

Spring 2016

Ion Exchange Experiments – Water Softening and Deionization

Darcy Geraud

University of Akron, dag48@uakron.edu

Please take a moment to share how this work helps you [through this survey](#). Your feedback will be important as we plan further development of our repository.

Follow this and additional works at: http://ideaexchange.uakron.edu/honors_research_projects

Recommended Citation

Geraud, Darcy, "Ion Exchange Experiments – Water Softening and Deionization" (2016). *Honors Research Projects*. 345.

http://ideaexchange.uakron.edu/honors_research_projects/345

This Honors Research Project is brought to you for free and open access by The Dr. Gary B. and Pamela S. Williams Honors College at IdeaExchange@UAkron, the institutional repository of The University of Akron in Akron, Ohio, USA. It has been accepted for inclusion in Honors Research Projects by an authorized administrator of IdeaExchange@UAkron. For more information, please contact mjon@uakron.edu, uapress@uakron.edu.

Ion Exchange Experiments – Water Softening and Deionization

Darcy Geraud

Department of Chemical and Biomolecular Engineering

Honors Research Project

Submitted to

The Honors College

Contents

Introduction:.....	7
Laboratory Objective	7
Materials and Components	7
Components	8
Chemicals.....	8
Safety Considerations	10
Day 1: Filling the Column	11
Background	11
Lab Instructions:	18
Create a Calibration Curve:.....	18
Fill the column with resin (only if needed as explained in the background section):	18
Backwash the column:	19
Experimental Schematic:	20
Cation Backwash Schematic and Valve Positions:	21
Cation Filling the Freeboard Schematic and Valve Positions:	22
Anion Backwash Schematic and Valve Position:	23
Anion Filling the Freeboard Schematic and Valve Position:	23
Background	25
Lab Instructions:	32
Cation Regeneration.....	32
Anion Regeneration	34
Experimental Schematic:	35
Cation Regeneration Schematic and Valve Position:	35
Anion Regeneration Schematic and Valve Position:	36
Background:	37
Lab Instructions:	43
Backwash Directions:	43
Fill the Freeboard:	43
Creating a break through curve:	44
Experimental Schematic:	45
Day 4 – Lab Measurements	46
Background:	46
Lab Instructions:	48
Soap Test:.....	48
Conductivity:.....	48
Titration:	49
Day 5 – Water Deionization	50
Background:	50
Lab Instructions:	52
Create a Calibration Curve:.....	52
Column Preparation:	52
Water Deionization	53
Experimental Schematic:	54
Assignments:	54
Design/Proposal Presentation	55
Day to Day Assignments	56
References:.....	58

Executive Summary:

Ion exchange is the exchange of charged mobile ions with a fixed ion. Ion exchange is most often used in water-softening and other purification and separation processes. It has become more popular as more and more homes acquire water softeners to remove Ca^{2+} and Mg^{2+} from water. Currently multiple separation processes are studied in Mass Transfer Operations (MTO). By offering an ion exchange laboratory, students will have a chance to learn another separation option through hands on approach.

The project's purpose was to create ion exchange experiments to be used by junior chemical engineering students in their junior lab. The experiments were designed to imitate the ion exchange process at the laboratory scale. Using the experimental results, parts of the industrial design could be determined, such as column size, breakthrough volume, and breakthrough time. The experiments had three main objectives: to understand the characteristics of an ion exchange column, to be able to determine the breakthrough of an ion exchanger, and to utilize laboratory testing in the design process. Some other ion exchange techniques, capacity testing, resin swelling, and elution testing were considered outside of scope for the labs.

The students will work through multiple steps of design and ion exchange, beginning with the basic theories and working up to using two ion exchangers in series. The final assignment will be the uses of the tools the students were taught throughout the experiments to design a column. Each student will give a 7-10 minute design proposal presentation. The presentation will include steps taught such as choosing a type of resin, deciding on a type of regeneration, sizing a column from lab data, and finding a market/industry for the process.

Both co-current and counter current regeneration were considered for the lab. Co-current is most often used in industry because of its associated low cost of equipment. Co-current

regeneration has some leakage, but provides adequate results for non-stringent systems. For these reasons, co-current regeneration was chosen to change the form of the resin and subsequently restore the resin back to that form after use.

Students create breakthrough curves by running simulated 0.1M hard water through the cation exchanger. A breakthrough curve is a graphical representation of the laboratory data used to scale a column up to industry-sized columns. Breakthrough occurs when the effluent concentration is 5% of the influent concentration. The columns in lab were designed to have breakthrough occur and approach exhaustion within one hour. On average the breakthrough occurred at 10.3 minutes; the breakthrough time equates to an average breakthrough volume of 775 mL and a standard error of 52 mL. Exhaustion, 95% of the influent, occurred only one of three times; the other two reached 92% and 81% of the influent, respectively. With the data collected, there are two possible options to scale the system, kinetic and volume based. Kinetic scale up uses every data point to find the rate constant and scale to any breakthrough volume; volume based uses the breakthrough volume and time to scale a system to handle any volume.

Three different types of measurements techniques are used and compared. The first is conductivity to determine concentration. It is suggested to consider pH moving forward as that may provide results that are more accurate. The second measurement is based on the ASTM standard method of determining Ca^{2+} and Mg^{2+} in water. The final measurement is based on determining how many soap drops need to be added before the mixture will foam when shaken. For example, a soft water solution should foam after 1-2 drops of soap are added and the mixture is shaken. This measurement technique proved to be very rough and never matched up to the results from the other two forms. The inaccuracy is partly due to the detergent and dyes that are now added to soaps. The most accurate results were the ASTM standard.

The final day of lab is designated for water deionization; using two columns in series. The initial bed removes all cations from the solution and replaces them with H^+ , the second bed removes the anions and replaces them with OH^- . The result is pure H_2O . Students compare the concentration of the solution as it comes through both beds and determine if it was completely deionized. One preliminary test was run; the exchangers removed all of the ions for a duration of six minutes.

Several broader impacts, including technical and career skills as well as personal skills, were accomplished throughout the course of this research. The basis of the experiments was to purify water; this basis will help as I move into an engineering position in the Water Industry in June. In addition, I found where to get the ASTM water standards and the ASTM approved method for testing hardness in water. I learned how to use the results from a lab test to design the size of an ion exchange column; these same steps could be used for Reverse Osmosis which is often used at Nestle Waters. The personal skill I developed the most was decision making. The project allowed for room for creativity. There are multiple ways to use ion exchange and deciding on the option that highlight the most design aspects was difficult. I found that with more options, I had more ideas and struggled to narrow in the scope. Learning to discern when it was time to draw the line and make a decision was a personal skill I developed.

The use of ion exchange in lab is a commonly used separation method in industry. While this lab is a good baseline for what is involved, methods are always evolving. To keep the lab from becoming stagnant, it is best to stay up to date with water softening technology. Additional research opportunities may involve introducing an elution process or a better way to measure concentration of calcium. Overall, the experiments incorporate many of the aspects in designing an ion exchanger. It creates a basis of ion exchange knowledge for students moving forward.

Honors Abstracts Addendum:

The purpose of the project was to create ion exchange experiments to be used by junior chemical engineering students in Chemical Engineering Laboratory (4200:360). The lab activities are to build upon each other and closely resemble what is done in industry. A lab manual was created delineating each activity and its corresponding background, instructions, schematic, and assignment. Using the tools for designing an ion exchange system, taught throughout the experiments, the students will present a design proposal.

The ion exchange activities are based on labs currently being completed at other universities, as well as designed to illustrate the chemical engineering concepts behind ion exchange. Water softeners are one of the most common ion exchangers available on the market. They are also most often used for ion exchange labs because of their simplicity in nature. During the design of the activities, I strove to incorporate all the aspects of designing an ion exchanger. By incorporating all aspects of designing an ion exchanger I was able to determine step by step how to go from an idea to having all the information needed to create an industrial sized ion exchanger.

Ion Exchange Lab Manual

Introduction:

Ion exchange resins are solid polymer materials that hold fixed positive and negative charges. These charges are exchanged with mobile cations, or anions, in a process called ion exchange. Throughout the whole process, electro-neutrality is maintained in both the mobile liquid phase and the fixed solid phase. The process is reversible, through a process called regeneration, which allows the resin to be used multiple times.

Currently, two of the primary applications of ion exchange are water softening and deionization. The softening process used in industry and popular in homes, uses a cation exchange resin to remove the calcium and magnesium ions from water. Water deionization is slightly more complex as two exchangers are used concurrently. The first, a cation exchanger to remove all cations and replace with H^+ , the second, an anion exchanger to remove all anions and replace them with the OH^- fixed charge. This two-stage process produces pure H_2O .

Laboratory Objective

The Ion Exchange Experiments are designed to imitate the industrial design on the laboratory scale. With that intent, the objectives of the experiments are:

- I. To study the characteristics of an ion exchange column
- II. To calculate breakthrough capacities of the ion exchanger
- III. To understand and utilize laboratory testing in the ion exchange design process

Materials and Components

The materials and components section is to describe what went into setting up the lab for the ion exchange. The lab set up includes two columns with tubing set to run them concurrently as well as separately. A more detailed component list is provided in the section below. After

setting up, the chemical materials needed for the lab are included. The chemicals were purchased from Sigma Aldrich or the University of Akron chemical stores. The solution makeup is detailed below. Creating the materials and components lists was one of the first steps of design and is important when designing a lab scale test for industry.

Components¹

The following components are a list of large items needed to complete the experiments. The equipment setup also utilizes 3-way valves, tube fittings, and tubing. Beakers are used throughout the experiments to collect or move samples.

Table 1: Description and Pricing information for equipment used in the Ion Exchange Experiments for Chemical Engineering Laboratory. The column was purchased from Kimble Chase, all pump parts from Cole Parmer, the conductivity probe from Vernier, and everything else from The University of Akron chemical stores. The prices are subject to change and are based on prices pulled in March 2016.

Description	Quantity	Unit Price
Kontes Chromaflex Column (60 x 2.5 cm ID)	2	\$306.00
Masterflex L/S variable-speed modular drive (6 to 600 rpm, 115 VAC)	1	\$790.00
Masterflex L/S two-channel Easy-Load II pump head (L/S 16 tubing)	1	\$325.00
Vernier Conductivity Probe	1	\$95.00
25 mL Buret with stopcock	1	\$44.00
Buret Stand	1	\$13.00
Buret Clamp	1	\$7.00
Total:		\$1796.00

Chemicals

The following chemicals were used as the basis for all experiments. The calcium chloride and magnesium sulfate were used to make the hard water. The sodium hydroxide was

¹ The components list is for one lab set up; there are currently two set ups in Auburn Science and Engineering Center Room 81.

made in a 6% (w/v) solution for regeneration; the hydrochloric acid was 5% (v/v) also for regeneration. The second set of chemicals is the cation and anion resin. The third, and final, set are used for the Ethylenediaminetetraacetic acid (EDTA) titration to determine water hardness.

Table 2: Prices for chemicals used in the Ion Exchange Experiments in Chemical Engineering Laboratory. All chemicals were purchased from Sigma Aldrich or The University of Akron Chemical Stores. Prices are subject to change and are based on prices pulled March 2016.

Description	Quantity	Price
Sodium Hydroxide (pellet form)	0.5 (g)	\$15.00
Hydrochloric Acid	2.5 (L)	\$17.00
Calcium Chloride (pellet form)	0.5 (g)	\$19.00
Magnesium Sulfate (anhydrous)	0.5 (g)	\$22.00
Amberlite IR120 (Na ⁺ Form)	1.0 (Kg)	\$98.00
Amberlite IRA-410 (Cl ⁻ Form)	0.5 (Kg)	\$69.00
pH 10 buffer (Borax/NaOH)	100 (mL)	\$23.00
Eriochrome Black T Indicator (0.5% w/v)	120 (mL)	\$19.00
Ethylenediaminetetraacetic acid (EDTA)	0.1 (Kg)	\$21.00
Total:		\$303.00

The hard water used in lab is simulated by a solution of calcium chloride and magnesium sulfate. The solution is an adequate simulation of permanent hard water; permanent hard water is the type of hard water removed in an ion exchange column²⁵. Using the solution helps to standardize experiments. If tap water were used, it would be harder to quantify amount removed and compare experiments. Procedure for creating hard water solution can be found in the Appendix.

Safety Considerations

There are several hazards that are associated with the chemicals used in Ion Exchange Experiments. Table 3 shows the NFPA rating, required personal protective equipment, and safety concern for each chemical/material used in the ion exchange laboratory. When working with flammable materials, they should be monitored to ensure the flammability hazard is limited. Flammable hazards need to be stored in a UL-approved flammable storage cabinet. The Eriochrome Black T indicator is flammable and must be regarded as such; it should be stored in a flammable storage cabinet. Another way to limit flammable hazards could include possible cooling during experiment time; for the experiment, cooling is not necessary as long as the indicator is put back in the cabinet once used. The pH 10 buffer should be added in a hood for proper ventilation. For any further safety information see the safety data sheets (SDS) in the appendix. It is important to be familiar with any safety concerns the chemicals may offer.

Table 3: Safety Hazard Summary for the components used in the Ion Exchange Experiments

Materials	NFPA	PPE Level	Safety Concerns
Sodium Hydroxide	3,0,0	Protective gloves, eye protection	Serious eye damage, severe skin burns
Hydrochloric Acid	3,0,0	Tight fitting safety glasses, gloves	Severe skin burns and eye damage, possible respiratory irritation
Calcium Chloride	2,0,0	Protective gloves, eye protection	Serious eye irritation
Magnesium Sulfate	0,0,0	Protective gloves, eye protection	none
Amberlite IR120	2,0,0	Protective gloves, eye protection, respirator for long periods of exposure	Serious eye irritation, possible skin irritation
Amberlite IRA-410	2,0,0		
pH 10 buffer	0,0,0	Protective gloves, eye protection, use in a hood	Eye irritation
Eriochrome Black T Indicator	2,2,0	Protective gloves, eye protection	Flammable, harmful if swallowed, eye irritation,
Ethylenediaminetetraacetic acid (EDTA)	2,0,0	Protective gloves, eye protection	Serious eye irritation

Day 1: Filling the Column

Background

For this lab, the column will already be filled with the resin. In order to fill the column correctly, a specific procedure needs to be followed. If the procedure is not followed accurately, it is possible for air to be introduced to the column. Air bubbles limit contact with the exchange resin, which in turn will impede the flow of ions through the column. Ion exchange depends upon uniform contact with the resin; if the flow is impeded, the contact will not be uniform and pathways of less resistance will exist. These pathways of less resistance can cause inefficiencies and errors in exchange; for this reason¹, it is important to fill the column limiting the amount of air allowed in. If air does get in the column during filling, lightly tap the column forcing the air towards the top of the resin. In the short clip “*Air Bubble in Column*” the release of the air can be seen. During the backwash stage, the column will be reset to account for this slight redistribution of resin.

Ion exchange is the process of a fixed charge exchanging with a mobile ion from solution. Resins fixed with negative charges will exchange with positive mobile ions, or cations, in a cation exchanger. In an anion exchanger, the opposite is true; fixed positive ions will exchange with mobile negative ions². The ion exchange resins are actually a cross-linked polymer matrix with fixed ions attached to it. Ideally, the matrix will have a uniform distribution of the fixed ion active sites³.

Resins are most often in the spherical form, shown in Figure 1: Magnified image of a cationic exchange resin.. This form allows for uniform contact of the solution and resin⁴, it also has a lower pressure drop than the other irregularly shaped particles.



*Figure 1: Magnified image of a cationic exchange resin.
Source: Wikipedia "Ion-Exchange Resins"*

Currently there are resins being made into sheet like membranes. These resins are most often used in reverse osmosis and electrodialysis. This style of resin is not very common, but it is an additional option in design.

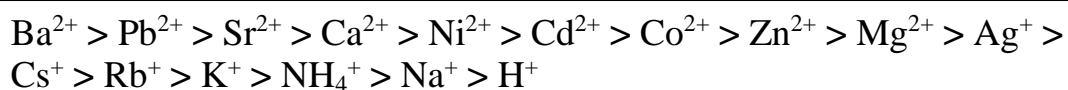
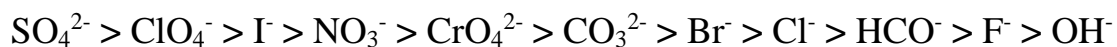
Ion Exchange is used for a number of purposes. On the lab scale, ion exchange chromatography is used to determine the makeup of solutions. Hospitals use ion exchange for clinical diagnosis with respect to amino acids. Because the acids elute at different rates, the protein concentrations can be determined². In the food industry, ion exchange is used for wine making, sugar production, etc⁵. Most often in the food industry, ion exchange is used to remove the bad tasting metallic flavor. There are numerous other uses for ion exchange. The first step of designing a separation is to determine the purpose; by knowing the purpose, the options for resins can be narrowed. For this lab, the purpose is to remove calcium and magnesium from the water and purify it. Over the course of the three-week lab activity, your assignment, described at the end of the paper, is to find one of the uses for ion exchange and create a market and design plan.

Once a purpose has been identified, the next step is to choose the resin for the exchange. Ion Exchange Resins can be simplified to four different types: Strong Acid Cation (SAC) Resin, Weak Acid Cation (WAC) Resin, Strong Base Anion (SBA) Resin, and Weak Base Anion

(WBA) Resin. All four types are made of the same base organic polymer; their difference is the ionizable group attached to the polymer's hydrocarbon network⁶. SAC resins are most highly ionized in the acid and salt form; H^+ and Na^+ forms of the resin are readily available for exchange for all pH's. WAC resins, on the other hand, are strongly influenced by the pH of the solution. Using a WAC is unsuitable for deionizing some waste waters because they have a limited exchange capacity below a pH of 6.0⁶. The Base Anion Resins work mostly the same way, except WBA resins have limited capacity above a pH of 7.0. The other major difference is that WBA resins are never in the hydroxyl form.

These four types of resins are all useful in certain situations. SAC in the H^+ form are used for the hydrolysis of starch and sucrose, they are also used for water softening and deionization. Weak Acid Cation resins are chosen when the hardness to alkalinity ratio is greater than one, they are not normally used in water softening²⁶. WAC resins are not used because they normally remove only the temporary hardness, rather than the permanent, Ca^{2+} and Mg^{2+} . Weak Base Anion resins allow silica and bicarbonate to pass through the exchanger. They should not be used for pure deionization as they only remove free mineral acids²⁶. WBA resins are used for blood preservation when waiting on testing. Strong Base Anion resins in the OH^- form are used in making wine; WBA resins would not work here as they are never in the hydroxyl form. The previous are just some uses of the different types of resins. In order to choose the correct resin, the purpose has to be known, also comparing to past tests and uses can help.

