

7-3-2012

# Selective salt recovery from reverse osmosis concentrate using inter-stage ion exchange

Joshua E. Goldman

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**Selective Salt Recovery from Reverse Osmosis Concentrate  
Using Inter-stage Ion Exchange**

**BY**

**Joshua E. Goldman**

B.A., Anthropology, State University of New York at Stony Brook, 2000

M.S, Environmental Science, University of South Florida, 2007

DISSERTATION

Submitted in Partial Fulfillment of the  
Requirements for the Degree of  
**Doctor of Philosophy**  
**Engineering**

The University of New Mexico  
Albuquerque, New Mexico

**May, 2012**

## **DEDICATION**

This dissertation is dedicated to the loving memory of my grandmother, Henriette Stein.

## ACKNOWLEDGMENTS

This project was funded by the WateReuse Research Foundation. Resins were donated by ResinTech and Purolite. Francis Boodoo of ResinTech provided technical consultation for the pilot design. CDM wrote the Salt Market Analysis and helped with pilot operations. Robert Fowlie of CDM was responsible for the Salt Market Analysis and Doug Brown, Tim Rynders, and Chris Stillwell helped with pilot operations. Angela Montoya of the University of New Mexico, wrote the MATLAB model code, and Lana Mitchell assisted with laboratory analyses.

I offer my sincerest gratitude to the following individuals.

To my adviser, Dr. Kerry Howe, I thank you so much for mentoring me over the last five years and for the many hours you spent working on this project with me. Your guidance made this project possible.

I would also like to thank my committee member, Dr. Bruce Thomson, for always having his office door open for questions and for providing his critical comments.

It was only with the encouragement of Dr. Jeff Cunningham, of the University of South Florida, that I gained the confidence to pursue this degree. Thank you, Jeff, for believing in me.

I am deeply grateful for the unwavering support of my family. Thank you for being there for me through everything. It is impossible to express the extent of my gratitude. I love you all so much.

And finally, to my partner, Gabe Torres, thank you for the patience you have shown over the last two years. Your love sustained me.

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**ABSTRACT**

A treatment process for reverse osmosis concentrate was developed to recover selected salts and increase fresh water recovery. The process utilizes cation and anion exchange to exchange all ions in the concentrate stream for sodium and chloride. The sodium chloride stream, with reduced scaling potential, can be treated further by a second reverse osmosis stage or another volume reduction technique to recover additional fresh water. The resulting concentrated sodium chloride stream can be used as ion exchange regeneration solution. Regeneration solutions from the cation and anion exchange columns are mixed to precipitate specific salts. In order to demonstrate the concepts behind this process, several phases of research were conducted. First, ion exchange batch isotherms were measured to characterize resin selectivity under ionic strength conditions common to reverse osmosis concentrate. A mathematical model was developed in which these isotherms were used to predict breakthrough curves. Regressions relationships developed from the batch tests were used in conjunction with the model to predict the number of bed volumes to breakthrough of

calcium, magnesium, and sulfate. Model and regression relationships were verified by a series of column experiments. Attempts to separate ions during the regeneration process were not successful. Ion distribution within a loaded column was characterized using a specially designed column from which resin samples could be taken along the longitudinal axis. Third, simulated cation and anion regeneration solutions were combined to precipitate selected salts which were analyzed to determine their constituents. Finally, the process was tested with a continuously operated pilot scale system. Mixing of simulated and pilot generated cation and anion regeneration solutions resulted in precipitation of calcium sulfate when mixed at pH below 4.5 and mixed carbonate salts when pH was not adjusted. The pilot system can produce 12 kg of precipitate per cubic meter of regeneration solution and recover approximately 45% of the calcium and 28% of the sulfate.

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# **CHAPTER 1**

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## **1.1 INTRODUCTION**

Across the United States and the world, the issue of water scarcity is gaining importance as communities struggle to provide water to their constituents. The Reverse Osmosis (RO) treatment process removes dissolved salts from water, producing drinking water from sources that cannot be treated conventionally. However, it is more wasteful than conventional treatment and can only recover 50 % to 75% of the water diverted to the treatment process. RO concentrate, as the waste volume is called, is difficult to treat or dispose of because it contains high concentrations of dissolved salts. The National Research Council identified concentrate management as an area in which significant research is needed [1]. As water demand increases for limited water resources, RO treatment will become more widespread, especially in arid areas where water resources are already scarce.

Regulatory and economic constraints to traditional concentrate disposal methods are driving research on alternate concentrate management strategies. This dissertation describes development of a treatment process for RO concentrate to recover salts for beneficial reuse and increase water recovery.

### **1.11 Background**

The principle behind the RO process is that salt water and fresh water are separated by a membrane that is more permeable to water than it is to salts. In a non-pressurized system, fresh water would diffuse into the salt water solution. In the RO process, pressure is applied to the salt water side of the membrane, overcoming the osmotic pressure and forcing water through the membrane to the fresh water side. As a result, the salt water becomes saltier and fresh water is recovered.

There are two main limitations to the RO process that limit recovery. First, as the salt concentration in the RO feed water increases, more pressure is required to push fresh water through the membrane. A mechanical limit exists at approximately 1200psi above which the pressure differential will damage the membrane. This limit is significant in

seawater applications in which feed water salt concentrations can reach 35,000 mg/L. The second factor which limits is the scaling potential. As freshwater is recovered from the feed water, the salt concentration in the concentrate increases. Scaling occurs when mineral deposits form on the membrane surface as salts reach their solubility limit. Recoveries from hard and brackish water applications are typically around 75%.

Concentrate management is a major challenge in the RO process. A seawater RO (SWRO) facility may be able to discharge the concentrate stream into the ocean, but inland brackish water RO (BWRO) facilities must use alternative disposal options. Traditional concentrate disposal methods include discharge to surface water, evaporation, discharge to waste water treatment plants, and deep well injection[2]. High costs are driving municipalities to look for better options such as the recovery of salts for beneficial reuse. The sale of such products may subsidize the RO process. Additionally, the reduction in fouling potential allows water to be treated further by RO or another process, resulting in increased water recovery.

## **1.12 Objectives**

The goal of this project was to develop a complete treatment train for RO concentrate using sequential ion exchange and chemical precipitation in order to recover selected salts for beneficial reuse and increase water recovery.

The overall goal of the project has been met through focus on the following specific objectives:

- The effect of ionic strength and ion proportions on resin selectivity was examined because RO concentrate has higher ionic strength than waters typically treated by ion exchange.
- A computer model using MATLAB was developed to simulate ion distribution in an ion exchange column based on separation factors found in the resin selectivity investigation. Visual MINTEQ was used to calculate saturation indices in mixed cation and anion regeneration solutions.
- The spatial distribution of ions in an ion exchange column was characterized by analysis of resin along the length of an exhausted column.

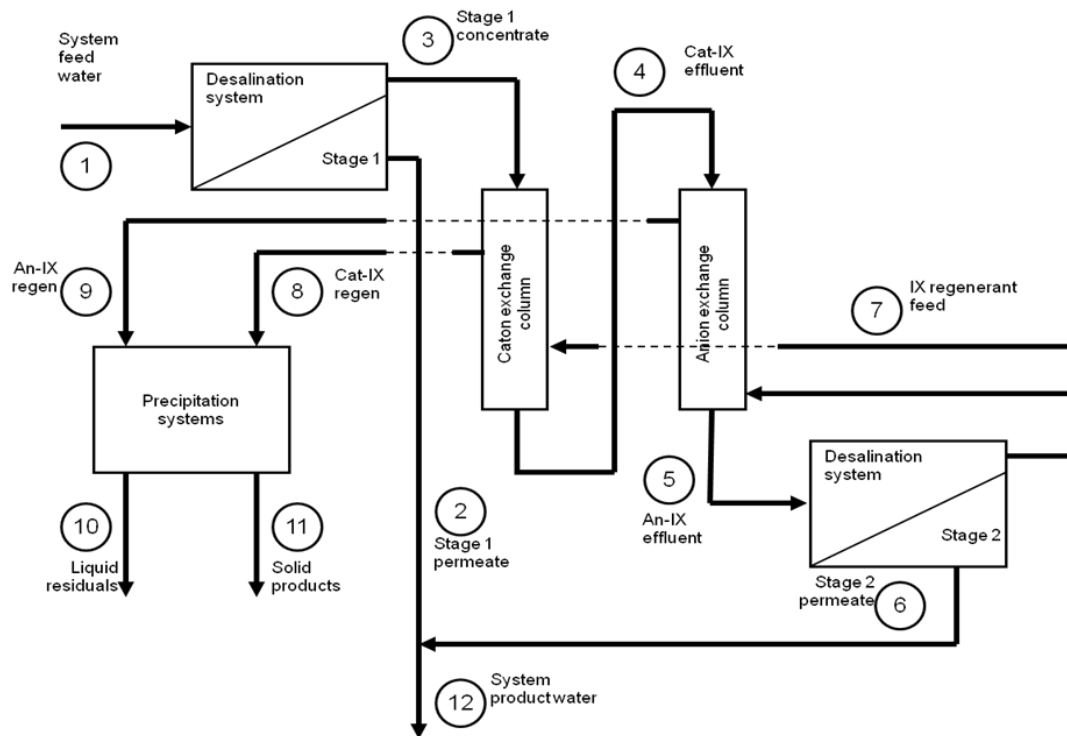
- Selected salts with potential resale value or recyclability were recovered by precipitation from mixed regeneration solutions from ion exchange columns.
- Sodium chloride solution produced by sequential ion exchange and passed through a second RO stage was recycled for use as ion exchange regeneration solution. Use of this second stage RO concentrate was evaluated for its effectiveness as ion exchange regeneration solution.

In addition, project partner CDM, Inc. evaluated the national salt market to determine the feasibility of marketing recovered salts in the different regions of the United States.

### 1.13 Proposed Treatment

The fundamentals of the treatment train outlined in Figure 1 were verified experimentally by this research, and the entire process was evaluated by pilot scale testing.

Figure 1: Proposed RO Concentrate Treatment Train



Each of the unit processes in the proposed treatment train is in widespread use in water treatment, but the particular sequence and suggested operation is novel. This study investigated sequential ion exchange to remove all cations and anions from an RO concentrate stream and replace them with sodium and chloride. The benefit of ion replacement is that sodium and chloride are highly soluble, so the concentrated sodium chloride effluent solution can more easily pass through some form of volume reduction using RO, membrane distillation, or another relevant process to produce more potable water. The resulting brine solution may be concentrated enough to be used as regeneration solution. As the ion exchange columns are regenerated, they will release the cations and anions from the resin phase, resulting in a concentrated solution of cations and chloride from one column and a concentrated solution of anions with sodium from the other column. Depending on the constituents, it may be possible to recover valuable salts with commercial by combining these solutions.

To determine the feasibility of the process, a mass balance was performed to calculate the likely sodium chloride concentration of the Stage 2 RO concentrate for use as ion exchange regeneration solution. Table 1 lists the input parameters for the RO stages. The model assumes that cations and anions listed in Table 2 are present in the feed water. Their concentrations are meant to be representative of a brackish groundwater. Preliminary experiments showed that a 10% sodium chloride solution will effectively regenerate a cation exchange column. The sodium chloride concentration in the ion exchange effluent is a function of the initial feed water ion concentrations. If calcium and magnesium are present at 200 mg/L and 100 mg/L respectively, in the initial feed water, the initial sodium concentration must be greater than or equal to 580 mg/L in order to produce brine that can be further treated to produce usable ion exchange regeneration solution without further salt addition. Table 3 shows the water flow and ion concentrations at each stage of the process. The process numbers correspond to those in Figure 1.



**Table 1: RO Parameters**

Stage 1 recovery	0.75
Stage 1 rejection	0.99
Stage 2 recovery	0.9
Stage 2 rejection	0.99

**Table 2: Cations and Anions in Feed Water**

Ion	Sodium	Calcium	Magnesium	Chloride	Sulfate	Carbonate
Concentration (mg/L)	580	200	100	894	479	247

**Table 3: Salt Balance**

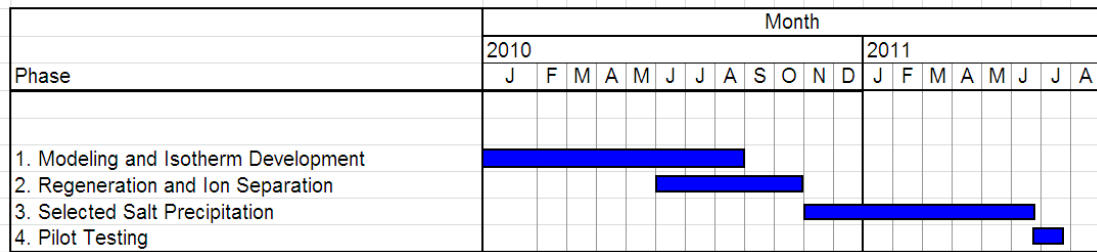
Cations		Water Flow	Sodium Conc.	Calcium Conc.	Magnesium Conc.
Flow	Description	(m3/d)	(meq/L)	(meq/L)	(meq/L)
1	System feed	1000.00	25.23	9.98	8.23
2	Stage 1 permeate	750.00	0.25	0.10	0.08
3	Stage 1 concentrate	250.00	100.16	39.62	32.67
4	Cat-IX effluent	250.00	172.45	0.00	0.00
5	An-IX effluent	250.00	172.45	0.00	0.00
6	Stage 2 permeate	225.00	1.72	0.00	0.00
7	IX regeneration feed	25.00	1709.00	0.00	0.00
8	Cat-IX regen waste	12.50	263.09	792.42	653.50
9	An-IX regen waste	12.50	1709.00	0.00	0.00
10	Liquid residuals	25.00	850.30	24.00	21.00
11	Solid products	0.00	--	--	--
12	System product water	975.00	0.59	0.08	0.06
Anions		Water Flow	Chloride Conc.	Sulfate Conc.	Carbonate Conc.
Flow	Description	(m3/d)	(meq/L)	(meq/L)	(meq/L)
1	System feed	1000.00	25.23	9.98	8.23
2	Stage 1 permeate	750.00	0.25	0.10	0.08
3	Stage 1 concentrate	250.00	100.16	39.62	32.67
4	Cat-IX effluent	250.00	100.16	39.62	32.67
5	An-IX effluent	250.00	172.45	0.00	0.00

6	Stage 2 permeate	225.00	1.72	0.00	0.00
7	IX regeneration feed	25.00	1714.46	0.00	0.00
8	Cat-IX regen waste	12.50	1714.46	0.00	0.00
9	An-IX regen waste	12.50	268.54	792.42	653.50
10	Liquid residuals	25.00	852.70	244.00	2.00
11	Solid products	0.00	--	--	--
12	System product water	975.00	0.59	0.08	0.06

This project investigated the use of sequential cation and anion exchange followed by chemical precipitation to recover selected salts from RO concentrate. The following section provides a background on these technologies and discusses their potential for this usage.

The experimental methods and results for this research are divided into four phases, and each is presented as a separate chapter. Chapter 2 describes a mathematical model developed to describe column loading based on resin selectivity and influent ion concentrations. Chapter 3 describes batch isotherm tests done to characterize ion exchange resin selectivity with changing ionic strength and ionic ratio to determine its feasibility for use in treatment of reverse osmosis concentrate. Regressions relationships were developed for separation factor as a function of ionic strength and equivalent fraction of exchanging ion. Chapter 4 presents the results of column testing to verify the regression developed in Chapter 3 and to verify the model described in Chapter 2. It also reports on column tests to separate resin phase ions chromatographically during regeneration and to characterize the distribution of ions within a loaded ion exchange column. Chapter 5 presents the results of experiments designed to precipitate selected salts from laboratory simulated mixed regeneration solutions from cation and anion exchange columns. Chapter 6 is a report on pilot scale testing of the proposed process. The pilot testing was conducted in conjunction with CDM at a water treatment facility operated by East Cherry Creek Valley Water and Sanitation District located in Brighton, CO. The experimental work was completed according the time table in Figure 2. All experimental work and analysis was performed at the UNM environmental engineering laboratories excepting the pilot. Ion exchange resins were donated by ResinTech<sup>®</sup> and Purolite (see Table 4).

**Figure 2: Research Schedule**



**Table 4: Resin Characteristics**

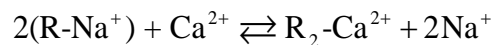
Name	Manufacturer	Type	Important Properties
CG-10	ResinTech	Strong Acid Cation	high capacity, gelular, sulfonated
SBG-1	ResinTech	Strong Base Anion	high capacity, gelular, type 1
SST65	Purolite	Strong Acid Cation	Gel polystyrene cross-linked with divinylbenzene, sulfonated
A850	Purolite	Strong Base Anion	Gel Polyacrylic crosslinked with divinylbenzene, quaternary Ammonium function groups

## 1.2 LITERATURE REVIEW

### 1.21 Ion Exchange

Synthetic ion exchange resins have been engineered specifically for water treatment since the 1950s. These resins contain charged functional groups on their surfaces which attract oppositely charged “counter-ions” from a solution. The functional groups on the resin are pre-saturated by contact with a solution containing a high concentration of ions that have relatively low affinity for the resin. Ion exchange occurs when “counter-ions” in a solution displace the ions on the resin [3-6]. This is shown in Equation 1 where R indicates an active site on the resin.

**Equation 1: Ion Exchange Reaction**



When all exchange sites are filled to capacity, an ion exchange resin can be “regenerated” by immersion in a highly concentrated acid, base, or salt solution. During regeneration, counter-ions removed from the treated solution are displaced by the presaturant ion in the concentrated solution.

There are four categories of synthetic resins which are distinguished by the types of functional groups on the resin surface. Strong acid cation (SAC) resins usually contain sulfonate groups which exchange over a large pH range while weak acid cation resins tend to contain carboxylic groups which only exchange within a limited pH range [5]. Weak acid resins can be regenerated by a less concentrated solution than strong acid resins [5]. Strong base anion resins often contain quaternary amine groups which exchange over a large pH range while weak base anion resins contain tertiary amine groups that exchange over a limited pH range. The tertiary amine groups act as Lewis bases. In solution, they release a hydroxide and take up another anion in its place. Strong base anion resins are not as stable as strong acid resins and are often characterized by a fishy odor [5]. Ion exchange resin particles have diameters ranging from .04-1.0 mm, and their uniformity coefficient usually lies between 1.4 and 1.6 [5].

### **1.211 Selectivity**

The affinity for a particular ion by a particular resin can be described mechanistically or operationally. The operational description of ion affinity is called the separation factor and is represented by the Greek character,  $\alpha$ . The separation factor is described by Equation 2, which is based on solution and resin phase concentrations [4]. Rational ionic fractions in each phase can also be used to calculate this factor. The separation factor is simply a ratio between phase distribution coefficients for the two ions in question. It does not account for any other variables in a system such as ionic strength or ionic ratio and is therefore system specific. It is generally used in practical applications in which solution characteristics are unlikely to change. The selectivity coefficient (Equation 4), on the other hand, is used to quantify selectivity based on the mass action law. It is the equilibrium constant of a mass action equation describing an ion exchange reaction (Equation 3) [4]. Because the selectivity coefficient is based on a

chemical equation, in principle it has a thermodynamic significance and can represent equilibria at high ionic strength.

For systems in which ions of the same valence are being exchanged, the separation factor and the selectivity coefficient are identical. In systems in which the valences of the exchange ions are different, Equation 5 can be used to convert between the two.

<b>Equation 2: Separation Factor, <math>\alpha</math> (Equivalent based)</b>	$\alpha_A^B = \frac{(X_B)_r \times (X_A)_s}{(X_A)_r \times (X_B)_s}$
<b>Equation 3: Ion Exchange Chemical Reaction</b>	$z_B RA^{z_A} + z_A B^{z_B} \rightarrow z_A RB^{z_B} + z_B A^{z_A}$
<b>Equation 4: Selectivity Coefficient</b>	$K_A^B = \frac{[RB^{z_B}]^{z_A} [A^{z_A}]^{z_B}}{[B^{z_B}]^{z_A} [RA^{z_A}]^{z_B}}$
<b>Equation 5: Conversion Between Separation Factor and Selectivity Coefficient</b>	$(\alpha_A^B)^{z_B} = K_A^B \left( \frac{[RB^{z_B}]}{[B^{z_B}]} \right)^{z_B - z_A}$

Ion exchange resin selectivity is complicated by its dependence on several parameters, but there are some general trends that can be recognized. Resins tend to have more affinity for ions with greater charge due to increased electrostatic attraction. For ions of equal charge, ions with a smaller hydrated radius are preferred. Hydrated radius is dependent on the size to charge ratio of the ion. Larger ions have a greater surface area over which to distribute charge density which reduces the field strength. For this reason, they do not coordinate with water molecules as strongly as ions with smaller size to charge ratios, which tend to have larger relative hydrated radii [5, 7]. This physical explanation fits well with thermodynamic data from Marton [8] showing the dependence of parameters  $g_0$  and  $g_1$  (which affect resin phase molar excess free energies) from Equation 9.

The effect of ionic strength on selectivity can be difficult to predict due to competing processes. When higher concentrations of ions exist in solution, neutral

complexes can form, reducing the concentration of ions free to interact. Charged complexes may also form which could have the effect of increasing or decreasing interactions with the resin, depending on the charge. Increased ionic strength also has the effect of reducing double layer length, requiring ions to move closer to reactants in order to interact. If water activity becomes very low, ions may not be able to form a full hydration shell, reducing the size of the hydrated radii. The combined outcome of all these effects is that high ionic strength selectivity is difficult to model [4]. An extreme example is that which occurs during regeneration. Resin is contacted by a very high ionic strength solution containing monovalent lower selectivity ions. The activity of divalent and trivalent ions decreases more with ionic strength than monovalent ions, so the selectivity of the monovalent ion increases. This selectivity reversal combined with the overwhelming concentration of the monovalent ion reverses the direction of ion exchange.

