# ABSTRACT

Title of Document:        SUSTAINABLE LOW ENERGY DESALINATION OF ROAD SALT RUNOFF USING ION EXCHANGE RESINS

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NaCl is used to deice roads during winter storms, but the resulting salty runoff has detrimental environmental effects. A novel low-energy approach for desalinating snowmelt runoff using ion exchange resins was explored. Strong-acid cation and strong-base anion resins were tested in parallel gravity flow columns to determine their efficacy in removing $Na^+$ and $Cl^-$ from saline solutions of varying concentrations (0%, 1%, 5%, 10% w/w). Ion exchange was quantified via pH measurements of column effluent samples. Cation resin capacity was positively correlated with influent $Na^+$ concentration, while removal efficiency was negatively correlated with $Na^+$ concentration. Neither the anion resins' capacity nor removal efficiency followed any correlation with $Cl^-$ concentrations. More 1% influent solution compared to 5% or 10% was required to exhaust both resins. Future research should confirm current findings, test resins in realistic field conditions, explore resin regeneration, and examine engineering efficacy in a field setting.

SUSTAINABLE LOW ENERGY DESALINATION OF ROAD SALT RUNOFF

USING ION EXCHANGE RESINS

by

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Proposal submitted in partial fulfillment of the requirements of the Gemstone Program,

University of Maryland, 2019

*We pledge on our honor that no unauthorized assistance was given or received on this*

*assignment.*

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Acknowledgements

**TABLE OF CONTENTS**

**LIST OF TABLES**

**LIST OF FIGURES**

# CHAPTER 1: BACKGROUND

## *1.1 Introduction*

As a society that relies heavily on motor vehicles for transportation, it is essential to provide safe driving conditions at any cost. In the winter months, this reliance leads to the need to clear roadways of increasing winter precipitation. The use of chloride salts, commonly known as road salts, to melt snow and ice on roads has been a consistent practice since the 1940's (Daley, Potter, & McDowell, 2009). The most common of these road salts is sodium chloride (or NaCl). The U.S. alone applies eighteen million metric tons of salt each year in efforts to abate the inherent risks of winter storms (Jackson & Jobbagy, 2005).

Once sodium chloride dissolves and melts the road ice, it is carried by snowmelt and rain runoff from the treated pavements into the surrounding freshwater, land, and infrastructure. As each year passes, more salt accumulates in the environment from continuous use of salt throughout the winter.

Road salts can be be placed into the same category as other environmental hazards such as microplastics and pesticides as an overarching class of emerging contaminants. Emerging contaminants can be defined in multiple ways, typically as a contaminant which has recently emerged in the environment; or, in scientific literature, as a substance which has always existed in the environment, but has recently started to become problematic (Sauve & Desrosiers, 2014). Salts and other ionic compounds fall into the second category, as the continuous application of salt to roads has resulted in a buildup of component sodium and chloride ions ($Na^+$ and $Cl^-$) in the surrounding soil and freshwater sources. Much of the current body of research focuses on the buildup of chloride and its harmful effects, including declines in the quality of water, infrastructure, and local plants (Marsalek, 2003).

Due to the difficulty of decreasing salinity levels once they become high, road salt continues to accumulate in natural resources throughout the United States, slowly and progressively degrading the environment. As each year passes, more salt runs off into the surrounding environment. Without any remediation, the environment is unable to naturally desalinate, leading to a gradual accumulation of road salt from its continuous winter usage.
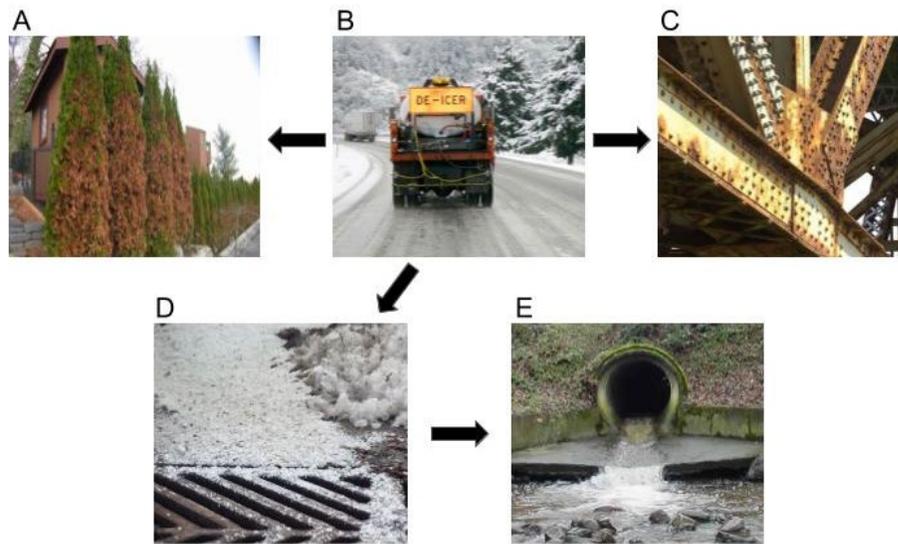


Figure 1-1. (B) Salt is used to deice roads during winter storms because it is extremely cheap and effective, however once this salt dissolves, it runs off into the surrounding environment. (A) It leaches into soil and dehydrates plants. (C) The chloride corrodes automobiles, planes, and crucial infrastructure such as bridges and piping systems. (D) Salt also runs off into storm drains that feed into (E) freshwater bodies, raising salinity levels which can make conditions uninhabitable for aquatic organisms.

Although road salts offer a societal benefit, they have a negative environment impact following their application. Once sodium chloride dissolves and melts the roadway ice, it runs off into the surrounding water, land, and infrastructure.

## 1.2 Research Objectives

Due to the novelty of the proposed hypothesis, this research project focuses solely on evaluating the desalination potential of the resins rather than the implementation of a roadside desalination system; therefore, any challenges associated with such were beyond the scope of this project. Regarding the desalination potential of the selected resins, the following research questions were proposed:

1) How effectively can ion exchange resins desalinate saltwater at concentrations similar to road salt runoff in a flow through gravity fed system?

2) How does the concentration of salt in the influent affect the total number of ions exchanged by the resins?

3) How does the ion exchange performance of the cation and anion exchange resins compare?

4) Can ion exchange resins be effectively regenerated using a strong acid or base; if so, how many times can it be regenerated, and how is desalination performance affected afterwards?

5) Can the effluent of the regeneration process be collected and reused as a concentrated brine for future road salting application, allowing for a sustainable cyclic process of using, capturing, and reusing road salt?

The following experimental methods were created to answer these questions surrounding the potential of ion exchange resins for desalination. Given the time constraints placed on the project, the team decided to focus primarily on investigation into the first three proposed goals of the project. These primary research questions addressed

the very basis of the team's goals, focusing on examining the effectiveness of the resins at desalination, the effects of influent concentration, and the variable efficiencies of the two resin types. The latter two questions were unable to be explored in the lab over the duration of the project, but are important questions to consider when thinking about implementation of such a desalination system. As such, they are discussed in the future directions section at the end of this report.

**CHAPTER 2: LITERATURE REVIEW**

*2.1 Environmental Effects of Road Salt*

Excessive sodium and chloride concentrations from road salt runoff alter both natural and built environments. Much of the snowmelt runoff travels into stormwater drains, through pipes, and into nearby freshwater bodies, such as streams or lakes. Sodium chloride alters the natural water chemistry by increasing salinity levels in these sensitive ecosystems. In a U.S. Geological Survey in Wisconsin, it was found that 72% of sampled streams exhibited toxicity, and that the chloride concentrations exceeded the U.S. Environmental Protection Agency (U.S. EPA) acute (860000 µg/L) and chronic (230000 µg/L) water quality at all of the monitored sites during winter runoff periods (Corsi, 2010).

Increased sodium and chloride concentrations negatively affect sensitive freshwater organisms accustomed to living in or drinking this freshwater. Organisms especially vulnerable to the effects of increased salt concentration are those with permeable skin, such as amphibians.  Defects in larval and early stages of life have been correlated to higher conductivity in freshwater bodies, leading certain populations of these animals to develop defects as they reach maturity. I addition, the effects of winter storms remain even after the winter is over. Animals live in and are harmed by these saline solutions all year as the salt is not effectively cleared out over the following months (Sanzo & Hecnar, 2006).

A 2015 study involving wood frogs found that larval stage frogs were scarcer in Northeastern Ohio wetlands where there was high conductivity in the water. When found and allowed to reach maturity, the frogs had reduced immune defenses and other defects (Dananay, Krynak, Krynak, & Bernard 2015). Another study conducted in 2016 found that salt can negatively affect some invertebrate species as well, The study reported 12% slower

growth in detritivores in areas with higher than normal salinity (Tyree, Clay, Polaskey, & Entrekin, 2016). The continuous leaching of salt into bodies of water can affect freshwater aquatic organisms at all stages of their life, and there may be much more damage researchers do not yet know about.

Sodium ions also have negative effects on soil quality and plant nutrient uptake. Sodium shifts the ion exchange processes in soils, which decreases the available nutrients that plants can uptake. In addition, high concentrations of sodium can disperse soil colloids, possibly causing accumulations of heavy metals in the soil to enter into the groundwater (Norrström & Bergstedt, 2001). These issues have been increasingly reported near roadsides of heavily salted highways (Turer, Maynard, & Sansalone, 2000).

Finally dissolved chloride ions accelerate the corrosion of metals, damaging vehicles and valuable infrastructure. Salt increases water conductivity and chloride ions break the protective coating on metals, resulting in electrochemical corrosion (Kelting & Laxson, 2010). Results of an experiment by Fishel (2001) showed that sodium chloride corrodes steel at a rate of 52.49 MPY (millimeters per year), while distilled water was measured to corrode steel by only 3.82 MPY. This experiment displays how sodium chloride can accelerate the decline of infrastructure such as highway bridges, pipelines, and utilities. Copper pipes transporting highly salinated water can corrode and become structurally weaker (Lin, Torrents, Davis, Zeinali, & Taylor, 1997). Furthermore, the corrosion of metallic pipelines can release toxic metals to the water. For example, the lead solder in pipes can dissolve in water with higher electric currents caused by salt, posing a health hazard (Nguyen, Clark, Stone, & Edwards, 2011).

*2.2 Current Efforts to Amend Environmental Issues*

There are two paths to address the many environmental problems caused by road salt– one is preventative and the other is reactionary. The preventative method involves using a new alternative deicer to replace road salt that would have less detrimental effects. Since the 1970s researchers have tested different methods of applying deicers to the roadways as well as a variety of deicing compounds. The development of prewetting and brine solutions has been relatively successful in reducing the amount of salt used per length of road. Pre-wetting salt is a common practice that involves initially applying a liquid brine solution containing freshwater and typically 23 by weight (wt.%) of either calcium chloride or magnesium chloride to dry salt (Donahay & Burkheimer, 1996). Before pre-wetting, dry salts were applied alone and in much larger quantities, as up to 20% of the salt applied would bounce off the road and into the roadside landscape (Burtwell, 2001). Pre--wetting the salt acts to make the wet salt solution heavier and stickier, and therefore more likely to stay on the road. Both prewetting and the application of liquid brine solutions also increase the overall effectiveness of the salt, as they provide the moisture needed for the salt to dissolve into aqueous form and become an effective deicer. Without the brine, dry salt would fail to melt the snow at low temperatures or when no moisture is present, thus rendering it ineffective (Burtwell, 2001).

A few compounds have been tested as possible deicer alternatives. The most common materials applied to roadways include chlorides, acetates, and formates. Chlorides are the primary deicer used in the United States, the most common of which used today is sodium chloride, also known as rock salt (Fay & Shi, 2012). Calcium chloride and magnesium chloride are also used, both generally in aqueous brine forms as the pre-wetting

complement to dry rock salt, and occasionally in solid form as deicers (MDOT SHA, 2016). Some less common deicing substances include acetates and formates. Potassium acetate, sodium acetate, potassium formate, and sodium formate have become more popular than the previously used urea for use as a runway/airport pavement deicer because they are more effective at lower temperatures (Fay & Shi, 2012; Shi, 2008). After chloride salts, potassium acetate (KAc) is the most commonly used deicer in areas deemed more susceptible to the negative effects of road salt because it has proven to be less damaging to the environment. However, the production and use of acetates is costly, both financially and environmentally, as they require more substance to melt ice, produce more byproduct greenhouse gases, and are more corrosive to concrete than road salts (Fay & Shi, 2012). Though formates are biodegradable at low temperatures, both acetates and formates increase the hardness and pH of water, have negative consequences on vegetation, and can lead to fish abnormalities (Fay & Shi, 2012). Use of calcium magnesium acetate (CMA) results in less heavy metal leaching than sodium chloride, but it is more expensive and has the same consequences of the acetates stated above (Amrhein & Strong, 1990).

