

Flowable-Electrode Capacitive Deionization for Treatment of Mining Process-Affected Water

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Chemical Engineering (Nanotechnology)

Waterloo, Ontario, Canada, 2019

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Water is a critical resource in the mining and resources sector. It enables the extraction and materials processing operations that underpin this primary industry, and therefore everyday life. Water's value in mining means substantial amounts of water are used over the lifetime of a mine, from initial exploration, to mine operations, to long-term closure. The generation of process-affected water in mining is a key part of the environmental impact of each mining site.

Canada's the energy industry is built upon surface mining of bitumen containing oil sands. The water-based extraction of oil from the strip mined sands has led to the accumulation of over 1 billion cubic metres of water stored in tailings ponds. This process-affected water has increased salinity through successive reuses in the extraction process and exposure to minerals in the sand. The dissolve solids in this impacted water affects the ability to safely return the water and land to its natural state, as well as causing corrosion and reduced bitumen extraction efficiency in active operations. Managing these water stocks and reducing dissolve solids accumulated within it is a key operational and remediation challenge for oil sands operators.

Deionization technologies such as thermal and membrane processes are most commonly applied in drinking water production applications. However, for complex water streams with a variety of contaminants and relatively low levels of dissolved solids, conventional processes are typically too energy intensive and operationally demanding to be suitable for use in oil sands mining applications. Emerging deionization technologies, such as capacitive deionization (CDI), present an opportunity to reduce the energy demand and increase treatment efficacy for these applications.

This thesis studies a novel flowable-electrode capacitive deionization (FCDI) process towards development of a prototype treatment cell, characterization of the prototype performance, and analysis of the application of FCDI to treat dissolved solids in oil sands process-affected water (OSPW). Iterative design of the prototype is shown to generate comparable performance to prior FCDI systems and new analysis is presented for FCDI's treatment of varied dissolved ions. The studies show FCDI's efficacy for treatment of all dissolved solids in complex mixtures.

Towards its application in OSPW treatment, the FCDI system is tested on representative field samples and demonstrates treatment to below typical water intake quality and analyze treatment on a speciated basis. The treatment study successfully identifies FCDI as a method capable of treating OSPW without

substantial pre-processing and at an energy cost below conventional methods. The study concludes that FCDI is well suited for OSPW treatment compared to conventional methods.

The thesis demonstrates a new FCDI prototype, treatment of a variety of dissolved ions, variation in key operational parameters, and application of the technology towards treatment of a mining-impacted water. The current work concludes that enhancement and development of the FCDI system should continue towards detailed development of flowable electrode media, characterization of new operational modes, long term treatment study with OSPW, and subsequent scale up of the prototype to a next generation system.

Acknowledgements

The opportunity to explore and develop new sustainable technology for clean water has been a great privilege enabled by my supporters and community inside and outside of the University of Waterloo.

I first thank my supervisor and mentor Prof. Frank Gu for providing guidance, research support, and challenging questions to further this research topic. From initial engagement with an idea to bring together a novel treatment technology and impactful treatment challenge, Prof. Gu was a key support for me to complete this research and grow as both academically and personally. I also thank Prof. Ting Tsui and Prof. Ali Elkamel for their review of this thesis and providing feedback.

I would also like to thank my research group colleagues in the Frank Gu Lab, particularly the water treatment research team including Dr. Tim Leshuk, Dr. Stuart Linley, and Dr. Andrew Holmes. Their support, expertise and camaraderie was integral in advancing my work and building on new ideas. I also thank the many staff and advisors in the Department of Chemical Engineering and the Waterloo Institute for Nanotechnology, who supported my learning and provided the facilities for me to advance my education.

This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Toward Environmentally Responsible Resource Extraction Network (TERRE-NET). Additional research support provided by the Waterloo Institute for Nanotechnology (WIN) and Canada's Oil Sands Innovation Alliance (COSIA).

Beyond the University, I am grateful for the support of family and friends to keep me balanced, provide support, and endure long days and nights pursuing my goals in research and entrepreneurship. I thank my wife, Leah, for her steadfast support and helping to keep my spirits high. Thanks as well to my great network of friends, including Jacob Terry, who was a key confidant through the whole journey, and to Rob Reid and Jimmy Ehrman, for providing advice and sharing a breather on many bike rides between work hours.

Finally, thanks to my parents Darla and Jeff, and sister, Heather, for always supporting my ambitions and my pursuit of new adventures. Your encouragement to value hard work, academics, and most importantly, development of my character is the foundation that my studies have been built upon.

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List of Abbreviations

AEM – Anion-Exchange Membrane

AR – Ammeter Recorder

CAD – Computer Assisted Design

CDI – Capacitive Deionization

CEM – Cation-Exchange Membrane

CT – Conductivity Transmitter

ED – Electrodialysis

EDR – Electrodialysis reversal

EDL – Electrical Double Layer

FDCI – Flowable-Electrode Capacitive Deionization

IEM – Ion-Exchange Membrane

MCDI – Membrane Capacitive Deionization

OSPW – Oil Sands Process-Affected Water

PAC – Powdered Activated Carbon

RO – Reverse Osmosis

SAGD – Steam-assisted gravity drainage

1 Introduction

1.1 Study Overview

Extraction of valuable resources in mining operations and use of water are closely linked. Water is an important tool to recover solid minerals, liquid fuels, and natural gas, as well as conduct material transportation and waste sequestration. In a world of growing water scarcity where, by 2030, water supply is expected to be 60 % greater than the available supply with “business as usual” increases¹, new approaches to water management and treatment for intensive industries are needed.

Process-affected water generated by active mining operations and through contact with mined formations is often reused, with fresh water added to maintain an acceptable water quality. Mining, particularly in surface strip mining, involves exposing large volumes of mined ores with high surface area, and the use of water in extracting valuable minerals and fuels leads to the generation of process-affected water that accumulates during mine operations. The impacted water typically concentrates dissolved ions, elemental metals, and dissolved organics. Water contaminants can cause risks to the local environment and business continuity. Environmentally, the contaminants can lead to toxic or acidic waters that impact wildlife and pose risks to the watershed during accidental releases. In addition to environmental liabilities, increases in salinity can lead to process equipment corrosion, reduced process efficiency, and complications to end of mine life closure.

One of the largest mining operations in the world is the Canadian Oil Sands, where unconventional oil reserves are found in bitumen-laden sand. The heavy crude oil is extracted by surface mining of sand deposits, which uses the “Clark hot water process” to separate bitumen, or by in-situ mining, which uses a steam-activated gravity drainage (SAGD) process to flow out heated, reduced viscosity bitumen². Both processes rely on water for operation, using approximately 2 barrels and 0.2 barrels of water per barrel of bitumen, respectively³. While continued innovation has greatly reduced water use intensities, the large scale of operations continues to generate large water stores.

In surface mining, operations have generated large stocks of oil sands process-water (OSPW), which is a complex saline solution of suspended clays, dissolved organics and solvents, and trace heavy metals. Fresh water use in the oil sands mining was over 245 million m³ in 2018⁴. These large volumes are required in addition to 80-85 % of process make-up water reused from OSPW stores, for a total water throughput of over 990 million m³ in 2018⁴. Increased salinity in OSPW contributes to reduced

bitumen extraction efficiency and increased corrosion and wear on process equipment. In addition to the cost of lower efficiencies and reduced reliability, concentrating salinity threatens the viability of mine closure plans and return of OSPW to the watershed, as heightened salinity reaches levels that may not be viable for local flora and fauna.

The treatment of dissolved solids to reduce salinity in OSPW is a challenge facing both Canadian industry in the Athabasca Oil Sands, and mining operations around the world^{2,5}. Management of mining process-affected water is different from conventional desalination for water supply, requiring technologies to handle complex input water chemistry, operate resiliently, and enable low-cost treatment in niche applications. New deionization technologies can both increase the efficiency and economics of dissolved solids management, while reducing the complexity of pre-treatment needed to operate deionization systems in water reuse and remediation.

Capacitive deionization (CDI) is an emerging technology that can solve the need of efficient and economical dissolved solids treatment. This technology uses the principles of electro-deionization to extract, concentrate, and ultimately remove dissolved ions from water. It is well suited to lightly to brackish salinity waters, providing high-efficiency removal of dissolved ions compared to high pressure membrane filtration and thermal evaporation processes, which are more energy intensive and commonly applied in seawater and brine treatment. CDI builds upon established electro-dialysis techniques that are often applied to low salinity waters by increasing the rate and efficiency of removal through use of electric-double layer capacitive storage of dissolved ions.

Recent advances in capacitive deionization have also shown promise for more efficient and continuous operating systems using ‘flowable electrodes’, modelled after flow battery technology, where solutions of conductive media are used as dynamic, continuously regenerated electrodes. These advances may unlock higher operating efficiencies and closed-circuit energy recovery, further decreasing the energy use, increasing scalability, and improving the reliability of capacitive deionization systems.

1.2 Research Scope and Objectives

The objective of this research project was to develop a novel deionization technology for treatment of dissolved ions in mining process-affected water. The research herein addresses the system design, fabrication, validation, and application of flowable-electrode capacitive deionization (FCDI) towards

the treatment of dissolved solids in OSPW. The aim of these studies is to develop an operational FCDI prototype that is comparable to the state of the art and examine its performance and design selections towards application in industrial water treatment. This includes characterization of treatment for a variety of dissolved ion species, evaluation of electrical power requirements, and assessment of the specific benefits and applicability of FCDI in the application of OSPW treatment.

1.3 Structure of Thesis

The thesis composed in six sections detailing the development and testing of the FCDI prototype and its application for OSPW treatment.

Sections 1 and 2 detail the scope of research, background in deionization technology, capacitive deionization, and mining process-affected water treatment needs. A review of relevant literature and background in the development of CDI technology provides the basis for design selections and conventions in the prototype design.

Section 3 details the mechanical and process engineering and development of the FCDI prototype. Design principles from former CDI and FCDI studies are applied to develop two prototype flow cells, the second integrating design improvements to the first enabling effective operation. This section also details the specifications of products and materials integrated in the FCDI system.

Section 4 and 5 include the validation and characterization of the FCDI system. This section includes initial start-up design changes in order to enable deionization operation and assesses treatment performance using number of salt solutions. Following performance validation, operational parameter analysis is conducted for the concentration of solids in the flowable-electrodes and operating voltage.

Section 6 examines the application of FCDI system towards treatment of dissolved solids in OSPW. The sample OSPW is characterized and treatment testing is analyzed to a treatment extent below endemic water dissolved solids concentrations, including energy input analysis. The treated OSPW is further analyzed by dissolved ion species to demonstrate the treatment efficacy of FCDI for all dissolved solids constituents.

Section 7 provides key conclusions from the studies contemplated in the thesis and provides recommendations for further study on topics that are outside the scope of this project and that may be most valuable to advancing the application of FCDI in an industrial treatment setting.

2 Literature Review

2.1 Mining and Oil Sands Process-Affected Water

Management of water is an integral part of all mining operations from initial site development, through active operations, to long term remediation and site closure. As all mining involves extraction of resources from natural land formations – often using water as a useful tool for extraction, transport, and processing of material – the generation of process-affected water containing dissolved ions is an inherent impact of mining operations. Effective management of dissolved ions in process water has important implications both in reducing costly corrosion and wear on process equipment, as well as reducing the overall impact of mines on the local environment.

One such application relevant to Canadian natural resources sectors is the treatment of dissolved ions in OSPW in surface mining³. In this mining process, bitumen-laden sands are strip-mined from near-surface deposits and processed using a hot water extraction method to recover heavy oil contained in the sands. Through this process, minerals in the sands are dissolved into the process water and concentrate over regular reuse of the water. Surface mining operations reuse up to 85 % of process-affected water in water make-up⁶, leading to concentration over time to a typical level of 1000 - 5000 mg/L total dissolved solids^{2,7}. This poses a challenge to maintaining plant infrastructure and poses a threat to effective management of water at the end of mine life as salinity may become limiting for re-integration with the local watershed^{2,8}.

Towards OSPW treatment and other mining process-affected water treatment applications, further development of deionization technologies specialized for applications beyond of water production from seawater and for drinking water have important economic value.

2.2 Dissolved Solids Treatment & Deionization

Deionization technologies come in many forms for many different applications. In mining process-affected water treatment, the requirement is generally to minimize energy cost and improve resiliency with complex waters and for lower concentration streams, as compared to seawater desalination. A few natural resources applications, such as hydraulic fracturing in oil and gas, have highly concentrated water streams⁹. Both settings call upon a unique set of treatment options compared to the conventional

methods. For the purposes of this review, lower concentration treatments suitable for OSPW will be the focus.

2.2.1. Types of Dissolve Solids Treatment Technologies

The oldest methods of deionization for purification of water are thermal techniques using evaporation. While modern thermal and flash distillation technologies are far more advanced than a simple distillation still, the fundamental principles remain the same. In the mid-1900s, membrane processes such as reverse osmosis became increasingly popular by removing the need to generate large amounts of heat, and instead using high pumping pressure to separate water from dissolved ions. Further development of membrane processes such as nanofiltration have furthered this technology, with reverse osmosis becoming a highly popular method today.

Along with these two most conventional methods, other methods using membranes, electric fields, and chemical reactions have been developed as alternative methods with unique benefits. The comparative application of common technologies for deionization are shown in **Table 1**.

Table 1 – Comparison of deionization techniques for low to brackish salinity applications¹⁰⁻¹².

Type	Method	Energy Intensity	Typical TDS Range
Thermal	Multi-Effect Distillation	High	High
Thermal	Multi-Stage Flash	High	High
Membrane	Reverse Osmosis	Moderate	Medium - High
Membrane	Forward Osmosis	Low	Medium - High
Electrochemical	Electrodialysis	Moderate	Low
Electrochemical	Capacitive Deionization	Low	Low - Medium

2.2.2. Methods for Low to Brackish Salinity Applications

The major challenge in selecting methods for lower salinity applications, such as process-affected water treatment, is mediating the total cost of energy and treatment infrastructure with the low economic value of process water. The primary focus of desalination and deionization technology

development is towards water production from seawater or other saline aquifers. As such, leading technologies such as thermal and membrane processes are generally tailored toward this type of application. These methods, while effective and well-established, are often most cost-effective when in operation with higher salinity streams, and do not scale proportional to the concentration of dissolved ions, making their energy cost higher on a concentration normalized basis for lower salinities^{13,14}.

For low to brackish salinity applications, treatment can be more effectively deployed using alternatives such as electrochemical methods like electrodialysis¹⁵ and capacitive deionization¹⁴. Given the strong alignment of electrochemical methods for low to brackish salinity applications by scaling with salinity, and suitability for treatment in complex water streams, analysis following will focus on the emerging area of capacitive deionization, and its versions therein, for application in process-affected water treatment^{12,16}.

2.3 Capacitive Deionization

Capacitive deionization (CDI) is an electrochemical method of transporting, concentrating, and electrically absorbing dissolved ions from a solution¹⁷. The emergence of CDI as a water treatment process follows the development of capacitive energy storage devices, wherein ion charge separation between two electrodes is used to store energy capacitively. The development of CDI has used the principles of these electro-chemical energy storage devices, where CDI utilizes “electro-sorption” to capture ions in the electrical double layers (EDLs) of opposing electrode surfaces, separating ions from solutions passing through the system. The process is similar to conventional electrodialysis using electrical forces to transport ions out of a deionized solution, but instead storing the ions capacitively, as opposed to simply concentrating them into a parallel brine stream.

A key benefit of CDI, shared with electrodialysis, is the removal ions from the water solution, as opposed to of removing the water from solution as a majority component. The latter is the operating principle for membrane and thermal methods of deionization, which causes them to be inherently energy intensive processes that do not scale as proportionally to salinity, as compared to CDI. For treatment of light to brackish salinity waters (<1000 – 5000 mg/L), this means that CDI often exhibits greater efficiency per volume of water treated^{12,18}. However, compared to electrodialysis, CDI offers key advantages through its ion electro-sorption process, wherein separated ion concentrations can be

much higher and electrical efficiency of separation therefore greater. Further, CDI offers potential for energy recapture during regeneration, whereas electro dialysis does not fundamentally integrate the same capacitive energy storage¹².

