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Electrodeionization versus Electrodialysis: A Clean-Up of Produced Water in Hydraulic Fracturing

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Citation

Electrodeionization versus Electrodialysis: A Clean-Up of Produced Water in Hydraulic Fracturing

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By

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Abstract

Electrodeionization (EDI) is a widely studied process ranging from applications in wastewater clean-up in the food and beverage industry to purifying organic compounds. To date, there are no apparent studies on applying this technology to produced wastewater recovered from hydraulic fracking sites. Water consumption within hydraulic fracturing sites can reach in the upwards of millions of gallons per site, so a need for a water recycling process becomes necessary within areas where water requirements are scarce. Implementation of an EDI module that is capable of handling high salt solutions from produced wastewater in subsequent fracturing practices will decrease overall water demands, making this an environmentally sustainable process as well. This study will focus on the selective removal of high concentrations of ions using ion-selective membranes and ion exchange wafers in Wafer-Enhanced Electrodeionization (WE-EDI) of hydraulic fracturing solutions for improved water recovery and reuse within industrial applications. Experiments were performed using a WE-EDI setup with varied wafer composition and thickness in comparison with electrodialysis for selective removal of divalent ions (Ca^{2+}) over monovalent ions (Na^+) from simulated and fracking solutions. Research sought to show that when increasing the wafer thickness and changing the composition (weak acid compared to strong acid resins) there would be a greater overall current efficiency observed and subsequently lower power consumption. This research concluded that there is some degree of enhanced selectivity with increased wafer size, as well as varied composition compared to a traditional ED system. Continued research is recommended to conclude uncertainties, eliminate areas of system performance error and to further solidify all hypothesises within this research.

Acknowledgements

Special thanks go to my advisor through this process, Dr. Jamie Hestekin. Your persistence and faith in me as a graduate student afforded me an opportunity I wouldn't of had otherwise and your kindness and encouragement saw me through these past two years. For being a mentor, boss and friend, I am forever grateful.

I would also like to thank Dmytro Demydov, postdoctoral and research guru. You kept the labs running smoothly and your expert input was unquestionably a reason for this research getting from start to finish and through every mishap in between.

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Dedication

To my mother, father, sister, and brother. You four have been my foundation for 25 years and I thank you for imparting in me the strength to complete this journey. I am truly blessed to call you my family.

Table of Contents

Introduction

Electrodeionization (EDI) is a process typically studied for the removal of low ion concentrations from solution. This study sets focus on the selective removal of high concentrations of ions using ion-selective membranes and ion exchange wafers in Wafer-Enhanced Electrodeionization (WE-EDI) of hydraulic fracturing solutions for improved water recovery and reuse within industrial applications. Water consumption within hydraulic fracturing sites can reach anywhere between 2-13 million gallons per site (1-2) creating a need for a water recycling process within areas where these high water requirements are hard to meet. Approximately 90% of the fracturing fluid injected remains bounded within the shale development, while the remaining 10%, known as flowback returns to the surface as a mixture of various metals, radionuclides, and organic compounds (3-4). These include high concentrations of Na, Ca, and Cl being the most likely ions detected, while Sr, Ba, and Br are more highly specific compounds found within flowback waters. Table 1 (below) details the typical range of concentrations for common constituents of flowback water within the Marcellus Shale. In addition, radioactive radium is commonly present in produced waters, yielding low concentration radioactive waste that has a potential for on-site human health implications if not handled appropriately (4). This water is referred to as "produced water" upon the well producing gas and is subsequently recovered throughout the well's lifetime (3). This process can produce wastewater with widely varied water quality characteristics across different regions, most notably total dissolved solids (TDS) levels ranging from approximately 10,000 to 300,000 ppm (1, 4-6). Treatment and management strategies for this produced/flowback water are constrained by environmental regulations, government, economics and overall technology performance and advancement (5). There are multiple methods for disposing of produced water include deep-well injection, industrial or municipal waste treatment, and reuse (4, 7). Currently, deep-well injection is the most utilized method

for produced water disposal. However, the availability of adequate deep-well disposal capacity can be an important constraining factor for shale gas development. Another treatment method studied in the clean-up of produced waters is reverse osmosis, which is considered economically infeasible for waters containing more than 40,000 mg/L TDS. There is also the option to discharge to publicly owned treatment works (POTWs) for dilution disposal, but the amount of high-TDS flowback water that can be accepted by POTWs is usually limited by regulations (5). On-site reuse for hydraulic fracturing has shown to be one of the most promising technologies for management of produced waters and is particularly attractive in regions where deep-well disposal is not readily available or where water is scarce. Implementation of an EDI module that is capable of handling high salt solutions from fractured water for reuse in subsequent fracturing will cut on overall water demands. WE-EDI setup was studied with varied wafer composition and thickness in comparison to electrodialysis for selective removal of divalent ions to meet standard EPA requirements for reuse and to save on operational costs.

The purpose of this study was to test the favourability of a WE-EDI setup in comparison to electrodialysis with ion exchange membranes for selective separation of high ionic concentrations in produced water recovered from hydraulic fracturing sites. Electrodialysis (ED) is a process that promotes ionic transfer through a semi-permeable membrane by applying opposing electric fields on either end of the system to act as a driving force. Ionic separation by ED has been a desirable study for a multitude of water and wastewater treatment practices with focus being placed on improving overall TDS removal and water recovery in these specific applications (8-16). These include extensive studies on high removal rates (95-99%) of both monovalent (Na, K, Cl) and divalent (Zn, Ca, Pb, Mg) ions within the system. Current efficiency was found to be in the lower range of 60-80% and upwards of 85-90% depending on solution concentration levels (13-14, 17-18). One

experiment by Sirivedhin et. al. studied salt removal by electrodialysis and noted that excessive sodium in proportion to calcium and magnesium cause water penetration to decrease overall and power required to treat high TDS water was approximately 23 times higher than power required for low TDS water (9). Electrodialysis has also been studied as a means of concentrating solutions as a cost effective alternative in organic acid purification within the chemical industry (19-20).

Implementing ion-exchange resins further improves this purification process and improves acid recovery through selective transport (21-22). EDI combines this selective separation of ions with the continuous processing of electrodialysis by incorporating ion-exchange resins within the diluate compartment (23). This application of resins in the diluate compartment has multiple advantages, including water dissociation that leads to an electrochemical regeneration of the resin and promotes removal efficiency (24-33), enhanced solution conductivity and ionic transport across the system. This also counteracts the concentration polarization occurring within ED setups, which is evidenced by an increase in the maximum ion separation efficiency (34).

