Lithium Transport in Monovalent Selective Electrodialysis: Effect of Brine Salinity, Acidity and Composition

by

John Thomas

Submitted to the Department of Mechanical Engineering
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Abstract

Lithium is an increasingly important resource for electrification but current supply will not keep up with expected demand. Monovalent selective electrodialysis (MSED) offers a potential method to separate lithium from other elements from salt lake brine. A monovalent selective electrodialysis setup was used to test conditions of pH, salinity, coexisting cations, and current density in the effectiveness in lithium extraction from salt lake brines. MSED of multi-component brines containing more coexisting ions is shown to be less effective than brines with only one coexisting cation. The study shows that pH 7 had significantly higher separation coefficient than lower pH without significant negative impact on current efficiency. The lowest salinity brines of 10 g/L showed the highest separation coefficient, approaching 10 for the Chinese brine, while still having similar current efficiency to the higher salinity brines. Current density is also shown to increase the separation coefficient 3x while only only reducing current efficiency by 50% or less.

Thesis Supervisor: John H. Lienhard
Title: Abdul Latif Jameel Professor of Mechanical Engineering and Water

Acknowledgments

Thank you to Professor Lienhard for his support and the opportunity to do this project, my family for helping me through the challenges and especially to Zi Hao Foo for his mentor-ship in completing this thesis.

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Statement of Originality

This study was conducted in the Rohsenow Kendall Heat Transfer Laboratory from September 2022 to December 2022. Water sample analysis was conducted in the Materials Research Laboratory. The author received supervision from Professor John Lienhard and his team of graduate students. The experiments and result analyses presented in this thesis are original and have not been previously published.

Chapter 1

Introduction

Lithium is a critical resource used extensively in the clean energy sector, primarily as the key element in rechargeable lithium batteries. Despite being a central component for many applications across the world, lithium can only be sustainably harvested from a limited set of mines or salt-lakes, primarily located in South America, Asia and Australia. Majority of the lithium production in the world today (~ 60 %) originates from the mining industry in Australia [5].

As an alternative to mining, lithium can be harvested from hypersaline salt lakes located in Chile, Argentina, Bolivia, China and the United States. Most of the lithium from those brines today is extracted by pumping the brine into evaporation ponds. Once the water evaporates out, a number of salts are left behind, including lithium salts and salts of other elements such as magnesium, sodium and calcium. The residual salts have to be post-processed to remove impurities and to increase lithium purity. The majority of these methods involve the use of chemical solvents or energy intensive separation processes that are powered by fossil fuels [3].

To improve separation efficacy and allow for the use of sustainable energy sources, monovalent selective electrodialysis (MSED) is a potential method for separating lithium from the other elements in brine. Monovalent selective electrodialysis differs from conventional electrodialysis in that the cation-exchange membrane is designed to allow for the selective migration of monovalent cations, separating them from the multivalent ions [4]. As a monovalent ion, lithium is expected to penetrate through the MSED membranes, allowing for its recovery in the concentrate stream while retaining the undesirable multivalent ions in the diluate stream.

Despite promising applications, there remains open questions about the practicality of lithium extraction with MSED. Firstly, the cost of extracting lithium with MSED, compared to the cost of conventional lithium production, is unclear. This is because the extraction efficacy of MSED under the harsh acidity and high salinity of salt-lake brines encountered during commercial operation has yet to be studied. Consequently, the optimal conditions for extracting lithium from the salt-lake brines with MSED are unquantified [2]. As a start, this study seeks to further our understanding of how the process conditions affect the separation and energy efficiency of MSED. In this thesis, through direct experimentation, we document the influence of brine composition, salinity and acidity, and current density on lithium selectivity. The presented experimental results may be useful for future transport mechanism or process optimization studies.

Chapter 2

Materials and Methods

2.1 Experimental Design

The goal of the experiments is to determine conditions that allow for the most effective and efficient extraction of lithium in practical settings. Therefore, the brines used in this study mimic the compositions of the salt-lake brines at Salar de Atacama in Chile, and Lake Qaidam in China.

The MSED setup is used with different synthetic brine solution compositions, as displayed in Tables 2.1, 2.2, and 2.3. Brines are diluted with deionized water (MilliQ) to achieve the desired composition while keeping the relative ionic ratios constant. The electrode rinse is composed of a 0.2 M sodium sulfate solution. The synthetic brine and rinse solutions are prepared with anhydrous ReagantPlus-Grade NaCl, KCl, LiCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, K_2So_4, Li_2SO_4, $MgSO_4$ and $CaSO_4$ with > 99 % purity. The pH of the solutions are controlled by dropwise addition of NaOH and HCl solutions, prepared using anhydrous NaOH (> 98 % purity) and HCl (12 M). The monovalent selective electrodialysis membranes, Neosepta CMS and ACS, are obtained from Amerida. The membrane stack is procured from PCCell, Germany.

Table 2.1: Nominal ionic composition of feed solution based on simplified brine from Salar de Atacama, at solution molarity of 0.35 M.

Brine Composition (Abbreviation)	Nominal Composition (g/L)					Solution Molarity (M)
	Li^+	Mg^{2+}	Cl^-	SO_4^{2-}	TDS	
Li^+-Mg^{2+}-Cl^- (LM-C)	0.34	2.05	7.70	—	10.09	0.35
Li^+-Mg^{2+}-SO_4^{2-} (LM-S)	0.49	2.98	—	15.13	18.59	0.35
Li^+-Mg^{2+}-Cl^--SO_4^{2-} (LM-CS)	0.34	2.09	7.39	0.62	10.44	0.35

Table 2.2: Nominal ionic composition of feed solution based on brine from Salar de Atacama, at total dissolved concentrations of 10, 30, 70 g/L. [6]

Salt Lake, Location	Nominal Composition (g/L)							
	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	TDS
Salar de Atacama, Chile	0.33	19.23	4.99	2.04	—	40.10	3.36	70.00
	0.14	8.24	2.14	0.87	—	17.17	1.44	30.00
	0.05	2.75	0.71	0.29	—	5.72	0.48	10.00

Table 2.3: Nominal ionic composition of feed solution based on brine from Qaidam Lake, at total dissolved concentrations of 10, 30, and 70 g/L. [6]

Salt Lake, Location	Nominal Composition (g/L)							
	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	TDS
Qaidam Lake, China	0.09	15.79	1.23	5.67	—	37.65	9.57	70.00
	0.04	6.77	0.53	2.43	—	16.14	4.10	30.00
	0.01	2.26	0.18	0.81	—	5.38	1.37	10.00

The brines in Table 2.1 are binary solutions, with magnesium as a coexisting cation to lithium. These brines are used to provide a baseline to compare the impact of introducing additional coexisting cations. The brine compositions representing Lake Qaidam in China are shown in Table 2.3. Similarly, the brine compositions representing Salar de Atacama in Chile are shown in Table 2.2.

During operation, the diluate and concentrate solutions are initially composed of the same brine composition. As the MSED process progresses, monovalent cations and anions migrate from the diluate into the concentrate, across the monovalent selective membrane. By using the same concentration in the diluate and concentrate streams initially, it prevents diffusion from a concentration gradient that would affect the effectiveness of the MSED. Figure 2-1 shows how the diluate and concentrates are fed through the MSED system. The divalent magnesium ions are expected to have more difficulty migrating across the membranes while the monovalent ions such lithium will cross the cation exchange membrane.

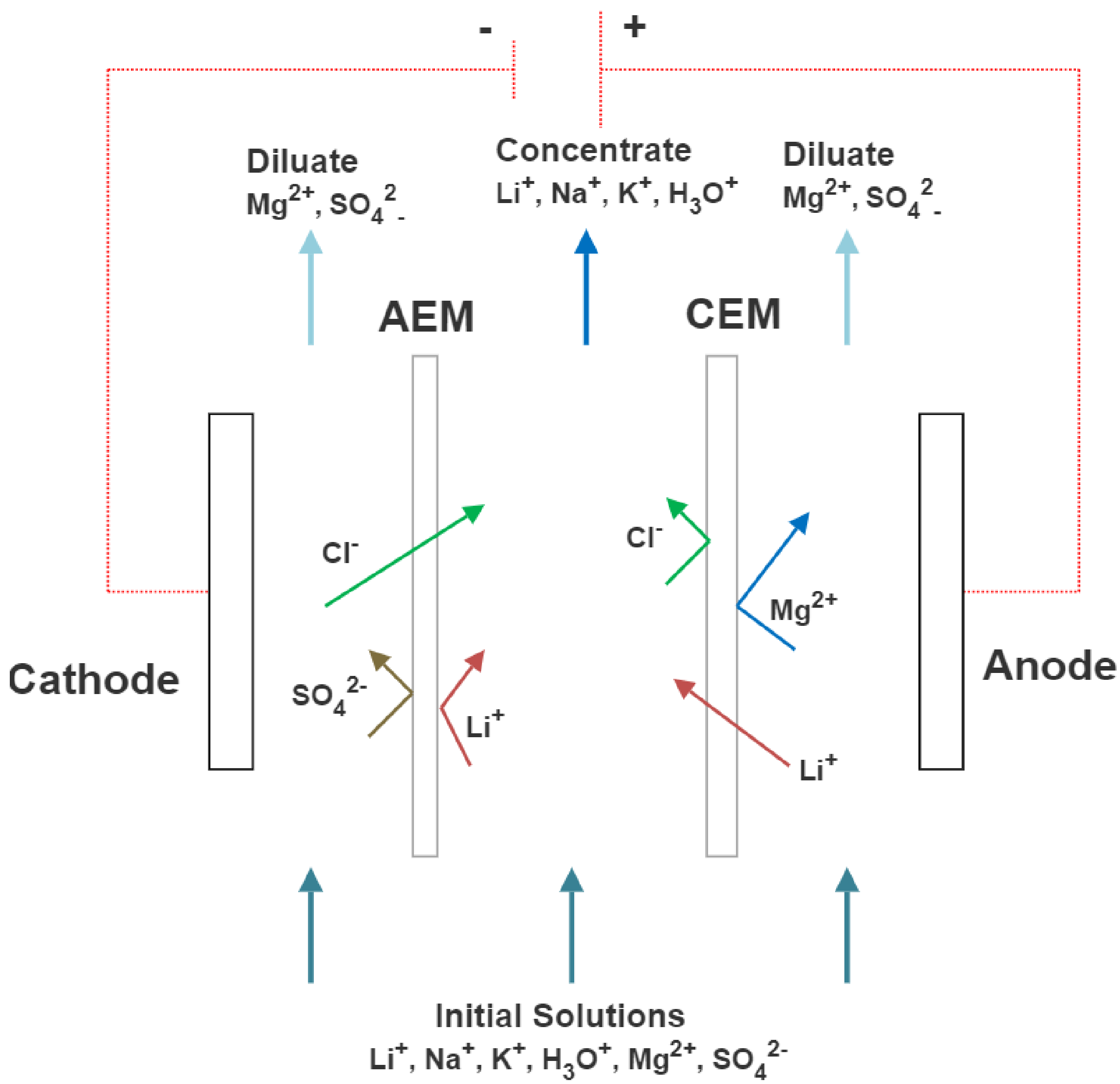


Figure 2-1: Simplified MSED diagram with an applied voltage across the electrode causing migration of ions across the membranes. The diagram shows only one set of membranes instead of the 10 in the actual setup. The cation exchange membrane (CEM) allows monovalent ions such as lithium, sodium and potassium to migrate from the diluate to the concentrate but prevents divalent ions such as magnesium from migrating. The anion exchange membrane (AEM) allows monovalent chlorine to cross the membrane while preventing divalent sulfates from migrating.

The binary solution brines are tested with an initial of pH 7, with a current of 0.5 A over a period of 150 minutes. The multi-component brines are each tested with an initial pH 3, 5, and 7, with a current of 0.5 A and 3.0 A. The multi-component brines are also tested at different concentrations of total dissolved solid (TDS) of 10 g/L, 30 g/L and 70 g/L.

During each MSED trial, 10 mL samples of both the diluate and the concentrate streams are taken to evaluate their composition at 15 - 30 minute intervals. The compositions are analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES). The mass of both the concentrate and diluate tanks are measured using scales, which are then recorded using a data acquisition unit. The migration rate of each cation and anion from the diluate to the concentrate streams at each time interval are calculated using the mass of each solution tank and the ion concentration in the water samples.

The pH of both diluate and concentrate streams are measured using the pH sensors and are recorded during trials. The voltage drop across the electrode is measured using a voltmeter. Based on the fixed current and the voltage measurements, the resistance of the solutions can be calculated. As ions are removed from the diluate stream, the voltage drop across the system is expected to increase as the solution resistance increases with depletion.

2.2 Experimental Apparatus

The MSED setup is shown in Figure 2-2. The rinse, concentrate and diluate loops are run through a PCCell ED 200 electrodialysis unit using Iwaki MD-55R centrifugal pumps. The tank for each loop contain 4 L, 4 L and 2 L of solution, respectively. The monovalent selective membranes are a set of 10 cell pairs of Neosepta membranes of 1 mm thickness each. Between each cell membrane pair is a 2 mm spacer. The volumetric flow rate is fixed and limited to 9.5 liters per hour through the diluate

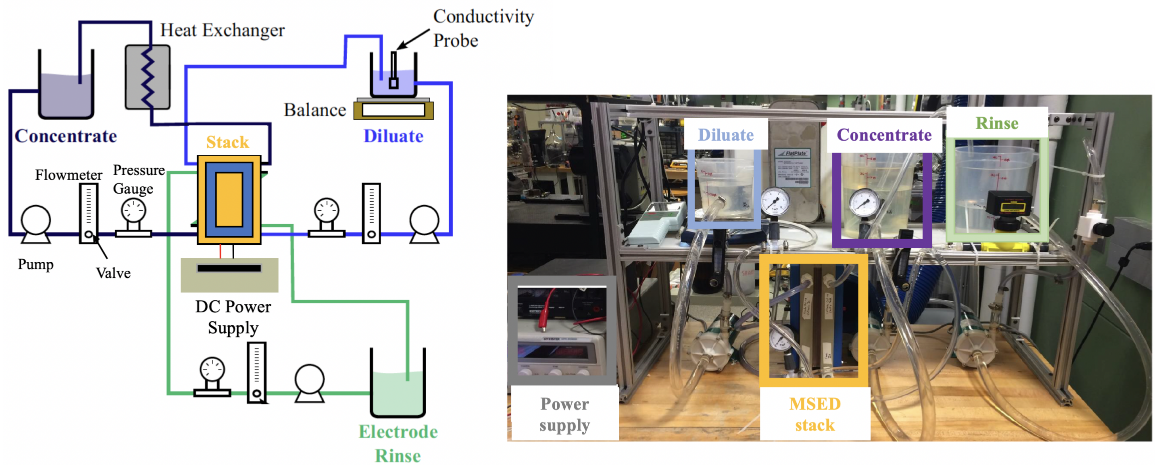


Figure 2-2: MSED apparatus using the PCCELL ED200 cell with Neosepta membranes. Rinse, concentrate and diluate loops feeding into the MSED stack [1].

and concentrate channels using variable area flow meters to prevent migration from pressure gradients. The temperature of the concentrate loop is controlled to about 20 °C using an external heat exchanger. The concentrate loop then acts as a heat exchanger loop through the MSED unit to the cool the diluate stream.