CDI utilizes highly mesoporous, high specific surface area electrode materials, which provide a large quantity of sites for capacitively storing immobilized ions in the EDLs of mesopores and micropores. Standard pore size definitions, as determined by IUPAC¹⁹, are summarized in **Table 2**. This primarily occurs through a non-Faradaic and reversible process of charge balanced storage near the surface of the electrode, in a volume known as the Stern layer, and in a dispersion of ions away from the surface, as described by the Guoy-Chapman theory, when an electrical potential is applied between electrodes^{17,20,21}. The combined Stern-Guoy-Chapman storage of ions describes a non-ideal charge compensation the electrodes, including losses caused by co-ion diffusion away from the electrode, which results in a less than one-to-one charge to ion absorption that may otherwise be expected in a Helmholtz model of the capacitive ion storage¹⁷. In the most common arrangement, electrodes are arranged at opposing sides of a water channel, flowing perpendicular to the electrical field^{17,22}. The fundamental principle of CDI operation is the concentrated storage of positive and negative ions at electrodes, in a process where the removal of the applied potential reversibly releases the ions from the mesopore and micropore EDLs²¹.

Table 2 – Definitions of porosity and pore sizes.

Pore Size Classification	Diameter (nm)
Macropores	> 50
Mesopores	2 - 50
Micropores	< 2

Electrode materials have a finite storage capacity for ions, which is reached when the EDLs throughout the mesoporous media saturate with ions¹⁷. The stored ions may be expelled from the EDLs either by removing the electric potential to permit diffusion away, or in an alternative operating mode, applying an inverse potential to drive ions away at a faster rate^{17,23}. In typical CDI operation, the process of electrode regeneration concentrates stored ions into the same channel of water formerly used for deionization, creating a brine stream. The control of separating the deionized and concentrate streams may be done through switching of fluidic inputs and outputs to the cell. A semi-continuous

operation can be achieved using two parallel cells – one deionizing and one regenerating²¹. This process enables the CDI system’s electrodes to return to a neutral or co-ion deficient state, ready to extract ions from solution again at peak efficiency.

The basic principles of CDI were first studied in 1960 by Blair, Murphy et al.^{24,25}, and furthered by Johnson et al.²⁶ through detailed study and characterization of the EDLs, which more clearly described the mechanism of operation. These methods focused on the above basic architecture of electrodes around a flowing water channel, commonly known as “flow-by”. A similar process, using “flow-through” electrodes was included in the study by Johnson et al.¹⁸, by eliminating the spacer channel and instead flowing water through the electrode media, and orienting the electric field parallel to the deionized water flow direction, reducing the path-length for ion diffusion^{27,28}. However, this required new considerations for electrode media, enabling effective flux of treated water and managing potential foulants. Schematics of these two processes for these basic CDI systems are shown in **Figure 1**. In both modes, mesoporous electrodes attract dissolved anions and cations and store them in the electrode pore EDLs, generating deionized water.

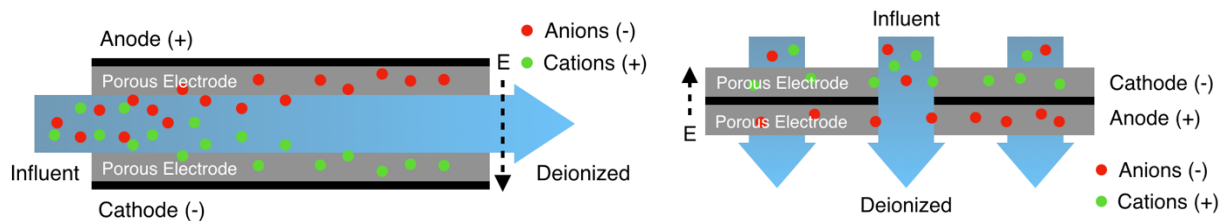


Figure 1 – Schematic of two CDI treatment systems: flow-by CDI (left) and flow-through CDI (right).

CDI was advanced by Farmer et al. in the 1990s, using carbon aerogel electrodes for a substantial improvement compared to traditional activated carbon electrodes^{29,30}. This research evaluating new electrode materials preceded a major increase in scientific interest for CDI in the mid-2000s, primarily with a focus on new electrode materials with optimized conductivity, surface area, mesopore and micropore distribution, and resistance to fouling or unwanted Faradaic reactions^{17,22}.

Further research has developed new approaches to this basic CDI design, involving several areas of iteration, from improved electrode materials with greater efficiency and capacity^{31,32}; to various modes of electrical operation^{27,33,34}; to new CDI architectures and operational designs^{18,22}. With CDI identified as the research project focus, the latter area of development – architecture and operational design –

presents an immediate design selection question: what system design may be most advantageous? Two notable innovations for increased CDI efficacy iterating upon the basic CDI model include membrane CDI (MCDI), and its further iteration, flowable-electrode CDI (FCDI). Both methods aim to improve the overall efficiency of deionization using the principle of CDI with improved system dynamics.

2.3.1. Membrane Capacitive Deionization

For basic flow-by CDI, applying a potential to the electrodes both attracts counter-ions (opposing charge) from the water channel to the EDLs in mesopores and micropores of the electrode, while also expelling co-ions (same charge) out of the mesopores, into the spacer channel and, depending on the time for diffusion, to the opposing electrode. A key innovation, pioneered by Lee et al., utilizes ion exchange membranes (IEMs), typically applied to separate concentrate and deionized streams in electrodialysis, between CDI electrodes and the water channel volume³⁵. This schematic is shown in **Figure 2**. The IEMs, anion (AEM) and cation exchange membranes (CEM) at the anode and cathode respectively, utilize strong internal charges from functional groups in the membrane polymers to effectively block the transport of co-ions across the membrane^{17,36}. The MCDI design uses IEMs to block the discharge of co-ions away from the electrodes, making flux of counter-ions from of the treated water towards the electrode the only trans-membrane ion transport during discharging.

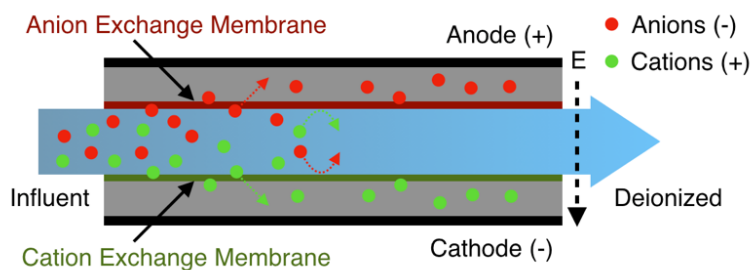


Figure 2 – Schematic of an MCDI treatment system.

The use of IEMs in MCDI can enable faster and more efficient deionization compared to similar CDI systems. Co-ion transport away from and towards the opposing electrode leads to lower deionization efficiency, as co-ions contribute to charge migration towards opposing electrodes, using electric potential and saturating EDLs faster³⁷. This also reduces the co-ion charge concentration in macropores and the volume surrounding each electrode, which in turn reduces the counter-ion concentration in the charge-neutral macropores, further reducing efficiency^{17,37}. This effect has been

shown to lead to up to a 20-40% increase in efficiency, compared with equivalent flow-by CDI systems^{36,38}.

A secondary benefit of the MCDI design is that the treated water volume is separated from the porous electrode media. This can improve performance in complex water streams where suspended solids and organic media can lead to fouling of the electrode materials more readily than membranes³⁹. The IEMs provide a physical barrier that can be cleaned and maintained in more effective manner than the porous electrode materials, using techniques developed for electro dialysis systems. The mesoporous media used in electrode materials are often similar in material type and morphology to other materials specifically designed for high absorption for water foulants, such as activated carbon beds³¹.

MCDI also offers a benefit relevant to deionization targeting specific problematic ions. Ion exchange membranes can be selected to preferentially deionize certain ionic species, such as selectively separating between divalent and monovalent species^{40,41}. For some industrial wastewater processes, this may be advantageous to specifically target a problem ion species or condition water for reuse.

However, MCDI maintains the limitation of requiring a charge-discharge cycle within the same cell, leading to complexity in the overall system design and fluid handling for each cell, as well as leading to trade-offs in the operational design of the system. A key trade-off is selecting regeneration thresholds where longer deionization time can incur a penalty of operating in a lower efficiency regime of partial electrode saturation⁴². An ideal CDI or MCDI system could be one that is able to operate in a zero to low-saturation regime at all times and maintain a continuous operating mode to be similar in operation to electro dialysis systems, which typically use continuous flowing parallel streams of deionized and concentrated brine waters.

2.3.2. Flowable-Electrode Capacitive Deionization

The solution to this challenge is an iteration of the MCDI design, replacing solid electrode materials with flowable slurries of similar mesoporous, conductive media. This design, called flowable-electrode CDI (FCDI) uses the IEMs from MCDI as both a co-ion barrier, as well as a physical barrier to retain the conductive slurry between a charged current collector and the treated water stream. A schematic of this design is shown in **Figure 3** below. Flowable electrode slurries, comprised of powdered,

mesoporous media and electrolyte flow by current collectors. Ions are stored capacitively in the moving mesoporous activated carbon particles, which are continuously cycled through the system.

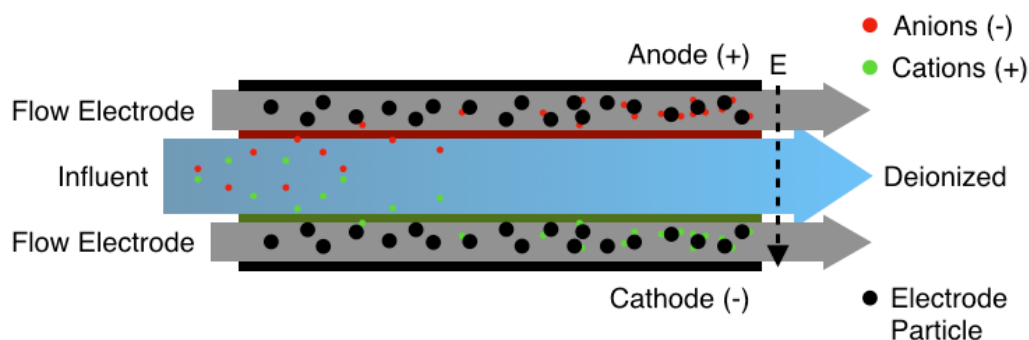


Figure 3 – Schematic of an FCDI treatment system.

The design theory for FCDI, pioneered by Jeon et al., uses the flowable electrode to continuously feed unsaturated electrode media into an electrode channel, charged by contact with a current collector⁴³. This continuous injection of fresh electrode media enables the cell to deionize continuously and in a high efficiency regime. FCDI both enables deionization near the peak efficiency of a cell for continuous periods for higher overall efficiency, as well as the potential to address higher salinity streams where solid electrodes may saturate too quickly, or require an excessive total electrode volume for a required deionization extent^{22,42,44}. Concentrated ions stored in the EDLs of the porous particulate in the slurry are transported at a rate determined by the flowable electrode stream, where the saturated slurry may be stored and regenerated externally by mixing the two streams, using a regeneration cell, or simply by extending the charge-discharge cycles of a single FCDI cell^{44,45}.

Flowable electrode slurry is comprised of powdered activated carbon or other mesoporous conductive materials and composites that, at sufficient solids concentration, are sufficiently conductive to mimic the operation of a solid electrode. The overall charge efficiency is derived from complex interactions between the conductive solids, their concentration, flow channel dynamics, and charge carriers that may be added to reduce resistive losses. Typically, a flowable slurry will sacrifice conductivity and coulombic efficiency compared to solid electrodes¹⁸ in exchange for the ability to operate in a continuous mode, with unsaturated electrodes. This trade-off gives the potential for a system of higher overall efficiency and effective system design compared to the limitations of MCDI.

A variety of flowable media have been selected for use in this FCDI applications, the most common selection and readily produced materials being high conductivity, high specific surface area powdered activated carbons (PACs), often developed for use in supercapacitive energy storage and as conductive additives. These slurry particulate materials, along with other slurry additives, enable performance that compares favorably to common solid electrodes in CDI and MCDI applications¹⁸.

2.3.3. CDI Energy Recovery Design

The shared principles of electrochemical energy storage and CDI extend to the ability to recovery energy from a CDI cell during electrode regeneration. Stored electrical potential from the capacitive storage of ions in the opposing electrodes presents an opportunity for recovering this energy during electrode regeneration^{46,47}. The net efficiency of the deionization process depends on the losses during charging and discharging phases, which dictate the “round-trip” energy cost for a given deionization cycle. The relationship of the work applied in a standard CDI treatment cycle is:

$$W_{round-trip} = W_{charge} - W_{discharge} \quad (1)$$

The two phases of charging and discharging may have differing efficiencies based on the design and operation of the system and may change over time based on degeneration from repeated charge and discharge cycles. Each is determined as:

$$W_{charge} = \frac{E_{charge}}{\eta_{charge}} \quad (2)$$

where E_{charge} is the energy required for the charge cycle of the CDI cell, η_{charge} is the is thermodynamic efficiency, relative to the minimum theoretical thermodynamic energy of moving ions to the electrode EDL¹². This minimum theoretical energy in ideal conditions is defined as:

$$\Delta G = G_{fresh} + G_{conc} - G_{feed} \quad (3)$$

$$G_i = RT\phi_{v,i}c_i \cdot \ln c_i \quad (4)$$

where ΔG is the change in the free energy of the system by performing deionization (increased free energy by reduced entropy), as it relates to the free energy of the fresh, concentrated, and feed water free energies. The free energy components are determined by the concentrations (c_i) in each stream

and the flow rate ($\phi_{v,i}$)^{17,48}. Therefore, the efficiency of the cell (η_{charge}) can be determined as a ratio of actual energy compared to the theoretical requirement. As a figure of merit for the total energy consumed in a round trip, the ratios of the two charging and discharging steps can be compared¹²:

$$\eta_{round-trip} = \eta_{charge} \cdot \eta_{discharge} = \frac{W_{discharge}}{W_{charge}} \quad (5)$$

While CDI systems are not optimized for maximum round-trip efficiency compared to supercapacitor energy store devices, capturing the stored energy during regeneration has been shown to recapture energy for the treated volume by up to 83%, as shown by Dlugolecki and van der Wal for a standard flow-by MCDI system²³. However, this thermodynamic efficiency varies depending on the deionization extent and operational conditions, especially the inlet salinity, where more saline streams make regeneration less complete^{49,50}. For FCDI systems, this premise can be further extended using the design principles of flow-batteries. Demonstrated by Gendel et al., the FCDI system can operate in a closed loop with a deionizing and recovery cell, operating on two parallel water streams (i.e. – deionized and brine concentrate)⁵¹. This mode of operation is shown in **Figure 4**. The flowable electrode slurry first capacitively stores separated ions in the deionizing cell and then flows to the recovery cell where slurry is regenerated, and capacitive stored energy is partially recaptured. Slurry may be stored in bulk vessels reduce round trip time or defer regeneration.

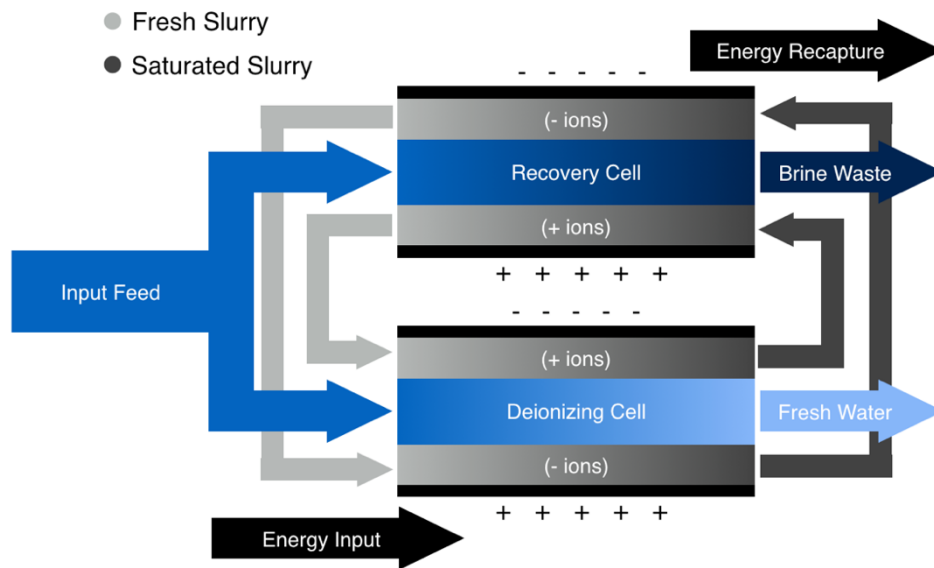


Figure 4 – Schematic of a closed-loop recovery system for parallel FCDI cells.

