1 Fouling and *in-situ* cleaning of ion-exchange membranes during the
2 electrodialysis of fresh acid and sweet whey
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Abstract

This work investigated the fouling of ion-exchange membranes during the electrodialysis of sweet and acid dairy whey. Fresh whey was used, rather than solutions made up in the laboratory, giving a unique perspective. While membrane fouling occurred in all experiments, the effects on system performance were limited. Reductions in the current during pure NaCl circulation fell to a minimum of 80% of the original value after 5 hours of whey processing. The use of an alkaline concentrate resulted in the strongest increase in system resistance, but the mineral deposits formed appeared to detach readily, thereby reducing these effects. The use of an acidic concentrate gave significantly greater rates of lactic acid removal, which is important in industrial applications. A solution of HCl with a pH of 1.0 ± 0.15 was effective for *in-situ* cleaning of the mineral deposits. However, protein deposits were not readily removed using the recommended base cleaning formula of 3% NaCl at a pH of 9.2 ± 0.2 .

Keywords: Ion-exchange membranes; Electrodialysis; Whey; Protein fouling; Mineral scaling; lactic acid

1.0 Introduction

Sweet whey (SW) is readily processed within dairy operations through membrane concentration, evaporation and spray drying. However, the processing of acid whey (AW) is much more difficult due to the high mineral content and the presence of lactic acid (LA) (Chandrapala et al., 2016; Wijayasinghe et al., 2016). Acid whey is lower in pH than sweet whey, and it contains greater amounts of calcium phosphate due to its greater solubility at low pH conditions (Williams and Kline, 1980). Furthermore, the low pH promotes protein precipitation (Jelen, 2011), which reduces the protein content to almost half of the amount found in sweet whey. In our recent publication (Chen et al., 2016), we proposed that acid whey processing could be enhanced by partial removal of minerals and lactic acid using electrodialysis (ED) equipped with ion-exchange membranes (IEMs).

Dairy products such as acid whey contain colloidal matter and inorganic compounds, including calcium, carbonate, phosphate, and protein (Kumar et al., 2013), which can deposit either on the surface or inside a membrane, resulting in membrane fouling (Lin et al., 2008). In ED, fouling can compromise the membrane integrity, cause a reduction in ion migration and result in an increase in energy consumption (Bazinet and Araya-Farias, 2005a; Wang et al., 2011). Several factors affect or promote membrane fouling in an ED unit including the mineral content of the feed solution (Ayala-Bribiesca et al., 2007; Bazinet and Araya-Farias, 2005a; Casademont et al., 2007), the mode of operation (batch or continuous) (Ayala-Bribiesca et al., 2007; Casademont et al., 2008; Lin et al., 2008), and the concentrate pH (Ayala-Bribiesca et al., 2006a, 2006b, 2007; Casademont et al., 2007).

Protein fouling is expected to dominate on the diluate side of anion exchange membranes (AEMs) in dairy applications (Ayala-Bribiesca et al., 2007). The main whey proteins, β -lactoglobulin and α -lactalbumin, are negatively charged above their isoelectric points (pH 5.2 and 4.8, respectively) and so deposit on the positively charged surface of the AEM membrane. Mineral fouling is also possible on the side of the AEM facing the concentrate compartment as phosphates migrate into this channel (Ayala-Bribiesca et al., 2007; Casademont et al., 2008).

For similar reasons, mineral scales, consisting mainly of calcium salts, have been observed on cation exchange membranes (CEMs) facing the concentrate compartment, particularly under

alkaline concentrate pH (Bazinet et al., 2001; Bazinet and Araya-Farias, 2005a). However, the presence of proteins in the feed stream can also result in CEM fouling facing the diluate compartment, when the concentrate is maintained at acidic pH (Ayala-Bribiesca et al., 2006a). Leakage of H^+ ions from the concentrate compartment through the CEM reduces the pH on the diluate side of the CEM membrane surface, thus decreasing protein solubility and promoting its precipitation (Ayala-Bribiesca et al., 2006b; Bazinet et al., 2003; Diblíková et al., 2013).