Compared to electrodialysis, WE-EDI is capable of concentrating solutions of high salt concentrations down to significantly lower concentrations through the addition of ion exchange resins (25, 34). Ionic exchange is a diffusive process between cations and anions within solution. Compacted wafers are comprised of both cationic and anionic exchange resins bonded by polymer and sugar to create a porous material, which aids in attracting and transporting ions from solution more efficiently. EDI operates without the addition of regenerative agents or other chemicals due to this ion-exchange process (35). Multiple methods have been formulated for creating ionic exchange wafers from resins (23, 36-37). Ion exchange wafers are comprised of both anion and cation exchange resins, polymer, and sucrose in a 23:23:15:10 ratio (anion:cation:sugar:polymer). Resin compositions utilized in

studies will be strongly acidic anion exchange resins, weakly acidic anion exchange resins, and strongly basic cation exchange resins. For the purpose of this study, the same ratio (polyethylene, sugar, resins) will be used for all experimental runs with only variations in resin composition. Ion removal can progress well beyond the limiting current density obtained through electrodialysis and a higher recovery of ionic products can be obtained through WE-EDI (23, 34). Although EDI has been studied in great length on a multitude of water treatment applications, it has not yet been applied to the treatment of produced water from hydraulic fracturing sites. As such a patent application has been filed for this innovative wastewater treatment system and method. The patent claims include a first sub-system that removes suspended solids and free/soluble oil from wastewater and a second sub-system that removes targeted ions, including calcium and sodium tested within this thesis, from wastewater. Other claims include ED and EDI wastewater treatment systems and methods associated with these processes, including one or more ion exchange wafers configured to selectively remove a targeted ion to a predetermined maximum level of concentration (40). This research will examine the various wafer compositions, including resins and wafer thickness, and their overall affect on ion selectivity, current efficiency and power consumption within an EDI system. Furthermore, this will be compared for advantages to the more traditional method of wastewater clean-up, electrodialysis.

Constituent	Low[2] (mg/L)	Medium[2] (mg/L)	High[3] (mg/L)
Total dissolved solids	66,000	150,000	261,000
Total suspended solids	27	380	3200
Hardness (as $CaCO_3$)	9100	29,000	55,000
Alkalinity (as $CaCO_3$)	200	200	1100
Chloride	32,000	76,000	148,000
Sulfate	ND[5]	7	500
Sodium	18,000	33,000	44,000
Calcium, total[4]	3000	9800	31,000
Strontium, total	1400	2100	6800
Barium, total	2300	3300	4700
Bromide	720	1200	1600
Iron, total	25	48	55
Manganese, total	3	7	7
Oil and grease	10	18	260
Total radioactivity	ND[5]	ND	ND

Table 1. Typical range of concentrations for some common constituents of flowback water from natural gas development in the Marcellus Shale (5)

Experimental

I. Wafer Composition and Production

Each ion exchange wafer utilized were comprised of both anion and cation exchange resins, polymer (Polyethylene, 500 micron), and sucrose in a 23:23:15:10 gram ratio of anion:cation:sugar:polymer (23). The mixture was uniformly combined using a FlackTek Inc. SpeedMixer^{TM} (model: DAC 150 SP) at a rate of 300rpm for 3-5 seconds. This mixture was doubled to compensate for a 4 mm wafer. Anionic and cationic resins used included Amberlite® IR120 Na$^+$ form (strongly acidic), Dowex® MAC-3 hydrogen form (weakly acidic), and Amberlite® IRA-400 chloride form. Anionic resin was chosen based on desired wafer composition needed to carry out experimentation and similarities in exchange capacity volumes. Combined mixture was cast in a steel mold and placed in a Carver press (model 3851-0) heated to 237 °F at 10,000 psi for ninety minutes. This was followed by a twenty minute cooling period via pressurized air treatment. The wafer was pre-soaked in deionized water for approximately 24 hours to insure that the sucrose completely dissolved and then cut to size to fit within the spacer of equal dimensions (2mm or 4mm). Both ED and EDI were performed within the same Micro Flow Cell (ElectroCell North America, Inc.) for consistency purposes and the wafer was simply replaced with a turbulence grate for ED. The Micro Flow Cell was tightened to 30 in-lbs across all bolts to ensure even flow throughout the system and prevent leaking outside of the cell.

II. ED/EDI Setup and Sample Collection

Setup for wastewater clean-up required preparation of four separate solution chambers of equal volume but varied concentration. The concentrate chamber was 250 mL of 2% wt. (20g/L DI water) sodium chloride solution and both rinse chambers were 250 mL of 0.3M (27g/2L DI water) sodium sulphate (Na_2SO_4) solution. The permeate chamber varied to allow

for both pure fractured water and simulated solution to be tested within the cell stack. Pure fractured wastewater from Beasley, Texas was pre-treated by membrane separation technology known as vibratory shear-enhanced processing (VSEP). In this process, flat membranes are arranged as discs in parallel are separated by gaskets. Shear is then created by vibration, which lifts solids and fouling material off the membrane surface (5). Simulated solution was created to focus solely on sodium and calcium concentrations typically found in fracking wastewater. To create a mixed solution, 10,000 ppm (10 g/L DI water) of calcium chloride and 50,000ppm (50g/L) of sodium chloride was combined and 250 mL was added to the permeate chamber. This was also altered to solely test 10,000 ppm calcium chloride and 50,000 ppm sodium chloride.

All experiments were performed using this batch mode with varied diluate chambers. To ensure control of the experiments and to avoid over-heating and destroying the membranes, the electrical current was kept constant at 0.2 Amps for both ED and EDI runs to allow a voltage range appropriate for the membranes within the one cell stack. Typical experiments ran for 48 hours, with samples collected at the initial (0-hr), 3-hr, 6-hr, 24-hr and 48-hr mark to provide adequate data points and trends for each run. The system was cleared with deionized water and cleaned following each run and new wafers were utilized in each run. Membranes were replaced pending damage due to fouling or drying to ensure each consecutive run was at desired conditions. Visuals and schematics of system setup and ion movement can be seen in figures 1-4.

III.   Sample Dilutions

Preparation for sample analysis by atomic absorption involves a dilution of each sample collected across 48-hours. Samples are diluted to fit within the optimum working range listed for the particular element to be analysed. This information can be found within the flame methods manual for atomic absorption by GBC Scientific Equipment. This also includes

details on standards preparation, instrument requirements and interferences. Calcium is found within an optimum working range of 180-760 µg/ml and is diluted 20 times from original sample (10,000-16,000 ppm) to fit range. Sodium has an optimum range of 100-380 µg/ml and is diluted 100 times from original sample (50,000 ppm) to fit range.

IV.   Atomic Absorption

Flame spectroscopy is an analytical technique to qualitatively and quantitatively determine an element in a sample. A liquid sample is introduced into a flame where thermal and chemical reactions create free atoms capable of absorbing, emitting or fluorescing at characteristic wavelengths (38). Concentrations of element analysis were assessed throughout all four chambers using this analytical technique and the program analysis software GBC Avanta. Each element to be tested had varying analytical data associated with the elements optimum working range and wavelength to gather concentration data. Standards were prepared for each element tested and analysed prior to each run to ensure proper calibration and accuracy in data. Flame type varied between air acetylene (sodium) and nitrous-oxide acetylene (calcium). Mean absolute concentrations were input graphically within excel to gather a specific trendline for individual runs and changes in concentration across the system were based off of each elements dilution from this data.