As with any product implemented on such a wide scale, there will always be a balance between environmental friendliness, effectiveness, and cost. So far, the effort has been made to preserve cost as much as possible, leading to the generous use of sodium chloride to treat roads after a storm, and there does not seem to be a decrease in the near future of the amount of salt used. Therefore, a reactionary approach, which entails cleaning the runoff water after salt is applied to the roads, to mitigate the issues of sodium chloride pollution could prove more successful than the preventative approach of reducing and substituting the deicing chemicals in use. One such approach would be to remove a portion

of the salt from the water before it runs off into the surrounding area. Currently, there is no form of desalinating filtration taking place and all salinated road salt runoff leeches directly into the environment. Other avenues of desalination do exist, but all are significantly more expensive and energy-intensive than the application of road salt.

## *2.3 Desalination Techniques*

As alternative deicers no longer seemed promising, other methods of lowering the salinity levels of freshwater bodies were explored. At this point focus shifted from looking for a solution before the deicer was placed on the road to mitigating its effects afterwards. As the primary issue is the rise of salinity levels in freshwater bodies near heavily salted roadways, the team decided to investigate potential desalination methods. When it comes to the most common forms of desalination, most prove to be very energy intensive and are generally used for turning saltwater, typically seawater, into fresh and potable water. The goal of this project was not to create potable water as current desalination methods do; instead the proposed desalination method would be purposed for environmental remediation to reduce the salinity of the runoff water as much as possible without using a high energy input. The team's idea for the simplest desalination effort was a targeted approach on the salty concentrated runoff itself before it enters larger water bodies and becomes diluted. It was also deemed important to filter the runoff in a natural setting rather than expending energy to move it to and through a treatment plant. This goal meant that the runoff would most effectively be treated at areas to which it drains. Thus the optimal desalination would likely occur in or around stormwater drains. With this ultimate objective in mind, research was guided by creating a small-scale low energy desalination

system that could address many of the environmental effects previously discussed. Several existing water purification methods were researched and compared for this possible implementation. These methods included: reverse osmosis, electrodialysis, other membrane-based desalination, and ion exchange resins.

Reverse osmosis is one of the most commonly used forms of potable water production from saltwater, accounting for 60% of the world's desalination market in 2017 (Johnson, 2018). This method works by countering osmotic pressure that occurs between two bodies of water on either side of a semi-permeable membrane. Osmotic pressure is the pressure difference that exists over the membrane due to differences in salinity levels, as water will be drawn to the body with a higher salt concentration. Reverse osmosis forces a pressure across this membrane that water can cross but salt cannot. This pressure pushes the water to the less saline body further reducing its salinity (Khawaji, Kutubkhanah, & Wie, 2008). While this process works well for producing water that is drinkable, it is also energy intensive due to the high-pressure differential required. In addition, this method is generally done on a larger scale than would be reasonable for road salt runoff. Thus, reverse osmosis is not suitable for desalination of winter stormwater runoff.

Electrodialysis is another widely used desalination method for producing high purity water. The idea behind electrodialysis is to use an electric charge gradient across a stream. On one side of the stream, there is a negatively charged cathode plate, while the other side has a positively charged anode plate. These two plates create an electric field that draws positive sodium and negative chloride ions away from each other. Between the two charged plates there are also membranes that the salt ions can cross selectively as they move toward their respective plates. Thus the water nearest to the plates increases in

salinity while that of the water in the center decreases (Strathmann, 2010). Similar to reverse osmosis, this method is also more energy intensive than is needed for producing non-potable water. Other drawbacks of electrodialysis include the need for pretreatment of the inlet streams to prevent fouling and scaling on the membranes and plates within the separator. The largest risk is the possible production of chlorine gas that can occur due to the presence of chloride ions along with the voltage gradient (Schlumpberger, Lu, Suss, & Bazant, 2015; Schlumpberger, 2016).

Distillation is a commonly-used technique used to not only remove both salt and other impurities from water. Two advantages for this method are that liquid impurities can also be separated from the water since different liquids have different boiling points, and that no membranes are required, leading to a lower chance of fouling. When separating salt, distillation becomes especially simple since sodium chloride and other ionic compounds do not boil at the same temperature as water. After the water is distilled and collected via a condenser apparatus, the process can be repeated in succession to yield higher purity water. However, major drawbacks of distillation are found in its high energy requirements and low efficiency. Estimates put separation via distillation as a low thermodynamic efficiency method of purification, with efficiency typically around 20-30% for the entire process (Kiss, Landaeta, & Ferreira, 2012). The majority of the energy required is used to heat the solution itself, but much of the energy is also lost to the surroundings in the process. There has been new research in the field of distillation, producing a technique called membrane distillation to increase the thermodynamic efficiency of this method. Though some research looks promising with these membranes, a challenge researchers still face is their fouling (Drioli, Ali, & Macedonio, 2015).

One last novel idea that was explored was the use of hydrogels for separating the water from the salt. Hydrogels are materials that are able to absorb quantities of water and other liquids far beyond their own original volume (Ali et al., 2015). The team looked into the idea that the hydrogels could be used to absorb much of the water from a saltwater mixture and leave behind a smaller, more concentrated saline solution. The clean water from the hydrogels would then be desorbed and allowed to flow into the environment while the high salinity solution would be reused for deicing. One problem with this idea was that the second step of separating the water from hydrogels (known as dewatering) would be very energy intensive **(**University of Texas News, 2018). There are a number of ways to do this including heating the gel or putting pressure on them but these methods are not suited for small scale environmental remediation. Therefore hydrogels were also rejected as a desalination method for the team's goals.

### 2.4 Ion Exchange Resins for Desalination

Ion exchange resins are another tool that has been used for water purification. These resins are small millimeter size beads made up of a crosslinked porous polymer with either positively charged (anion exchange resins) or negatively charged (cation exchange resins) fixed side chains. These charged side chains attract mobile ions of the opposite charge that are dissolved in the surrounding solution. For water purification, these ions have been used for both water softening and ion removal (Apell & Boyer, 2010).

Ion exchange works by separating ions based on their binding affinity for the resin itself. Binding affinity is based on the strength of attraction between two compounds and is based primarily on the charge of the ion. Ions with a larger charge will have higher

affinity for an oppositely charged resin. During ion exchange a solution containing ions flows over the resins, and if the ions in this solution have a higher binding affinity with the fixed resin side chains than the already present mobile ion in the resin, the introduced mobile ion will displace the original ion and bind electrostatically to the fixed side chains. This keeps them attached to the resins as the solution flows through with a decreased concentration of the introduced ion, but an increased concentration of the ion originally bound to the resin (Apell & Boyer, 2010). This process is depicted in Figure 2-1. However, if an ion with a lower affinity for the resin has a significantly higher concentration than the ion with higher affinity, a large portion of the weaker ion will bind to the resin and not be displaced by the stronger ion.
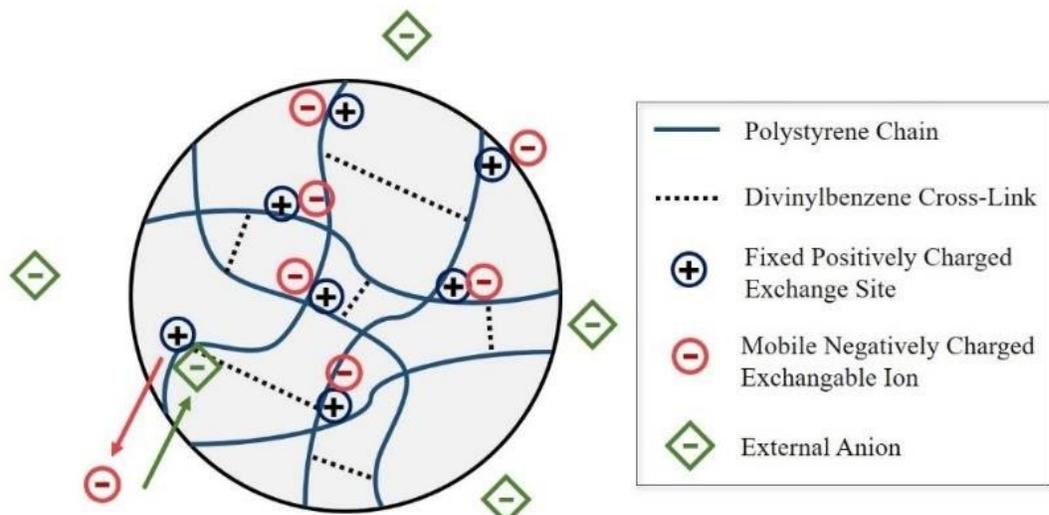


Figure 2-1. Depiction of the exchange of monovalent anions over a polystyrene based resin with monovalent cationic side chains. Reproduced from Lee, Lee, Jung, Cheng, and Lim (2018).

In the case of water softening, calcium and magnesium are exchanged for sodium ions. This is done to prevent the buildup of limescale, which can damage pipes on a residential scale and harm other purification systems (such as reverse osmosis membranes)

on an industrial scale through membrane fouling and galvanic corrosion (Soft Water Lab, 2017). This process is possible because the calcium and magnesium ions have a higher binding affinity for the fixed resin side chains than the sodium ions. There are a variety of ionic side chains used for ion exchange. The majority contain sulfonyl groups ($-SO3^-$) for cation exchange and ammonium groups ($-NH_4^+$) for anion exchange (Guide to Ion Exchange Chromatography, n.d.). It is important to note that the side chains will always have some amount of mobile ion bound to them (Ion Exchange Resins, 2018). Generally speaking, these ion exchange-based water softeners are able to reduce water hardening to a suitable level with only one pass. However, since some systems require even lower levels of calcium, a serial softening system has been developed involving a "lead" softener followed by a "polishing" softener. These systems can reduce calcium levels to below 1 ppm (Bennett, 2007). Similar levels of purity might be achievable for salt removal systems.

Ion exchange resins have also been used for general ion removal. The term general ion removal refers to the exchange of any form of metal or nonmetal ions in solution for hydroxide ($OH^-$) and hydronium ($H_3O^+$) ions, respectively, in order to produce deionized (DI) water. After passing through the resins, these new hydroxide and hydronium mobile ions will then exchange a hydrogen between themselves and form two water molecules. Because two ions react to form electrostatically neutral water, this process ultimately removes a net positive amount of ions hence why it is used in the production of DI water (Fu, 2011). This process can be represented by the following reactions:

$$nAR\!-\!H + CM^{n+} \rightarrow (AR^-)_n CM^{n+} + nH^+$$

$$nCR\!-\!OH + AM^{n-} \rightarrow (CR^+)_n AM^{n-} + nOH^-$$

$$nH^+ + nOH^- \rightarrow nH_2O$$
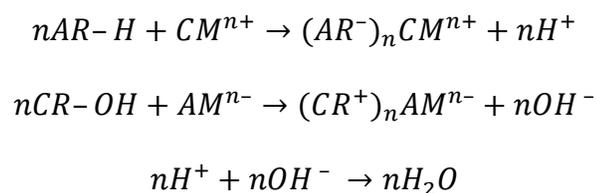
where AR and CR represent the anion and cation fixed resin side chains, respectively; CM and AM represent the cation and anion mobile ions being removed from solution, respectively; and n is an integer value representing the charge of the mobile ion being removed. After the exchange has occurred, the resins can then be regenerated with hydrochloric acid for the cation exchange resin and sodium hydroxide for the anion exchange resin. The higher concentration of hydronium and hydroxide ions in these solutions will remove the previously bound ions despite their higher affinity for the resin.

Nevertheless, the capability of these resins to remove monovalent ions in exchange for other types of monovalent ions in a passive manner for stormwater remediation is not well researched. Because ion exchange resins can function simply upon contact with an ionic solution, they can remove monovalent ions, such as sodium and chloride. These ions could be exchanged for hydronium and hydroxide ions, respectively, that can combine in the right proportions to form water as a clean effluent. Because of the aforementioned reasons, the resins' ability to exchange ions solely through gravity, and their lack of external energy requirements, they have potential to treat salinated snowmelt runoff in a roadside desalination system. Although ion exchange resins effectiveness likely does not compare well to current high purity drinking water desalination methods, any ion removal would be environmentally beneficial, and as such, should be investigated and quantified. Another important distinction between the use of these resins in this work and in DI water production is the fact that in this work the ions will be exchanging relatively high concentrations of salt. On the other hand, when DI water is typically produced the influent to the resins is distilled first in order to lower the amount of salt in the water before further purification (Bennett, 2007).