This demonstrates promise for utilizing the FCEDI system not only in a continuously recoverable fashion, but also the potential to store charged media and regenerate with energy recapture during deferred periods. Further, flow rate bias towards the deionizing cell show that up to 90/10 ratios of deionized to concentrate flow rates are possible while maintaining a high treatment performance in continuous treatment⁵¹. FCEDI systems' endemic limitations for reaching solid-electrode charge efficiencies mean that the round-trip recovery may be less efficient overall, such as shown by Jeon et al. for an energy recovery of 20%⁴⁴. However, the energy recovery is only one part of the net efficiency, and continuous operation may contribute further to the utility of the FCEDI process design to decrease the cost of energy and the size of a deionization system. Improvements to slurry materials selection, current collector design, and operational design can improve FCEDI energy recovery.

2.4 Flowable-Electrode Capacitive Deionization Design

FCEDI shows strong potential for application in the area of low to brackish salinity deionization, including with benefits for complex water streams that would otherwise require more significant pre-treatment. Within the area of FCEDI, there are a number of approaches to the design of the treatment unit, referred to generally as the “flow-cell”, with respect to orientation of flows, physical dimensions, material selection, and the operational design.

2.4.1. Flow-Cell Mechanical Design and Architecture

CDI system architectures are abundant, translating design concepts from a variety of other electro-chemical energy storage and water treatment systems. FCEDI similarly has several notable design variations, which have consequences on the overall performance of the system in conjunction with materials selection.

i. Electrode and Water Channel Design

A fundamental design consideration for flow electrodes is their shape, size, and flow-path. A basic design is two electrode channels flowing parallel on opposing sides for the deionized water channel^{46,52}, as generally represented in **Figure 3**. Ideally, the flow electrode behaves as an ideal plug flow through the electrode channel, minimizing decoupling and dead-zones in the stream where saturated slurry media may accumulate and operate ineffectively. Variations on the parallel flow streams emerge for this reason, particularly with increasing flow cell aspect ratio and slurry viscosity, both of which would

limit the effectiveness of a single, wide stream. As demonstrated from the first FCEDI cell designs by Jeon et al., serpentine flow pathways can enable small electrode depth coupled to a large membrane-to-deionized water interface, minimizing ohmic losses through the electrode layer while ensuring effective transport of the viscous slurry media^{43,51}.

However, smaller channels and serpentine designs can incur greater pressure drops across the flow-cell, which manifest as a limitation on slurry solids loading (where lower solids content correlates with higher ohmic losses)^{42,52} and greater pumping energy requirements (where it constitutes a non-trivial component of the total energy costs for FCEDI)⁵². For simple demonstration cells, the single channel and parallel flow design may be most convenient to evaluate the merits of FCEDI in new treatment applications and new materials selections. In addition to channel geometries reducing dead-zones, optimized contact with current collector surfaces can reduce net ohmic losses.

ii. Electrode and Water Channel Dimensions

The selection of the channel dimensions is also important. FCEDI systems are generally limited by electrolysis of water above 1.2V, and the sizing of the channels have a key impact on the resistive losses across the cell. For instance, the deionized water channel is the primary source of resistive losses in the cell⁵³, and a wider channel requires longer transport distances for ions to reach the IEM interface⁴². Practically, the benefits of reduced channel width and increased aspect ratio must be weighed against maintaining effective pumping and reducing dead-zones in both the slurry and water channels⁵⁴.

Electrode channels have similar trade-offs, especially in FCEDI where electrodes are naturally higher resistivity relying on slurry conductivity¹⁸. However, smaller electrode volumes mean that saturation is achieved at a higher rate due to the finite EDL surface area. This can be mitigated by higher rate of slurry pumping and replacement, at the cost of added pumping energy⁵². Each channel design relates to the slurry composition trade-offs as well, as higher solids loading slurries with greater viscosity become more difficult to pump in a small channel cross-section but do provide benefits for reduced ohmic losses.

iii. Alternative FCDI Flow Cell Architectures

In addition to the above FCDI designs, which have emerged as the flowable electrode variant of the common flow-by MCDI architecture, there exist additional creative design approaches. One variant, proposed by Hatzell et al., eliminates the separated deionized water channel by directly integrating the flowable electrode media with the deionized water streams⁵⁵. The two electrode streams are separated by a non-ion selective porous membrane, and after capacitive storage of ions, the slurry media is separated by a filtration step. This mimics the benefits of the flow-through CDI system by reducing the ion transport distance and effect of ohmic losses²⁸, which is especially important in FCDI systems where ohmic losses are typically increased. It also reduces the total number of pumped fluid streams, though it incurs an energy penalty for filtration recovery of the charged slurry media.

Another approach, proposed by Porada et al., utilizes specially designed cylindrical IEMs to create flow electrode tubes with wire current collectors in the center⁴². The design theory presents a more scalable design premise for large reactors, as compared to the conventional flat plate systems, and a large electrode-water interface. However, practical challenges such as poor contact with single wire current collectors and custom extruded IEMs presented overall ohmic losses of 2 orders higher than a comparative flat plate system.

Finally, while similar to the design of a common FCDI cell, Doornbusch et al. demonstrated an FCDI variant with fluidized bed electrodes, enabling much higher solids loading with larger mesoporous particle media (100 μm beads compared to a typical 10 μm FCDI slurry particle) for benefits to conductivity without sacrificing high pumping requirements⁵⁶. The vertical cell orientation and pumping direction, paired with the large beads, creates a high solids loading in a fluidized bed electrode, while maintaining a low solids loading in the rest of the system, reducing pumping requirements. Novel approaches such as these represent the diverse approaches to FCDI seeking performance enhancement.

2.4.2. FCDI Flow Cell and Electrode Material Selection

FCDI cell materials selection is important for the overall performance and reliability of the system. The key materials comprise: the composition of the flowable-electrode slurry; the ion exchange membranes; the current collector; and other spacing and fluidic contact materials.

i. Flowable-Electrode Slurry

The selection of materials for the flowable-electrode is perhaps the most fundamental part of the FCDI system. Materials selection is firstly focused on the mesoporous, conductive media used to absorb ions. High specific surface area materials provide high capacitive storage per volume of slurry. Generally, small micrometer scale ($\sim 10 \mu\text{m}$ dia.) powdered activated carbon (PAC) media is utilized^{22,52,56}, typically of similar grade to other applications in superconductors or conductive additives⁴⁵, and loadings typically up to 20-25% by weight^{43,52,57}.

Mesoporous electrodes used in CDI and FCDI benefit from specific morphologies that encourage efficient and abundant charge storage in the EDLs. The pore structures forming surface area are an important parameter. CDI electrode media should have pores that are open (continuous communication with the external surface) and should comprise an abundant mesoporosity (2-50 nm) connected to a macroporous network to encourage efficient charge transport¹⁹. Pores should ideally have EDLs do not overlap yet be small enough in their distribution that the total porosity is maximized. Overlap of the EDLs is detrimental because it reduces ion transport, which subsequently reduces overall salt capacity¹⁷. Highly mesoporous and macroporous materials are ideal, along with small particle diameters, in order to achieve effective transport through short pore depth and a high quantity of open pores^{58,59}.

Additives and modifications to the slurry can also be advantageous. Modifications to improve the flowability of the slurry particles such as chemical oxidation⁵² or surface functionalization of the PAC particles⁶⁰. Higher flowability enables greater solids loading while maintaining operations, increasing conductivity and capacitance. Other slurry additives such as conductive carbon black particles^{46,61} or dosing electrolytes have also been shown to benefit overall performance by reducing ohmic losses^{57,62}. The addition of electrolytes has the benefit of not incurring additional energy penalties by increase of viscosity.

2.4.3. FCDI Operational Design

The operation of a given flow cell is also an important engineered design. While the selection of materials and architecture create the characteristic performance of a flow cell, the selection of

operational regime, as it relates to the electric and fluidic parameters and their modulation, are important to maintaining optimal efficiency.

The most common electrical operation mode for CDI is a constant voltage of 1.2V applied to the cell during charging, and a zero charge regeneration step^{17,22}. The charging mode is generally limited by hydrolysis, however greater potentials can be used at the risk of impacts from Faradaic reactions^{20,57}. In theory, maximized potential will increase the capacity of the cell for ion storage and rate of ion separation. However, due to limitations on ion transport to the electrode, as well as the scaling of ohmic losses, CDI flow cells may perform more efficiently at lower potentials⁵⁸.

With the implementation of MCDI limiting co-ion transport away from the electrode, the charging step can instead be operated in constant current mode¹⁷. This is especially advantageous for maintaining a steady single pass effluent concentration with solid electrodes, where potential instead follows maintaining the same rate of ion removal²². However, it has been shown that practically, constant voltage and constant current perform with similar overall efficiencies, and instead enable different rates of removal⁶³. For FCDI, constant current operation may be less impactful in the cell no longer has the same finite capacity as a solid electrode. As such, constant voltage mode is more typical for these systems, though both constant current mode and modulating the flow rate of the electrode can also be used to maintain an optimized single pass removal.

In discharge, a CDI cell can be operated in either no charge, or reverse charge modes (including both constant voltage or constant current). While no charge is most common²², energy recovery schemes and fast discharging of the cell may suggest that operating with a reverse potential could be effective to maximize round trip performance³³. This is theorized to potentially “pre-charge” the electrodes by means of creating a counter-ion deficiency³⁷.

For FCDI, regeneration is typically completed using a parallel cell⁵¹ or otherwise cycling a charge and discharge of two stored volumes of flow electrode media (separating charges)⁴⁴. While the prevailing theory of operation suggests energy recovery and regeneration may occur in a similar cell design to deionization, acting similar to a capacitive energy storage system, research proposed by Porada et al. and Hatzell et al. suggest other schemes such as capacitive mixing, the generation of energy by switching the salinity of a stream⁶⁴, can be employed for regeneration as well^{42,46}. In another variation,

Rommerskirchen et al. demonstrated creative arrangement of parallel deionized and concentrated streams in a single cell could create a closed loop operation with up to 80% water recovery⁶⁵.

Fluidic operation for CDI also affects performance in connection with electrical parameters: the flow rate through the deionized water channel determines the extent of single-pass deionization, set by the rate of removal by the cell. While in-field applications of CDI will likely be single-pass and continuous, batch mode recycling of effluent for additional cycles can be used to simulate a larger flow cell system¹⁷. Both batch mode and single-pass experiments can be useful to determine the characteristics of a flow cell (e.g. – single pass rates vs. total deionization capacities).

For flow-electrodes, the direction and rate of flow can affect the overall performance. Flow rate of the electrode determines the rate of replacement for flow-electrode media. Selection of an appropriate flow rate may be determined by evaluating the specific capacitance of the cell, and optimizing the maintenance high separation efficiency (i.e. – low saturation electrodes) and sufficient loading of the flow electrode for practical implementation (i.e. – not consuming an excess of pumping energy or generating large volumes of lowly saturated slurry). In FCDI operations, flow electrodes may utilize the IEM in order to facilitate a counter-flow or transverse flow operations (with respect to deionized channel flow direction)^{43,51,65}. This, coupled with aforementioned designs for electrode flow paths, may ensure that electrode media is loaded evenly through its transit of the flow cell. However, most FCDI studies have not focused on flow direction as a key design parameter.

In general, FCDI performance must be characterized and determined to suit the design of the flow cell and water to be deionized. Further exploration and novel approaches to electrical and fluidic parameters may enable more pragmatic design selection for FCDI systems

2.5 Industrial Application of CDI Technology

FCDI systems have had no significant implementations at a commercial scale. However, CDI and MCDI systems, along with analogous flow-battery energy storage similar to FCDI, have demonstrated potential for scale-up. These applications include their demonstration in both laboratory in in-field settings for both water supply and wastewater processing.

One of the first attempts to scale up CDI systems was completed by Welgemoed et al. in partnership with the Lawrence-Livermore National Laboratories towards desalination for water production⁶⁶. The

performance at this time in the 1990s to early 2000s was still limited by early carbon aerogel electrodes, however the scale-up demonstration demonstrated a pathway to implementation and identified key process challenges such as corrosion prevention in electrical contacts, and the need to focus on electrode material performance.

MCDI has been successfully commercialized for small scale application in drinking water purification and low-level salinity applications by Voltea B.V. in the Netherlands. Their field of applications includes industrial treatments of dissolved solids, such as in feed water for cooling towers⁶⁷ and sulfate removal from wastewater⁶⁸. These show promise for industrial applications and further improvement through FCDI technology. Other specialty industrial and mining water treatment ventures such as Saltworks Technologies Inc. and Enpar Technologies Inc. show a market for electrochemical water treatment outside of drinking water applications.

CDI has also been applied in settings for water softening⁶⁹, brackish water treatment for in-land water supply⁷⁰, and treatment of produced water from natural gas production⁷¹, which shows similar promise in real-world applications. However, the bottom line for all CDI competitiveness is increasing the overall energetic benefit over more established membrane and thermal technologies. This illuminates a path for further improvement using FCDI methods compared to CDI in scale-up. FCDI can leverage the same secondary benefits of fouling resistance and ability to scale to lower salinity or targeted extraction applications.

2.6 Conclusions

Capacitive deionization, and further, flowable-electrode variations therein, are a high potential and emerging option for deionization of low to brackish salinity mining process-affected waters. FCDI technology builds upon an early but demonstrated potential for CDI systems by increasing the performance and scalability of the treatment process, and presenting an alternative that scales in deionization performance compared to conventional thermal and membrane processes^{12,16,18}. However, the number of research studies evaluating practical applications of the technology and in particular, the implementation of novel systems such as FCDI, are limited. This presents an addressable research gap in evaluating their applied performance for applications such as process-affected water.

3 Design and Methods for Flowable-Electrode Capacitive Deionization

The design of the FCDI prototype system was selected with precedent from prior art in flowable supercapacitor and battery technology, as well as other flowable electrode systems, such as those by Jeon et al.⁴³ The concept of the FCDI cell is to provide a robust and simple combination of current collectors, flowable electrode channels, and membrane support to create the three selectively connected flow channels that create the deionization cell. The FCDI system used to conduct treatment studies in this thesis was developed through design iteration of the flow cell architecture, selection of materials, integration of monitoring devices, and improvements to designs after initial testing validation, as discussed in **Section 4**.

3.1 FCDI Process Flow Design

The process flow of an FCDI system is relatively simple, including the three flow paths for electrode media and treated water, and the design of their flow and materials handling. The major consideration for the study of the FCDI system is operation in continuous (single pass) or batch mode (multi-pass) treatment modalities. For study of greater treatment extent using a single module, the batch mode process is generally preferred and can be extrapolated to a larger FCDI system with greater treatment contact time. Batch mode operation was primarily used in the studies conducted herein.

A process flow diagram representing the FCDI system used in these studies is shown in **Figure 5**. Here, the flow paths of the electrode media are shown to operate in a closed loop, where the electrode media is provided in excess to maintain a high rate of de-ionization performance. The system utilizes both inline conductivity transmitters (CT), as illustrated on the treated water return, as well as sensors in the water sample vessel and flow electrode vessel(s) to monitor the rate of deionization. Finally, the power electronics are notated for clarity, including the integration of an ammeter data recorder (AR) at the cathodes. Together, the conductivity and current data logging system allows for measurement of treatment performance on a per-pass and batch treatment basis, as well as the corresponding energy consumption for all operational conditions tested.