Figure 1 shows a side view of the ElectroCell system setup with platinized titanium electrodes, gaskets, and spacers. The titanium electrodes are assembled in opposite directions on either end of the system with the positive lead attaching to the electrode on the diluate side and negative lead attaching to the electrode on the concentrate side. There are four compartments within the system that are divided by alternating spacers (white) and gaskets (green). The spacers act as a opening for solution to pass through various chambers, including the wafer comprised of ionic exchange resins within the diluate compartment. The gaskets act as a sealant between each spacer to prevent leaks across the system, as well as they have openings of closing to allow or divert flow between compartments. Each side of the system includes four total inlet and outlet ports where silicon tubing is attached and fed through either a respective peristaltic pump or back into the corresponding solution chamber. Figure 3 gives a more detailed view of solution movement through the spacers and gaskets.
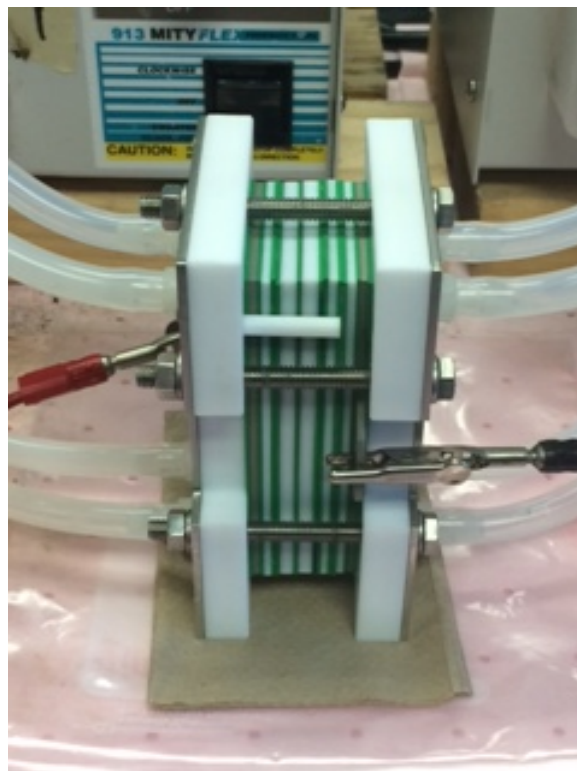

Fig. 1. Side view of ElectroCell system setup with electrodes, gaskets, and spacers

Figure 2 displays the front view of the ElectroCell system with 1/8" inlet and outlet connections for silicon tubing. To make setup easier to track, each of the four corners have been labelled for their respective compartment inlet and outlet flow. This figure displays the concentrate side. The diluate side is the reversed view of the concentrate (i.e. diluate inlet would be on the bottom left and outlet would be on the top right). Silicon tubing with 3/16" inner diameter and 3/8" outer diameter was attached to each connector on both sides of the system. Tubing fed from the respective solution chamber through high viscosity peristaltic pumps (Mcmaster-Carr ®) and attached to the inlet connectors. Solution flows through the system, leaves through the outlet connectors by silicon tubing fed back into the respective solution compartment.

Fig. 2. Front view of ElectroCell system with 1/8" inlet and outlet connections

Figure 3 is a schematic of WE-EDI with breakdown of compartments by spacers and membranes. This can also be visualized for electrodialysis with the removal of the ion exchange wafer within the diluate compartment. On both the left and right side of the system, the lighter and shorter arrows denote solution movement through the rinse compartments of the system. Both rinses are blocked off by closed gaskets from diffusing across the anionic exchange membranes (AMX) within the system. The next, longer set of arrows, denote solution movement across the concentrate and diluate compartment within the system. From here, gaskets and spacers are open on opposing ends to allow for the streams to cross once diffused across the cationic exchange membrane (CMX). There is an ion exchange wafer within the diluate compartment for WE-EDI (removed for ED setup) to enhance ion movement across the system. Ions from the diluate compartment that cross the cationic exchange membrane are picked up within the concentrate solution in consecutive samples.
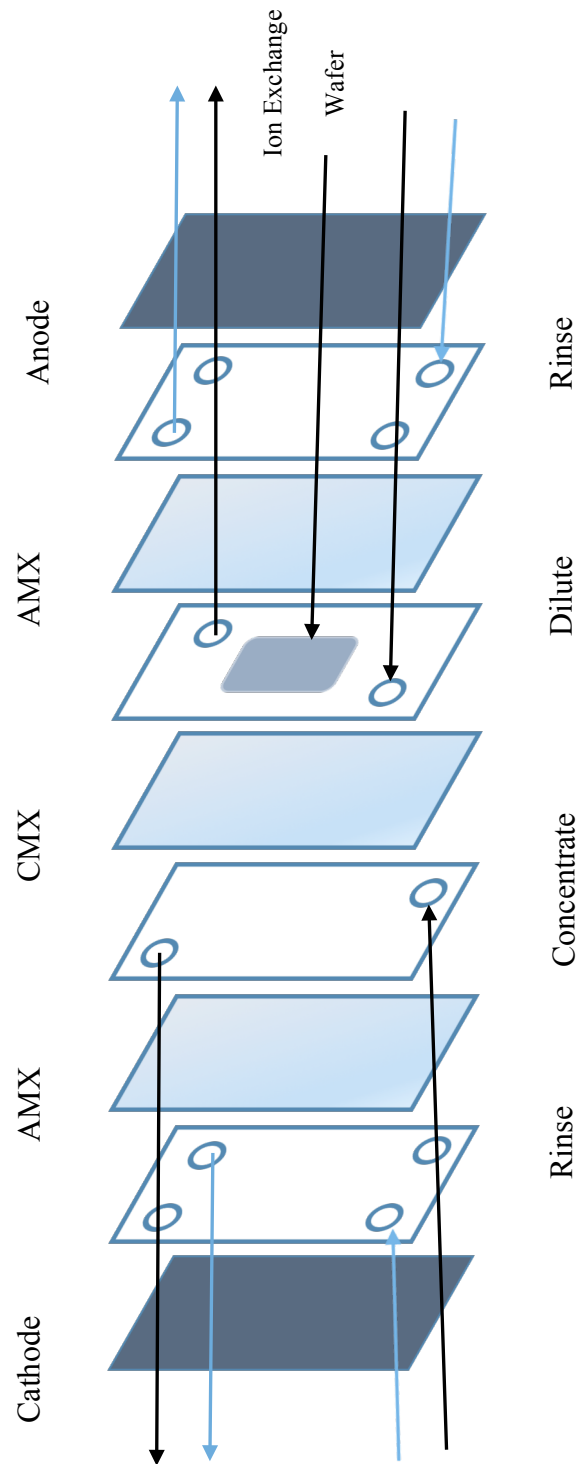
Fig. 3. Schematic of WE-EDI experimental set-up for 2mm and 4mm runs. Electrodes are labelled anode and cathode. AMX: Anionic exchange membrane. CMX: Cationic exchange membrane