2.3 Data Analysis

This section presents a summary of the metrics used to evaluate the separation and energy efficiencies of the MSED process. From the ICP-OES experiments, the ion concentrations in the diluate and concentrate streams are derived at each time interval. Following which, the extent of ion movement for Li^+, Mg^{2+}, Cl^- and SO_4^{2-} can be calculated through direct subtraction. The ion concentrations are subsequently used to calculate the separation coefficients and current utilization efficiencies.

2.3.1 Separation Coefficient

$$F_{\text{M–Li}} = \frac{(C_M/C_{Li})_t}{(C_M/C_{Li})_i} \tag{2.1}$$

The separation coefficient is the change in the ratio of concentrations between two ions, at a specified time relative to a reference time. C_M is the concentration of some coexisting cation in mol/L while C_{Li} refers to the concentration of lithium in mol/L. A high separation coefficient (> 1) corresponds to lithium migrating at a faster rate compared to the coexisting cation. A separation coefficient of one means there is no net change in the ratio of concentrations. Similarly, a separation coefficient of less than 1 corresponds to the case of the coexisting cation migrating at a faster rate than lithium.

2.3.2 Current Efficiency

Current efficiency is defined as how much charge was consumed in transporting Li^+ across the membrane divided by the total electric charge consumed by the MSED process.

$$I_{\text{eff}} = \frac{Z * F * dN_{Li^+}}{n * I * t} \tag{2.2}$$

where Z is $+1$ for the Li^+, n is the number of membrane pairs, F is the Faraday constant (96,475 C/mol), dN_{Li^+} is the change in lithium molar concentration, t is time (s) and I is the current passing through the MSED stack.

A current efficiency approaching 1 signifies that every charge provided was consumed in transporting Li^+ across the membrane, while an efficiency approaching 0 means very little of the charge provided was used in transporting Li^+.

Chapter 3

Results and Discussion

3.1 Impact of Co-existing Ions: Comparing Chilean and Chinese Brine

The Chilean brine has a Li concentration of 0.05 g/L in 10 g/L TDS solution while the Chinese brine has a Li concentration of 0.01 g/L in the 10 g/L solution. The mass ratio of magnesium to lithium is roughly 6 in the Chilean brines and 63 in the Chinese brine. The Chinese brine, therefore, has more coexisting cations that can compete in the migration across the membrane.

A compilation of the experimental results is provided in Figures 3-1 to 3-20, with concentrations ranging from 10 g/L to 70 g/L, current ranging from 0.5 A to 3.0 A, and pH ranging from 3 to 7. In each figure, the separation coefficient of Li^+ to Mg^{2+} based on the fitted line is provided in the upper left quadrant. The lines are fit using a least squares linear fit with an initial concentration of 1. The error bars are calculated using known errors from the ICP-OES concentration measurement.

In each of the figures, the concentrations of the ion decrease with time. The faster the rate of ion depletion in the solution, the more selective the membrane is towards that particular ion. By comparing the separation coefficient of Li^+ to Mg^{2+} from the fit, we can correlate effects of varying the operating parameters on the lithium selectivity of MSED.

The potential impact of cation ratios can be seen by comparing figures showing concentration over time of the Chilean brines (Figure 3-1, 3-4, 3-5, 3-5) and those of the Chinese brines (Figure 3-11, 3-14, 3-15, 3-15). The Chinese brines and Chilean brines generally have the same trend in lithium concentration over time. For example, the Chilean brine at 10 g/L, pH 3 and 0.5 A (Figure 3-1) has a slope $\frac{-3C(Li^{+})}{hr}$, while the corresponding Chinese brine (Figure 3-11) also has a slope of about $\frac{-3C(Li^{+})}{hr}$ where $C(\mathrm{Li}^{+})$ is the normalized concentration of lithium in the diluate. The normalized concentration is the concentration at that point in time divided by the initial concentration in the solution. The competing cations, however, migrate at a higher rate in the Chinese brine compared to the Chilean brine. This is seen in the ratio of the slopes of lithium to magnesium and is also displayed in Table 3.1, where the ratio of slopes of lithium to magnesium is higher in the Chilean brine to each corresponding Chinese brine.

From inspection, for a given operating current, solution pH and salinity, the $\mathrm{Li}^{+}/\mathrm{Mg}^{2+}$ separation efficiency of MSED is approximately 30 % higher on average with the Chilean brines as compared to the Chinese brines. The results suggest that the presence of Mg^{2+} reduces the selectivity mechanism of the membrane. Further, for a given operating current and solution composition, it is evident that the separation efficiency of MSED declines with decreasing pH.

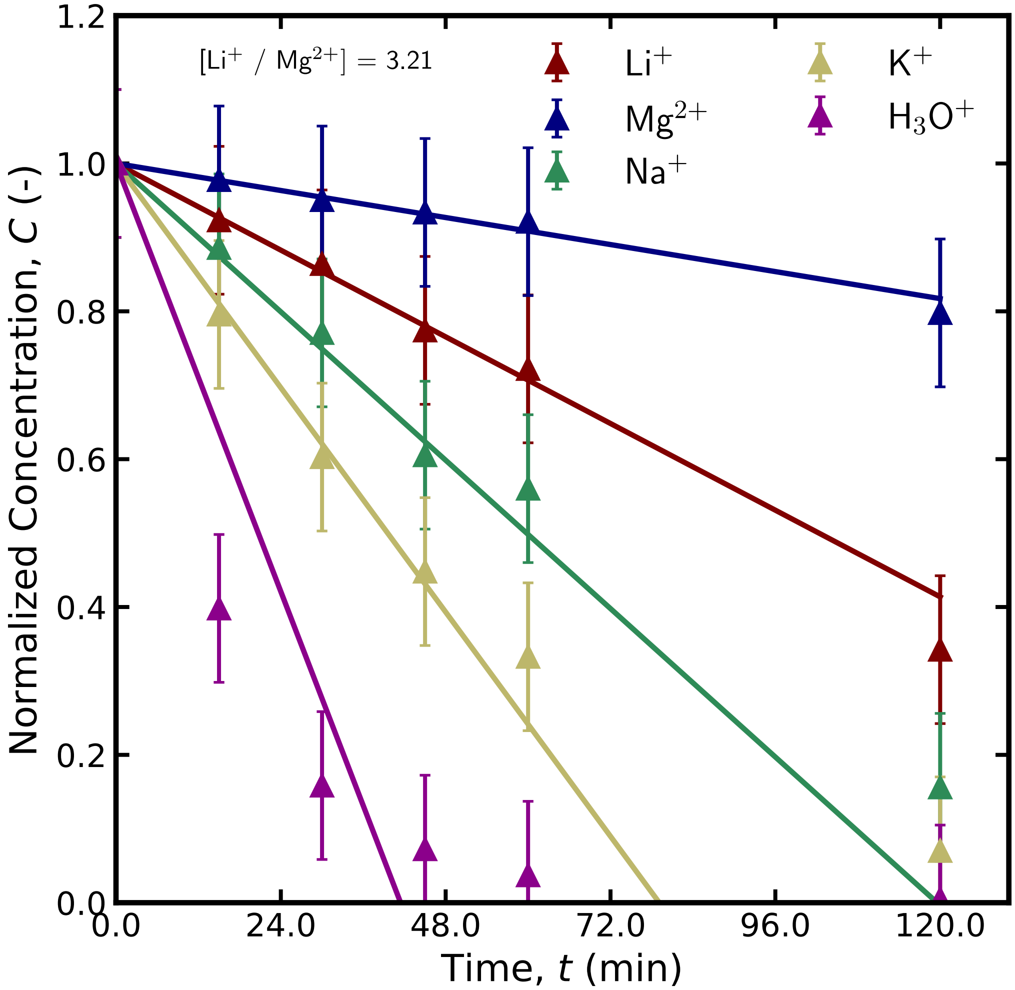


Figure 3-1: Normalized concentration over time in MSED trials of Chilean brine at 10 g/L, pH of 3, and current density of 0.5 A over 120 minutes. Concentrations shown are Li^+, Mg^{2+}, K^+, H_3O^+. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

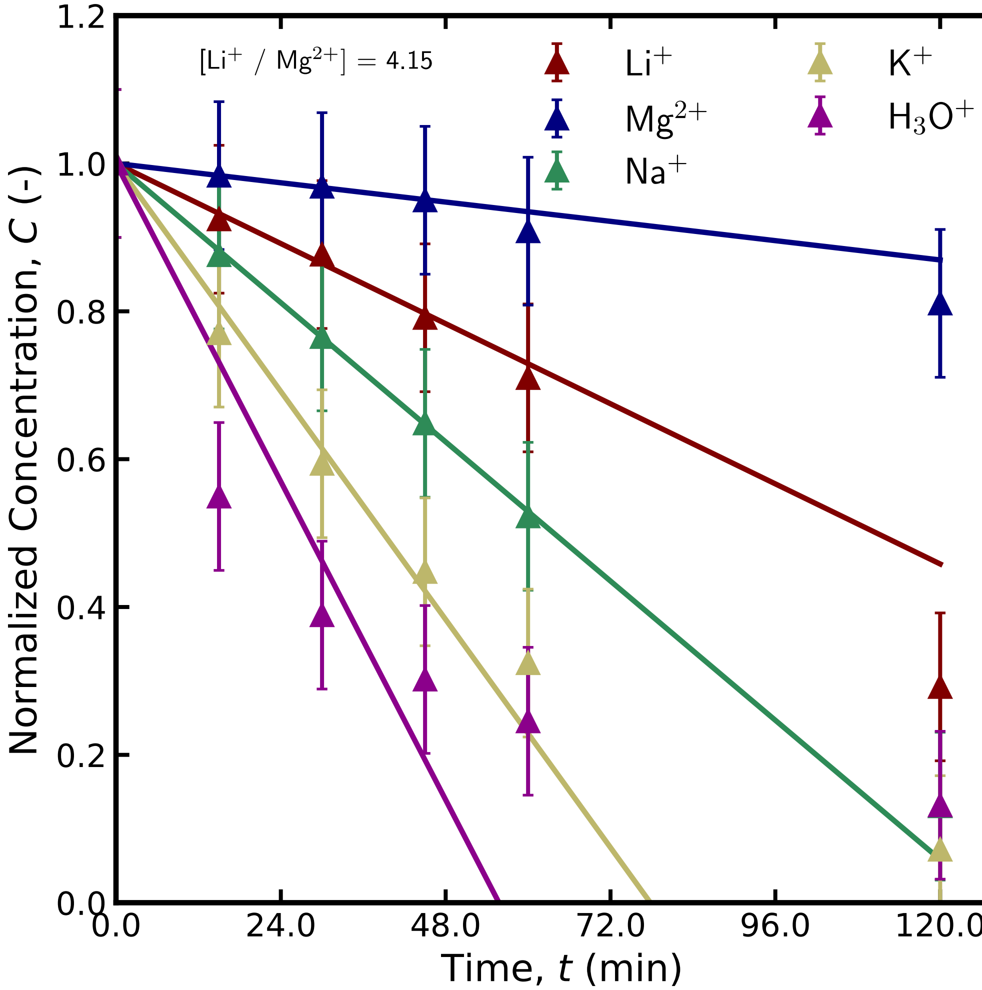


Figure 3-2: Normalized concentration over time in MSED trials of Chilean brine at 10 g/L, pH of 5 and current density of 0.5 A over 120 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

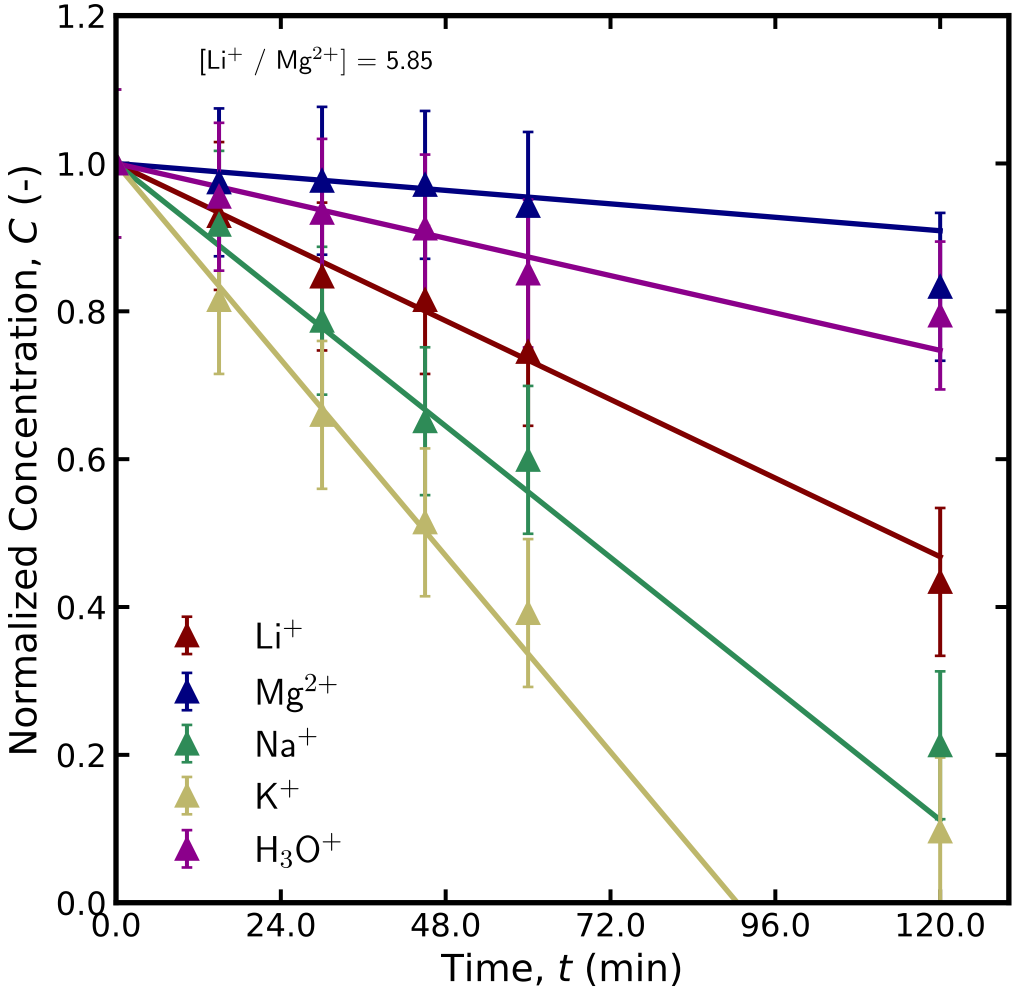


Figure 3-3: Normalized concentration over time in MSED trials of Chilean brine at 10 g/L , pH of 7 and current density of 0.5 A over 120 minutes. Concentrations shown are Li^+, Mg^{2+}, K^+, H_3O^+. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