The literature lacks consensus on the type and sequence of acid and base agents used for cleaning these IEMs after fouling (Bdiri et al., 2018, 2018; Bylund, 2003; Garcia-Vasquez et al., 2016; Guo et al., 2015; Lujan-Facundo et al., 2016; Wang et al., 2011). However, the American Water Works Association (AWWA) claims that a 2-5% HCl solution for acid cleaning, a 3-5% NaCl solution adjusted to a pH of 8-10 using NaOH for alkali cleaning, and a 10-50 mg/L chlorine solution are the only chemicals that should be used (American Water Work Associations, 1995).

In this work, the extent of membrane fouling is studied during the electrodialysis of fresh acid and sweet whey obtained from a dairy plant in Victoria, Australia. We have shown in comparable work with nanofiltration that this approach gives significantly different results than the use of re-solubilised powders as commonly used in the scientific literature (Rice et al., 2009). Furthermore, the effectiveness of the cleaning agents suggested by AWWA during *in-situ* cleaning of the fouled membranes is examined. Finally, since the ED unit is not disassembled after each cleaning step, a new method is proposed to monitor membrane performance. In this method, the current in a pure NaCl solution is recorded after each step. This is similar to the approach used to assess the performance of pressure-driven membranes using a clean water flux.

2.0 Methods and Materials

2.1 Materials

Raw acid whey and skimmed sweet whey samples were obtained from Bega Cheese Pty. Ltd. (Victoria, Australia). The acid whey samples were skimmed in the laboratory using a centrifuge separator (Milky cream separator; Model FJ 130 ERR; MilkyDay, Czech Republic) to remove fat and whey cream. All the whey samples were refrigerated at 4 ± 1 °C and used within two weeks. The sample compositions (Table 1) were consistent with the values reported by Chen *et al.* (Chen *et al.*, 2016).

Table 1. The composition of skimmed sweet and acid whey used in this work.

Component	Unit	Sweet whey	Acid whey
pH	-	6.1 ± 0.2	4.4 ± 0.3
Conductivity	mS/cm	6.1 ± 0.3	7.8 ± 0.3
Total protein *	% (m/v)	0.85 ± 0.05	0.36 ± 0.01
K	mg/100mL	114 ± 7	125 ± 8
Na	mg/100mL	38 ± 4	47 ± 4
Ca	mg/100 mL	34 ± 8	121 ± 8
Mg	mg/100 mL	8.3 ± 0.6	13 ± 1
P	mg/100 mL	43 ± 4	71 ± 2
LA	mg/100 mL	86 ± 2	570 ± 3

* Total protein = Total nitrogen $\times$ 6.38

Purified water (>8.6 M Ω cm; Merck Millipore KGaA, Germany) was used to prepare solutions of 20 g/L sodium sulphate (Na₂SO₄; $>99\%$; Thermo Fisher Scientific Australia Pty., Ltd., Australia) and 5.5 g/L sodium chloride (NaCl; $>99.5\%$; Merck KGaA, Germany) as the electrolyte and the concentrate solutions, respectively. The pH adjustment of the concentrate was performed using appropriate amounts of 5M hydrochloric acid (36% HCl; Thermo Fisher Scientific Australia Pty., Ltd., Australia) and 5M sodium hydroxide (NaOH; Chem-Supply Pty. Ltd., Australia), while the conductivity was adjusted using high purity water (18.2 M Ω cm; Merck Millipore KGaA, Germany). Acid and base cleaning steps were performed using an HCl solution with a pH of 1.0 ± 0.15 and a solution of 3% NaCl adjusted to a pH of 9.15 ± 0.15 using NaOH, respectively. Although 2-5% HCl is recommended by AWWA, a less concentrated HCl solution was used to

ensure operation was well within the pH tolerance range specified by the membrane manufacturer (0-14).

