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Intensification of demineralization process and decrease in scaling by application of pulsed electric field with short pulse/pause conditions

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ABSTRACT

Pulsed electric field (PEF) can affect positively the membrane scaling mitigation and the intensification of electrodialytic (ED) process. Recent studies considered the use of PEF with relatively long pulse/pause conditions (5–40 s). The present work was focused on the application of specific PEF conditions with short pulse/pause duration as a following perspective step in improving demineralization. Therefore, in this study six conditions were tested (1 s/0.33 s, 1 s/1 s, 2 s/0.5 s, 2 s/0.67 s, 3 s/0.33 s, 3 s/1 s) in order to investigate the influence of short PEF lapses and to find the optimum among all PEF conditions. Results indicate that PEF conditions of 2 s/0.5 s and 2 s/0.67 s allowed the highest demineralization rates. A decrease of scaling on the cation-exchange membrane surface in comparison with previous data was observed in all PEF conditions. In addition, absence of scaling on the anion-exchange membrane was observed for the first time in such extreme conditions of demineralization and solution composition. These results highlighted the successful use of short pulse/pause lapses during electrodialysis.

1. Introduction

The main lockers for electrodialysis (ED) development are concentration polarization (CP) phenomena and fouling formation at ion-exchange membrane (IEM) interfaces [1]. CP arises due to the ability of IEM to readily transport ionic species. As a result, the salt concentration decreases at one side of the membrane and increases at the other [2]. If a sufficiently high voltage is applied, the electrolyte concentration near the diluate side of the membrane becomes close to zero: the limiting current density (LCD) is then reached. It means that with increasing the voltage the mass transfer of ionic species is no more improved and water splitting phenomenon occurred. Thus CP is influenced by the state of flow in the desalting cell [3] and provides generation of H^+ and OH^- ions as current carriers [4]. Further voltage increase leads to the development of current-induced convection (electroconvection and gravitational convection) which improves ion transport to the membrane surface and hampers water splitting. Concerning membrane fouling, its formation includes the adsorption of foulants at the interfaces of the membrane (diluate or concentrate sides) or inside the membrane. The main difference between the types of fouling (colloidal fouling, organic fouling, scaling and biofouling) is the nature of the particles that cause the fouling [5]. In addition, fouling can be a physical and/or chemical phenomenon [6].

Among all methods which can help to solve both types of limitations, pulsed electric field (PEF) is considered as one of the most effective [2,7,8]. PEF perturbations may scale down the CP, because during pause lapse ion transport from the bulk of solution to the membrane layer is continued by means of diffusion and convection; thereby the concentration gradient decreases before application of the pulse lapse [2]. Furthermore, inertial properties of liquid movement can exist after pulse lapse, which can intensify ion transfer [7]. Successful uses of PEF for reducing membrane fouling were reported by Ruiz et al. [8] for a protein deposit, Lee at al. [9] and Park et al. [10] for humate deposit, and by Casademont et al. [11] and Cifuentes-Araya et al. [12] for scaling. After the thorough investigations of the mineral deposit structure, the scaling formation mechanism was proposed by Cifuentes-Araya et al. [12]. Two main factors were indicated as the most important for building up the membrane deposit: OH^- generation during the water splitting phenomenon and OH^- leakage. These hydroxyl ions can create the necessary environment for precipitation of two

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Abbreviations: AEM, anion exchange membrane; CEM, cation exchange membrane; CP, concentration polarization; EC, energy consumption; ED, electrodialysis; DBL, diffusion boundary layer; DR, demineralization rate; SC, scaling content; IEM, ion exchange membrane; LCD, limiting current density; PEF, pulsed electric field

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main mineral foulant agents Mg^{2+} and Ca^{2+} ions in the different polymorphic forms of $Mg(OH)_2$ and $CaCO_3$. From the identified mechanisms and polymorphic forms generated during ED in different PEF conditions [12,13], it was proposed to use short pulse/pause lapses (less than 5 s) instead of long pulse/pause lapses (5–40 s) [7,8,12–14]. In addition, the use of pause lapse values less than pulse lapse values may also have a positive effect on scaling prevention [13]. Furthermore, recent investigations by Malek et al. [15] revealed the feasibility of using short PEF regimes for improving the ED performance by suppression of water splitting phenomenon. However, their experiments were performed on an ideal system containing only NaCl and thus provided no information on the possible benefits of this approach to limiting fouling.

Thus, the present work will focus on PEF application combining different short pulse/pause lapses conditions in order to intensify the desalination process and decrease the membrane scaling as well as to find the optimal PEF conditions during ED treatment of more complex solutions containing Mg^{2+} and Ca^{2+} salts.

2. Experimental methods

2.1. Material

$CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, NaCl and KCl (ACS grade) were obtained from Laboratoire MAT (Quebec, QC, Canada). Na_2CO_3 was obtained from EMD (EMD Chemicals, Gibbstown, NJ), NaOH (1 M) and HCl (1 M) from Fisher Scientific (Nepean, ONT, Canada).