Temperature has also been shown to increase ion exchange selectivity for calcium and magnesium over sodium. A study of real and laboratory simulated seawater exchange with two weak acid resins found a significant increase in calcium and magnesium selectivity as the temperature increased from 10°C to 80°C [9]. However, varying temperature is impractical for water treatment purposes.

Surface modification of ion exchange resins has been a popular area of research. Research indicates that modification of an anion exchange resin surface by addition of an anionic polyelectrolyte slows the rate of reaction with divalent ions in comparison to that of monovalent ions. This has an overall effect of increasing affinity for nitrate over sulfate. The change in selectivity was thought to be caused by size exclusion and electrostatic repulsion [10]. In another experiment, a cation exchange resin was modified by exposure to polyethyleneimine resulting in an increased affinity for heavy metals over alkaline metals. Researchers concluded that the change in selectivity was due to an increased chelating capacity by the modified resin which tended to favor ions that form complexes with an amine group [11]. Surface modifications tend to increase separation potential for ions with specific chemical properties such as bond formation with amines or physical properties such as molecular size but have not been developed to separate ions with similar properties such as calcium and magnesium.

## 1.212 Selectivity Modeling

The thermodynamic approach for predicting ion exchange selectivity is based on the fact that the change in Gibbs energy at equilibrium is equal to zero. Equation 6 shows the pertinent Gibbs energy calculation for a standard ion exchange reaction [8]. The terms in the equation are the chemical potentials of the ions in the solution and resin phases. These can be calculated for the solution phase using Equation 7 and for the resin phase using Equation 8 [8]. Resin phase partial molar excess free energies in Equation 8 can be calculated using the concentrated electrolyte solution model. Equation 9 describes the calculation of the excess Gibbs free energy of the whole system which is then used to calculate the partial molar free energies in a two-component system by Equation 10 and Equation 11. The thermodynamic model of selectivity described previously and other similar methods work well as approximations of selectivity of a resin, but they do not take into account the specific qualities of the resin such as the degree of cross-linking [12]. Depending on the method used, they may not account well for the low activity of ions in the solution and resin phases and the effects of different ionic ratios in solution. Other methods have been developed to deal with these parameters by including the swelling pressure due to high degrees of cross-linking and the low activity of water in highly concentrated solutions in the calculations [12, 13]. Marina et al, developed a model to predict selectivity based on the degree of cross-linking of the resin, the water activity of the solution, and the concentration ratio of the two counter-ions. He related these parameters to selectivity using Equation 12 where  $K_A^B$  is the selectivity coefficient with regards to ions B and A,  $K_A^{OB}$  is the thermodynamic constant of ion exchange,  $\bar{y}$  and  $y$  are the activity coefficients of the species in the resin and solution phases, respectively,  $\pi$  is the resin phase swelling pressure, and  $V$  is the partial molar volume. The activity coefficients are functions of water activity as shown by Equation 13 where  $a_w$  is the water activity and  $\sigma$  is the total concentration of dissolved species in solution. The water activity is a function of swelling pressure, as shown by Equation 14 where  $V_w$  is the partial molar volume of water and  $a_w$  and  $\bar{a}_w$  are the water activities in the solution and

resin phases, respectively. He found that water activity in the solution was an important parameter in controlling selectivity.

Equation 6: Gibbs Energy Calculation for Ion Exchange Reaction	$\Delta G^o = -RT \ln K^T = \bar{\mu}_B^o - z\bar{\mu}_A^o + z\mu_A^o - \mu_B^o$
Equation 7: Calculation of Chemical Potential for Ions in Solution Phase	$\mu_i = \mu_i^o + RT \ln a_i$
Equation 8: Calculation of Chemical Potential for Ions in Resin Phase	$\bar{\mu}_i = \bar{\mu}_i^o + RT \ln \bar{x}_i + \bar{\mu}_i^E$
Equation 9: Calculation of Excess Free Energy Change	$\Delta \bar{G}^E = -RT \bar{x}_A \bar{x}_B \left[ g_o + g_1 (\bar{x}_A - \bar{x}_B) \right]$
Equation 10: Excess molar partial free energy of Ion A in Resin Phase	$\bar{\mu}_A^E = \Delta \bar{G}^E + (1 - \bar{x}_A) \left( \frac{\partial \Delta \bar{G}^E}{\partial \bar{x}_A} \right)_{T,I,\bar{x}_B}$
Equation 11: Excess molar partial free energy of Ion B in Resin Phase	$\frac{\bar{\mu}_B^E}{z} = \Delta \bar{G}^E + (\bar{x}_A) \left( \frac{\partial \Delta \bar{G}^E}{\partial \bar{x}_A} \right)_{T,I,\bar{x}_B}$
Equation 12: Selectivity Function from Marina	$K_A^B = K_A^{OB} \left[ \frac{(\bar{y}_{AR} \bar{y}_{BX})}{(\bar{y}_{BR} \bar{y}_{AX})} \right] \exp \left[ -\pi \left( \frac{\bar{V}_{BR} - \bar{V}_{AR}}{RT} \right) \right]$
Equation 13: Dependence of Activity Coefficient on Water Activity	$y = f \frac{(a_w)}{\sigma}$
Equation 14: Water Activity as a Function of Swelling Pressure	$\frac{\bar{a}_w}{a_w} = \exp \left( \frac{-\pi V_w}{RT} \right)$

In dilute solutions, activities are very similar to molar concentrations and may be assumed to be unity, but for higher ionic strength solutions, activity coefficients must be calculated using a model. The extended Debye-Huckel model can be used to predict activity coefficients for solution with ionic strength up to 0.1 M, and the Davies model can be used for solutions with ionic strength up to 0.5 M. Activity coefficients in



solutions with ionic strength greater than 0.5 M can be calculated using the specific interaction model which takes into account the interaction between ions in the solution [14]. The Bromley method also considers the interactions of all cations and anions in solution and can be used for solutions with ionic strength up to 6 mol/kg [15].

The calculation of resin phase activities can be performed using the Wilson model which was originally proposed in 1964 for liquid-vapor equilibrium but was first applied to resin phase activities in by Smith and Woodburn in 1978 and has since been used in many studies [16, 17]. This model requires binary interaction parameters to be known in order to calculate activities, and several methods have been developed over the years since then to determine them more accurately [16]. Melis, et al, proposed an entirely different approach by considering ion exchange as a phase equilibrium rather than a mass action law. In this model, the resin phase contains a statistical distribution of ideally behaving active sites with different adsorption energies. Adsorption at each site can be described by a simple Langmuir isotherm [18].

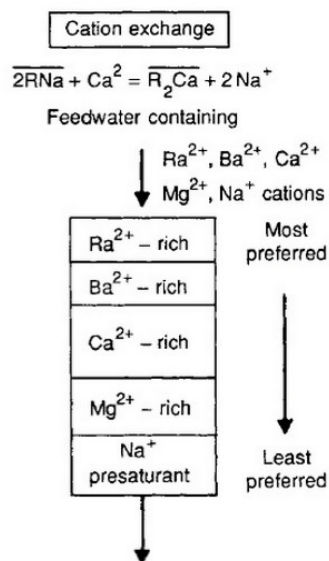
### **1.213 Column Processes**

The determination of selectivity properties for a particular resin is often done using batch reactor experiments, but most operational configurations utilize a column because of the increased efficiency it provides. Column processes can be thought of as series of batch reactors in which the solution continually encounters a fresh resin bed. This forces the equilibrium reaction in a favorable direction [3]. As the solution passes through the column, the resin in contact with the solution becomes exhausted. The mass transfer zone, the area in the column in which the exchange reaction is occurring at a specific time, moves through the column in the direction of flow until it exits the column at breakthrough. Process efficiency, as defined here, is the fraction of the column in equilibrium with the influent solution at the time of breakthrough. This fraction is determined by the length of the mass transfer zone. If hydrodynamics, column dimensions, and ion concentrations are held constant, the length of the mass transfer zone is primarily dependent on the selectivity of a particular ion. Consider the lengths of the mass transfer zones of a high and low selectivity ion moving through a column. A larger fraction of the high selectivity ion concentration will exchange to the resin in column

segment, resulting in a smaller fraction being passed to the next segment. Therefore, fewer reactors are required to completely remove the high selectivity ion compared to the lower selectivity ion [3]. Resin in which the mass transfer zone has already passed is completely exhausted for a particular ion, so long mass transfer zones result in poorer column efficiency [3, 6]. For an ion with infinitely high selectivity in a column in which diffusion and dispersion are neglected, the mass transfer zone would be infinitely small, which would result in a perfectly rectangular plug front. Dispersion and diffusion will cause curve broadening of the mass transfer zone [3].

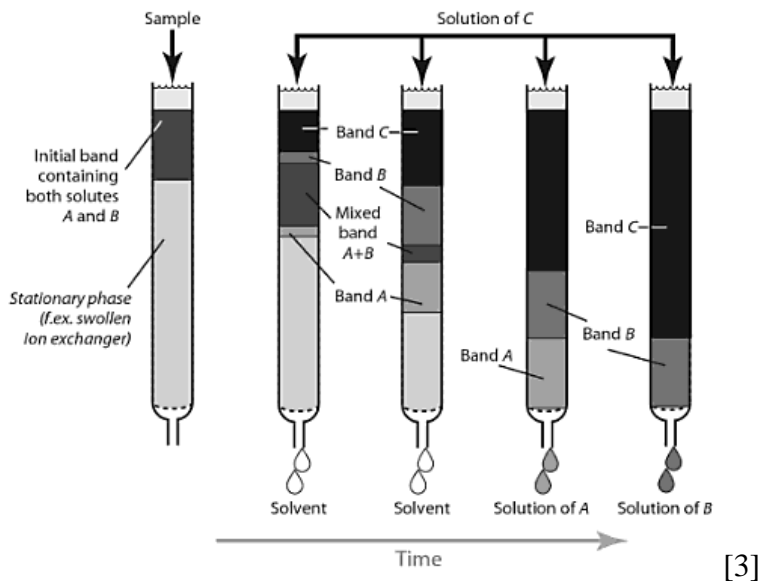
Due to differences in selectivity, ions move through ion exchange columns at different rates and have different shapes to their breakthrough curves [19]. The least selective ion is the first to exit the column at breakthrough [3]. Higher selectivity ions concentrate at the column inlet, and the result is a banding effect in which plugs of ions form in a column, in the direction of flow, according to selectivity sequence. In an infinitely long column, in which wave fronts have time to separate based on selectivity, the concentration profile of ions in the resin during loading would resemble Figure 3. Later on in the column process, the resin at the topmost portion of the column is in equilibrium with the influent solution, and the resin contains the equilibrium concentrations of ions predicted by the separation factor.

Figure 3: Ideal Resin Phase Concentration Profile from [17]



Ions are eluted from an exhausted column through one of two processes. Regeneration is done by flowing a concentrated acid, base, or salt solution through the column to drive all ions into the solution phase and out of the column. This process is used when the ions in the column are not intended for recovery. Elution is the process of removing ions of interest from the column [3]. A variety of solutions can be used to achieve this end, but they all are based on the process of exchanging ions in the solution phase for one or more ions in the resin phase. This can either be done with a concentrated solution or with a solution containing ions that are more highly selective than those on the resin. Figure 4 shows the loading and regeneration of ion exchange column. Note the ion banding effect and the displacement of the lower selectivity ions, A and B, by ion C.

Figure 4: Loading and Regeneration of an Ion Exchange Column



### 1.214 Modeling of Column Processes

The modeling of ion exchange processes in a column is a complex problem. In 1962, Helfferich [6] thought a rigorous solution to be hardly feasible. Over the intervening years, however, many column models have emerged. Column models can be divided into two main categories: equilibrium models and rate based models.

Equilibrium models assume that equilibrium is attained instantaneously between the resin and liquid phases as they come into contact. Column operation is modeled by dividing the column in segments which come into equilibrium in succession as the liquid moves through the column. This type of model may or may not consider the effects of advection. Equilibrium models have the advantage of simplicity, but the disadvantage is that the number of segments is an empirical quantity that cannot be predicted. The model must be calibrated to each set of specific column conditions [6]. Rate models take into account non-equilibrium conditions, making them much more mathematically intense [6]. They have the advantage of being able to be predicted from fundamental data and need no empirical correlation. Rate models account for diffusion rates as well as material balances and ion exchange equilibrium.

The model written by Wilson in 1986 is an equilibrium model that works by dividing the column into a number of theoretical plates [20]. As Wilson contends, there is no simple interpretation of the number of theoretical plates used. Each segment is assumed to be well mixed, and it is noted that numerical dispersion occurs that results in front broadening. A non-linear numerical solver was written to solve for concentrations in each segment based on concentration, selectivity, and electro-neutrality. Selectivity was assumed to be constant although Wilson noted that a function to solve for selectivity based on solution concentrations could be added later. Wilson noted that the relationship between the broadness of the front and the number of segments is such that decreasing front width by a factor of  $1/x$  requires increasing the number of segments by  $x^2$ . Increasing the number of segments also required the use of very small time segments, resulting in increased processing costs. In response to this problem, several simplified algorithms were developed to represent advection, and the required number of segments was decreased. By today processing standards, these modifications are not necessary, and equilibrium models such as this one can be run with many segments without excessive computer processing.

Computer processing costs are rarely considered to be a major factor in model development anymore. Modern modeling efforts are much more focused on accurate prediction based on fundamental data. Ostoski et al [15], developed a model for column processes including mass transfer kinetics. His model defined selectivity by the mass

action equation including activities. The activities in the solution phase were estimated using the Bromley [21] method and resin phase activities were estimated using the Wilson model [22]. The column was divided into equally sized elements in which a mass balance equation including bed density, interstitial velocity, axial dispersion mass transfer coefficient, total voidage, time and space was included. The equation also included mass transfer terms for the external liquid film and the inside of a particle of resin. Mass transfer was modeled as having two distinct parts, 1) the movement of ions from the bulk phase through liquid film and 2) the diffusion of ions into the micro-pores of the resin. The exchange reaction itself was considered to be instantaneous. The finite volume method was used to solve the mass balance equations. His results matched well to experimental data of ion exchange columns in which zinc was exchanged for sodium. He concluded that the initial stage of mass transfer is controlled mainly by film resistance but the overall mass transfer process is inter-particle resistance.

Nakamura [23] modeled a column containing a hydrogen-sodium-ammonia system. He defined selectivity in terms of molarity and divided the column in equal volume segments. In his model, total resin capacity and selectivity were determined as fitting parameters, and he found that the exchange rate depended on the overall liquid phase mass transfer coefficient and the surface area of particle. Film diffusion resistance was found to control the overall rate of mass transfer.

Another application of the mass action law to model of ion exchange in a fixed bed column was put forth by Borba et al [24]. This model considered thermodynamic equilibrium at the liquid-solid interface, the external mass transfer resistance and internal diffusion resistance (in series), and the concentration profile within pores described by linear driving force (LDF) to predict ion exchange capacity. The column was divided into equal volume segments and the following calculations were completed for each segment using the finite volume method: liquid phase mass balance, external film mass transfer, liquid phase charge balance, diffusion of species within particles, resin phase charge balance, and mass balance between external mass transfer and diffusion mass transfer. The Langmuir and the mass action law of equilibrium were compared to see which fit the data better, and both were found to fit the data well. A column model

general enough to predict performance over a wide range of solutions, resins, and geometries has not yet been developed.

## 1.22 Chemical Precipitation

The process of chemical precipitation involves adjusting the chemical and physical parameters of a solution to form solids from dissolved species. The chemical principles are well understood, and chemical precipitation has been used in water treatment for more than a hundred years. A familiar water treatment example is the use of lime softening, the removal of calcium carbonate by increasing solution pH to promote calcium carbonate precipitation. This was discovered in 1841 by Thomas Clark, a professor of Chemistry at Aberdeen University in Scotland. It was endorsed by the British Water Commission on Water Supply in 1869 and has been widely used in the United States since the 1940s. [25]

The equilibrium of dissolved ions in solution with a solid precipitate occurs when the Gibbs energy of reaction is equal to zero (see Equation 15). Relating equilibrium to Gibbs energy allows the solubility constant to be determined based upon thermodynamics rather than by empirical correlation. The solubility product (Equation 15) depends on temperature and is function of the enthalpy of the solubility reaction. The Ion Activity Product (IAP) (Equation 16) uses the activities of ions in the mass action equation and, when compared to the equilibrium constant, indicates the degree of saturation. The logarithm of the ratio of the IAP to the equilibrium constant is the Saturation Index (SI).

Equation 15: Solubility Constant	$\overline{\Delta G}_r = RT \ln(K_{SO})$
Equation 16: Ion Activity Product	$IAP = \{Cation\}\{Anion\}$ where $Cation + Anion \rightarrow Solid$
Equation 17: Saturation Index	$SI = \log\left(\frac{IAP}{K_{SO}}\right)$

If the SI is greater than zero, precipitation will occur [25]. Table 5 shows the  $pK_{SO}$  values of some common salt precipitates.

**Table 5: Solubility Constants for Common Precipitates**

Solid	pK <sub>SO</sub>
CaCO <sub>3</sub>	8.48
CaSO <sub>4</sub>	4.36
MgCO <sub>3</sub>	7.46
MgSO <sub>4</sub> ·7H <sub>2</sub> O	2.13

There are two cases for which the solubility of a mineral is a function of pH: 1) if one of the ions reacting to form the precipitate is H<sup>+</sup> or OH<sup>-</sup>, 2) if one of the ions is a weak acid or base, such as carbonate.

Precipitation may not occur instantaneously even if the SI indicates that a particular salt is supersaturated. The rate of precipitation depends on reaction kinetics, mass transfer, and available surface area for reaction. For crystals to form in suspension, small particles must exist in the suspension for crystals to grow around. Tiny crystals will eventually form spontaneously as ion concentrations increases, but this could occur at concentrations much above those specified by solubility constant. Providing tiny particles or crystals for this purpose is called seeding and is common practice in precipitation processes[26].

Complexes forming in solution may affect solubility. Complexes are dissolved species in waters consisting of a metal and a ligand. Ligands are ions or molecules that form bonds with the central metal atom. These bonds may be electrostatic, covalent, or other types such as van der Waals, dipole-dipole, etc. Metal ligand complexes also exist in equilibrium with the free ions and precipitated salt in the system[14]. The mass of ions contained in these complexes at equilibrium cannot be neglected when considering solubility.

### **1.221 Precipitation in Combination with RO**

Precipitation has been used in water treatment for more than a hundred years, but more recently, as RO treatment has become widespread, it has been optimized to pretreat water to limit membrane fouling. Membrane fouling generally takes one of four forms, depending on the nature of the foulant: colloidal, organic, biological, or scaling [27].

Scaling in RO is most commonly caused by the precipitation of sparingly soluble salts on the membrane surface. This occurs as the salts reach their solubility limit. Precipitation can be used in combination with RO to reduce scaling potential by removing the sparingly soluble salts from the water before it undergoes RO treatment.

Intermediate precipitation was proposed by Gabelich, et al (2007) as another way to increase RO recovery. In this process, precipitation of hardness ions is an intermediate step between two RO stages [28]. Precipitation was induced by pH adjustment only. Gabelich observed some interesting trends in this study. First, the presence of non-carbonate hardness resulted in lower calcium removal. Second, there was a high degree of mixed salt precipitate such as barium and strontium precipitating with calcium. Third, general cation removal increased with increasing pH [28]. Fourth, anti-scalants were required to prevent scaling in the secondary RO process.

The SAL-PROC™ system has been developed by Geo-Processors, Inc. over the last 15 years [29]. The goal of the process is to produce usable and possibly marketable salts and slurries from RO concentrate through accelerated precipitation. Many details of the process are proprietary, but it is reported to include heating, cooling, and chemical addition [29]. According to product literature, the process utilizes sequential concentration steps which may include further RO treatment or evaporation. The SAL-PROC™ process relies entirely on chemical precipitation to recovery salts. For this reason, pH control, temperature control, and chemical addition are essential to the process.

A study by Heijman in 2009 proposed a system combining precipitation with sedimentation, ion exchange, and nanofiltration to treat groundwater to zero liquid discharge. A cation exchanger was used to remove any hardness ions not removed by chemical precipitation. The study concluded that the combination of the two technologies reduces the amount of chemicals required for treatment and increased water recovery to 97% [30].

The Accelerated Precipitation Softening process includes primary RO treatment, followed by pH increase and calcite seeding, microfiltration to remove crystals, pH decrease, and secondary RO treatment. No recoverable salts are created in the process,



and it requires extensive treatment for pH adjustment and scale protection, but 98% water recovery was reported for the process [26].

## **CHAPTER 2**

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### **MODELING**

One of the objectives of this project was to develop a mathematical model to describe ion exchange in a column over time. Modeling is a convenient way to see the effects of changes in selectivity, solution characteristics, and operation time on the column process. The model is described in the first section because results from each phase of the project are compared to model predictions.

#### **2.1 Chapter Objectives**

The purpose of this chapter is to describe the mathematical model developed to describe the ion exchange column process. The inner workings of the program will be explained in terms of computer language, functions, inputs, and outputs. The goal of this section is to impart an understanding of the model and its results, so they can be compared to experimental results in a meaningful way in later sections.

#### **2.2 Chapter Summary**

The key results and conclusions from this chapter are as follows:

1. Model assumptions:
  - a. The model is based on charge balances and selectivity only. Kinetics and hydrodynamic dispersion were not included.
  - b. One bed volume of operation occurs when the number of time steps is equal to the number of segments.
2. Model inputs include solution phase ion concentrations, resin separation factors, column dimensions, the number of segments in the column, and time steps.
3. The model outputs two, three dimensional arrays. The first includes time, segment number, and resin phase ion concentration. The second includes time, segment number, and solution phase ion concentration. The arrays can be queried in several useful ways to produce snapshots of the entire column, resin phase concentration at any time, and breakthrough curves.