Figure 4 is an extension of figure 3 in that it displays the particular ion movement and water splitting that happens in solution across the respective compartment membranes. The diluate solution is comprised of produced hydraulic fractured wastewater, which includes many more compounds than examined within this thesis, or simulated solutions including comparable concentrations of sodium chloride or calcium chloride to fracking solution. The concentrate solution is comprised of 2 wt% sodium chloride. The leads are set up respectively on both ends of the system to pull either negative or positive charges. Within the concentrate compartment, 2 wt% sodium chloride does not cross either anionic or cationic membrane. Divalents (Ca and Na) within the diluate solution cross the cationic membrane and the ion exchange wafer, comprised of both cation and anion resins, and subsequently increases the concentrate solution over time. Water splitting also occurs to some degree within all membrane compartments. Combined with the high concentrations of solution within the diluate chamber, a result of highly acidic or highly basic solutions in adjacent chambers can be observed. This can be noted by a decrease in the overall pH within the rinse compartment adjacent to the diluate compartment because of a increase of chloride ions reacting with hydrogen ions (a result of water dissociation within compartment) to form a highly acidic compound, hydrogen chloride. By contrast, a highly basic compound, sodium hydroxide is formed within the concentrate chamber.
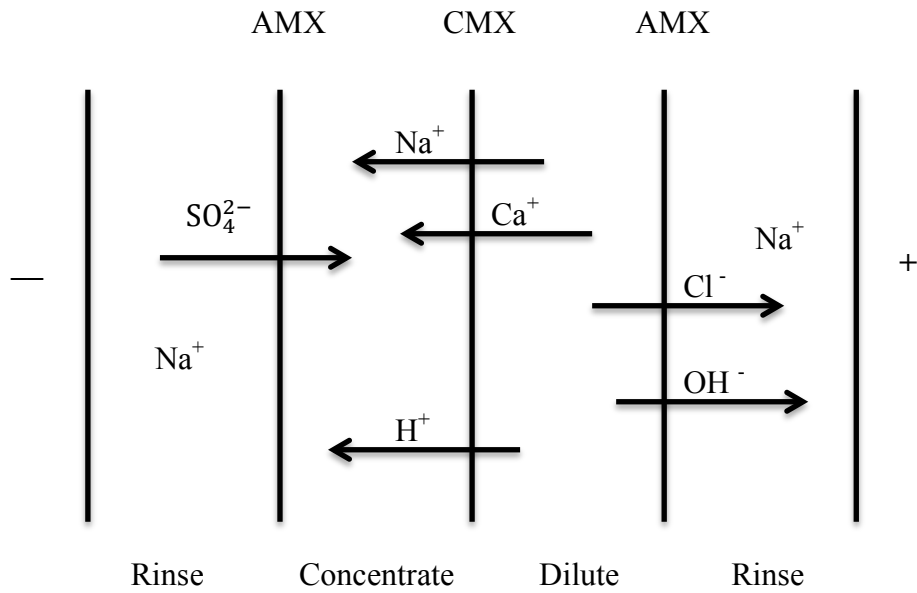
Fig. 4. Schematic of ion movement across chambers (4) and water splitting within WE-EDI. Electrodes are cathode (negative end) or anode (positive end). Concentrate contains 2 wt% NaCl solution. Dilute contains 50,000 ppm NaCl, 10,000 ppm CaCl, or produced wastewater from Beasley, TX

Theory and Equations

I.   *Current Efficiency, Power Consumption and Selectivity*

Performance of both ED and EDI was monitored during each run by analysing concentrations from the diluate chamber for current efficiency and power consumption of both calcium and sodium within the system. Current efficiency is defined as the following:

$$\eta = \frac{zFV(C_f - C_i)}{tIMw} \times 100\%$$ (1)

where z is the ionic valence, F is Faradays constant, V is the volume within the diluate chamber, C_f is the final concentration in the diluate chamber, C_i is the initial concentration in the diluate chamber, t is the total system operation time, I is the current, and Mw is the molecular weight of the ion. This monitors how efficiently the system is transferring a particular ion across the membranes and wafer due to electrochemical reactions. Maximum current efficiency begins at 100% and decreases as a result of heat loss and/or water dissociation within the diluate compartment (a side chemical reaction within the system) of WE-EDI or concentration polarization within ED setups. Within this thesis, current efficiency is graphically denoted in a percentage measurement.

Another calculation used to quantify the energy consumed through the ED and EDI process was power consumption, which is defined as the following:

$$PC = \frac{V_t I t}{(C_f - C_i)\eta}$$ (2)

where Vt is the system voltage applied and η is the current efficiency (not percent efficiency). This is measured because the system does not operate within 100% efficiency at any one time and some amount of power is lost as heat. The unit of measurement for power consumption is kilowatt hours (kWh).

The separation coefficient is calculated to determine the selectivity of one ion over another to compare the rate of removal of calcium ions over the rate of removal of sodium ions with varied wafer thickness and composition. The selectivity is defined as the following:

$$\alpha = \frac{(C_i^e - C_i^s)/D_i^s}{(C_j^e - C_j^s)/D_j^s}$$

(3)

where C_i^s is the starting concentration of ion i (calcium ion), C_i^e is the final concentration of ion i, D_i^s is starting concentration in the diluate chamber of ion i, C_j^s is the starting concentration of ion j (sodium ion), C_j^e is the final concentration of ion j, and D_j^s is the starting concentration in diluate chamber of ion j. The separation coefficient will be greater than one if the movement of calcium is larger than that of sodium and it will be less than one if the movement of sodium exceeds that of calcium across the membrane. The movement of calcium and sodium across the system are of equal value if the selectivity is exactly one.

II. Ion Exchange Resins and Theory

Wafers were comprised of both anionic and cationic resins in various compositions (strongly acidic or strongly basic) with polymer and sucrose to create a porous ion-exchange wafer for application in EDI. The principle goal for implementing a wafer comprised of strongly acidic resins and another of weakly acidic resins is to test the respective selectivity of each within an EDI module. Sulfonic acid functional groups are immobilized onto polystyrene beads leading to the development of strongly acidic ion-exchange resins, while carboxylic acid is a much weaker functional group that comprises weakly acidic ion-exchange resins. While sulfonic acid is capable of exchanging with metal ions, it has relatively low selectivity and carboxylic acid displays greater selectivity for divalent ions (39). Volumes and final weights were calculated for each wafer composition within the respective spacer dimensions (2mm, 4mm and 8mm). This gives an insight on how much ion-exchange resin is present within the

16

spacer dimensions and thusly its contribution in ionic movement in the system.

Analysis of Results

The following figures detail and compares the results accumulated for both ED and WE-EDI runs, including their corresponding current efficiencies and power consumption across the system. In order to properly evaluate, error bars are included within system averages. Runs were repeated in sets of three to further eliminate potential questions of error on overall system performance. Data displays 2mm and 4mm wafers with both strong acid and weak acid compositions. Data will also be compared between simulated solutions and produced water from the Beasley, TX fracking site. Simulated runs were easier to replicate when compared to produced "fracking" wastewater runs, regardless of conditions remaining the same throughout all system runs. Most system runs were performed with new membranes and pump tubing to avoid scale build-up and all were performed with new wafers to avoid unnecessary ion movement between consecutive runs.

Figure 5 shows a comparison of percent current efficiencies and power consumption for ED and EDI runs with 50,000 ppm sodium chloride solution within the diluate compartment to replicate an average amount of sodium found within a sample of produced hydraulic fracturing solution from Texas. Observing the second and third experimental runs shows that current efficiency was greater across 4mm wafers comprised of strong acid and strong base resins than current efficiency across 2mm wafers. It is probable that there was less ionic transport within EDI runs comprised of 2mm strong acid wafers compared to a wafer of greater thickness, which, along with losses due to water dissociation, could be why current efficiency across the system is less within duplicates for 2mm runs compared to 4mm runs. Current efficiencies above 100% (the first run in ED and second run in 4mm EDI) are possibly due to system fouling or excessive water dissociation that occurred within the specific system run. An apparent rise in power consumption can be noted within the second and third 2mm WE-EDI runs, with lower power consumption in the corresponding duplicate

4mm runs. A single-factor ANOVA analysis was performed on both percent current efficiency and power consumption to determine the statistical difference between averages of the triplicate runs performed for ED, 2mm and 4mm EDI runs. There was determined to be no statistically significant difference between the three groups as determined by a one-way ANOVA ($F_{(2,6)}$ = 0.893, p = 0.458) for current efficiency and ($F_{(2,6)}$ = 1.383, p = 0.321) for power consumption for triplicates runs of 50,000 ppm NaCl of ED and strong acid only comprised EDI runs. The standard deviations for percent current efficiencies were $\pm$ 24.1 for ED, $\pm$ 7.7 for 2mm EDI, and $\pm$ 18.6 for 4mm EDI. The standard deviations for power consumption were $\pm$ 2.5 for ED, $\pm$ 4.0 for 2mm EDI, and $\pm$ 1.7 for 4mm EDI.