One of the other factors for choosing a resin is their preference for ion exchange. The resin wants the highest charge possible. For example, when Ca^{2+} flows through a cation exchanger charged with H^+ , the Ca^{2+} will replace the hydrogen and hydrogen will flow out.



Knowing the preferences of the exchanger can help determine what form the resin should be in.

The following are the ion preference series⁷ for anion and cation resins, respectively:

The purpose of the lab, as previously stated, is to remove the Ca^{2+} and Mg^{2+} from hard water and then further purify it. To remove these ions from water, a Strong Acid Cation resin in the Na^+ form is normally used in homes. By using a Na^+ resin the effluent becomes NaCl (a basic salt) which is fine to introduce to your pipes at home.

In lab, a Strong Acid Cation resin in the H^+ form will be used. During deionization, the cation exchanger needs to be in the hydrogen form, for this reason, during water softening it

will be in the same form. The change in form is completed by regeneration,

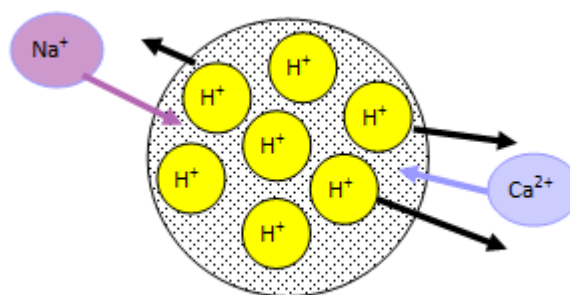


Figure 2: Softening of Water. The cations in the mobile phase replace the hydrogen (yellow) in the fixed phase.
Source: "Ion Exchange: An Introduction."

talked about in Lab 2. Figure 2, shows the column in a fixed H^+ form. The influent has both Na^+ and Ca^{2+} ions that exchange with the hydrogen. It can be seen that to keep electro-neutrality, the Ca^{2+} entering causes two hydrogen ions to leave²⁷ and occupies two exchange sites. The water is softened as the "Hard" characteristics of Ca^{2+} and Mg^{2+} are removed; however, the effluent, in lab, will be HCl and needs to be treated as a strong acid.

Sometimes, the hard water will contain a CO_3^{2-} group; hard water containing the CO_3^{2-} group is referred to as temporary hardness. The CO_3^{2-} could combine with calcium and create

calcium carbonate. The CO_3^- is most often ignored in testing because it can be removed with boiling. To include the temporary hardness aspect, the directions for making “complete” hard water can be seen in the appendix.

Purified, or deionized, water is made up of pure hydrogen and hydroxyl ions. In order to achieve this purification, two exchangers will be used. The first is the Strong Acid Cation resin in the H^+ form discussed in the last paragraph. This resin will remove all cations and leave only hydrogens. This solution will then move into the second exchanger, a column with a Strong Base Anion resin in the OH^- form. The resin will remove any anions in solution and release the hydroxyl groups. Figure 3, shows the resin beds at exhaustion²⁷. This leaves just H^+ and OH^- in the solution, when they recombine $\text{H}^+ + \text{OH}^- \rightarrow \text{HOH} \rightarrow \text{H}_2\text{O}$.

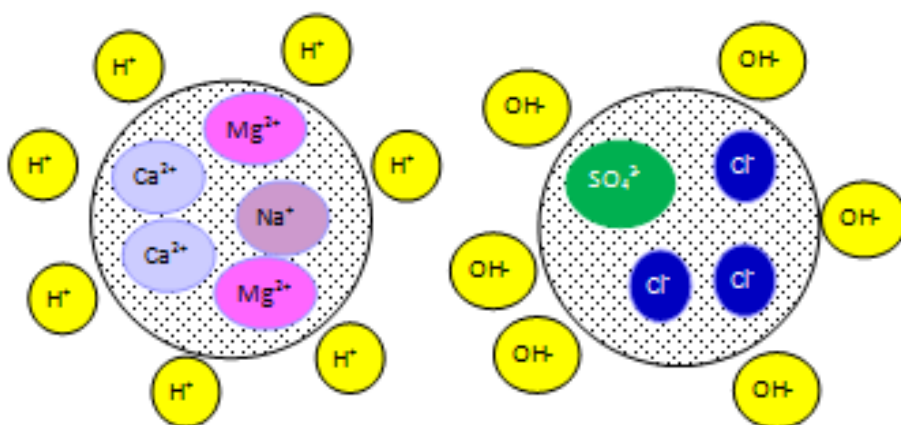


Figure 3: Both the cation and anion resin beads (grey) are exhausted. There is no hydrogen or hydroxyl left to release. Only H^+ and OH^- ions have been released into the water.
Source: "Ion Exchange: An Introduction."

Another important design decision is the capacity of the resin, that is, the number of sites available for exchange. The capacity is most often given when purchasing a resin; however, the capacity can be determined by experimentation. To determine capacity by experimentation, the resin is converted to an easily measured ion by regeneration. As the converted ions are removed from the solution, they are measured quantitatively to determine the capacity.³ The total ions

removed from solution divided by the weight of the resin tested gives the resin capacity.

Regeneration is the process of restoring the resin back to its original ionic state. For example, in home water softeners there is a mineral brine tank of NaCl; the NaCl is used to remove the Ca^{2+} from the exhausted resin and replace it with Na^+ . Once the mineral brine is finished, the resin will be back in its original state.

One of the final considerations in design is swelling. Based on the material of construction for the column, there will be constraints for how much pressure it can handle. As the resin takes in more of the mobile ions, the volume of the fixed ions changes. The resin volume changes depending on to which ionic form it is being converted³. This “swelling” will cause increased pressure in the column. Depending on what resin is being used, either the column will need to be made of a different material or a different resin with less swelling will be needed.

All of these design considerations can be addressed by experimenting at lab scale. Lab runs provide valuable data to use for scale up. It can determine how concentration changes over time and how concentration changes based on solution flow rate. Lab testing is used to determine how a breakthrough curve changes based on control variables. Capacity and swelling can be monitored and their effect on the lab results can be used to make good decisions for the industry scale process. Based on breakthrough time and regeneration time, the number of columns for operation can be determined. .

Today’s lab, backwashing the column, allows the resin bed to expand from its settled conditions. During this expansion, the resin is cleaned as any suspended solids are flushed out; the resins also brush against each other allowing any dirt from the surface to be cleaned off⁹.

The backwash cycle allows for better exchange once the experiment is run. Follow the instructions for backwashing the column.

Prior to putting the resin in the column, the resin needs to be hydrated and “exercised”; this means to wash it with a phase that will cause the most swelling. The resin is then poured, in slurry form, into the column; remember, it is important that there are no air bubbles in the column. The hydrating step was done for you during the filling of the column.

A common term in ion exchange is bed volume (BV). Bed volume is the equivalent solution volume as the volume of the resin in the column. The columns are 295 mL; they have an inner diameter (ID) of 2.5 cm with a length of 60 cm. The instructions for filling the column with resin are given below but you will not need to fill the column with resin for this activity.

Lab Instructions:

These procedures should be completed on both the anion and cation column.

Create a Calibration Curve:

During the water softening lab, you will be using conductivity to determine the concentration of calcium. The CaCl_2 will run through the column and the Ca^{2+} will exchange with the H^+ on the resin. Create a calibration curve in order to determine the concentration of Ca^{2+} . According to Global Water standards for hard water, 1 mg/L CaCO_3 is $2\mu\text{S}/\text{cm}$. There is an example of a possible calibration curve in the Appendix.

Fill the column with resin (only if needed as explained in the background section):

1. Place 125 mL of each resin in separate beakers with 100 ml of DI water for 30 minutes to precondition the resin.
2. Fill the column 1/3 to 1/2 way full of deionized water
 - a. It is important not to put resin into a dry column
 - b. Put a beaker in place in case any water leaves the exit tubing
3. Pour the resin slurry into the column, tapping to release any air bubbles
 - a. Make sure to keep the water about an inch above the resin
 - b. The resin may need extra water in order to pour into column

Equipment set up:

Each lab set up has extra tubing on the inlet side. The extra tubing is needed to go into the solution barrel. There is a section of MasterFlex tubing on that extra tubing. The section of MasterFlex tubing is the section of tube that must go into the pump head. Both lab set ups are using the same pump head so if the system should not have flow, the tubing must be removed from the pump head. When the pump head is opened, both systems will lose flow; make sure to talk to the other group before opening the pump head. It is best for both groups to go at the same pace. The pump should be between the two lab setups.

Fill a 2L beaker with DI Water and use it as the source for the backwashing.

Backwash the column:


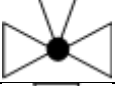


All of these steps are to be done for both columns. The directions are the same, but the schematics are different.

1. Place the extra tubing in the DI water supply, which will be the processing solution.
2. Turn the 3-way valves so that water will flow up the resin column
 - a. A schematic for this can be seen below (Backwash)
3. Turn on the pump to begin running DI water through at Level 1-2 (about 75mL/min)
4. Once the bed begins to fluidize, continue the backwash for 10 minutes
5. After 10 minutes, gradually reduce the flow to 0 ml/min
6. Allow the bed to gravity settle, keeping water a couple of inches above the resin.
7. Turn the 3-way valves so water is flowing down the column
 - a. A schematic for this can be seen below (Filling the Freeboard)
8. Restart the pump to start the water flowing
9. Begin flowing the water through very slowly in order to not disturb the resin bed
 - a. See clip “Disturbing the Resin” for what not to do
10. Run 2-3 BV’s of water through the column to rinse out any impurities.

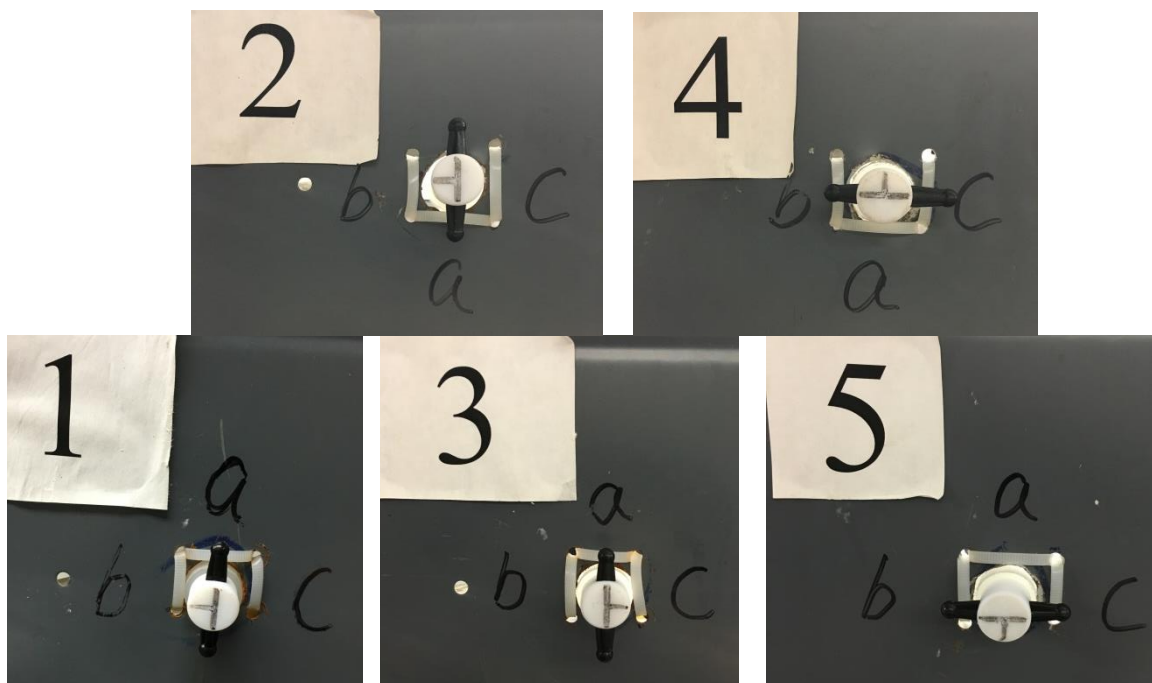
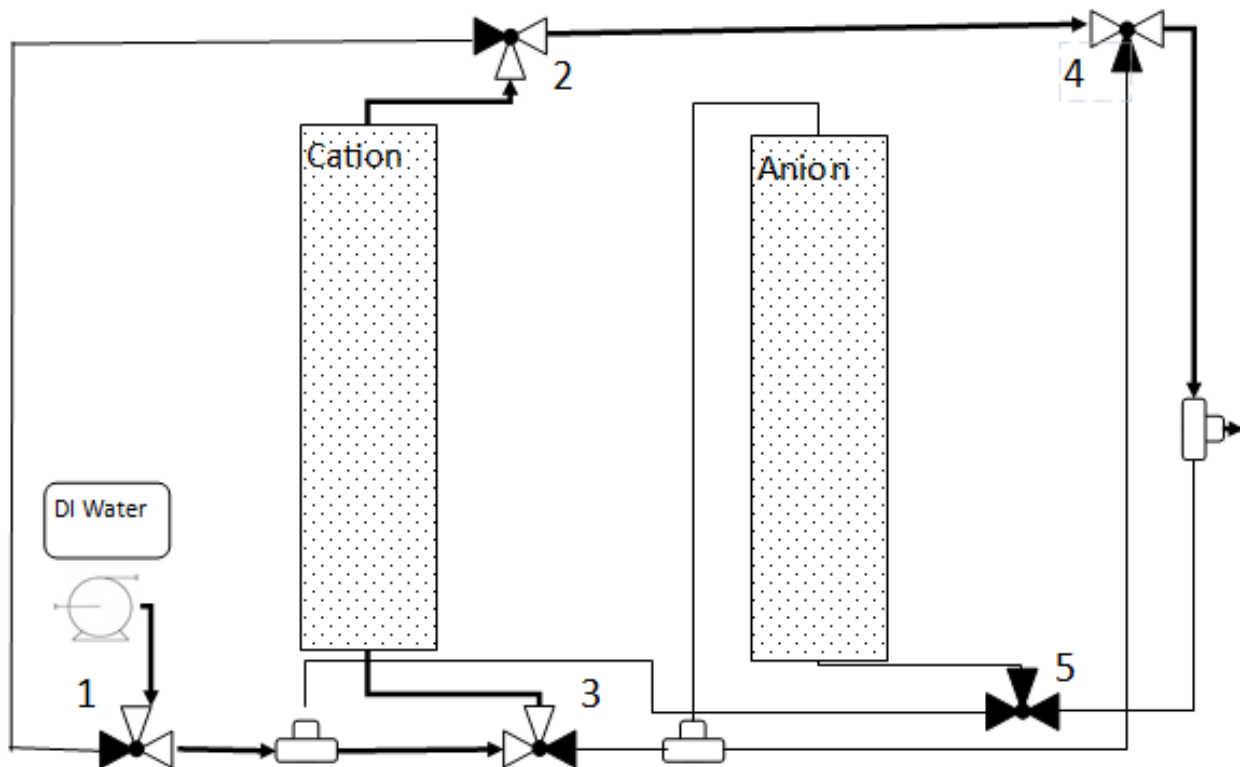
Experimental Schematic:

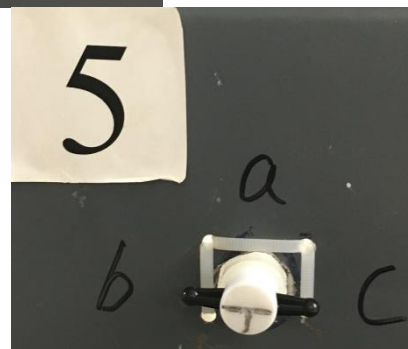
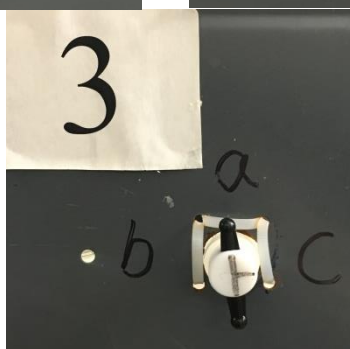
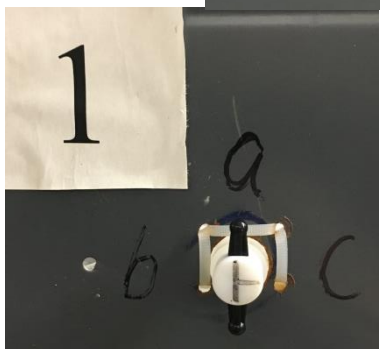
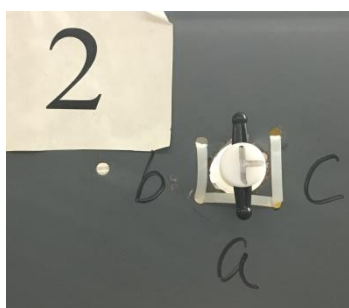
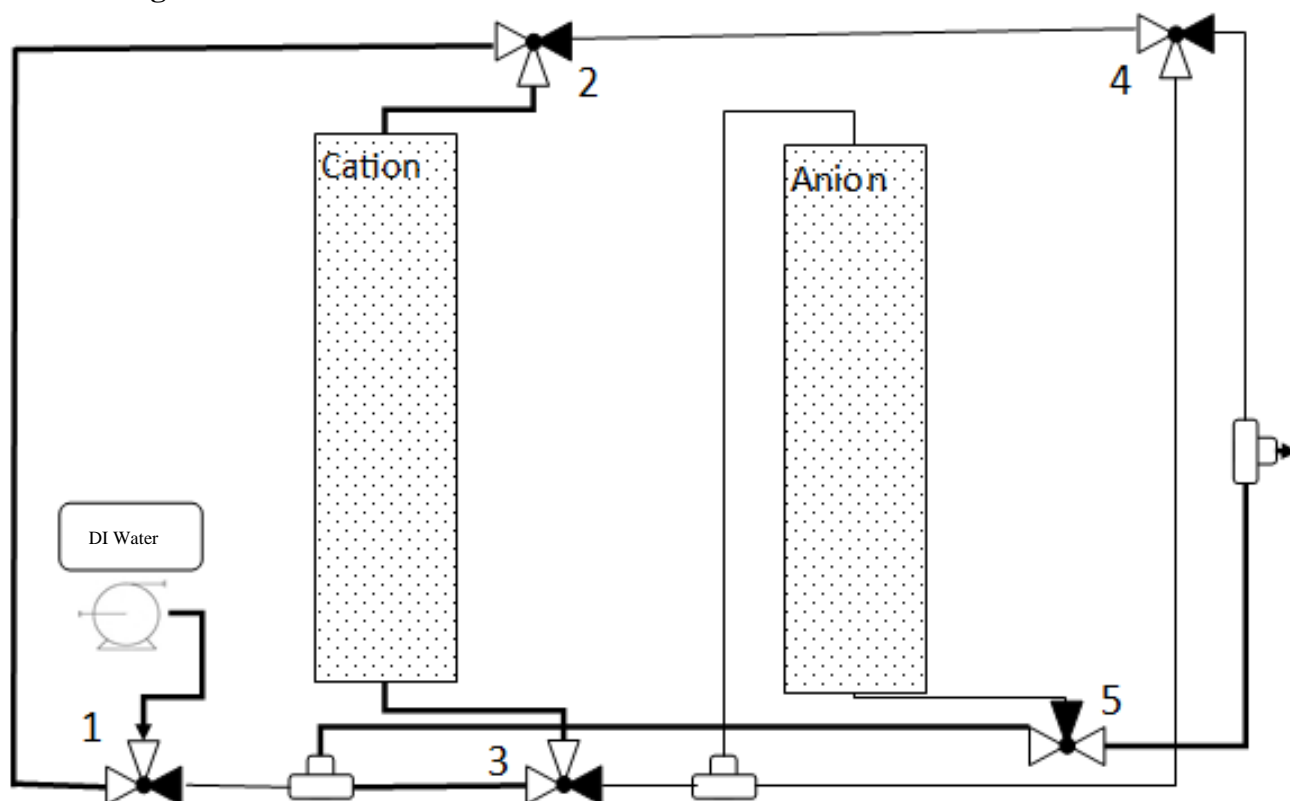
The following are schematics of one lab setup. The flow of solution is represented by a thick black line. There are five three-way valves numbered and used in the lab set up. Pictures of the valves, when in the correct position for the purpose noted (e.g., Cation Backwash), are provided for reference. The numbers in the schematic match the numbers in the pictures.