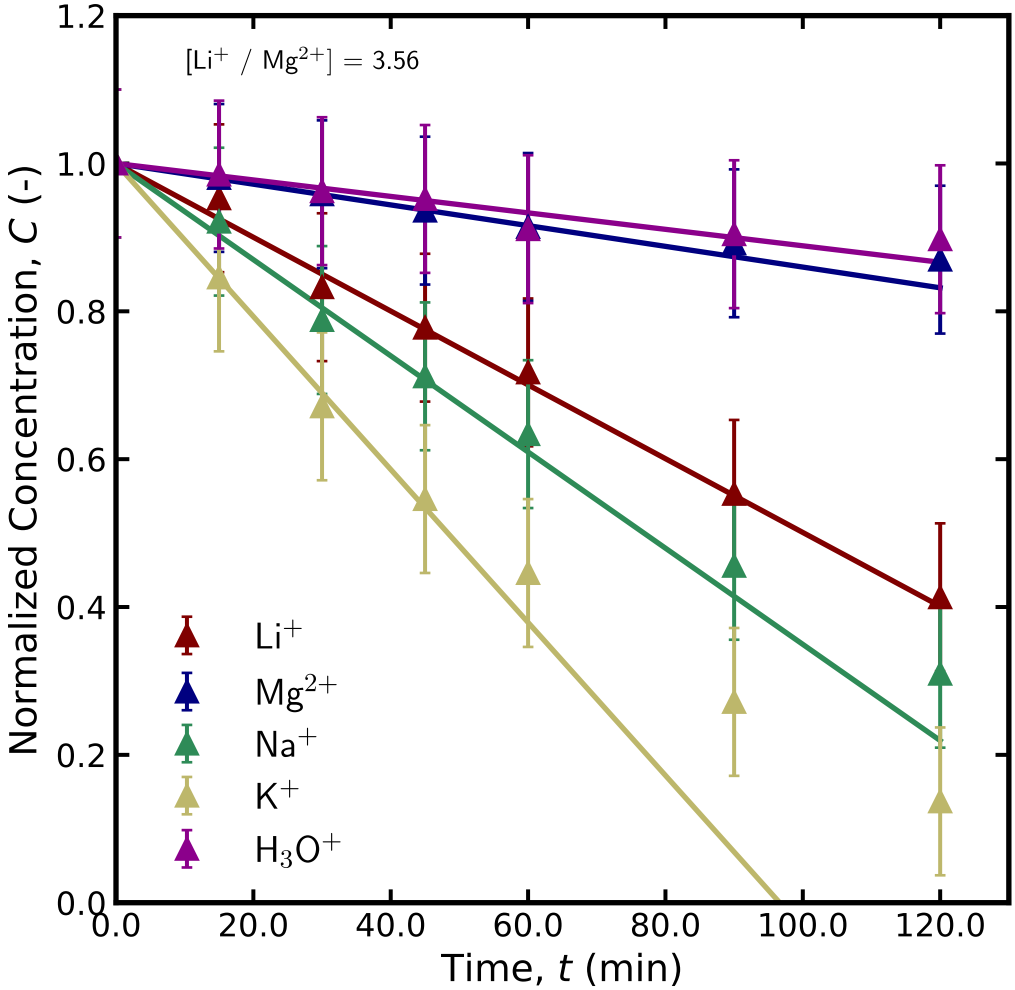


Figure 3-4: Normalized concentration over time in MSED trials of Chilean brine at 30 g/L , pH of 7 and current density of 0.5 A over 120 minutes. Concentrations shown are Li^+, Mg^{2+}, K^+, H_3O^+. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

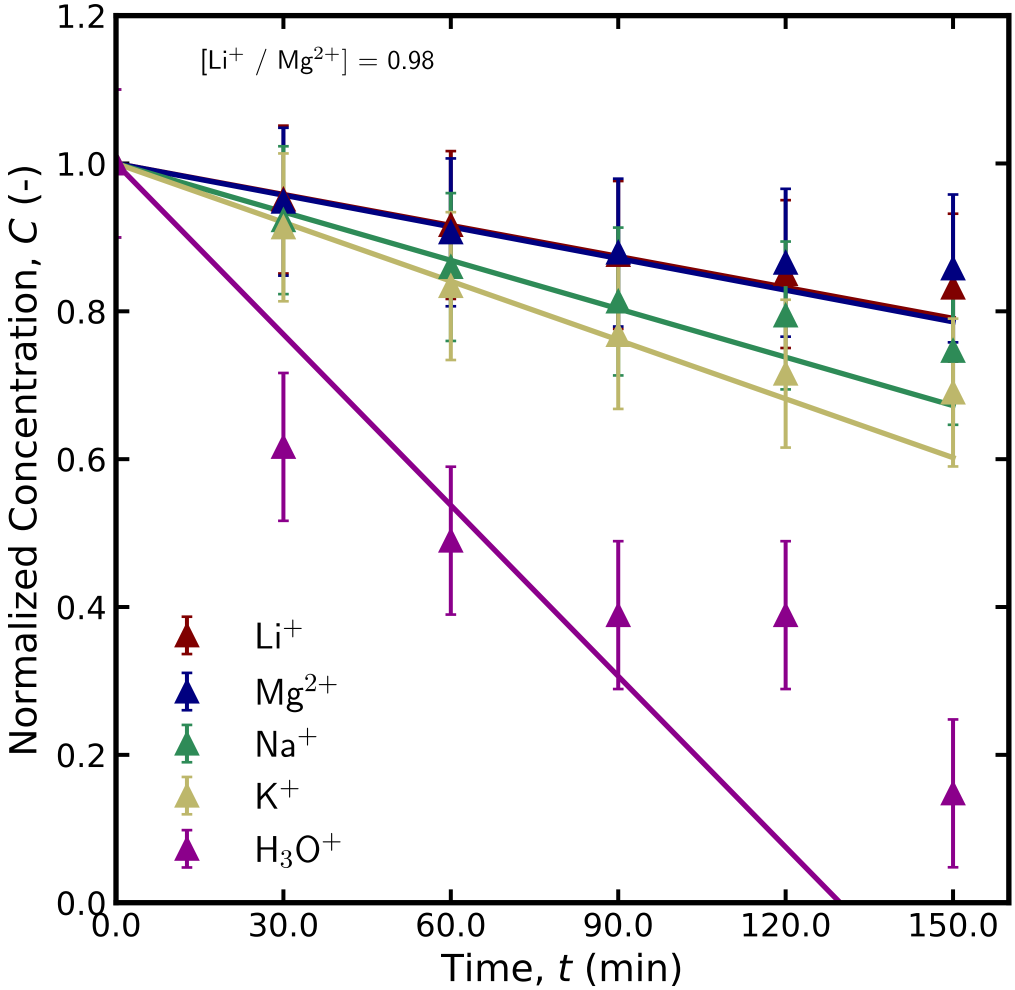


Figure 3-5: Normalized concentration over time in MSED trials of Chilean brine at 70 g/L , pH of 3 and current density of 0.5 A over 150 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

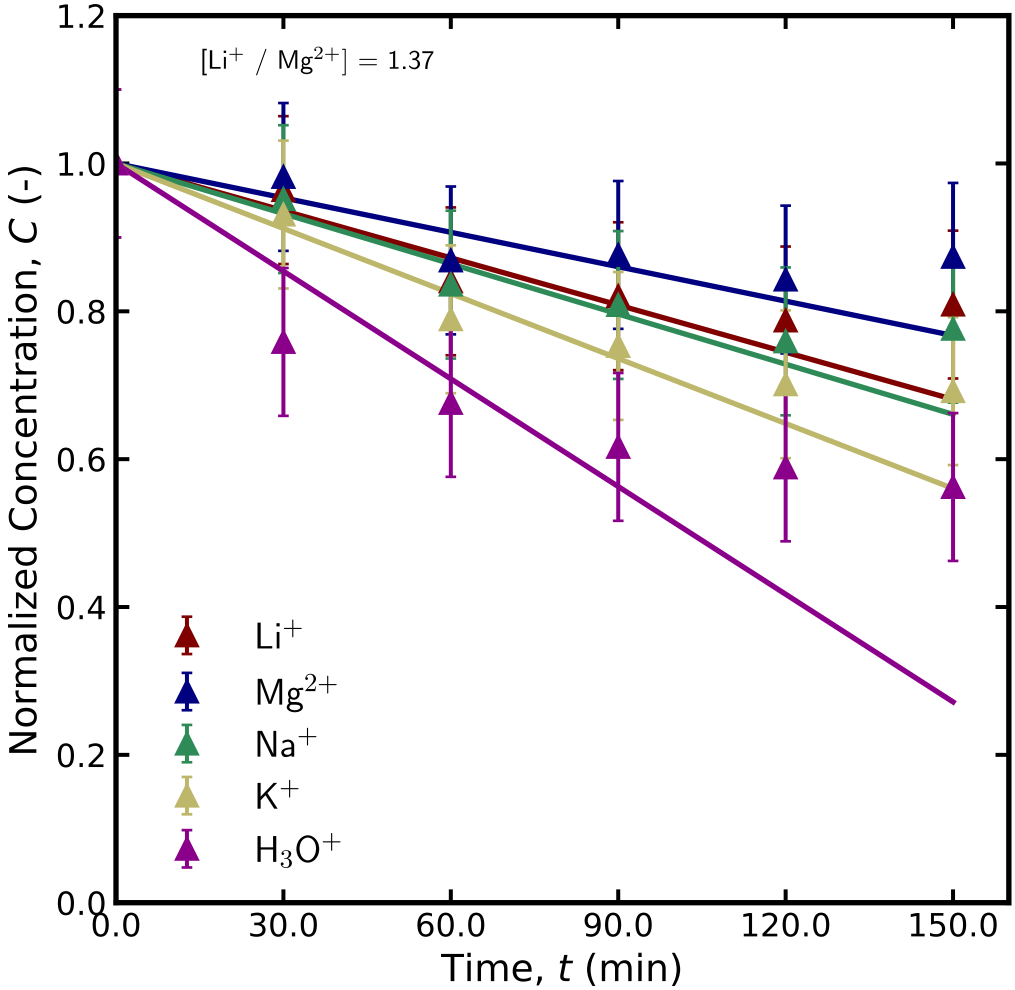


Figure 3-6: Normalized concentration over time in MSED trials of Chilean brine at 70 g/L , pH of 5 and current density of 0.5 A over 150 minutes. Concentrations shown are Li^+, Mg^{2+}, K^+, H_3O^+. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

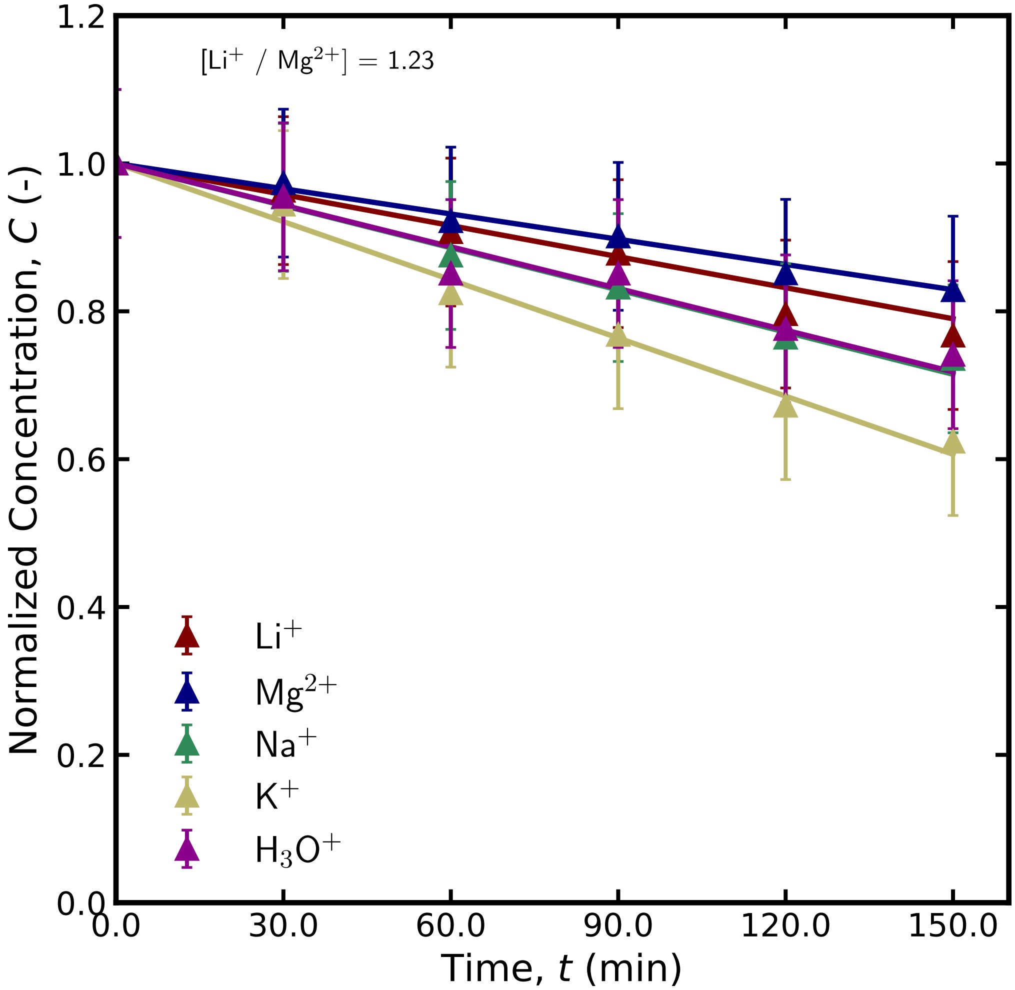


Figure 3-7: Normalized concentration over time in MSED trials of Chilean brine at 70 g/L, pH of 7 and current density of 0.5 A over 150 minutes. Concentrations shown are Li^+, Mg^{2+}, K^+, H_3O^+. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