Figure 6 displays the same comparisons as figure 5 with the exception that runs are performed with 10,000 ppm of calcium chloride solution within the diluate compartment to replicate calcium found within a Texas fracking site. This is below the average parts per million of calcium within Texas produced fracturing water due to the systems inability to handle 15,000 ppm of simulated solution without fouling. This is detailed in table 2 along with several other regions of produced wastewater and their corresponding reuse limits (EPA provided reuse limits). Highly varied results can be observed across ED, 2mm and 4mm EDI triplicate runs. It is known that calcium is more likely to precipitate within the system when it combines with sodium sulphate from the rinses and forms calcium sulphate, which will build up on both the wafers and membranes in the system, a probable, but not experimentally tested causation for system fouling in CaCl runs. A single-factor ANOVA analysis was performed on both percent current efficiency and power consumption to determine the statistical difference between averages of the triplicate runs performed for ED, 2mm and 4mm EDI runs. There was determined to be no statistically significant difference between the three groups as determined by a one-way ANOVA ($F_{(2,6)}$ = 0.007, p = 0.993) for current efficiency and ($F_{(2,6)}$ = 0.346, p = 0.721) for power consumption for triplicates runs of

10,000 ppm CaCl of ED and strong acid only comprised EDI runs. The standard deviations for percent current efficiencies were $\pm$ 45.1 for ED, $\pm$ 34.7 for 2mm EDI, and $\pm$ 38.5 for 4mm EDI. The standard deviations for power consumption were $\pm$ 127.7 for ED, $\pm$ 350.9 for 2mm EDI, and $\pm$ 75.0 for 4mm EDI.

Data on electrodialysis is displayed within figures 5 and 6 to give a comparison of ability on ED versus WE-EDI to efficiently transfer ions across the system over a 48-hour time period. It would appear that both 2mm and 4mm EDI runs are comparable to ED for sodium and calcium ion movement across triplicates in both figure 5 and 6. It is difficult to determine (without further runs) if calcium chloride for ED, 2mm and 4mm EDI runs are displaying high current efficiency or lower current efficiency due to system fouling. There is at least one instance of high percent current efficiency and low power consumption within ED, 2mm and 4mm EDI for CaCl. This could be a result of multiple issues within the system including fouling and ion loss within the wafer, explained in greater detail within the ion exchange resin theory.

Hydraulic Fracturing Wastewater		
	Sodium (ppm)	Calcium (ppm)
Texas	50,000	16,000
Oklahoma	43,000	8,100
Utah	17,200	113
North Dakota	18,200	8,700
Reuse Limit	<20,000	<2,000

Table 2. EPA standards and reuse limits for various regions of produced water
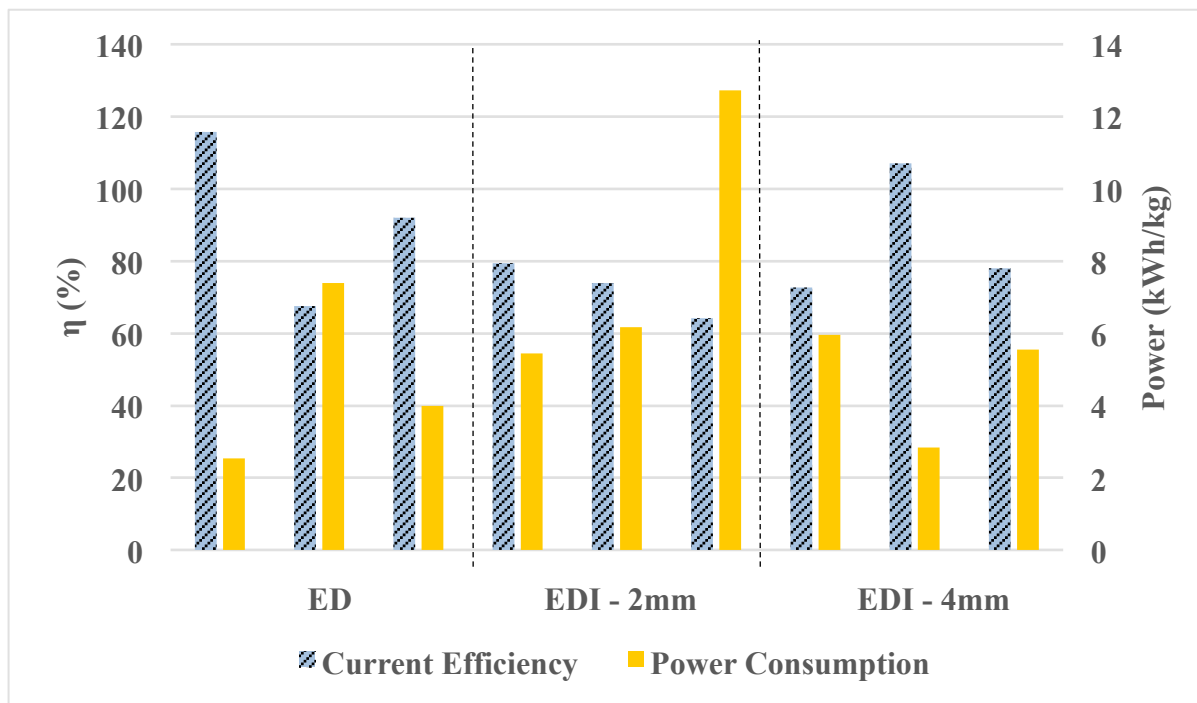
Fig. 5. A comparison of percent current efficiency and power consumption for sodium chloride runs across strong acid/strong base comprised wafers only (2mm vs. 4mm) compared to electrodialysis (ED). All ED and EDI are performed in triplicates.
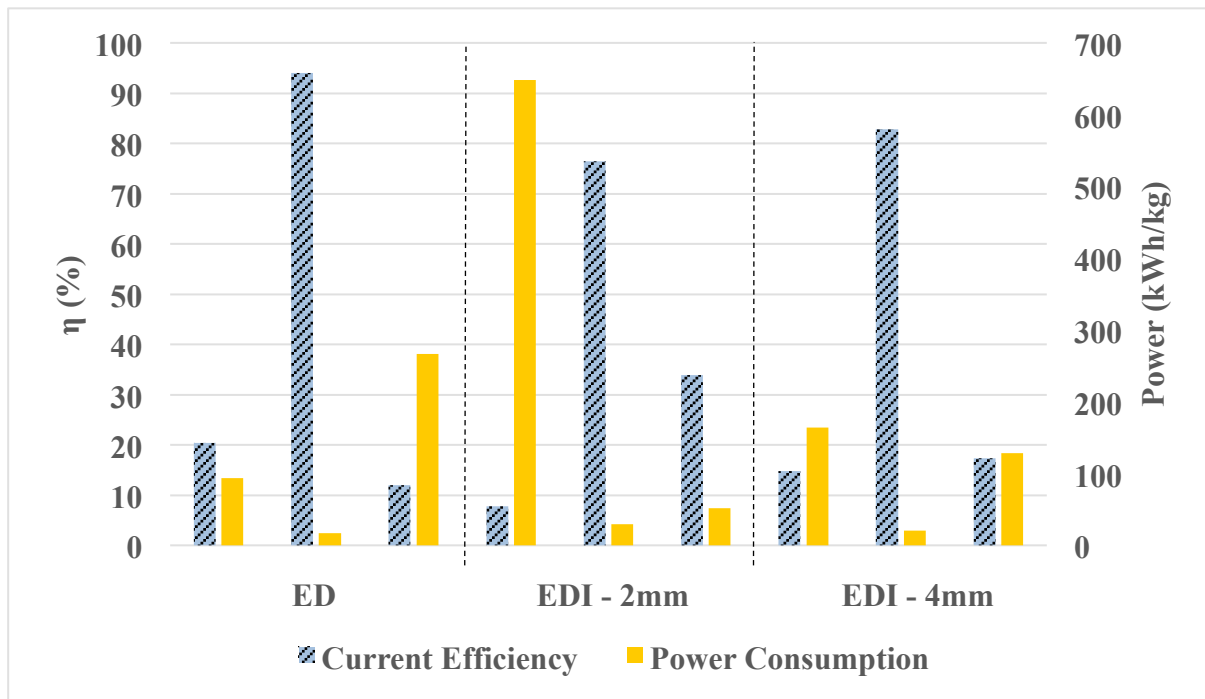
Fig. 6. A comparison of percent current efficiency and power consumption for calcium chloride runs across strong acid/strong base comprised wafers only (2mm vs. 4mm) compared to electrodialysis (ED). All ED and EDI are performed in triplicates.