4. The model code was written in MATLAB

### **2.3 - Modeling**

The model was developed using MATLAB, in conjunction with Angela Montoya, a programmer and graduate student at the UNM. It is a discretized mass balance model in which solution and resin equilibrium is found simultaneously using a non-linear solver.

The model is based on vector Equation 18 that combines the charge balance equations and the separation factor equations to solve for solution phase composition simultaneously for all ions in the system. The equation solver, `fsolve`, was used to solve the system of non-linear equations. Resin phase ion equivalents,  $R$ , are solved by subtracting the solution phase ion equivalents from the total ion equivalents in the system (Equation 19). The simulated column is split into a number of segments defined by the user. The equation works by looping over time and space to produce solution and resin phase ion equivalents for each time step in every column segment. Resin phase and solution phase ion equivalent totals are converted to concentrations by dividing by the segment volume (Equation 20). At the beginning of each time step, total ion equivalents are calculated by adding the equivalents on the resin to the equivalents in solution. At the next time step, solutions are advanced down the column to the next segment and used as influent initial ion concentrations for the equilibrium calculation for that time step.

<p><b>Equation 18: Vector Equation to Solve for Solution Phase Ion Equivalents, C</b></p>	$0 = \begin{bmatrix} q_T \\ q_T \\ q_T \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} - \left( \begin{bmatrix} T \\ T \\ T \end{bmatrix} - \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} \right) \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{bmatrix}$ <p>where <math>q_T</math> is resin capacity (meq, calculated by multiplying specific capacity by segment volume), <math>\alpha</math> is separation factor, <math>C</math>, total solution phase ion equivalents (meq), <math>T</math> is total ion equivalents in segment (meq, solution phase plus resin phase)</p>
<p><b>Equation 19: Vector Equation to Solve for Resin Phase Ion Equivalents</b></p>	$\begin{bmatrix} R_1 \\ R_2 \\ R_3 \end{bmatrix} = \begin{bmatrix} T \\ T \\ T \end{bmatrix} - \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix}$ <p>where <math>R</math> is resin phase ion equivalents</p>
<p><b>Equation 20: Conversion of Solution and Resin Phase Ion Equivalents to Concentrations</b></p>	$C_{\text{eq/L}} = \frac{C}{V_{\text{seg}}} \text{ and } R_{\text{eq/L}} = \frac{R}{V_{\text{seg}}}$ <p>where <math>V_{\text{seg}}</math> is segment volume (L)</p>
<p><b>Equation 21: Equation for Segment Volume</b></p>	$V_{\text{seg}} = \frac{q_T}{n}$ <p>where <math>n</math> is the user defined number of column segments</p>

The column is modeled similar to a “tanks in series” (TIS) arrangement. It is split into a number of segments (user defined,  $n$ ) containing an equal volume (see Equation 21 and Figure 5). As the number of elements increases, a closer and closer approximation of plug flow is reached. This can be seen in Figure 6 in which a tracer concentration is plotted as a function of the normalized time (time divided by average residence time) [31]. The TIS model is alternative and somewhat limited (one parameter) method of modeling dispersion in reactors in systems with small deviations from plug flow [32]. In an ideal plug flow column, ion sorption fronts are sharp, even for ions with low separation factors, although ions with larger separation factors will always have sharper curves than those with lower separation factors. In real columns, dispersion must be accounted for. Dispersion in the column results in peak broadening which is modeled by decreasing the number of column segments [20]. This can also be seen in Figure 6. A

direct comparison between the tanks in series model (Equation 22) and the MATLAB model shows very similar results (see Figure 7 and Figure 8).

Figure 5: Model Scheme

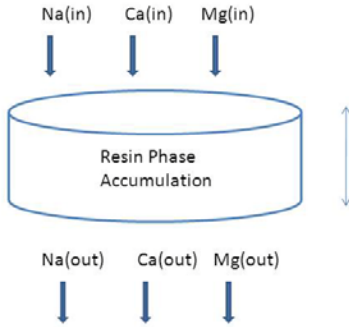
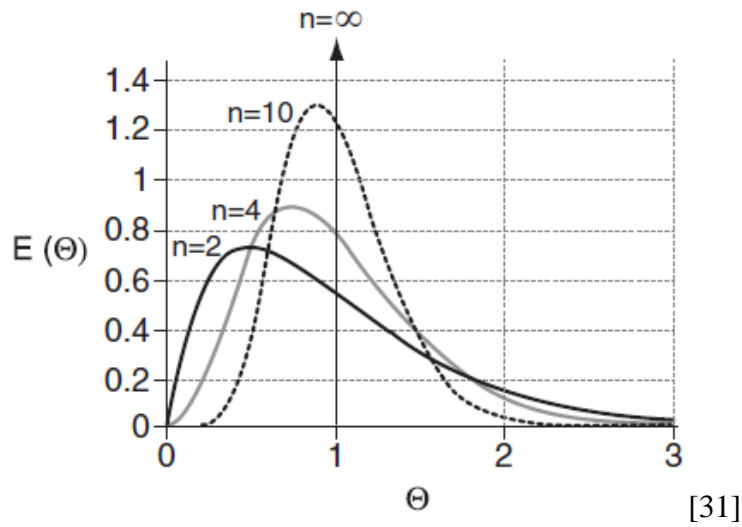


Figure 6: Response to Pulse Tracer Input for TIS Model with Differing Number of Tanks



Equation 22: Cumulative Time Distribution (F) and Relative Time Distribution (E) for the TIS Model

$$F(t) = \int_0^t E(t) dt \quad E(t) = \frac{t^{(n-1)}}{(n-1)! \tau^n} e^{-\frac{t}{\tau}}$$

Figure 7: Effluent Concentration Curve from TIS Model using Different Numbers of Tanks

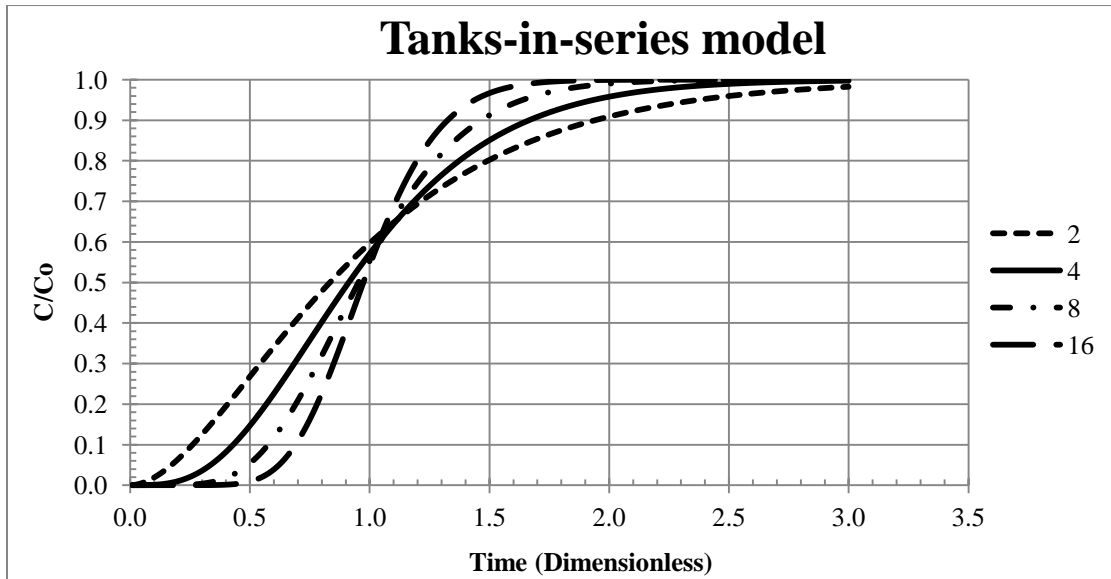
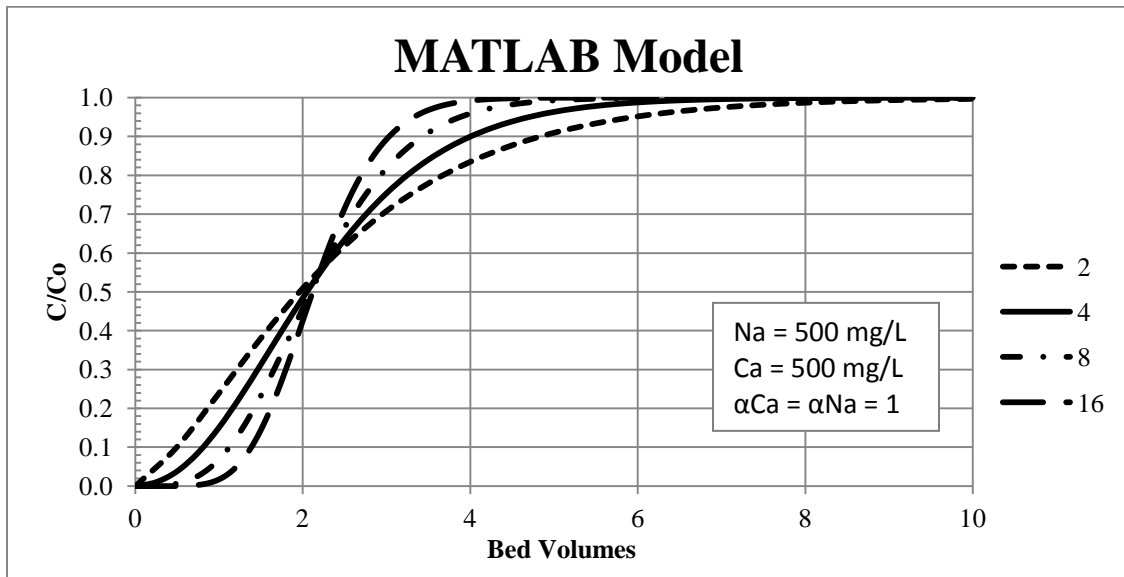


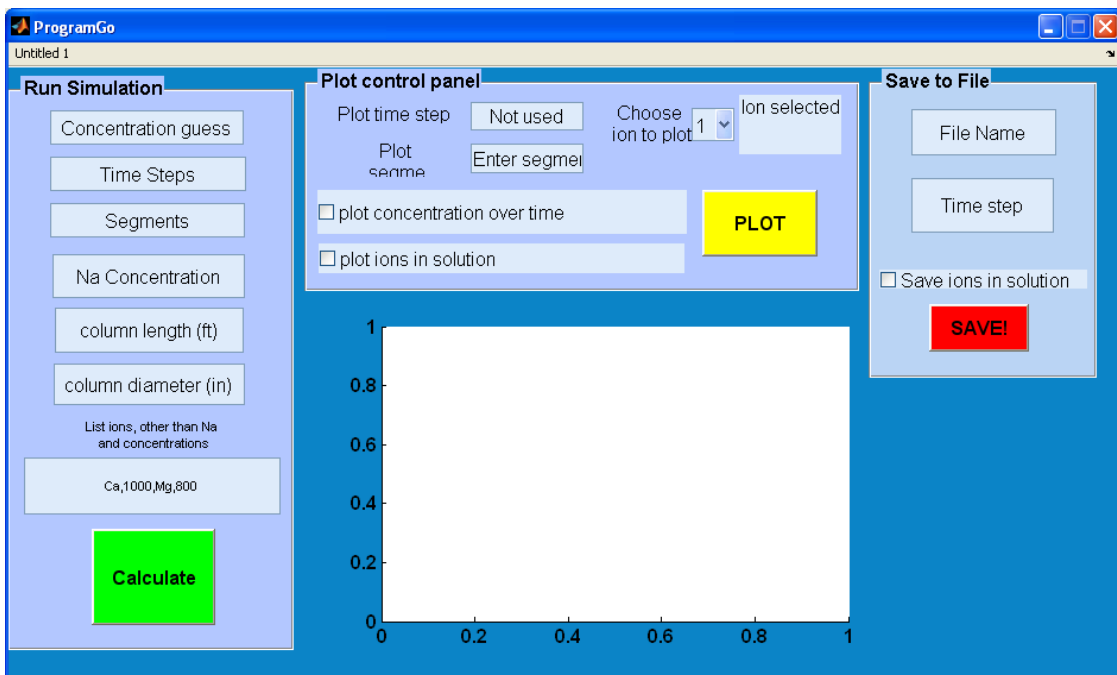
Figure 8: Effluent Concentration Curve from MATLAB Model using Different Numbers of Segments



A graphical user interface (GUI) was developed to simplify data input and export. The input area on the GUI (see Figure 9) is on the left hand side. Data inputs include the number of time steps, the number of column segments, the initial solution phase sodium concentration (mg/L), the column length (ft), the column diameter (in), and the concentration of other ions in solution (mg/L). There is also a field for concentration

guess. This field feeds fsolve, the non-linear solver, an initial guess for solution phase ion amounts (total meq). Since this number can vary greatly depending on the size of a particular element and the initial solution concentrations, this approach is better than hard coding a “one size fits all” guess into the function. It will not converge if the guess is too far from the actual value. The input guess is only used for the first time step in the first element. For all subsequent equations, the equilibrium concentration in the previous time step in the previous element is used as a guess.

Figure 9: Graphical User Interface for MATLAB model



The GUI also allows for graphing of solution and resin phase ion equivalents over time and space. This feature was added to allow the user to confirm that the calculations were successful and to get a quick overview of the system. Users can export the solution or resin phase ion equivalents at a specific time for all segments as text file that can be imported to any graphing program and can be plotted to show the distribution of ions within the column for any time (see Figure 10). The arrays can also be accessed directly from the MATLAB environment by using the functions employed by the GUI graphing feature. The function entitled `get_segment_data` allows the user to retrieve resin or

solution phase ion equivalents for all segments at a specific time. The function is called by specifying an array (resin or solution), a segment, and an ion (Ca, Mg, other). The other useful function, `get_time_data`, returns the solution or resin phase ion equivalents at all times for a specific segment. It is called by specifying an array, a segment number, and an ion. Using this function, the user can generate solution phase ion equivalents at all times for the final segment, which is very similar to a breakthrough curve (see Figure 11). Any ion can be added to the model by inputting its molecular weight, charge, and separation factor into a straightforward and well commented file. The model code is available upon request.

The effect of increasing the number of segments while keeping the number of bed volumes treated and the selectivity of the resin constant can be seen in Figure 12. Although the equilibrium distribution of ions is constant, the sorption front becomes sharper as the number of segments increases. Sharper peaks also result in a longer time to breakthrough and a corresponding increase in column efficiency. The number of segments suitable for modeling a real reactor can be found by matching the observed dispersion of a non-reactive tracer to that modeled by using a specific number of segments.



Figure 10: Example Column Snapshot from Model

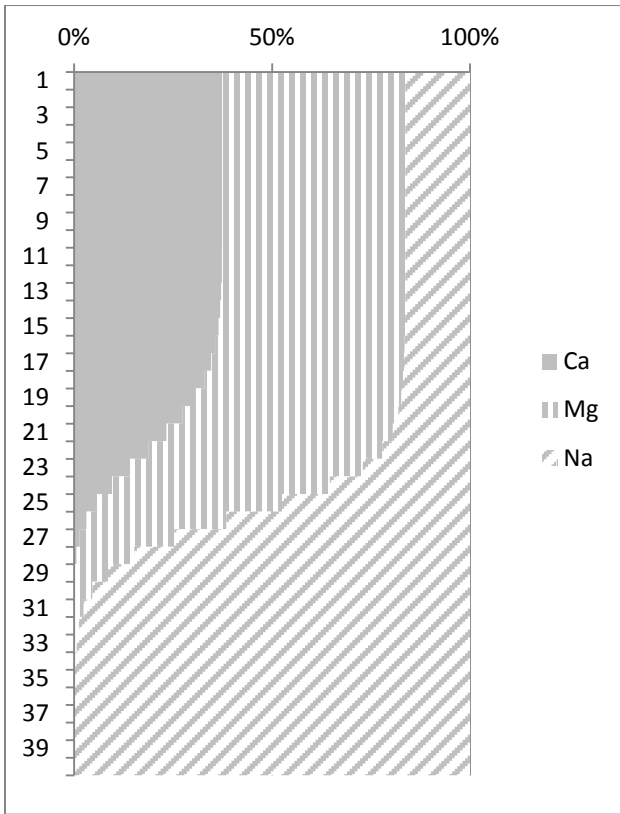


Figure 11: Example Breakthrough Curve from Model

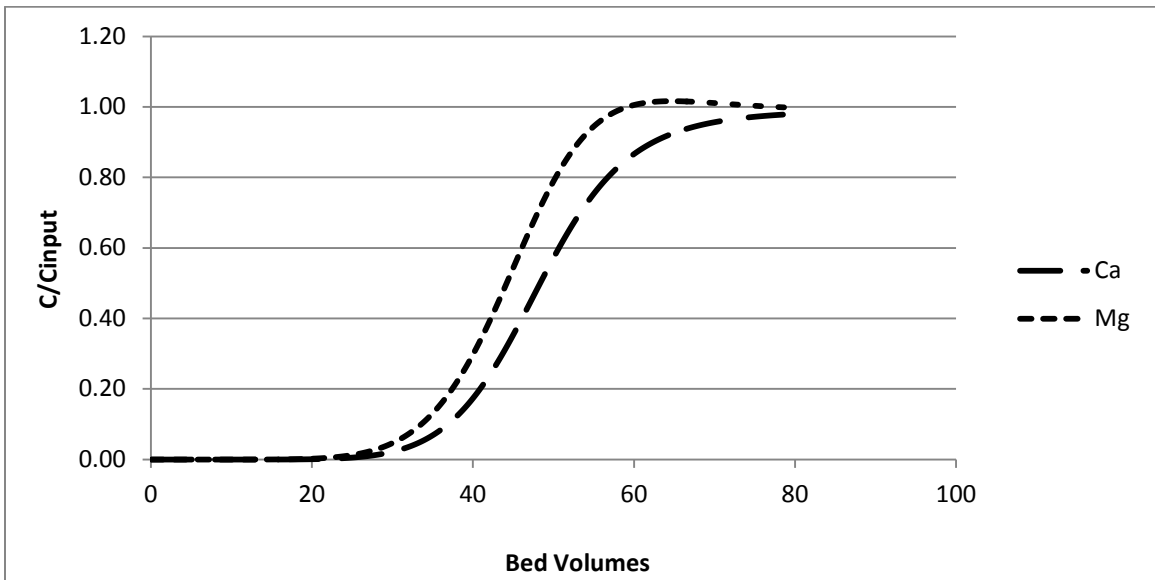
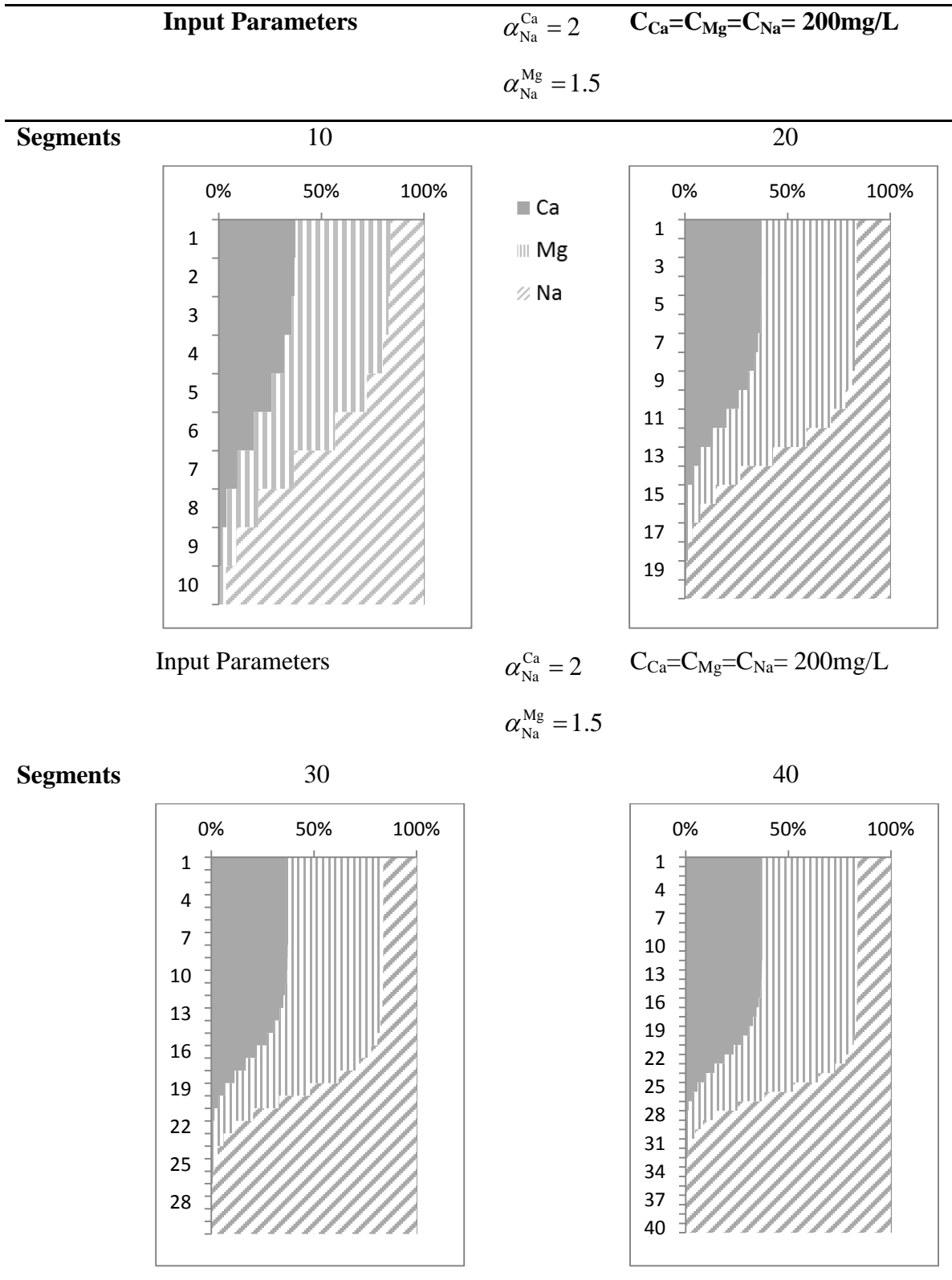