2.2 Electrodialysis unit

The electrodialysis experiments were conducted using an FTED-40 module manufactured by FuMA-Tech GmbH (Germany) as described in our earlier work (Chen et al., 2016). Cation exchange membranes (Neosepta CMB) and anion exchange membranes (Neosepta AHA) were purchased from Astom Co., Ltd., Japan. These membranes are well known for their wide pH tolerance and thermal stability. Information on the membrane characteristics can be found elsewhere (Chen et al., 2016). All membranes were pre-conditioned by soaking in 3% NaCl solution to allow for membrane hydration and expansion. After each trial the membranes were soaked in HCl (pH 1.0 ± 0.15) for two days, followed by subsequent soaking in 3% NaCl at pH values of 9.2 ± 0.2 and 5.5 ± 0.5 for two days each. This protocol ensured that the membranes were fully clean before re-use and had returned to their original ionic state.

2.3 Experimental Protocol

Through all the steps, the temperature was maintained at 45 ± 2 °C, since dairy streams are operated either below 10 °C or above 45 °C to minimize microbial growth (Beaton, 1979).

Experiments were conducted in both constant voltage and constant current modes of operation. For the constant voltage experiments, the operation was divided into five main steps as summarized in Table 2. The performance tests (Steps 1, 3, 4c and 5c) were conducted by circulating a solution of 5.5 g/L NaCl with a pH of 5.5 ± 0.5 through both diluate and concentrate channels in a batch mode from a single 20 L tank. Membrane fouling (Step 2) used sweet or acid whey circulating through the diluate channels from one 20 L tank, while 5.5 g/L NaCl at a specified pH (2.25, 6.25 or 9.25 ± 0.5) was circulated through the concentrate channels from a second 20 L tank. The diluate and concentrate flowrates were maintained at 500 mL/min, while the electrolyte flowrate was retained at 1000 mL/min as recommended by the manufacturer to minimize concentration polarization effects in the ED unit.

The concentrate and diluate were passed only once through the unit during cleaning and rinsing steps to prevent solution contamination. The flowrates of both the diluate and concentrate streams

were increased to 750 mL/min during these two steps. It is a common practice that cleaning is performed at higher flowrates, since under such conditions, the relaxed fouling layer is more susceptible to shear stress (Trägårdh, 1989).

In the constant current experiments, Step 2 was performed at a constant current (166 A/m², 305 A/m² or 444 A/m²) and variable voltage. In this case, the diluate and concentrate flowrates were maintained at either 300 mL/min or 500 mL/min to study the relationship between shear force and electrostatic interactions.

To provide an estimate of experimental error, the constant voltage experiment for acid whey at pH 9.25 was repeated twice and these replicates used to estimate error margins. Access to further quantities of sweet and acid whey limited our ability to conduct further replicate runs.

Table 2. Details of the main steps for constant voltage experiments

Step	Step length (min)	Diluate	Concentrate	Voltage (V)	Aim	Mode of operation
1	30	NaCl	NaCl	7	Initial membrane performance	Batch, single tank
2	300	Acid or sweet whey (no pH adjustment)	Concentrate (pH = 2.25, 6.25 and 9.25 ± 0.25)	7	Membrane fouling	Batch
3	30	NaCl	NaCl	7	Performance after fouling	Batch, single tank
4a	30	HCl (pH 1.0 ± 0.15)	HCl (pH 1.0 ± 0.15)	0	Acid cleaning	Continuous
4b	10	NaCl	NaCl	0	Rinse	Continuous
4c	30	NaCl	NaCl	7	Performance after acid clean	Batch, single tank
5a	30	3% NaCl (pH 9.15 ± 0.15)	3% NaCl (pH 9.15 ± 0.15)	0	Base cleaning	Continuous
5b	10	NaCl	NaCl	0	Rinse	Continuous
5c	30	NaCl	NaCl	7	Performance after base clean	Batch, single tank