The concept of current efficiency related to wafer composition is expanded upon in Figures 7 and 8 that follow. Both figures offer a comparison of simulated solutions and produced wastewater from Beasley, TX. This is further developed by exploring two separate resins that comprise both a 2mm and 4mm wafer. Similar to figures 5 and 6, data is presented on ED to display how effective ion transfer is in WE-EDI across the system in 48-hour runs.

Figure 7 shows a comparison of current efficiencies (percentage) and power consumption for ED and EDI runs with one setup being a solution of 50,000 ppm sodium chloride within the diluate compartment as a representation of a standard amount of sodium found within a sample of produced hydraulic fracturing solution within Texas (refer to Table 2). The second setup is 250 mL of produced wastewater from Beasley, TX within the diluate chamber. All other system conditions remain the same. On average, current efficiency was observed to be greater across 4mm wafers with both strong acid and weak acid compositions than of 2mm wafers, however, error was also far greater across 4mm system runs. This is comparable to what is seen within simulated solutions comprised of sodium chloride only in figure 5 above. Runs performed with 4mm strong acid wafers appear to out perform 2mm wafers and ED overall. It can also be noted that a weak acid and strong base wafer composition for both 2mm and 4mm wafers showed overall better current efficiency and lower power consumption within a WE-EDI system compared to ED. All system runs are at maximum current efficiency for ED and WE-EDI (2mm and 4mm) for sodium chloride. There is a significant rise in standard error along current efficiencies that exceed 100% overall. Power consumption remains very low, between 2-5 kWh/kg across all runs, which is comparable to power consumption observed in simulated runs only in figure 5 (above). Weak acid resins consume only between 2-3 kWh.kg of power compared to strong acid resins and ED, since weak acid resins are relatively more efficient at regenerating than strong acid or base resins are. Strong acid resins possess a higher affinity for monovalent ions and lower

affinity for hydrogen, requiring a larger quantity of acid to regenerate the resin. This, as well as the fact that weak acid resins are much more selective for alkaline salts (Ca and Mg), contributes to the much higher power requirements necessary for system operation with wafers comprised of strong acid resins (41). A two-way ANOVA analysis with replication was performed to confirm results in figure 7. It was found that there was no statistically significant interaction between the wafer composition and wafer thickness in current efficiency for ED and EDI, $F_{(2,6)} = 0.255$, $p = 0.783$. There was also found to be no statistically significant difference in power consumption for ED and EDI, $F_{(2,6)} = 0.374$, $p = 0.703$ within results for figure 7.

Figure 8 includes ED and EDI system runs performed with produced hydraulic wastewater in one setup and 10,000 ppm of calcium chloride solution in the second setup to replicate calcium found within a produced Texas wastewater (refer to table 2). It can be observed that weak acid and strong base wafer composition for both 2mm and 4mm appear to display better overall current efficiency and lower power consumption when compared to the strong acid wafer composition. However, higher error is present within the 4mm weak acid wafer composition than is present within 2mm or ED in either weak or strong acid wafer compositions. Current efficiency within 4mm runs for both compositions appears to be comparable with ED runs. This is similar to results observed in a comparison of current efficiency and power consumption for simulated solution of calcium chloride only (refer to figure 6 above). Simulated solutions of calcium chloride are just as unpredictable as experimental runs with hydraulic fracking solution. Current efficiency in fracking and simulated solution is approximately 19% for ED and 15% for 4mm strong acid wafers. This is comparable to the first simulated runs shown in figure 6 (strong acid only) for ED and 4mm EDI. As with figure 7, a two-way ANOVA analysis with replication was performed on figure 8 to statistically confirm comparable results between test groups. It was found that

there was no statistically significant interaction between wafer composition and wafer

thickness in current efficiency for ED and EDI, $F_{(2,6)} = 0.431$, $p = 0.668$. However, there

was found to be a statistically significant difference in wafer composition and wafer thickness