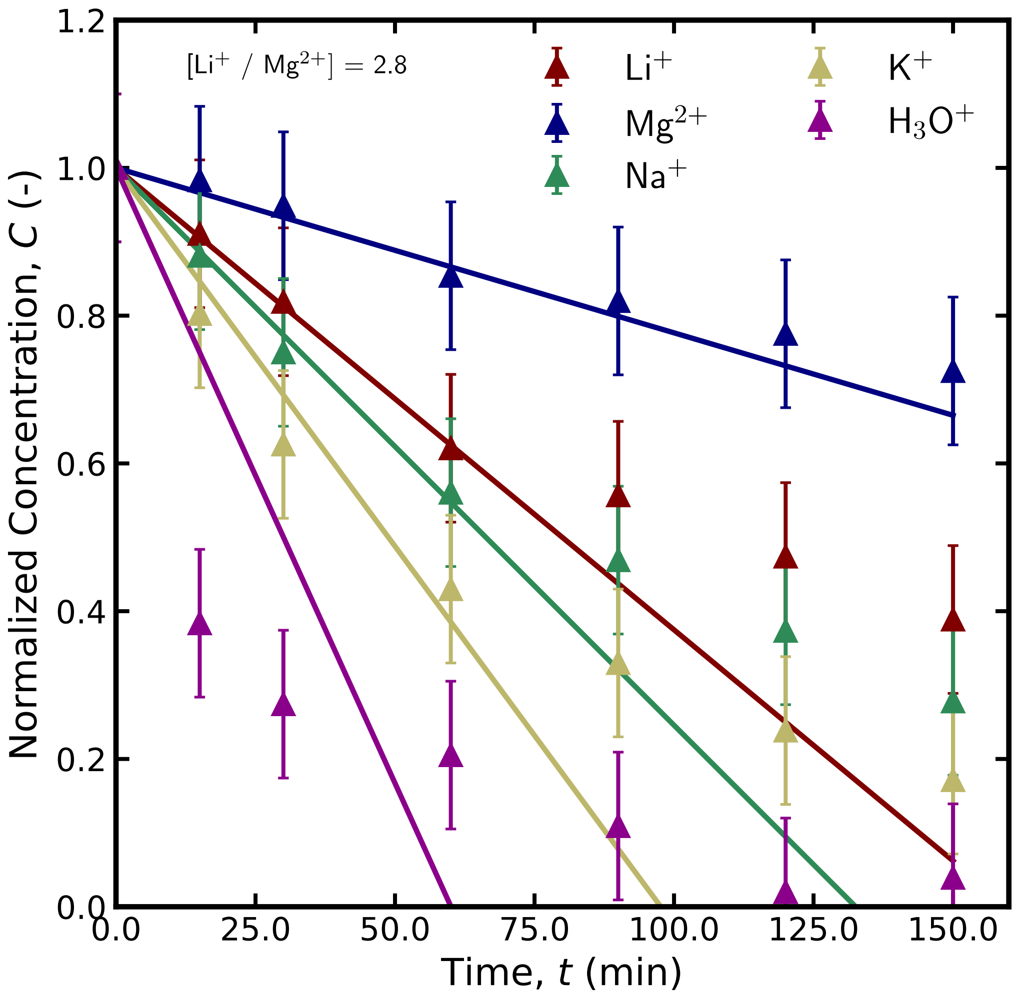


Figure 3-8: Normalized concentration over time in MSED trials of Chilean brine at 70 g/L, pH of 3 and current density of 3.0 A over 150 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

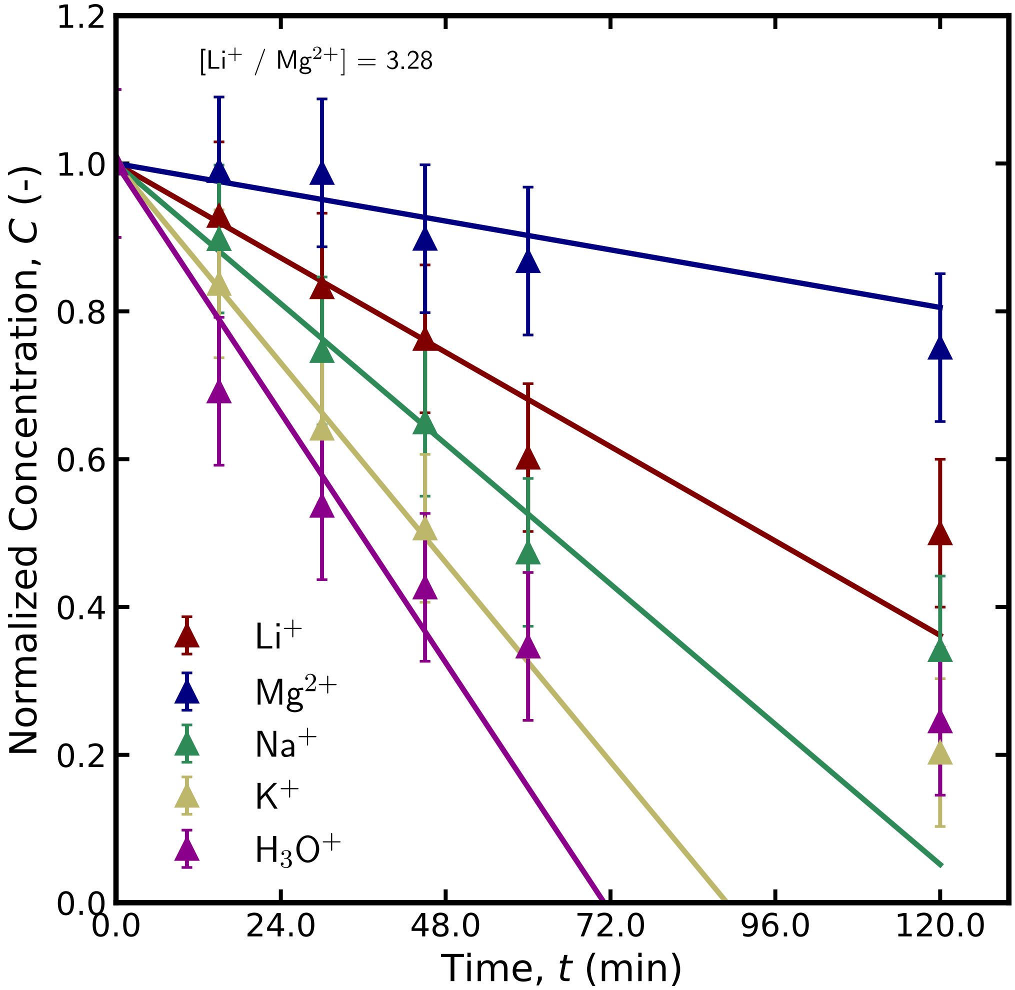


Figure 3-9: Normalized concentration over time in MSED trials of Chilean brine at 70 g/L, pH of 5 and current density of 3.0 A over 120 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

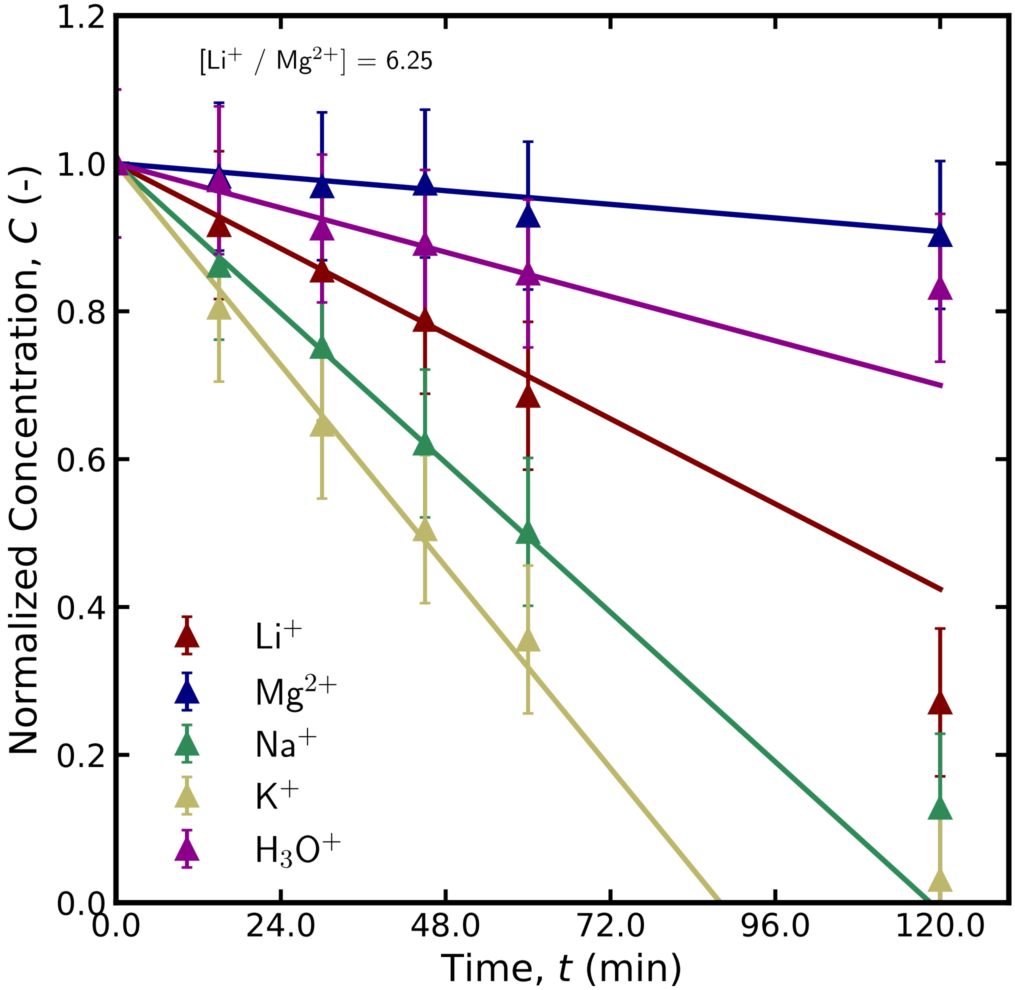


Figure 3-10: Normalized concentration over time in MSED trials of Chilean brine at 70 g/L, pH of 7 and current density of 3.0 A over 120 minutes. Concentrations shown are Li^+, Mg^{2+}, K^+, H_3O^+. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

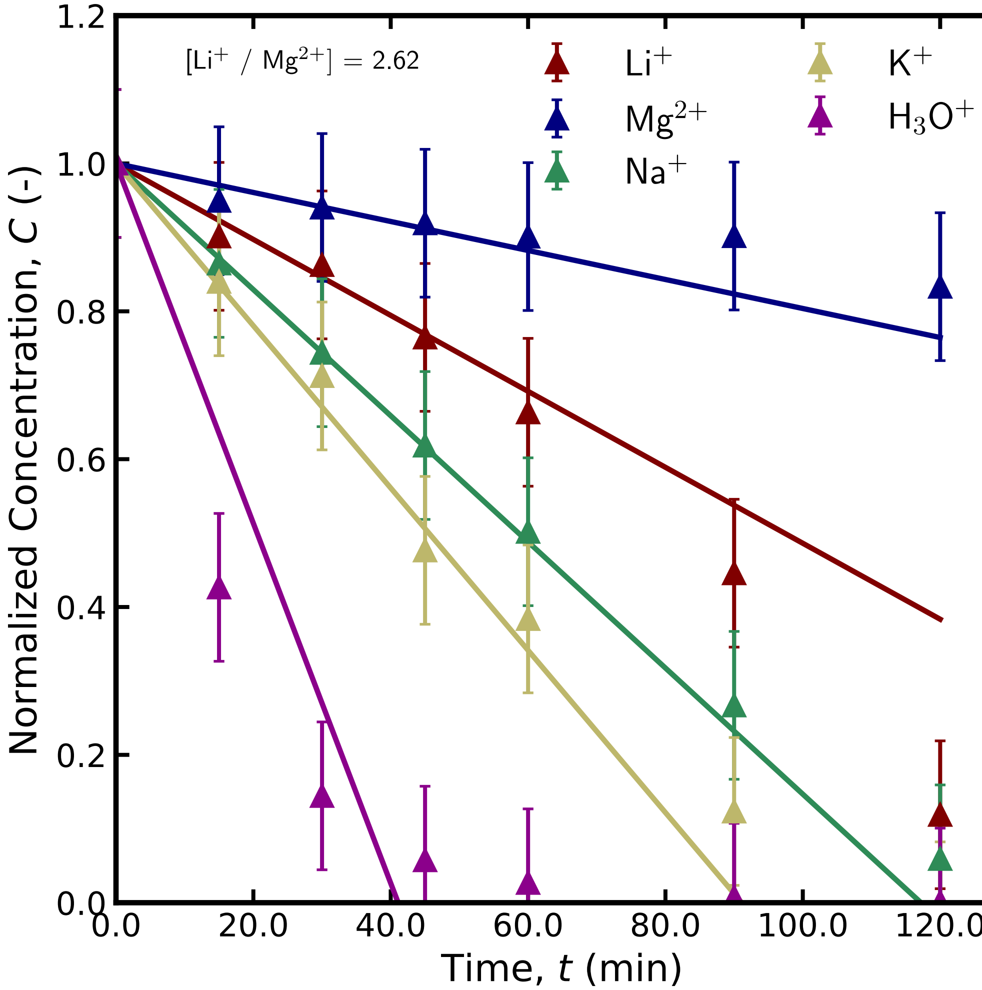


Figure 3-11: Normalized concentration over time in MSED trials of Chinese brine at 10 g/L, pH of 3 and current density of 0.5 A over 120 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

