



Mechanisms of mineral membrane fouling growth modulated by pulsed modes of current during electrodialysis: Evidences of water splitting implications in the appearance of the amorphous phases of magnesium hydroxide and calcium carbonate



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ABSTRACT

Experiments revealed the fouling nature evolutions along different electrodialysis (ED) trials, and how it disappears when current pulsation acts repetitively on the interfaces of ion-exchange membranes (IEMs). Fouling was totally controlled on the diluate side of cation-exchange membrane (CEM) by the repetitive pulsation frequency of the higher on-duty ratios applied. They created steady water splitting proton-barriers that neutralized OH⁻ leakage through the membrane, decreasing the interfacial pH, and fouling of the concentrate side. The anion-exchange membrane (AEM) on the diluate side was similarly protected, but it was fouled once water splitting OH⁻ generation became either intense enough or excessively weak. Interestingly, amorphous magnesium hydroxide (AMH) stemmed on the CEM-diluate side from brucite under intense water splitting OH⁻ generation, and/or strong OH⁻ leakage electromigration through the membrane. Water dissociation and overlimiting current regimes triggered drastic water molecule removal from crystal lattices through an accelerated cascade water splitting reaction. Also, amorphous calcium carbonate (ACC) appeared on CEM under intense water splitting reaction, and disappeared once intense OH⁻ leakage was allowed by the water splitting proton-barrier dissipation. Our findings have implications for membrane fouling control, as well as for the understanding of the growth behavior of CaCO₃ and Mg(OH)₂ species on electromembrane interfaces.

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1. Introduction

Recent findings have shown a rich variety of crystalline mineral mixtures growing on CEMs, crystals that are composed of calcium and magnesium hydroxides (Ca(OH)₂ (portlandite) and Mg(OH)₂ (amorphous magnesium hydroxide (AMH) and brucite), respectively), and also calcium carbonates (CaCO₃) (amorphous calcium carbonate (ACC), aragonite, and calcite) [1]. These reports showed the role of Mg²⁺ as an inhibitor factor of CaCO₃ growth and

important modifier of the evolution of its crystalline polymorphism [2–4]. In ED, minerals precipitate on IEMs due to concentration–polarization conditions that impart alkalinity at membrane boundaries through water splitting reaction [5–7]. The generation of OH⁻ current carriers is enhanced by high current densities, and especially in the case of OH⁻ leakage occurring through CEM when alkaline concentrate streams are used for demineralization [1,8].

Nowadays, one of the main problems of ED is fouling of membranes by minerals present in complex physiological solutions such as seawater, milk, and whey solutions. Moreover, there is currently a great need for reducing the energy requirements during electromembrane processing [1,9]. In consequence, the recent practice of ED evidences the interest in applying alternative current modes such as non-constant asymmetrical ones under high current densities [9]. Pulsed electric fields (PEFs) have been applied regarding the control of mineral fouling since they enhance the electrophoretic mobility of foulants at the membrane interfaces

Abbreviations: ED, electrodialysis; IEM, ion-exchange membrane; CEM, cation-exchange membrane; AEM, anion-exchange membrane; AMH, amorphous magnesium hydroxide; ACC, amorphous calcium carbonate; PEF, pulsed electric field; Ton, pulse time; Toff, pause time; HF, high frequency; LF, low frequency; SEM, scanning electron microscopy; XRD, X-ray diffraction; DR, demineralization rate.

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[10], interrupt the membrane CP phenomenon, and essentially intensify the process performance [11,12]. Indeed, the application of PEFs creates optimized underlimiting current regimes when the current density is high [12,13].

Further research steps discovered the way PEFs modulate the precipitation kinetics of a characteristic fouling growth occurring on CEM [1], and the way they handle water splitting proton-barriers against interfacial membrane alkalization [8,12]. A characteristic fouling growth composed by a complex mixture of crystalline phases of CaCO_3 and $\text{Mg}(\text{OH})_2$ was described, and its evolution kinetics were decelerated as long as the demineralization trials were driven under lower PEF on-duty ratios [1]. It was seen that for the classical ED configuration, AEM accumulates mineral scaling on the concentrate side when water splitting is steady enough and OH^- generation exalts divalent cations intending to cross the membrane from recirculated concentrate streams [8]. On the other hand, a steady H^+ generation by water splitting on the AEM-diluate side acted as a pH neutralization barrier protecting the membrane integrity. Nonetheless, this barrier vanished during excessively long pause lapses, and AEM was scaled [8]. The observations made in those investigations suggested that an accurate PEF on-duty ratio would control mineral fouling totally for the given ED system [12]. However, there is yet need to study the impact those PEFs frequencies might have on the electrochemical phenomena occurring on electromembrane interfaces, the behavior of the whole system along the demineralization trials, OH^- leakage behavior through CEM, and the nature and evolution of mineral fouling growth. The impact of Mg^{2+} on the character of the crystallization reactions and CaCO_3 structures [14] must also be further clarified. The recently reported appearance of an amorphous phase stemming from the partial dehydration of brucite under strong water splitting reaction [1,8] is not completely understood, and its elucidation calls for further investigation. The origin of the amorphous phase of CaCO_3 , and its linking to water splitting reaction and/or another parameter of the process remains an unexplored phenomenon.