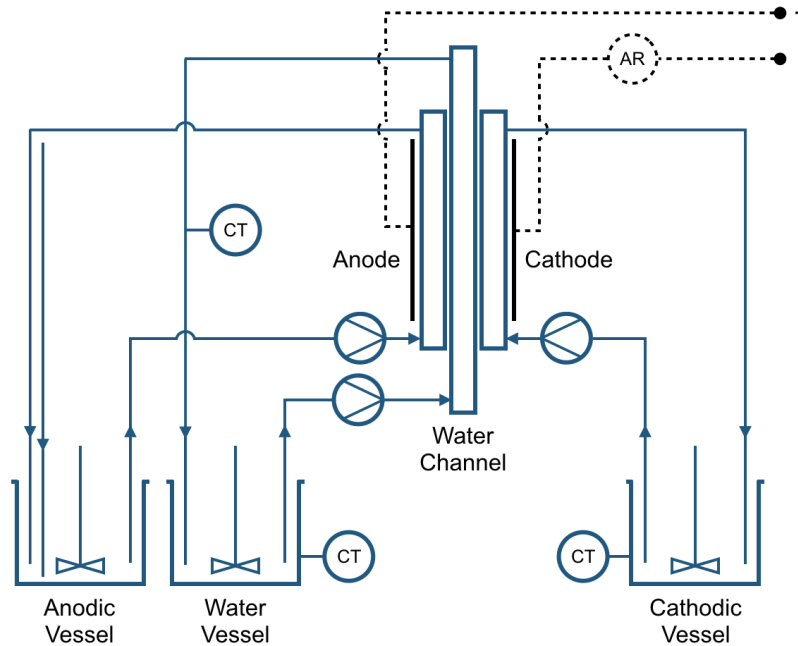


Figure 5 – Process flow diagram describing the design of the FCDI prototype cell configured in a batch treatment mode.

3.2 Mechanical Design & Selection of Materials

A critical design selection for the development of a FCDI system is materials composition and performance. Materials of the key system components – the current collector, electrode slurries, ion exchange membranes, and other interconnects – will dictate the rate of performance of the system. The development and optimization of materials for CDI systems is the most researched system component and design selections are important towards the operability and performance of the FCDI system^{31,32}.

3.2.1. Mechanical Design Iterations

Two flow cell designs were developed towards an effective prototype for testing the performance of the FCDI systems. The first iteration of design was developed using a machined current collector that positioned flow electrode slurry entry off axis from the direction of flow, and incorporated IEMs attached to the current collector by marine-grade epoxy resin in an inset section. This design aimed to reduce the number of gasket interfaces and enable a larger aspect ratio flow electrode chamber. A cross-section schematic of the system is shown in **Figure 6**. However, this design encountered

reliability and maintenance challenges between treatment trials due to the integrated IEM design. Delamination of the membrane-to-current connector interface and the adhesive used to bond them caused leaks into the treated water volume. Additionally, the semi-permanent bonding made inspection and servicing of the ion exchange membranes more difficult, particularly in a phase (discussed in a later section) where troubleshooting the flow electrode and membrane interface was important. A re-design of the system was completed towards greater reliability, simplicity of re-assembly, and fewer changes in channel aspect ratios and flow directions towards more effective mass transfer through the entire flow channel volume.

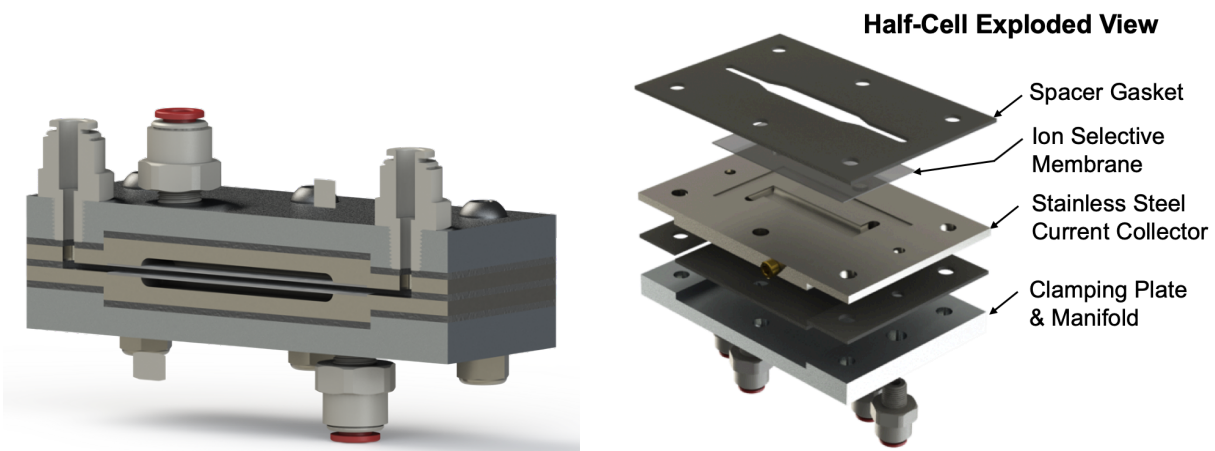


Figure 6 – Version 1 prototype FCDI cell shown in cross-section (left), and exploded view showing flow-electrode channel and integrated membrane (right).

The revised iteration, used in all of the studies examined in this thesis, is shown in **Figure 7**. This design incorporates straight, parallel flow channels for both the flow-electrodes and water channels, entering and exiting through perpendicular fitting interfaces. The IEMs are instead sized extend over the entire flow-cell plate area, and perforations in the membranes for clamping bolts are positioned to create tension force across the membranes. Gaskets in this configuration enable easier membrane removal, servicing, and replacement, and reduced leaks due to pumping pressure. The gaskets also enable simple alteration of flow channel depths by using varied gasket material thicknesses, and therefore increased spacing for the depth of the flow channels.

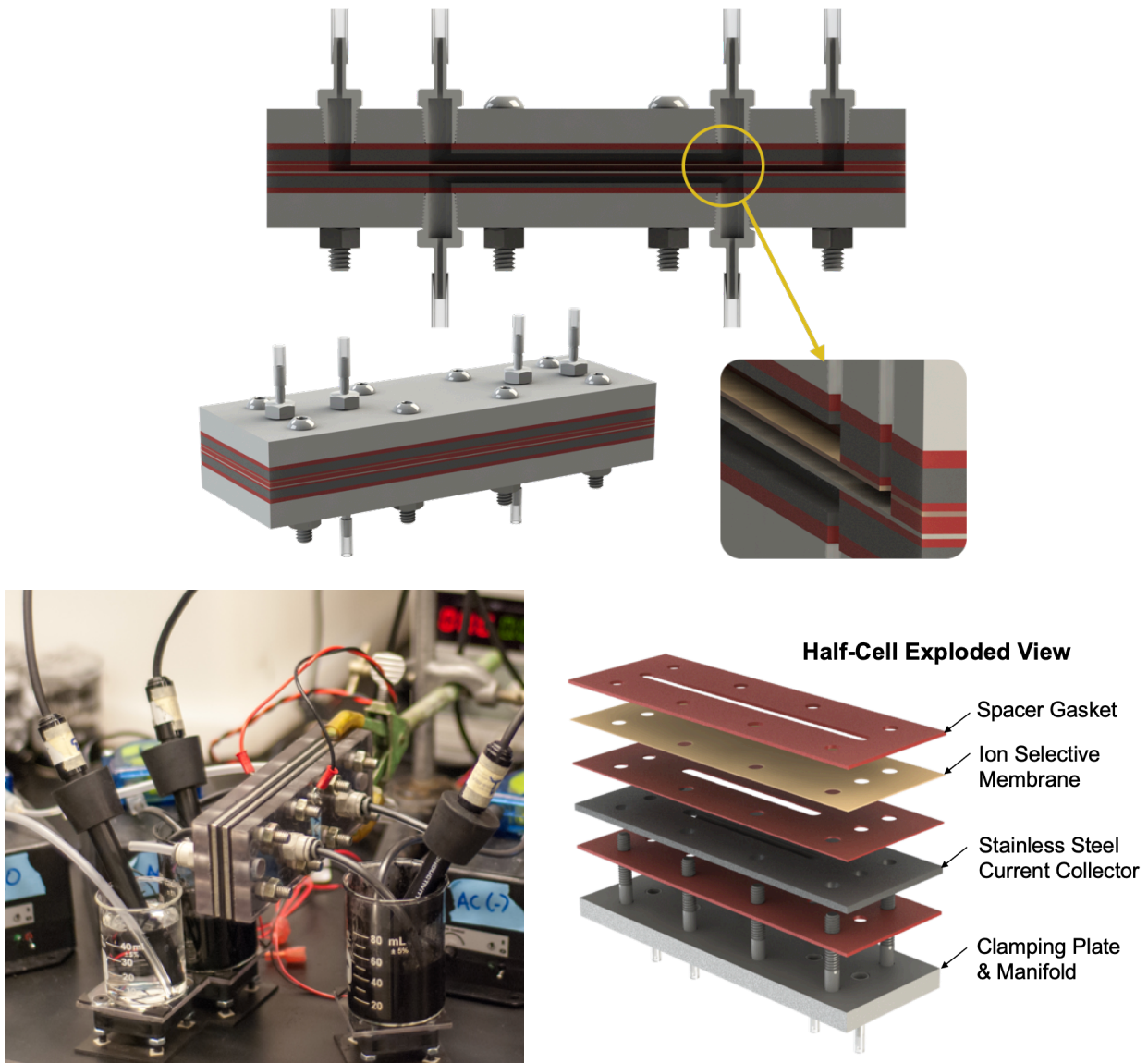


Figure 7 – Assembled and cross-section detail renders of the Version 2 prototype FCDI flow cell in normal configuration (top); the as-built and operating system is shown (bottom left); and exploded view of FCDI half-cell with key elements labelled (bottom right).

3.2.2. Current Collectors

The current collectors were constructed of 3.18 mm (0.125”) thick 316 stainless steel flat stock in order to provide high conductivity, ease of machining, and corrosion resistance in the presence of elevated total dissolved solids solutions. 316 stainless steel is commonly used in corrosive and saline

applications, and was selected to reduce the potential losses in ionic concentrations that may contribute to the deionization signal during testing.

The current collectors were machined to create the flow channels for the electrode slurry. The channel dimensions were selected to be 6.35 mm (0.25”) x 60 mm x 3 mm and were machined using a 3 mm ball end-mill to create a radius between the vertical channel walls and the top of the channel volume, reducing the dead volume. Further, the channel was milled to create a narrow center divider to provide additional support for the membrane and reduce the width of the channel. The channel dimensions and geometry was chosen to improve the flow of the viscous electrode slurries and reduce dead volume where mass transport of saturated electrode material may be lower, iterating from the original flow cell design. The current collectors were connected to the power supply using a screw terminal plug and insulating inserts were added to each current collector to separate the charged plate from conductive fasteners used to clamp the flow cell together.

3.2.3. Ion Exchange Membranes and Gaskets

The selection of IEMs was completed through a review of available anion and cation exchange membrane suppliers, including those demonstrated in previous MCDI and FCDI studies. Several different IEM products have been used in contemporary flow battery and deionization systems. A comparison of a selection of these membranes obtained for study are shown in **Table 3**.

Table 3 – Ion exchange membranes evaluated using FCDI prototype flow cell.

Specification		Membranes International	Snowpure Excellion	ASTOM Neosepta
Thickness (μm)		450	340	140
Burst Strength (psi, Mullen test)		>80	41 – 47	> 50
Electrical Resistance ($\text{ohm} \cdot \text{cm}^2$)	AEM	< 40	7.5 – 12.5	2.4
[0.5 N NaCl]	CEM	< 30	9.5 – 14.5	2.9
Exchange Capacity (meq/g)	AEM	1.3	2.4*	1.25
	CEM	1.6	1.3*	1.62

Data reported for both IEM types where specifications are similar.

*Approximation based on reported meq/m² using polypropylene density (primary membrane material).

The selected IEMs are shown to have similar mechanical, electrical and ion exchange properties. The Membranes International products (AMI-001 and CMI-7001) are the thickest and most robust, while maintaining a relatively similar exchange capacity. The Snowpure Excellion (MI-100 and MI-200) products are lower strength and have a rougher surface finish, however they compare more favorably based on the approximate conversion of exchange capacity, particularly for the AEM. The ASTOM Neosepta (ASE and CSE) are similar in exchange performance to the Membranes International products, but may have a lower electrical resistance which could increase effective potential across the deionization channel.

In comparing the products and their mechanical workability, the Membranes International IEMs were selected as the primary option for use in the FCDI cell. The high mechanical strength was advantageous to maintain a seal and channel dimensions under varied pumping modes. Testing confirmed similar performance between the membranes, such that their selection as general IEMs were acceptable.

The IEMs are utilized as selectively permeable membranes both to control the flow of ions in the FCDI system, as well as to separate the treated water stream from the electrode slurry solids. In order to great a thickness dimension to these channels, neoprene rubber gaskets were created from 1/8" and 1/16" flat sheet stock. Channel shapes and other perforations were created using computer assisted design (CAD) stencils and a combination of scalpel blades and hand punches.

As shown in **Figure 7**, the gaskets were placed between the outer clamping plates and the charged current collectors to act as insulation; between the membranes and current collector to create an effective seal for both interfaces; and in the center channel between membranes to create the treated water channel depth and act as an insulating interface. The center channel gasket was interchanged in experimentation examining the channel spacing and its effect on deionization efficiency.

3.2.4. Flowable Electrode Slurry

The composition of the flowable electrode slurry includes three components: water, powdered activated carbon (PAC), and an electrolyte. The particle size, surface area, and conductivity of the PAC selected are important parameters. Supercapacitor battery grade PAC is utilized for the FCDI flowable electrodes in order to obtain high purity and high conductivity materials. All three PAC suppliers evaluated for this study provide specialty grade PAC that is highly conductive, mesoporous, and small

particle size as compared to other powdered and granulated activated carbon otherwise found in absorbent applications. The PAC materials considered are shown in **Table 4**.

Table 4 – Comparison of powdered activated carbon (PAC) products evaluated for flowable electrodes.

Specification	Haycarb HCE 202	Cabot Norit DLC Supra 30	Calgon Carbon Elite C
Particle Diameter - D ₅₀ (μm)	5 - 7	5 - 10	5.5
Bulk Density (g/cm ³)	0.36 - 0.41	0.30	-
Surface Area - BET (m ² /g)	1750 - 1980	1900	>1600

All three PAC materials have similar mechanical properties including their particle size and surface area. These are the most critical attributes to determine the available surface area available for capacitive storage of ions. More complex analysis to determine the relative micro and meso-porosity of the materials along with comparisons of their durability through successive charge cycles (i.e. – rate of capacitance loss) may enable incremental improvements and modifications to the PAC materials. For the purposes of this prototype study, solutions of all three materials were found to be similarly flowable and stable, and conducted treatment on single salt concentrations with equal performance. For data reported in this study, the Haycarb HCE 202 was used unless otherwise noted due to ease of availability for successive experimentation studies.

The flowable electrode electrolyte was sodium chloride through all experiments, mixed at a concentration of 1000 mg/L unless otherwise noted. The inclusion of an electrolyte in the PAC slurry enables improved flowability, conductivity and overall performance of the FCDI cell. A similar magnitude of electrolyte compared to the treated influent water was used towards reducing any confounding effects of having a large differential in electrode and deionized channel dissolve solids concentration during treatment tests.

3.2.5. Other Flow Cell Components

The remaining FCDI prototype components include fluid interconnects and clamping components. The fluid interconnects were push-to-connect tube fittings, threaded into the clamping plates and connected to Tygon polypropylene tubing. The clamping plates, designed to provide structural strength and be non-conducting, were machined ½” clear polycarbonate flat stock and the completed

cell was clamped using $\frac{1}{4}$ "-20 x 3" 8-18 stainless steel bolts. The bolts were sheathed with insulating vinyl electrical tape to prevent connection between the two electrodes. Clamping force was provided by tightening with wrenches until initial visible deformation of the gasket layers under compression force.