**CHAPTER 3: METHODS**

***3.1 Ion Exchange Column Test***

<u>*3.1.1 Materials Selection*</u>

The resins chosen for testing were the SBG1P-OH-ID Anion Resin and the CG8-H-ID Cation Resin, which were purchased from ResinTech Incorporated. These resins were selected from the other commercially available options because of the attached mobile ions and color changing property for exhaustion indication. Color change allows a visible indication of when the resins have exhausted, which serves as a helpful observatory aid during laboratory testing and can also support the data collected. The cation and anion exchange resins come loaded with $H^+$ and $OH^-$ ions, respectively. This not only serves to fulfill a goal of the project– form water through exchange of captured ions– but also conveniently enables the ion exchange of the resins to be quantitatively measured using a pH meter. Any sodium ion that binds to the resin will take the place of an $H^+$ ion, which goes into the effluent (Wheaton & Lefevre, 2000). Both the $Na^+$ and $H^+$ ions have a '+1' charge. Thus, the moles of $H^+$ displaced from the resins and measured in the effluent indicates the moles of $Na^+$ removed from the influent solution. This is also true with the anion exchange resins, in which $OH^-$ ions in the effluent allow for the measurement of $Cl^-$ ions bound to the resins. Measuring the ion exchange of each resin as it becomes exhausted is crucial for comparing the overall effectiveness of the ion exchange resins in different experimental scenarios. Strong acid ($H^+$ loaded) and base ($OH^-$ loaded) resins were chosen over weak resins. The effectiveness of weak acid resins is decreased by variability in pH (Dow Chemical Company, 2019), which makes weak acid resins a poor choice when

considering the implementation of this method in practice. In practice, the columns would be set up in a chronological series or as a mixed bed of both cation and anion exchange resins, such that the effluent flows through both resin types. Thus, the $Na^+$ and $Cl^-$ ions would both be trapped by the resins and displace the $H^+$ and $OH^-$ ions into the effluent. For the team's experiments, these methods were not chosen, as their effectiveness would be more difficult to quantify. In these practical layouts, the $H^+$ and $OH^-$ in the effluent are allowed to react with each other to form $H_2O$. Because the team chose to measure moles of $Na^+$ and $Cl^-$ removed using a pH meter, this neutralization would lower the amount of ions in the effluent solution and reduce the accuracy of the results.

In order to test the ion exchange of the resins, the resins must be set in a container that allows for the passage of liquid, but does not allow for the passage of solid resin beads. The team selected the DWK Life Sciences Kimble™ Kontes™ FlexColumn™ Economy Column from Fisher Scientific. The chosen gravity-fed column itself is composed of Type I Class A Borosilicate Glass with supports made from high-density polyethylene (HDPE) as well as an end-cap housing a male luer lock connector. It has an inner diameter of 25 mm, a length of 200 mm, and a capacity of 98 mL. This gravity flow column contains a pre-installed semipermeable membrane with a pore size of 20 μm and a cross-sectional area of 4.91 cm$^3$ that keeps the resin particles in place while allowing free passage of both sodium and chloride ions. The radii of these ions are well under even a single nanometer– sodium is 0.095 nm while chloride is 0.181 nm– and will be able to pass freely through the larger pores in the column's membrane (Size of Atoms). Unlike certain desalinating

membranes developed to remove the targeted ions themselves, the team's membrane is thus simply stabilizing the resins, so that all desalination is provided by the resins alone.

### 3.1.2 Test Solutions

Although road salt snowmelt runoff would contain a multitude of other ions (both monovalent and polyvalent), organic matter, and other particulates (Denning, Baron, Mast, & Arthur, 1991), the research focus was on the effectiveness of ion exchange resins to bind only sodium and chloride ions; thus pure sodium chloride solutions were used for testing. Solutions of sodium chloride (NaCl) in deionized water (DI) were prepared in 1 L volumetric flasks based on percentage of salt by weight. The solutions used for experimentation included NaCl concentrations of 0% (0M NaCl), 1% (0.172M NaCl), 5% (0.883M NaCl), and 10% (1.829M NaCl). The maximum solubility of salt in water is 357 g/L, or approximately 26% by weight at 25°C (Cohen, 1994; Density of Water, 2004; Dorn, 1987; McGuire, 1998; Sodium chloride, n.d.). The team chose these influent concentrations to account for the variability of salt concentration in road salt runoff that would likely be more dilute than the maximum concentration. The experimental conditions in the lab, were around room temperature, ranging from 21 to 23°C. A 0% salt solution of pure DI water was used as a control to demonstrate that the exchange of $H^+$ and $OH^-$ was due to the

presence of $Na^+$ and $Cl^-$ ions and not simply the flow of water through the resins.

### 3.1.3 Experimental Setup

For each experiment, each resin type was added to separate gravity flow column. Each column was packed to contain 20.0 ± 0.5 mL of resin, as follows. To prepare the correct amount of resin for each column, 20 mL of deionized water (DI water) was first added to a graduated cylinder. Then the resin was transferred from its commercial container to the water in the graduated cylinder until the difference between the total volume in the graduated cylinder and the volume of initial DI added equaled the desired amount of resin volume. Following the displacement, the resin was mixed in the graduated cylinder and the resin-water solution was poured into the column. The resulting effluent was collected, measured for volume, and discarded. Before running ionic solutions through the resins, each packed column was washed with a total of 100 mL of DI water, including the portion that was originally used to make and transfer the resin solution. 100 mL of DI water was chosen to remove any potential impurities as it was observed to clean the effluent to an acceptable clear color. A diagram of the experimental setup can be seen in Figure 3-1.
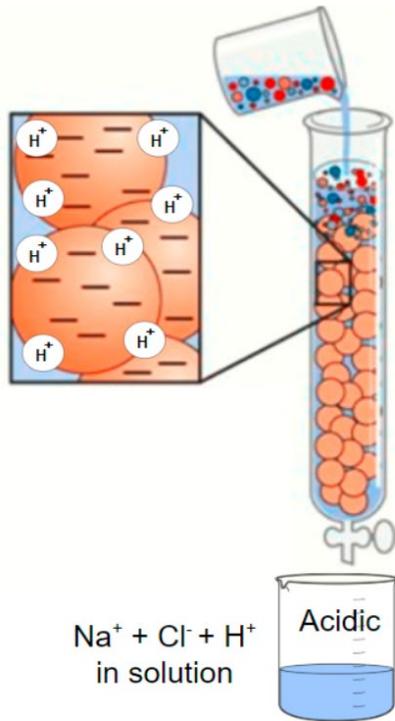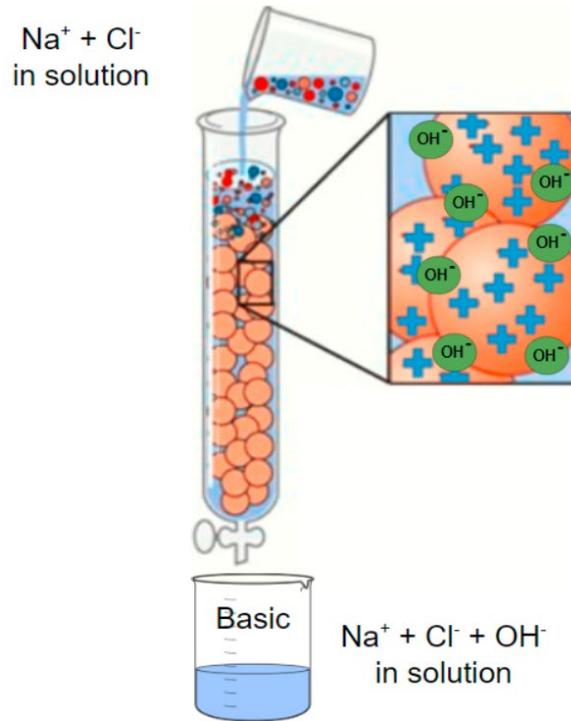
Figure 3-1. Ion Exchange Test Experimental Setup: Two parallel gravity flow through columns were set up with equal amounts of the cation exchange resin in one and anion exchange resin in the other. NaCl solutions of varying concentrations were poured through the resins in increments of 50 mL for a total of 750 mL. The cation exchange resins exchanged $Na^+$ for $H^+$ and the anion exchange resins exchanged $Cl^-$ for $OH^-$. The pH of the effluent solution was measured in order to determine the efficacy of ion exchange.

### 3.1.4 Column Tests

The goal of this experiment was to simulate the continuous flow of salty snowmelt runoff through a gravity flow column; however, in order to quantify ion exchange over time, an incremental flow was used. Three replicates for each influent percentage and resin type were conducted. For each replicate, a total of 750 mL NaCl solution (including 0% NaCl) was added to the resin in 50 mL increments with the goal of exhausting the resin. Resins became exhausted when the number of moles exchanged approached zero, which

is when the pH of the effluent approached the pH of the DI water. Based on the pH of each increment, the number of moles of sodium and chloride exchanged could be quantified. In preliminary tests, exhaustion occurred in the range of 500 – 1000 mL; but to keep the procedure simple and consistent for all salt solution percentages, the volume of 750 mL was chosen. Measuring the effluent in increments allows for the quantitative comparison of the effectiveness of each resin by plotting the change in the number of moles of each ion exchanged per unit volume of resin used versus the total volume of influent salt solution. A 50 mL increment volume ("or run") was chosen because it is a small enough volume to allow enough data points (15) to enable good curve-fitting of the data.

In order to quantify the moles of $H^+/Na^+$ exchanged, pH measurements of the effluent volume were needed. A beaker was used to collect the column effluent from the resin, which was then transferred to a graduated cylinder for volume measurements with an uncertainty value of 0.5 mL. An aliquot of each effluent was then poured into a labeled sample vial and kept for a future pH measurements.

The resin columns act as plug flow reactors moving the solution continuously through a reactive cylinder of resin. In a plug flow reactor the contact time is an important engineered factor in concentration reduction. Because the columns operate under gravity only, flow out of the columns was limited by the column bottom opening, not the resin media. The flow rate was calculated by measuring the time it took for the influent 50 mL of solution to pass through the column. This flow rate was then used with the resin volume (not including porosity of resins) to find the resin contact time for the flow through solution.

*3.2 Sample Testing*

*3.2.1 Materials Selection*

A Hanna Instruments HI2002-01edge® Dedicated pH/ORP Meter with a HI11311Digital Glass Body pH Electrode with Matching Pin for General Purpose was used. Before each use, the pH meter was calibrated using a 5-point calibration with Hanna Instruments Calibration buffer solutions at pH values of 1, 4.01, 7.01, 10.01, and 13.

*3.2.2 Dilution and Measurement*

For pH measurement, an aliquot from each effluent sample vial was serially diluted by a factor of 1000 or 10000 with DI water until the pH was between 4 and 10. Samples were diluted into the pH 4 to 10 range in order to minimize alkaline and acidity errors with the pH meter and to protect the pH probe from damage. Alkaline errors occur at high pHs (pH > 10) when the hydrogen ion concentration of the solution is significantly lower than the sodium ion concentration. The pH meter then begins to read the sodium ions as hydrogen ions and the pH reading is lower than the actual pH of the solution ("The Theory of pH Measurement," 2004). On the other hand, the acid error starts occurring at around pH 2; the acid error causes the pH meter measurement to be higher than the actual pH of the solution (Improved Process Measurement & Control, n.d.; Skoog, Holler, & Crouch, 2017). As the acid error is especially not well understood, the team elected to dilute samples into a safer range of pH 4 to 10 to further avoid it.

The resin exhaustion was measured quantitatively using pH and visually monitored using resin color change. The pH of the flow through from both the anion and cation

exchange resins approached the pH of the DI water and read consistent values as the resins became exhausted. A more neutral pH in the effluent indicated resin exhaustion because it showed that less $H^+$ or $OH^-$ ions were in solution, meaning that less $Na^+$ or $Cl^-$ were exchanged on the resin. In runs of higher concentration, a color change acted as a visual indicator that a resin was exhausted. Once the pH of the effluent ceased to change, measurements were stopped as this indicated that the resin was exhausted and a significant number of moles of $Na^+$ or $Cl^-$ were no longer being removed. Hence for more concentrated NaCl solutions, measured results may not extend to the same number of runs or total influent volume through as for the less concentrated solutions.

Importantly, the team recognized that there are other methods that could be used to quantify the amount of sodium and chloride ions exchanged. Previously, the team attempted to use Ion Chromatography (IC) for quantifying the exchanged chloride ions and Inductively Coupled Plasma Mass Spectrometry (ICP MS) for sodium quantification. However, due to instrumental function problems and time constraints, the team was unable to use these instruments to quantify sodium and chloride. Additionally, the team is aware that a conductivity meter can be used to quantify sodium chloride concentration, but the conductivity meter is unable to quantify individual ions and can only measure the total ion concentration.

### 3.2.3 Data Calculations

The results from this experimental procedure enabled the quantification of the ion exchange capacity and the kinetics of the resins for each salt solution. The moles of $Na^+$

removed by the cation exchange resin and the moles of Cl⁻ removed by the anion exchange

resin (the operating capacities) were calculated from volume and pH measurements of the

subsequent flow through increments during the column exhaustion process. The influent

$H^+$ and $OH^-$ moles were considered negligible and therefore not included in the mole

balance because the concentration would be about almost equal to zero ($10^{-6}$ M and $10^{-7}$

M). Since the pH of each sample was diluted to be in the pH range of 4 - 10, the dilution

factor is taken into account in the calculations for the number of moles of $Na^+$ and $Cl^-$

removed. Because many samples had pH values on the extreme end of the pH scale they

required large dilutions and thus the diluted samples had a large fraction of DI water

volume to sample volume. Therefore, the DI of the pH was not negligible in the total pH

of the diluted sample and thus had to be measured and accounted for in all calculations.

Using a mole balance and the ratio of equivalent 1:1 exchange of monovalent ions, a series

of equations were used to calculate moles removed for each sample. For ease of comparison

and practical understanding, the moles removed data were normalized per one liter of resin

volume; this normalization is reflected in the following equations.

Dilution of samples was considered using the equations:

$$f_{effluent} = 1 \ / \ DF \tag{1}$$

$$f_{DI} = (DF - 1) \ / \ DF \tag{2}$$

where DF is the total dilution factor and $f$ is the fraction by volume of DI or effluent sample

in the measured diluted sample.