for power consumption for ED and EDI runs, $F_{(2,6)} = 8.50$, $p = 0.018$.
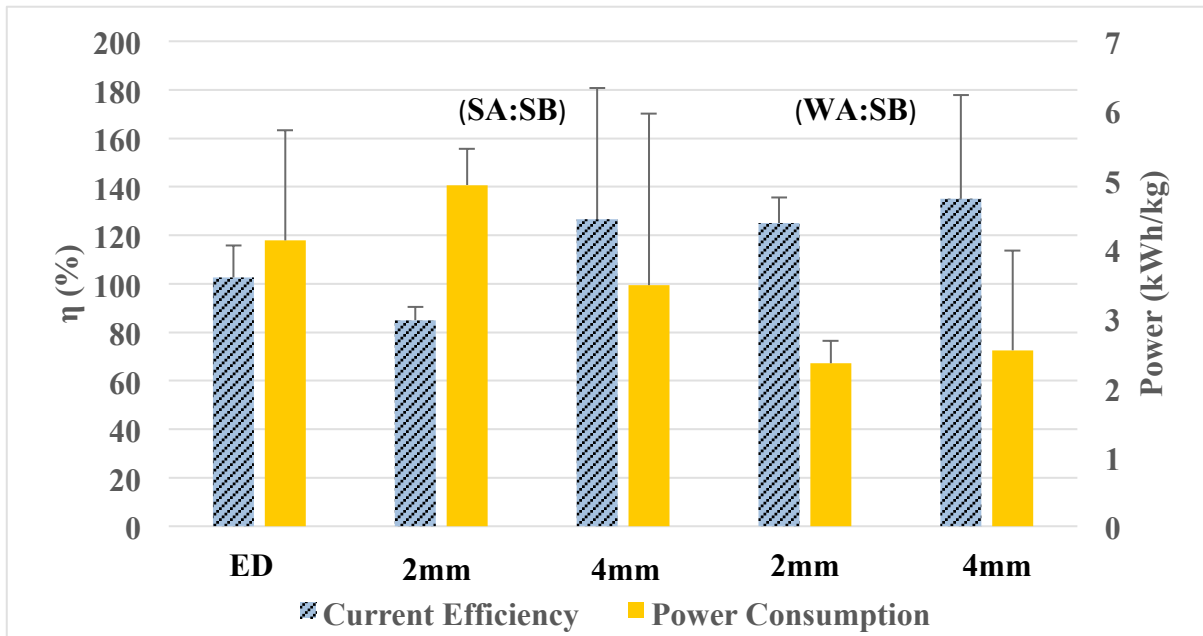
Fig. 7. A comparison of percent current efficiency and power consumption for both sodium chloride and hydraulic fracturing runs (averaged together) across strong acid/strong base (SA:SB) and weak acid/strong base (WA:SB) comprised wafers (2mm vs. 4mm). All EDI runs are compared to ED averages.
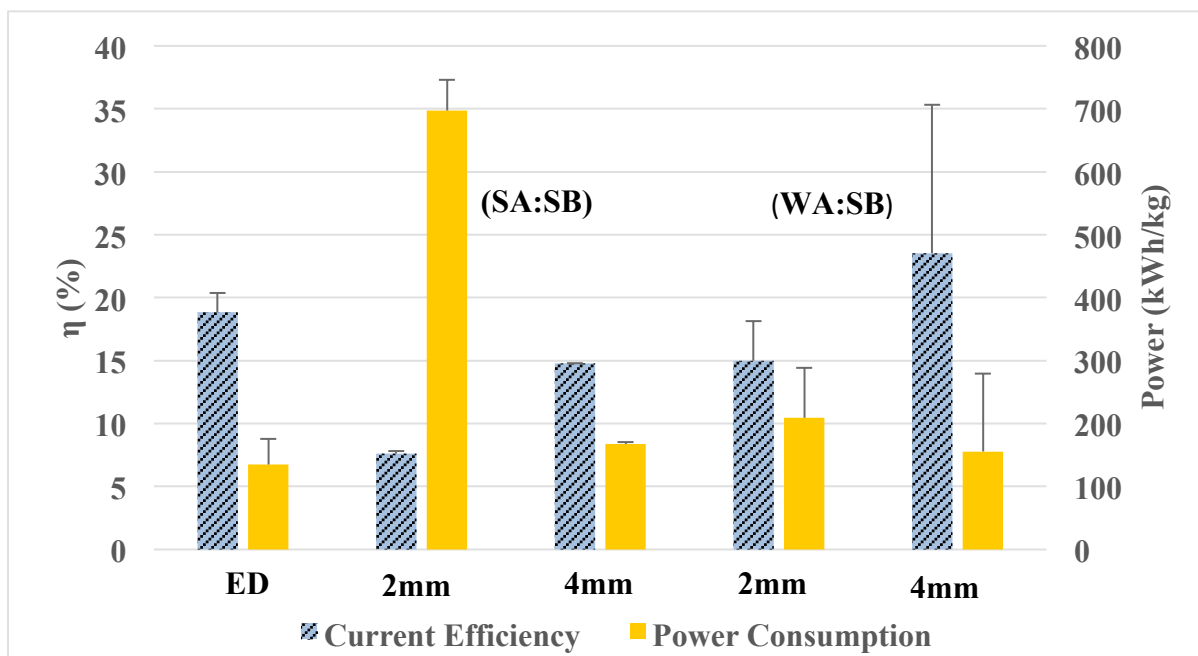
Fig. 8. A comparison of percent current efficiency and power consumption for both calcium chloride and hydraulic fracturing runs (averaged together) across strong acid/strong base (SA:SB) and weak acid/strong base (WA:SB) comprised wafers (2mm vs. 4mm). All EDI runs are compared to ED averages.

Figures 9 and 10 display concentration change over a 48-hour run for WE-EDI comprised of strongly acidic resins. This is for 2mm and 4mm wafers for produced wastewater from Beasley, TX. Analysing figure 9 shows a change in concentration for sodium ions between the concentrate and diluate chambers. The 4mm runs decreased by approximately 6,000 ppm and the concentrate increased by approximately 2,600 ppm, this equates to a 43% overall cation transport across the wafer and ion exchange membrane (CMX). This can be compared to 2mm runs that decreased by approximately 3,000 ppm and increased within the concentrate by 2,300 ppm, equating to a 77% cation transport across the wafer and ion exchange membrane (CMX). This larger loss of sodium ions within the 4mm wafer can be equated to the increased wafer thickness or a potential lack of adequate porosity for ion transfer.