3.3 Controls, Monitoring, and Analysis Methods

In order to operate the prototype FCEDI cell and monitor its performance, a basic arrangement of power electronics, sensors and data loggers were integrated into the testing set-up, including the use of custom designed parts. An overall schematic of the demonstration set-up is shown in

3.3.1. Pumping and Flow Control

Pumping for the flowable electrode slurries and water samples used for experimentation were provided by three variable flow rate peristaltic pumps from APT Instruments (SP201V1) using chemical resistant Norprene rubber tubing. Flow rate settings were validated using a balance and timer to confirm flow rate settings.

The slurry media was typically continuously suspended in mixture using small magnetic stir bars in 50 mL borosilicate glass beakers, with tubing inserted vertically at the beaker walls and tube ends located at the lower third of the beaker volume. Water samples were operated in batch mode and continuously mixed with effluent from the FCEDI cell unless otherwise noted in experimentation.

3.3.2. Power Electronics and Monitoring

The electrical input used for operating the FCEDI prototype was supplied by a 24 V, 2 A adjustable power supply from Tenma Test Equipment (72-8335A). The system was typically operated using a constant voltage setting and connected to the current collectors of the FCEDI cell. In order to monitor energy consumption, a ± 160 mA (5 μ A resolution) current data logger from Madgetech (Process101A) was placed in line with the current collector anode and power supply. Due to the pump selection not being optimized for the operating range, pumping energy was generally not considered in the figure of merit for operation, and was less than 1.5 A for all three pumps in full operation.

3.3.3. Deionization Monitoring and Water Analysis

Measurement of total dissolved solids and changes to their concentration was recorded in real time during experimentation using conductivity probes (0 - 20,000 $\mu\text{S}/\text{cm}$) from Vernier Software & Technology (CON-BTA) connected to a LabQuest 2 Data Logger (LABQ2). The conductivity probes were inserted into the water sample reservoir in typical operation. For single salt batch testing, conversion of solution conductivity to ionic concentration was completed using molar conductivity references for the treatment range tested⁷². Conductivity probes were calibrated using 100 or 1000 mg/L sodium chloride standards supplied by Vernier depending on the treatment range being studied.

In tests assessing the single-pass deionization, a custom flow cell mounted at the effluent port of the FCDI prototype cell was used to capture changes in conductivity per-pass. Calibration was completed using sodium chloride standards provided by Vernier.

Selected test results were validated using analytical services provided by ALS Environmental Inc., including analysis of dissolved cation and anion species and other water quality analytics included in the characterization of industrial water sources using ion

4 Validation of FCDI Treatment & System Design

The second iteration of the FCDI prototype was validated and characterized using various solutions of dissolved salts in order to demonstrate deionization performance, compare removal, and consider changes to the design configuration to enable effective operation. The follow section details start-up testing and design changes made to the FCDI prototype, and analysis of performance to characterize the expected ion removal performance towards the application of FCDI in treatment of industrial wastewaters.

4.1 System Validation and Iteration

The FCDI prototype was tested in a series of iterative studies to validate its capability as designed and fabricated to deionize water. The primary requirement of the testing validated that the treatment was measurable and correlated with expected performance of the system (i.e. – transport and storage of ions into the flowable electrode slurries). The secondary requirements were to compare against expected rates of deionization from contemporaneous examples of similar FCDI systems prior to testing the technology's application in industrial wastewater conditioning with OSPW.

4.1.1. Start-Up Testing and Electrode Modifications

Initial operation of the system used a 1000 mg/L sodium chloride spiked water solutions to test a basic monovalent salt solution in the FCDI system. The first tests encountered an issue where, under operating conditions, it appeared that a small quantity of ions would be removed from the water solution and would not be further deionized. Evaluation of the disassembled FCDI prototype revealed that the activated carbon particles were becoming immobilized on the surface of the IEM. This observation suggested that this layer of activated carbon may have been saturated quickly and then acted as a blocking layer between the water stream and the rest of the electrode slurry volume.

The activated carbon layer remained adhered under moderate shear force from running water, suggesting that increased rate of slurry pumping may not provide a solution, as shown in **Figure 8**. However, the accumulated layer was mostly removed with a scrubbing force. The presence of this layer was repeated under varied process conditions such as increasing the slurry flow rate, changing the electrolyte concentration in the slurry, and deploying alternative IEMs from other manufacturers with differing physical surface properties (such as surface roughness, flexibility, and thickness).

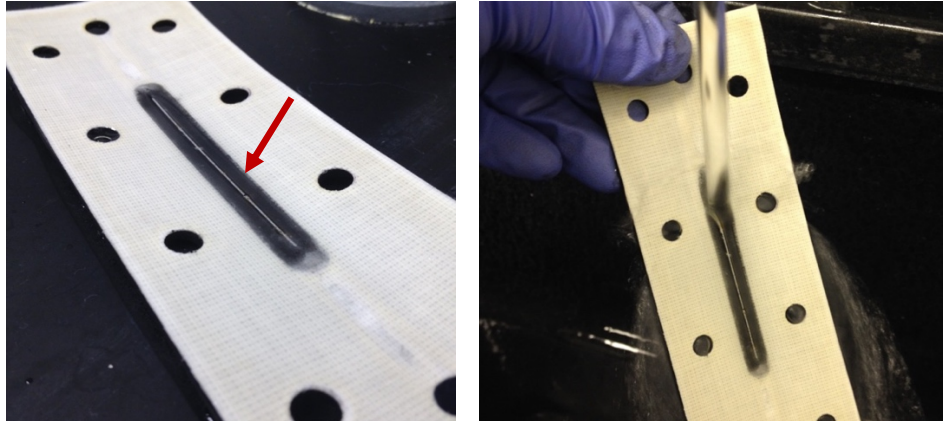


Figure 8 – CEM (Membranes International) immediately following disassembly from the FCDI system after a single salt treatment trial showing activated carbon layer (left), and AEM (Membranes International) showing adhesion under flowing water (right).

In order to reduce the direct contact between activated carbon particles the surface of the IEMs – thereby reducing or eliminating the accumulation of saturated electrode mass – a physical separator between slurry and IEM was devised and tested. Modifications to flow rate, flow cell orientation, and other process conditions did not indicate that a change to cell geometry or operating parameters would enable treatment results.

Testing of separation media included the use of glass microfiber filter sheet, polymeric felt sheet, and stainless steel microporous meshes, the latter selected with precedent from Gendel et al.⁵¹. Experimentation revealed that the addition of a separator layer both enabled deionization of the water and that the 316L stainless steel mesh (5 μm pore size, via Utah Biodiesel Supply) was the highest performing separator. The comparative deionization for each separator is shown in **Figure 9** for deionization of 1000 mg/L sodium chloride spiked water.

This result concluded that use of the stainless-steel mesh would be used for all future testing of the FCDI system. Testing using this system without the activated carbon and analysis of the FCDI operation with the stainless steel mesh, including validation of ion transport and preservation of mass to the PAC slurry concluded that the deionization mechanism was not through oxidation of the mesh media, however future substitution with non-metallic materials or alternative ion exchange or PAC media may enable more resilient materials to be used in higher salinity or acidic operating environments.

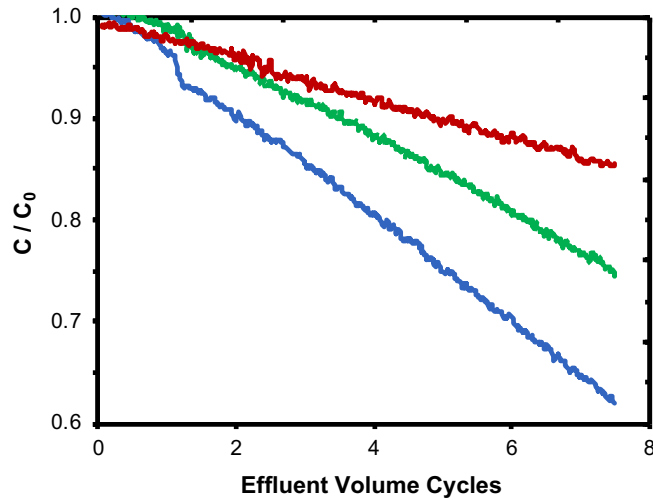


Figure 9 – Comparison of PAC slurry and membrane separation materials including stainless steel microporous mesh (blue), polymeric felt sheet (green), and glass microfiber sheet (red).

4.1.2. Validation of Deionization with Activated Carbon Electrodes

Initial characterization of the FCDI prototype was conducted using spiked solutions of selected salts in order to study the operation of the system in controlled conditions and compare performance for different operational parameters and ions. The first trial studied the operation of the system for removal of 1000 mg/L of sodium chloride operating the system with and without PAC slurry in the electrodes (i.e. – comparing treatment with and without the capacitive storage media). The test without PAC was operated with electrodes starting at the same sodium chloride concentration of 1000 mg/L, and the tests conducted with PAC used this water matrix with the addition of 1000 mg/L of sodium chloride. Flowable electrodes were operated at 6 mL/min, from a 60mL volume of flowable electrode media per electrode. The flowable electrode media was replaced for each successive test to ensure an equivalent initial operating condition. These flowable electrode conditions were used for all studies unless otherwise noted. The results of this test are shown in **Figure 10** for batch treatment of 1000 mg/L sodium chloride solution. The operation of the FCDI with PAC was conducted at a slow (1 mL/min) and fast (1.5 mL/min) feed rate in order to test the effect of rate on removal. The variation in rate did not have a substantial effect given the 50% change in flow speed through the cell.

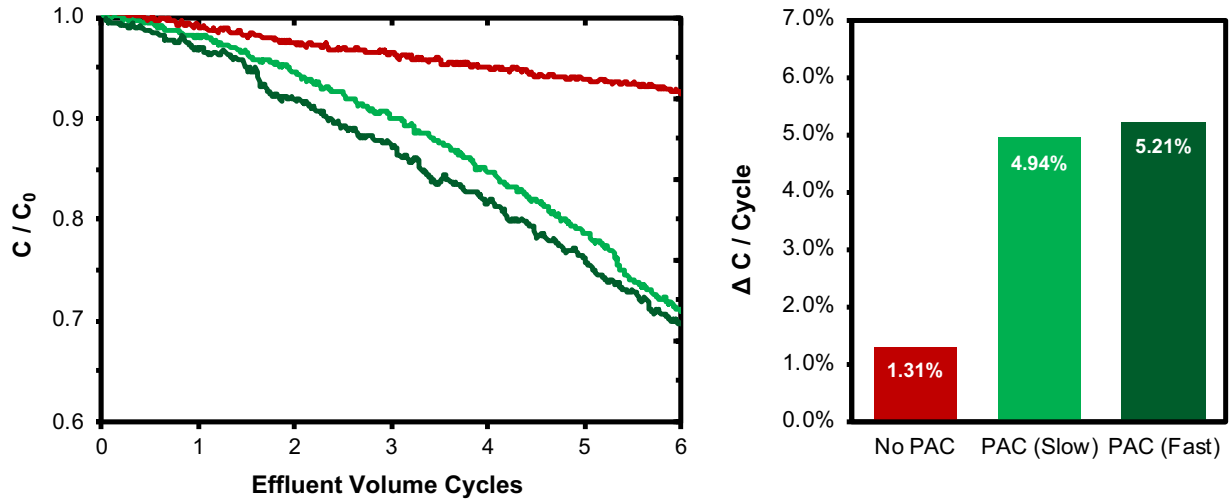


Figure 10 – Comparison of ion removal without PAC in electrode channels (red) and with 10% w/w PAC (green).

The trial with and without PAC demonstrated that the operation of the system with capacitive storage, compared with a pseudo-electrodialysis operation without, showed a higher rate of ion separation from the treated water volume. The ion concentration was monitored using a conductivity probe in the batch volume treated in a continuous cycle mode. The increase in rate of circulation for the electrode slurry media did not show a substantial change in performance in this test. Overall, the FCEDI system both demonstrated the ability to separate ions from the treated water solution, and the utility of the flowable electrode slurry to impart a higher rate of separation.

4.2 Model Water Deionization Testing and Optimization

Deionization treatment of industrial wastewater typically comprises complex, multi-ion separations aiming to reduce total dissolved solids or reduce target ion species. In order to characterize the FCEDI system in the present study, variations in dissolved ion composition including valency and concentration were studied, including with variation of the key ion transport component – the ion exchange membranes.

4.2.1. Comparison of Cation Species Removal

Typical industrial applications of the FCEDI system will treat a variety of ionic species with varied valency and molecular weight. In order to examine these two attributes, chloride salts of sodium (Na^+), potassium (K^+), and calcium (Ca^{2+}) were tested in single salt solutions at 1000 mg/L in order to

examine the relative rates of removal from water. Each batch test used a new batch of the same PAC slurry electrodes (1 g/L sodium chloride) and deionization was monitored using conductivity probes in the spiked watch batch volume (with concentration adjusted based on molar conductivity of each salt). The comparison of these three cationic species removal from solution, as measured by batch volume conductivity decrease, is shown in **Figure 11**.

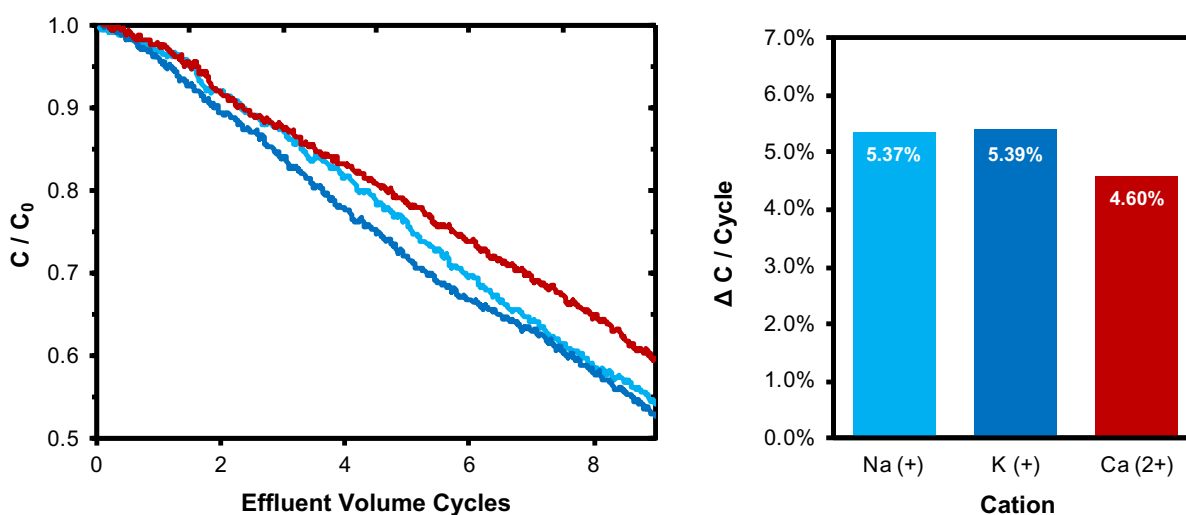


Figure 11 – Comparison of monovalent (blue) and divalent (red) cation removal for chloride salts of sodium, potassium and calcium at 1000 mg/L.

The comparison of cationic species showed similar rates of removal for monovalent species of differing molecular weight, and a higher rate of removal for monovalent species (Na⁺, K⁺) compared to divalent species (Ca²⁺). However, a key conclusion is that the difference in deionization rates are not substantial or demonstrating selectivity, as was expected using non-selective IEMs.

The rate of removal is also linear across of 40 - 50 % reduction in the dissolved solids concentration during the treatment of each solution. This treatment behavior is consistent with the theoretical treatment mechanism for capacitive deionization. For solutions with a complex mixture of ions, such as the target OSPW compositions, the non-selective treatment mechanism and linear treatment at relatively low concentrations is suitable for treatment.

4.2.2. Comparison of Anion Species Removal

In counterpart to the cation species removal comparison, two anion species commonly found in industrial wastewater were tested as salts of sodium: chloride (Cl⁻) and sulfate (SO₄²⁻). The chloride

test used the same results as demonstrated in the cationic comparison. The rates of removal in equivalent operating conditions for both anions, as measured by batch volume conductivity, are shown in **Figure 12**.