2.4 Analysis methods

The pH and conductivity of the concentrate tank were measured continuously during the fouling run (Step 2) using a pH (Mettler-Toledo Ltd., Switzerland) and conductivity meter (Crison, Switzerland). When the conductivity value of the concentrate tank increased by 10% of its initial value, the conductivity was adjusted by adding 1.7 ± 0.3 L of high purity water and removing an identical volume of concentrate solution. The adjustment of concentrate conductivity in this manner is a common practice used in the industry (Fidaleo and Moresi, 2006). Similarly, the pH of the concentrate tank was adjusted if it deviated by more than 0.25 pH units from the target value, through addition of NaOH or HCl. The conductivity of the diluate stream was measured using a second conductivity meter (Mettler-Toledo Ltd., Switzerland), which allowed the calculation of the demineralization rate (DR) according to Eq. (1) (Cifuentes-Araya et al., 2013).

$$DR = \frac{\chi_i - \chi_f}{\chi_i} \times 100 = 1 - \frac{\chi_f}{\chi_i} \times 100 \quad \text{Eq. (1)}$$

where χ is the conductivity of the diluate solution in $\mu\text{S}/\text{cm}$, and i and f refer to the initial and final conductivity values of the diluate solution, respectively.

The total system resistance was calculated using Ohm's law from the voltage and current values obtained directly from the indicator on the power supply. The performance of the membranes was evaluated by averaging the last 20 min of the current data collected during Steps 1, 3, 4c and 5c. Each value was then normalized with respect to the initial current (value obtained in Step 1).

Samples were taken on an hourly basis from both the diluate tank and outlet pipe and analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES 720ES, Varian, USA) to measure the concentration of calcium (Ca), sodium (Na), magnesium (Mg), potassium (K) and phosphorus (P). High-performance liquid chromatography (HPLC, Shimadzu, Japan) was used to measure lactic acid concentrations in samples collected hourly from the diluate output. The samples were filtered to remove proteins but were not diluted. Information on the operating parameters of the ICP-OES and HPLC can be found elsewhere (Chen et al., 2016).

3.0 Results and discussion

3.1 Effect of concentrate pH and feed composition on fouling rates

The resistance in the ED unit is initially due to the membranes (Bazinet and Araya-Farias, 2005b) and the solutions (Casademont et al., 2008). For the system reported in this paper, the resistance of the concentrate, electrolyte solution, and membranes should be consistent for all experiments, thus making the diluate solution the main differentiating resistance. As shown in Figure 1, acid whey has a lower initial resistance compared to sweet whey. This is due to the higher conductivity of the former. The increase observed in the resistance with time is either due to whey demineralization and/or membrane fouling (Bazinet and Araya-Farias, 2005b; Casademont et al., 2008; Lin et al., 2008). The extent of fouling was evaluated based upon this increase in resistance with time as well as the drop in the current while using pure 5.5 g/L NaCl solution in both the compartments after Step 2 (see Figure 2).

Figure 1. Changes in the resistance of ED unit as a function of time during whey demineralization (Step 2, refer to Table 2). The pH value refers to the pH of the concentrate solution. AW and SW are acid and sweet whey, respectively. Replicate experiments were conducted for acid whey at concentrate pH of 9.25.

Figure 2. The current observed in an NaCl solution after membrane fouling (Step 3, refer to Table 2), normalized to the initial value (Step 1). AW and SW are acid and sweet whey, respectively.

In all experiments, the extent of fouling is relatively low, with the current remaining above 80% of the initial value after 5 hours of fouling (Figure 2). When an acidic concentrate was used, protein fouling was expected (Ayala-Bribiesca et al., 2006b; Bazinet et al., 2003; Diblíková et al., 2013). Indeed, protein deposits were observed on the AEM membranes facing the diluate compartment after disassembling the ED unit at the end of Step 5. However, the extent of protein fouling for both acid and sweet whey is relatively small, as the rate of increase in resistance is lower than at other pH values (Figure 1). A greater difference in both the normalized current and the system resistance was expected for sweet whey compared to acid whey, since the protein content in sweet whey is almost double the amount in acid whey. However, the greater proportions of calcium in acid whey also appeared to promote protein precipitation, as there is only a small difference in current drop (Figure 2), as well as in the final system resistance (Figure 1) or demineralisation rate (Figure 3). Casademont *et al.* observed a greater demineralisation rate when using acidic concentrate rather than that at higher pH values (Casademont et al., 2008), but within experimental error this trend is not observed here (Figure 3).