For the **<u>cation</u>** samples the following equations were used:

$$[H^+]_{measured} = 10^{-pH_{diluted\ sample}} \tag{3}$$

$$[H^+]_{DI} = 10^{-pH_{DI}} \tag{4}$$

$$[H^+]_{measured} = [H^+]_{DI} \times f_{DI} + [H^+]_{effluent} \times f_{effluent} \tag{5}$$

$$[H^+]_{effluent} = 1/f_{effluent} \times ([H^+]_{measured} - [H^+]_{DI} \times f_{DI}) \tag{6}$$

$$Moles\ H^+ = [H^+]_{effluent} \times V \tag{7}$$

where V is measured volume of effluent (L), and

$$Moles\ Na^+{}_{removed} = Moles\ H^+{}_{effluent} \tag{8}$$

$$Moles\ Na^+{}_{removed/L\ resin} = Moles\ Na^+{}_{removed} \times 1000\ /\ RV \tag{9}$$

where RV is the resin volume used (mL).


For the **anion** samples the following equations were used:

$$[OH^-]_{measured} = 10^{-(14-pH_{diluted\ sample})} \tag{10}$$

$$[OH^-]_{DI} = 10^{-(14-pH_{DI})} \tag{11}$$

$$[OH^-]_{measured} = [OH^-]_{DI} \times f_{DI} + [OH^-]_{effluent} \times f_{effluent} \tag{12}$$

$$[OH^-]_{effluent} = 1/f_{effluent} \times ([OH^-]_{measured} - [OH^-]_{DI} \times f_{DI}) \tag{13}$$


where f is the fraction by volume of DI or effluent sample in the measured diluted sample,

$$Moles\ OH^- = [OH^-]_{effluent} \times V \tag{14}$$

where V is measured volume of effluent (L), and

$$Moles\ Cl^-{}_{removed} = Moles\ OH^-{}_{effluent} \tag{15}$$

$$Moles\ Cl = Moles\ Cl^-{}_{removed} \times 1000\ /\ RV \tag{16}$$

where RV is the resin volume used (mL).

To determine the cumulative moles removed at a given cumulative volume the incremental moles removed were summed up to that given data point, as shown in equations (18) and (19). Total moles removed was equated to the cumulative moles removed value of the final run.

$$Cumulative\ Moles\ Na^+{}_{removed/L\ resin} = \sum_{i=1}^{n} Moles\ Na^+_{removed/L\ resin} \quad \textbf{(18)}$$

$$Cumulative\ Moles\ Cl^-{}_{removed/L\ resin} = \sum_{i=1}^{n} Moles\ Cl^-_{removed/Lresin} \quad \textbf{(19)}$$

where n is the number of influent runs at any given data point.

From the moles removed data set the cumulative moles removed, incremental percent removal efficiency, along with total removal efficiency before exhaustion were all determined to evaluate the overall performance of the resins relative to the proposed research question. Incremental removal efficiency was found by dividing the moles of each ion by the influent moles of each ion.

$$\%\ Moles\ Na^+ = \frac{Moles\ Na^+_{removed}}{Moles\ Na^+_{Influent}} \quad \textbf{(20)}$$

$$\%\ Moles\ Cl^- = \frac{Moles\ Cl^-_{removed}}{Moles\ Cl^-_{Influent}} \quad \textbf{(21)}$$

To determine the total percent of moles removed at the point of resin exhaustion/ L resin (i.e. resin removal efficiency / L resin), equations (22) and (23) were used.

$$Cation\ Exchange\ Resin\ RE = \%Mol\ Na^+_{removed/\ L\ resin} = \frac{\sum_{i=1}^{ne} Na^+_{removed/Lresin}}{\sum_{i=1}^{ne} Na^+_{influent}} \quad \textbf{(22)}$$

$$Anion\ Exchange\ Resin\ RE = \%Mol\ Cl^-_{removed/\ L\ resin} = \frac{\sum_{i=1}^{ne} Cl^-_{removed/Lresin}}{\sum_{i=1}^{ne} Cl^-_{influent}} \quad \textbf{(23)}$$

where RE is the removal efficiency and $n_e$ is the number of influent runs at the point of exhaustion. The point of exhaustion for calculation purposes was chosen as the last run in which >0.01 moles were exchanged.

Total effluent concentration from the column before exhaustion was calculated using equations (24) and (25). This concentration refers to the collection of all increments (before exhaustion) in a single volume, as would be the case in a continuous flow through system in the field.

$$[Na^+]_{effluent} = [Na^+]_{Influent} \left( 100 - \% \, Moles \, Na^+_{removed/L \, resin} \right)/100$$

(24)

$$[Cl^-]_{effluent} = [Cl^-]_{Influent} \left( 100 - \% \, Moles \, Cl^-_{removed/L \, resin} \right)/100 \quad \textbf{(25)}$$

The flow rate of the influent solution through the column was calculated using the continuity equation:

$$Q = V \, / \, t \tag{26}$$

Where Q is flow rate (mL/s), V is the volume of the influent salt solution (mL), and t is the residence time (s).

The contact time of the influent solution through the resins was calculated using the continuity equation:

$$tc = RV / Q \qquad\qquad \textbf{(27)}$$

Where tc is the residence time (s), RV is the resin volume (mL), Q is flow rate (mL/s).

**CHAPTER 4: RESULTS**

*4.1 Cumulative Ion Removal*

The collected data were used to create cumulative ion removal graphs with respect to cumulative influent salt solution to emulate a continuous system (Figures 4-1 and 4-2). This allowed for analysis of the relationship among concentrations for each resin and between the cation and anion exchange resins. Although samples were collected every 50 mL up to 750 mL, the graphs only display data points that were measured, and since measurements were stopped at apparent resin exhaustion, 750 mL was not always reached. Each data point is shown with standard error bars for the moles removed for the three replicates of each incremental measurement. The point of exhaustion (defined as the last run in which > 0.01 moles of the ion of concern was removed) is highlighted in red.
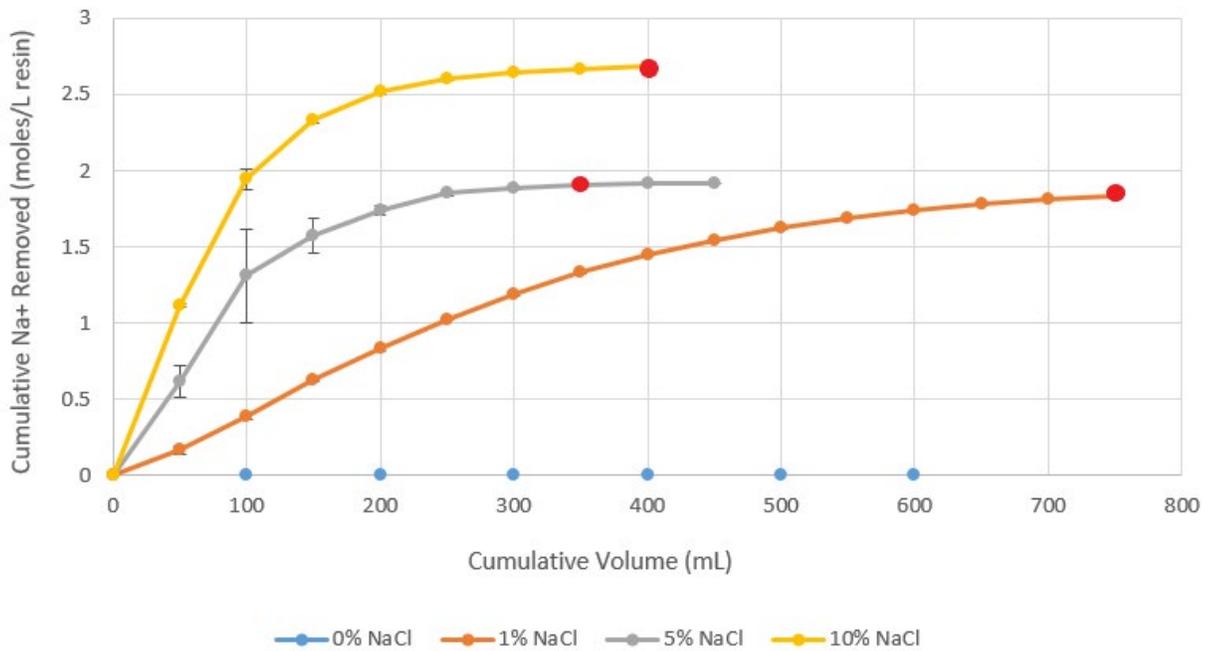


Figure 4-1. The cumulative moles of sodium ion removed per liter of resin as 50 mL increments were subsequently run through the resin. For each sodium chloride solution percentage, the point of exhaustion is marked with a red dot. (Each curve represents the mean of 3 replicates; error bar is 1 standard error).
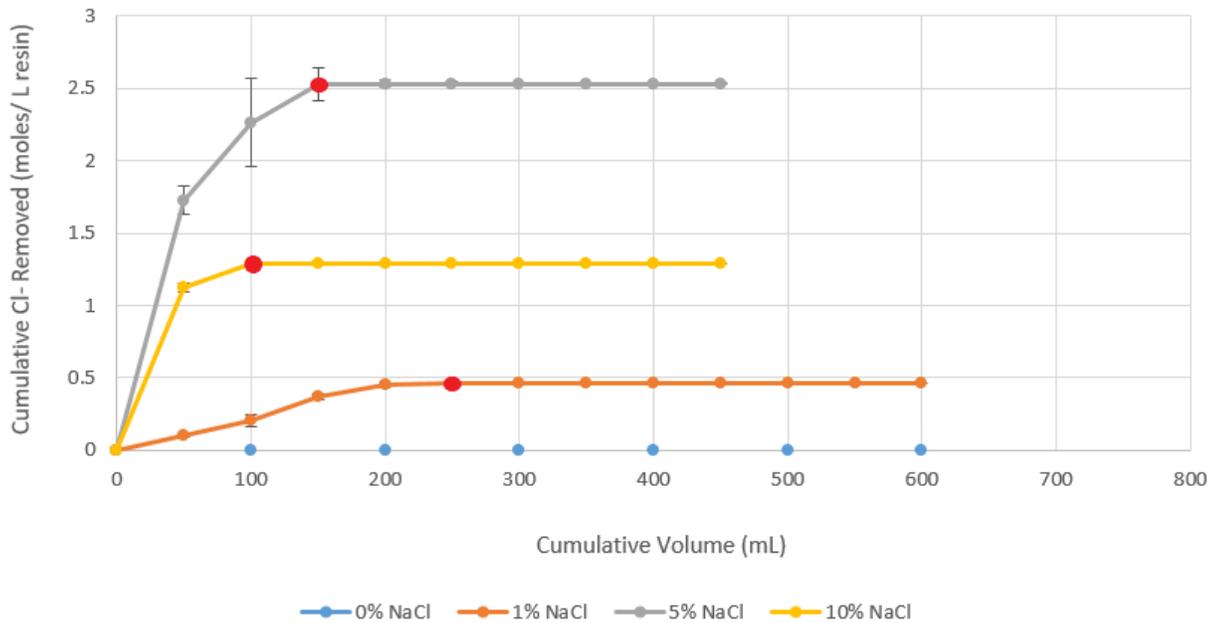
Figure 4-2. The cumulative moles of chloride ion removed per liter of resin as 50 mL increments were subsequently run through the resin. For each sodium chloride solution percentage, the point of exhaustion is marked with a red dot. (Each curve represents the mean of 3 replicates; error bar is 1 standard error plus or minus).