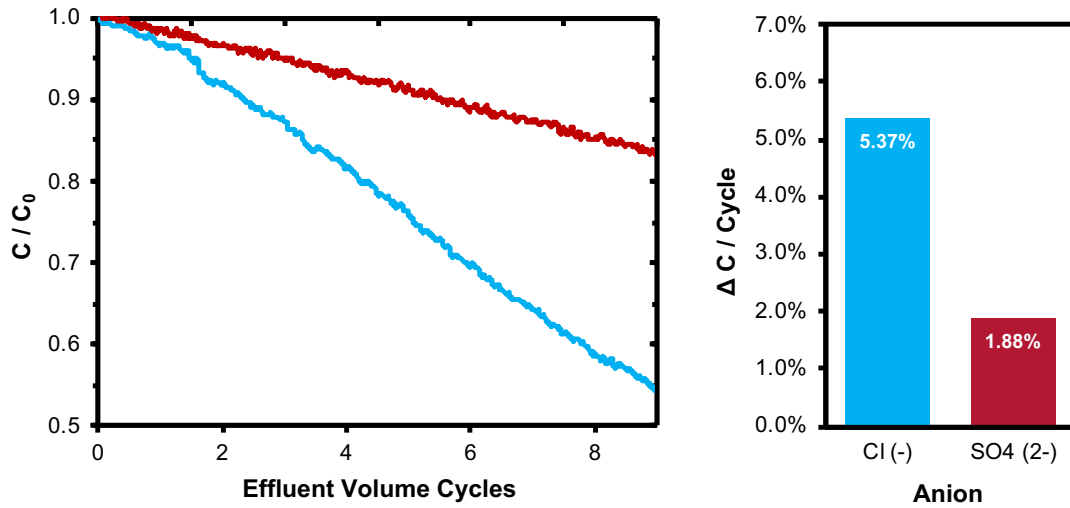


Figure 12 – Comparison of monovalent (blue) and divalent (red) anion removal using sodium salts of chloride and sulphate at 1000 mg/L.

The anion variation in ion separation showed more significant deviation in rate of separation compared to cation varied solutions. Sodium sulphate separation was substantially lower at only 35% of the rate of separation compared with sodium chloride. The sodium sulphate separation rate was found in repeated tests at varied concentrations, including reduction to 200 mg/L. The rate of removal appeared limited by a fixed mass flux to the flowable electrode, with similar magnitude of separation at both 200 and 1000 mg/L. Similar rates of removal were also found with alternative membrane selection, as summarized below.

Further analysis of the differential in rate of separation found in complex mixtures of dissolve solids is examined further in the OSPW treatment study. For design application of the FCDI system, the varied rate of removal found in the test suggests that for treatment applications with high concentrations of specific ions or for selective conditioning applications, characterization of rate is required. The lower separation rates did, however, maintain a similar linear treatment rate across varied concentrations.

4.2.3. Effect of Influent Dissolved Solids Concentration

To evaluate the rate of separation for dissolved ions at varied concentrations in the FCDI system, solutions with varied concentrations of sodium chloride. Solutions of 1, 2, and 10 g/L of sodium chloride were prepared and treated partially to generate a rate of removal for each concentration start point. The treatment performance is shown in **Figure 13**, as measured by change in batch volume conductivity and shown as linear trendlines due to varied magnitudes of noise in the conductivity sensor data different concentration magnitudes.

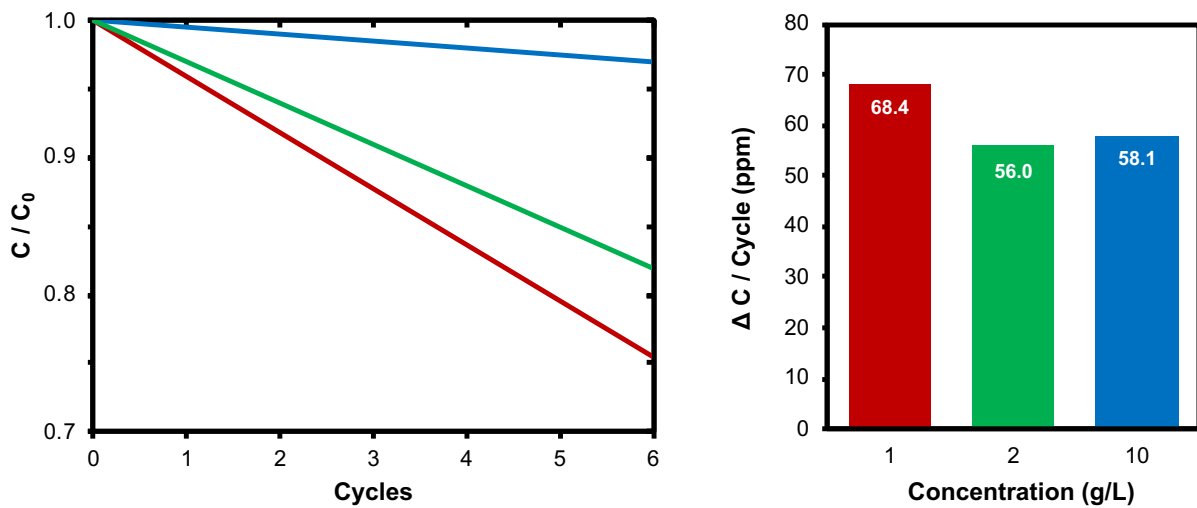


Figure 13 – Comparison of relative concentration change and per cycle removal of sodium chloride solution by FCDI at varied batch concentrations of 1, 2 and 10 g/L.

The varied concentration test reveals two important characteristics of the system. At all sodium chloride concentrations tested, the rate of concentration decrease was consistent and linear. The rate of removal was also relatively consistent across the varied concentrations tested. Treatment at different orders of magnitude of input dissolved solids (1 g/L and 10 g/L) showed equivalent rates of separation. This represents a similar trend found in prior results showing a separation with a characteristic mass transport in the FCDI system for a given ion composition.

This test was repeated using sodium sulphate at 0.2 and 2 g/L, as shown in **Figure 14**. The rate of removal during the test was again shown to be linear, and the reported rate of separation showed a higher flux at higher concentration. The rate of removal was 33 % higher at 2 g/L and indicates that at low concentrations, the variation in rate of separation may be more substantial where diffusion to

the flow-electrodes becomes more dominant compared to the rate of flux through the IEMs and in storage within the EDLs of the flowable electrode media.

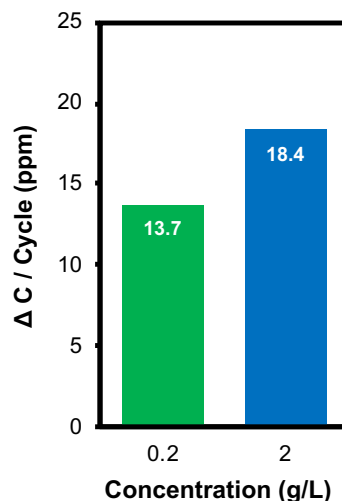


Figure 14 – Comparison of per cycle deionization removal of sodium sulphate by FCDI at varied batch concentrations of 200 and 2000 mg/L.

4.2.4. Comparison of Ion Exchange Membranes

The FCDI prototype has been shown to remove a variety of dissolved solids using IEMs supplied by Membranes International. These membranes were selected for having comparable performance to competing alternatives, a low surface roughness, and a relatively higher stiffness that was considered advantageous for maintaining consistent water channel thicknesses in the FCDI cell (i.e. – less z-axis deviation under pumping pressure).

In order to assess that the performance of the Membranes International IEMs were reasonable, particularly accounting for a substantial difference in the rate of removal between chloride and sulphate shown in **Section 4.2.2.**, the FCDI system was tested using two divalent salts using IEMs supplied by Snowpure in order to compare the rate of removal under equal operating conditions. The results of this comparison are shown in **Figure 15**, as measured by concentration reduction of treated water per cycle in the FCDI system.

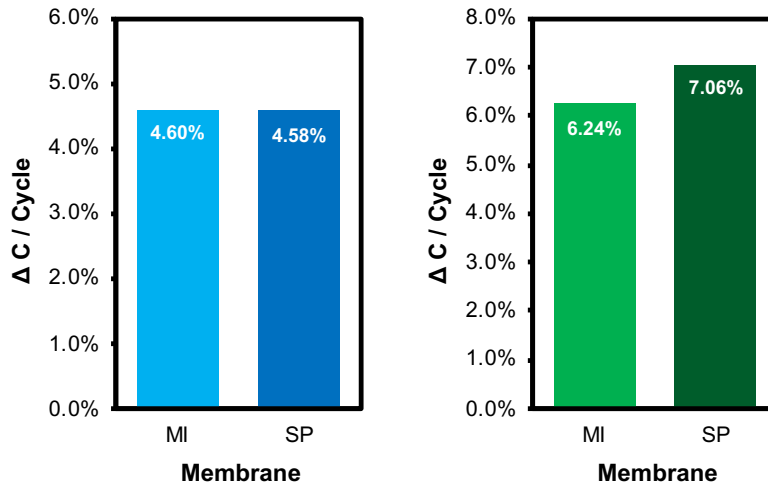


Figure 15 – Comparison of ion exchange membranes supplied by Membranes International (MI) and Snowpure (SP) for treatment of 1000 mg/L CaCl₂ (left) and 200 mg/L Na₂SO₄ (right).

The rate of removal for 1000 mg/L of calcium chloride was not significantly different between the Membranes International and Snowpure membranes. For removal of 200 mg/L of sodium sulphate, the Snowpure membranes showed a higher rate of separation. The difference in rate of separation for sodium sulphate suggests that the higher AEM exchange capacity, reported in **Table 3**, may permit a higher rate of transport for the sodium sulphate. However, the differential in the rate of removal is small – 0.82% per cycle, accounting for an increase of 13% – which suggests that the rates deionization are representative of the FCDI system and not solely the IEM selection.

The mechanical properties of the Membranes International product making assembly and operation of the FCDI cell more effective are a comparable benefit to increased transport in by the Snowpure membranes. As such, the Membranes International IEMs were selected for use for OSPW treatment experiments unless otherwise noted.

4.3 Conclusions

The FCDI prototype successfully demonstrated capability to conduct deionization of a variety of dissolved salts, including monovalent and divalent species. With the addition of a physical interface separation, the flowable electrodes were capable of consistent and repeatable treatment results in a variety of treatment conditions. Testing demonstrated that the FCDI system has a characteristic treatment rate for a given dissolved solids make-up and treatment proceeds in a linear fashion in the

tested range of 200-10,000 mg/L. Use of alternative IEMs demonstrated a repeatable performance that does not appear to be substantially affected by IEM selection. Further study on the variation in key operational parameters for the flow electrode and electrical operation are considered in **Section 5**.

5 Evaluation of Selected FCDI Operational Parameters

A key performance metric for FCDI in comparison with competing methods is the energetic cost of operation for deionization. As noted in Section 2, for low concentration solutions of dissolved solids, CDI technology provides a benefit through reducing energy input requirements compared to membrane and thermal methods. Towards the industrial research for OSPW treatment with FCDI, parameters affecting the energy cost of treatment for the FCDI prototype are examined to select a representative mode of operation for OSPW treatment evaluation. The performance is evaluated with respect to applied potential and concentration of PAC in slurry, and their net effect on energy consumption per dissolve ion mass removed.

5.1 Effect of Applied Potential on Single-Pass Deionization

In order to evaluate the effect of the electric potential applied in a continuous voltage operation of the FCDI system, a continuous treatment monitoring test was conducted. A conductivity sensor was placed in-line to the influent and effluent lines of the flow cell and a constant feed of 500 mg/L sodium chloride spiked water was pumped through the system. The difference in conductivity between influent and effluent as 30-minute average was correlated to the total dissolved solids removed per-pass in the system at the given applied potential in order to evaluate the effect of differing potentials in the system. The treatment performance for each potential tested is shown in **Figure 16**.

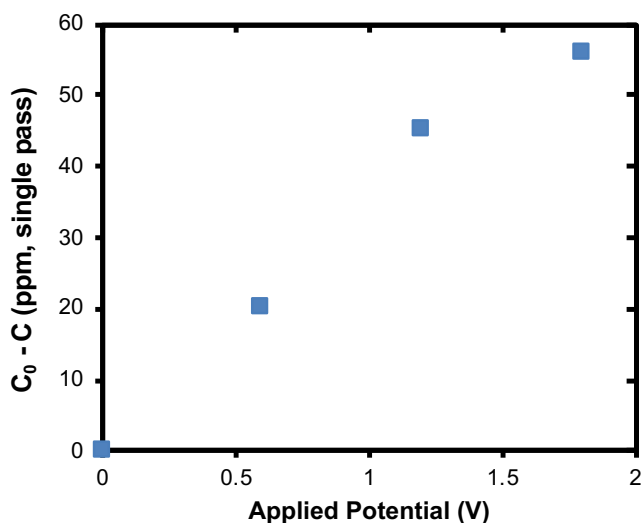


Figure 16 – Effect of applied potential on the differential of influent and effluent water conductivity during treatment of 500 mg/L sodium chloride solution.

The applied potential variation demonstrated a linear increase in the rate of removal from 0 to 1.2 V of applied potential, and further increase above 1.2 V at a decreasing rate of improvement. The operation above 1.2 V may incur potential for hydrolysis, however the presence of the conductive slurry reduces the effective potential and may enable over-voltage operations to be sustained. This increase in removal for greater applied potential is expected and the linear rate of increase matches the operating theory of capacitive storage of ions in the PAC slurry media, such that increased potential is proportionally compensated by greater transport of ions to the electrode.

However, the decreased efficiency at the increased voltage suggested that operation at 1.2 V for industrial application research would be most ideal and eliminate potential for confounding effects from operation in this range on evaluating efficiency and energy cost for treatment in industrial water streams where operating >1.2 V is less well characterised.

5.2 Effect of Flowable Electrode Solids Concentration and Applied Potential

The second key operational variable evaluated is concentration of PAC in the flowable electrode slurry. Prior studies demonstrating comparable FCDI architectures have operated with a range of PAC concentrations from as low as 5 % to up to 23 % by weight. In this study, the most suitable PAC composition for the current FCDI system is considered on the basis of removal of ions on a per pass basis.

An initial test of flowability for the slurry and PAC material used in the present FCDI prototype was tested to evaluate the operability of the system, including concentrations of 5, 10, 15, and 20 % by weight. The flowable electrode slurries were created using the same electrolytic solution of 500 mg/L sodium chloride dissolved in deionized water. Each test utilized a volume of 40 mL of solution operated in a continuously stirred reservoir and recycled through the system. The flowability test demonstrated that the concentrations of 5 – 15 % PAC by weight were effective at flowing through the FCDI flow cell and pumping systems without any notable issues in 30-minute operating tests.

However, the 20 % by weight solution was observed to flow with visible intermittence and analysis of the flow cell after operation showed substantial accumulation of PAC media not observed at lower concentrations. For this reason, the 20 % by weight PAC electrode composition was excluded from further study. Additional development outside the scope of this work may enable viscosity reduction

in the PAC solution, or changes to the pump and flow cell design selections to enable reliable operation, as has been demonstrated in other studies.

The expected benefit of higher concentration PAC solutions is a greater solution conductivity (and therefore lower ohmic losses and higher effective potential in the water channel), and greater capacitive storage, both contributing to a higher effective rate of deionization for the FCDI system. As shown in **Figure 17**, this effect was observed within the tests conducted at 5, 10 and 15 % weight solutions.

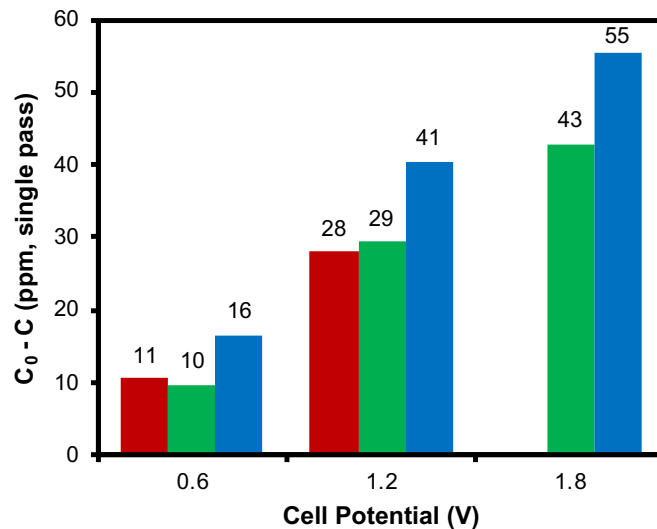


Figure 17 – Effect of flowable electrode PAC concentration (by weight) at 5 % (red), 10 % (green), and 15 % (blue) for single pass deionization of 500 mg/L sodium chloride solution.