Figure 3. Overall demineralisation rate (DR) calculated using Eq. (1). AW and SW are acid and sweet whey, respectively.

When the concentrate pH was maintained at 6.25 ± 0.25 , only small overall levels of fouling were observed, with the current in pure NaCl remaining at around 90% of its original value for both acid and sweet whey (Figure 2). Under such pH conditions, both mineral and protein fouling were expected to take place as reported by the literature (Ayala-Bribiesca et al., 2006a). The increase in resistance as a function of time was much greater for acid whey (Figure 1), which might be related to a greater extent of mineral fouling due to the higher concentrations of calcium and phosphate in these samples. This is also suggested by the lower overall demineralisation rate for acid whey determined from diluate conductivity measurements (Figure 3). In the last 50 minutes of the run, fluctuations in the resistance are observed for acid whey (Figure 1). Such fluctuations might arise from the displacement or partial removal of the fouling layer as the electrostatic interaction between the mineral fouling layer and the membranes becomes weaker than the shear force exerted by the fluid. This hypothesis is discussed further in section 3.5 of this paper.

At alkaline pH and a processing temperature of 45 ± 2 °C, mineral deposits of calcium salts dominated due to the reduction in solubility. For the sweet whey, there was a steady increase in

the system resistance. The final value was significantly higher than that for the other sweet whey experiments. The final salt concentration in the diluate was not particularly low, indicating that mineral fouling was the main source of this increased system resistance. In the initial minutes of the fouling step, the system resistance increased even faster for the acid whey, again probably reflecting greater mineral scaling. However, as observed in Figure 1, this resistance dropped dramatically at the 70-minute mark (first run) and 17-minute mark (replicate run), which was possibly due to the dislodgement of the fouling layer. The removal of this fouling layer led to a net increase in the current flow for acid whey relative to that for the sweet whey at Step 3 (Figure 2). The overall rates of demineralisation were comparable (Figure 3) for both whey types and similar to that at $\text{pH } 2.25 \pm 0.25$, again suggesting that while fouling occurred, the overall effect on performance was not severe.

3.2 Ion migration

In most experiments, the cation migration (Figure 4) reflected that reported previously in the literature, as the monovalent ions migrated faster than the divalent ions following an descending order: $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ (Ayala-Bribiesca et al., 2006a; Diblíková et al., 2013; Šímová et al., 2010). The percentage of phosphorus removed over a period of 5 hours was generally greater than that of lactic acid, which differs from our prior work where these percentage removals were comparable (Chen et al., 2016).

The Na^+ and K^+ migration was generally higher for acid whey compared to sweet whey (Figures 4 and 5), which could be due to the high initial concentration of minerals and lower solution pH (see Table 1). Higher initial concentration results in a greater concentration difference between the diluate and concentrate streams, thus allowing ion transport through diffusion. Furthermore, the major proteins will be uncharged at the acid whey pH (Fidaleo and Moresi, 2006), thus enhancing cation and anion transport. On the other hand, significantly greater lactic acid removal was achieved at acidic concentrate pH (Figures 4 and 5) for both types of whey. This may be because lactate ions crossing from the diluate to the concentrate channel immediately combine with hydrogen ions, thus reducing the lactate concentration in this channel. In turn, this maintains a strong diffusional driving force for more lactate to cross the AEM. This is useful for acid whey treatment where the removal of lactate is known to enhance downstream processing (Chandrapala et al., 2017). No obvious difference was noted in the lactic acid removal at other pH conditions.

The trends in calcium and phosphate migration are difficult to explain and probably reflect a complex interplay between the speciation of calcium as well as fouling effects. The calcium in the acid whey diluate ($\text{pH } 4.4 \pm 0.3$) will be present entirely as Ca^{2+} . Conversely, the calcium in the sweet whey diluate at $\text{pH } 6.1 \pm 0.2$ could be present partly as a monovalent anion complex of calcium citrate and possibly as neutral colloidal calcium phosphate (Rice et al., 2010). Upon crossing into the concentrate channel at $\text{pH } 9.25 \pm 0.25$, more neutral calcium phosphate species will form, as well as monovalent CaPO_4^- . These changes in speciation can affect migration rates.

