however, the molar concentrations of monovalent and divalent are, unlike seawater, equal [21,22,24] or relative close to each other [22]. Moreover, only the selectivity of the cation exchange membrane (CEM) was investigated. In the studies performed by Kabay et al. [21,22] the investigated applied potential range was small. Kim et al. were performing their study in a much broader current range (0–200 A/m²) but also did not apply a constant current.

In the present study, ED is applied on feed water with seawater ion concentrations and the effect of applied current density on the preferential removal of multivalent ions is investigated over a broad current density range (10–300 A/m²). Furthermore, both the anion and the cation transport are considered.

2. Theory

To describe ion transport in electrochemical systems the Nernst–Planck (NP) flux equation is widely used (e.g. [24–31]). In the present study Eq. (2.1) is used, both in the SDL in front of the membrane, and in the membrane itself. Here, the NP equation contains a diffusion term and a migration term:

$$J_i = -D_i \left[\frac{dc_i(x)}{dx} + c_i(x) z_i \frac{d\varphi}{dx} \right] \quad (2.1)$$

here J is the ion flux (mol/m² s), D is the diffusion coefficient (m²/s), φ is the electrical potential in the SDL or membrane (made dimensionless by scaling the potential to the thermal voltage, $V_T = RT/F$), c_i is the concentration of species i (mol/m³), z is the valence (dimensionless), F is the Faraday constant (C/mol), R is the gas constant (J/mol K), T is the temperature (K) and x is the distance from a reference point (m). The convection term ($+c_i v$) was neglected as the convective transport in the direction perpendicular to the membranes is negligible in comparison with the

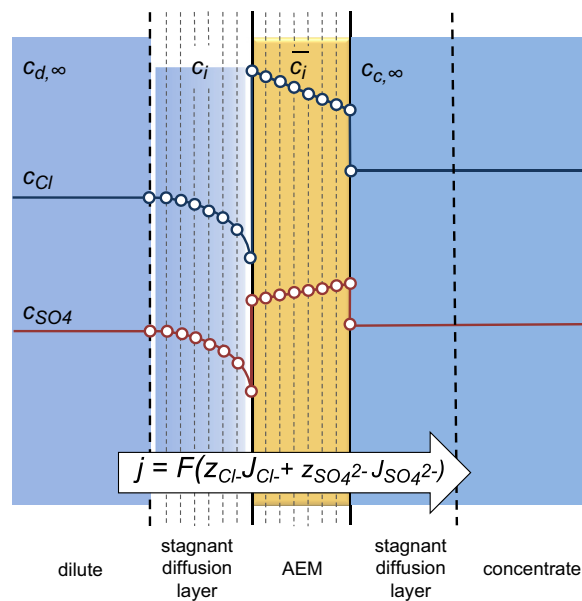


Fig. 1. Schematic representation of the dilute, stagnant diffusion layer (SDL), anion exchange membrane (AEM), concentrate stage and the calculation planes (dotted lines) used by the model.

diffusion and migration term [24–26,31]. Based on this NP flux equation, the transport of e.g. chloride and sulphate through an anion exchange membrane (AEM) can be calculated with a fairly simple model. The CEM can be modelled in the same way.

In the model four phases are distinguished: (i) a dilute bulk solution phase (dilute), (ii) a stagnant diffusion layer (SDL) phase at the dilute side of the membrane, (iii) an AEM and (iv) a concentrate bulk solution phase (concentrate). These four phases are schematically shown in Fig. 1. Dilute and concentrate phases are regarded as completely stirred solutions with a concentration changing in time (transient state) from an initial situation where they have the same composition. In the mathematical model, the SDL and AEM are divided in a number of planes (or nodes) where Eq. (2.1) is discretized and solved. The transport through the SDL and membrane is assumed to be in steady state, and thus for each ion the flux J of Eq. (2.1) is [30,32] unchanging across SDL and membrane.

An AEM has not only a selectivity towards counterions (anions) or co-ions (cations) but it can also be more selective towards a specific counterion when several counterions are present in the solution [3,33]. In this model, the affinity of the membrane towards specific counter-ions is estimated from experimental data by introducing a ratio r_i between the diffusion coefficient of the species in the bulk solution and the SDL (D_i) and the diffusion coefficient in the membrane matrix (\bar{D}_i). \bar{D}_i is taken as a function of the value in the (bulk, external) solution, D_i , as described by

$$\bar{D}_i = \frac{D_i}{r_i} \quad (2.2)$$

where the values of r_i are empirically obtained for each ion separately from fitting model to data (see Table 4). As we will discuss, for divalent anions in an AEM, a current-dependent value of this r_i must be used.

For the sake of simplicity the membrane is considered perfectly selective for counterions, (no co-ions are allowed in or through the membrane) and is assumed that no water transport through the membrane takes place. Everywhere in the system electro-neutrality is assumed and accumulation of ions is absent. Because the co-ion is blocked entry in the membrane, in Eq. (2.1), the co-ion flux J is zero, and Eq. (2.1) simplifies for the co-ions to

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