Figure 12: Comparison of Column Snapshots with Different Numbers of Segments



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Input Parameters

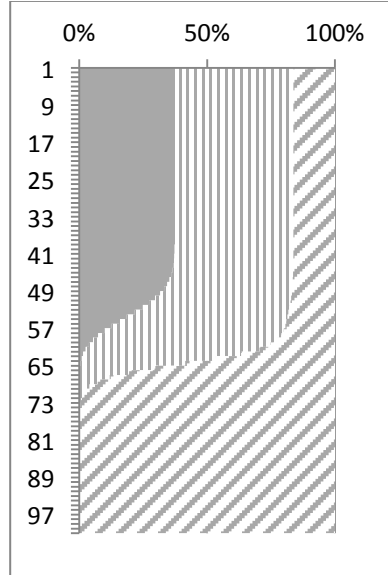
$$\alpha_{\text{Na}}^{\text{Ca}} = 2$$

$$C_{\text{Ca}} = C_{\text{Mg}} = C_{\text{Na}} = 200 \text{mg/L}$$

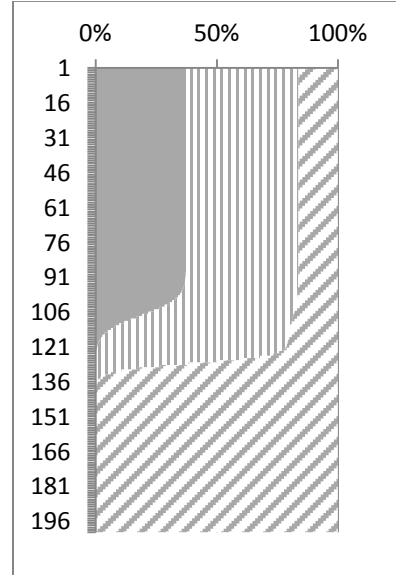
$$\alpha_{\text{Na}}^{\text{Mg}} = 1.5$$

Segments

100



200



## **CHAPTER 3**

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### **DEPENDENCE OF RESIN SELECTIVITY ON IONIC STRENGTH AND SOLUTION COMPOSITION**

#### **3.1 Chapter Objectives**

The purpose of this chapter is to describe the methods and results from batch studies performed to determine the effect of changing ionic strength and ionic composition on the selectivity of cation and anion ion exchange resins for common ions present in most reverse osmosis concentrate including calcium, magnesium, carbonate, bicarbonate, and sulfate. Ion selectivity directly relates to the feasibility of using these resins to treat reverse osmosis concentrate.

#### **3.2 Chapter Summary**

The key results and conclusion from the batch isotherm experiments are as follows:

1. Selectivity for all divalent ions decreases with ionic strength.
2. Selectivity for all divalent ions decreases with solution phase equivalent fraction.
3. The best predictor of separation factors is a regression based on these two factors.
4. Cation and anion exchange resins have adequate selectivity for the major ions of interest in a broad range of solutions.

#### **3.3 Methods**

The objective of the first phase of the project was to determine how resin selectivity is affected by fundamental variables including ionic strength and initial ion proportions. To achieve this objective, several ion exchange isotherms were measured using anion and cation exchange resins donated by ResinTech<sup>®</sup> and Purolite. Based on manufacturer's specification from ResinTech<sup>®</sup> which detailed ranges of working conditions, selectivity, and exchange capacity, a SAC resin, CG-10, was selected for use (see Figure 13). Purolite A850, a SBA resin, was also selected. The solutions prepared for the isotherms were designed to test resin properties at a variety of ionic strengths and ion ratios, using ions common to brackish water sources and therefore likely to be in RO concentrate including sodium, calcium, magnesium, chloride, sulfate, and carbonate.

These ions are also components of several possible salts that may be recovered for beneficial reuse such as calcium and magnesium carbonate or sulfate.

Ion exchange resins in the  $\text{Na}^+$  or  $\text{Cl}^-$  form were rinsed and dried in a lab oven at  $104^\circ\text{C}$ . Solutions were prepared by mixing together concentrated stock solutions of various salts. 50 mL of each solution was poured into a 50 mL vial. Using a Mettler Toledo AB104-S balance, 0.5 g or 1 g of dried resin was weighed and added to each 50 mL vial.

Figure 13: Resin Samples



Vials were placed on a VWR DS2-500-1 laboratory shaker or a vertical rotating disk for a 24 hour period. Metals were analyzed by flame AA spectroscopy using a Varian SpectrAA 55BB Atomic Absorption Spectrometer (AAS) (see Figure 14). Specific ion lamps were newly purchased for this work including those for calcium, magnesium, potassium, and barium. Sodium was measured using atomic emissions spectrometry. Anions were by ion chromatography using a Dionex DX series Ion Chromatography System (IC) using a newly purchased AS-14 column. The equilibrated solution concentrations were compared to the initial concentrations of the solutions and the mass of ions exchanged was determined by the difference. In the final the cation exchange isotherm, the equilibrated resin was washed with de-ionized (DI) water and then stripped with 2N HCl. The resulting liquid was analyzed for calcium, magnesium, and sodium. These measurements were used to verify the measurements taken from initial and equilibrated solutions. The matrix of isotherm experiments is shown in Table 6 and results are presented in the next section.

Figure 14: Atomic Absorption Spectrometer (left) and Ion Chromatography System (right)



Table 6: Matrix of Isotherm Experiments (Ratios are based on molarity)

<b>Isotherm Type</b>	<b>Ions</b>	<b>Initial Ratio (Counterions:Na or Cl)</b>	<b>Ratio (Ca:Mg) or (SO<sub>4</sub>/CO<sub>3</sub>)</b>	<b>Ionic Strength (M)</b>
<b>Binary</b>	Ca/Na	1:3, 1:1, 3:1	N/A	0.15, 0.5, 1.0, 1.5
<b>Binary</b>	Ca/Na	1:3, 3:1	N/A	0.10, 0.15, 0.20, 0.25
<b>Binary</b>	Mg/Na	1:3, 1:1, 3:1	N/A	0.15, 0.5, 1.0, 1.5
<b>Binary</b>	Mg/Na	1:3, 3:1	N/A	0.10, 0.15, 0.20, 0.25
<b>Ternary</b>	Ca/Mg/Na	1:3, 1:1, 3:1	4:1	0.15, 0.5, 1.0, 1.5
<b>Ternary</b>	Ca/Mg/Na	1:3, 3:1	1:3	0.10, 0.15, 0.20, 0.25
<b>Ternary</b>	Ca/Mg/Na	1:3, 1:1, 3:1	1:4	0.15, 0.5, 1.0, 1.5
<b>Binary</b>	SO <sub>4</sub> /Cl	1:3, 3:1	N/A	0.10, 0.15, 0.20, 0.25
<b>Binary</b>	CO <sub>3</sub> /Cl	1:3, 3:1	N/A	0.10, 0.15, 0.20, 0.25
<b>Ternary</b>	SO <sub>4</sub> / CO <sub>3</sub> /Cl	1:3, 3:1	1:1	0.10, 0.15, 0.20, 0.25

Experiments in Phase 1 were designed to quantify changes in rein selectivity due to variations in ionic strength and solution equivalent fraction of exchanging ion. Initial ionic ratios were calculated by dividing the concentration (M) of counter-ions by the

concentration (M) of sodium or chloride. The ratio of the initial concentration of competing counter-ions was also varied. In cationic ternary systems, for example, two different ionic ratios were quantified: the ratio between the sum of the calcium and magnesium to sodium and the ratio of calcium to magnesium. It should be noted that ionic ratios change when solutions equilibrate with resins. Since it was not possible to predict ionic ratios for equilibrated solutions, solutions were designed to specific ionic ratios in their initial condition.

### 3.4 Results

The objective of this experimental phase was to determine the effect of changing ionic strength and ionic composition on the selectivity of ion exchange resins for common ions found in reverse osmosis concentrate. Preliminary batch isotherms were conducted at ionic strengths up to 1.5 M, but column tests demonstrated that the service cycle of a column process would be too short to be practical at that ionic strength, so later experiments were done at lower ionic strengths. .

#### 3.41 Cation Exchange Isotherms

Several cation exchange tests were performed over the course of the research. The different tests varied in terms of range of ion concentrations, number of points, and the ions included. As lab experience increased, experimental procedures and data analysis improved. In particular, the concentration range of the exchanging ions decreased, and the number of points in the isotherm increased. This allowed for a more precise measurement of changes in selectivity over a smaller range of ionic strengths. Isotherm test parameters are listed Table 7.

Table 7: Cation Exchange Isotherm Tests

Test #	Exchanging Ions	Experimental Notes	Initial Concentration Range (M)
1	Mg, Na	12 points	Mg: 0.020 – 0.526 Na: 0.013 – 0.719

<b>2</b>	Ca, Na	12 points	Ca: 0.018 – 0.413 Na: 0.009 – 0.687
<b>3</b>	Ca, Mg, Na	12 points	Ca: 0.015 – 0.323 Mg: 0.005 – 0.116 Na: 0.011 – 0.611
<b>4</b>	Ca, Mg, Na	24 points, stripped resin w/ HCl to measure resin phase concentrations	Ca: 0.003 – 0.077 Mg: 0.011 – 0.065 Na: 0.021-0.141

For the first three isotherm tests, exchanging ion concentrations were measured in the solution before and after equilibration with the resin. Equivalents of exchanged ions per gram of resin were calculated from these two values. For the last isotherm, concentrations of exchanging ions were measured in the initial solution and in the 2N HCl solution used to strip the equilibrated and washed resin. These two values were used to calculate the concentration of exchanging ions in the equilibrated solution. Ion concentrations were used to calculate separation factors and ionic strengths for each point on the isotherm. The equations used to calculate these values are shown in Table 8.

Separation factors for calcium and magnesium were calculated for all tests. Calcium separation factors are plotted against ionic strength and equivalent fraction in Figure 15 and Figure 16. There was a general pattern of decreasing selectivity with both increasing equivalent fraction and ionic strength, but neither relationship was strong enough to be predictive. In both cases, the decrease appeared to be exponential, so a log based regression was performed for separation factors with both variables, and a strong correlation was observed. The resulting equation and the associated regression statistics are shown in Table 9. The dotted line in the figure has a slope of 1. To illustrate this correlation, predicted separation factors are plotted against calculated separation factors in Figure 17.



**Table 8: Values Calculated for Isotherms Tests with Relevant Equations**

<i>Value</i>	<i>Equation</i>
<b>Equation 23: Resin Phase Ion Concentration (Tests 1-3)</b>	$q_i = \frac{([i]_{\text{init}} - [i]_{\text{final}}) * V}{M}$ <p>where <math>q_i</math> is the resin phase ion equivalent concentration, <math>[i]</math> is the solution phase ion equivalent concentration, <math>V</math> is the solution volume, and <math>M</math> is the resin mass</p>
<b>Equation 24: Resin Phase Ion Concentration (Test 4)</b>	$q_i = \frac{[i]_{\text{stripped solution}} * V}{M}$
<b>Equation 25: Solution Phase Ion Concentration (Test 4)</b>	$C_i = \frac{([i]_{\text{init}} * V + q_i * M)}{V}$ <p>where <math>C_i</math> is the solution phase ion equivalent concentration</p>
<b>Equation 26: Solution Phase Equivalent Fraction</b>	$(X_1)_s = \frac{[1] z_1}{[1] z_1 + [2] z_2 + [3] z_3}$ <p>where <math>(X_1)_s</math> is the equivalent fraction of ion 1 in solution and <math>z_1</math> is the charge of ion 1</p>
<b>Equation 27: Separation Factor</b>	$\alpha_1^2 = \frac{(X_2)_r * (X_1)_s}{(X_1)_r * (X_2)_s}$ <p>where <math>(X_1)_r</math> is the resin phase equivalent fraction of ion 2</p>
<b>Equation 28: Ionic Strength</b>	$IS = 0.5 * \sum (C_i z_i^2)$ <p>Note: Co-ion concentration was estimated by sum of counter-ions.</p>

Figure 15: Calcium Separation Factors vs. Equivalent Fraction of Calcium

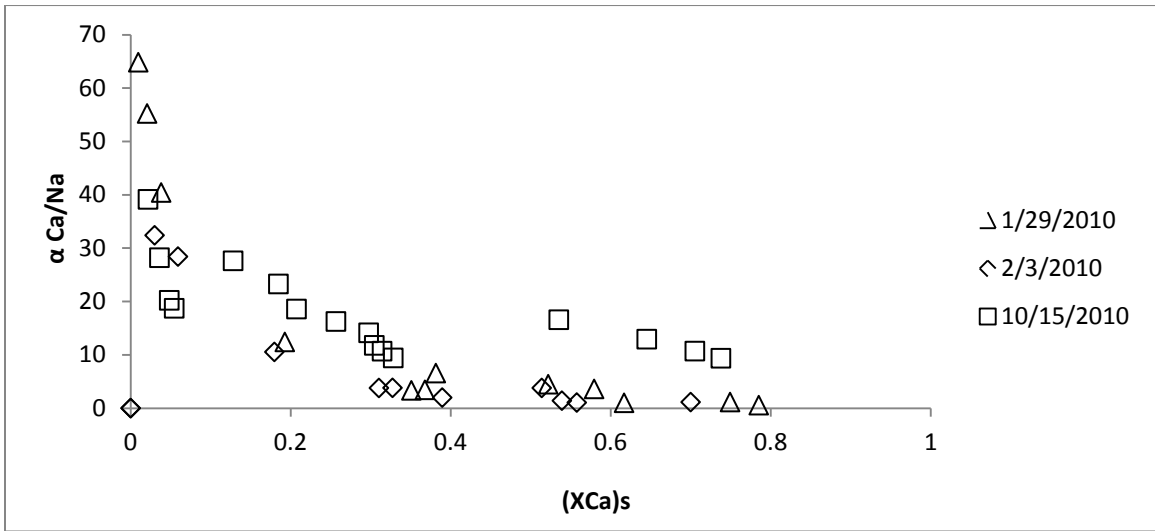


Figure 16: Calcium Separation Factors vs. Solution Ionic Strength

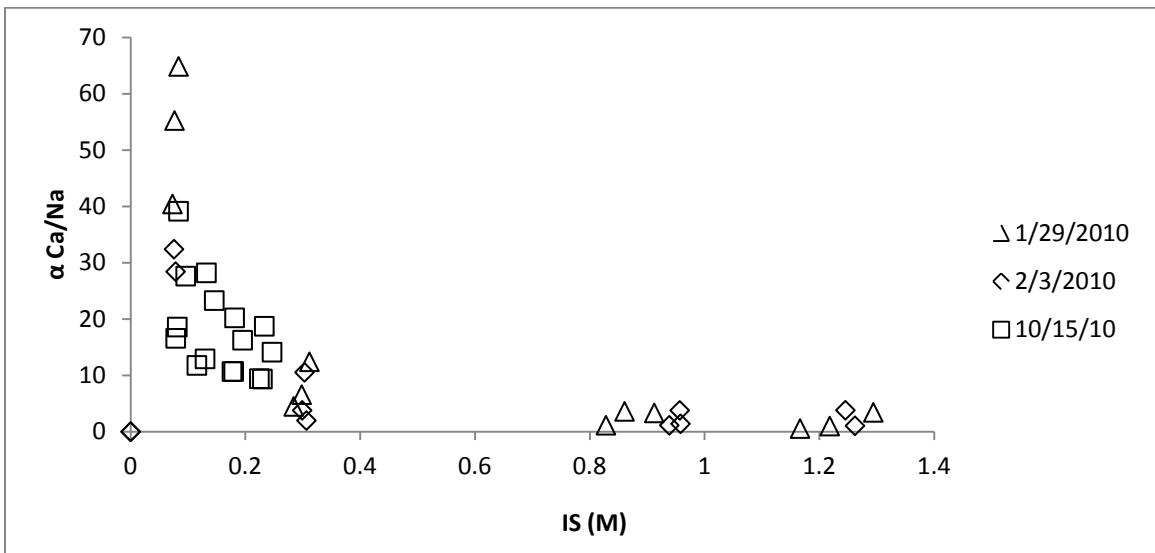


Table 9: Regression Equation and Associated Statistics for Calcium Separation Factors

Equation 29: Regression Equation for Calcium Separation Factor

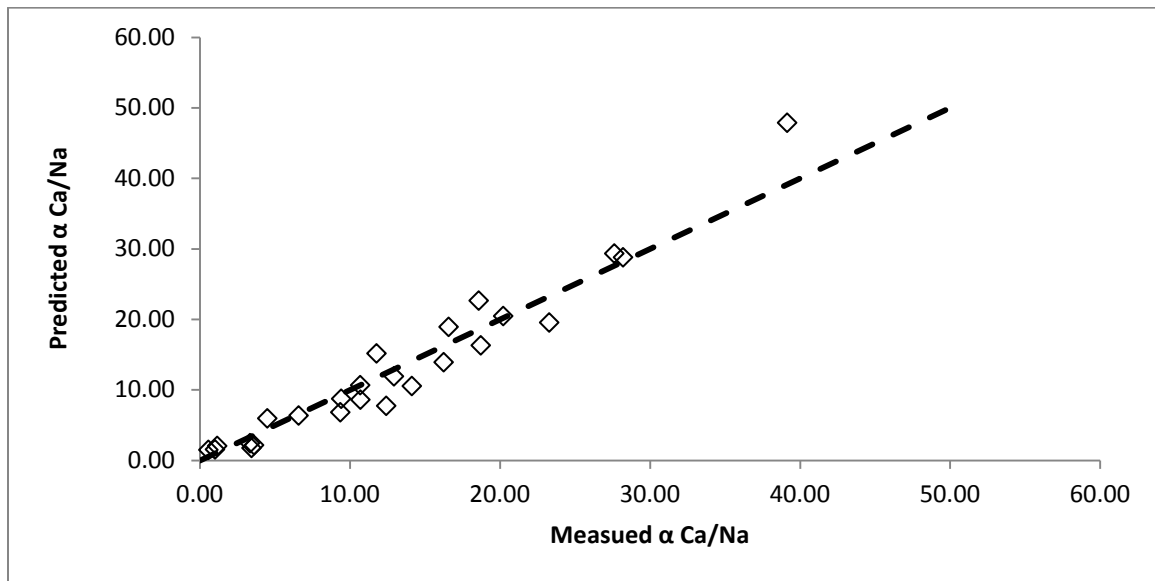
$$\log(\alpha_{Na}^{Ca}) = -0.344 * \log((X_{Ca})_s) - .885 * \log(IS) + 0.193$$

*Regression Statistics*

Multiple R 0.96

R Square	0.92
Adjusted R Square	0.91
Standard Error	0.15
Observations	28

Figure 17: Predicted Calcium Separation Factors vs. Measured Calcium Separation Factors



Selectivity decreases with ionic strength due to the corresponding decrease in ion activity. It is also explained by the concept of Donnan potential which is built up in response to the concentration gradient of co-ions between the solution and resin phase [3, 4, 6]. The gradient and the corresponding electrical potential generated at the resin-solution interface (Donnan potential) is largest when the resin is in contact with very dilute solutions. It excludes multivalent ions more efficiently than monovalent ions, and this effect becomes more pronounced as the solution becomes more dilute [3, 4].

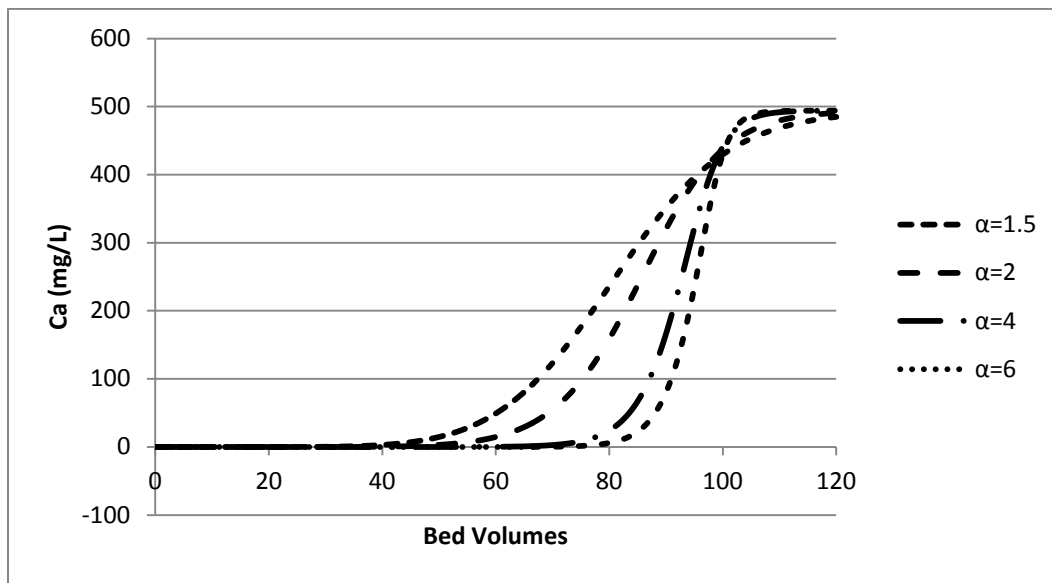
Using the multiple regression equation, a matrix of predicted separation factors with changing ionic strength and solution phase equivalent fraction was created. Using the MATLAB model, the number of bed volumes to breakthrough was calculated. For the purposes of this investigation, breakthrough was defined as an effluent calcium concentration of  $C/C_0 = 0.1$  which was equal to 5 mg/L. The parameters of the system

used in the model are shown in Table 10. Breakthrough curves for 4 systems with separation factors ranging from 1.5 to 8 are shown in Figure 18.