For the acid whey run at a concentrate pH of 6.25 ± 0.25 , the calcium and phosphate migration appear particularly high and the corresponding Na^+ and K^+ migration appear low (Figures 4 and 5). These changes in ion migration possibly also reflect mineral fouling. That is, the ion migration is determined from the loss of these species from the diluate, rather than the gain in the concentrate. As the pH on the membrane surface increases, phosphate will transition from neutral H_3PO_4 to H_2PO_4^- and HPO_4^{2-} , which are less soluble ions and hence more likely to precipitate. If these calcium phosphate complexes precipitate on the membrane surface, then this loss will appear larger. Conversely, potassium and sodium migration may be reduced by the presence of this fouling, which results in an overall lower demineralisation rate (Figure 3). Similar effects may have occurred at a concentrate pH of 9.25 ± 0.25 in the first minutes of the run, but the apparent release of the calcium phosphate back into the diluate tank as this dislodgement occurred may also have explained the reduced removal of the calcium ions from the acid whey, relative to the case at $\text{pH } 6.5 \pm 0.25$.

Migration of H^+ and OH^- possibly also occurred during these experiments. As the whey solutions are naturally buffered, it is not possible to determine these migration rates from changes in the diluate pH, which remained constant during all experiments. The concentrate pH did vary but was adjusted throughout the experiment to maintain a value within 0.25 pH units of the target value. The number of times an adjustment was required gives an approximation of the pH changes that occurred (Table 3).

At the concentrate pH of 2.25 ± 0.25 , uncharged lactic acid and phosphoric acid are favoured over phosphate and lactate ions. The addition of HCl for the two runs at pH 2.25 thus probably reflects the combination of H^+ ions with lactate and phosphate as they cross from the less acidic diluate. Conversely, as phosphate crosses the membranes into a concentrate at $\text{pH } 9.25 \pm 0.25$, it will

310 change speciation from H_2PO_4^- to HPO_4^{2-} and PO_4^{3-} thus releasing H^+ , leading to the need for
 311 NaOH addition.

312 **Figure 4.** Percentage removal of the major cations and anions as a function of whey type and
 313 concentrate pH. AW and SW are acid and sweet whey, respectively.

Figure 5. Total cations and anions removed from the diluate over a period of 5 hours (Step 2, refer to Table 2) under the application of a constant voltage. AW and SW are acid and sweet whey, respectively.

Table 3. Concentrate pH adjustment frequency during membrane fouling run (Step 2, refer to Table 2).

Whey type	Concentrate pH target range	No. of pH adjustments	
		NaOH addition	HCl addition
SW	2.25 ± 0.25	-	1
	6.25 ± 0.25	-	7
	9.25 ± 0.25	1	-
AW	2.25 ± 0.25	-	2
	6.25 ± 0.25	4	-
	9.25 ± 0.25	6, 23*	-

* This run was repeated twice, with 6 adjustments in the first trial and 23 adjustments in the second.