2.2. Electrodialysis cell

The electrodialysis cell was a Microflow-type cell (Electro-Cell AB, Täby, Sweden) comprising two Neosepta CMX-SB cation-exchange membranes and two Neosepta AMX-SB anion-exchange membranes (Tokuyama Soda Ltd., Tokyo, Japan). The anode was a dimensionally stable electrode (DSA) and the cathode a 316 stainless-steel electrode. This arrangement defines three closed loops (Fig. 1) containing the diluate model salt solution (330 ml, flow rate of 600 mL/min), a 2 g/L KCl aqueous concentrate solution at constant pH (330 mL, 600 mL/min) and a 20 g/L NaCl electrolyte solution (500 mL, 900 mL/min). The membranes tested, of 10 cm^2 membrane effective surface, were in contact with the model salt solution on one side and the pH-controlled KCl solution on the other side (Fig. 1). Each closed loop was connected to a separated external plastic reservoir, allowing continuous recirculation. The electrodialysis system was not equipped to maintain constant temperature, but this parameter undergoes low variations.

2.3. Protocol

Preliminary tests were performed to determine the limiting current density according to the method described by Cowan and Brown [16]. Limiting current density value was 21 mA/cm^2. ED was carried out in batch process at a constant current density of 40 mA/cm^2 using a Xantrex power supply (Model HPD 60-5SX; Burnaby, BC, Canada). This current density was chosen in order to explore a possible scaling mitigation when water splitting and current-induced convection occurred and to compare our results with those reported by Cifuentes-Araya et al. [12,13]. The model salt solution was composed of Na_2CO_3 (1000 mg/L), KCl (800 mg/L), $CaCl_2$ (800 mg/L) and $MgCl_2$ (452 mg/L) in order to respect a Mg/Ca ratio of 2/5 [14]: this ratio is double as the one contained in milk [17] to ensure membrane scaling formation [12,13]. The model salt solution was prepared just before the beginning of ED process. The initial pH of the model salt solution was fixed at 6.5 by manual addition of HCl (1 M). The pH of concentrate solution was maintained constant (pH=12) during the whole ED process by manual additions of NaOH (1 M) to ensure the continuous precipitation of minerals [12,13]. The ED treatments were stopped after the maximum voltage capacity of the power supply was reached (62.5 V). To find the optimal PEF conditions the following regimes were performed: $T_{on}/T_{off}=3$ s/1 s (PEF ratio 3), $T_{on}/T_{off}=2$ s/0.67 s (PEF ratio 3), $T_{on}/T_{off}=1$ s/0.33 s (PEF ratio 3), $T_{on}/T_{off}=3$ s/0.3 s (PEF ratio 10), $T_{on}/T_{off}=2$ s/0.5 s (PEF ratio 4) and $T_{on}/T_{off}=1$ s/1 s (PEF ratio 1). These PEF modes were selected based on the data obtained by Ruiz et al. [8], and Cifuentes-Araya et al. [13]. Four repetitions were carried out for each PEF condition. ED parameters (current intensity, voltage, solution conductivities) were recorded every five minutes all along the treatments. After

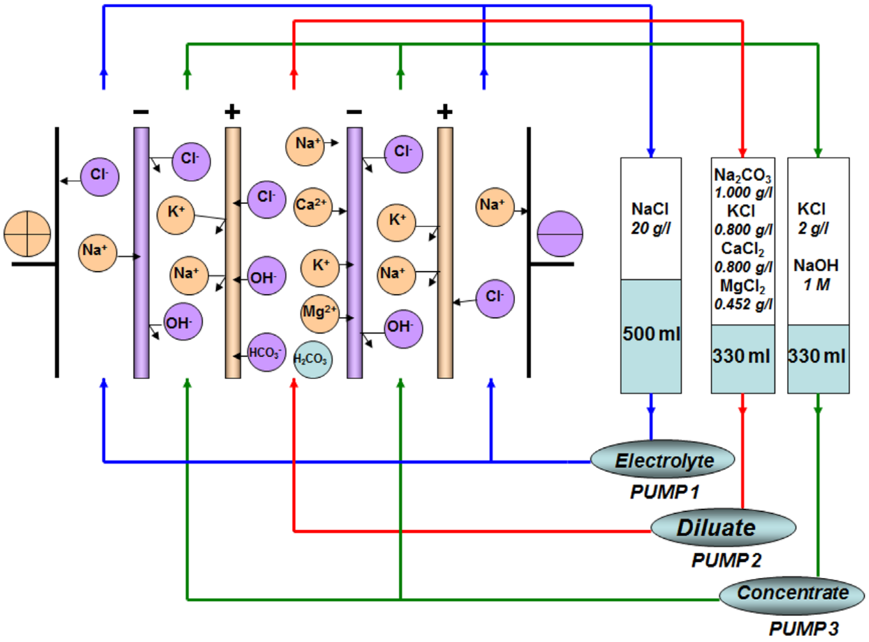

Fig. 1. Electrodialysis cell configuration.