Testing showed that at the typical applied potential of 1.2 V, the 15 % by weight solution substantially increased the per-pass average removal (30-minute continuous average) compared to the lower concentration solutions. The results also presented similar rates of removal for the 5 % and 10 % by weight tests both at 0.6 V and 1.2 V, which may suggest reaching a threshold of solids concentration at 15 % by weight for measurable reduction of the ohmic losses and charge distribution in the slurry.

The FCDI cell was also operated at 1.8 V using the 10 % and 15 % by weight solutions to assess whether this improvement in per-pass removal was consistent at an over-voltage operating range. While the relative degree of improvement was lower – 24 % higher removal at 1.8 V compared to 29 % higher at 1.2 V – the overall trend was found to be similar. The operation at varied PAC concentrations concludes that a higher PAC concentration in the flowable electrodes is advantageous,

and the highest concentration practical for maintaining consistent and reliable operation should be utilised in order to maintain the highest rate of deionization.

5.3 Operational Parameter Effects on Energy Consumption

The higher rate of removal at constant voltage operation suggests that the removal efficiency may be higher for increased PAC concentration in the flowable electrode slurry. However, as noted in Section 5.1, the rate of improvement is not necessarily linear with increased voltage and PAC concentration on an energetic basis. To evaluate the relative energy efficiency of varied PAC concentration and applied potential for the FCDI system, the same 500 mg/L sodium chloride treatment study was operated while measuring the current supplied from the power supply to the FCDI cell during deionization. Using the measured change in conductivity, and correlated ion removal, and the energy consumed, the total energy cost per ionic concentration removal can be devised, as shown in **Figure 18**.

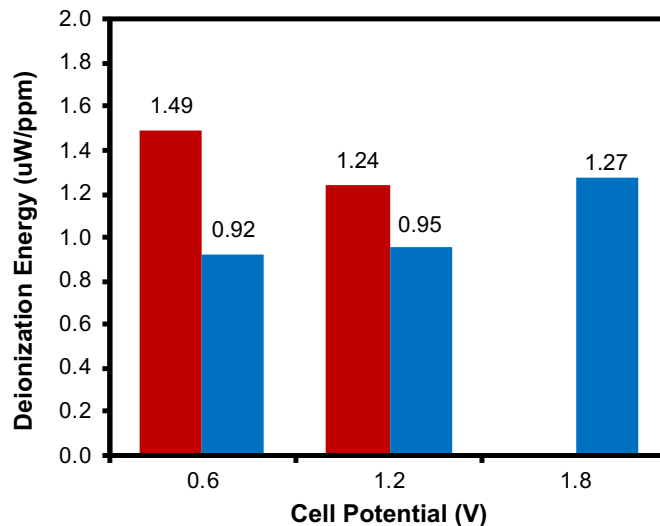


Figure 18 – Effect of flowable electrode PAC concentration (by weight) at 5 % (red) and 15 % (blue) on the energy input per mass removal of sodium chloride from 500 mg/L solution at constant voltage.

The energy efficiency study examined the 5 % and 15 % by weight solutions to compare the energy efficiency through varied operating potential, and between extrema of the PAC concentrations considered. The results demonstrate that indeed, the operation of 15 % by weight PAC solutions in flowable electrodes is most energy efficient, with similar removal efficiencies at 0.6 V and 1.2 V. The higher total per pass removal at 1.2 V makes this operational mode most ideal. Further, operation at

1.8 V was shown to be less efficient, as suggested in **Section 5.1**. The lower concentration flowable electrode tests showed that on a per mass removal basis the rate of change was not linearly improved at 5 % versus 15 % by weight, and suggests that further optimization in scale up considering pumping and mixing energy, that lower concentration slurries may be suitable where the per pass magnitude of removal is a suitable trade-off for whole system energy efficiency and reliability.

5.4 Conclusions

Through characterisation of two key operational parameters of applied potential and electrode slurry PAC concentration, it was found that operating at a constant voltage 1.2 V and a PAC concentration of 15 % by weight was most optimal for the prototype system. These parameters will be used in the FCDI evaluation for OSPW treatment in **Section 6**.

The FCDI prototype performance and operational parameters were found to be comparable to other FCDI systems shown in literature for model water deionization and were found to be acceptable to proceed to evaluate merit in the industrial application chosen. These comparisons are summarized in **Table 5**.

Table 5 – Comparison of FCDI prototype with demonstrations of similar flowable-electrode designs.

Study Reported	PAC Conc. (w/w %)	Electrolyte Conc. (g/L)	Influent Depth (mm)	Flow Speed (cm/s)	Input Conc. (g/L)	Removal Rate (mg/m ² -s)
Present	10	1.00	1.5	0.25	1.00	11.57
Jeon et al., 2013 ⁴³	5	5.84	1.8	0.09	1.10	6.67
					5.90	31.67
Hatzell et al., 2015 ⁵²	15	10.00	1.5	1.05	5.00	9.39

Further analysis of changes to the prototype geometry, pumping systems, slurry additives, and alternative electrical operational modes may enable additional optimization beyond the scope of this study and for enhancement to FCDI systems, as contemplated in other literature.

6 Application for Oil Sands Process-Affected Water Treatment

The industrial application objective for the FCDI system is towards treatment of dissolved solids in oil sands process-affected water (OSPW). Following iterative improvements and validation of functionality for the FCDI prototype on model waters, an industrial sample of OSPW was treated using FCDI and the resulting treated water analyzed. The target demonstration range was treatment to typical Athabasca River water quality ², with typical operation of the FCDI in practical applications being between the current tailings pond water quality and the influent fresh water composing the oil extraction process water feed stream. The treatment demonstration was successful in showing that the FCDI system could reduce total dissolved solids by up to 90%, including reduction of both monovalent and divalent cation and anion species.

6.1 Characterization of Oil Sands Process-Affected Water

OSPW has varying compositions depending on many production factors including the mine geology, ore quality, water reuse intensity, and age of the mine and tailings pond, including its use in active operations. For the FCDI treatment study, a sample was obtained from one a tailings pond of the major surface mining projects in the Athabasca Oil Sands. The sampled water is representative of a typical composition of OSPW for dissolved and suspended solids, as well as organics and total metals composition.

For the purposes of this treatment study, overall water composition is analyzed, as well as detailed dissolved anion and cation speciation. The samples used in FCDI studies were, unless otherwise noted, pre-processed using a settling period and centrifugation to simulate a solids pre-treatment process prior to FCDI treatment. The initial OSPW characteristics, analyzed by ALS Environmental Inc. following centrifugation removal of suspended solids, are captured in **Table 6**. This source of OSPW was the sole sample utilized through all FCDI treatment experiments.

The overall composition of the water is lightly saline, as observed in other OSPW literature, and includes a low level of organic content. The analysis of dissolve anion and cation species reduces the impact of settling or other removal of remaining non-dissolved metals in the OSPW samples during the treatment study that would otherwise contribute to changes in the total metals content.

Table 6 – Composition analysis for oil sands process-affected water sample used in FCDI studies.

Parameter	Units	Lowest Detection Limit	OSPW Sample - Initial
pH	-	0.10	8.26
Total Dissolved Solids (TDS)	mg / L	20	872
Total Suspended Solids (TSS)	mg / L	2.0	< 2.0
Total Organic Carbon (TOC)	mg / L	1.0	35.8
Alkalinity, Total	mg / L	10	412
Dissolved Species			
Sodium	mg / L	5.0	281
Potassium	mg / L	0.5	19.3
Magnesium	mg / L	0.5	13.0
Calcium	mg / L	0.5	23.6
Fluoride	mg / L	0.10	3.55
Chloride	mg / L	2.5	143
Sulfate	mg / L	1.5	204

6.2 Treatment of OSPW with FCDI

The treatment of OSPW using the FCDI prototype was studied in two batch mode treatments. These tests studied the extent of treatment towards treatment to approximately 90% reduction in total dissolved solids (as measured by conductivity) and analysis of the treatment study compared the relative separation of dissolved ion species. Treated OSPW quality was compared with to water from the Athabasca River and the power consumption data showed efficient deionization in comparison with competing membrane separation processes.

6.2.1. Methodology

The two OSPW treatment studies were conducted in a batch mode configuration. The first trial was conducted in a single operating run and monitored continuously using a conductivity sensor immersed in the 40 mL OSPW sample and treated until reduction of >90% of the solution conductivity.

The second trial to study removal rate by species was conducted in four sequential batch treatment studies in order to generate sufficient effluent sample quantity for dissolve solids analysis. The sample analysis was conducted using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC). Each batch study was conducted using 100 mL of centrifugated OSPW as the input water, and 40 mL of 10 %^{w/w} activated carbon slurry as electrode media. The electrode media was replaced with a fresh quantity for each batch of OSPW treated.

In both tests, the FCDI cell was operated at 1.2 V and the current draw recorded using the current data logger connected to the cathode and power supply in order to measure the energy consumption of the cell. The conductivity of the water sample was recorded using a conductivity probe immersed in the sample vessel through the full duration of each treatment batch. For the second trial, the conductivity was averaged for the four tests.

Following treatment, the samples requiring speciated analysis were sent to ALS Environmental for analysis using ICP-MS and IC for species analysis of cations and anions in the treated OSPW.

6.2.2. Demonstration of Treatment Extent by FCDI

The treatment of total dissolved solids in the first study demonstrated that it was possible to reduce the dissolved solids to < 10.2 % measured by the whole solution conductivity, as shown in **Figure 19**. The initial total dissolved solids in the OSPW sample was 872 mg/L and the measurement of conductivity reduction provides an estimated TDS reduction to < 100 mg/L.

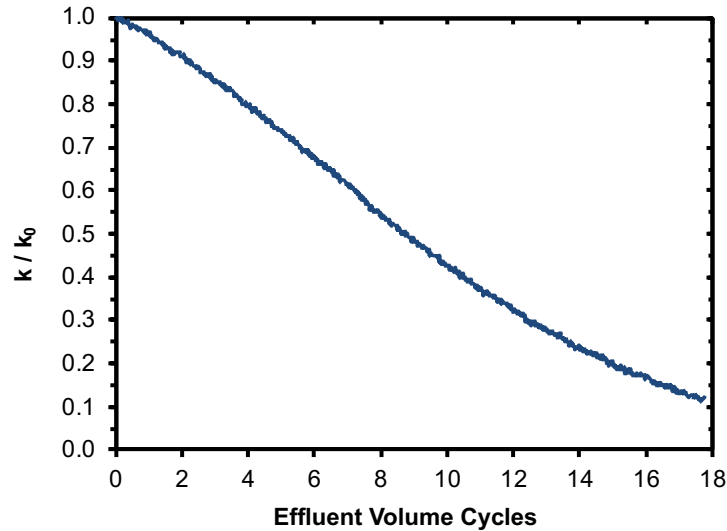


Figure 19 – Conductivity change in FCDI processed OSPW through re-cycled batch mode treatment.

The average total dissolved solids content in the Athabasca River is 140 mg/L and an average conductivity of 245 μ S/cm. In this test, the FCDI system treated OSPW to < 245 μ S/cm after 16 sample volume cycles through the FCDI cell. This demonstrates that the FCDI system is capable of treating a complex solution of dissolved solids from the elevated level in OSPW to a comparable concentration to endemic water sources. Analysis of the cation species in the treated OSPW was conducted by inductively coupled plasma optical emission spectrometry (ICP-OES) at the University of Waterloo Department of Chemical Engineering. The cationic species data in **Table 7** demonstrates that the rate of removal is similar for all major cations tested, and the reduction in conductivity is correlated with reduction in these species.

Table 7 – FCDI treated OSPW cation species composition.

Ion Species	Units	Initial Concentration	Treated Concentration	Removal (%)
Na ⁽⁺⁾	mg / L	249	28.5	88
K ⁽⁺⁾	mg / L	23.23	1.88	92
Mg ⁽²⁺⁾	mg / L	7.18	0.36	95
Ca ⁽²⁺⁾	mg / L	10.07	2.01	80

In this test, the initial composition of OSPW species varied from the initial composition measured by ALS Environmental Inc. for the primary OSPW characterization and analysis for the second trial

below. This variance may be due to method variations in the OSPW preparation. Initial and final concentrations are completed by the same analysis process for consistency in ion removal reference points.

Towards application in a practical setting, this test demonstrated that FCDI treatment is capable of reducing the conductivity and total dissolved solids to levels typical of intake water used for process water make-up. Treatment may also be possible beyond this level; however existing operations do not typically employ water conditioning for dissolved solids for intake water.

In order to reduce the accumulation of dissolved solids in OSPW at current water reuse intensity, which is 80-85% recycled OSPW combined by volume, the extent of treatment required would be lower than demonstrated above. The rate of salination of OSPW stored in tailings ponds is not readily available, also affected by natural water accumulation and evaporation, variations in ore quality, and operational variations. The linear rate of treatment demonstrated by the FCDI system suggests it is suitable as a water conditioning process to control the accumulation of total dissolved solids in OSPW.

6.2.3. Analysis of OSPW Ion Separation Profile by FCDI

In a second test, partial treatment of OSPW completed in four replicates and the effluent analyzed by inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC) to compare the ionic species removal, as shown in **Table 8** and **Figure 20**. The OSPW was treated through eight treatment cycles and analysis conducted by ALS Environmental Inc.

Table 8 – FCDI treated OSPW dissolved species composition following 8 treatment cycles.

Ion Species	Units	Lowest Detection Limit	Initial Concentration	Treated Concentration	Removal (%)
Na ⁽⁺⁾	mg / L	5.0	281	182	35
K ⁽⁺⁾	mg / L	0.5	19.3	8.41	55
Mg ⁽²⁺⁾	mg / L	0.5	13.0	5.48	54
Ca ⁽²⁺⁾	mg / L	0.5	23.6	9.1	59
F ⁽⁻⁾	mg / L	0.10	3.55	2.15	39
Cl ⁽⁻⁾	mg / L	2.5	143	70.07	51
SO ₄ ⁽²⁻⁾	mg / L	1.5	204	109	47

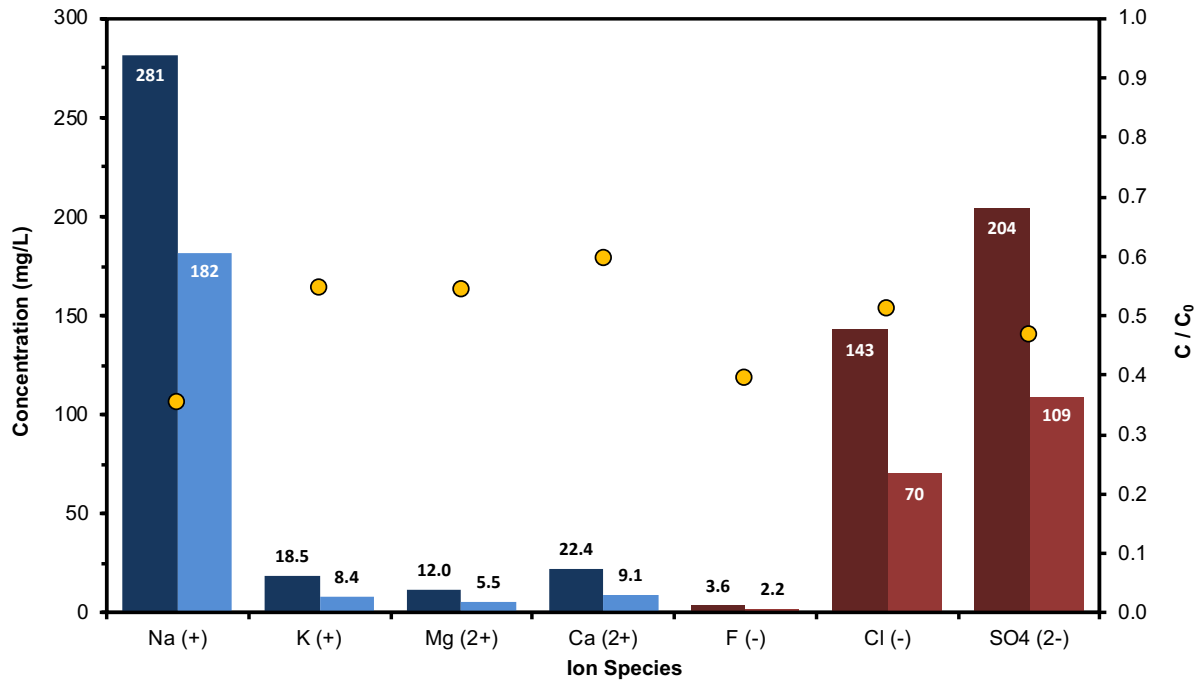


Figure 20 – Dissolved cation (blue) and anion (red) species of interest in partially treated OPSW showing initial (dark), treated (light) concentrations, and concentration change (dots).