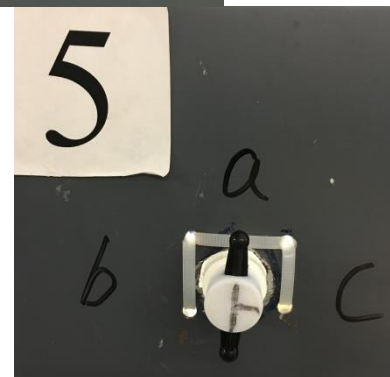
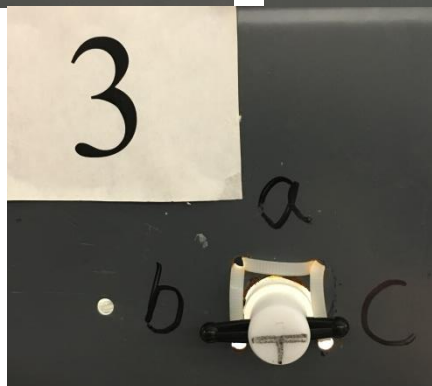
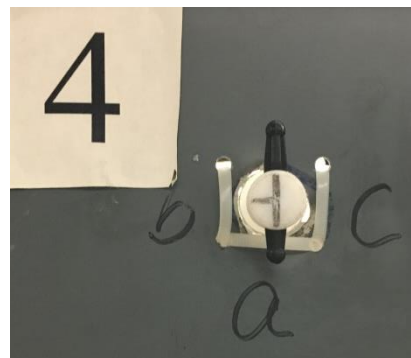
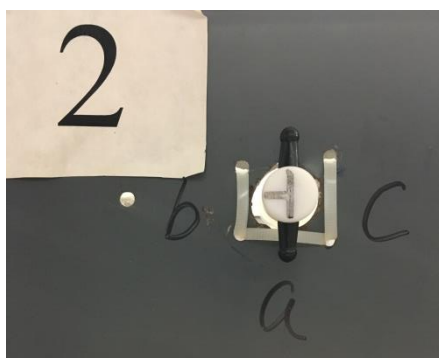
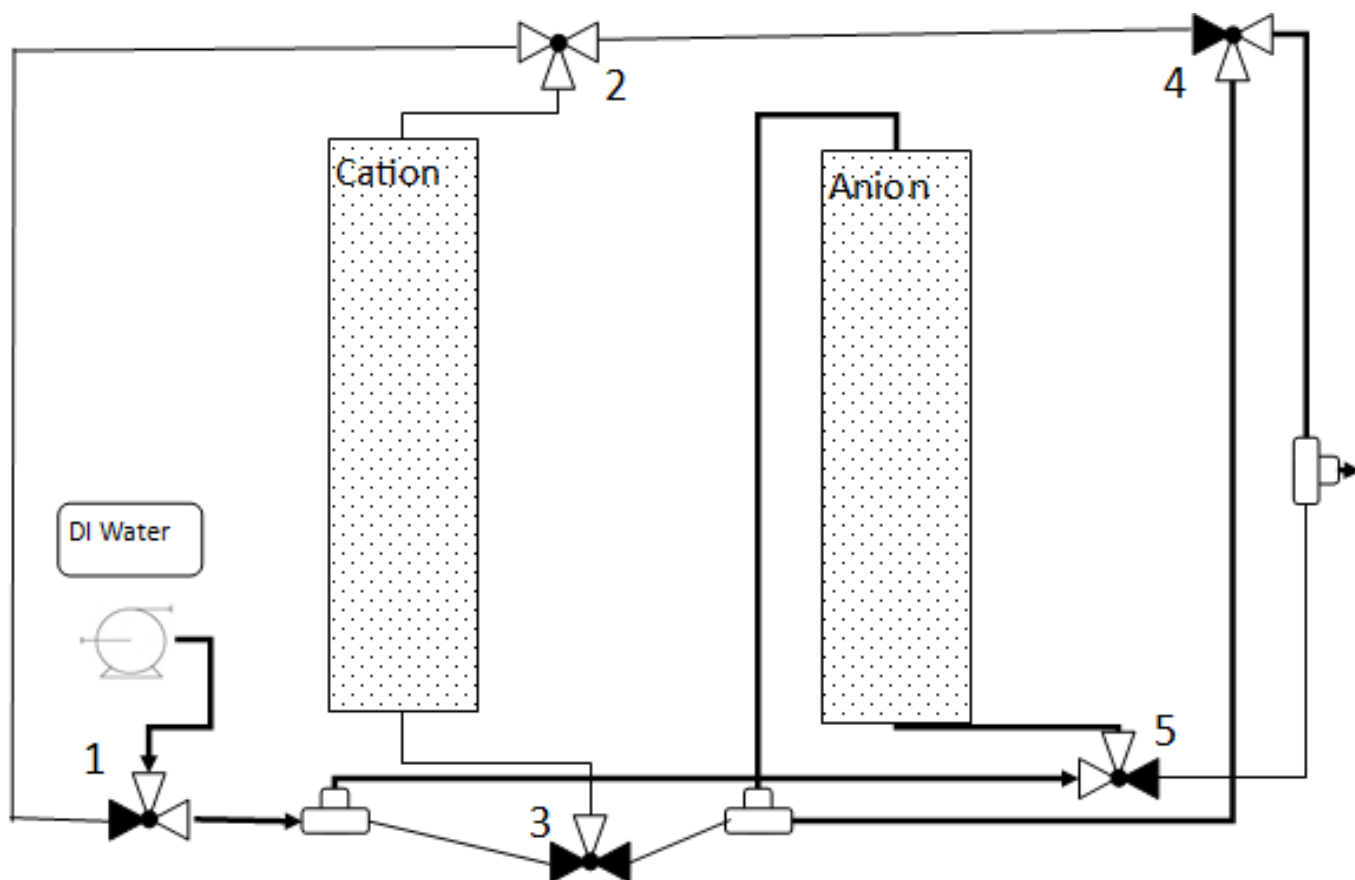
Table 4: Schematic Diagram units and symbols. The same symbols are used in all schematics throughout the lab.

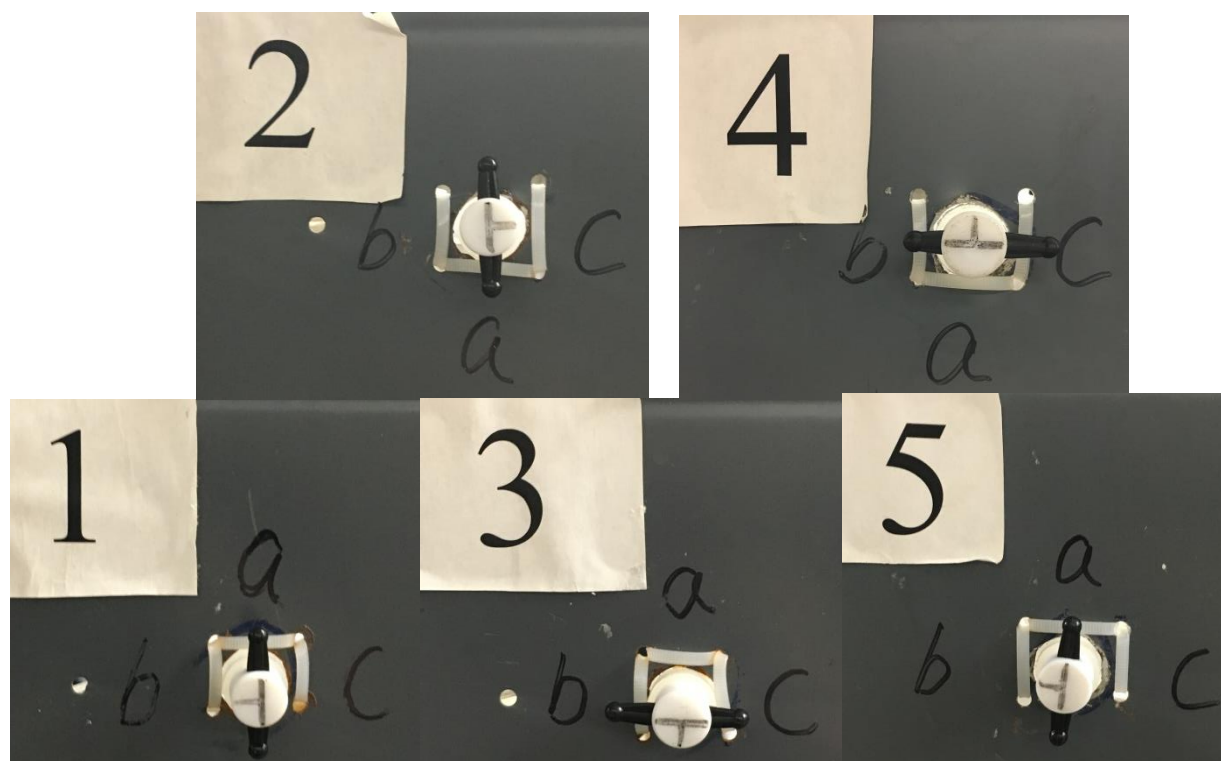
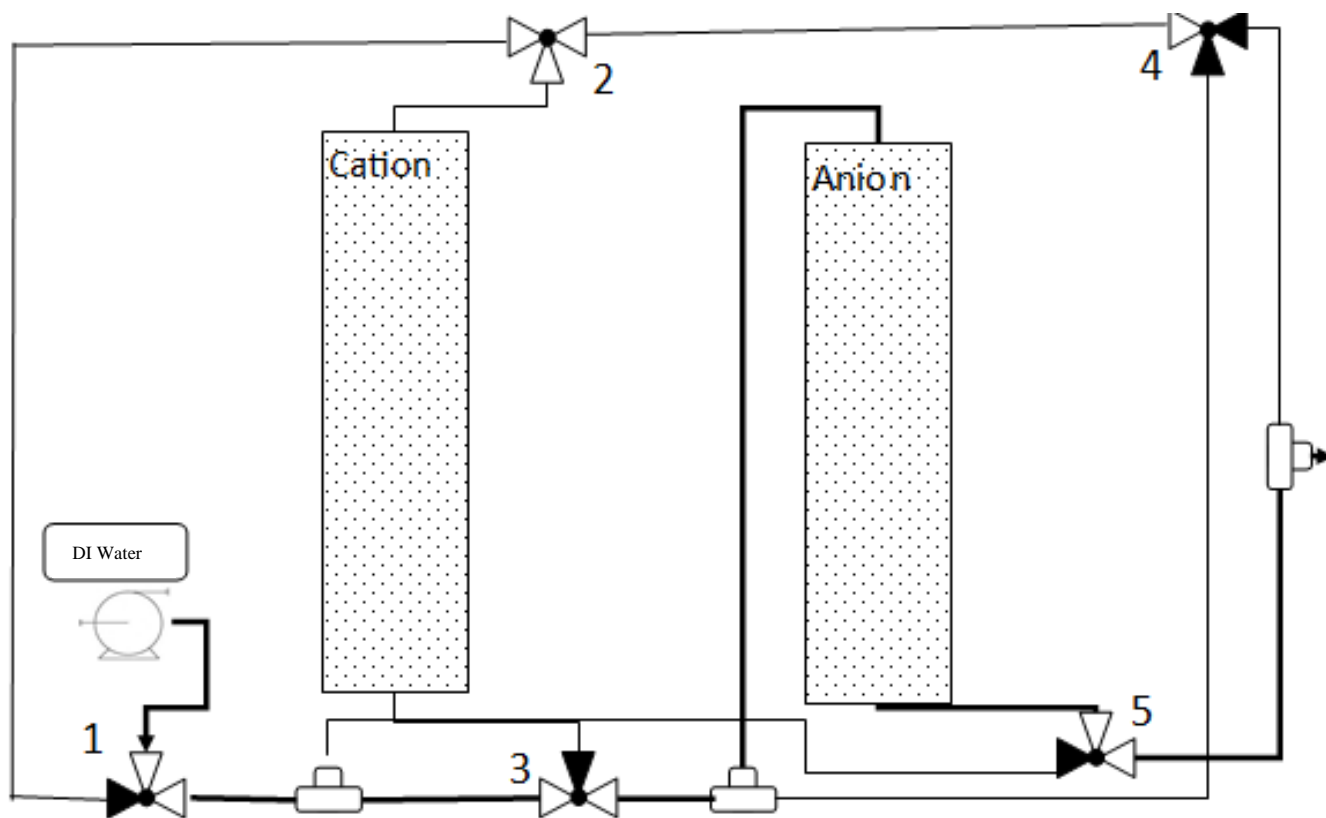
Symbol	Description
	Peristaltic Pump
	3-way valve with all ports open
	3-way valve with left flow closed
	3-way joint

Cation Backwash Schematic and Valve Positions:



Cation Filling the Freeboard Schematic and Valve Positions:

Anion Backwash Schematic and Valve Position:

Anion Filling the Freeboard Schematic and Valve Position:

Day 2: Regeneration of the Resin

Background

Backwashing's purpose is to clean the resin of any loose particles, regeneration's purpose is to restore the resins back to their original ionic forms⁹; however, regeneration can also be used to change the ionic form of a resin. During the experiment today, the ionic form of the resins will be converted. The same process can be used to restore the resins later when breakthrough occurs. Breakthrough is when the resin is considered exhausted and the majority of the “hard” elements are breaking through into the solution. The detection of this exhaustion is normally found by a change in conductivity, which indicates the ionic breakthrough¹⁰. Once the breakthrough time is known, scheduled regeneration times can be determined. One of the ways this is done is by having two exchange columns. While one is running production, the other is regenerating. By running production, this way there is no downtime.

There are three different types of home water softeners when it comes to regeneration. Some softening systems regenerate based on time passed since the previous regeneration; during the regeneration, soft water is not available to the home. The second, is slightly more advanced, a computer triggers regeneration. A computer triggered softener normally has reserve resin capacity to allow the softener to work during regeneration. The final type of home water softener bases the regeneration on water usage measured with a mechanical water meter. Most of the water softeners of this type are equipped with two resin columns so that there is always soft water available.

In industry, ion exchange resins are normally regenerated every 12 to 48 hours depending on the application. It is important to regenerate at the first sign of breakthrough. For example, in a two-bed deionizer, if the cation resin is not regenerated, $\text{Na}^+/\text{Ca}^{2+}/\text{Mg}^{2+}$ may pass into the anion

resin. Using the example of sodium, Na^+ will pass through the anion resin and the effluent will not be pure H_2O , but rather, NaOH ¹⁰. Having NaOH in the effluent could be a problem, depending on what type of water quality is needed. Complete regeneration is normally not practical because large amounts of regenerate are needed. Normally, resins are regenerated to a certain percentage of their total capacity.

The percentage of capacity achieved during regeneration is based on cost of regeneration, water quality standards, and the costs of new resin. There is an American Society for Testing and Materials (ASTM) document that specifies the quality standards for reagent water. It is the most often referenced document when discussing standards of water needed in industry. The document, D-1193, separates water into four different types, Type I and II are prepared by distillation, Type III and IV can be prepared by ion exchange⁸. One of the examples is that to be able to use Type IV in your system, the water must have a pH between 5.0-8.0 and no organic compounds are allowed. When designing regeneration, the leakage must be considered, as Type III allows a much smaller conductivity than Type IV. There are other standards out there, depending on what application the water is being used, the ion exchange effluent must be monitored to stay within standards.

There are two types of regeneration systems, co-current and counter current. Co-current runs the regenerate through in the same direction as the processing solution. Counter current regeneration will regenerate the same way as when the system is being backwashed; opposite of the direction of production. Figure 4 is an example of the difference between the two types of systems. It is important to notice that in part A (co-current regeneration), the non-regenerated resin ends up by the exit of the column, once feed is added to it this Na^+ will leak out into the

effluent. In part B, the Na^+ that was not regenerated is at the top of the column, the area of non-regenerated resin is already spent and will not exchange with the water.