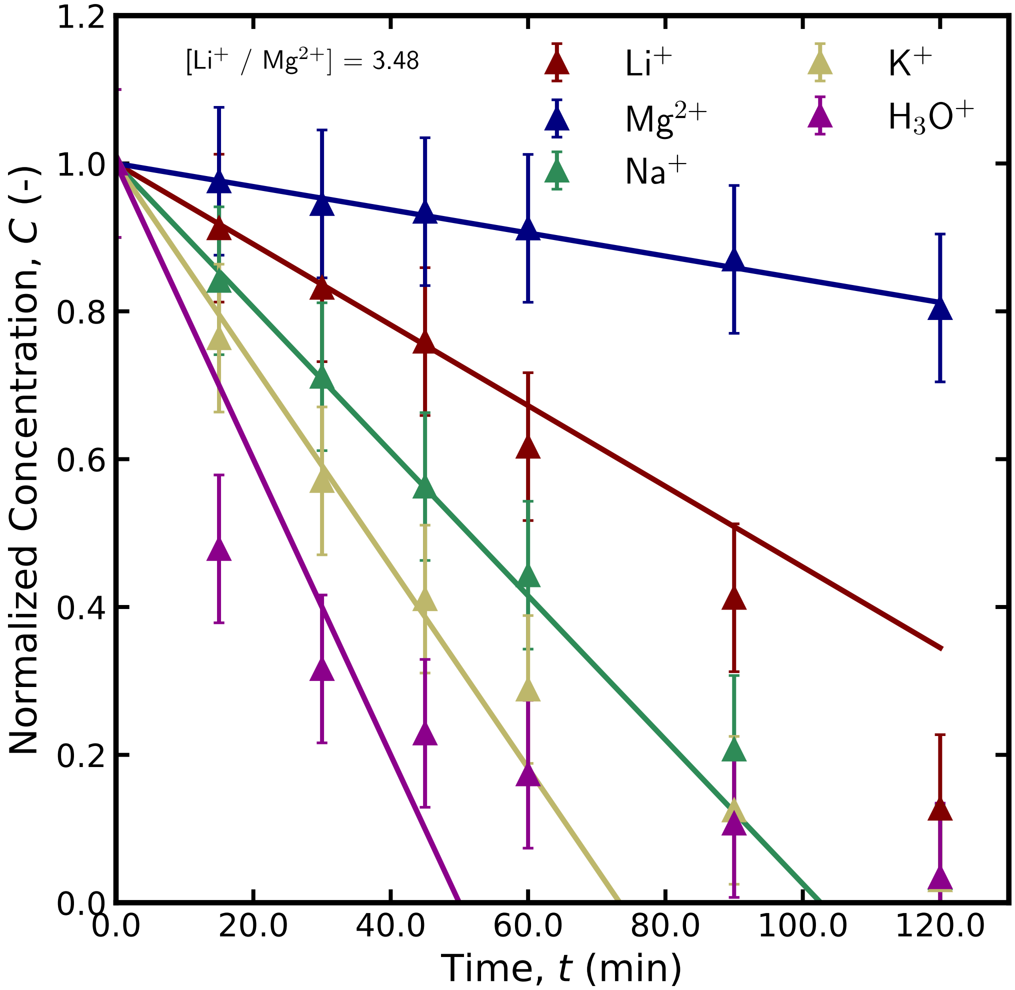


Figure 3-12: Normalized concentration over time in MSED trials of Chinese brine at 10 g/L, pH of 5 and current density of 0.5 A over 120 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

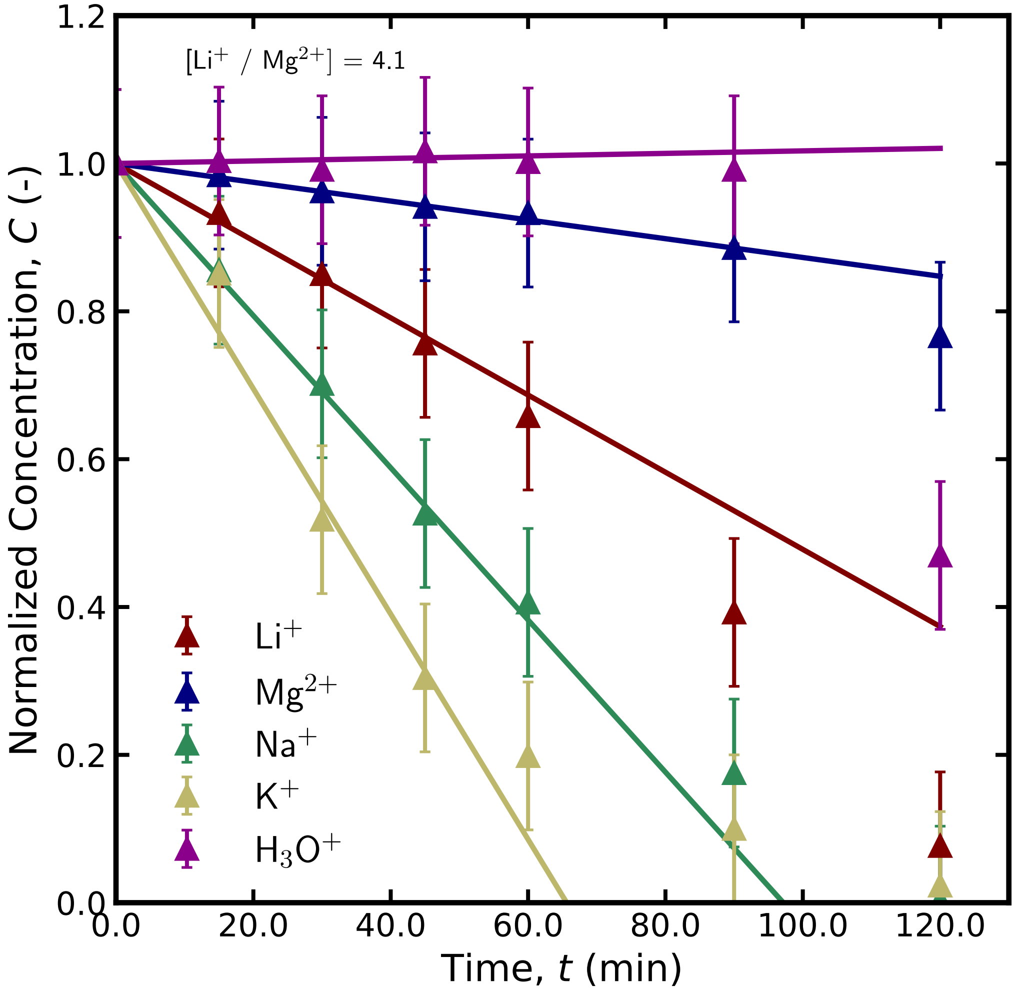


Figure 3-13: Normalized concentration over time in MSED trials of Chinese brine at 10 g/L, pH of 7, and current density of 0.5 A over 120 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

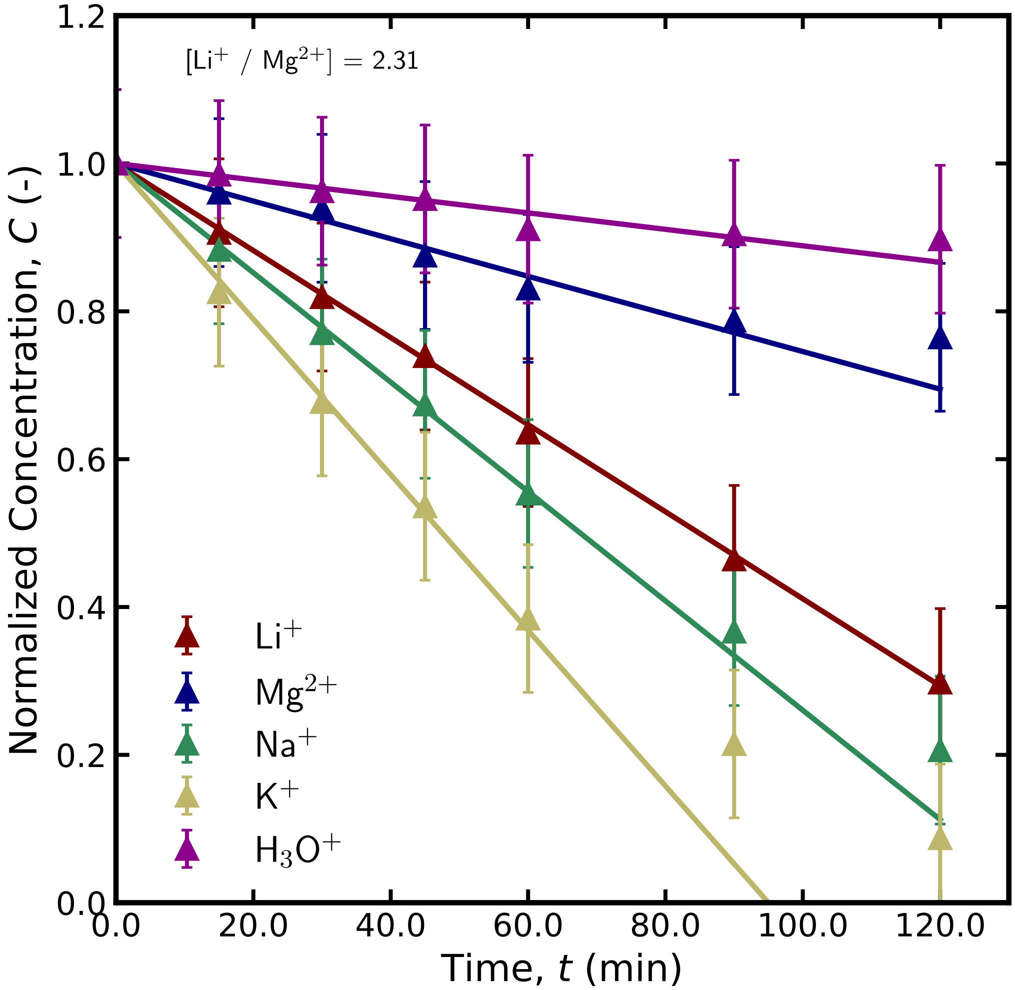


Figure 3-14: Normalized concentration over time in MSED trials of Chinese brine at 30 g/L, pH of 7, and current density of 0.5 A and pH 7 over 120 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

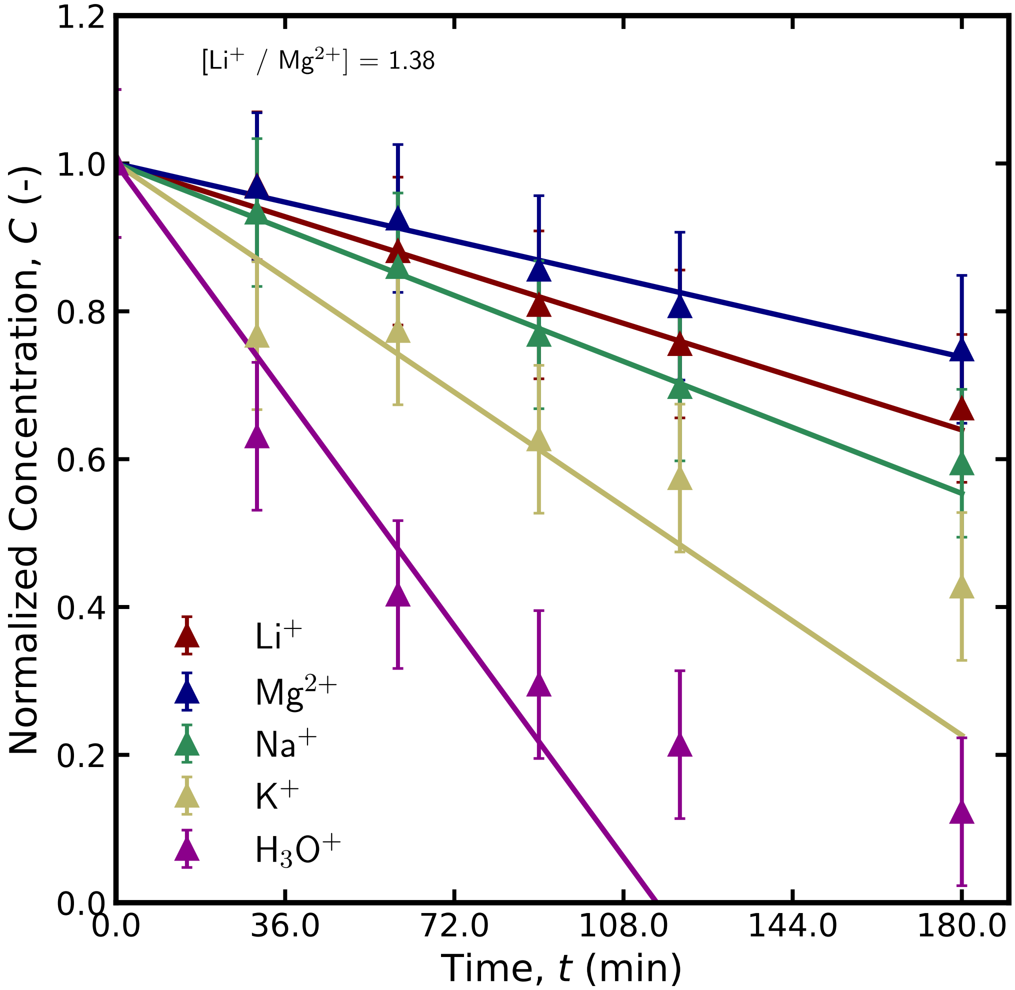


Figure 3-15: Normalized concentration over time in MSED trials of Chinese brine at 70 g/L, pH of 3, and current density of 0.5 A over 180 minutes. Concentrations shown are Li^+, Mg^{2+}, K^+, H_3O^+. Ratio of slopes of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