In this study, it shown that the FCDI provided removal of the ions of interest at varied magnitudes of concentration. No species removal showed a substantial bias, as monovalent and divalent species, and those of varied molar mass, were shown to have similar removal relative to initial concentrations. The similar extent of removal for all species is a positive indication that the capacitive storage is affected for an array of ions, and suggests that the FCDI system would be effective at a range of species concentrations and matrix compositions.

The comparatively lower rate of removal for sodium for cationic species indicates that there may be competitive effects for storage of sodium ions. This effect of differing rates of removal for different ions has been demonstrated in other CDI system characterization studies⁷⁰. Further, while the chloride removal extent is comparable to other cation and anion species, the use of sodium chloride as an electrolyte in the flowable electrode slurry may have an effect on diffusion of additional sodium to the electrode solution volume. However, in spite of the lower apparent removal in **Figure 20**, the treatment using the FCDI prototype has shown in the cationic removal comparison in **Table 7** shows that sodium can be reduced to a further extent (up to 88% shown).

Compared to anion removal efficiency comparison in **Section 4.2.2**, the separation of chloride and sulfate ions is similar in this study. The sulfate removal, while lesser, is not 35 % of the chloride removal rate, as shown in the prior single salt characterization tests. The difference in the comparative rates of removal may be due to the lower concentrations of each ion compared to the single salt tests or the combination of salts and their competition for capacitive storage sites on the electrode media.

The IEMs selected for the FCDI prototype are not designed to be ion selective or promote preferential transport any ion species. However, for applications where specific ion separations may be preferable, this characterization indicates that the FCDI system is not selective without this designed component in its semi-permeable membranes. Given the performance of the FCDI system with non-selective membranes effectively removing all studied ions, introduction of ion selective membranes would likely not similarly effective performance for those species transported to the electrodes.

6.3 FCDI Energy Requirement and Application for OSPW Treatment

All deionization treatments necessarily have capital and operational expenditure associated with use of the selected process. For FCDI, the objective is to reduce the energy requirement for operation, as well as pre-treatment and reliability concerns for membrane processes treating turbid and untreated OSPW. I

To evaluate this energetic benefit, the FCDI system was monitored with the same current logging process at constant voltage operation as shown in **Section 5.3**. The energy requirement for treatment of the OSPW was recorded during the OSPW treatment extent test conducted in **Figure 19**. The treated was conducted at 1.2 V and consumed an energy equivalent to 0.18 kWh/m³. With a comparable starting TDS range, notwithstanding differences in pre-treatment requirements, a RO system may be expected to have an energy input of approximately 0.8 - 1.0 kWh/m³¹⁴, while an electrodialysis reversal (EDR) system that is typically suited for brackish water levels, may be approximately 0.4 - 1.0 kWh/m³⁷³. While the energy consumption for FCDI would necessarily be higher for pumping energy in a full-scale system, these comparisons suggest that the FCDI method may be competitive with optimization and addition of energy recovery.

The preceding studies for treatment of OSPW using an FCDI system have shown it is an effective method of removing dissolved solids species to at or below endemic water concentrations. FCDI treatment efficiently reduces all dissolved ion concentrations in a repeatable and linear treatment

process without substantial pre-treatment. This treatment capability could enable surface mining operators to treat OSPW in reuse applications in order to either partially reduce dissolved solids to remove round trip accumulation in the bitumen extraction process, or treat water to meet the intake water quality from the local watershed. Both applications of deionization conditioning of OSPW for reuse or return to the environment could reduce the overall water use intensity and environmental footprint of operations.

7 Conclusions and Future Study

A new flowable-electrode capacitive deionization prototype has demonstrated effective and efficient treatment of oil sands process-affected water dissolved solids. The system was successively developed through two iterative designs to develop a reliable FCDI cell, including the addition of key functional components such as a spacer between IEMs and the flowable electrode PAC slurry. The resulting FCDI system produced repeatable treatment results consistent with capacitive deionization theory demonstrated in prior work.

Characterization of the FCDI system demonstrated capability to treat a variety of single salt solutions containing monovalent and divalent cations and anions, including through the use of multiple IEM products in the same FCDI system. A slower treatment rate was found for sulphate anions, while cation species had less deviation in rate. Treatment at different ion concentrations from 200 – 10,000 mg/L demonstrated a typically linear deionization process with a consistent magnitude of mass transport in the FCDI cell in the tested ranges.

Variation of key operational parameters including PAC solids concentration in the flowable electrode solution and operating voltage demonstrated that higher solids loading, up to a mechanical limit of flowability, and operation at 1.2 - 1.8 V was an ideal performance range for constant voltage operation.

Treatment of centrifugated OSPW demonstrated that FCDI was suitable to decrease the lightly saline matrix of 872 mg/L to below 100 mg/L. FCDI was capable of removing all major dissolved ions species analyzed with relatively equivalent efficacy and at energy cost that demonstrates competitiveness with conventional deionization technologies. The impact of this result shows an energy efficient method whereby oil sands operators or other mining applications can treat process water with limited pre-treatment to local water quality levels. Based on demonstrations with single salt solutions, FCDI may be applicable to additional treatment applications and variations in dissolved solids content in OSPW.

In order to further characterize and optimize the FCDI system, as well as explore its application in an OSPW treatment setting, the following areas are proposed for future study:

1. Further analysis of flowable-electrode PAC solutions, including the materials composition of the PAC and modifications thereto in order to generate flowable high concentration slurry

that is durable through successive treatment cycles. The optimization of materials composition has enabled improvement in other CDI systems, and study of the cost-benefit and performance enhancement in the context of industrial application will enhance FCDI's competitiveness.

2. Characterization of operational modes for electrode recovery and variation in operating voltage. A next step to improve the performance of the FCDI prototype would examine the ideal electrical operating modes to achieve the most efficient separation. These modes have been well characterized for solid electrode CDI systems, and may reveal new operating strategies in FCDI.
3. Evaluation of continuous treatment for OSPW for analysis of performance reliability, fouling prevention, and control of effluent quality. The testing in this study has shown FCDI is a high potential process for OSPW treatment and practical application will require analysis of failure modes and methods of maintaining efficient operation with minimized pre-treatment. A key advantage for FCDI would be to add resilience to deionization treatment in complex industrial waters.
4. Scaling up the FCDI prototype to include a larger treatment volume and flow cell length towards demonstrating the scaling relationships of the treatment. This may enable the development of scaling factors and limitations for flow cell size and architecture to inform development of pilot scale systems for testing in-field. Mechanical challenges such as maintaining low dead volume and uniformity of flow in larger channels may require additional innovation in the flow cell design.

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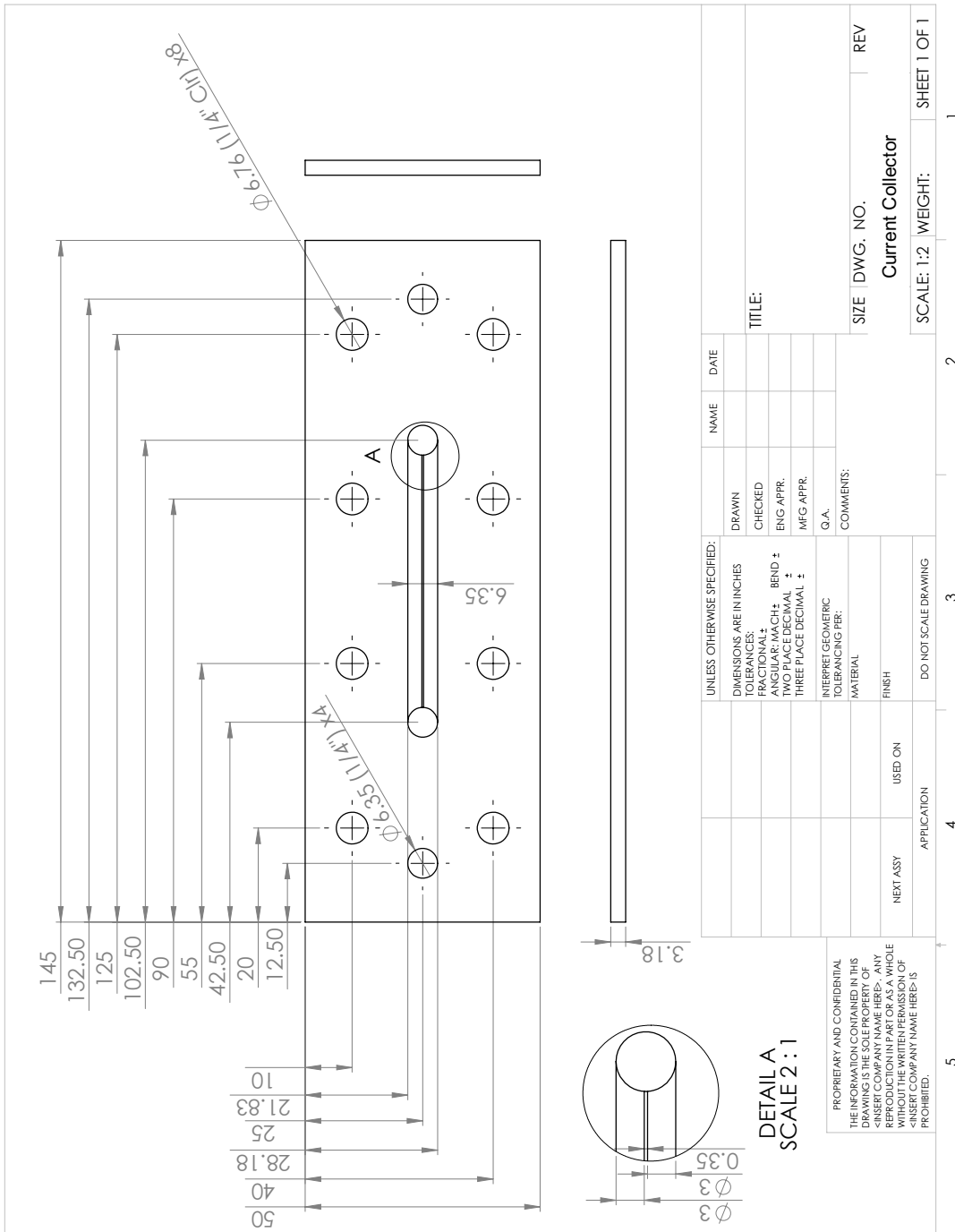
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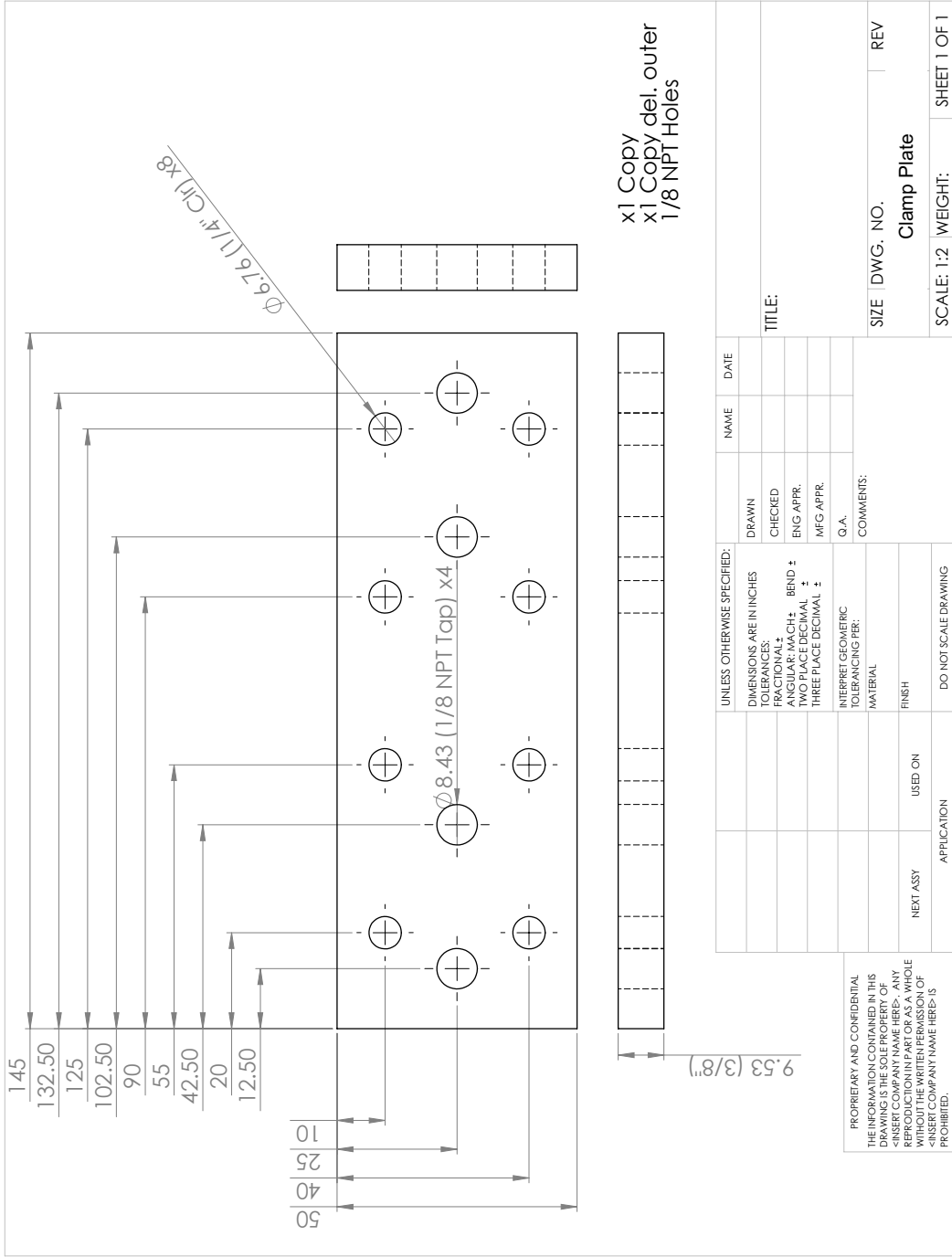
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Appendix A: Drawings for FCDI Prototype Machined Parts





x1 Copy
 x1 Copy del. outer
 1/8 NPT Holes

UNLESS OTHERWISE SPECIFIED:		NAME	DATE
DIMENSIONS ARE IN INCHES	DRAWN		
TOLERANCES:	CHECKED		
FRACTIONAL ±	ENG APPR.		
ANGULAR: MACH ± BEND ±	MFG APPR.		
TWO PLACE DECIMAL ±	Q.A.		
THREE PLACE DECIMAL ±	COMMENTS:		
INTERPRET GEOMETRIC TOLERANCING PER:			
MATERIAL			
FINISH			
USED ON			
NEXT ASSY			
APPLICATION			

TITLE:
 SIZE DWG. NO. REV
Clamp Plate
 SCALE: 1:2 WEIGHT: SHEET 1 OF 1

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