## *4.2 Incremental Removal Efficiency*

The incremental removal efficiency for each run (50 mL influent salt solution) in terms of the 20 mL of resin used is also expressed to display how resin performance changes normalized relative to the influent rather than on a basis of moles removed per liter of resin (Figure 4-3).
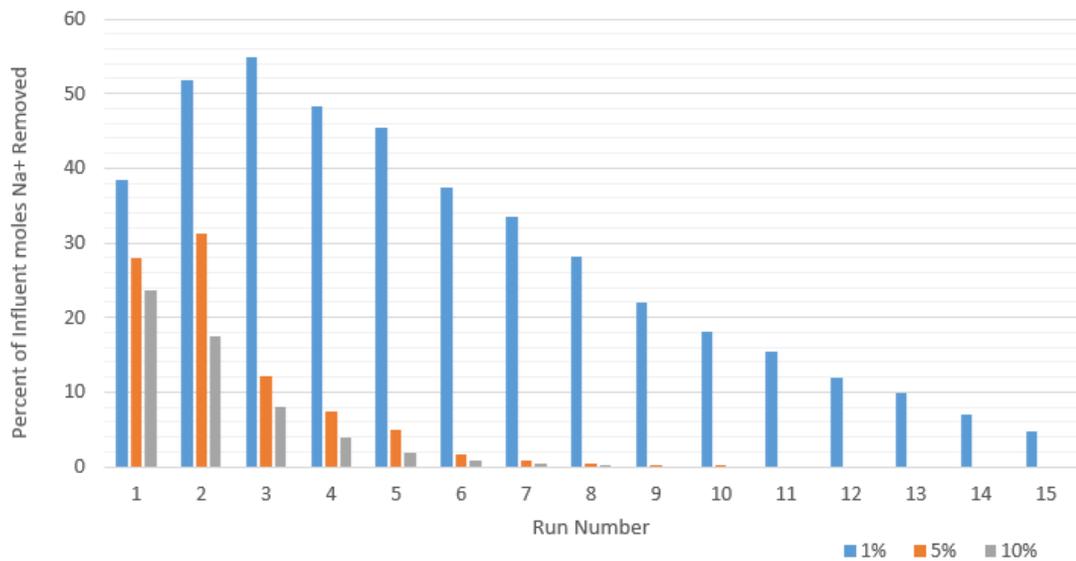
Figure 4-3. Grouped incremental Na$^+$ removal efficiency for each subsequent 50 mL increment is displayed. Each number on the x-axis represents one of the 50 mL increments run through the column during the test (total of 400-750 mL).
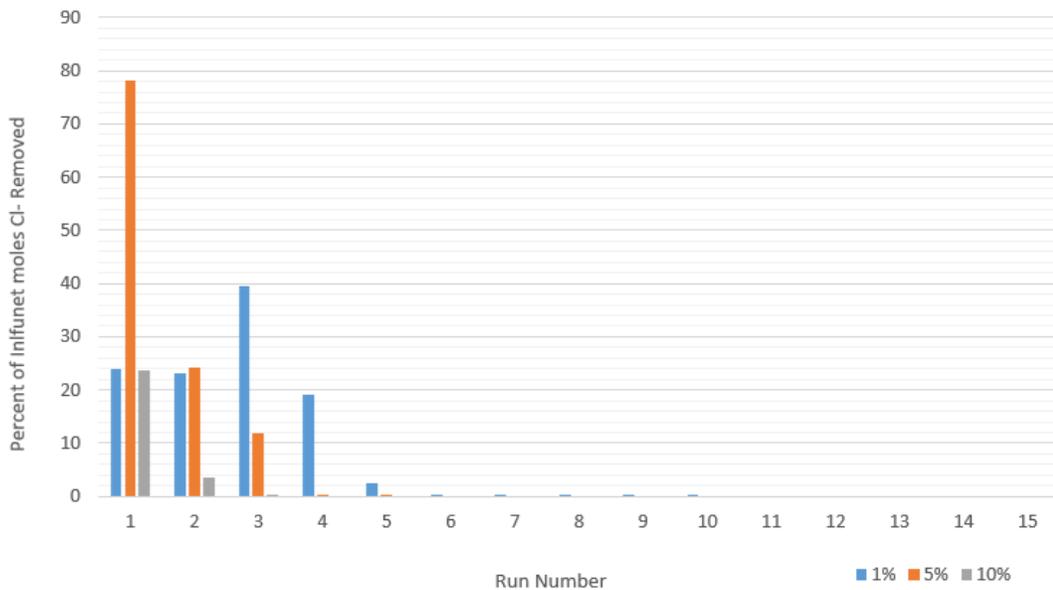


Figure 4-4. Grouped incremental Cl$^-$ removal efficiency for each subsequent 50 mL increment is displayed. Each number on the x-axis represents one of the 50 mL increments run through the column during the test (total of 450-600 mL).

## 4.3 Cumulative Ion Removal Per Liter

The total moles of $Na^+$ and $Cl^-$ removed by one liter of cation and anion exchange

resin respectively are shown in Tables 4-1 and 4-2. These values can also be interpreted as

the operating capacity of the resins (meq/mL resin).

Table 4-1. Cumulative Moles Na+ Removed Per Liter Cation Exchange Resin (i.e. Resin Operating Capacity meq/mL)

| Influent NaCl %w/w (Molarity) | 0% (0M) | 1% (0.172M) | 5% (0.883M) | 10% (1.892M) |
|---|---|---|---|---|
| Cumulative Na+ Removed (Moles/L resin) or Resin Operating Capacity (meq/mL resin) | 0.0001* ± 0.00001 | 1.836 ± 0.006 | 1.919 ± 0.001 | 2.683 ± 0.002 |

*Note: The 0% value reported is the $H^+$ released not the $Na^+$ removed, since the two cannot be equated

Table 4-2. Cumulative Moles $Cl^-$ Removed Per Liter of Anion Exchange Resin (i.e. Resin Operating Capacity meq/mL)

| Influent NaCl %w/w (Molarity) | 0% (0M) | 1% (0.172M) | 5% (0.883M) | 10% (1.892M) |
|---|---|---|---|---|
| Cumulative $Cl^-$ Removed (Moles/L resin) or Resin Operating Capacity (meq/mL resin) | 0.0008* ± 0.00001 | 0.4666 ± 0.00001 | 2.5318 ± 0.000001 | 1.2903 ± 0.000001 |

*Note: The 0% value reported is the $OH^-$ released not the $Cl^-$ removed, since the two cannot be equated

## 4.4 Hypothesis Testing

In order to determine if the total moles $Na^+$ or $Cl^-$ removed for each concentration was significantly different, T-tests were performed on the following null hypothesis of equality using a 90% level of significance ($\alpha$=0.1).

Null Hypothesis:

$$\%A\ Total\ Moles\ Na^+{}_{removed/L\ resin} = \%B\ Total\ Moles\ Na^+{}_{removed/L\ resin}$$

Alternative Hypothesis:

$$\%A\ Total\ Moles\ Na^+{}_{removed/L\ resin} \neq \%B\ Total\ Moles\ Na^+{}_{removed/L\ resin}$$

where %A and %B refers to the two concentrations being compared. The t-test calculations were performed in Microsoft Excel (two-tailed, unequal variance). The results are shown in Tables 4-3 and 4-4.

Table 4-3. T-Tests for difference between two concentrations mean cumulative moles $Na^+$ removed

| | P value | 1/2 Alpha | Result | Decision | Answer |
|---|---|---|---|---|---|
| 0% and 1% | 0.0007 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 0% and 5% | 0.0417 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 0% and 10% | 0.0006 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 1% and 5% | 0.8580 | 0.0500 | P > 1/2 alpha | fail to reject H0 | no significant difference |
| 1% and 10% | 0.0036 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 5% and 10% | 0.2383 | 0.0500 | P > 1/2 alpha | fail to reject H0 | no significant difference |

Table 4-4. T-Tests for difference between two concentrations mean cumulative moles $Cl^-$ removed

| | P value | 1/2 Alpha | Result | Decision | Answer |
|---|---|---|---|---|---|
| 0% and 1% | 0.0081 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 0% and 5% | 0.0049 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 0% and 10% | 0.0005 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 1% and 5% | 0.0063 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 1% and 10% | 0.0063 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |
| 5% and 10% | 0.0217 | 0.0500 | P < 1/2 alpha | reject H0 | significant difference |

*Note: See Appendix A for the data from all three replicates used for the t-tests

## 4.5 Percent Total Moles Removed

The percent total moles removed per liter of resin from the cumulative influent volume at the point of exhaustion is seen in Figure 4-5. These values can also be interpreted as the percent concentration reduction before exhaustion. The 0% control was not included because there were no influent $Na^+$ or $Cl^-$ ions and so there was no percent removal.
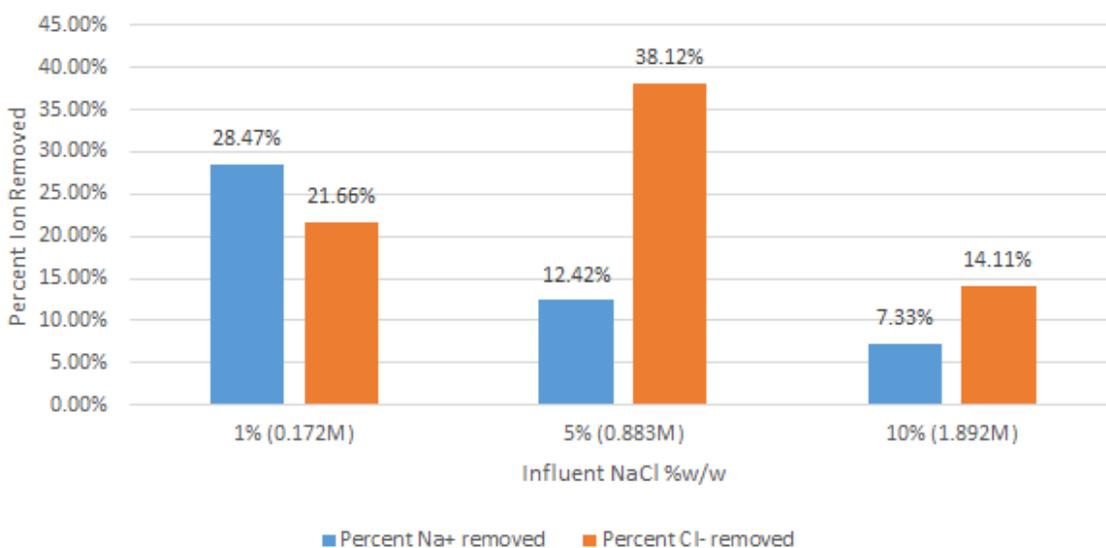


Figure 4-5. A bar graph of the averaged percent of influent moles (percent concentration reduction) of sodium and chloride removed until column exhaustion for each influent concentration.

The total effluent concentration, as defined by equations (24) and (25), for each column at the point of resin exhaustion is seen in Tables 4-5 and 4-6.

Table 4-5. Concentration of total effluent [Na$^+$] before resin exhaustion for each influent sodium chloride concentration

| Influent NaCl %w/w | 0% (0M) | 1% (0.172M) | 5% (0.883M) | 10% (1.892M) |
|---|---|---|---|---|
| Effluent [Na+] | 0.0000 | 0.1230 | 0.7733 | 1.6949 |

Table 4-6. Concentration of total effluent [Cl$^-$] before resin exhaustion for each influent sodium chloride concentration

| Influent NaCl %w/w | 0% (0M) | 1% (0.172M) | 5% (0.883M) | 10% (1.892M) |
|---|---|---|---|---|
| Effluent [Cl$^-$] | 0.0000 | 0.1347 | 0.5464 | 1.5709 |

Residence time for the 50 mL of influent through the column was measured four times with an average value of $33.5 \pm 0.6$ seconds. The flow rate through the resins is found by the flow continuity equation (Eq. 26) to be 1.5 mL/s. Using this flow value and the resin volume of 20 mL, the contact time was calculated to be 13.33s.

**CHAPTER 5: DISCUSSION**

*5.1 Capacity Analysis*

<u>5.1.1 Comparison Between Resins</u>

The operating capacity (total moles removed / L resin) of the cation exchange resins with the 0% NaCl solution was 0.000 moles/L, as was expected because there are very few, if any, sodium ions in DI water. The operating capacity was relatively constant for the 1% and 5% NaCl solutions, which removed $1.836 \pm 0.006$ moles/L and $1.919 \pm 0.001$ moles/L, respectively. The 10% NaCl solution removed the most moles of sodium ions at $2.683 \pm 0.002$ moles/L. This upward trend indicates that the resins remove more ions at higher concentrations of NaCl solution. An opposite trend can be seen for the influent volume at which the resins exhausted and could exchange no more ions. This occurred at 750 mL, 350 mL, and 400 mL for the 1%, 5%, and 10% NaCl solutions, respectively.

Though the trend of the total moles removed seems promising, when calculating the percent removal efficiency at which the resins exhausted, it is clear that introducing more concentrated NaCl solutions to the cation exchange resins resulted in a lower removal efficiency. For 0%, the removal efficiency was 0%; however, for 1%, 5%, and 10% NaCl solutions, the removal efficiencies were 28.47%, 12.42%, and 7.33%, respectively. Even though more total moles were removed with increasing concentration of the NaCl solution, the total percent of the influent moles removed actually decreased with increasing concentration of the NaCl solution.

It is possible that for 1% NaCl solution, more ions could have been exchanged past a volume of 750 mL. These results show that strong acid cation exchange resins chosen for

this experiment are more efficient when NaCl solutions with low concentrations (1%) are run through the resins.

The data for the strong base anion exchange resins were less consistent than the strong acid cation exchange resins. Similar to the cation exchange resins, the operating capacity of the anion exchange resins with the 0% NaCl solution was 0.000 moles/L. However the operating capacity for the resins with the 1%, 5%, and 10% NaCl solutions was 0.4666 mole/L, 2.5318 mole/L, and 1.2903 moles/L. Though there is an increase in the operating capacity from the 1% to the 5% NaCl solutions, it decreases again at 10%, which was not expected. The volume at which the resins exhausted decreased with increasing influent concentration. This occurred at 250 mL, 150 mL, and 100 mL for the 1%, 5%, and 10% NaCl solutions, respectively.

The data for the total percent removed show that for the 5% NaCl solution the anion exchange resin was most efficient, removing 38.12% of the chloride ions from the total influent solution. For the 1% NaCl solution, the anion exchange resins removed 21.66% of the chloride ions from the total influent solution, while for the 10% NaCl solution, the anion exchange resins removed 14.11% of the chloride ions in the total influent solution.

The data for the 5% NaCl solution have an outlier in its triplicate data set, so it is important that the experiment be repeated to determine if this is a true outlier or if there was error in the data collection for the anion exchange resins with this percent. However, it is also possible that the data for the 1% or the 10% NaCl solutions are very low.