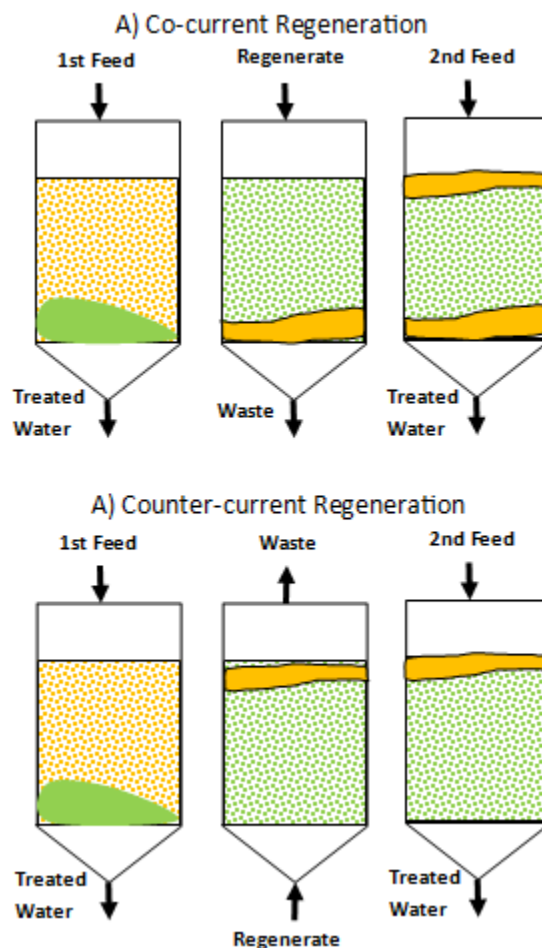


Figure 4: Ion Leakage in a Fixed-Bed Column for a H^+ form (green) bed with Ca^{2+} (gold) removal.
Source: "Fundamentals of Ion Exchange."

Co-current regeneration is considered easier because the piping already exists to run the flow this way. In Figure 4 part a, whatever non-regenerated resin that is left after regeneration is near the exit flow of solution. The non-regenerated resin allows for leakage during the resumption of process flow¹¹. In co-current regeneration, in order to reduce leakage, a larger amount of the regenerate is needed to decrease the amount of non-regenerated resin. The process, however, is generally lower cost because no additional equipment or piping is needed to

change the flow. Most processes that do not need a super pure product will use co-current because of its lower cost¹¹.

Leakage is very common because of incomplete regeneration. It regularly occurs when production is restarted after regeneration because there is still Ca^{2+} on the resin closest to the exit. Generally the leakage is short lived, but it could affect production. For this reason, it is important to know if the system has leakage and how much it will affect production.

Counter Current regeneration is used in processes which have much more stringent product specifications. Because the flow is run counter to the process, the highest quality of resin is at the process outlet after regeneration. Counter current regeneration also requires less regenerate because the percentage of non-regenerated is at the top of the column.

Regeneration is also used to change the form of the resin. The cation and anion resins used in lab are Amberlite® IR120 and Amberlite® IRA410, respectively. The IR120 comes in sodium form, and the IRA410 comes in chlorine form. SAC resins can be regenerated with a strong acid in order to convert the resins to hydrogen form. All the cations (including the fixed Na^+) are exchanged with the H^+ ion from HCl ¹². SBA resins can be regenerated with a strong base, by using sodium hydroxide the resin will convert from the Cl^- form to OH^- . Using these solutions to regenerate the resins before deionizing will convert the resins into the correct form to produce pure H_2O .

Calculating resin regeneration and efficiency is based on selectivity coefficients and exchange. The exchange is summarized as the following, where the barred terms are the fixed phase and the others are the mobile phase: $A^+ + B_{bar}^+ \leftrightarrow B^+ + A_{bar}^+$

For this exchange the equilibrium constant (selectivity coefficient) would be:

$$K_{B^+}^{A^+} = \frac{[A_{bar}][B^+]}{[B_{bar}][A^+]} \quad (1)$$

A_{bar} = moles of A^+ on a resin/liter resin basis (bulk volume)

B_{bar} = moles of B^+ on a resin/liter resin basis (bulk volume)

A^+ = moles A^+ per liter of liquid

B^+ = moles B^+ per liter of liquid

It is important to note that these coefficients are only constant over a narrow range of concentrations. The exchangeable capacity for the resins is denoted as C_{bar} . Using the exchangeable capacity of the resin and the solution, the equivalent fraction for the ions in each phase can be defined.

$$X_{A^+} = \frac{[A^+]}{C} \text{ or } X_{A_{bar},+} = \frac{[A_{bar}^+]}{C_{bar}} \quad (2)$$

Most often for water softening, the ion is calcium and has a 2+ charge. The monovalent/divalent exchange is summarized as the following, where the barred terms are the fixed phase and the others are the mobile phase. The Equilibrium constant would also change.

$$A^{2+} + 2B_{bar}^+ \leftrightarrow 2B^+ + A_{bar}^{2+}$$

$$K_{B^+}^{A^{2+}} = \frac{[A_{bar}^{2+}][B^+]^2}{[B_{bar}]^2[A^{2+}]} \quad (3)$$

In order to keep charge balance the equations would become:

$$X_{A^{2+}} = \frac{2[A^{2+}]}{C} \text{ or } X_{bar,2+} = \frac{2[A_{bar}^{2+}]}{C_{bar}} \quad (4)$$

Using the equivalent fraction, the selectivity coefficient, and the monovalent (H^+) and divalent (Ca^{2+}) exchange, the mass transfer expression is:

$$\frac{X_{Ca^{2+}}}{(1-X_{Ca^{2+}})^2} = \frac{1}{K_{H^+}^{Ca^{2+}}} \frac{C}{C_{bar}} \frac{X_{bar,Ca^{2+}}}{(1-X_{bar,Ca^{2+}})^2} \quad (5)$$

$X_{Ca^{2+}}$ = equivalent fraction of Ca^{2+} in solution

C_{bar} = total concentration of exchangeable sites on the resin (fixed ions)

C = total concentration of exchangeable sites in solution (mobile ions)

$X_{bar,Ca^{2+}}$ = equivalent fraction of Ca^{2+} on resin

$K_{H^+}^{Ca^{2+}}$ = equilibrium constant

The following is the step by step derivation of the mass transfer expression:

$$C = [Ca^{2+}] + [H^+]$$

$$C_{bar} = [Ca_{bar}^{2+}] + [H_{bar}^+]$$

$$[A_{bar}^{2+}] = \frac{X_{bar,A} C_{bar}}{2} \text{ and } [A^{2+}] = \frac{X_A C}{2}$$

$$[B_{bar}^+] = C_{bar}(1 - X_{bar,A}) \text{ and } [B^+] = C(1 - X_A)$$

$$\text{Combine the above equations: } K_{B^+}^{A^{2+}} = \frac{\frac{X_{bar,A} C_{bar}}{2} C^2 (1 - X_A)^2}{C_{bar}^2 (1 - X_{bar,A})^2 \frac{X_A C}{2}}$$

$$\text{Simplifying the above: } K_{B^+}^{A^{2+}} = \frac{X_{bar,A} C (1 - X_A)^2}{C_{bar} (1 - X_{bar,A})^2 X_A}$$

$$\text{Rearranging gives equation 5: } \frac{X_{Ca^{2+}}}{(1 - X_{Ca^{2+}})^2} = \frac{1}{K_{H^+}^{Ca^{2+}}} \frac{C}{C_{bar}} \frac{X_{bar,Ca^{2+}}}{(1 - X_{bar,Ca^{2+}})^2}$$

At some point, usually based on years of use, the resin will swell and begin to break down. For a typical home water softener, the resin can last up to 10 years¹³. One of the best ways to know the resin needs to be replaced is to notice that regeneration is no longer resulting in the correct purity during processing. Another way is that the resin begins to emit a foul smelling odor. The odor happens a lot when the resin sits, unused, for a long period. Finally, the resin may need to be replaced if the effluent leaving the cation exchanger begins to take an orange color. In this scenario, the cation resin has begun breaking down and the resin fines are leaving in the effluent.

The lab setup that is being used in lab was previously used for ion exchange. The resin had been sitting in the column, partially soaked, for at least a year. At this point the resin had the start of a foul odor and the effluent was emitting the color of the resin. Figures 5 and 6 show the “bad” resin on the left, and the new resin added to the column on the right.

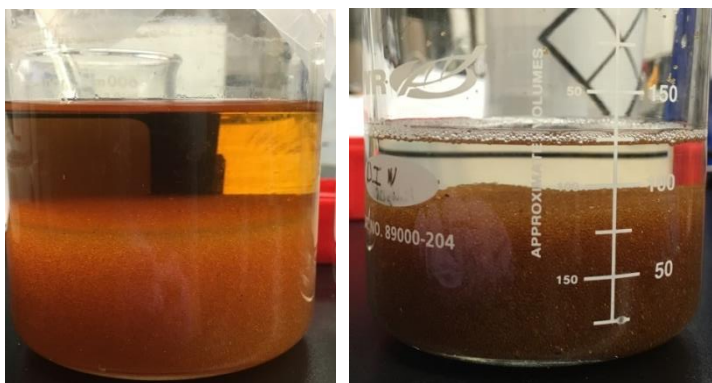


Figure 5: Comparison of the old anion resin (left) and the new resin (right). The new resin was fresh from Sigma Aldrich. The old resin was creating cloudy smelly effluent.

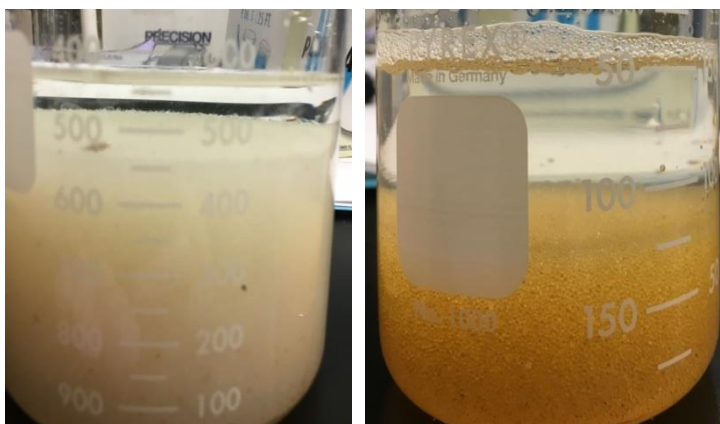


Figure 6: Comparison of the disintegrating resin (left) and the new resin (right). The resin on the left was also emitting a foul smell. The new resin was fresh from Sigma Aldrich

Lab Instructions:

Equipment set up:

Each lab set up has extra tubing on the inlet side. The extra tubing is made to go into the solution barrel. There is a section of MasterFlex tubing on that extra tubing. The section of MasterFlex tubing is the section of tube that must go into the pump. Both lab set ups are using the same pump head so if the system should not have flow, the tubing must be removed from the pump head. The pump should be between the two lab setups.

The HCl will be in a clearly labeled 2L beaker. This solution will be shared between the two set ups, pay attention if it is running low. It is 5% (v/v) and easy to make more. The NaOH will also be in a clearly labeled 2L beaker. This solution will be shared but probably not emptied, pay attention if more needs to be made. It is a 6% (w/v) solution.

Cation Regeneration

Use the 5% HCl solution as the processing solution.

Backwash Directions:

1. Place the tubing in the DI Water solution. The water should be labeled, but the conductivity can be checked to verify that it is DI Water.
2. Turn the 3-way valves so fluid is flowing up the resin column
 - a. Follow the schematics from lab 1
3. Set flowrate of DI Water to Level 1-2 (about 75 mL/min) for a duration of 10 minutes
4. At the end of ten minutes shut off backwash

Acid Brine:

1. Move the tubing to the 5% HCl solution.
2. Turn the 3-way valves so fluid is flowing through the column
 - a. A schematic for this can be seen below (Cation Regeneration)

3. Set the HCl flow to Level 1 (50 mL/min) to not disturb the resin
4. Allow HCl to flow for 30 minutes
5. Track conductivity throughout the 30 minutes, taking a reading at least every minute

DI Water Rinse

1. After the 30 minutes of HCl flow is over, switch the processing solution back to DI water
2. Set the DI Water flow for about Level 1.5 (75 mL/min)
3. Allow water to flow through the tower for 1-2 BV (about 15 minutes)
4. Track the conductivity, it should move back towards that of DI Water
5. At the end of 15 minutes, measure the effluent pH to compare it to DI Water

Anion Regeneration

Use the 6% NaOH as the processing solution

Backwash Directions:

1. Keep the processing tube in the DI water to start this part
2. Turn the 3-way valves so fluid is flowing up the resin column
 - a. Follow the schematic from lab 1
3. Set flowrate of DI Water to Level 1-2 (about 75 mL/min) for a duration of 10 minutes
4. At the end of ten minutes shut off backwash

Acid Brine:

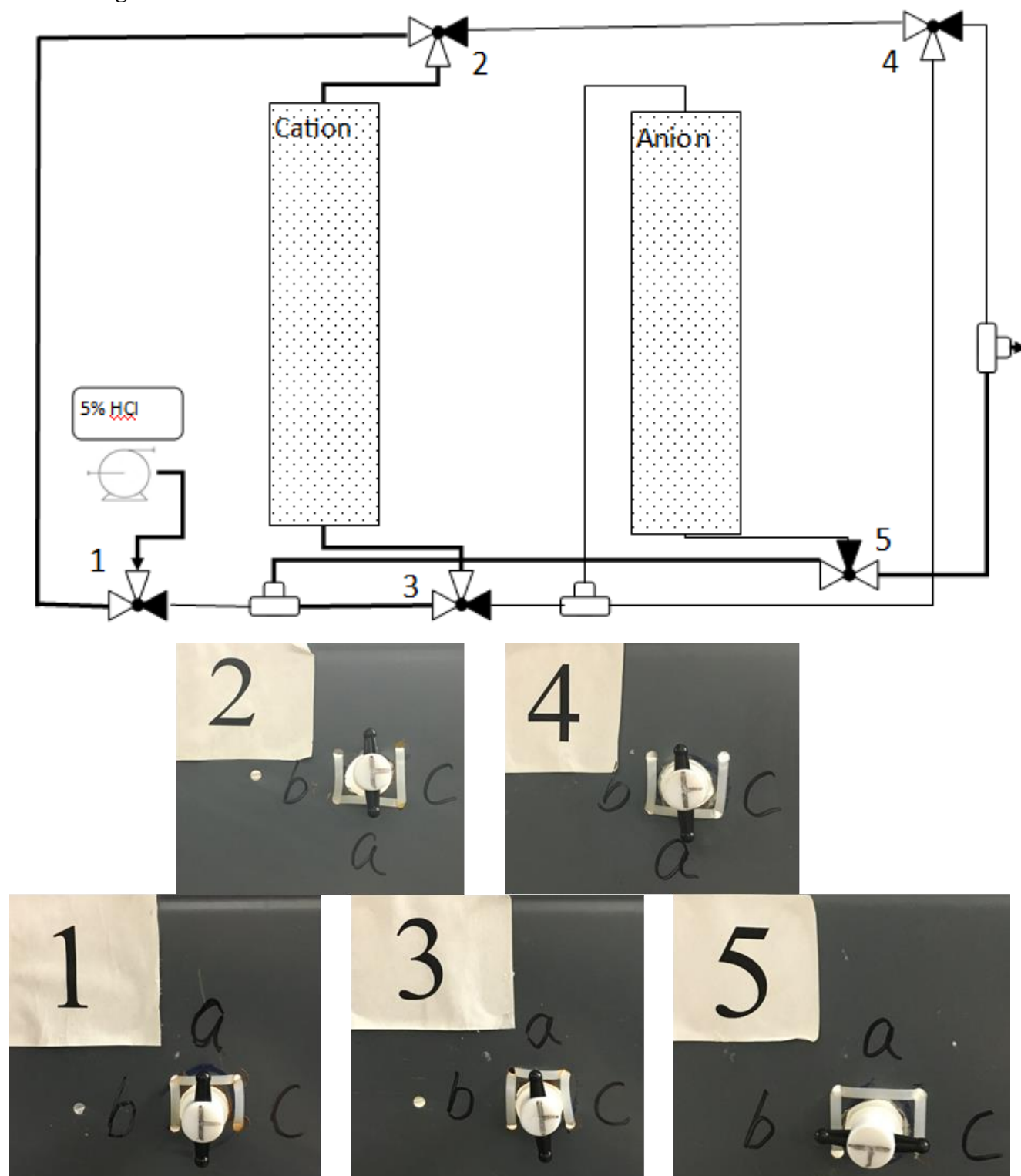
1. Move the tubing to the 6% NaOH.
2. Turn the 3-way valves so fluid is flowing through the column
 - a. A schematic for this can be seen below (Anion Regeneration)
3. Set the NaOH flow to Level 1 (50 mL/min) to not disturb the resin
4. Allow NaOH to flow for 30 minutes
5. Track conductivity throughout the 30 minutes, taking a reading at least every minute