3.3 Effect of mode of operation

The mode, in which the ED unit is operated (batch or semi-continuous), also affects the membrane fouling. Ayala-Bribiesca *et al.* (Ayala-Bribiesca et al., 2006a, 2007) claimed that operating the ED unit in batch mode, as often is the case in laboratory scale experiments, contributes significantly to the precipitation of calcium salts. These authors found calcium phosphate deposits on the AEMs facing the concentrate compartment, while calcium hydroxide and calcium carbonate were found on the CEM facing the concentrate compartment. The authors (Ayala-Bribiesca et al., 2006a, 2007) explained that during the demineralization step, Ca^{2+} ions will migrate through the CEMs from the diluate to the concentrate stream. When the concentrate is recycled back to the ED unit, the Ca^{2+} ions come into contact with phosphorus ions migrating through the AEMs from the diluate stream, resulting in the formation and precipitation of calcium phosphate under alkaline conditions (Ayala-Bribiesca et al., 2007; Casademont et al., 2008). They argued that this phenomenon will not take place if the concentrate stream is passed only once through the unit. However, according to Fidaleo and Moresi (Fidaleo and Moresi, 2006), most industrial ED units are operated in a semi-continuous mode, in which the diluate stream flows continuously, while the concentrate stream is operated in a feed and bleed mode. This means that Ca^{2+} recirculation and contact with AEM cannot be avoided. Conversely speaking, adjusting the conductivity of concentrate stream to a standard value is a common practice in industrial ED units. We believe that adjusting the concentrate conductivity during the fouling step (Step 2) diluted the Ca^{2+} ion concentration, which was recycled back to the unit, and hence, reduced the potential for this effect to occur. To investigate this issue, a separate experiment was conducted with sweet whey at the pH of 9.25 ± 0.25 , where the concentrate conductivity was not adjusted, and hence increased during the fouling run (Step 2) from 10.2 to 12.5 mS/cm. Under these conditions, fouling was observed on the AEM after cleaning the unit (see Supporting Information Figure S1), while no deposits were observed when the concentrate conductivity was adjusted throughout the experiment.

3.4 Cleaning efficiency

For experiments where the concentrate conductivity was adjusted, no mineral deposits were observed on the members after cleaning, indicating that the acid cleaning was effective in removing the mineral deposits. Furthermore, protein deposits were only observed after cleaning for the experiment with sweet whey under acidic concentrate conditions. Whey protein precipitation is expected to be reversible, if it is sorbed on the membrane either by relatively weak dipole-dipole interactions or by hydrogen bonding. However, the sites, where electrostatic bonds have formed between the charged sites on the protein and the functional groups on the membrane (Bleha et al., 1992), require chemical cleaning under high ionic strength and high pH conditions. In the present case, the use of an alkaline solution of 3% NaCl at a pH of 9.2 ± 0.2 for 30 minutes was insufficient to remove the protein deposits formed when sweet whey was processed under acidic concentrate conditions. Organic fouling is usually avoided in such cases by modifying the mode of current supply to the ED unit. This is commonly achieved by using either a pulsed electrical field or electrodialysis reversal.

As noted from the results reported in Figure 6, it is difficult to assess the effectiveness of chemical cleaning by monitoring the current in a pure NaCl solution. From the acid whey replicate experiment, the recorded current values after fouling of the unit are in close proximity to each other, while the measured values after both the acid and base cleaning deviate in both experiments, and do not exhibit a clear trend.

Such behaviour is probably a result of the contact of membranes with different solutions during the five steps in each experiment. IEMs contain high concentrations of counter-ions to balance the fixed charges. The CEMs and AEMs were pre-soaked before use to ensure that these counter-ions are Na^+ and Cl^- , respectively. However, during the cleaning step, these counter-ions would be replaced with H^+ (during the acid cleaning) and OH^- (during the alkali cleaning). We aimed to return these counter ions to Na^+ and Cl^- by a 10-minute NaCl rinse prior to the current measurements. However, we believe that the high mobility of residual H^+ and OH^- ions led to the variability in the observed current after acid and base cleaning, affecting the results seen in Figure 6. A longer period of operation would be required to obtain the true current under these conditions.

Figure 6. Membrane performance check using NaCl solution (Steps 1, 3, 4c and 5c, refer to Table 2). The pH value refers to the pH of the concentrate solution. AW and SW are acid and sweet whey, respectively.

3.5 Constant current mode

We believe that the fluctuations observed in the resistance during whey processing (Figure 1) are related to the shear stress exhibited by the flow and electrostatic interactions between the membrane surface and foulant. As the current falls during the demineralization process, the electrostatic interactions reduce until they are less than the shear forces exerted by the liquid flow. This allows partial or even total removal of the fouling layer from the membrane surface. This in turn reduces the contribution of membrane fouling to the total resistance of the unit. To test this hypothesis, a series of fouling runs were performed using acid whey and alkaline concentrate at constant current (166, 305, 444 A/m²) and varying voltage. The use of constant current is more likely to be the mode of operation in an industrial environment.