The cation exchange resin results show a statistically significant difference between the total moles of $Na^+$ removed for 0% compared to 1%, 5%, and 10%. This shows that the cation exchange resins do exchange significantly more sodium ions when exposed to a

concentrated salt solution than pure DI water. Additionally 1% and 10% were different. However, 5% was not significantly different from 1% or 10%, even though 5% has a greater average moles $Na^+$ removed than the 1%. This is likely due to a single outlier measurement (see Appendix B) in the second data point of replicate three that is skewing the entire third replicate and thus causing a large variance in the 5% data set. Unfortunately this outlier makes it difficult to tell whether the 5% data set is significantly different from 1% and 10% because of the outlier or not.

Each anion concentration was statistically significantly different from the others, confirming not only that the anion exchange resins do exchange significantly more chloride ions when exposed to a concentrated salt solution than pure DI water, but also that the resins function differently (have different capacities) when exposed to different concentrations of monovalent ionic solution.

### 5.1.2 Comparison Among Percents

As expected, for the 0% salt solution the operating capacity of the cation and anion exchange resins was 0% because there were no sodium or chloride ions that needed to be removed from the DI water.

For the 1% NaCl solution, the cation exchange resins seemed to be more effective at removing sodium from the given solution than the anion exchange resins were at removing chloride ions. The cation exchange resins removed, in total, more moles of sodium at $1.836 \pm 0.006$ moles/L, while the anion exchange resins removed a total of 0.4666 moles/L. The cation exchange resins also exhausted at 750 mL while the anion exchange resins exhausted at 250 mL. At their respective exhaustion points, the cation

exchange resins filtered 3 times as much NaCl solution and removed 4 times as many moles as compared to the anion exchange resins under the experimental conditions. At an influent volume of 250 mL for the cation, 1.0270 moles of sodium were removed (Figure 4-1). At the same influent value for the anion exchange resins, slightly less than half of this number of moles, 0.4666 moles/L, was removed (Figure 4-2). In terms of the percent removed, the values were somewhat comparable. The removal efficiency for the cation exchange resins was 28.47%, while this value was only 21.66% for the anion exchange resins, indicating that the cation exchange resins were slightly more efficient. A system would need approximately 2.5 times as much anion exchange resin at the point of exhaustion to remove moles of chloride equal to the moles of sodium removed by the cation exchange resin.

For the 5% NaCl solution, the cation exchange resins were less effective at removing sodium from the given solution than the anion exchange resins were at removing chloride. The cation exchange resins removed, in total, $1.919 \pm 0.001$ moles/L while the anion exchange resins removed a total of 2.5318 moles/L. At their respective exhaustion points, the cation exchange resins filtered about 2.5 times as much NaCl solution but removed half a mole of ions less than the anion exchange resins. At an influent volume of 150 mL for the cation, 1.5753 moles of sodium were removed. At the same influent value for the anion exchange resins, about one more mole of ion was removed. The percent total moles removed for the cation exchange resins was 12.42%, and 38.12% for the anion exchange resins, indicating that the anion exchange resins were more efficient. However, this result disagrees with the trends for the cation and anion exchange resins for the 1% and 10% NaCl solutions.

For the 10% NaCl solution, the cation exchange resins were more effective at removing sodium from the given solution than the anion exchange resins were at removing chloride. The cation exchange resins removed, in total, $2.683 \pm 0.002$ moles/L while the anion exchange resins removed a total of 1.2903 moles/L. The cation exchange resins also exhausted at 400 mL while the anion exchange resins exhausted at 150 mL. At their respective exhaustion points, the cation exchange resins filtered 2.5 times as much NaCl solution and removed twice as many moles than anion exchange resins. At an influent volume of 150 mL for the cation, 2.3300 moles of sodium were removed. At the same influent value for the anion exchange resins, about half of this number of moles was removed. In terms of the removal efficiency, the values were somewhat comparable. The removal efficiency for the cation exchange resins was 7.33% and 9.47% for the anion exchange resins, indicating that the anions resins were slightly more efficient. However, overall, the anion exchange resins used were not as effective at removing chloride than the cation exchange resins were at removing sodium. A system would need twice as much anion exchange resin under the same conditions of exhaustion to remove moles of chloride equal to the moles of sodium removed by the cation exchange resin.

Anion exchange resins are less dense than cation exchange resins and thus have smaller exchange capacities (Ion Exchange, n.d.). The observed differences are consistent with the manufacturer's stated exchange capacities for the resins. The Resintech website from which the tested resins were purchased listed capacities of the cation exchange resin at >1.8 meq/mL and >1.0 meq/mL for the anion exchange resin. The cation column test results show a capacity that decreases with decreasing influent concentration to around 1.8 meq/mL, confirming the minimum capacity information listed by Resintech. This indicates

that the capacity of the resins for a low concentrated ionic solution is 1.8 meq/mL, but as the concentration increases the capacity increases as well, perhaps because a higher influent solution activity forces greater exchange. There is an upper limit of total ion binding sites, but this is not something that can be found through tests and may only be proprietary information.

The anion column test results do not follow a clear decreasing trend towards the listed capacity of >1 meq/mL. The 1% influent is only about half the minimum capacity (0.4666 moles $Cl^-$), while 5% is more than double (2.5318 moles $Cl^-$). The 10% influent is the closest to the minimum capacity (1.2903 moles $Cl^-$). It is not clear why the cation data confirm the manufacturer's value while the anion data do not. It is possible that the anion exchange resin was affected by non ideal conditions such as dry $CO_2$ in the air. Thus it did not follow reasonable trends and did not reach its listed capacity for 1%.

### 5.2 Kinetics Analysis

To further analyze the kinetics of this ion exchange process, a regression was run comparing the cumulative ion removal to a logistic function of the form

$$N = \frac{L}{1+exp(-k(x-x_o))} + y_o - \frac{L}{2} \tag{28}$$

where L is the maximum value of the curve, k is the logistic growth rate or steepness of the curve, and $x_o$ and $y_o$ represent the x and y coordinates of the midpoint of the sigmoid. The regression was run by varying these values in order to minimize the sum squared error of the expression with the measured data. For all data sets, error was normalized based on the maximum number of moles absorbed as this value represents 100% saturation of the

resin. The sum squared error for each set was found to be below 0.002 meaning the expression very accurately fit the curve with the exception of the 1% Cl⁻ expression which

had a sum squared error of 0.0299 since the curve did not fit the early data well. From these regressions the logistic growth factor of each data set was found. These are presented in Table 5-1. These values represent the rate at which the resins reached exhaustion.

Table 5-1. Logistic Growth Factors k (mol/mL), representing the rate at which the resins exhausted. The sum squared error for each set was found to be below 0.002, except the for the 1% Cl⁻ which has a sum squared error of 0.0299.

| Concentration (w/w) | $Na^+$ | $Cl^-$ |
| --- | --- | --- |
| 1% | 0.00613 | 0.036185 |
| 5% | 0.021074 | 0.025247 |
| 10% | 0.018608 | 0.162266 |

The logistic growth factors in Table 5-1 show that as the concentration of the solution increases, both the anion and cation exchange resins exhaust at a higher rate. In comparison to one another, the anion resin is more efficient than the cation exchange resin. While it is shown that the removal efficiency is not very high in the anion and cation exchange resins, the removal efficiency would be improved in more energy intensive processes like thermal or pressure gradient.

## 5.3 Overall Desalination Effectiveness

An overall assessment of resin ability to remove $Na^+$ and $Cl^-$ ions in this flow through gravity fed system is helpful to answer the three tested research questions. Based on the data collected, the resins can function to remove sodium and chloride in a flowthrough system as seen by the total percent of ions removed and the incremental removal efficiency graphs in the results (Figures 4-3, 4-4, and 4-5). Before the resins exhausted, they effectively removed many ions from the solution, ranging from 7.33% (10% salt influent) to 28.47% (1% salt influent) for cation exchange resins and from 14.11% (10% salt influent) to 38.12% (5% salt influent) for anion exchange resins (Figure 4-5). It makes sense that the 10% influent results in the lowest percent removal because this solution had the most ions. One would expect that the resins would remove the highest percent ions for 1% influent solutions before exhaustion since there are less ions to remove. Though this is true for the cation exchange resins, it is not the case for the anion exchange resin because this resin removed 38.12% of chloride ions before exhaustion for 5% influent, which is nearly double the 21.66% chloride removed for 1% ion solutions. Though there is a trend in percent removal for the sodium ions removed by the cation exchange resins, a similar trend is not present for the anion exchange resins.

After exhaustion, the incremental removal efficiency of the resins declines (Figure 4-5). The incremental removal efficiency results show that the effectiveness of the resins to remove salt significantly drops after just 200-250 mL of salt solution is run through them (Figures 4-3 and 4-4) with the exception of cation exchange resin for the 1% salt solution. The cation $Na^+$ removal efficiency for the 1% influent declines, but not as quickly as it

does for the other influent conditions. The cation exchange resins are still removing about 5% of $Na^+$ ions after 15 runs (Figure 4-3). This result for 1% cation removal efficiency is intriguing and warrants further investigation. With all of this said, however, the resins would be implemented as a low energy removal system and any type of salt removal would be beneficial for the water quality.

Figures 4-1 and 4-2 provide further interesting analysis for resin performance in terms of the differences in cumulative moles of salt removed with each influent concentration. For the cation exchange resins, the order of cumulative moles of sodium removed at exhaustion by solution salt percentage is 0%<1%<5%<10% (Figure 4-1). It makes sense that more moles of sodium are removed when the resins are exposed to higher concentrations of sodium at higher percentage salt solutions, as higher concentrations force more exchange to occur. On the other hand, the anion exchange resins do not follow this trend as the order of total cumulative chloride moles removed at exhaustion by solution salt percentage is 0%<1%<10%<5% (Figure 4-2). This trend for anion exchange resins indicates that the effectiveness of chloride removal by the resins is not solely dependent on the amount of chloride present in solution. For this reason, more experimentation should be performed to determine other factors, besides influent salt solution concentration, that affect ion removal ability. If the effectiveness of the resins can be optimized, then their feasibility for implementation into the environment will be improved.

Another aspect in which the efficiency of cation and anion exchange resins can be compared is in terms of resin exhaustion volume. The red dots in Figures 4-1 and 4-2 show where the resin has reached capacity, or the point of exhaustion. For the cation exchange resins, the volume of exhaustion is the largest (750 mL). This means that it can it can filter

a larger volume of solution before it loses the ability to exchange ions. However, this volume decreases as the influent concentration increases from 1% to 5% (350 mL) and 10% (400 mL). A similar trend exists for the anion exchange resins, but to a much smaller degree. The 1% influent solution still exhausts the resins after the largest volume (250 mL), while 5% (150 mL) exhausts next, and 10% (100 mL) exhausts after the smallest volume of influent. Compared to the cation exchange resins, the 1% influent solution exhausts the resins after a much smaller volume, indicating that the cation exchange resins are more effective at a low salt concentration of 1%.

### 5.4 Limitations and Sources of Error

It is suspected that there was error in the collection of the 5% NaCl solution with the anion exchange resin because of the outlier in the replicates. This may have been due to an unknown error in data collection at some point. As stated before, there is also the possibility that the data for the 1% or 10% NaCl solution with the anion exchange resins were too low due to a similar error. Other sources of error include extraneous variables that may have affected the results, including salt residue remaining in the physical column after washing. Though the columns were thoroughly washed with DI water several times, there may have been some salt residue left in the columns, especially from the more highly concentrated salt solutions. Exposure of the resins to the air and $CO_2$ may have affected their function, however, this exposure was limited to very short periods of time and resins were never fully dried out then rewetted. Instrumental error in the balance used for weighing, the graduated cylinders used for measuring and pouring the salt solutions, and the volumetric flasks used to store the salt solutions may have been present. There was also

propagated error from the multiple dilutions made to get the effluent pH between 4 and 10. Finally, DI water is not completely free of ions, and the presence of small traces of other competing ions may have affected the results.

One of the biggest limitations to this research was in the methodology. As mentioned in the Methods Chapter and detailed in Appendix B, using a pH meter to estimate ion removal introduced with many errors and complications that needed to be adjusted for and accounted for in the experiment. Because pH meters measure relative voltage differences to determine the pH of a solution, it may be difficult to determine the exact $H^+$ concentration. The team attempted to employ more accurate tests: an Ion Chromatography (IC) instrument to measure chloride ion concentration and Inductively Coupled Plasma (ICP) to measure sodium ion concentration. Each of these methods measures the concentration of ions in the solution directly and provides a more accurate measurement of the amount of ions in a solution. Preliminary use of the ICP machine for runs with the 1% NaCl solution with the cation exchange resins indicated more exchange than what was determined using only the pH meters. Unfortunately, the ICP machine broke and was not repaired in time in order for the team to continue using, but it proved to be a useful instrument for more accurate measurement and should be considered for future experiments. The team was not able to use the IC to collect data for the chloride ions.