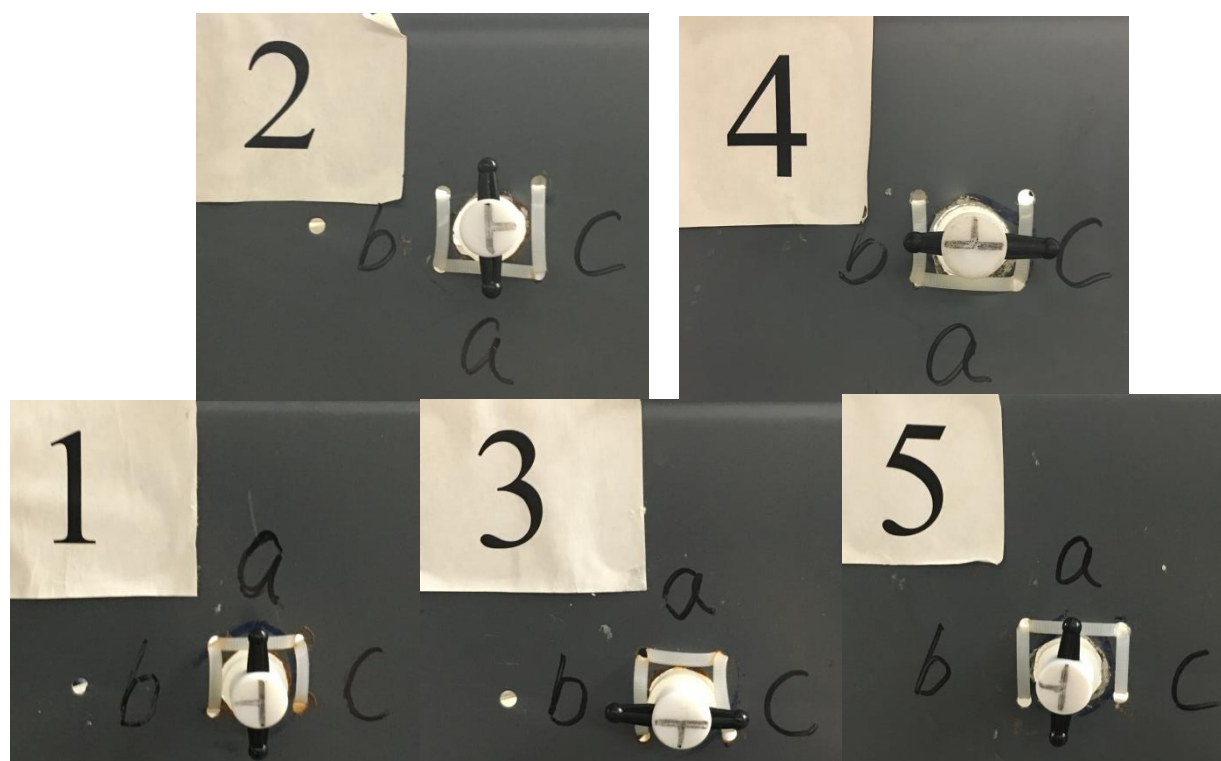
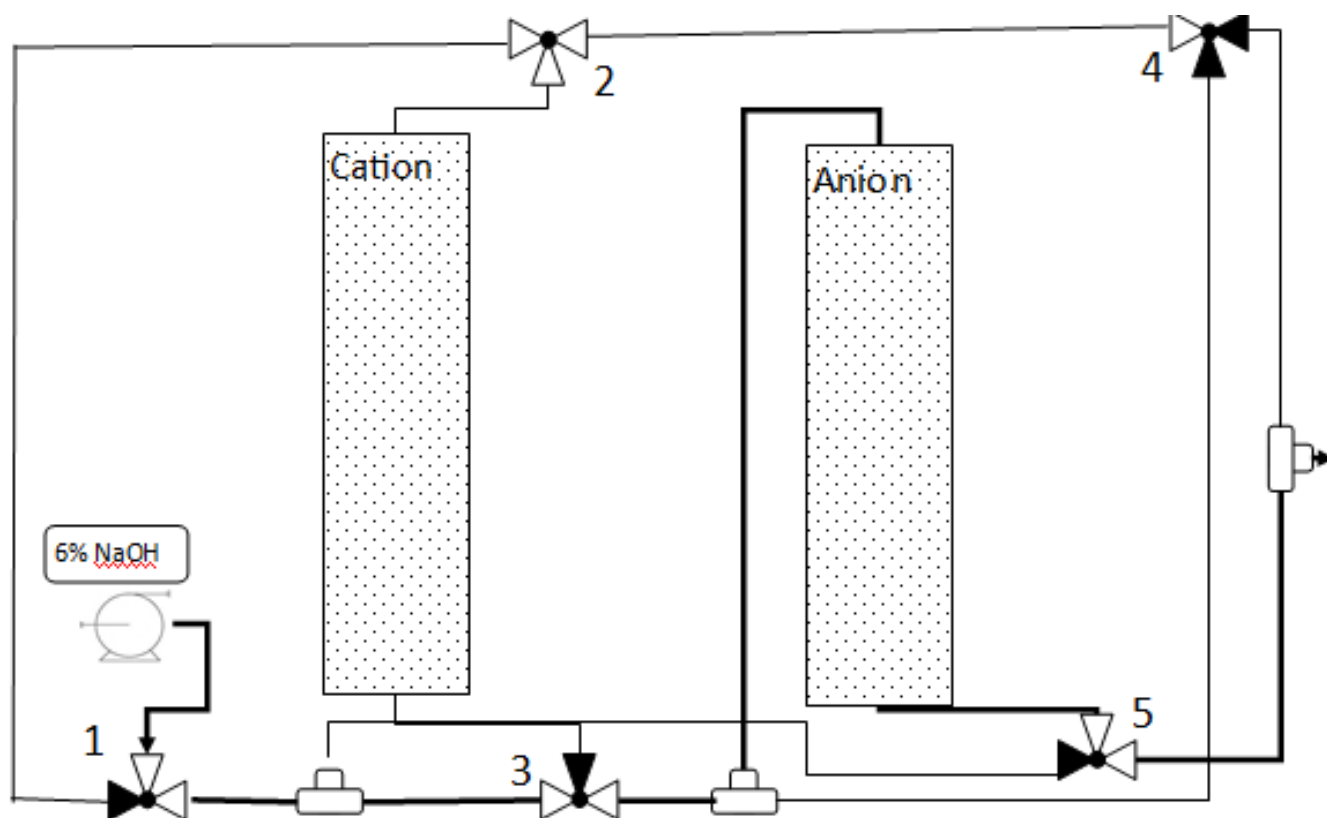
DI Water Rinse

1. After the 30 minutes of NaOH flow is over, switch the processing solution to DI water
2. Set the DI Water flow for about Level 1.5 (about 75 mL/min)
3. Allow water to flow through the tower for 1-2 BV (about 15 minutes)
4. Track the conductivity, it should move back towards that of DI Water
5. At the end of 15 minutes, measure the effluent pH to compare it to DI Water

Experimental Schematic:

Cation Regeneration Schematic and Valve Position:



Anion Regeneration Schematic and Valve Position:

Day 3: Creating a Breakthrough Curve

Background:

The purpose of lab scale simulations is to find the breakthrough. Using the results of the breakthrough curve, a better idea of what will happen at pilot scale, and then industry size, can be determined. A breakthrough curve is created by looking at the effluent concentration profile as a function of the volume of liquid processed; Figure 7 is a good example of a breakthrough curve. The top of the figure shows the change in the column as the exchange happens. For this part, the dark green is the exhausted column, the light green is the mass transfer zone, and the blue is the clean resin. The breakthrough is shown by the green line; it continues almost linearly until the breakthrough happens. Once breakthrough occurs the concentration in the effluent increases until exhaustion. At exhaustion, the clean resin is all gone. The shape of the

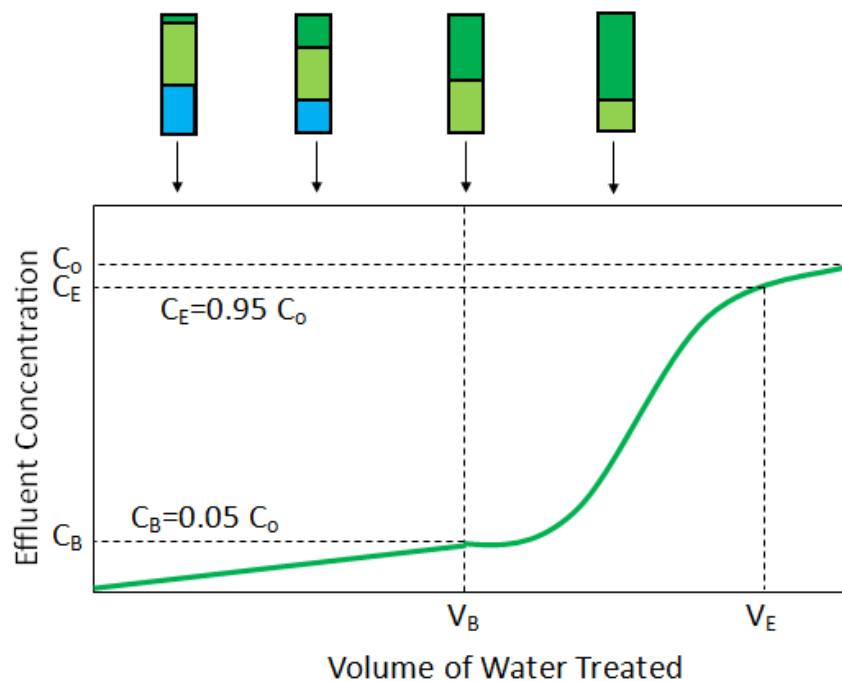


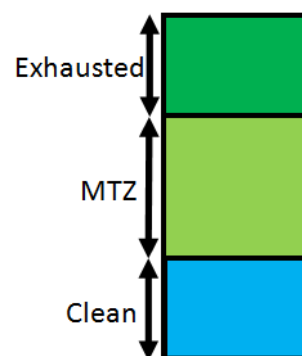
Figure 7: Breakthrough curve of a solution. Depicts how the zones move through the bed throughout a full breakthrough curve

Source: "Water Resources Engineering."

breakthrough curve depends on several factors, equilibrium relationship between solution and fixed phases, rate-limiting mass transfer mechanism (i.e. diffusion, dispersion, or reaction kinetics), fluid flow velocity, and bed volume.

The analytical way to fit the data is to find the convective diffusion equation in terms of time and column position¹⁴; this method is normally possible only for very simple systems. Most columns are designed by fitting experimental data or solving transport equations.

Figure 7, showed the column over time, while Figure 8⁷ is a snapshot of the ion exchange column around the time of breakthrough; the solution is flowing down through the column in Figure 8. The resin starts as “clean”. As more solution flows through the column, it becomes the light green, the mass transfer zone (MTZ). The mass transfer zone is the area in which the ion exchange occurs; it moves through the column leaving behind exhausted resin (dark green). The exhausted resin does not allow mass transfer as all of the fixed ions have already exchanged with mobile ions.



*Figure 8: The three zones of an ion exchange column are shown. The zones move through the column based on the amount of solution that has flown through.
Source: "Water Resources Engineering."*

Column tests are performed to determine the shape of the breakthrough curve. In order to change the shape or duration of the breakthrough, resin size, feed flow rate, operating temperature, and bed volume can be manipulated¹⁵. The column tests are used to elicit the shortest (on a volume basis) breakthrough zone. The breakthrough zone is the area of the curve between the first breakthrough and column exhaustion. There are many general guidelines for designing experiments and breakthrough curves. Slower flow velocities are normally favored as it gives more time for the fixed ions to exchange with the mobile ions; this results in shorter mass

transfer zones. Typically, higher temperatures are favorable; increasing temperature leads to an increase in diffusion rate of ions¹⁶. Diffusion, assuming isobaric and isothermal system, is given by Fick's First Law:

$$J_A = -D_{AB} \nabla c_A \quad (6)$$

$$D_{AB} \propto T^{3/2} \quad (7)$$

J_A = molar average velocity
 c_A = concentration of component A
 D_{AB} = diffusion coefficient
 T = temperature (absolute)

As stated, breakthrough happens when the clean zone disappears; breakthrough is when the effluent concentration reaches 5% of the influent concentration⁷. In Figure 7 breakthrough occurs at the vertical dashed line at V_B . Throughout typical experimentation, the length of the

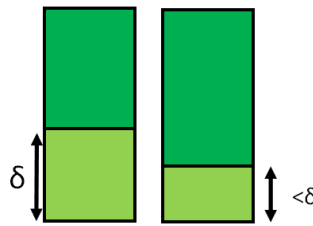


Figure 9: Change in MTZ as column moves closer to exhaustion. Only at this point does the MTZ change length. Source: "Water Resources Engineering."

MTZ remains constant; however, after the initial breakthrough, the effluent concentration increases and the MTZ starts to decrease as more of the column becomes exhausted. Once the MTZ disappears,

the bed is considered exhausted; this is also when the

concentration of the effluent is 95% of the influent. In Figure 7

exhaustion occurs at the vertical dashed line at V_E . The change in

MTZ length is shown in Figure 9. The MTZ length is calculated

by the following equation and represented as "δ" in Figure 9⁷:

$$H_{MTZ} = L \left[\frac{V_E - V_B}{V_E - 0.5(V_E - V_B)} \right] \quad (8)$$

H_{MTZ} = length of mass transfer zone
 L = length of the bed
 V_E = volumetric throughput to exhaustion
 V_B = volumetric throughput to breakthrough

As the bed length increases, the MTZ becomes a smaller fraction of the whole bed. The breakthrough time is calculated based on the ideal time and the fraction of the bed being utilized.

Using the breakthrough time, the amount of bed left unused can be determined.

$$t_b = t^* \left(1 - \frac{LUB}{L}\right) \quad \text{or} \quad LUB = L \left(1 - \frac{t_b}{t^*}\right) \quad (9)$$

t_b = time at break point

t^* = ideal adsorption time

LUB = length of unused bed

L = length of bed

The length of unused bed is important because systems have the same breakthrough curve shape for different lengths of bed. During scale up of the system, the fraction of unused bed to length of bed stays constant for different bed lengths. The length of unused bed can also be calculated from a breakthrough curve. Using integration, the total solute absorbed up to the breakthrough point can be determined. The capacity of the resin is also found through integration of the complete breakthrough curve; it can also be given by the manufacturer. The unused fraction of the bed is found by 1.0 minus the ratio of the two.

As shown with the effect of temperature, the rate of exchange between ions is limited by the diffusivity of the mobile ions and resin particles. In order to predict concentration changes in an ion exchanger, the unsteady-state diffusion equations must be solved. According to McCabe, the overall mass transfer coefficient can be approximated using a driving forced based equation¹⁷.

$$r = K_c a (c - c^*) \quad (10)$$

K_c = overall mass transfer coefficient (m/s)

a = external area per unit bed volume

c = concentration in solution

c^* = concentration in equilibrium with the average particle concentration

The overall mass transfer coefficient depends on both the external and internal coefficient. Diffusion is an unsteady state process; therefore, the internal coefficient decreases

with time. The effective diffusivity depends on the resin porosity; surface diffusion often contributes more to the total flux than diffusion in the gas phase. The average coefficient can be approximated with the following equation fit to data for spheres:

$$k_{c,int} \approx \frac{10De}{D_p} \quad (11)$$

D_p = diameter of the particle
 De = effective diffusivity

$$\frac{1}{K_c} = \frac{1}{K_{c,ext}} + \frac{1}{mK_{c,int}} \quad (12)$$

The external mass transfer coefficient is predicted based on the correlation of packed beds. Sherwoods number is equivalent to the external mass transfer coefficient. This equation should not be used for Reynolds numbers less than 10.

$$Sh = 1.17Re^{0.585}Sc^{1/3} \quad (13)$$

Chapter 17 in McCabe¹⁷ is a good review of these equations. For reference:

$$Sc = \frac{v}{D_v} = \frac{\mu}{\rho D_v} \quad (14)$$

μ = viscosity
 ρ = density
 v = kinematic viscosity
 D_v = volumetric diffusivity

$$Re = \frac{\rho v D}{\mu} \quad (15)$$

μ = viscosity
 ρ = density
 v = kinematic viscosity
 D = Diameter of particles

Combining the above equations:

$$\frac{K_{c,ext}D}{D_v} = 1.17 \left(\frac{\rho v D}{\mu} \right)^{0.585} \left(\frac{\mu}{\rho D_v} \right)^{\frac{1}{3}} \quad (16)$$

The internal resistance is most often negligible. A low concentration in the external solution will make the ratio of internal to external concentrations very large; the external

resistance would be controlling the diffusivity. From there the rate of mass transfer can be determined.

Lab Instructions:

Equipment set up:

Each lab set up has extra tubing on the inlet side. The extra tubing is made to go into the solution barrel. There is a section of MasterFlex tubing on that extra tubing. The section of MasterFlex tubing is the section of tube that must go into the pump. Both lab set ups are using the same pump head so if the system should not have flow, the tubing must be removed from the pump head. The pump should be between the two lab setups.

Fill a 2L beaker with DI Water and use it as the source for the backwashing. The hard water will be created for you, it is a 0.1 M solution of CaCl_2 and MgSO_4 . The tubing will need to be moved between the two solutions as needed.

Backwash Directions:

1. Place the extra tubing in the DI water beaker.
2. Turn the 3-way valves so fluid is flowing up the resin column
 - b. Follow the schematic from lab 1
3. Set flowrate of DI Water to Level 1-2 (about 75 mL/min) for a duration of 10 minutes
4. At the end of ten minutes shut off backwash

Fill the Freeboard:

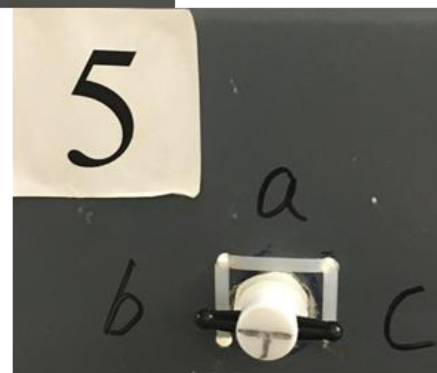
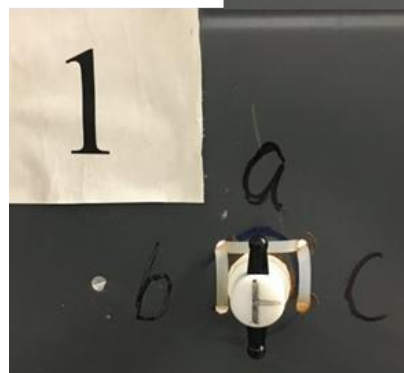
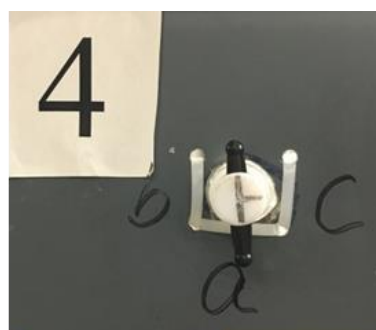
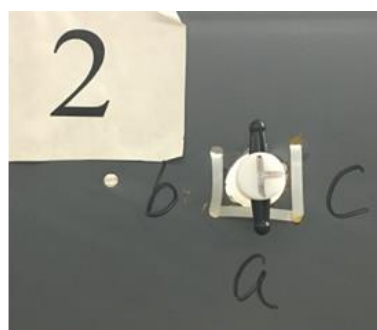
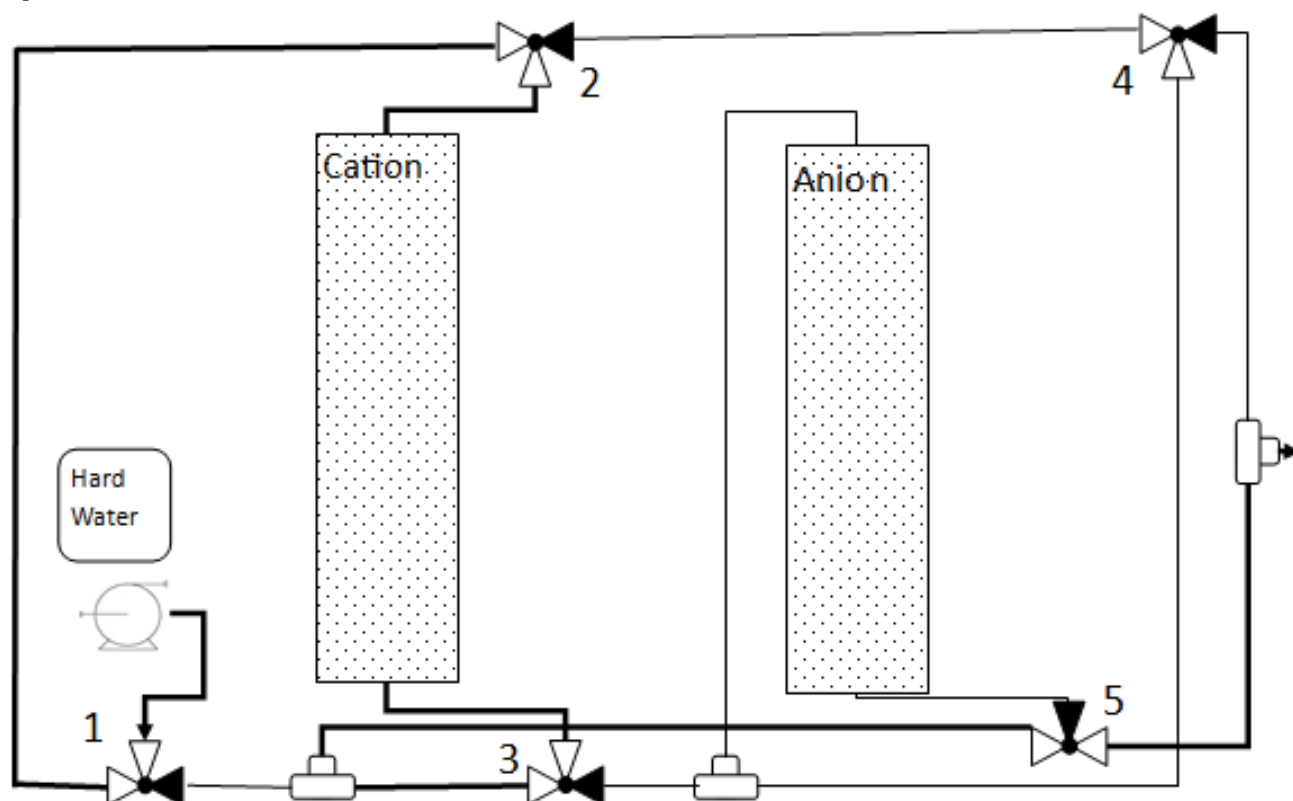
1. Move the tubing from the DI water to the hard water. The conductivity can be checked if the solutions are not labeled.
2. Turn the 3-way valves so fluid is flowing through the column
 - a. See schematic from lab 1 (Cation Fill the Freeboard)
3. Begin flowing the hard water through very slowly at Level 1 (50 mL/min)
4. Continue filling until at least four inches above the resin is filled

Creating a break through curve:

To create an adequate breakthrough curve, at least 10-15 samples need collected.

1. Set the flow of Hard water to Level 1.5 (about 75 mL/min) for the pump
2. Turn the pump on, 3-way valves should be in same position as during the previous step
 - a. A schematic can be seen below
3. The conductivity needs recorded at least every minute
 - a. At the end of every four minutes, two sample vials need to be filled (ex. minute 4, minute 8, etc.)
 - i. Make sure to label the time duration at which you took the sample (minute 4, minute 8, etc)
 - ii. These vials will be used in tomorrow's lab to compare measurement techniques
4. Continue on until the conductivity increases to that of HCl then remains constant
 - a. if this does not happen, stop at 60 minutes
5. Shut off the pump
6. Make sure the water is above the resin before leaving

Experimental Schematic:



Day 4 – Lab Measurements

Background:

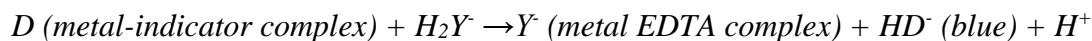
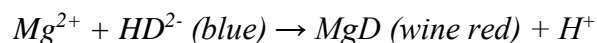
The hardness in “hard” water is actually the characteristic, which prevents soap from lathering²⁰. This characteristic is caused by the presence of calcium, magnesium, and other salts/heavy metals dissolved in the water. Hard water, instead of lathering, forms a white precipitate; the white precipitate is most often referred to as scale. Water softeners are used in home environments to remove the scale that shows up in pipes and bathrooms.

With all the home water softeners currently in use, there needed to be a less analytical way to determine the calcium present in the water. One of the most crude measurement options is called the “Soap Test”. Because hardness in water keeps the soap from lathering, to test the hardness soap is added to solution and shaken to see if suds appear²⁰. Table 5 shows the correlation of water hardness to the number of drops of soap added to the sample. It is important to use soap without detergent, as soaps formulated with detergent lather no matter what²¹. As well as without detergent, it is best to use soap without any perfumes or dyes. Another home testing option is a water strip with a color chart. The strips are put in the water and matched to the color on the chart²⁰; this method is assumed to work better because most soap has detergent or dyes.

Often, in industry, conductivity meters and ion selective electrodes are used as an online control. Another control option is a pH meter; hard water typically has a high pH. By monitoring pH in a water softener or deionizer, the resin life is also monitored. When the resin needs regenerated, the pH will begin to rise towards that of the hard water feed. At this time, regeneration is needed.

Titration is a type of offline measurement. Total hardness can be determined by using an EDTA solution to titrate the Ca^{2+} and Mg^{2+} ; a 10 pH buffer solution and a metal indicator are also used.

The resulting reactions are¹⁹:



The Eriochrome black T is added to a pH 10 aqueous solution containing Ca^{2+} and Mg^{2+} ions in order to turn the solution wine red. By using EDTA as the titrant, the Ca^{2+} and Mg^{2+} become complex; the solution will turn from the red to blue when the titration has reached its endpoint¹⁹.

Today's lab will compare the three different types of methods: crude, online, and offline. The online results were taken during the last lab. The other two tests will be performed following the procedure below.

Lab Instructions:

Soap Test:

1. Take the first sample, measure out 35 mL
2. Add a drop of soap
3. Shake to look for suds
4. Repeat until suds form
5. Mark down how many drops were used
 - a. use Table 5 to determine hardness level and ppm
6. Repeat steps 1-5 for all samples taken

Table 5: Water Hardness measurements based on the soap test

Soap drops	Grains/gallon (GPG)	Ppm (mg/L)	Softness of the Water
2	0-1	0-17.1	Very Soft
4	1-3.5	17.1-60	Slightly Hard
6	3.5-7.0	60-120	Medium Hard
8	7.0-10.5	120-180	Hard
10	10.5+	180+	Very Hard

Conductivity:

Using Table 6 determine hardness areas of water

Table 6: Water Hardness measurements based on average conductivity given by Vernier software

CaCO ₃ (mg/L)	Conductivity (uS/cm)	Hardness
0-70	0-140	Very Soft
70-150	140-300	Soft
150-250	300-500	Slightly Hard
250-320	500-640	Medium Hard
320-420	640-840	Hard
420+	840+	Very Hard

Titration:

1. Fill a clean burette to the zero mark with standard 0.005 M EDTA
2. Measure 10 mL of the first sample and add to a 250 mL Erlenmeyer Flask
3. To the same flask add 20 drops of the pH 10 buffer
 - a. Swirl the flask to make sure it is mixed
4. Place the flask under the burette and turn the stopcock adding the EDTA to the water solution drop by drop until the red color turns blue.
5. When blue, record the amount of EDTA added
 - a. If the solution is already blue: record 0 mL's were added
6. Calculate the amount of CaCO_3 in solution by multiplying by 50
7. Repeat steps 1-6 for all samples

Day 5 – Water Deionization

Background:

Deionized water is used often in industry. It is also used for flushing cooling systems, for dilution of anti-freeze, for rinses of circuit boards, and many other reasons². There are two ways to produce deionized water using ion exchange: mixed bed and two bed deionizing²². Mixed bed deionizers use one tower and a resin mixture of anionic and cationic resins; this allows the water to contact both the cation and anion in succession. Water is deionized continually resulting in the highest purity of deionized water.

One of the reasons mixed beds are not typically used in industry is their high costs. Even though one column is used for the exchange process, the resins then need to be separated into two different columns for regeneration²². After the regeneration process, the resins are mixed again in the original column. Because of their high cost, mixed bed deionizers are rarely used unless ultra-pure water is needed.

Two-bed deionizers are most often used for deionization. The water is run through a Strong Acid Cation resin in H^+ form and then through a Strong Base Anion Resin in OH^- form². During the regeneration lab, the SAC resin was changed from Na^+ to H^+ ; the Anion Resin went from Cl^- to OH^- . This was done in preparation for the deionization.

The cation resin, as in the water-softening lab, removes the positively charged impurities. The Ca^{2+} , Mg^{2+} , and Na^+ attach themselves to the ion exchange resin, which then elutes off H^+ from the previous acid regeneration. The solution leaving the cation exchanger is mostly acidic because of the H^+ interacting with the anionic impurities still left in the water²². To remove those anionic impurities, the solution is run through the anion exchanger.

The anion resin is used to remove the negatively charged impurities and replace them with OH^- . The impurities, Cl^- , SO_4^- , and CO_3^- , attach themselves to the ion exchange sites replacing the hydroxide attached to the resin. At this point in the process, there should only be the H^+ ions from the cation resin and the OH^- ions from the anion resin. These two ions form the pure water that leaves the anion exchanger²²:



Just as in the mixed bed, at exhaustion the resins will need to be regenerated. This process is cheaper because there is no separation to be done beforehand. The resins are regenerated as in the previous lab and then the two columns can be run again. The resins can be used for a long time unless there is oxidation or buildup of organic matter².

Lab Instructions:

Equipment set up:

Each lab set up has extra tubing on the inlet side. The extra tubing is made to go into the solution barrel. There is a section of MasterFlex tubing on that extra tubing. The section of MasterFlex tubing is the section of tube that must go into the pump. Both lab set ups are using the same pump head so if the system should not have flow, the tubing must be removed from the pump head. Communication is key to make this work. The pump should be between the two lab setups.

Fill a 2L beaker with DI Water and use it as the source for the backwashing. The 5% (v/v) HCl will be used during the regeneration. The lab will have pre-made hard water for processing to deionize.

Create a Calibration Curve:

Most of this lab is a repeat of the past labs. In order to determine how efficient the series of exchangers are, a calibration curve for concentration must be determined. The influent is 0.1 M hard water and the effluent should be deionized water. A calibration curve is made up of at least 3 data points.

Column Preparation:

Backwash Directions:

1. Place the extra tubing in the DI water beaker.
2. Turn the 3-way valves so fluid is flowing up the resin column
 - c. Follow the schematics from lab 1
3. Set flowrate of DI Water to Level 1-2 (about 75 mL/min) for a duration of 10 minutes
4. At the end of ten minutes shut off backwash

Regeneration of Cation Resin:

1. Move the tubing so the 5% HCl is now the processing solution
2. Turn the 3-way valves so fluid is flowing through the column
 - b. A schematic for this can be seen in the Cation Regeneration lab
3. Set the HCl flow to Level 1 (50 mL/min) to not disturb the resin
4. Allow HCl to flow for 30 minutes
5. Track conductivity throughout the 30 minutes, taking a reading at least every minute

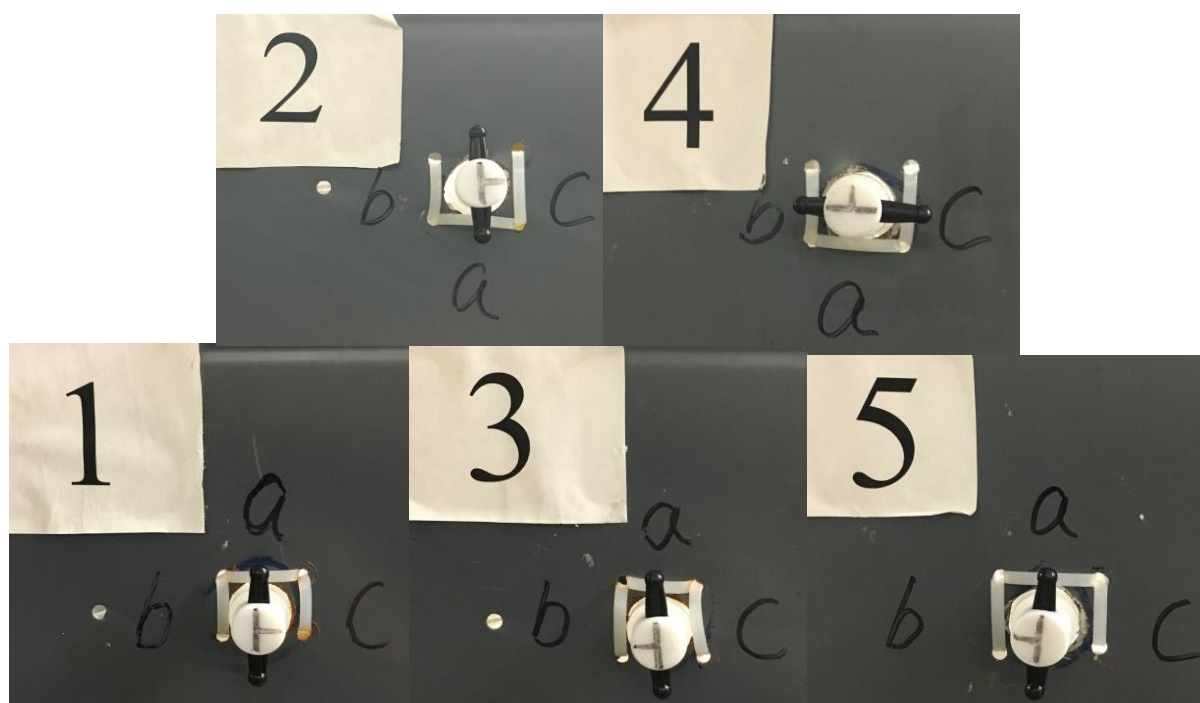
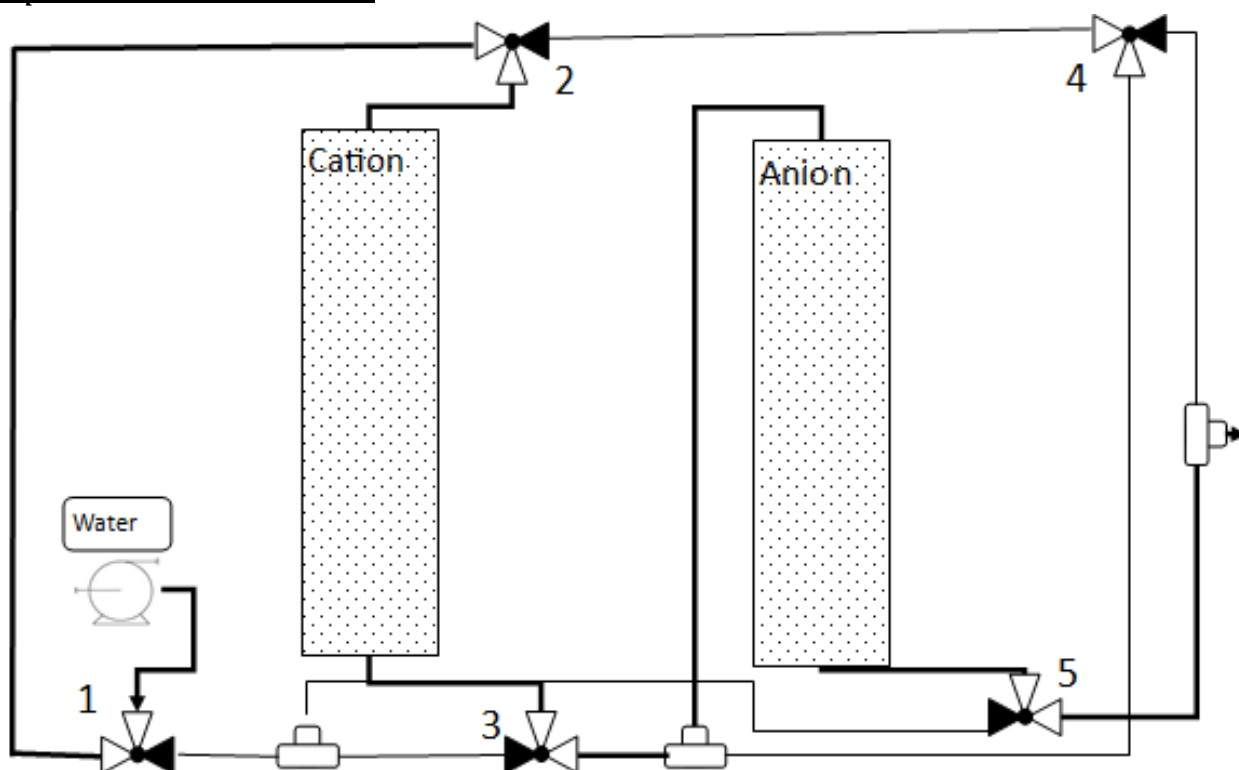
DI Water Rinse

1. After the 30 minutes of HCl flow is over, switch the processing solution back to DI water
2. Set the DI Water flow for about Level 1.5 (75 mL/min)
3. Allow water to flow through the tower for 1-2 BV (about 15 minutes)
4. Track the conductivity, it should move back towards that of DI Water
5. At the end of 15 minutes, measure the effluent pH to compare it to DI Water

Water Deionization

1. Turn the 3-way valves so fluid is flowing through both columns
 - a. A schematic for this can be seen below
2. Switch the processing solution to hard water. Set the flow of hard water to Level 1.5 (about 75 mL/min) for the pump
3. Turn on the pump and begin to run hard water through the bed
4. Record the conductivity of the outlet
5. Continue on until the conductivity increases then remains constant
6. Shut off the pump
7. Make sure the freeboard is filled before leaving.