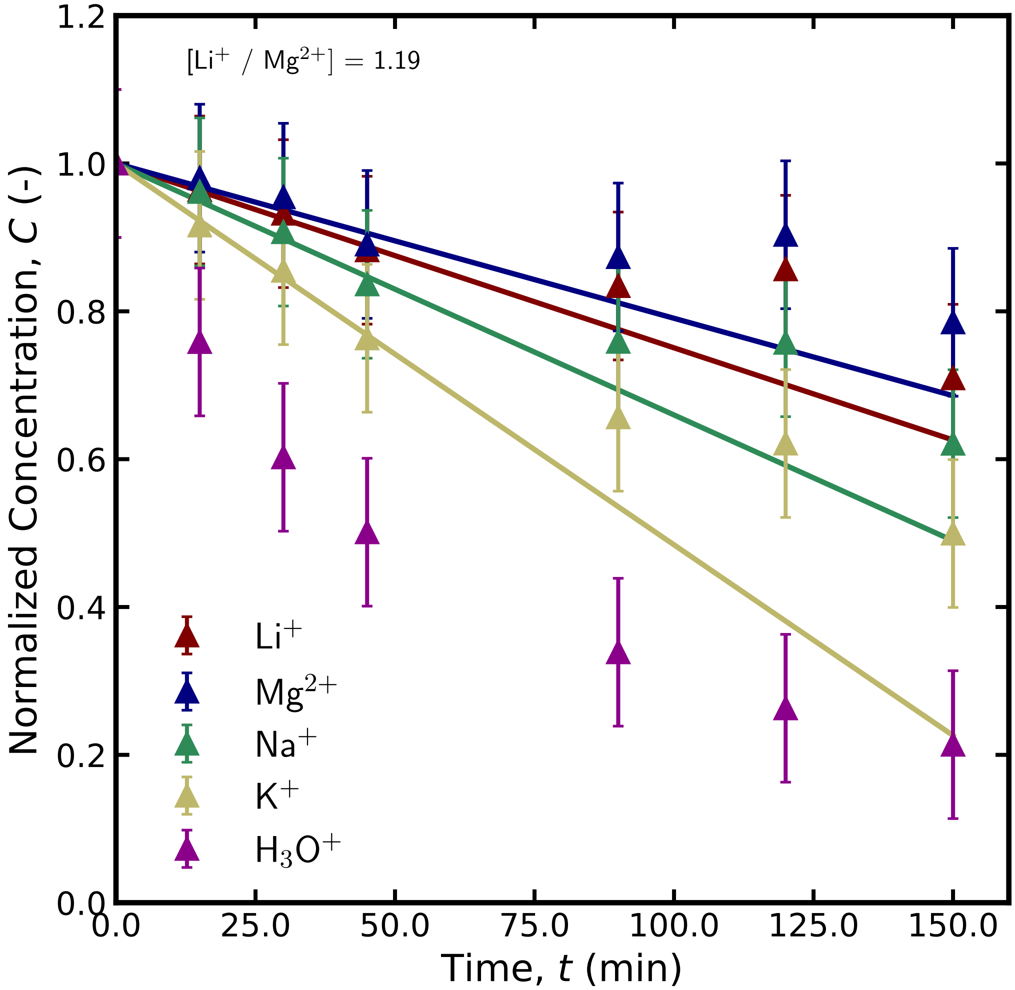


Figure 3-16: Normalized concentration over time in MSED trials of Chinese brine at 70 g/L, pH of 5, and current density of 0.5 A over 150 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

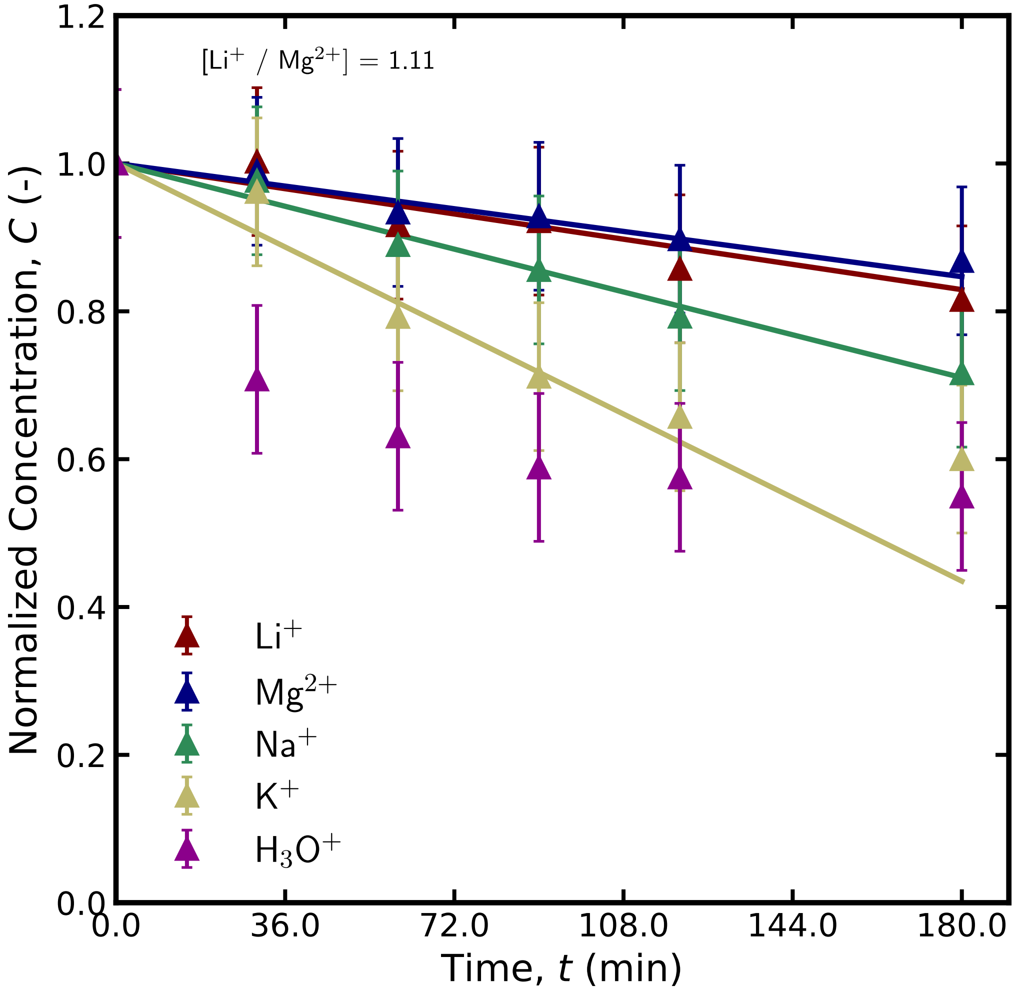


Figure 3-17: Normalized concentration over time in MSED trials of Chinese brine at 70 g/L, pH of 7, and current density of 0.5 A over 180 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

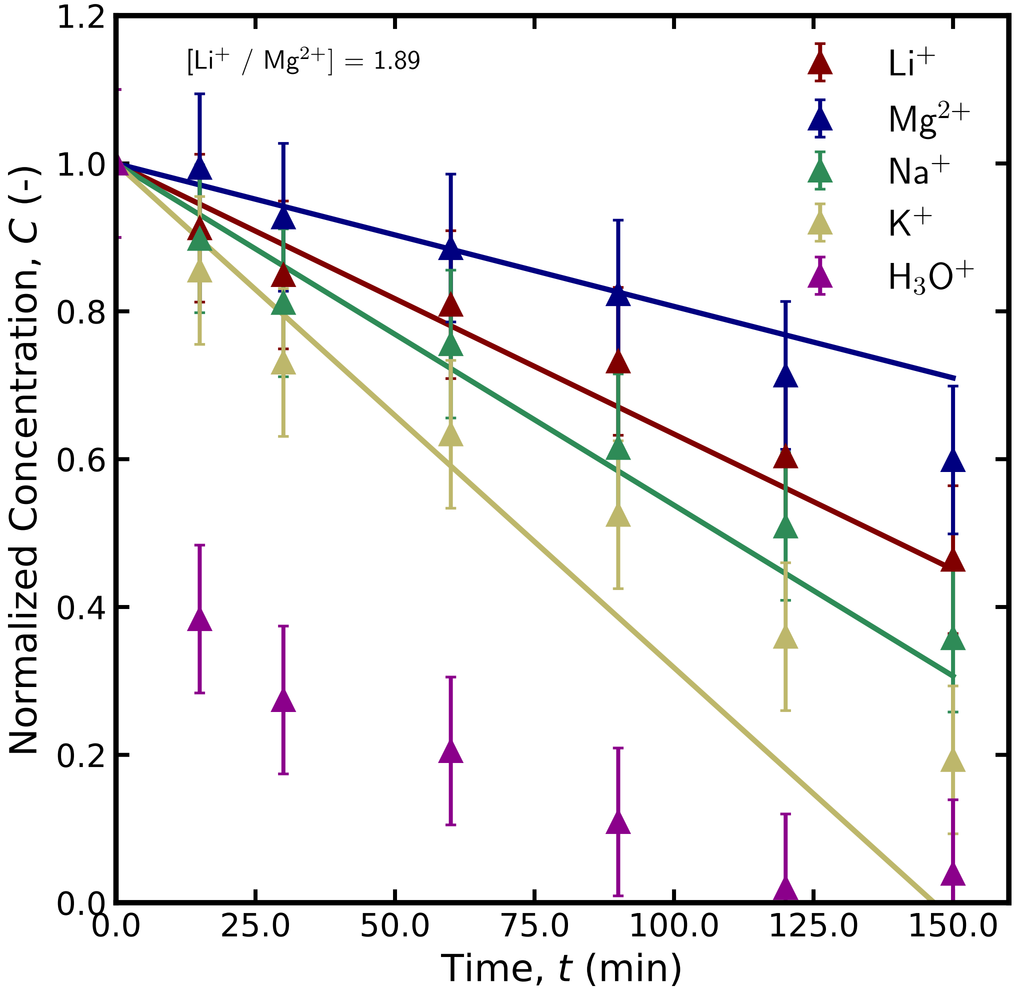


Figure 3-18: Normalized concentration over time in MSED trials of Chinese brine at 70 g/L and current density of 3.0 A, pH of 3, over 150 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficients of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

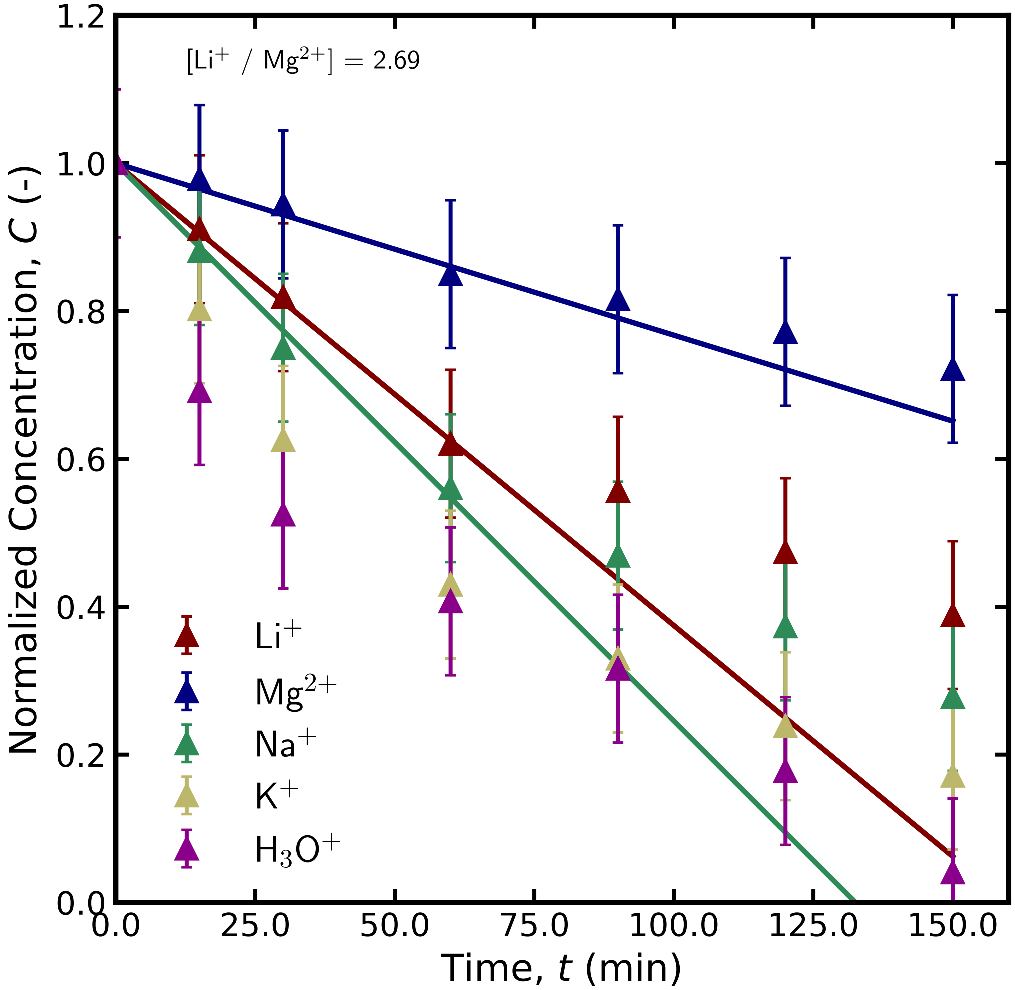


Figure 3-19: Normalized concentration over time in MSED trials of Chinese brine at 70 g/L, pH of 5, and current density of 3.0 A over 150 minutes. Concentrations shown are Li^+, Mg^{2+}, K^+, H_3O^+. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

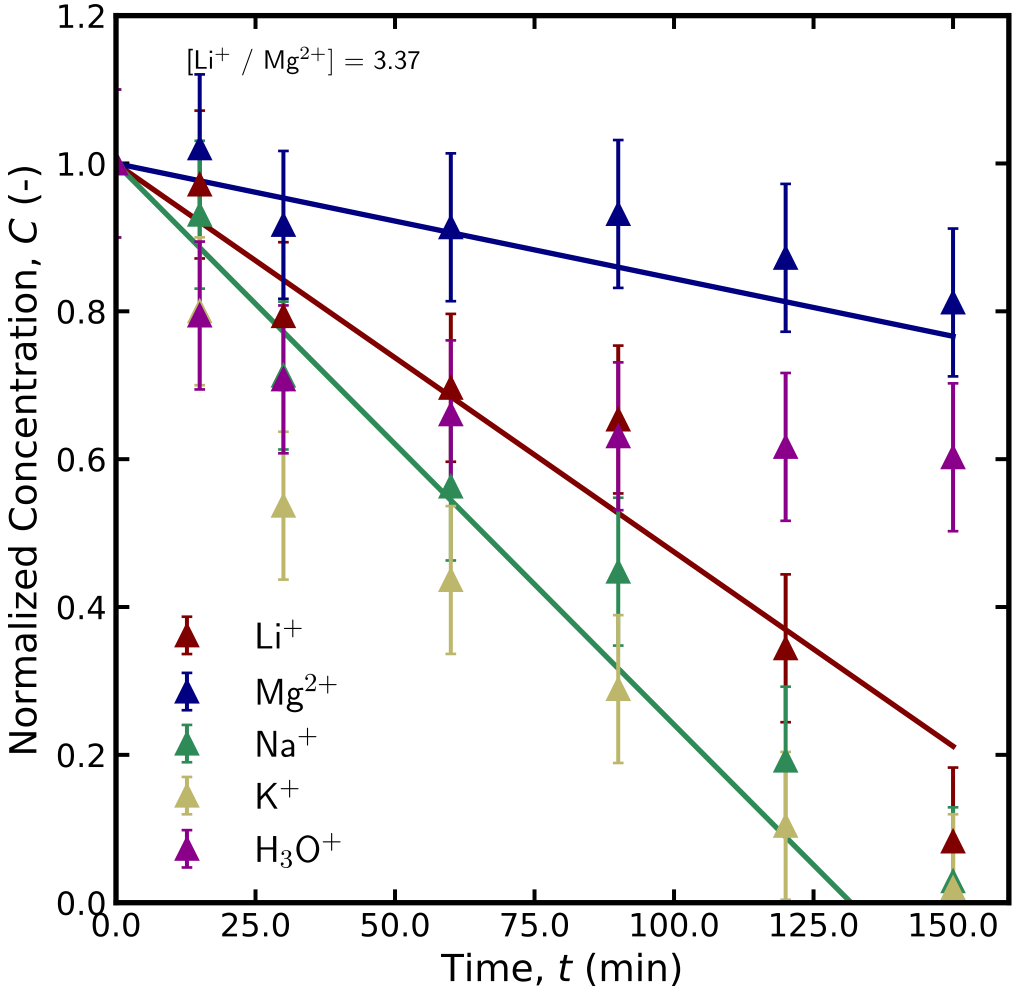


Figure 3-20: Normalized concentration over time in MSED trials of Chinese brine at 70 g/L, pH of 7, and current density of 3.0 A over 150 minutes. Concentrations shown are Li^{+}, Mg^{2+}, K^{+}, H_3O^{+}. The average separation coefficient of magnesium and lithium concentrations included showing lithium concentration dropping faster than magnesium concentration in the diluate.