**Table 10: Parameters for Modeling the Bed Volumes to Breakthrough for Different Separation Factors**

	mg/L	meq/L
<b>Ca</b>	500	0.02
<b>Na</b>	200	0.01
<b>Eq Fraction Ca</b>	0.74	
<b>IS</b>	0.04	

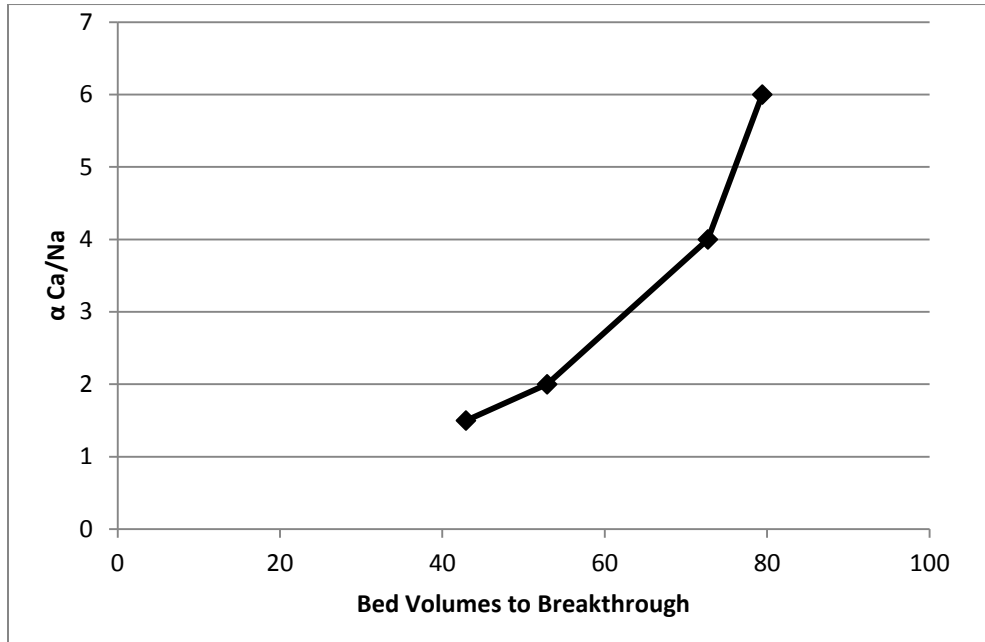
**Figure 18: Modeled Breakthrough Curves for Systems with Separation Factors Ranging from 1.5 to 6**



Decrease in separation factor results in a broader mass transfer zone (MTZ) which can be visualized as the difference in bed volumes between initial breakthrough and the point at which the influent calcium concentration is equal to the effluent concentration. As the MTZ gets broader, more column capacity is unused at breakthrough. The length of the MTZ is also dependent on dispersion, but if dispersion is constant, a decrease in the separation factor will result in a decrease of column capacity. Figure 19 shows model predictions of the number of bed volumes to breakthrough as a function of the calcium

separation factor using the number of column segments (20) that best fit the dispersion that existed in the laboratory columns discussed in the next section. The figure shows that the number of bed volumes to breakthrough decreases more quickly in response to changes in separation factor below 4.

Figure 19: Bed Volumes to Breakthrough as a Function of Calcium Separation Factor



When the regression is plotted as a surface (Figure 20), it is evident that the separation factor changes more quickly with ionic strength than with equivalent ionic fraction and that the most rapid changes with both variables occur at the lower ranges. At ionic strengths of 0.35 and below, separation factors are predicted to be above 4 even at very high equivalent fractions of calcium in solution. Resin selectivity is not a limiting factor for treatment of a wide range of reverse osmosis concentrates.

The same analysis was done for magnesium isotherm measurements and similar results were found. Separation factor is plotted against equivalent fraction and ionic strength in Figure 22. There is general trend of decreasing selectivity with both ionic strength and equivalent fraction. A multiple log regression of separation factor as a function of equivalent fraction and ionic strength showed a strong correlation between predicted and calculated separation factors. The regression equation and associated

statistics are shown in Table 11, and Figure 23 shows the correlation between calculated and predicted separation factors.

Figure 20: Separation Factor as a Function of Ionic Strength and Equivalent Ionic Fraction of Calcium

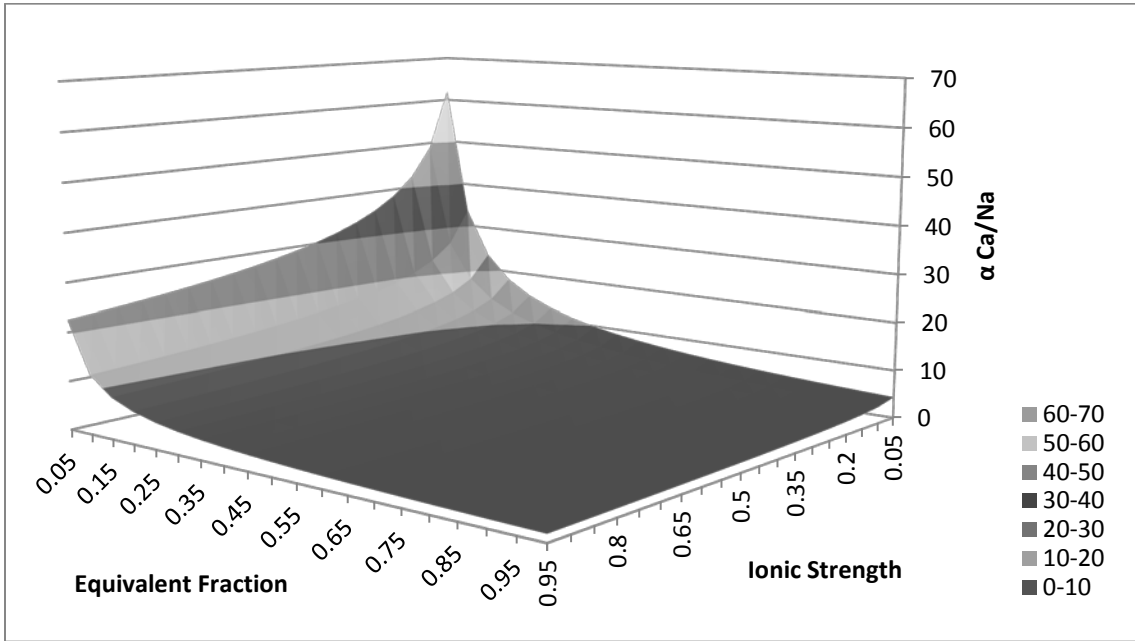


Figure 21: Magnesium Separation Factors vs. Equivalent Fraction of Magnesium

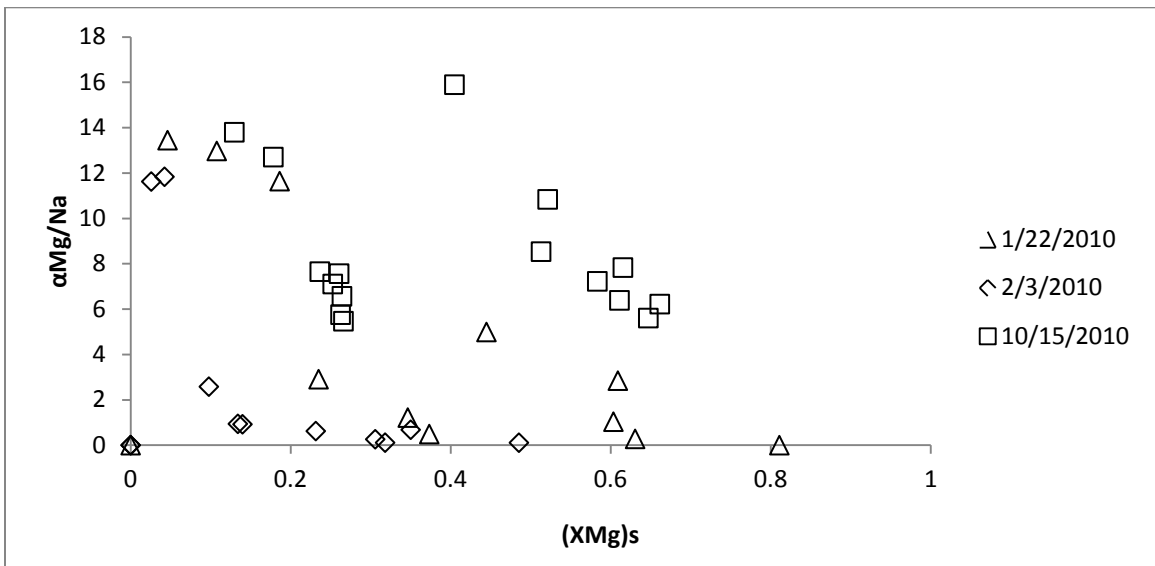


Figure 22: Magnesium Separation Factors vs. Ionic Strength

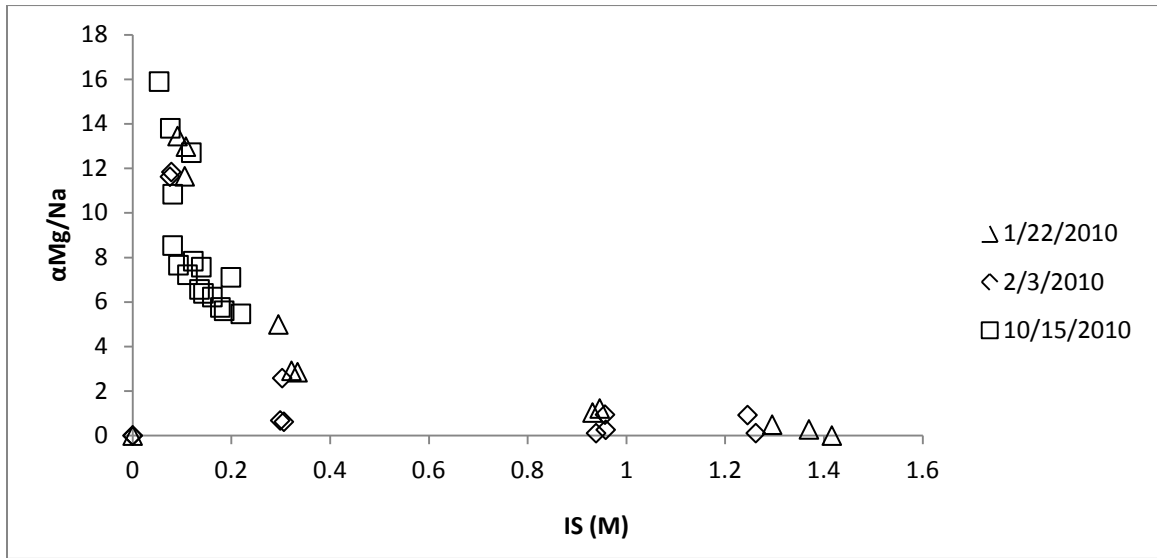


Table 11: Regression Equation and Associated Statistics for Magnesium Separation Factors

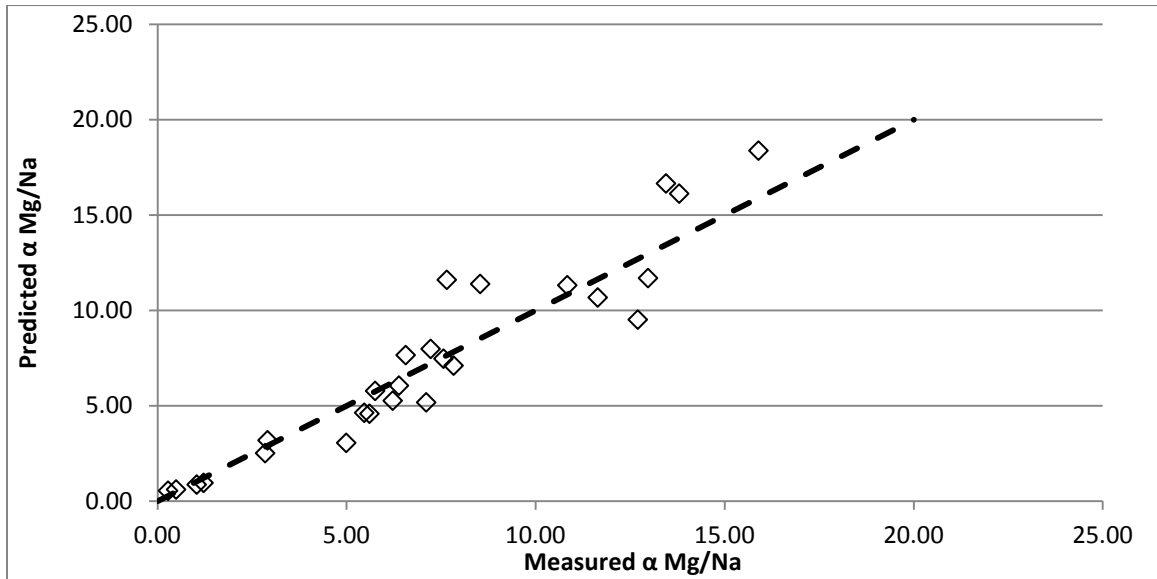
Equation 30: Regression Equation for Magnesium Separation Factor

$$\log(\alpha_a^b) = -0.208 * \log((X_b)_s) - 1.040 * \log(\text{IS}) - 0.139$$

*Regression Statistics*

Multiple R	0.97
R Square	0.94
Adjusted R Square	0.94
Standard Error	0.11
Observations	26

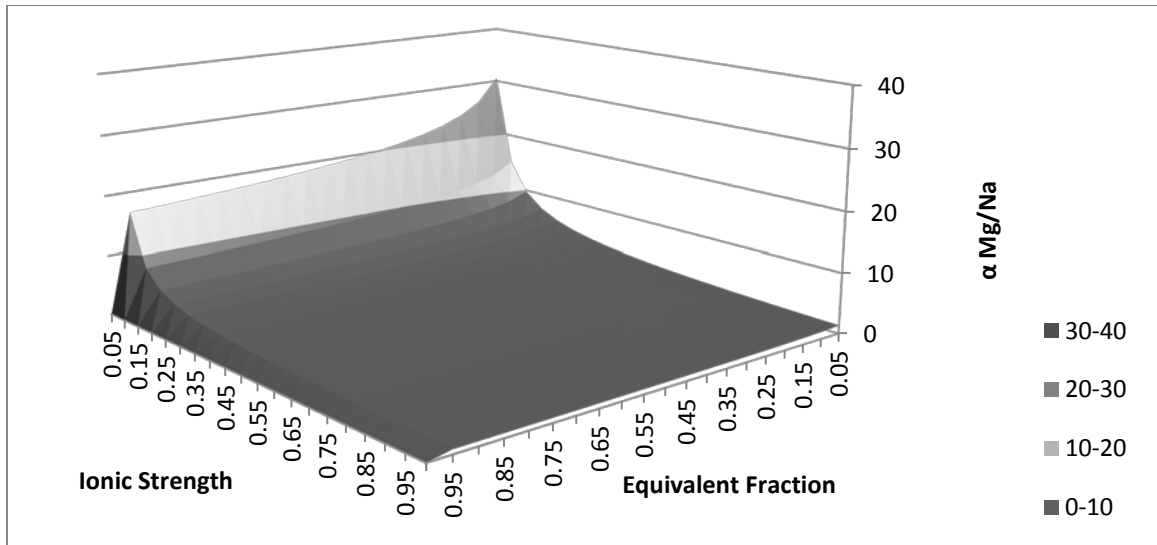
Figure 23: Predicted Magnesium Separation Factors vs. Measured Magnesium Separation Factors



A surface was plotted to show how magnesium separation factors change as a function of ionic strength and equivalent fraction (see Figure 24). Magnesium separation factors react similarly to calcium separation factors as solution characteristics change. Both show a more rapid decrease in selectivity with increasing ionic strength than with increasing equivalent fraction in solution. Although the resin selectivity for both ions responds similarly to changes in ionic strength and equivalent ratio, calcium selectivity is always greater than magnesium selectivity. This is a well-established selectivity sequence for SAC resins and was discussed previously.



Figure 24: Surface Plot Showing Changing Separation Factor with Ionic Strength and Equivalent Ionic Fraction



From cation exchange isotherm measurement, it was established that separation values for calcium and magnesium can be predicted by a log multiple regression on equivalent fraction in solution and ionic strength. For both ions, there is a more rapid decrease in selectivity with ionic strength than with equivalent fraction. Both regressions show a strong correlation. For both ions, selectivity values are adequate for efficient ion exchange in solutions with ionic strengths above 0.25 M. To put this in perspective, an example feed water containing calcium, magnesium, potassium, sodium, sulfate and chloride with an ionic strength of 0.27, has about 4500 mg/L of total dissolved solids (TDS). For solutions with high ionic strength, ion exchange may still be feasible if the equivalent fraction of divalent ions in solution is low. However, selectivity is not the only factor to consider in the application of ion exchange to reverse osmosis concentrate. If resin loading is very high, the number of bed volumes to exhaustion may not be high enough to make the process efficient. This issue was addressed in Phase 2 in which lab scale columns tests were conducted.

### 3.42 Anion Exchange Isotherms

An 18 point anion exchange batch isotherm was measured. Isotherm test numbers and parameters are listed Table 12.

Table 12: Anion Exchange Isotherm Tests

Test #	Exchanging Ions	Experimental Notes	Initial Concentration Range (M)
1	SO <sub>4</sub> , CO <sub>3</sub>	18 points	SO <sub>4</sub> : 0.017-0.192 TOTCO <sub>3</sub> : 0.017-0.083

Separation factors for sulfate and carbonate were calculated for all tests. The concentration of bicarbonate in solution did not change significantly, so separation factors were not calculated for bicarbonate. Sulfate separation factors are plotted against ionic strength and equivalent fraction in Figure 25 and Figure 26. Carbonate separation factors are plotted against ionic strength and equivalent fraction in Figure 25 and Figure 26.

Figure 25: Sulfate Separation Factor as a Function of Ionic Strength

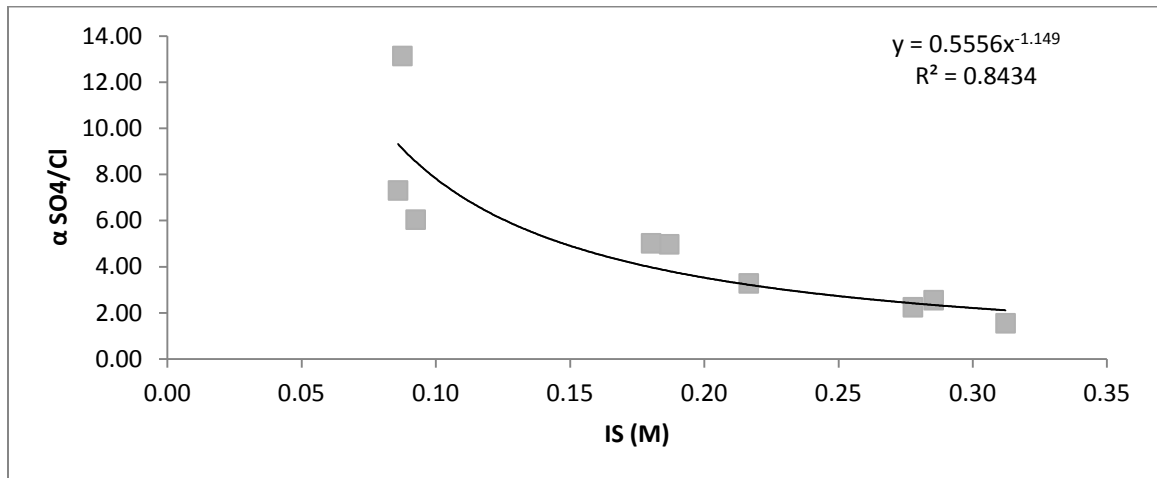
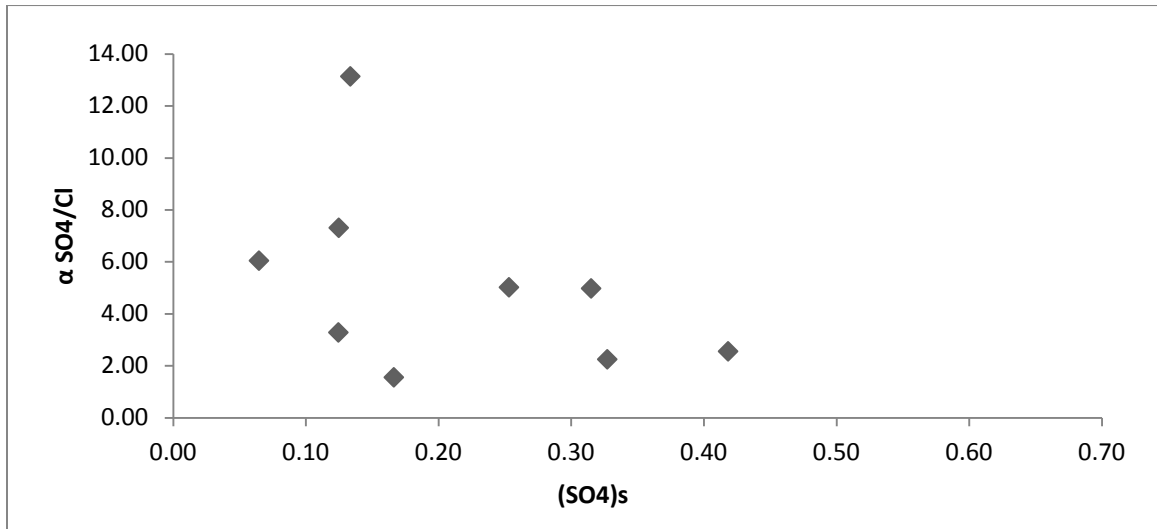


Figure 26: Sulfate Separation Factor as a Function of Ionic Fraction



The sulfate separation factor is better correlated with ionic strength than with equivalent fraction, and a multiple regression on separation factor as a function of both variables did not produce a strong correlation. However, it was possible to fit a power function to the relationship between separation factor and ionic strength (see Figure 25). The same pattern of relationships was seen with carbonate separation factors (see Figure 27 and Figure 28), but the correlation between ionic strength and separation factor was not as strong. This may be due to the fact that the dependence of carbonate speciation on pH made concentrations more difficult to measure. The predictive power of the relationship between sulfate separation and ionic strength is tested in the next section in which it is applied to column tests.