Experimental Schematic:



Assignments:

Design/Proposal Presentation

One of the objectives of the lab is to understand how laboratory testing is used in designing ion exchangers. In, “*Ion-Exchange Resins: A Retrospective from Industrial and Engineering Chemistry Research*” by Spiro D. Alexandratos, multiple industries which use Ion Exchange are discussed. The assignment is to:

- 1) Choose an industry to present on
- 2) Create a proposal for why your company should go into this market
 - a. Who are your biggest competitors?
 - b. What sort of market size is there?
- 3) Determine some of the basic design principles for your Ion Exchange²
 - a. What form of resin will you use?
 - b. Has this been done before?
 - i. Give an estimate of the size of column needed
 1. referencing other research papers may give data to help with this
 - c. What type of regenerant will you use?

This is just a proposal so plan for a 7-10 minute presentation. Include relevant figures and tables to help answer the 5W's & 1 H (Who, what, where, when, why, and how). Plan on having 5-8 minutes of questions from your classmates and instructor. This is meant to foster creativity by exploring what is happening in industry and using those ideas; there is no need to reinvent the wheel. Make sure to reference all companies or ideas you use to avoid plagiarism.

² DOW Chemical has a website called “*How to Design an Ion Exchange Resin System*”, it would be a good starting point.

Day to Day Assignments

For Day 2 (Regeneration)

1. Estimate the percentage of regeneration of the following system. A column used to remove Ca^{2+} is spent with a concentration of 0.1M. A 2M brine of HCl is used for regeneration.

Given: $K_{H^+}^{\text{Ca}^{2+}} = 3$ and $\dot{C} = 2 \text{ meq/mL}$

2. Estimate the Leakage in the following system. Determine if this amount should be a problem.

Given: $K_{H^+}^{\text{Ca}^{2+}} = 3$, $\dot{C} = 2 \text{ meq/mL}$, $[\text{H}^+] = 30 \text{ meq/L}$, and $[\text{Ca}^{2+}] = 40 \text{ meq/L}$,

$$c = 0.074 \text{ meq/L}$$

For Day 3 (Breakthrough Curve)

1. List of three Ion Exchange applications you would like to present
2. Solve the following problems:
 - a. We want to remove Ca^{2+} using a strong acid cation resin in the H^+ form. How much water can be run before the column reaches exhaustion²². Remember the column is filled with 125 mL of resin.

Given: $K_{H^+}^{\text{Ca}^{2+}} = 4$, $\dot{C} = 2 \text{ meq/mL}$, $[\text{H}^+] = 3 \text{ meq/L}$, and $[\text{Ca}^{2+}] = 1.5 \text{ meq/L}$

- b. The bed is 125 mL with a diameter of 2.5 cm. The flow rate is set at 50 mL/min and reaches breakthrough after 27 minutes. It is exhausted at 1 hour and 3 minutes. What was the mass transfer zone?

3. If you would like extra practice, problem 25.10 utilizes the mass transfer taught in Unit Operation of Chemical Engineering.

For Day 4 (Laboratory Comparison)

1. Create the breakthrough curve from the data found in lab.
 - a. Using your breakthrough curve, what is the length of unused bed? Assume an ideal time (t^*) or 0.5 hours.
2. Using the created breakthrough curve, create an industry sized water softener. Assume it needs to work for an apartment of 8 families, and that each family uses an average of 400 gal/day of water. Remember that a typical regeneration period is between 12-48 hours.

For Day 5 (Deionization):

1. Create a visual representation to compare the results of the conductivity vs titration vs crude method.
 - a. Why are the results different or the same?
 - b. Where could error have occurred?
2. Turn in completed presentation slides

For Day 6:

1. Create the calibration curve for the deionized water
 - a. include a regression analysis and error bars
2. Create a graph of the effluent concentration versus the throughput volume.
 - a. Write a paragraph explaining the results
 - i. Include any statistical analysis that may be pertinent.

References:

- [1] "TECH TIP #7." Thermo Fisher Scientific Inc. Pierce Biotechnology, 2008. Web. 24 Feb. 2016.
- [2] Walton, Harold F. "Ion-Exchange Reaction." Encyclopedia Britannica Online. Encyclopedia Britannica, 8 Jan. 2015. Web. 24 Jan. 2016.
- [3] Wheaton, R. M., and L. J. Lefevre. "Fundamentals of Ion Exchange." Dow Liquid Separations. DOW Chemical USA, June 2000. Web. 16 Jan. 2016.
- [4] Golden, L. S. "Ion Exchange Resins: Characterizations Of." Academic Press. Purolite International Ltd., 2000. Web. 24 Jan. 2016.
- [5] DuHamel, Deanna, and Kathy Graczyk. "Applications of Ion Exchange." Ion Exchange. Rensselaer Polytechnic Institute, 5 Apr. 1997. Web. 16 Feb. 2016.
- [6] "Ion Exchange - Resin Types." Adsorption Chap 04. Separation Processes. Web. 16 Feb. 2016.
- [7] Rabah, Fahid, Dr. "Water Resources Engineering." Water Treatment Technology. Water Treatment Technology. Web. 8 Mar. 2016.
- [8] "Standard Specification for Reagent Water." ASTM International. 2011. Web. 13 Apr. 2016.
- [9] Desilva, Frank. "Resin Regeneration Fundamentals." Water Quality Products. Scranton Gillette Communications, 1 Apr. 2006. Web. 24 Feb. 2016.
- [10] Alchin, David. "Ion Exchange Resins." Chem Processes - Water. New Zealand Institute of Chemistry, 2008. Web. 24 Jan. 2016.
- [11] Woolley, Joe. "Ion Exchange Process Design." Watercare International Ltd. SCI. Web. 24 Feb. 2016.
- [12] Patil, Arvind, Gary Hatch, Charles Michaud, Mark Brotman, P. Regunathan, Rebecca Tallon, Richard Andrew, Shannon Murphy, Steve VerStrat, Pauli Undesser, and Kimberly Redden. "Ion Exchange." WQA Technical Fact Sheet. Water Quality Association, 2013. Web. 24 Feb. 2016.
- [13] "Resin Replacement." Softener Parts. 2016. Web. 03 Apr. 2016.
- [14] Robinson, S. M., W. D. Arnold, and C. H. Byers. "Design of Fixed-Bed Ion Exchange Columns for Wastewater Treatment." Waste Management

- Symposia. Oak Ridge National Laboratory, 1990. Web. 1 Mar. 2016.
- [15] "Lab Guide: Column Separations Using Resins and Adsorbents." Dow Water Solutions. DOW Chemical USA, Feb. 2011. Web. 2 Mar. 2016.
- [16] Desilva, Frank, and Bill Koebel. "Some Like It Hot, Some Like It Cold." Water Quality Products Aug. 2000. Print.
- [17] McCabe, Warren L., and Julian C. Smith. Unit Operations of Chemical Engineering. New York: McGraw-Hill, 1976. Print.
- [18] Sanjeev Kumar and Sapna Jain, "History, Introduction, and Kinetics of Ion Exchange Materials," Journal of Chemistry, vol. 2013, Article ID 957647. Web. 6 Mar. 2016.
- [19] "Water Analysis - Determination of Chemical Parameters." Amrita Vishwa Vidyapeetham Virtual Lab. Virtual Amrita Laboratories, 2013. Web. 24 Feb. 2016.
- [20] "Water Hardness Test Procedures & Water Mineral Content Tests." How to Measure Water Hardness. InspectAPedia, 2014. Web. 24 Feb. 2016.
- [21] Garwell, Jerry. "Where To Use Deionized Water." Distilled and Deionized Water. 27 Jan. 2012. Web. 24 Feb. 2016.
- [22] "Deionized Water (DI)." Industrial Water Purification. Cal Water. Web. 24 Jan. 2016.
- [23] JJB. Ion Exchange. PowerPoint Presentation. Cornell University, 19 Apr. 2004. Web. 6 Mar. 2016.
- [24] S, Will. "How Can I Artificially Create 'Hard Water'?" Chemical Forums. 2005. Web. 13 Apr. 2016.
- [25] Brown, Phil, Dr. "Hard and Soft Water." Aqueous Chemistry. Web. 13 Apr. 2016.
- [26] Slagt, Marc. "Ion Exchange: Resin Selection." SCI. DOW Water and Process Solutions. Web. 13 Apr. 2016.
- [27] Haas, and Rohm. "Ion Exchange: An Introduction." Water Treatment Solutions. LennTech, Sept. 2008. Web.

Appendix 1: Creating Hard Water for Testing

Temporary Hard Water:

Temporary hard water is modeled as Calcium Bicarbonate. It is not a stable compound and must be created. First, add a couple of grams of Ca(OH)_2 to 1L of water. For 24 hours, mix/shake it at least once every hour. At the end of the 24 hours, pour off the clear solution on top. Next, bubble CO_2 through the Ca(OH)_2 solution. This will first turn the solution a milky consistency, continue until the solution turns back to clear. Save the solution as the temporary hard water.

Permanent Hard Water:

Create a 0.1M solution of CaCl_2 and MgSO_4 .

Hard Water:

Choose a consistent volume for mixing (for example, 1L). Mix 3L of temporary hard water and 1 L of the permanent hard water. Add 2L of DI water. If too weak, omit the DI water.

Notes from pretesting:

1. 0.1M hard water was used for all testing
2. Temporary hard water is normally removed by boiling and not by ion exchange
 - a. it was ignored for the experiments
3. Moving forward, the 0.1M should still be diluted (2-3 times) to get hardness levels more realistic to an actual home water softener.

Appendix 2: Calibration of Peristaltic Pump

Procedure:

The pump level was set and the flow out was measured in a 50 mL graduated cylinder over a period of 60 seconds. If the flow out reached 50 mL before the period was over, the time was stopped and that time was marked. Three flows were measured for each level setting. The level settings were changed between 1 and 3; at this point it was decided the flow was fast enough and did not need to continue.

Results:

Table 1: Raw data from the lab using the peristaltic pump. Amount of flow out was measured in mL and time in seconds. Using this data the flow was found in mL/min

Setting	Time (s)	Amount (mL)	Flow (mL/min)
1	58	50	51.72
1	57	50	52.63
1	56	50	53.57
2	30	50	100.00
2	27	50	111.11
2	27	50	111.11
3	20	50	150.00
3	20	50	150.00
3	19	50	157.89

An Anova was also completed for the raw data. The F value, 41.7, was greater than the F_{crit} value, 4.41; this signifies a significant correlation between the change in setting and the flow.

Table 2: Average, standard deviation, and standard error of the raw data for calibrating the peristaltic pump.

Setting	Average Flow (mL/min)	STDEV	StError
1	52.64	0.92	0.31
2	107.41	6.42	2.14
3	152.63	4.56	1.52

Using the averages of the flow and the sitting, a positive linear relationship was found. This relationship is presented on the following figure.

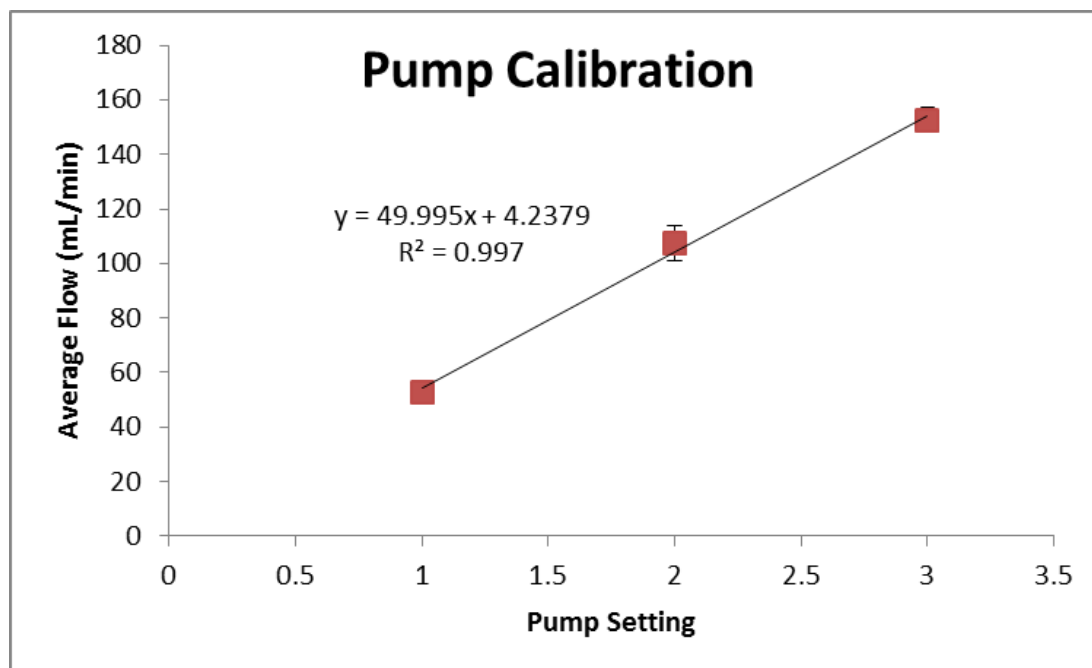


Figure 1: Average flow from the pump versus the pump setting. Each value represents the average of three flows. Error bars represent the standard deviation at each pump setting. The calculated values have an R^2 value of 0.997.

Appendix 3: Example of Concentration Calibration

Procedure:

Two solutions were made, a 0.1M solution of Hard water was created based on the instructions given in the paper, and a 5% (v/v) HCl solution. The conductivities of both solutions were taken 3 times to account for error. The HCl solution had a large error in the first three measurements so a fourth was taken. After the initial solutions were measured, three more solutions were created, one with 25% (v/v) hard water and HCl, one with 50% (v/v) hard water and HCl, and one with 75% (v/v) hard water and HCl. The three measurements per solution was repeated for each solution.

Results:

The raw data, as well as averages and standard deviations are below. An Anova was completed for the raw data. The F value, 156917, was greater than the F_{crit} value, 4.17; this signifies a significant correlation between the conductivity and the concentration of calcium in solution. The P value is essentially zero.

Table 1: Raw data for the concentration calibration curve. From this data the following were found: averages, standard deviations, standard error, F values, and P values.

.1 M Hard Water					
Reading	V (DC)				
1	4.276				
2	4.274				
3	4.282				
Average	4.277				
StDEV	0.004				
		75% Hard Water, 25% HCl			
		Reading	V (DC)		
		1	4.290		
		2	4.289		
		3	4.293		
		Average	4.291		
		StDEV	0.002		
		50% Hard Water, 50% HCl			
		Reading	V (DC)		
		1	4.294		
		2	4.301		
		3	4.309		
		Average	4.301		
		StDEV	0.008		
		75% HCl, 25% Hard Water			
		Reading	V (DC)		
		1	4.307		
		2	4.323		
		3	4.318		
		Average	4.316		
		StDEV	0.008		
5% HCl					
Reading	V (DC)				
1	4.330				
2	4.321				
3	4.333				
4	4.342				
Average	4.332				
StDEV	0.009				

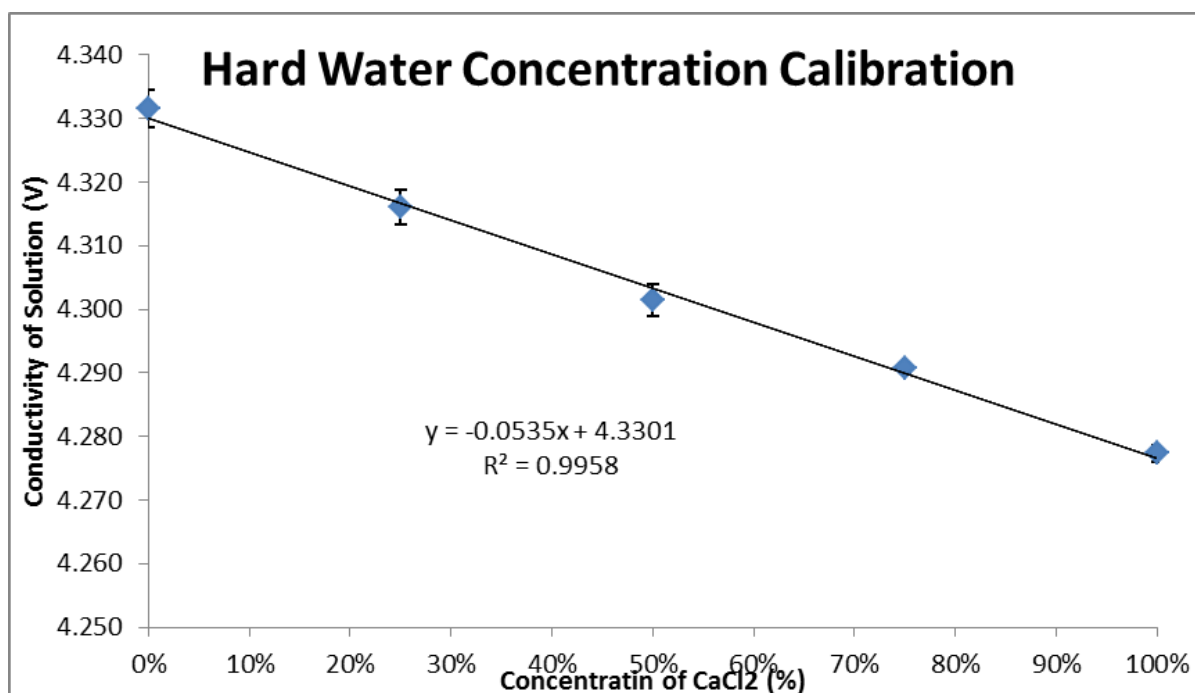


Figure 1: Conductivity data was collected at five different concentrations of Hard Water in solution with HCl. Each point on the graph represents the average of three conductivities. Standard errors are represented by error bars. This was all completed with solution at room temperature.

Appendix 4: Designing an Ion exchanger using Lab Data

Introduction:

There are currently two well-known approaches to designing an ion exchange column using lab data. They are the kinetic approach and the scaled approach. The kinetic approach has a particular advantage, the breakthrough volume of the scaled column can be chosen rather than found. The scaled approach on the other hand uses a ratio of the breakthrough volume and the volume of resin. For this reason, the scaled approach allows less room for design and is a more symmetrical design. Nevertheless, both are accepted as options in design.

During the creation of the lab, the water softener was run three times to collect data. The averages of the concentration at each time were used to scale. The following paper is the results of the column design in both methods. Instructions and comments were put throughout to help with steps along the way.