In this respect, this study investigated the way six different PEF on-duty ratios of moderately low and also highly repetitive frequencies modulate the system behavior during demineralization, the crystallization kinetics of mineral fouling, and the evolution of its polymorphism while growing on IEMs.

2. Experimental section

2.1. Material

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl and KCl (ACS grade) were purchased at Laboratoire MAT (Quebec, QC, Canada). Na_2CO_3 was obtained from EMD (EMD Chemicals, Gibbstown, NJ) and NaOH (1 M) and HCl (1 M) from Fisher Scientific (Nepean, ONT, Canada).

2.2. Electrodialysis cell

The electrodialysis cell consisted in 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. A (supporting information)) containing the diluate model salt solution (370 mL, flow rate of 600 mL/min), a 2 g/L KCl aqueous concentrate solution at constant pH (370 mL, 600 mL/min), and a 20 g/L NaCl electrolyte solution (500 mL, 900 mL/min). The membranes tested, of 10 cm^2 effective surface were both in contact with the model salt solution on one side, and the pH-controlled KCl solution on the other side (Fig. A (supporting information)). Each

closed loop was connected to a particular external plastic reservoir allowing for continuous recirculation. The electrodialysis system was not equipped to maintain constant temperature since this parameter underwent low variations.

2.3. Protocol

ED was carried-out in batch process using a constant current density of 40 mA/cm^2 generated by a Xantrex power supply (Model HPD 60-5SX; Burnaby, BC, Canada) with a maximum voltage capacity of 62.5 V. The high current density value was chosen in order to ensure membrane fouling formation [8], and to study the impact of PEF regimes of repetitive pulsation frequency on a possible fouling mitigation effect and the crystal precipitation mechanisms. Six different PEF on-duty ratios were evaluated (Ton/Toff = 5 s/10 s (PEF ratio 0.5HF), Ton/Toff = 10 s/20 s (PEF ratio 0.5LF), Ton/Toff = 5 s/5 s (PEF ratio 1HF), Ton/Toff = 10 s/10 s (PEF ratio 1LF), Ton/Toff = 10 s/5 s (PEF ratio 2HF), Ton/Toff = 20 s/10 s (PEF ratio 2LF)) (abbreviations HF and LF denote the high and low frequencies for equal on-duty ratios). The PEF ratios were selected to further optimize the process in terms of performance and fouling mitigation according to previous studies [1,8,12], and to impart different process variables for the investigation of mineral crystallization phenomena. 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) to respect a Mg/Ca ratio of 2/5, this one inducing a significant fouling formation [1,8]. The model salt solution was prepared immediately before the beginning of each ED process, and its initial pH value was adjusted to 6.5 by manual addition of HCl (1 M). All the ED treatments were stopped immediately after the maximum voltage capacity of the power supplier was reached (62.5 V). The value of limiting current density was previously determined as 21 mA/cm^2 . The amount of charge transported was calculated as the product of the time elapsed (s) and the current intensity (A) indicated in the power supply [15]. The concentrate pH was kept alkaline (pH = 12) during the demineralization trials by manual addition of NaOH (1 M). On 4-cm² dried membrane samples, electron microscopy images, X-ray elemental analysis and X-ray diffraction were performed. CEM and AEM surfaces in contact with the concentrate and diluate solutions were examined to identify the nature and to characterize the precipitation mechanisms ruling membrane fouling growth.

2.4. Analysis methods

2.4.1. Scanning electron microscopy (SEM) and X-ray elemental analysis

Images were taken with a scanning electron microscope (JEOL (Japan Electro Optic Laboratory), model JSM840A, Peabody, Massachusetts, USA) equipped with an energy dispersive spectrometer (EDS) (PGT (Princeton Gamma Tech.), Princeton, New Jersey, USA). The EDS conditions were 15 kV accelerating voltage with a 13 mm working distance. The samples were coated with a thin layer of gold/palladium in order to render them electrically conductive, and thus increase the quality of the photographs.

2.4.2. X-ray diffraction (XRD)

X-ray powder diffraction analyses were performed using a D5000 Siemens diffractometer (Montreal, QC, Canada) equipped with a curved graphite crystal monochromator and a goniometer theta–theta (in reflection) with a rotating sample holder. The radiation source (Cu K α) was a copper lamp with a wavelength of $\lambda = 1.5406 \text{ \AA}$, and the copper K α radiation was generated at 30 mA and 40 kV. The scan rate of $0.02^\circ (2\theta)$ was applied to record patterns for 2θ ranging between 20° and 70° , with a counting time of 1.2 s per step.

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