Figure 10 displays a change in concentration for calcium ions between the concentrate and diluate chambers. The 4mm runs decreased by approximately 1,100 ppm and increased in the concentrate by approximately 50 ppm, which is only a 5% cation transport across the system. This ratio of concentration loss to gain is far greater than what is seen within sodium movement across the strongly acidic 4mm wafer. This can be related back to the ion exchange resins theory stating that strongly acidic resins have a lower selectivity towards divalent ions, or in this case, calcium. Comparing 2mm runs for calcium transfer displays a decrease in the dilute chamber by 200 ppm and an increase in the concentrate by 70 ppm, which is an ion transport of 35% compared to an only 5% cation transport across the 4mm wafer and ion exchange membrane (CMX). The ratio of concentration loss to gain within 2mm wafers is comparable for both calcium and sodium ion transfer in WE-EDI.
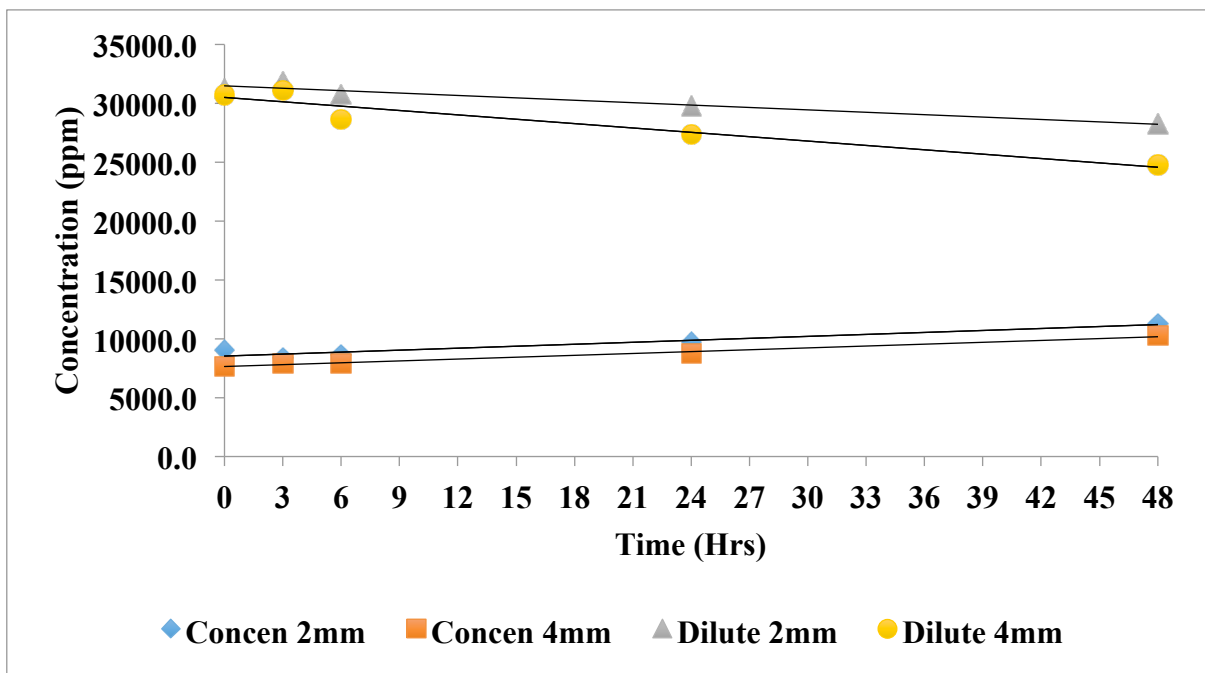
Fig. 9. A comparison of sodium concentration within concentrate and diluate chambers for hydraulic fracturing runs in batch mode across strong acid/strong base comprised wafers (2mm vs. 4mm)
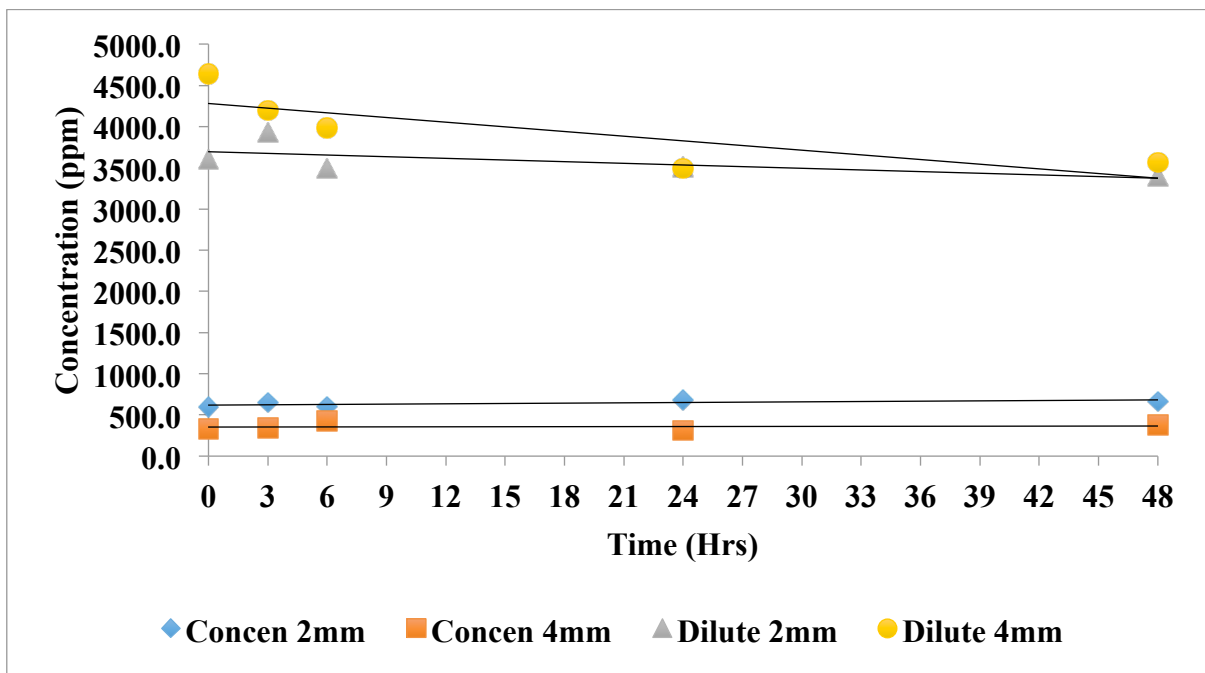
Fig. 10. A comparison of calcium concentration within concentrate and diluate chambers for hydraulic fracturing runs in batch mode across strong acid/strong base comprised wafers (2mm vs. 4mm)

Table 3 displays a comparison of selectivity's for 2mm, 4mm, and 8mm WE-EDI for calcium over sodium ions. Selectivity calculations are detailed in the theory and equations section within this thesis. Experimental runs were performed for both strong acid and weak acid wafer compositions for all three thicknesses. Duplicates were carried out on most runs were produced hydraulic wastewater was the permeate utilized for the experimental run. Selectivity was also analysed for simulated solution comprised of a mixture of sodium chloride and calcium chloride.

First, comparing selectivity's across simulated solution for WE-EDI it can be determined that there was a greater selectivity of calcium in the 2mm strongly acidic wafer and comparable selectivity within both the 2mm and 4mm weakly acidic wafer composition. However, electrodialysis showed to have better selectivity overall for simulated solution than EDI. This is was not the projected result as the wafer should enhance ion movement, making WE-EDI the favourable option for ion transfer when compared to ED. Duplicates will be necessary within both simulated ED and EDI to determine if this was caused by system fouling or ion loss within the wafers.

Next, selectivity of calcium within produced hydraulic frack water is compared. This included WE-EDI runs with 2mm, 4mm, and 8mm wafers. An 8mm wafer was configured by placing two 4mm wafers back to back within the diluate chamber of the system. Duplicates and triplicates were performed for all strong acidic wafer compositions. This shows a much more favourable trend within the strong acidic wafers with selectivity getting greater with an increase in wafer thickness. While selectivity's for 8mm exceed the 4mm wafer, there is an outlier at 1.75 for the 2mm wafer for strong acid resins. Both selectivity results for 8mm runs exceed the selectivity of the ED run for produced wastewater and therefore confirm hypothesized theory within this research. Selectivity for weakly acidic wafer compositions across all three thicknesses did not validly exceed selectivity for ED with the exception of

one 4mm run at 1.23. This can be related by to the ion exchange resins and theory that explains the weakly acidic resins preference for divalent ions compared to strongly acidic resins. It is probably that there was a greater loss of calcium ions within wafers comprised weakly acidic resins contributing to unrepeatable selectivity's within this EDI system.

Selectivity		
Simulated		
ED	4.06	
EDI	**SA:SB**	**WA:SB**
2mm	3.58	2.60
4mm	0.81	2.61
Produced Hydraulic Frack Water		
ED	0.65	
EDI	**SA:SB**	**WA:SB**
2mm	0.27	0.47
	1.75	---
4mm	0.13	1.23
	0.31	---
	0.77	---
8mm	1.86	0.69
	1.13	0.20

Table 3. Comparisons of selectivity within ED and EDI systems for both produced wastewater and simulated solution

Discussion and Future Work

While there are various treatment and disposal practices in place for produced wastewater from hydraulic fracturing sites, membrane separation is becoming a more competitive option in regards to cost efficiency and sustainability. This research sought to apply and optimize an available process known as electrodeionization. It was hypothesized that by altering wafer chemistry and membrane setup within a WE-EDI system, then ion transfer of calcium and sodium could exceed the ability of other available technologies including electrodialysis. However, data displayed loss of ions within the wafer compositions, as well as possible system fouling due to calcium precipitation. Since this research was performed on a small tabletop ED/EDI system, highly corrosive solution, such as the produced water from Beasley, Texas, becomes difficult for a small membrane system to adequately handle and run to completion, regardless of VSEP pretreatment performed on this hydraulic wastewater.

It is suggested that future work proceed by performing duplicates and triplicates on both simulated and produced wastewater solutions to create a more accurate trendline of this systems ability in treating corrosive solution. The concentrate solution of 2% sodium chloride should also be tested at higher concentrations between increments of 6-15%. It is also suggested to reformulate wafer composition ratios to allow for greater porosity, especially within 4mm and 8mm wafer compositions.

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