Another limitation was time. The team independently developed the experimental methods by applying their growing knowledge of the science and through trial and error because of a lack of literature pertaining to the team's methodology. This reduced the amount of time spent actually collecting data once the methods were finalized. In addition, setbacks due to the discovery of the sodium error (see Appendix C) and damage to the pH

meter further limited the amount of time spent collecting data. In addition, due to time constraints, it was not possible to test more salt solutions with different concentrations of other ions that could compete with the NaCl for the binding sites on the resins. These ions include magnesium and calcium for the cation exchange resins and nitrate and sulfate for the anion exchange resins. Using these ions, it would be possible to determine the efficacy of the resins to remove salt against competing ions. In addition, further experiments would test under realistic environmental conditions. These include near freezing temperatures and usage of commercial road salt (to test the effect of impurities on exchange ability).

Finally, there were limitations in terms of the resin used for the experiments. There were several types of resins that differed in their polymer type, functional group, capacity, water retention percent, and swelling percent. In each category, the anion exchange resins differed from each other more than the cation exchange resins did, which could explain differences in the results between the resins. The team was not able to compare multiple $OH^-$ anion exchange resins or multiple $H^+$ cation exchange resins to each other in order to determine which one was the most effective. This is something that should be done in future experiments to determine the best combination of cation and anion exchange resins.

**CHAPTER 6: FUTURE DIRECTIONS**

*6.1 Resin Regeneration*

The next phase of the research was to look into the possibility of regenerating the resins (see Research Objectives, pg 18) using a strong acid (HCl) or strong base (NaOH) after they have exhausted and can no longer exchange any more ions (What to Know About Ion Exchange Resin Regeneration, 2017). The idea is that the concentrated solution of acid or base will remove the sodium and chloride ions bound to the cation and anion exchange resins, respectively, and replace them with $H^+$ and $OH^-$ ions again. The

resulting effluent would be a concentrated brine solution that could be collected and reused for road salt prewetting. This is an important sustainability aspect of the project that could decrease the amount of salt used on the roads that ends up in the environment. After running the concentrated solution of acid or base through the respective resins, they would be tested again to see how effectively they removed sodium chloride from the brine solution.

Ion exchange resins are commonly regenerated in order to extend their use (Resin Regeneration Fundamentals, 2006; What to Know About Ion Exchange Resin Regeneration, 2017). There are two major types of regeneration: Co-Flow and Reverse Flow. In Co-flow, the regenerant solution flows in the same direction through the column as the treated solution. In Reverse Flow, the regenerant solution flows in the opposite direction through the column. The two types of regeneration can be seen in Figure 6-1. Co-flow is not ideal for strong acid cation and strong base anion exchange resins because a large amount of regenerant solution would be needed to fully regenerate all resins. In addition, a lack of full regeneration could result in a leakage of contaminant ions into the

flowthrough. This leakage would result from from the $H^+$ ions in the regenerated resins being exchanged for the $Na^+$ ions in the non-regenerated resins. For reverse flow regeneration, the less exhausted resins are regenerated first, followed by the more exhausted ones. This reduces the chances of leakage (de Dardel & Arden, 2003; What to Know About Ion Exchange Resin Regeneration, 2017).

A                                                                                    B
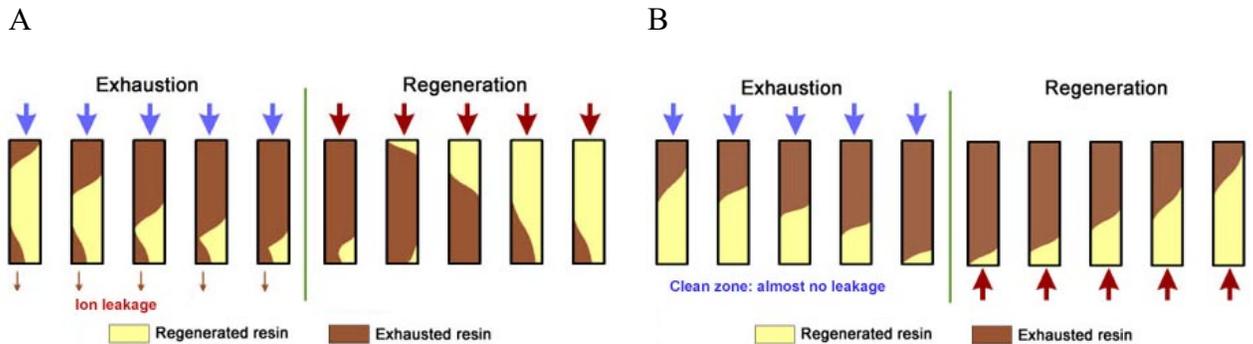


Figure 6-1. Types of Regeneration: (A) Co-flow
regeneration– the regenerant solution runs in the same direction of the treated solution and
(B) reverse flow regeneration– the regenerant solution runs in the opposite direction of the
treated solution. Image reproduced from de Dardel (2018).

The ideal regeneration procedure for the resins used in the experiment would be reverse flow regeneration. Regeneration consists of four steps (What to Know About Ion Exchange Resin Regeneration, 2017):

1) Backwash (only used for coflow): agitates the resin beads in order to remove any solids

2) Rinse with regeneration solution at a low flow rate in order to maximize contact with the resin.

3) Rinse with dilution water to rinse off any remaining regeneration solution.

4) Rinse with the treatment solution until the desired quality level is reached.

A resin can only be regenerated to 60-80% of its original exchange capacity (The Basics of Resin Regeneration, 2019; de Dardel & Arden, 2003), so subsequent regenerations will only produce about 60-80% exchange of the total capacity of the resin. The regeneration efficiency is the ratio of the operating capacity to the amount of regenerant used (both in equivalents per liter). The regenerant ratio or regenerant usage is the reciprocal of this. All values are expressed as percentages (de Dardel & Arden, 2003).

The chemical composition, concentration, and volume of the regenerant solution is important when regenerating. The amount of regenerant used has the greatest effect on operating capacity (de Dardel & Arden, 2003). It is also vital that more than the stoichiometric amount, yet still an economically reasonable amount of the regenerant, is used in order to ensure as much regeneration as possible. In addition, the type of regenerant used matters. NaOH is the most common and effective regenerant used for strong base anion exchange resins and produces a reasonable operating capacity after regeneration. For strong acid cation exchange resin, HCl is more effective than $H_2SO_4$. This is because sulfuric acid has a lower operating capacity, is not completely dissociated at the concentration needed, and, if there is a lot of calcium present in or on the resin, there is a risk for the development of the precipitate calcium sulfate during regeneration (de Dardel & Arden, 2003).

### 6.2 Limitations of Resin Use in the Environment

The potential use of the resins in the environment has several limitations. First, since road salt and brine solutions are placed directly on the roads themselves, use of these

resins to treat captured runoff may not be able to limit the damage to asphalt roads, bridges, motor vehicles, and other infrastructure. However, they could be strategically placed to avoid excess salt exposure to more sensitive infrastructure. The resins may also not be able to limit damage to soil and vegetation adjacent to roads on which salt or brine has been applied. Splash and runoff from the application of the deicer and vehicles driving over the road will directly affect the vegetation. However proper placement can still prevent salt levels from increasing in groundwater and aquatic vegetation farther from roadsides. Other solutions to the damage road salt inflicts upon infrastructure and vegetation must be researched in order to continue to provide a more well rounded approach to tackling this problem.

### 6.3 Implementation

The ultimate goal of this research is to determine the potential of ion exchange resins to desalinate runoff in a small scale stormwater drain setting during a winter storm. The results obtained from lab tests show the resins have desalination potential. If their legitimacy can be further demonstrated using more realistic influent solutions then it becomes necessary to start evaluating feasibility from a stormwater engineering standpoint, specifically the needed sizing of a storm drain resin reactor. If the volume of resin needed is a reasonable size for a storm drain then this idea may warrant further research, but if not then the idea may need to be reevaluated.

For this exercise the sizing was determined for a typical snowfall storm event in central Maryland. As previously mentioned, the runoff of road salt laden snowmelt can have a varying concentration and no exact measurements exist to give any type of idea as

to expected ranges. Because of this, runoff concentration approximations can only be made from salt usage rate information and measured snow totals. As of winter 2018-2019 in Baltimore County, road salt is applied at a rate of 1.2 tons per lane mile per storm (Strachan & Davis, 2009) over 6,774.25 lane miles (Baltimore County Government, 2019). This equates to about 126 million moles of NaCl for an average storm. At BWI airport (located adjacent to Baltimore County), the average snowfall event in the winter of 2018-2019 was 1.6 inches (Iowa State Department of Agronomy, 2019). Every inch of snow corresponds to approximately 1/13th in. of liquid water (National Severe Storms Laboratory, 2019); thus 1.6 in. of snow yield 0.12 in. of snowmelt. Using the length of lane miles and the average lane width of 12 ft. (Maryland Department of Transportation, State Highway Administration, 2019), a total volume of 121 million L of snowmelt is found for the average storm. From this information the concentration is conveniently found to be approximately 1 M NaCl. This value is relatively close to the 0.883 M (5% w/w) salt solution tested and thus can reasonably be related to the 5% data set. The cumulative moles removed curve for 5% NaCl for each resin gives the cumulative influent volume for which the resin will exhaust for a typical storm event: 0.35 L 5% solution/L cation exchange resin and 0.15 L 5% solution/L anion exchange resin.

Next, the volume of this influent snowmelt concentration that will flow into a drain for an average Maryland snow event was determined. As previously found, the average snowelt depth is about 0.12 inches. According to the Wisconsin DOT, runoff should not travel more than 300-600 ft. depending on the speed of roadway, so the average value of 450ft was used along with the 12ft road lane width to find an average drainage area of 0.12 acres (5227 ft$^2$). Using this information the total volume of ~5% snowmelt that will flow

into a typical stormwater drain is about 764 L (27 ft$^3$). This total snowmelt volume divided by the cumulative influent volume at exhaustion, as previously mentioned, yields the required number of liters of cation exchange resin: 2180 L (77 ft$^3$), and anion exchange resin: 5090 L (180ft$^3$). A mixed bed resin design would thus be the sum of the two: 7270 L (257 ft$^3$) with a volume ratio of 1 L cation exchange resin to 3.3 L anion exchange resin. An option for the approximate dimension of the total volume would be 16 ft. x 4 ft. x 4 ft. This does not account for porosity of the resin (resin volume was measured by submersion in water), as this would increase the size slightly. Because this size would be prohibitively large, implementation would require smaller reactors at the cost of exhaustion before a storm ends, which would translate to decreased salt removal from the listed efficiencies found in the column tests. This does not mean the resins will remove less salt before exhaustion, just that once they exhaust they will not be removing salt and the snowmelt will still be flowing in. A smaller more realistic size could be used to calculate what percent of a storm the resins could treat and from this information the loss of salt removal could be determined so that a decision could be made on whether installation is worth the cost. Alternatively, a smaller reactor could be used and then replaced during a storm event to provide the total volume needed. The large volume of resin needed to treat an average snowfall event is not ideal, but could be accommodated for if the technology continues to show promise and a community has high concerns over salty runoff and or is committed to improving its water quality. An example of how a resin reactor could be inputted into a storm drain is shown below in Figure 6-2. Here the resin column shown is as a mixed bed and designed to fit in a storm drain. This design would allow for ease of resin placement

and replacement in a storm drain while also preventing flow or resin blockage by debris/sediment carried in the stormwater.
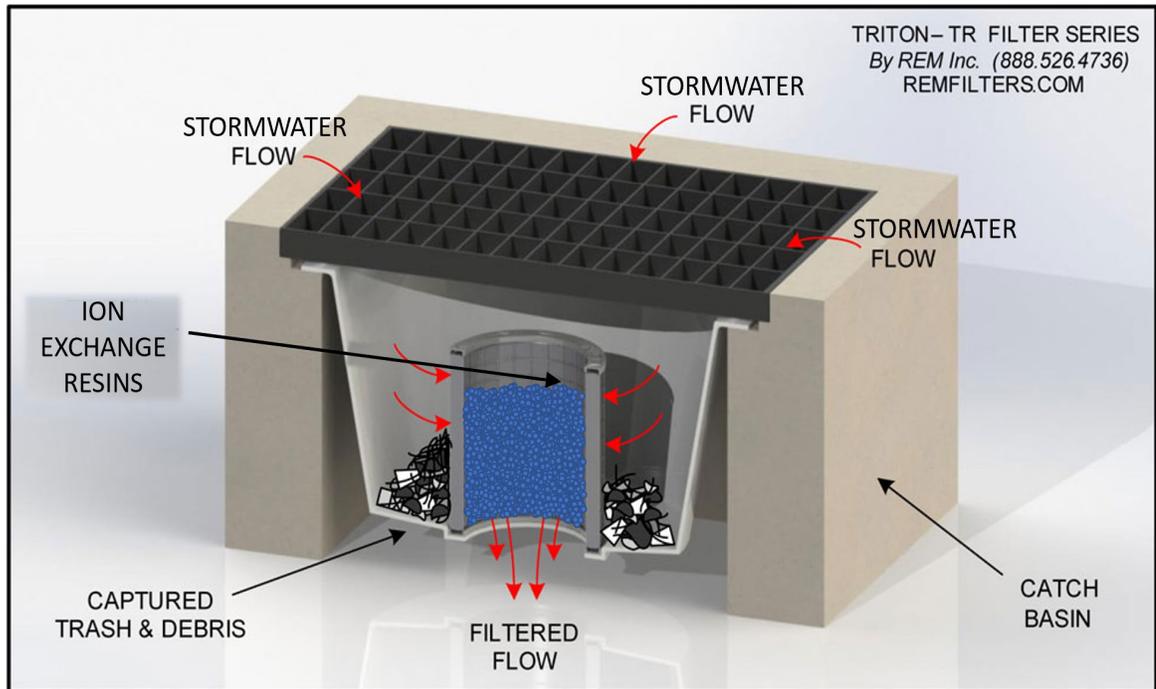


Figure 6-2. A representation of a possible configuration of a catch basin in a grate opening storm drain. Water flows into the area around the center column fills up and then flow in the top of the center column while undesirable debris is settles collected laterally next to the desalination chamber thus preventing blockage of the resins. A mixed bed of ion exchange resins are placed in the center in a column type design so flow can come in the top and through the bed and runoff can be desalinated. Image courtesy of REMFilters.com

Using resins for desalination would add another cost to winter storm roadway maintenance beyond the deicing chemicals. For this reason it likely will only be applicable in cold weather urban areas with frequent winter precipitation. These regions may be willing to invest as their road salt use would be having a much greater environmental impact than a region with infrequent snowfall. The ability to regenerate the resin, although not free, would allow for resins reuse and recovery of a concentrated salt brine, which would decrease the total cost of the system and to some minor extent even pay for itself.