Kinetic Approach:

The Thomas Kinetic Equation is a widely accepted way to model Ion Exchangers⁷. The following equation is the overriding kinetics of the system:

$$\frac{C}{C_o} = \frac{1}{(1 + E \frac{k_1}{Q} (q_o M - C_o V))}$$

C = effluent concentration

C_o = influent concentration

k_1 = rate constant

q_o = maximum concentration of the sorbed solute

M = mass of the resin

V = volume of throughput

Q = flow rate of influent

Try linearizing the equation yourself for practice. After completing the linearization, it can be seen that this is an equation in typical, $y=mX+b$ form, where the X variable is the volumetric throughput of solution.

$$\ln\left(\frac{C_o}{C} - 1\right) = \frac{k_1 q_o M}{Q} - \frac{k_1 C_o}{Q} V$$

Step 1: Using the Data collected in Lab, create the following table:

V (L)	C (mg/L)	C _o /C	C _o /C-1	Ln(C _o /C - 1)
-------	----------	-------------------	---------------------	----------------------------

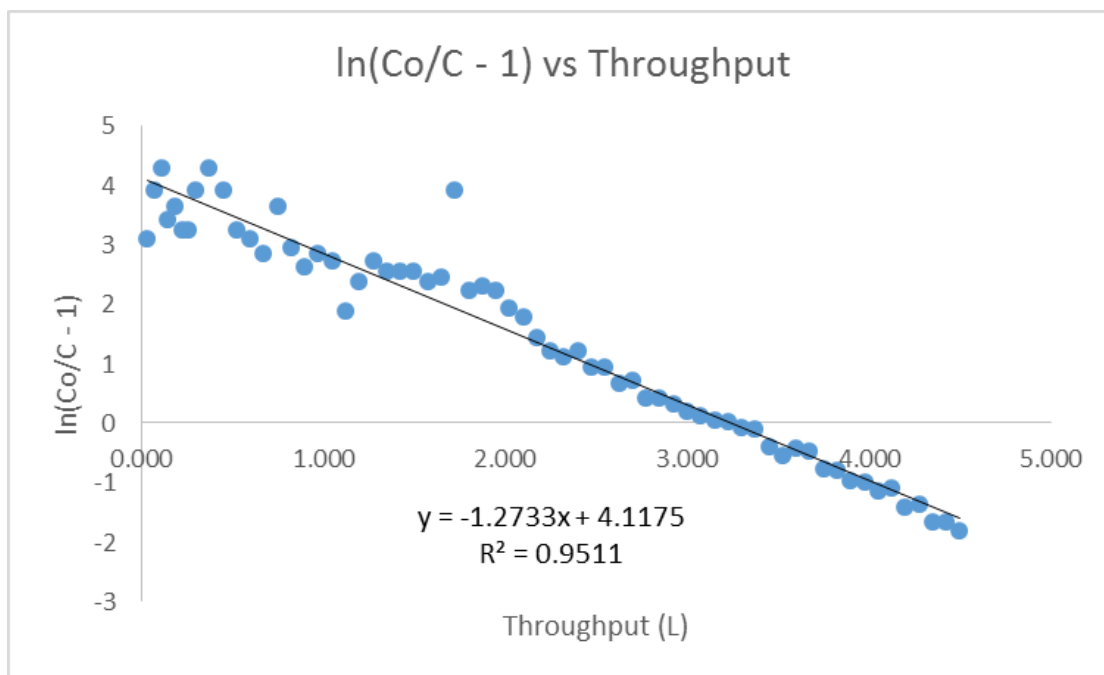
Using the data collected during preliminary work, here are the results. Note that only the first half of the data is shown to save space.

Throughput (L)	C (mg/L)	C/Co	Co/C	Co/C - 1	ln(Co/C - 1)
0.04	487	0.04	22.80	21.80	3.08
0.08	220	0.02	50.45	49.45	3.90
0.11	153	0.01	72.38	71.38	4.27
0.15	353	0.03	31.41	30.41	3.41
0.19	287	0.03	38.71	37.71	3.63
0.23	420	0.04	26.42	25.42	3.24
0.26	420	0.04	26.42	25.42	3.24
0.30	220	0.02	50.45	49.45	3.90
0.38	153	0.01	72.38	71.38	4.27
0.45	220	0.02	50.45	49.45	3.90
0.53	420	0.04	26.42	25.42	3.24
0.60	487	0.04	22.80	21.80	3.08
0.68	620	0.06	17.90	16.90	2.83
0.75	287	0.03	38.71	37.71	3.63
0.83	553	0.05	20.06	19.06	2.95
0.90	753	0.07	14.73	13.73	2.62
0.98	620	0.06	17.90	16.90	2.83
1.05	687	0.06	16.16	15.16	2.72
1.13	1487	0.13	7.47	6.47	1.87
1.20	953	0.09	11.64	10.64	2.36
1.28	687	0.06	16.16	15.16	2.72
1.35	820	0.07	13.53	12.53	2.53
1.43	820	0.07	13.53	12.53	2.53
1.50	820	0.07	13.53	12.53	2.53
1.58	953	0.09	11.64	10.64	2.36
1.65	887	0.08	12.52	11.52	2.44
1.73	220	0.02	50.45	49.45	3.90
1.80	1087	0.10	10.21	9.21	2.22
1.88	1020	0.09	10.88	9.88	2.29
1.95	1087	0.10	10.21	9.21	2.22
2.03	1420	0.13	7.82	6.82	1.92
2.10	1620	0.15	6.85	5.85	1.77
2.18	2153	0.19	5.15	4.15	1.42
2.25	2553	0.23	4.35	3.35	1.21

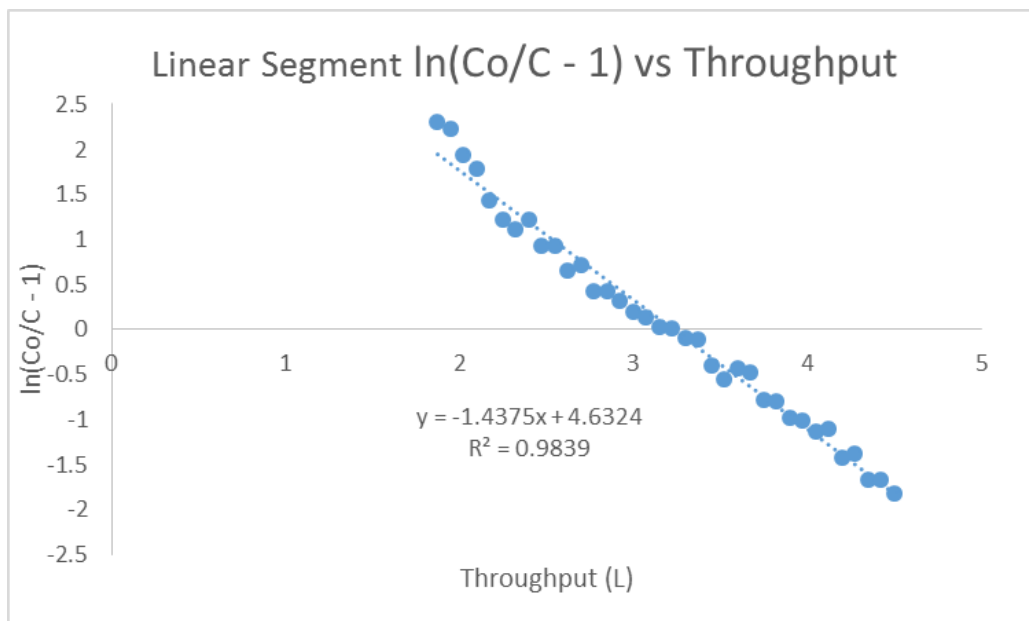
Step 2: Find the regression line

As shown earlier, we are looking to linearize the data in order to find the kinetics of the system. This step is completed in two parts. First, all the data is graphed. Second, the linear part is re-graphed to find regression. Why is it important to narrow in to the more linearized part?

A) Graph $\ln(C_0/C - 1)$ vs throughput.



B) Identify where the graph is linear.



Step 3: Solve for k_1 and q_o

Now would be an opportune time to go over the knowns for the lab scale system. Let us answer a few questions; the answers will be based on the preliminary experiments.

What was your influent concentration? The hard water was 11098 mg/L.

What was the mass of your resin? By looking at the spec sheet for the resin, you find the density is 1.28 g/cm³.

What was your influent flow? My pump level was set to 1.5, so 75 mL/min.

$$1.4375 (L^{-1}) = \frac{k_1 C_o}{Q}$$

$$k_1 = \frac{1.4375 (L^{-1}) * 4.5 (\frac{L}{hr})}{11098 (\frac{mg}{L})} * \frac{10^6}{3600} = 0.162 \frac{L}{kg * s}$$

$$4.6324 = \frac{k_1 q_o M}{Q}$$

$$q_o = \frac{4.6324 * 4.5 (\frac{L}{hr})}{0.162 (\frac{L}{kg * s}) * 0.160 (kg)} = 0.224 \frac{kg}{kg}$$

Step 4: Begin the scaleup

For the system being scaled, the flow rate it needs to handle is 630 L/hr. This is based on an average family using 400 gal/day of water. The water softener that needs to handle this capacity is in an apartment building with 10 apartments. Each apartment shares the one water softener. The breakthrough volume was chosen to be about 15000 liters; this would allow the system to be regenerated once a day.

M is the mass of the resin needed.

$$M = \frac{630 (\frac{L}{hr})}{0.162 (\frac{L}{kg * s}) * 0.224 (\frac{kg}{kg})} \left(\ln \left(\frac{11098}{555} - 1 \right) + \frac{0.162 (\frac{L}{kg * s}) * 11098 (\frac{mg}{L}) * 15000 (L)}{630 (\frac{L}{hr})} \right)$$

$$M=759 \text{ kg}$$

Using the density Find the volume:

$$V=0.59 \text{ m}^3$$

The ratio of the lab column is the diameter is $1/24^{\text{th}}$ of the Height. Using this ratio and the equation for the volume of a cylinder.

$$H= 7.62 \text{ m}$$

$$D= 0.315 \text{ m}$$

The breakthrough time is found:

$$t_b = \frac{15000 (L)}{630 (\frac{L}{hr})} = 24 \text{ hours}$$

The breakthrough time proves the design plan works. After 24 hours the breakthrough occurs, allowing the system to be regenerated once a day.

Scale Up Approach:

Assume the designed flow in lab scale was 1.5 BV/hr. The actual system ran at 36 BV/hr in order to speed up the process while still allowing the exchange to take place. A typical flow is about 1-3 BV/hr; however, this was not done because breakthrough and exhaustion would not occur in the standard 3 hour lab period. The design for both lab scale flows are included in order to show the difference in systems.

For 1.5 BV/hr:

Step 1: Find the Scaled Bed Volume

$$1.5 \frac{BV}{hr} = 630 \frac{L}{hr} \rightarrow \rightarrow BV = 420 L$$

Step 2: Find the volume of the resin exhausted per hour.

This step uses the breakthrough curve found in lab. Find the throughput volume at which the breakthrough occurred, 825 mL for preliminary testing. Then recall that the column used 125 mL of resin.

$$\text{Solution Treated per mL of resin: } \frac{825 \text{ (mL solution)}}{125 \text{ (mL resin)}} = 6.6 \frac{\text{mL solution}}{\text{mL resin}}$$

$$\text{Exhausted resin per hour: } V_t = \frac{630 \frac{\text{L solution}}{\text{hr}}}{6.6 \frac{\text{L solution}}{\text{L resin}}} = 95 \frac{\text{L resin}}{\text{hr}} \text{ exhausted}$$

Step 3: Breakthrough Time

$$t_b = \frac{V_{\text{column}}}{V_t} = \frac{420 \text{ L}}{95 \frac{\text{L}}{\text{hr}}} = 4.4 \text{ hours}$$

Step 4: Breakthrough Volume

$$V_B = t_b * Q = 4.4 \text{ (hr)} * 630 \left(\frac{\text{L}}{\text{hr}} \right) = 2772 \text{ L}$$

For 36 BV/hr:

Step 1: Find the Scaled Bed Volume

$$36 \frac{\text{BV}}{\text{hr}} = 630 \frac{\text{L}}{\text{hr}} \rightarrow \rightarrow \text{BV} = 17.5 \text{ L}$$

Step 2: Find the Resin exhausted per hour (note this step is the same for both systems)

$$\text{Solution Treated per mL of resin: } \frac{825 \text{ (mL solution)}}{125 \text{ (mL resin)}} = 6.6 \frac{\text{mL solution}}{\text{mL resin}}$$

$$\text{Exhausted resin per hour: } V_t = \frac{630 \frac{\text{L solution}}{\text{hr}}}{6.6 \frac{\text{L solution}}{\text{L resin}}} = 95 \frac{\text{L resin}}{\text{hr}} \text{ exhausted}$$

Step 3: Breakthrough Time

$$t_b = \frac{V_{\text{column}}}{V_t} = \frac{17.5 \text{ L}}{95 \frac{\text{L}}{\text{hr}}} = 0.18 \text{ hours}$$

Step 4: Breakthrough Volume

$$V_B = t_b * Q = 0.18 \text{ (hr)} * 630 \left(\frac{\text{L}}{\text{hr}} \right) = 115.5 \text{ L}$$

Discussion of Results

At this time, it is important to note some key differences between the two approaches. For the scaled approach, there is a number that represents “Based on the lab data, we can treat this much water per the amount of resin we had in the column”. The 6.6 mL solution/mL resin, step 2, is used no matter what BV/hr flow is used. No matter what volume of column or flow is chosen in design, it will all depend on that 6.6. That is why it is important in design to choose the flow based on a scale. In lab, a BV/hr was used for lab and another would have been assumed for industry. These two different numbers would still be affected by the 6.6 factor.

The other key figure in the scaled approach is, as the BV/hr increases, the volume of the actual bed stays the same. When designing a column first came into question, multiple examples and practice problems were perused and normally the flow rate was higher than 630 L/hr, most were in the thousands. During calculations, no matter how the flow increased, the BV was based on the lab scaled flow. Therefore, the breakthrough time was consistently the same. The lack of change is why, as mentioned above, it is important to know what the flow should be in full scale, before designing the lab testing.

An explanation of why the kinetic data and scaled approach are so different was difficult to find. In most homework and book problem examples, the results are similar. The difference comes from the testing described. The first approach is based on the kinetics of the system. The kinetics take into account all changes of the system, rather than just where the breakthrough occurs. The scaled approach uses the BV/hr flow and the breakthrough volume. During testing, the BV/hr was scaled to allow breakthrough to occur in about an hour, rather than a typical 12-48 hour process. Based on iterations, in order to have near the same results for both approaches, the BV/hr flow must be about 0.28 BV/hr. Using the 0.28 BV/hr flow will keep the 6.6 Lresin/hr from affecting the system as much and allow a breakthrough time of 23.5 hours and a

breakthrough volume of 14850. These numbers would be relatively close to the kinetic approach result.

For most testing, the kinetic approach for design seems to be more optimal. It is the more popular approach and allows the designer to choose the regeneration time and breakthrough volume after testing.

Here's a food for thought, "How would changing the flow rate and temperature of the influent affect the design of your column"?

Design Software:

At this point in your chemical engineering education, you have been introduced to certain modeling software. ChemCad and Aspen are two of the more popular modeling software's in design. ChemCad is used in Process Design helps to model the whole project. Ion Exchangers are modeled as a "black box" in ChemCad. When saying, "Black Box" that refers to, no actual calculation is done. The component separator UnitOp will split the stream with whatever information was inputted. For example, a molecular sieve removes 98% of the ethanol in a solution. The separator would be told that 98% of the ethanol went out one stream and everything else exited the other stream. The same thing could be done using an ion exchanger, except as the resin removes Ca^{2+} it replaces it with another ion. That other ion is not modeled and must be added back to a stream through a mixing point.

Another possible option, using ChemCad, is a VBA UnitOp. Using excel, a VBA routine is programmed to calculate the ion exchange using some lab data. During the simulation, the ChemCad exchanger pulls VBA code from Excel to calculate the split of the influent and solves for the stream. This allows for more design but is much harder to program. The final way to model an ion exchanger in ChemCad is to add an Excel Data Map. This puts actual excel cells in a UnitOp to be used. Data mapping through excel is difficult and takes really understanding each aspect of the ChemCad data. The help manual goes over the basics.

Aspen also does not have an actual Ion Exchanger UnitOp. Most often a "ForTran" is programmed. Fortran is a subroutine run within the system. Multiple companies have adapted a fortran model to simulate ion exchanger beds. Aspen was outside of the scope of my knowledge, but the fortran programming guide is a good source for how to program it for ion exchangers.

The final possibility for software that utilizes ion exchange design is called CADIX (computer assisted design for ion exchange) created by DOW Chemical Solutions. CADIX allows for the modeling of all DOW resins. It allows for either type of regeneration as well as quality performance updates. The software is used very often in companies that utilize ion exchange. CADIX has three main goals: help to design/retrofit ion exchangers, predict plant performance, and compare/calculate economics of current systems.

Nestle Waters uses this technology and one of the key features is the stream selection. Most rivers and lakes are already in the stream selection with the analyzed components. Other water streams can be added to the extensive library. The operating manual gives an example for demineralization of water. It helps to show how the software is used. Another key feature is the economic comparison between options. As a design engineer, comparing cost opportunities is very important in making system recommendations. CADIX allows the opportunities to be compared against each other on one screen.

There is other software available. These three are just some of the most popular. They are all good building blocks when designing ion exchangers. CADIX is the most user friendly, while ChemCad and Aspen allow the integration into the whole system. Mostly they are a good starting point when using software to design an ion exchanger.

References:

- [1] "CADIX: A Practical Guide for Operating the Program." Dow Water Solutions. The DOW Chemical Company, 2012. Web. 30 Apr. 2016.
- [2] "Aspen Plus Steady State Simulation." Aspen Technology Inc, 1999. Web. 30 Apr. 2016.
- [3] "ChemCad Version 6: User Guide." Chemstations. Chemstations Incorporated, 2007. Web. 30 Apr. 2016.

Appendix 5: Safety Data Sheets – Anion Resin

Appendix 6: Safety Data Sheets – Cation Resin

Appendix 7: Safety Data Sheets – CaCl_2

Appendix 8: Safety Data Sheets – MgSO_4

Appendix 9: Safety Data Sheets –HCl

Appendix 10: Safety Data Sheets –NaOH

Appendix 11: Safety Data Sheets –EDTA

Appendix 12: Safety Data Sheets –pH 10 Buffer

Appendix 13: Safety Data Sheets – Eriochrome Black T