3.2 Impact of Solution Simplification: Comparing Binary and Multi-component Brines

Figures 3-21, 3-22, and 3-23 illustrate the plots of the ion concentration over time of the various MSED trials with the binary brines. The binary brines (Table 2.1), having only magnesium as an additional cation, are theoretically easier solutions for the MSED to separate. At a current density of 0.5 A, these diluate solutions approach a lithium concentration of 0 within 100 minutes. The separation coefficient of lithium to magnesium concentration is over 10 with these brines, as shown in Figures 3-21, 3-22, and 3-23. The Chinese and Chilean brines at 0.5 A and pH 7 (Figures 3-11 and 3-1), however, never approach a lithium concentration of 0 and have separation coefficients of 4.1 and 5.85, much lower than the binary solutions. This difference results from the presence of other competing cations that attenuate the rate of lithium transfer. These experiments demonstrate that the derived separation efficiencies from binary solutions do not translate well to actual applications with multi-component brines.

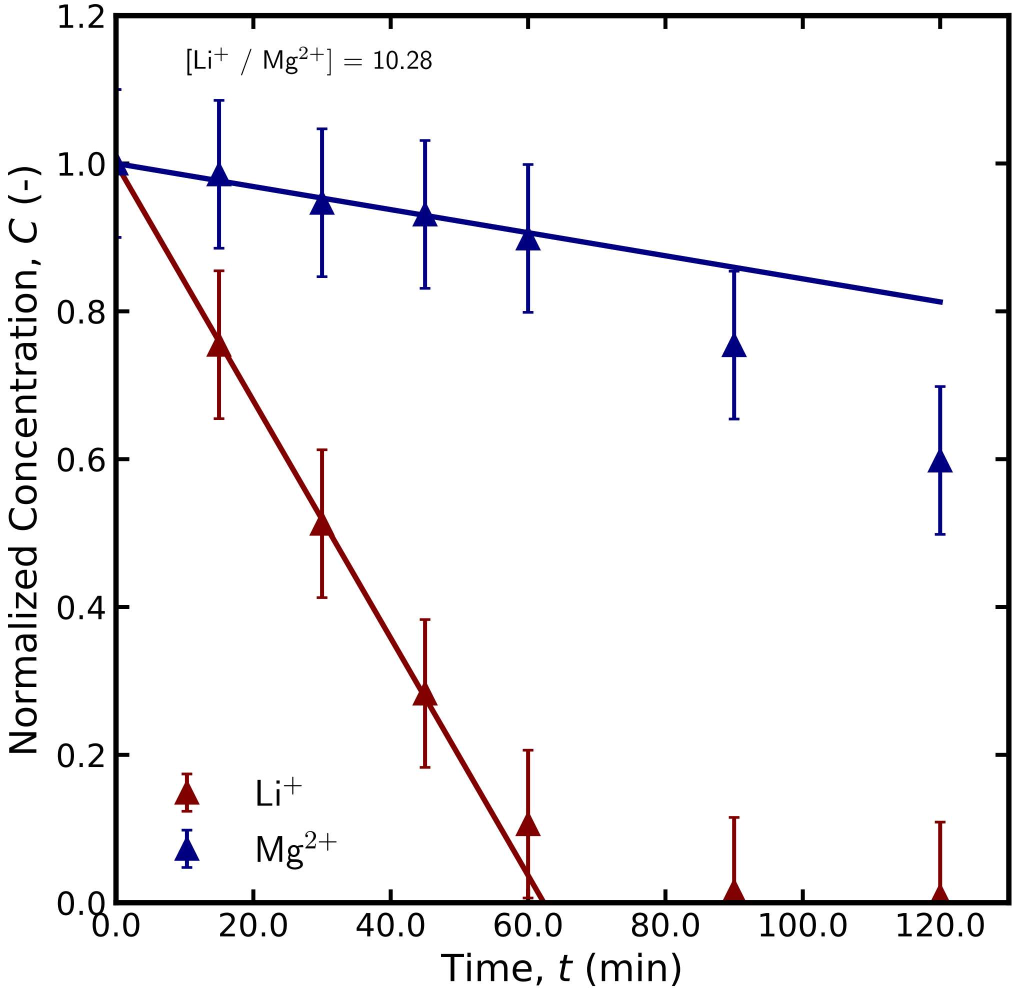


Figure 3-21: Normalized concentration over time in MSED trial of binary LM-C. Shown with MSED run at pH 7 and at 0.5 A current density over 120 minutes. Concentrations of cations shown decreasing over time, with the average separation coefficient of magnesium and lithium concentrations included showing that lithium concentration is dropping faster than magnesium.

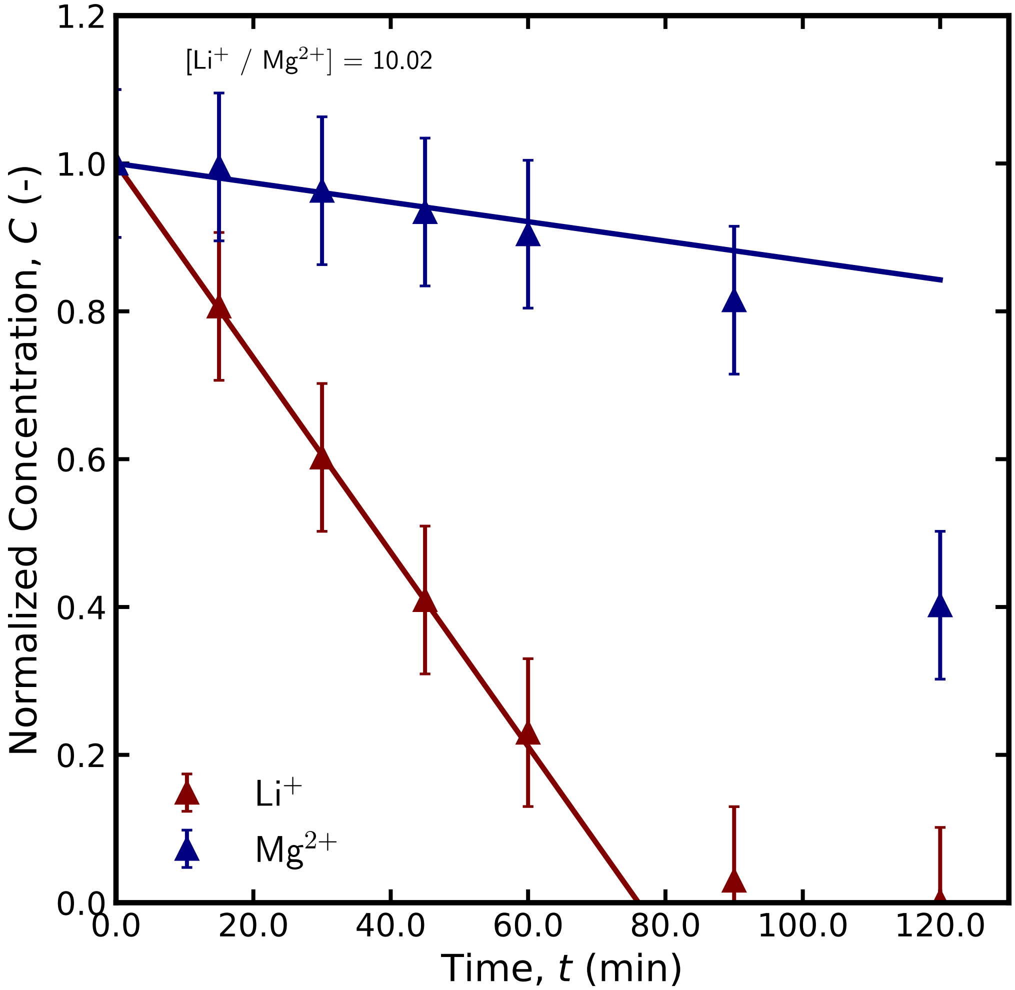


Figure 3-22: Normalized concentration over time in MSED trial of binary brine LM-S. Shown with MSED run at pH 7 and at 0.5 A current density over 120 minutes. Concentrations of cations shown decreasing over time, with the average separation coefficient of magnesium and lithium concentrations included showing that lithium concentration is dropping faster than magnesium.

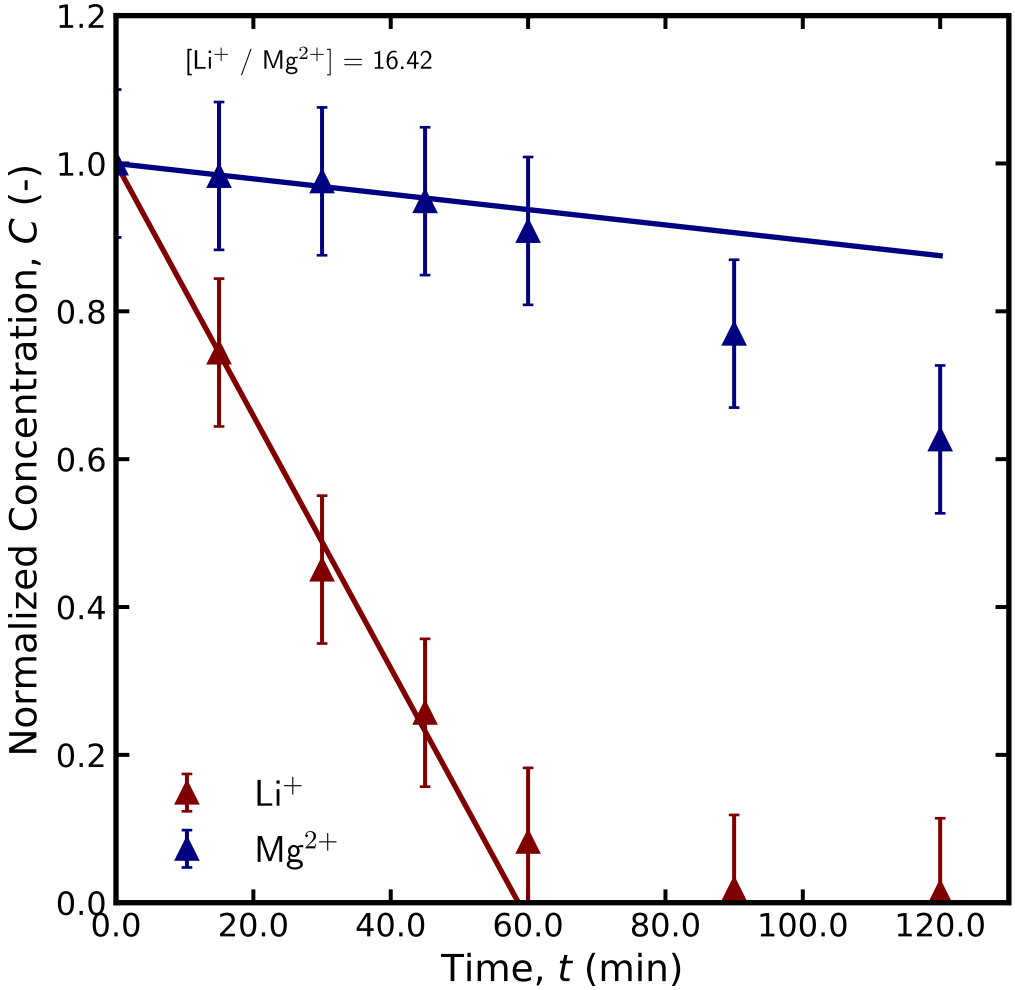
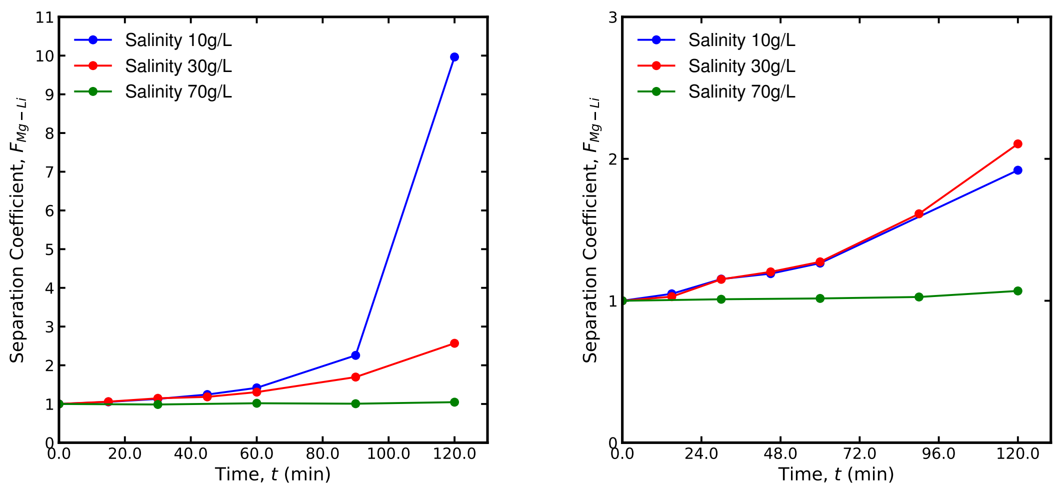


Figure 3-23: Normalized concentration over time in MSED trial of binary brine LM-CS. Shown with MSED run at pH 7 and at 0.5 A current density over 120 minutes. Concentrations of cations shown decreasing over time, with the average separation coefficient of magnesium and lithium concentrations included showing that lithium concentration is dropping faster than magnesium.