Figure 27: Carbonate Separation Factor as a Function of Ionic Strength

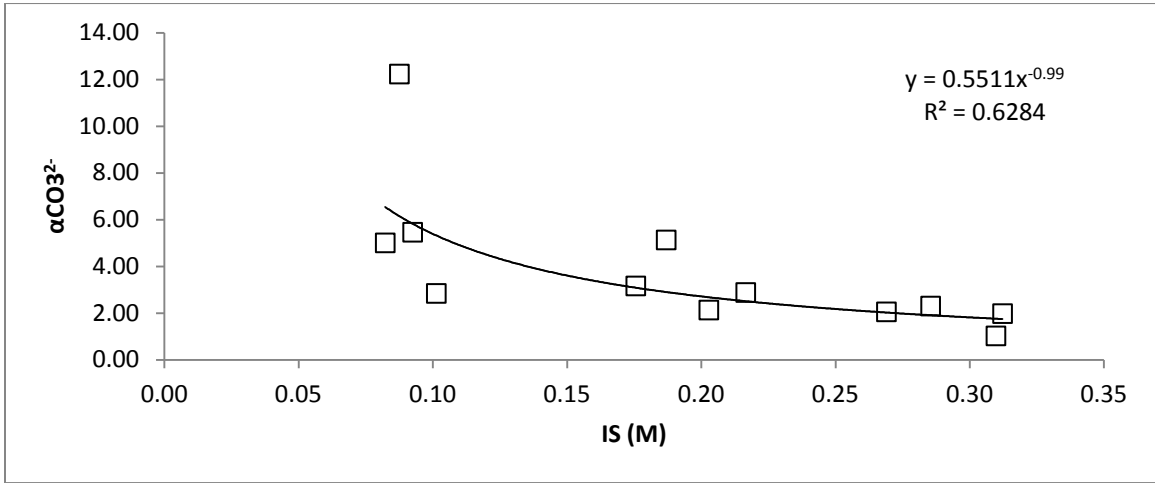
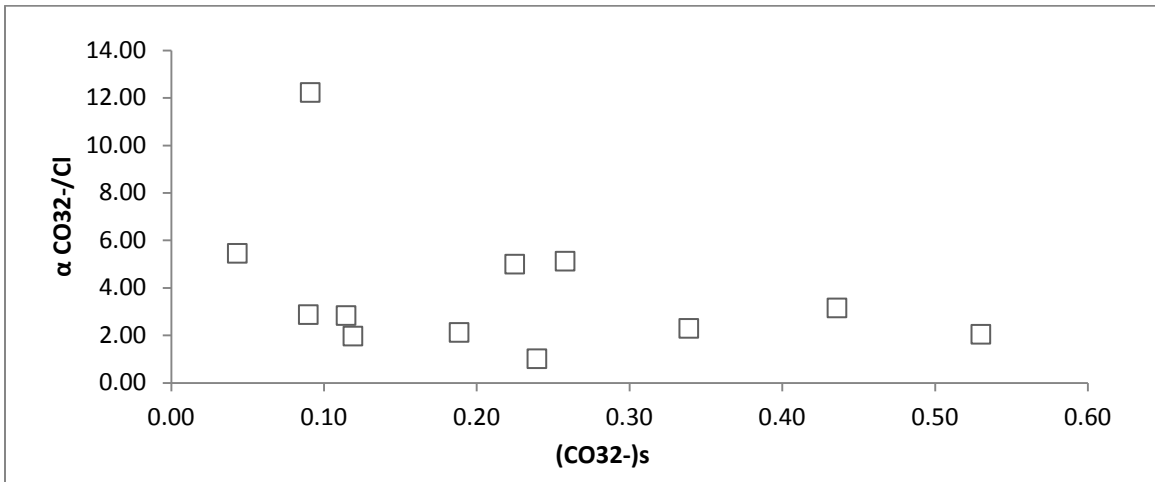


Figure 28: Carbonate Separation Factor as a Function of Equivalent Fraction



## **CHAPTER 4**

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### **PHASE 2 – COLUMN TESTING FOR SELECTIVITY VERIFICATION AND ION SEPARATION**

#### **4.1 Chapter Objectives**

The purpose of this section was to describe results from lab scale column testing of ion exchange resins with reference to three separate objectives.

1. To correlate column performance with selectivity values measured in batch isotherms for similar solutions.
2. To separate chromatographic peaks of ions during regeneration by varying regeneration flow rate, concentration, and direction.
3. To recover specific ions from a column by regeneration of a specific portion of a column. Resin phase concentrations of ions in a loaded column were measured using a specially designed column which allowed access to the resin along its longitudinal axis. Resin samples from along the column's length were analyzed to determine the concentrations of ions at each location.

#### **4.2 Chapter Summary**

The key results and conclusion from the lab scale column testing experiments are as follows:

1. Separation factors calculated in batch tests correlate well to separation factors estimated from column tests.
2. Elution curves show that chromatographic peaks for calcium and magnesium overlap when using standard regeneration flow rates and sodium chloride concentrations.
3. Variation of regeneration flow rate, concentration, and direction did not result in sufficient separation calcium and magnesium chromatographic peaks for separate ion capture.
4. Measurement of resin phase ion concentrations along the length of a loaded ion exchange column showed that discreet ion layers do not form during loading.

Instead equilibrium concentrations are propagated along the column, in the direction of flow.

### 4.3 Methods

A bench scale ion exchange system was constructed for Phase 2 experiments (see Figure 29). This system allowed the feed or regeneration solution to be pumped through two columns in series, in either direction. For example, fluid could move in a downward direction through Column 1 and then in an upward direction through Column 2. In addition, a third column could be regenerated while the other two columns were in use. Columns were held in place by re-usable clamps which allowed them to be moved or changed for other columns easily. This design also allowed for changes to the flow pattern without adjustments to the tubing.

Figure 29: Phase 2 Setup – Front (Top), Back (Bottom Left and Right)

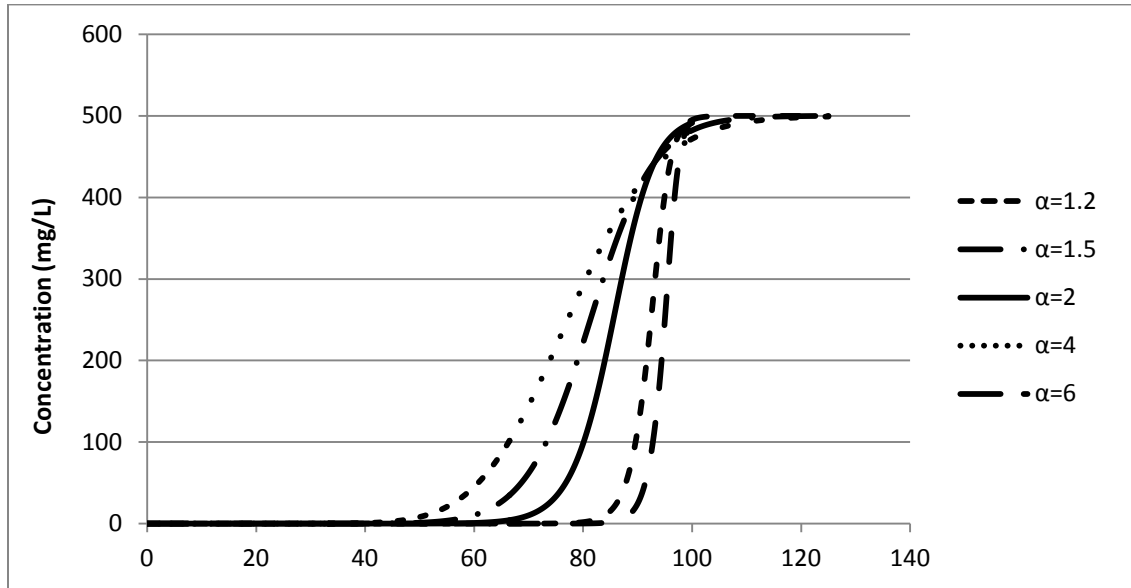


#### 4.3.1 Observed Column Compared to Predictions

The first step in the experimental process was to verify that the separation factors determined during the batch tests in Phase 1 were applicable to column processes. Similar solutions to those that were used during Phase 1 were fed into an ion exchange column until the column was exhausted. The regression relationship from Phase 1 was used to predict the separation factors based upon the ionic strength of the feed solution

and the solution phase equivalent fraction of exchanging ions(s). Equation 31 in Table 13 shows the calculation of solution phase equivalent fraction. Predictions from the MATLAB model show a relationship between the size of the mass transfer zone and the separation factor. This relationship is evident in the modeled breakthrough curves for a system with an influent solution containing 500 mg/L of calcium and 200 mg/L of sodium in Figure 30. The difference between the point of breakthrough and the point at which the effluent solution concentrations of calcium and magnesium are equal to the influent solution concentrations is the size of the mass transfer zone in the column (see Table 14). The column efficiency, as defined in this work, is the fraction of the column that is in equilibrium with the influent solution at breakthrough and is calculated using Equation 32 in Table 13.

Figure 30: Modeled Breakthrough Curves for Varied Separation Factors



**Table 13: Calculations Required to Design Phase 2 Experiments**

<p><b>Equation 31: Calculation of Equivalent Fraction in Solution</b></p> $(X_i)_s = \frac{C_i}{C_i + C_{\text{Na or Cl}}}$ <p>where <math>(X_i)_s</math> is the solution phase ionic fraction of exchanging ion</p>
<p><b>Equation 32: Calculation of Column Efficiency</b></p> $\text{Efficiency}(\%) = \frac{\# \text{ of BV to Breakthrough}}{\# \text{ of BV to Exhaustion}} * 100$ <p>where Exhaustion is defined as the point where effluent ion concentration is 75% of influent ion concentration and Breakthrough is defined at effluent ion concentration where <math>C/C_0 = .10</math></p>
<p><b>Equation 33: Calculation of Predicted Resin Phase Ion Concentration</b></p> $q_{i\text{predicted}} = \text{efficiency} \times q_{i\text{equilibrium}}$
<p><b>Equation 34: Calculation of Resin Phase Ion Equivalents of Exchanging Ions</b></p> $q_i = \frac{q_T C_i \alpha_k^i}{\sum_{k=1}^n \alpha_k^n C_n}$
<p><b>Equation 35: Calculation of Bed Volumes to Breakthrough</b></p> $BV_{BT} = \frac{q_{iBT}}{C_i}$ <p>where <math>q_{iBT}</math> is the estimated concentration of exchanging ion on the resin at breakthrough</p>



Figure 31: Relationship between Separation Factor and Column Efficiency

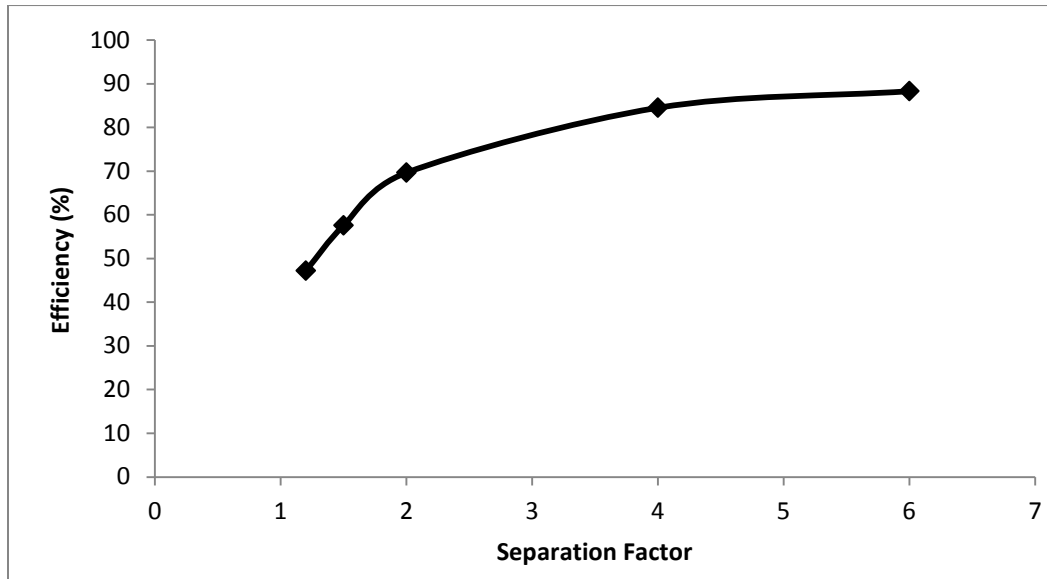


Table 14: Size of Mass Transfer Zone and Efficiency of Column at Varied Separation Factors

$\alpha$	BV to Breakthrough (A)	BV to $C=0.95 \cdot C_{in}$ (B)	Mass Transfer Zone Size (BV) (B-A)	Efficiency
1.2	47.7	101	53.3	47.23
1.5	56.5	98.1	41.6	57.59
2	67.1	96.3	29.2	69.68
4	82	97	15	84.54
6	87	98.5	11.5	88.32

The relationship between the column efficiency and the separation factor is shown in Figure 31. The amount (equivalents) of resin phase exchanging ion was predicted by multiplying the column efficiency by the amount of resin phase exchanging ion that would exist in the entire column at exhaustion. The equilibrium amount of exchanging ion on the resin was calculated using Equation 34. The number of bed volumes to breakthrough was calculated using the predicted amount of resin phase exchanging ion at breakthrough and the influent concentration, using Equation 35. For tests containing more than one exchanging ion, the number of bed volumes to breakthrough of each ion

was calculated. Determinations of sulfate and carbonate separation factors from Phase 1 was unsuccessful, but a pattern was evident in plotting the measured separation factor as function of ionic strength from Phase 1 (see Figure 32). A curve was fitted to the data and used to predict sulfate separation factors. These separation factors were correlated with column efficiency using the model, and the number of bed volumes to breakthrough was predicted (see Table 15). The flow rate for column tests in this section was 100 mL/min, and the column volume was 386 mL.

Figure 32: Sulfate Separation Factor as Function of Ionic Strength

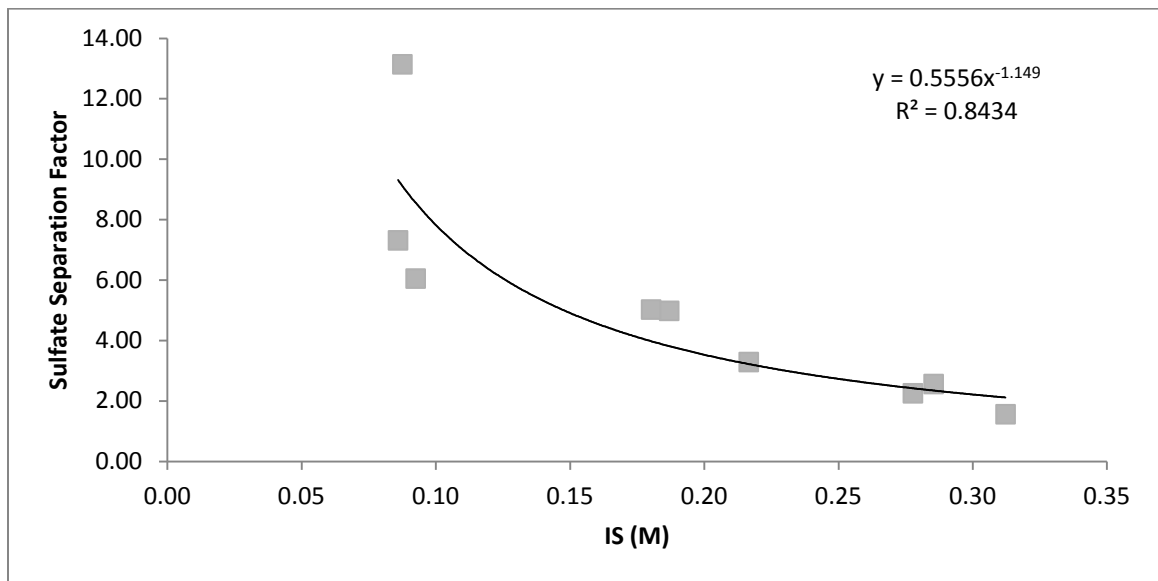


Table 15: Solution Ion Concentrations and Predicted Values for Selectivity Verification

Test #	[Ca]	[Na]	(XCa) <sub>s</sub>	IS (M)	Sep. Factor From Regression	Estimated Efficiency	Predicted qCa (eq/L)	BV <sub>BT</sub>
1	0.045	0.015	0.86	0.15	8.81	0.89	0.99	26.99
2	0.150	0.050	0.86	0.50	3.04	0.77	0.80	6.99
3	0.225	0.075	0.86	0.75	2.12	0.70	0.70	3.89
4	0.090	0.030	0.86	0.30	4.77	0.85	0.92	12.79
5	0.083	0.250	0.40	0.50	3.95	0.84	0.55	10.18
6	0.125	0.375	0.40	0.75	2.76	0.75	0.42	5.48

7	0.050	0.150	0.40	0.30	6.20	0.89	0.70	20.08
---	-------	-------	------	------	------	------	------	-------

Test #	[Mg]	[Na]	(XMg)s	IS (M)	Sep. Factor From Regression	Estimated Efficiency	Predicted qMg (eq/L)	BV <sub>BT</sub>
8	0.150	0.050	0.86	0.50	1.54	0.58	0.67	5.81
9	0.225	0.075	0.86	0.75	1.01	0.40	0.46	2.67
10	0.090	0.030	0.86	0.30	2.62	0.73	0.85	12.18
11	0.083	0.250	0.40	0.50	1.81	0.63	0.73	11.36

Test #	[Mg]	[Ca]	[Na]	(XCa)s	(XMg)s	IS (M)	Ca Sep. Factor From Regression	Mg Sep. Factor From Regression
12	0.009	0.036	0.015	0.83	0.55	0.15	8.92	5.92
13	0.015	0.060	0.025	0.83	0.55	0.25	5.68	3.48
14	0.021	0.084	0.035	0.83	0.55	0.35	4.21	2.45
15	0.009	0.036	0.015	0.83	0.55	0.15	8.92	5.92

Test #	Estimated Efficiency (Mg)	Predicted qMg (eq/L)	Predicted qCa (eq/L)	BV <sub>BT</sub>
12	0.88	0.14	0.86	20.50
13	0.80	0.13	0.83	10.32
14	0.72	0.11	0.78	6.27
15	0.88	.014	0.86	20.50

Test #	[SO4]	[Cl]	(XSO4)s	IS (M)	Predicted SO4 Sep. Factor	Efficiency SO4	Pred qSO4 (eq)	BV <sub>BT</sub>
17	0.045	0.030	0.750	0.30	1.9	0.69	0.21	5.47
18	0.045	0.030	0.750	0.30	1.76	0.63	0.17	4.85

Samples of column effluent were taken at short intervals to produce breakthrough and elution curves. These data were used to measure the actual number of bed volumes to breakthrough for each ion. These were compared to the predicted number of bed volumes to breakthrough in in the next section.

### **4.32 Separation of Ions by Varying Regeneration Conditions**

The second objective in this section was to separate chromatographic peaks of ions during regeneration by varying regeneration flow rate, concentration, and direction. This was only applied to the cation exchange column. Typical regeneration (25 mL/min and 12.5% sodium chloride solution) was performed on all exhausted columns from the selectivity verification experiments completed previously (Table 15 in the previous section). Effluent samples were taken during regeneration, and baseline elution curves were generated from these data. The process of regeneration is achieved by flooding the resin with a concentrated solution containing a low selectivity ion such as sodium. In order for complete regeneration to occur, a selectivity sequence reversal must occur. The resin preference for higher valence ions (electrostatic attraction) increases with greater solution dilution because of the increased Donnan Potential [4]. Contact with a highly concentrated solution reverses selectivity in favor of the lower valence ion, and it exchanges with higher valence on the resin

During regeneration, higher selectivity ions should theoretically elute from the column later than lower selectivity ions under normal conditions. Difference in selectivity is the basis for ion chromatography. However, in ion chromatography, columns are specifically designed for ion separation. Columns are packed and flow rates are optimized to limit the effects of dispersive and diffusive mixing within the column, so resin selectivity is the primary factor in the time that it takes each ion to exit the column. In standard ion exchange, columns are designed for water treatment rather than ion separation, and dispersion can lead to mixing of ions during elution. By reducing the strength of the regeneration solution, it was postulated that it would be possible to elute lower selectivity ions first and follow by eluting the higher selectivity ions with a more concentrated regeneration solution. It is important to note that as the difference between selectivity factors of any two ions become smaller, it will be become more difficult to

separate them during elution. Dispersion may be reduced by reducing the velocity of regeneration solution flowing through the column. For these reasons, regeneration solution concentration and flow rate were chosen as variables for this part of the experiment.