As expected, a higher applied current resulted in greater demineralisation and greater removal of monovalent ions (Figure 7). Although a DR close to 30% was achieved for 444 A/m² at a fluid flowrate of 500 mL/min, the concentrations of Ca and P removed were comparable to the amount removed at the applied current of 305 A/m² (DR of 20%). However, the extent of fouling observed on the membrane surface was much lower at 444 A/m² (see Supporting Information, Figure S2) than at 305 A/m². During the fouling run at 444 A/m², the frequency at which the concentrate pH was adjusted using NaOH was greater than at 305 A/m². This suggests that more H⁺ is migrating from the diluate, through both an increased migration rate and greater water splitting. When operating at this highest current density, the limiting current condition was probably exceeded, as noted by a significant increase in the system resistance in these experiments. The voltage was also observed to fluctuate in time at this highest current density, indicative of electroconvection occurring (Krol et al., 1999). The greater H⁺ concentrations at the membrane surface that arise from water splitting reduce the potential for calcium scaling due to localised lower pH values thus decreasing precipitation of calcium phosphate (Cifuentes-Araya et al., 2013; Mikhaylin and Bazinet, 2016). The electroconvection can also cause the fouling layer to be disrupted. Although Ayala-Bribiesca *et al.* (Ayala-Bribiesca et al., 2006a) reported that water splitting could contribute to protein and mineral fouling in the diluate compartment, this was not observed in the system under investigation.

When the applied current was limited to 166 A/m² at a flowrate of 500 mL/min, no scaling was observed, although a reasonable amount of Ca was removed from the diluate compartment (Figure 7). However, when the flowrates of both the diluate and concentrate streams were dropped to 300 mL/min, fouling was observed in the concentrate compartment (see Supporting Information, Figure S3). This fouling resistance was also reflected in lower migration rates for all ions (Figure 7). We believe that the increased fouling at lower flowrates reflects the reduced fluid shear stress that assists in foulant removal. The concentrate pH was adjusted 19 times for both 500 mL/min and 300 mL/min flowrates, indicating that only minimal water splitting occurred as the flowrate fell. However, the electrical resistance increased in a manner similar to that observed at 444 A/m² and voltage fluctuations were again observed, suggesting that water splitting was also occurring to some extent.

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433 **Figure 7.** Percentage of ions removed from the diluate tank under constant current operation
 434 over a period of 5 hours (Acid whey; concentrate pH of 9.25 ± 0.25).

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4.0 Conclusions

Fouling rates during electrodialysis of acid and sweet whey are generally low and comparable to each other. The current in 5.5 g/L NaCl retained over 80% of its initial value after a 5 hour fouling run under all conditions. Although, the protein content of acid whey is lower than that of sweet whey, protein precipitation in the diluate compartment was comparable for both solutions when operating with an acidic concentrate. When operating with an alkaline concentrate, greater increases in system resistance were observed with time due to mineral fouling. However, this mineral fouling was readily dislodged, leading to variability in the demineralization performance. Furthermore, the use of higher flowrates and lower current densities also proved effective in reducing mineral fouling. Maintaining a constant concentration of the concentrate stream through dilution of multivalent ions, especially calcium within the concentrate compartment, reduced the extent of mineral fouling on this side of the membranes. Cleaning with HCl solution at pH of 1.0 ± 0.15 was effective in removing mineral deposits. However, cleaning with 3% NaCl (pH of 9.2 ± 0.2) was ineffective in removing the strongly bound protein deposits that were formed when acidic concentrate was utilized.

When it comes to acid whey treatment using electrodialysis, the greatest migration rates for lactate anions were observed when an acidic concentrate was used. It is thus recommended to operate the concentrate stream at an acidic pH to avoid calcium phosphate precipitation and to achieve strong removal of lactate ions. The use of electrodialysis reversal, or a pulsed electric field, could be used in combination with this pH to reduce protein fouling that might occur under these conditions.

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