3.3 Effect of Salinity on Separation and Current Efficiency

In this section, we analyze the effect of varying solution concentration on the separation coefficient and the current efficiency. Figure 3-24 illustrate the trend in separation coefficient as a function of salinity and time, while Figure 3-25 analyzes the effect of the same parameters on the current efficiency.

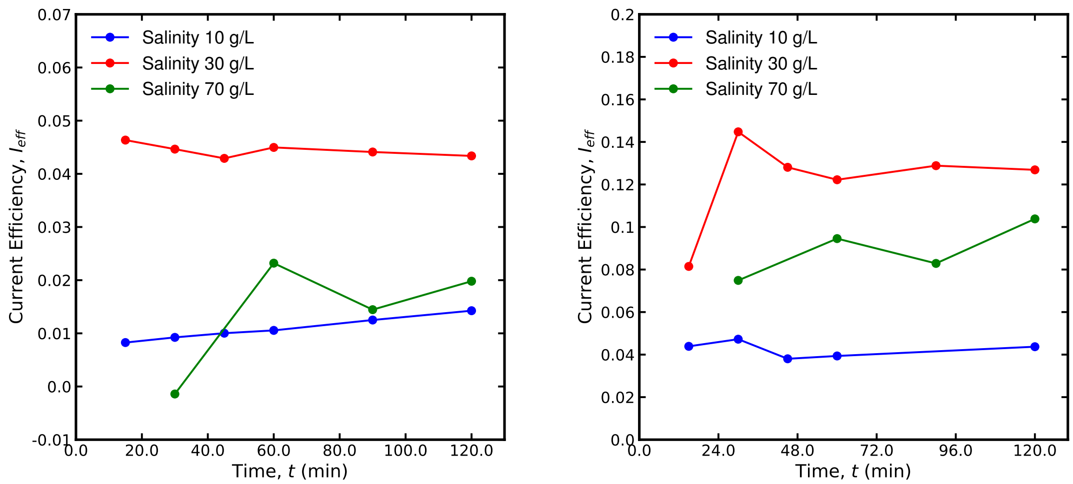


(a) Chinese Brine

(b) Chilean Brine

Figure 3-24: Separation Coefficients of MSED trials using 10 g/L, 30 g/L, and 70 g/L concentrations of brine. MSED performed at 0.5 A current density and pH 7.

Figure 3-24 shows that the separation coefficient decreases with increasing salinity for both the Chilean and Chinese brines. In both cases, brines at 70 g/L salinity has the lowest separation coefficient and the lowest current efficiency. In contrast, brines at 10 g/L salinity have the highest separation coefficient in the Chinese brine with higher current efficiency than the 30 g/L. The Chilean brine has similar separation coefficient at 30 g/L and 10 g/L but a lower current efficiency at 10 g/L. Both brines have the lowest current efficiency and separation coefficient at 70 g/L. These results indicate that the MSED is most effective with solutions of lower salinity and with lower concentrations of magnesium, supporting the conclusions from the earlier sections.



(a) Chinese Brine

(b) Chilean Brine

Figure 3-25: Current efficiencies of MSED trials using 10 g/L, 30 g/L, and 70 g/L concentrations of brine. MSED performed at 0.5 A current density and pH 7.

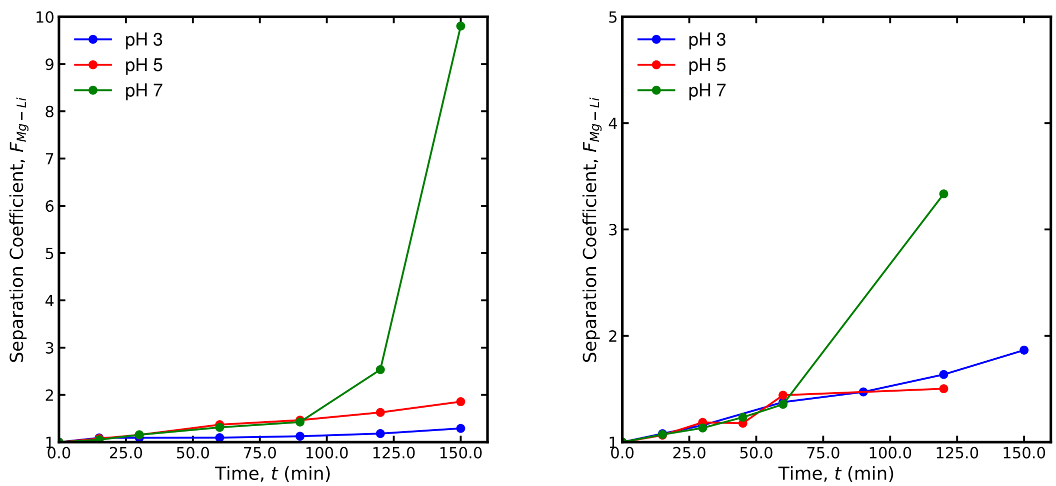
3.4 Effect of pH on Separation and Current Efficiency

In the earlier sections, the pH of the brine was shown to have a significant impact on the separation coefficient of MSED, as illustrated in Figure 3-26. The results indicate that brines with solution pH of 3 and 5 have similar separation coefficients while a solution pH of 7 has a much higher separation coefficient. The effect of the pH on the separation coefficients are summarized in Table 3.1, showing that the concentration of lithium dropped significantly faster in higher pH brines for both the Chinese and Chilean compositions.

Figure 3-27 shows the trend between the current efficiency as a function of solution pH and time, using experiments involving multi-component brines. Overall, the plot illustrates that the current efficiency for the different pHs are similar. Thus, for multi-component brines, it appears that no conclusive trends between pH and current efficiency can be drawn for MSED.

Table 3.1: Average rate of change of Li^{+}/Mg^{2+} concentration for MSED at 70 g/L with 3.0 A current density with varying pH.

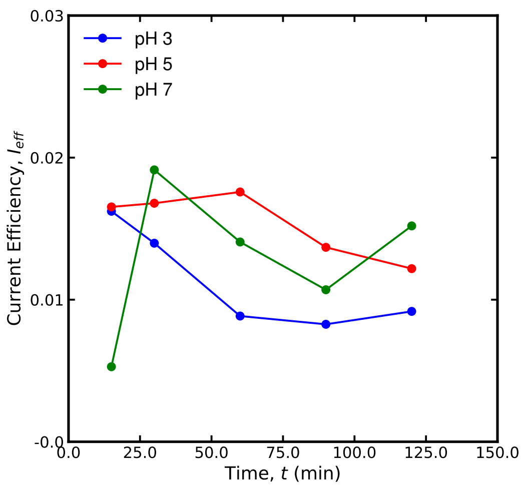
	pH 3	pH 5	pH 7
Chinese Brine	1.89	2.69	3.37
Chilean Brine	2.80	3.28	6.25



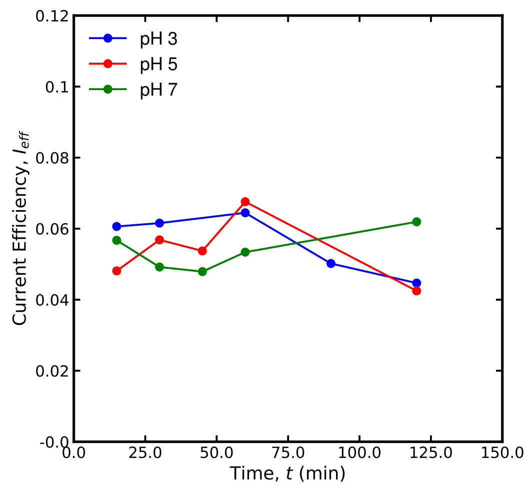
(a) Chinese Brine

(b) Chilean Brine

Figure 3-26: Separation Coefficients of MSED trials using brines of pH 3, pH 5, and pH 7. MSED performed at 3.0 A current density and 70 g/L salinity.



(a) Chinese Brine



(b) Chilean Brine

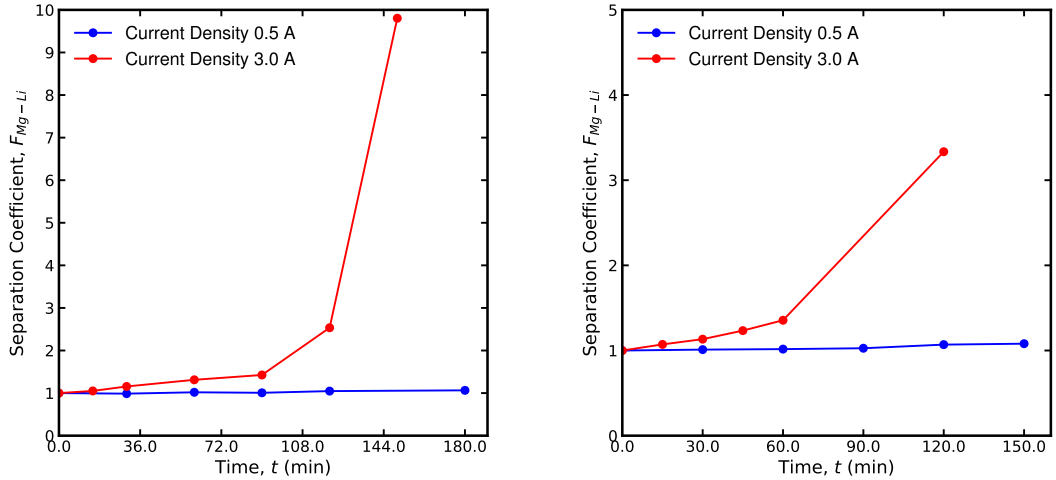
Figure 3-27: Current efficiency of MSED trials using brines of pH 3, pH 5, and pH 7. MSED performed at 3.0 A current density and 70 g/L salinity.

3.5 Effect of Current Density on Separation and Current Efficiency

The separation coefficients of current densities 0.5 A and 3.0 A for both Chinese and Chilean brines are shown in Figure 3-28. The separation coefficients demonstrate that, at higher current density, lithium is removed at at a much faster rate from the diluate solution. This is especially true with the Chinese brine which has a lower concentration of lithium as compared to the Chilean brine.

The current efficiencies of the experiments with current densities of 0.5 A and 3.0 A, for both Chinese and Chilean brines, are shown in 3-29. The general trend with these is that the lower current density yields to a slightly higher current efficiency. The separation coefficient, however, increases substantially with higher current density. The low initial concentration of lithium in the Chinese brine means that its separation coefficient increases dramatically as the concentration of lithium approaches 0.

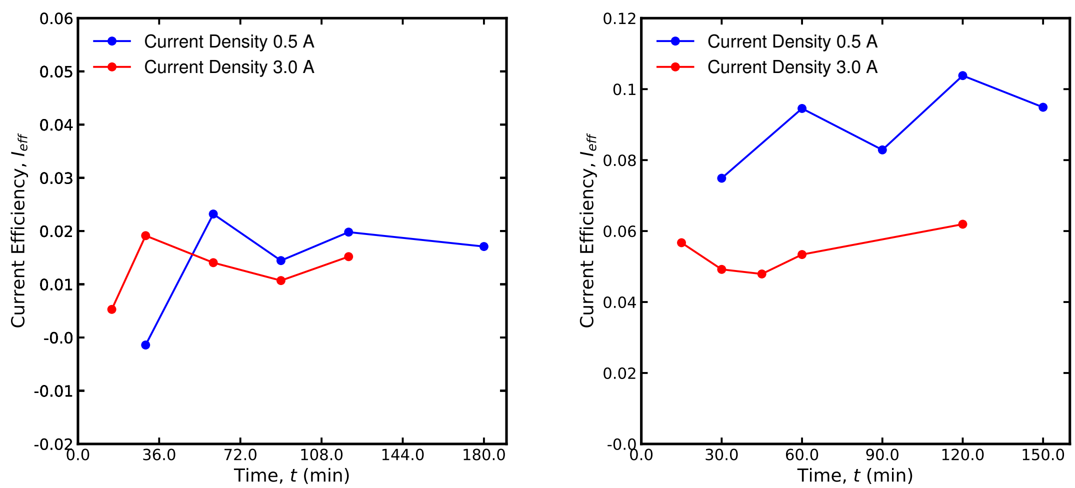
Since the separation coefficient improves with higher current density and the current efficiency drops, there is a trade off with running at a higher current density. The separation coefficient increased by at least 3x while the current efficiency dropped by less than 50%. The trade off of using the higher current density would be decided by the costs of the electricity and operating the MSED device but is beyond the scope of this study.



(a) Chinese brine

(b) Chilean brine

Figure 3-28: Separation Coefficients of MSED trials at current densities of 0.5 A and 3.0 A. MSED performed at 70 g/L salinity and pH 7.



(a) Chinese brine.

(b) Chilean Brine

Figure 3-29: Current Efficiency of MSED trials at current densities of 0.5 A and 3.0 A. MSED performed at 70 g/L salinity and pH 7.

Chapter 4

Conclusions

A monovalent selective electrodialysis setup was used to test conditions of pH, salinity, coexisting cations, and current density in the effectiveness in lithium extraction from salt lake brines. Higher salinity brine resulted in a 10x lower separation coefficient without a significant difference in current efficiency compared to low salinity brine in the Chines brine. Lower concentration of lithium, however, does mean that less lithium in total may be migrated. This efficiency is out of scope of the exercise but should be further evaluated.

A brine pH of 7 yielded at least 1.5x increased separation coefficient of lithium compared to pH 3 and 5, without an observable difference in current efficiency. Further trials would be required to determine whether a higher pH would further improve the effectiveness of the MSED. A current density of 3.0 A compared to 0.5 A resulted in over 3x higher separation coefficient while the current efficiency decreased by less than 50%. While there is not often control over the coexisting ions in brine, the multi-component studies show that limiting the number of coexisting ions results in 2x more effective separation of lithium from magnesium in MSED.

The results of this study show that lower salinity, higher pH and higher current density yield significantly more effective lithium migration in MSED without a comparable decrease in current efficiency. More experiments with pH, salinity, and current density would be required to determine the optimal conditions for MSED of each brine. This study shows that pH above 5, salinity below 70 g/L and current density above 0.5 A should be evaluated in future research to determine the ideal conditions of MSED for each brine. These conditions, combined with cost evaluations of the migration speed, separation coefficients, and energy consumed by MSED, would yield a comprehensive analysis of MSED of salt-lake brines that could be compared to other methods of lithium separation.

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