Many stormwater engineering challenges regarding the use of these resins in a natural environment need to be addressed before implementation. Of these, a main concern is the effluent pH. As previously discussed, this is critically important so that treated effluent does not become too acidic or basic and lead to damage of metallic pipes carrying the treated effluent or alter the water chemistry and threaten aquatic life once it enters freshwater bodies. More investigation is needed to address the impact on pipes and natural waters due to this temporary $H^+$ and $OH^-$ loading. Furthermore, if environmental effects of the effluent pH prove not to be negligible, then the resin reactors will have to be adjusted. Because the ratio of exchange of cation to anion exchange resins controls the effluent pH, then the resin volume ratio, relative exchange efficiencies and kinetics will control the pH. From the collected data, it was found that the removal efficiencies were not close to equivalent. Recall that removal efficiencies were not equivalent between the resins for any concentration, and nor were the kinetics (growth factors) equivalent either. Therefore, the volume ratio used in the aforementioned experiments (1:1) needs to be adjusted. The volume ratio needed for the neutral pH effluent may not match what is needed for the sizing example in the previous paragraph and thus desired pH or entire storm treatment may need to be compromised. How this volume ratio should be adjusted to account for these different factors is complicated to determine mathematically based on collected ion removal data and thus would likely be easier to determine by more experimental tests. Using a mixed bed resins with varying volume ratios, pH could be analyzed over time to find a an ideal ratio that produces a close to neutral pH effluent without compromising too much ion removal.

Another engineering challenge is the resistivity of the resin media which creates head loss through the system. This challenge is particularly important because if a resin desalination system interferes with the storm drains primary purpose of transporting water safely off the roads then it becomes impractical. The columns used for this research were sized for bench-scale convenience and some other types of container that allows a much higher flow would likely be needed. This would decrease the contact time which could possibly decreases ion removal and appropriate adjustments to the reactor design may have to be made. Additional flow tests would be needed to determine if the resins could be used without significantly slowing flow and causing backup problems.

Ion-exchange resins show promise as a desalination procedure, but more experiments must be conducted in order to confirm this conclusion. In addition to including regeneration experiments in future research into this topic, other realistic environmental conditions as well as more reliable methodology need to be incorporated into future tests to determine the resins' capacity to exchange in more realistic conditions. These include adjusting the temperature of the water and air to freezing or near freezing conditions to mimic winter runoff and creating salt solutions made with commercial road salt to test the resins' ability to exchange real road salt, not just a brine solution. Collecting samples of actual road salt runoff, determining their composition, and using the runoff in experiments is another way to mimic environmental conditions, in addition to possibly determining trends in road salt runoff concentration. It is expected that these in-situ conditions will lower the effectiveness of resins. If the percentage of ions removed is still considerable, then field implementation would becomes a possible focus. Since the resins seem to work best at lower salt solution concentrations, it is vital to ensure that, to some degree, the salty

solution that flows through the resins is at or below the maximum concentration at which the resins are most effective (have the highest percent total removed). In addition, improving the methodology to ensure accurate data collection is vital to better determining the capacity of the resins for $Na^+$ and $Cl^-$ exchange.

**CHAPTER 7: CONCLUSION**

The goal for this project was to investigate the desalination potential of ion exchange resins in a flow through gravity fed system. To compare the efficacy of the resins with influent concentration, a spread of concentrations (0%, 1%, 5%, and 10%) around the expected concentration of winter storm runoff were tested.

The results of the experiments indicated that while higher concentrations see the removal of more moles of ions, the resins removed a larger percentage of the $Na^+$ and $Cl^-$ moles at lower concentrations. The cation exchange resins removed a larger number of moles than the anion exchange resin, primarily due to the larger binding capacity of the cation exchange resin tested. The data indicated a substantial percentage of $Na^+$ or $Cl^-$ moles removed by the resins; however it is unclear whether the resins are feasible for practical use. While the percentages removed were significant, the resins themselves exhausted fairly rapidly and required large volumes of material. As explored in the implementation section of the team's analysis, the amount of physical mixed bed resin required to entirely desalinate winter storm runoff from one storm drain (16 x 4 x 4 ft$^3$) is prohibitively large to fit into the space within the drain. Thus, size adjustments would need to be made, resulting in a compromised rate of ion removal. Additionally after a storm or two of runoff, the resins in place would be almost entirely exhausted and saturated by the unwanted ions, requiring regular replacement. However, as discussed, there is the possibility to regenerate these resins by administering strong acids and bases through the system and collecting the effluent, a concentrated brine solution, for future deicing use.

With more research into regeneration and resin capacity, a stormwater management system of ion exchange resins could be created.

Without remediation, the road salt problem in the United States will continue to get worse. Sodium chloride from salinated runoff continues to accumulate in the country's waterways, harming local ecosystems and causing heavy corrosion damage to drainage pipes along the way. Desalination treatment of winter stormwater runoff is a possible step that could help to counteract the existing problems. Unlike other energy-intensive methods, this treatment promotes a strong level of sustainability by relying on gravity flow. The resins and brine solution flushed out are also able to be regenerated and re-used, minimizing cost and material waste. The results of the experiments have demonstrated that the method shows promise; however, additional research is required to progress to implementation. With further investigation into the desalination potential of ion exchange resins and intensive research into the real life application of such a system, ion exchange desalination for environmental remediation of road salt runoff can become feasible.

**APPENDICES**

*Appendix A. Replicate Total Moles Removed Data Used for T-Tests*

Table A-1. Cation exchange resin total Moles $Na^+$ removed for each replicate

| %Concentration | rep 1 | rep 2 | rep 3 |
|---|---|---|---|
| 0 | 3.87432E-05 | 6.20305E-05 | 6.44445E-05 |
| 1 | 1.909845437 | 1.74622427 | 1.852970162 |
| 5 | 1.378194424 | 1.669080253 | 2.710593158 |
| 10 | 2.81571 | 2.63449 | 2.59719 |

Table A-2. The data that shows the total Moles of $Cl^-$ removed for each replicate of anion resin.

| %Concentration | rep 1 | rep 2 | rep 3 |
|---|---|---|---|
| 0 | 0.000215022 | 0.000319026 | 9.77357E-05 |
| 1 | 0.402072057 | 0.451864419 | 0.545747011 |
| 5 | 2.20792897 | 2.823480947 | 2.563902688 |
| 10 | 1.27518 | 1.24884 | 1.34697 |

*Appendix B: Incremental Moles $Na^+$ removal for 5% Influent replicates*

Table B-1. Incremental Moles $Na^+$ removed / L resin for 5% Influent replicates (outlier highlighted in yellow)

| Volume in | Replicate 1 | Replicate 2 | Replicate 3 |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 50 | 0.7653 | 0.4273 | 0.6629 |
| 100 | 0.2652 | 0.5252 | 1.2825 |
| 150 | 0.0404 | 0.3773 | 0.3798 |
| 200 | 0.1756 | 0.1143 | 0.2073 |
| 250 | 0.0874 | 0.1252 | 0.1142 |
| 300 | 0.029 | 0.057 | 0.026 |
| 350 | 0.0122 | 0.0232 | 0.0267 |
| 400 | 0.0034 | 0.0158 | 0.0089 |
| 450 | 0 | 0.0026 | 0.0023 |
| 500 | 0 | 0.0011 | 0 |
| 550 | 0 | 0 | 0 |
| 600 | 0 | 0 | 0 |
| 650 | 0 | 0 | 0 |
| 700 | 0 | 0 | 0 |
| 750 | 0 | 0 | 0 |
| Total | 1.3782 | 1.6691 | 2.7106 |

*Appendix C: pH Meter Shortcomings and the Sodium Error*

The team's initial methodology was similar to the final methodology (i.e. using a gravity flow-through column to test the desalination capacity of ion exchange resins). However it differed in the following ways:

- The columns were packed so that theoretical milliequivalents matched instead of the volumes. The cation was packed with 15 mL of resin while the anion was packed with 27 mL of resin, so that both columns had similar milliequivalents of 27 meq/mL of resin. These were arbitrary values but were chosen based on the volume capacity of the resin in the column and the amount of saline solution to be poured through them. In addition, the volume of ion removed per mL of resin would be calculated so setting milliequivalents in the column was not necessary.

- 50 mL (nominal) plastic graduated cylinders which which were found to hold an actual volume of 49 mL were used to pour the salt solution down the column. This inaccuracy was corrected for in the initial calculations. These graduated cylinders were also used to pack the column with resin, so their volumes are slightly smaller than those stated above.

- Effluent volumes were collected and measured in 100 mL (nominal) plastic graduated cylinders which were found to hold an actual volume of 92 mL. This inaccuracy was corrected for in the calculations as well.

- A pH meter was used to determine the moles of salt removed due to the resins and pH values from as low as -0.13 to as high as 13.47 were obtained.

- A testing solution of 20% w/w NaCl was included.

The team identified three errors when using this method in the Fall of 2018:

- Due to a misunderstanding of information on the Hanna Instruments website which stated that the pH range was -2 to 16, the team was unaware that the pH probe and pH display meter did not have a similar range. The pH probe could only accurately measure values from pH 0 to pH 13 where as the display meter could give readings from pH -2 to pH 16. This caused the team to believe that the pH probe could measure a wider range of pHs than it actually could. In addition, the probe could only be calibrated for a pH range of 1-13.

- Damage to the pH probe from the very high and very low pH measurements most likely affected the results. High concentrations of the hydroxyl ions, or very caustic solutions, can deteriorate the conditions of a pH probe rapidly. pH measurements higher than 14, or 4% caustic soda, can lead to this irreversible damage ("The Theory of pH Measurement," 2004). In addition, pH measurements below 1 are very damaging to pH meters.

- The sodium error influenced the very high pH measurements as well. This systematic error produced underestimated pH readings.

What is the sodium error? And how did it affect pH measurements?

- The sodium ion error, also known as the alkali ion error, occurs at high pH (pH > 10) when the hydrogen ion concentration of the solution is significantly lower than the sodium ion concentration. The pH meter then begins to read the sodium ions as hydrogen ions and the pH reading is lower than it should be ("The Theory of pH Measurement," 2004; Werner & Wolfbeis, 1993).

- Multiple experiments confirmed this information by comparing measured values to theoretical values. The team did not have access to another pH meter with which to check the measurements, so further experiments into evaluating the sodium error should corroborate findings across multiple, undamaged meters.

- The team also found that a stronger sodium effect occurs for higher concentrations of sodium. This has been previously shown (Yue, 1986) and it is also important to note that at a fixed pH, the sodium error increases with an increase in sodium concentration.

- Though the sodium error affected high pH measurements and caused them to be lower than they truly were, there is also the possibility that the high concentrations of sodium also affected low pH measurements. It is possible that adding salt to a very high or very low pH solution pushes the pH to 7 regardless (Sheresti & Aliakbarzadeh, 2013).

- Because the pH readings were lower than they truly were, this means that the final moles of chloride removed were higher in reality. However, as there have been no attempts in the literature to quantify the sodium error, it was not possible for us to determine the true amount of chloride removed by performing any sort of standard check to compare the values to.
  - This may explain why the initial anion data did not fit the team's expectations. The initial data made it seem that the anion exchange resins were significantly less effective than the cation exchange resins, which the team initially attributed to the difference in milliequivalents (>1.0 meq/mL vs >1.8 meq/mL).

- ○ The initial cation results didn't necessarily match the teams predictions, either. This could have been due to measuring certain values out of the range of the probe.

- ○ This discrepancy in the anion data was confirmed by using an IC machine which accurately measures concentration of chloride ions in a solution. Though this was a promising method for collecting data, the machine became unusable and was not repaired in time for us to continue using it.

Several solutions were considered in order to correct for the error, but it was decided that the effluent solution would be diluted in order for the pH to fit within the 4-10 range.

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