A mixed solution containing calcium, magnesium, barium, sodium, and chloride was used to load the resin in the column. Solutions of different ionic ratios and ionic strengths were used. Initially, the same solutions were used to load the columns as were used during selectivity verification, but later it made sense to use more concentrated solutions to accelerate the loading process even though it resulted in decrease of column efficiency. The concentration of the ions in the solutions used to load the columns prior to the regeneration experiments is shown in Table 16. The regeneration operating conditions that were varied to elute ions individually are shown in Table 17. Effluent samples were taken at short intervals to create elution curves (ion concentration plotted against bed volumes of regeneration solution). Results are presented in the next section.

**Table 16: Ion Concentrations in Solutions Used to Load Column Prior to Regeneration Experiments**

<b>Test #</b>	<b>[Ca]</b>	<b>[Mg]</b>	<b>[Ba]</b>	<b>[Na]</b>
<b>1</b>	0.036	0.009	--	0.015
<b>2</b>	0.237	0.059	0.005	0.099
<b>3</b>	0.237	0.059	0.005	0.099
<b>4</b>	0.237	0.059	0.005	0.099
<b>5</b>	0.237	0.059	0.005	0.099
<b>6</b>	0.473	0.118	0.009	0.197
<b>7</b>	0.473	0.118	0.009	0.197
<b>8</b>	0.237	0.059	0.005	0.099
<b>9</b>	0.237	0.059	0.005	0.099
<b>10</b>	0.237	0.059	0.005	0.099

**Table 17: Regeneration Operating Conditions**

<b>Test #</b>	<b>Flow</b>	<b>Concentration</b>	<b>Flow Direction</b>
---------------	-------------	----------------------	-----------------------

<b>Rate</b>			
	mL/min	% NaCl	
<b>1</b>	25	12.5	co-current
<b>2</b>	25	0.5	co-current
<b>3</b>	25	0.25	co-current
<b>4</b>	6	0.5	co-current
<b>5</b>	6	0.5	co-current
<b>6</b>	6	12.5	co-current
<b>7</b>	6	12.5	co-current
<b>8</b>	10	12.5	counter-current
<b>9</b>	10	12.5	counter-current
<b>10</b>	10	12.5	counter-current

#### **4.32 Recovery of Specific Ions from a Loaded Column**

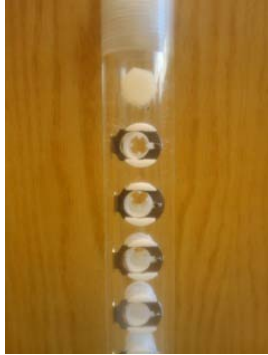
The hypothesis that led to experimentation with regeneration parameters was that ions distribute in bands or zones in a column, based on selectivity, with more selective ions located near the feed. The third objective was to quantify the distribution of ions within an exhausted column. A column was constructed (see Figure 33) featuring twenty ports along its length from which resin could be sampled or through which regeneration solution could be pumped. This allowed for selected portions of the column to be regenerated separately.

Figure 33: Specially Designed Research Column with Ports

Filled  
Column



Open Resin Ports  
Close-up



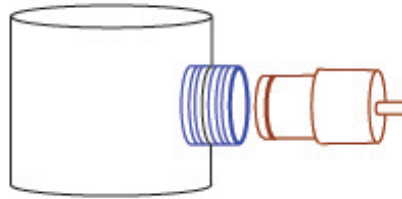
Closed Resin Ports



Full Column Schematic



Single Port Schematic



Feed solution was passed through the column until it was loaded with calcium and magnesium, and resin samples were collected from the ports along the length and analyzed to determine ion distribution. The feed solution concentrations, the number for

which solutions was treated, and the flow rate are shown in Table 18. Resin samples were thoroughly rinsed and then submerged in 2N HCl to strip off all exchangeable ions. The HCl solution was analyzed by Atomic Absorption Spectroscopy (AAS) to determine ion concentrations. Resin samples were separated from the HCl solution by filtration, then dried at 105°C and weighed.

**Table 18: Feed Solution Ion Concentrations and Number of Bed Volumes**

[Ca]	[Mg]	[Na]	IS	BV	Flow Rate (mL/min)
0.06	0.02	0.10	0.35	12.26	100

## 4.4 Results

### 4.41 Column Performance Compared to Predictions

The first objective of this phase was to correlate column performance with separation factors measured in batch isotherms for similar solutions. Data from the two phases were compared using a combination of modeling and regression of Phase 1 data. In Section 4.31, separation factors were predicted based on values of equivalent fraction of exchanging ion and ionic strength. Updated predictions of separation factors based on measured concentrations of ions in the mixed solution are shown in Table 19 .

**Table 19: Updated Versus Original Separation Factor Predictions for Column Tests**

Test #	Original Predicted $\alpha_{Ca}$	Original Predicted $\alpha_{Mg}$	Updated Predicted $\alpha_{Ca}$	Updated Predicted $\alpha_{Mg}$
1	8.81	N/A	8.25	N/A
2	3.04	N/A	4.04	N/A
3	2.12	N/A	1.93	N/A
4	4.77	N/A	4.50	N/A
5	3.95	N/A	3.74	N/A
6	2.76	N/A	2.63	N/A



<b>7</b>	6.20	N/A	5.91	N/A
<b>8</b>	N/A	1.54	N/A	1.84
<b>9</b>	N/A	1.01	N/A	0.97
<b>10</b>	N/A	2.62	N/A	2.60
<b>11</b>	N/A	1.81	N/A	1.97
<b>12</b>	8.92	5.92	8.99	6.06
<b>13</b>	5.68	3.48	5.60	3.43
<b>14</b>	4.21	2.45	4.41	2.56
<b>15</b>	8.92	5.92	8.37	5.50

<b>Test #</b>	<b>Original Predicted <math>\alpha</math>SO<sub>4</sub></b>	<b>Updated Predicted <math>\alpha</math>SO<sub>4</sub></b>
<b>16</b>	2.22	1.90
<b>17</b>	2.22	1.76

The number of bed volumes to breakthrough for each ion was predicted based upon the updated separation factors. Predicted number of bed volumes to breakthrough was compared to measured number of bed volumes to breakthrough to evaluate the applicability of separation factor regressions from batch isotherm test results to column processes. A measured breakthrough curve used to determine bed volumes to breakthrough is shown in Figure 34. Curves like these were measured for each column test. Correlations between measured and calculated values are shown in Figure 36. Values are listed in Table 20.

Figure 34: Breakthrough Curve from Test #14

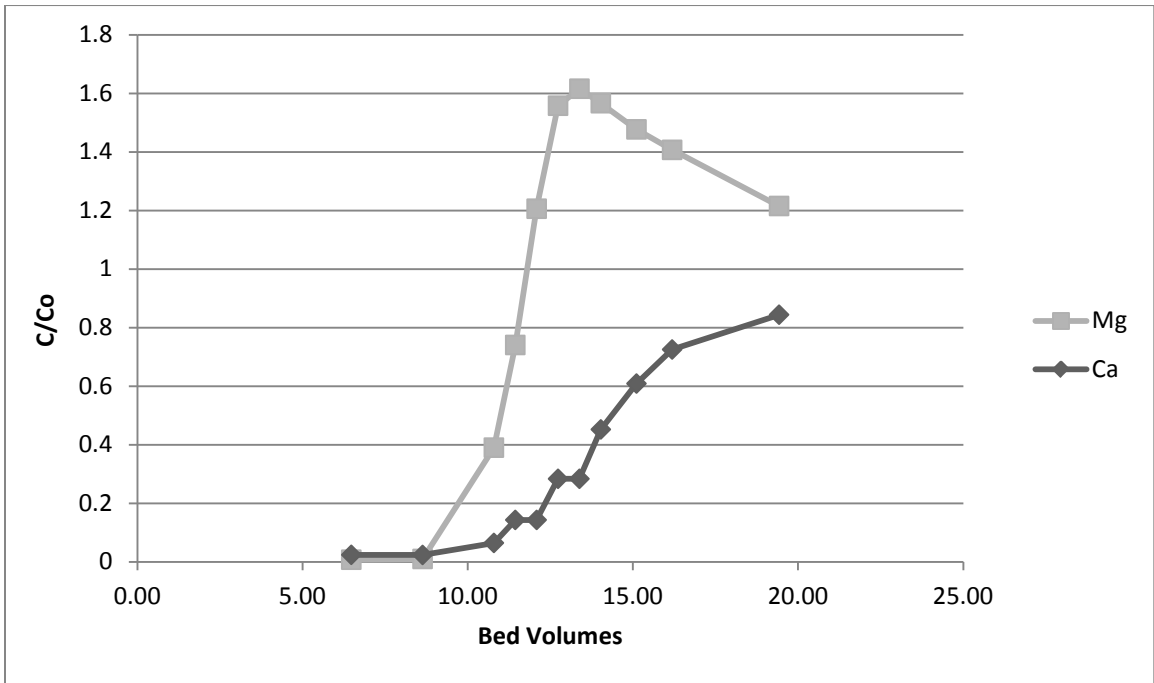
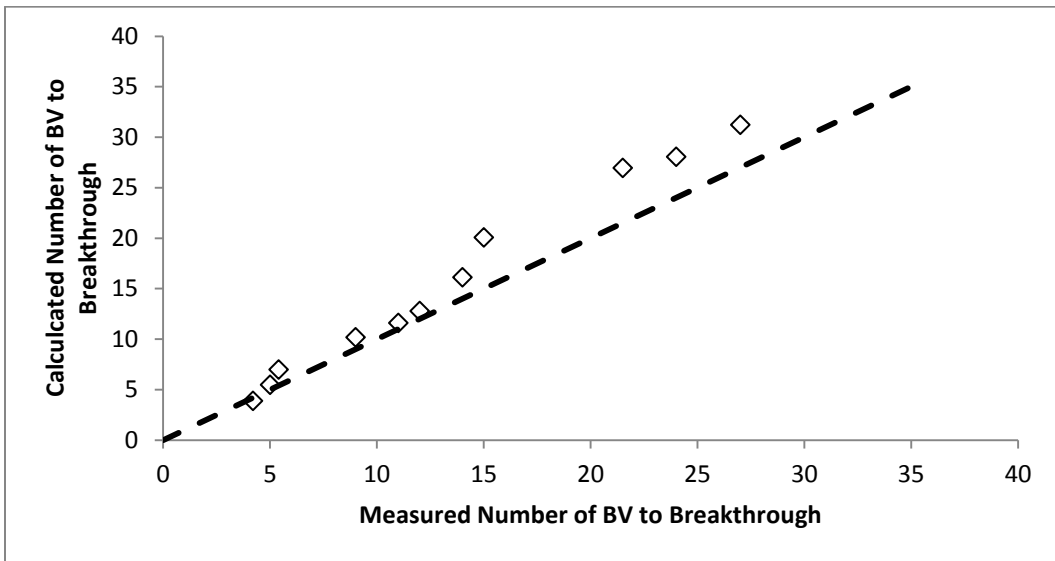
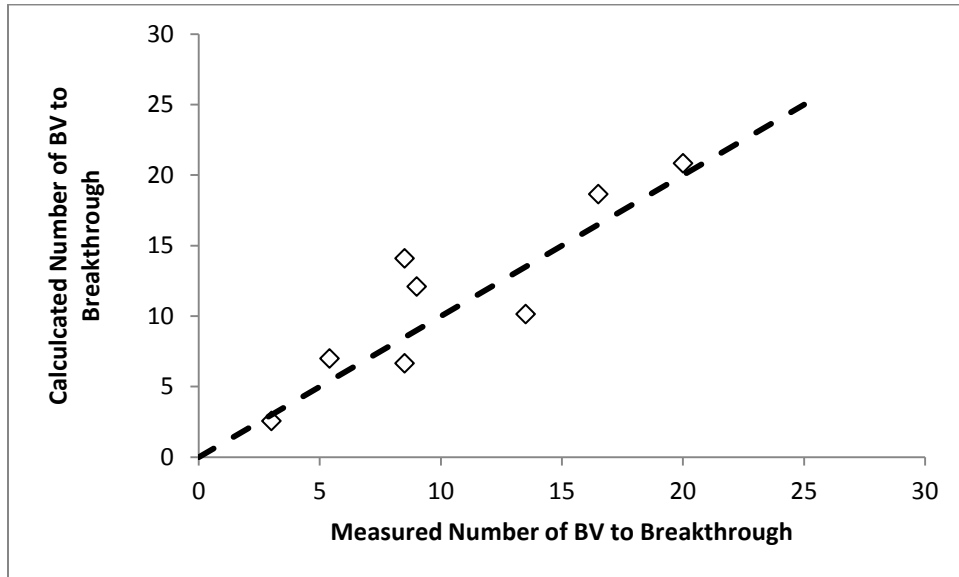


Figure 35: Correlation between Calculated and Measured Number of Bed Volumes to Calcium Breakthrough



**Figure 36: Correlation between Calculated and Measured Number of Bed Volumes to Magnesium Breakthrough**



**Table 20: Predicted Versus Measured Number of Bed Volumes to Breakthrough for Column Tests**

Test #	Ca		Mg	
	Predicted BV <sub>BT</sub>	Measured BV <sub>BT</sub>	Predicted BV <sub>BT</sub>	Measured BV <sub>BT</sub>
1	27.0	21.5	NA	NA
2	7.0	5.4	NA	NA
3	3.9	4.2	NA	NA
4	12.8	12	NA	NA
5	10.2	9	NA	NA
6	5.5	5	NA	NA
7	20.1	15	NA	NA
8	NA	NA	7.0	5.4
9	NA	NA	2.6	3
10	NA	NA	12.1	9
11	NA	NA	14.1	8.5
12	31.23	27	20.8	20
13	16.13	14	10.1	13.5
14	11.61	11	6.7	8.5
15	28.06	24	18.7	16.5

<b>SO4</b>		
<b>Test #</b>	<b>Predicted BV<sub>BT</sub></b>	<b>Measured BV<sub>BT</sub></b>
<b>16</b>	5.5	5
<b>17</b>	4.8	4.5

The correlation between measured and predicted number of bed volumes to breakthrough for the set based on calcium separation factors is very high. These results demonstrate that the regression relationship developed from batch isotherm data can predict separation accurately. The results also demonstrate that the correlation between column efficiency (size of the mass transfer zone) and the separation factor predicted by the MATLAB model is a useful in predicting the percentage of the column that is in equilibrium with the solution at the time of breakthrough. It is possible to predict the number of bed volumes to breakthrough for a column containing ResinTech<sup>®</sup> CG-10 resin using the separation factor regression from Phase 1 and the model, even for solutions that have higher ionic strengths than usually treated with ion exchange.

Correlations between measured and predicted number of bed volumes to breakthrough for magnesium are not as strong as those for calcium. Modeled column efficiency is a function of separation factor, not ion type, so the issue is either in the regression or the measurement. The batch isotherm results for separation factor had more variability in the separation factors for magnesium than for calcium, indicating that the separation factors for magnesium may be more difficult to predict.

Only two anion exchange column tests were performed, so it is not possible to make a significant correlation, but the number of bed volumes predicted is very close to the measured value for both tests. More data is necessary to draw a definite conclusion, but it does appear that the sulfate separation factor can be predicted as a function of ionic strength

Time to breakthrough of magnesium and calcium in column tests using solutions with ionic strengths up to 0.3 M are well predicted by combining regression of data from batch isotherms tests with column efficiency predicted by the MATLAB model. The measured time to breakthrough of sulfate agree well with that by calculated by combining the relationship from Phase 1 in which sulfate separation factor is a function of ionic

strength with the column efficiency predicted by the MATLAB model. Accurate prediction of separation factors and consequential time to breakthrough in ion exchange columns is very useful in design.

#### **4.42 Separation of Ions by Varying Regeneration Conditions**

The second objective of Phase 2 was to explore conditions that would allow ions to be eluted from the column separately during regeneration. Separation of ions during elution was investigated because it was hypothesized that this separation would facilitate the recovery of specific minerals from RO concentrate for beneficial reuse. The conditions that were investigated were the regeneration flow rate, concentration, and direction. Testing for this objective was done only for cation exchange columns. Elution curves were measured during regeneration of column testing for Objective 1 in order to see how ions elute under standard conditions. Manufacturer specifications indicated that regeneration solution should contain 10%- 15% sodium chloride and that the flow rate should be 0.5 to 1.5 gpm per cubic foot. All column tests performed for this objective were regenerated with 12.5% sodium chloride solution at 0.5 gpm per cubic foot until all ions had been eluted. For the laboratory column, that corresponded to 25 mL/min. Figure 37 shows calcium elution curves measured during standard regeneration (25 mL/min, 12.5% NaCl). On average, the peak calcium concentration occurred at approximately 1 bed volume, and the curves were asymmetrical. The calcium concentration increased quickly before the peak and declined more slowly afterward. As expected, due to its lower selectivity, magnesium peak concentration occur slightly sooner, but the shape of the elution curves follow a similar pattern.

Figure 37: Calcium Elution Curves Measured during Standard Regeneration

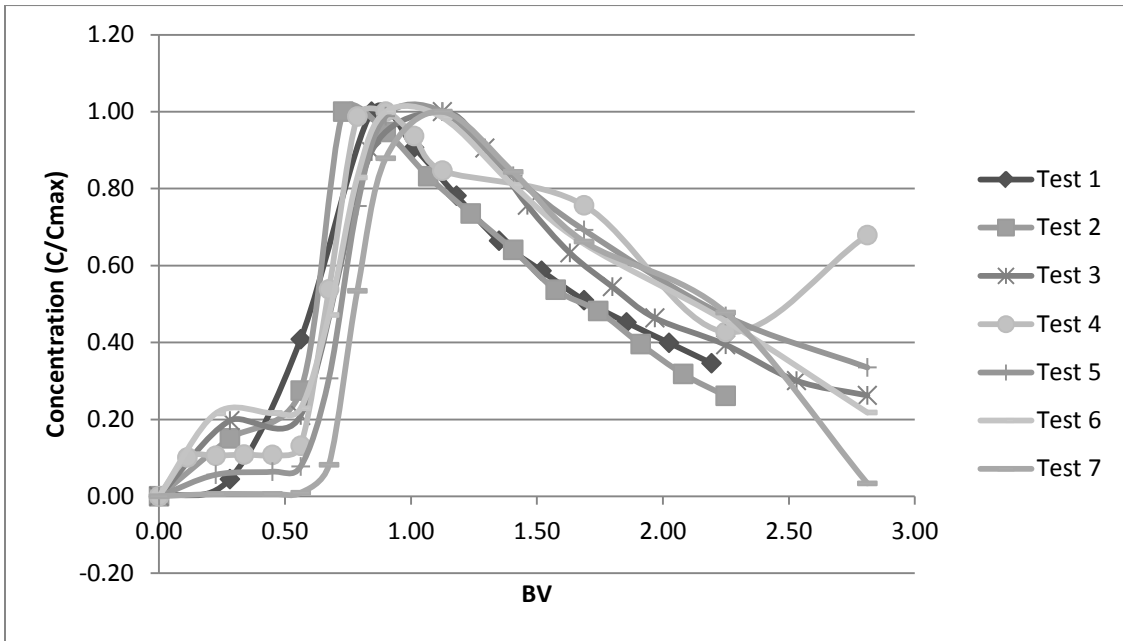
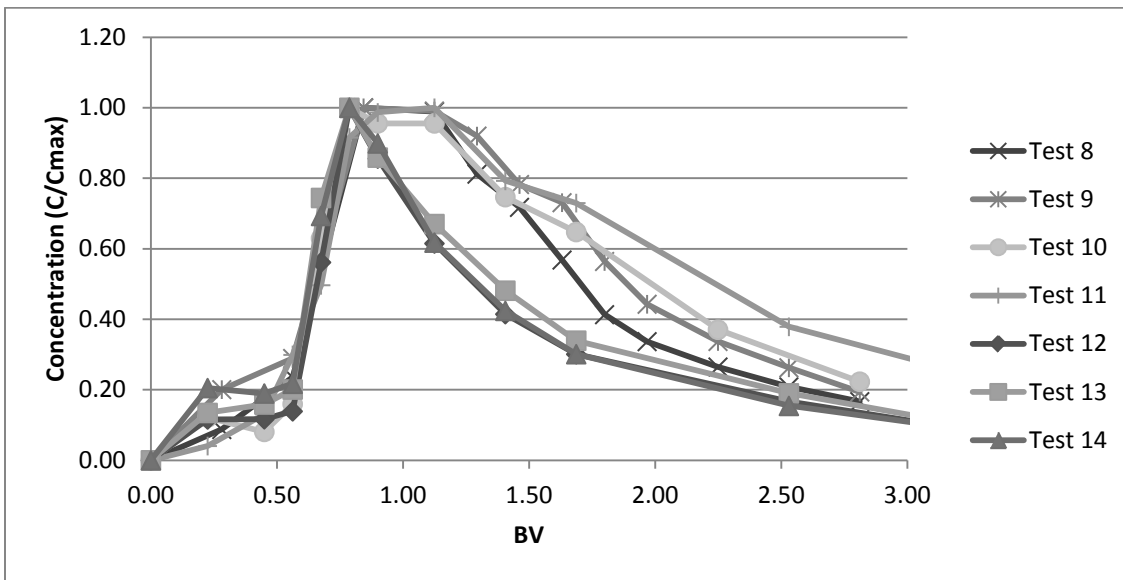


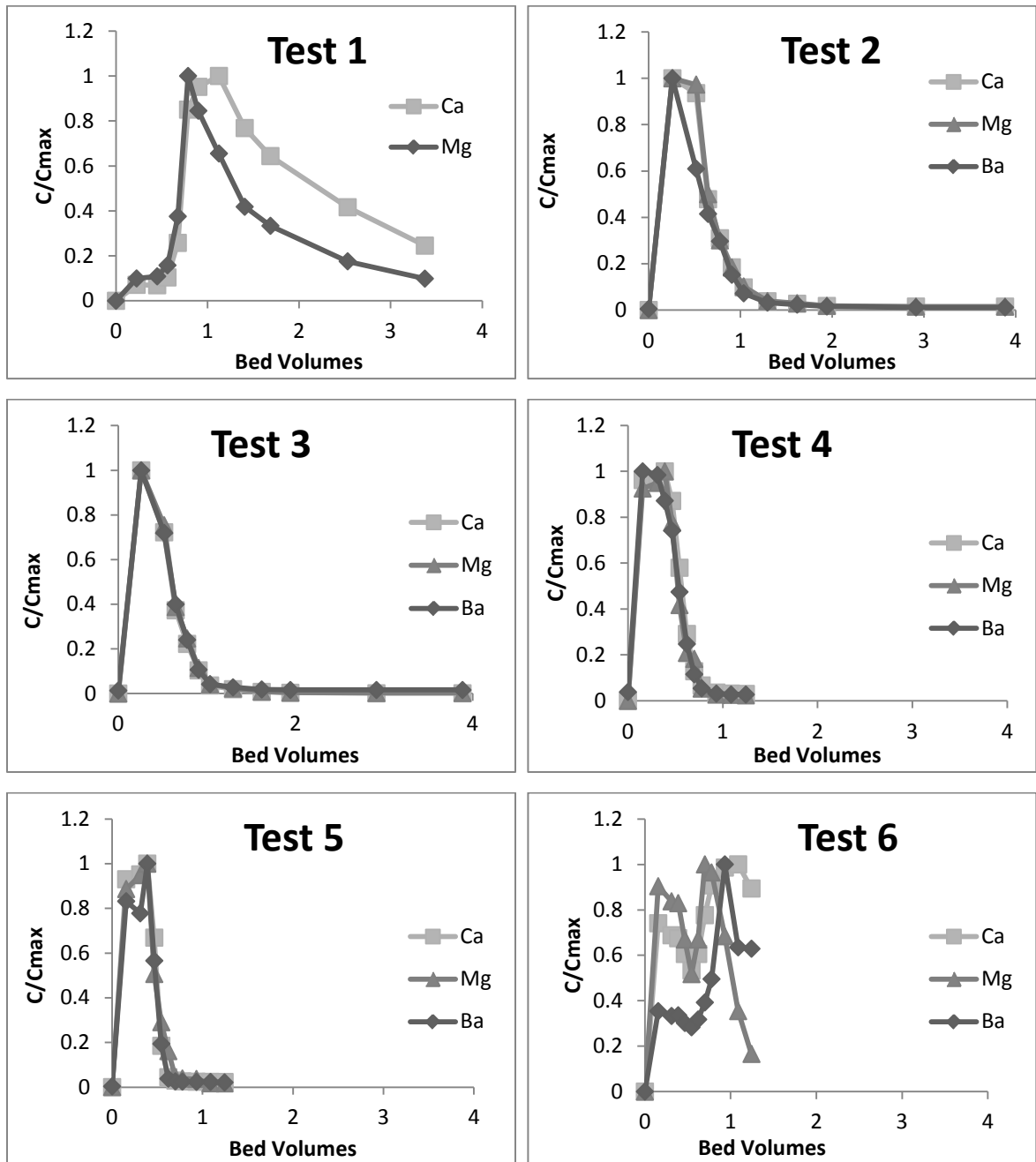
Figure 38: Magnesium Elution Curves Measured during Standard Regeneration

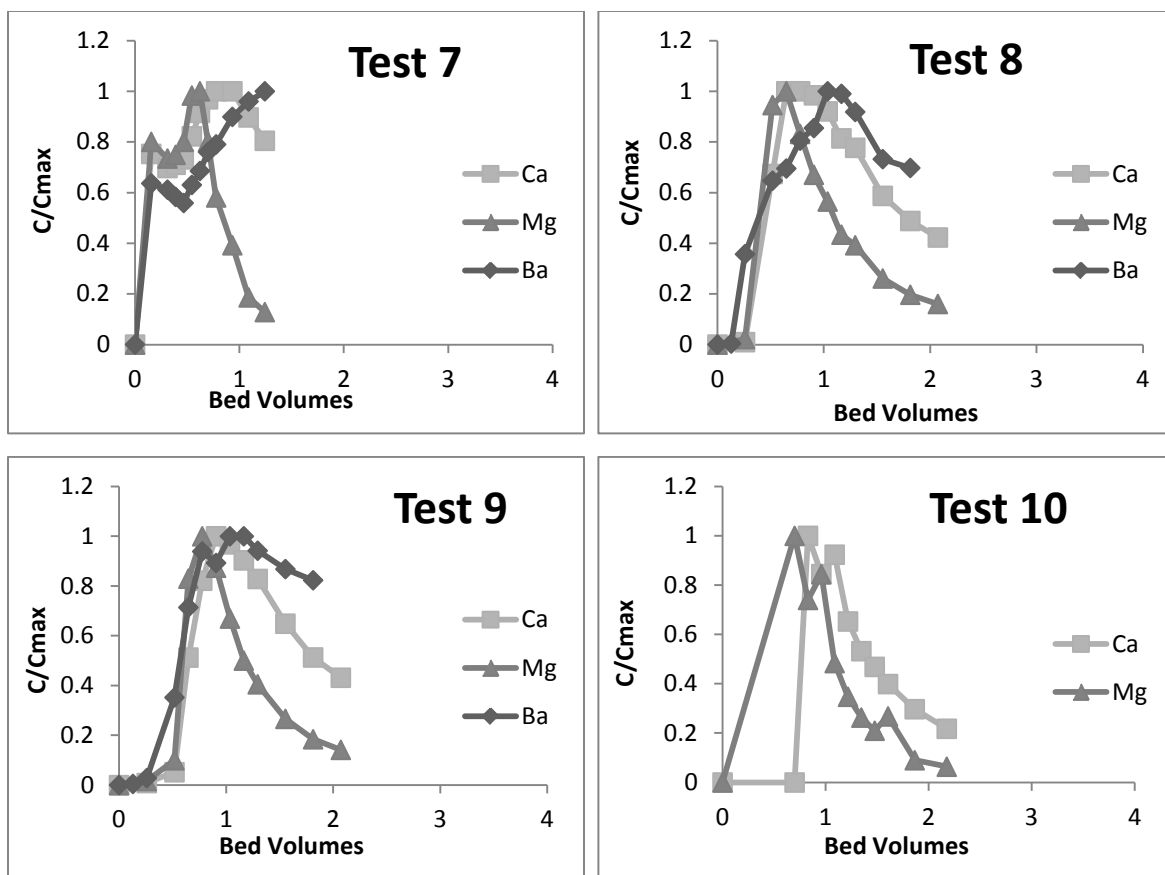


Based on the similarity of calcium and magnesium separation factors and the pronounced tailing of the elution curves, separating peaks enough to capture single cations would be difficult. In the next step, columns were loaded with solutions containing calcium, magnesium, barium, and sodium at the concentrations shown in

Table 16. The columns were then regenerated with varying concentrations of sodium chloride solution, flow rates, and regeneration direction as show in Table 17. Elution curves for the ten regeneration variation tests are shown in Figure 39.

Figure 39: Elution Curves for Regeneration Variation Tests





The most notable feature of all the tests is that despite changes in flow rate, direction, and solution concentration, there is significant overlap in ion peaks. Ions were not able to be separated by varying regeneration characteristics or direction of flow. There were however, interesting patterns that emerged from the data. In tests 2-5, sodium chloride concentration in the regeneration solution was less than 0.5%. Peak calcium concentrations occurred at 0.25 bed volumes, but they never exceeded the feed solution calcium concentration. It appears that the column was not actually being regenerated in these cases and that the peaks merely represent the solution phase ions in the pore space being flushed out by the regeneration solution. In test 6 and 7, the flow rate was reduced to 6 mL/min. The conclusion from this set of tests is that although some changes in elution can be attributed to changing regeneration operation conditions, elution of these ions from the resin as separate peaks was not successful.



### 4.43 Recovery of Specific Ions from a Loaded Column

The third objective of Phase 2 was to quantify the resin phase ion concentrations along the length of a loaded ion exchange column to evaluate whether it is possible to separate ions by regeneration of a specific portion of a column. Theory suggests that ions distribute in distinct layers in an ion exchange column during loading, based on upon their selectivity properties. .

The column containing ports along its length (described previously) was loaded by passing through a solution containing calcium, magnesium, and sodium, and resin was sampled from several points along the length of column. The resin samples were submerged in 2N HCl to determine the resin phase ion concentrations at each location in the column. Table 21 lists the resin phase ions concentrations measured from the stripped resin that was taken from the various sampling ports along the longitudinal axis of the column. Gray shaded rows indicate that resin was not sampled from the port. Instead, concentrations from the ports above and below it were averaged. Separation factors were calculated (see Table 22) under the assumption that the resin from the top most portion of the column was in equilibrium with the feed solution.

**Table 21: Resin Phase Ion Concentrations Measured From Stripped Resin**

<b>Location</b>	<b>Ca</b>	<b>Mg</b>	<b>Na</b>	<b>Sum</b>
	meq/g	meq/g	meq/g	
<b>1</b>	0.44	0.78	2.51	3.73
<b>2</b>	0.83	0.98	1.78	3.60
<b>3</b>	1.21	0.96	1.42	3.59
<b>4</b>	1.39	0.94	1.40	3.74
<b>5</b>	1.60	0.88	1.24	3.72
<b>6</b>	1.90	0.88	0.94	3.72
<b>7</b>	2.20	0.88	0.64	3.72
<b>8</b>	2.37	0.83	0.53	3.73
<b>9</b>	2.54	0.78	0.42	3.73
<b>10</b>	2.62	0.72	0.40	3.73

11	2.69	0.66	0.38	3.74
12	2.48	0.57	0.73	3.79
13	2.27	0.49	1.08	3.84
14	2.53	0.48	0.83	3.84
15	2.78	0.47	0.58	3.83
16	2.81	0.47	0.50	3.78
17	2.83	0.48	0.41	3.72
18	2.88	0.44	0.41	3.73
19	2.93	0.40	0.41	3.75

Table 22: Solution Concentration and Calculated Separation Factors

Ion	Separation Factor, $\alpha$	Solution Concentration (N)
Calcium	5.79	0.13
Magnesium	2.83	0.04
Sodium	1	0.10

Figure 40: Resin Phase Concentration Compared to Equilibrium Resin Phase Concentration

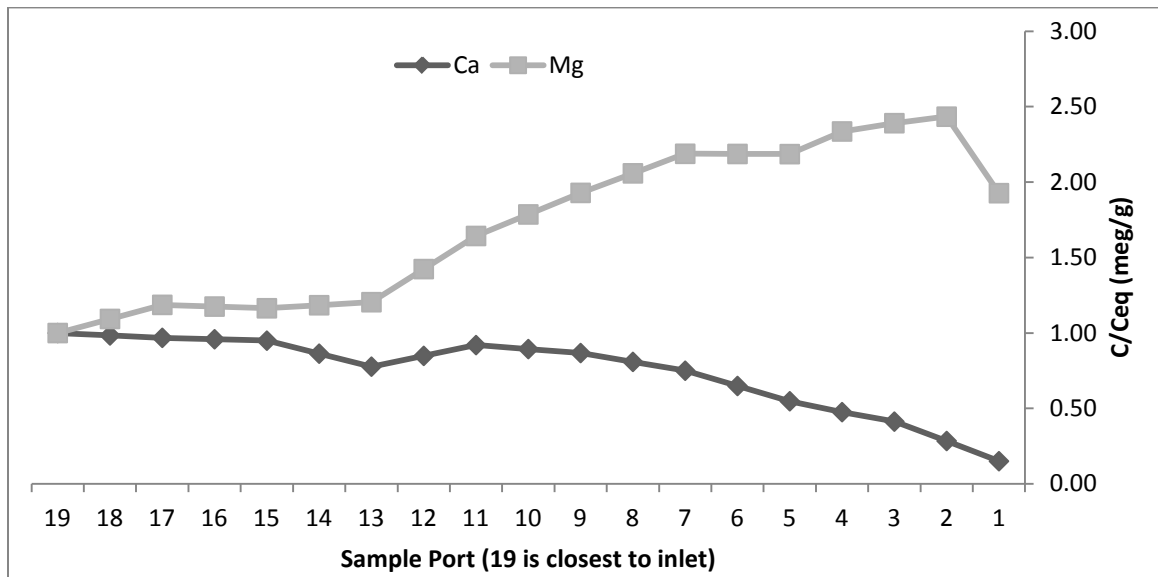
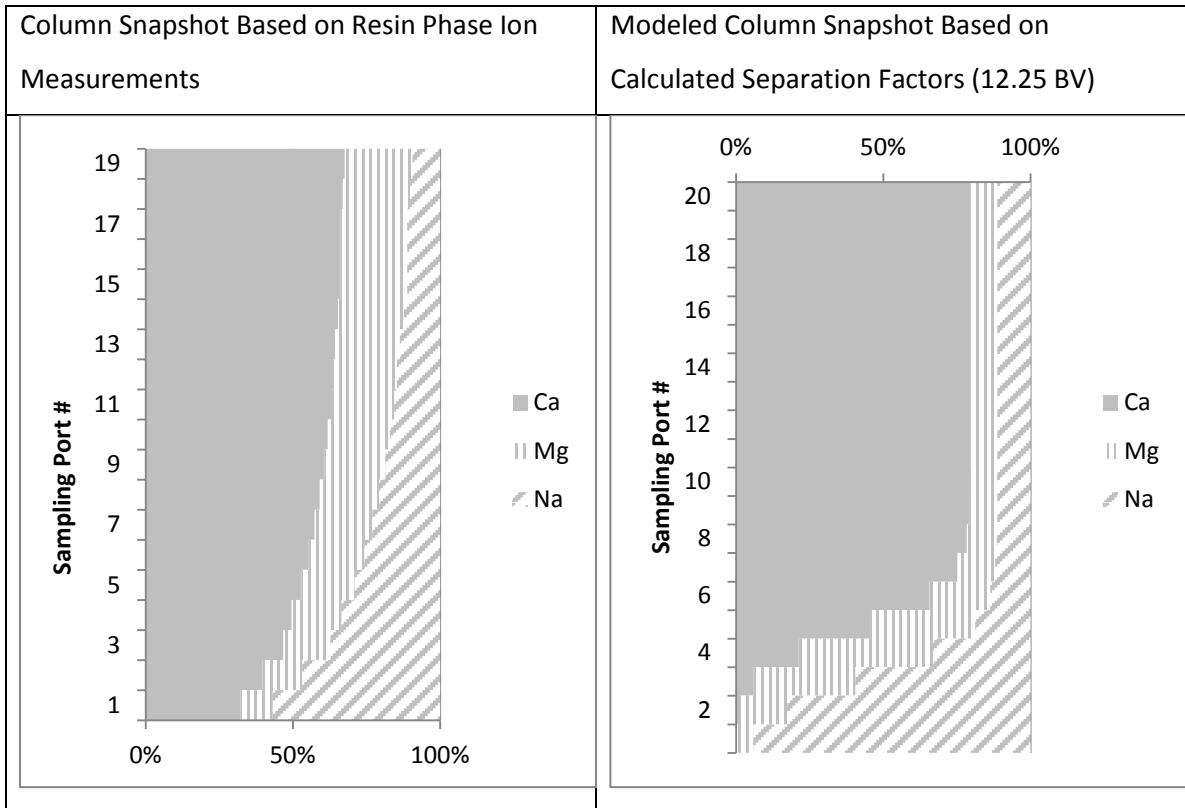


Figure 41: Distribution of Ions in the Resin Phase Axially Through a Column



Chromatographic peaking of magnesium can be observed by comparing the equilibrium resin phase concentration of magnesium to the resin phase concentration along the column length. While the calcium concentration decreases relative to the equilibrium concentration, the magnesium concentration increases (see Figure 40). Sample results indicate that ions were not present in distinct layers (Figure 41). Instead, there was a mix of ions in the resin phase, at all locations along the column. A comparison of the column snapshot based upon the measured results to one generated by the model for a column treated with the same solution for the same number of bed volumes and using the same separation factors, shows that the model is able to predict the resin phase concentrations well. Unfortunately, because the analysis did not reveal discreet ion banding or zoning, regeneration the lower portion of the column was not an option for ion separation. Since ions were not able to be separated using column processes, focus was moved to salt separation during precipitation, as described in the next section.

## **CHAPTER 5**

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### **PHASE 3 –SALT PRECIPITATION**

#### **5.1 Chapter Objectives**

The purpose of this section is to describe experiments in which laboratory simulated cation and anion regeneration solutions were mixed under different pH conditions to form precipitates. The goal of varying the pH during mixing was to precipitate carbonate and sulfate salts separately. Precipitates were analyzed by scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD) to determine their characteristics and mineralogy.

#### **5.2 Chapter Summary**

The key results and conclusions from precipitation testing experiments are as follows:

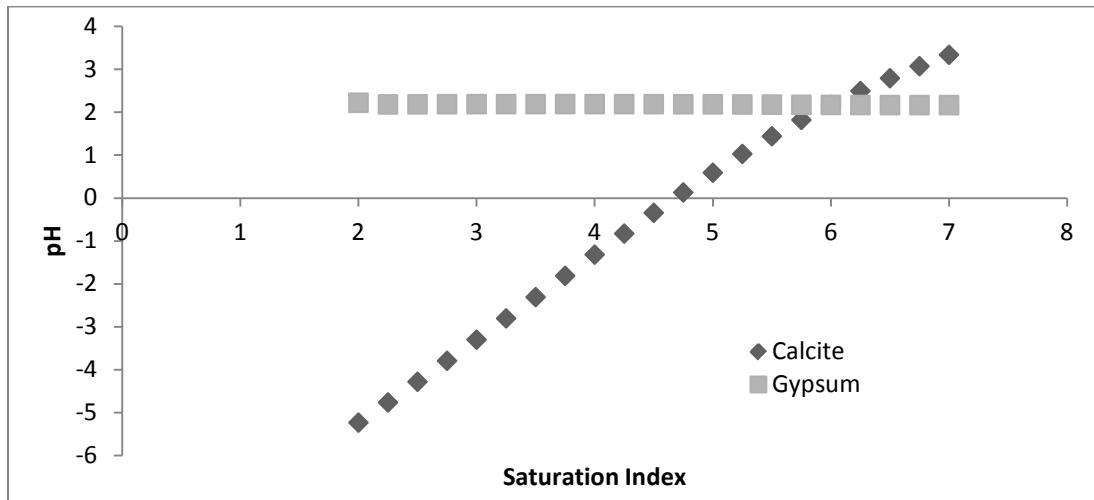
- Equilibrium modeling using Visual MINTEQ showed that that several salts are supersaturated in a mixture of cation and anion regeneration solutions.
- Visual MINTEQ modeling also showed that adjusting pH can control the precipitation of carbonate salts.
- A precipitate containing a heterogeneous mix of phases including halite, bassanite, bassirite, bischofite, and, calcium carbonate (CaCO<sub>3</sub>) is formed when cation and anion regeneration solutions are mixed without pH adjustment.
- Calcium sulfate precipitated in mixtures in which the pH of the anion regeneration solution was reduced below pH 5 prior to mixing with cation regeneration solution.
- A precipitate containing calcium, magnesium, and carbonate precipitated from the supernatant of the solution which had previously precipitated calcium sulfate when its pH was increased above 9.5

#### **5.3 Methods**

Chemical modeling in Visual MINTEQ showed that pH was an important variable in controlling the precipitation of specific salts from the mixture. Figure 42 shows the calcite and gypsum saturation indices as functions of pH as predicted by Visual

MINTEQ. Input calcium and carbonate concentration were 1M and the activity corrections were made using the specific ion interaction theory model. For this model solids are allowed to be supersaturated rather than precipitating. Saturation indexes greater than zero indicate that the solution is supersaturated. The figure shows that calcite precipitation is predicted to occur when pH is equal to 4.4. Gypsum precipitation is predicted to occur regardless of pH (between 2 and 7). By adjusting the pH of a mixed solution containing calcium, carbonate, and sulfate to between 2 and 4.4, gypsum precipitation should occur while carbonate stays in solution. If sufficient calcium is left after calcium sulfate precipitate comes to equilibrium with the solution, the pH can be increased and the calcium should precipitate as a carbonate salt. This was the basis of experiments with simulated regeneration solutions.

Figure 42: Calcite Saturation Index as a Function of pH



The procedure for these experiments was as follows. Synthetic cation and anion regeneration solutions were created in the lab. They were made to represent the regeneration solutions that would be recovered from anion and cation exchange columns that had treated RO concentrate with a 3:1 ratio of divalent cations to sodium with an ionic strength of 0.25. Regeneration solution ionic concentrations are listed in Table 23. Regeneration solutions were mixed together (volumes are listed in Table 24) and solids

were allowed to precipitate. Table 24, Table 25, and Table 26 list the parameters and notes for experiments in Phase 3.

**Table 23: Anion and Cation Regeneration Solution Concentrations**

<b>Cation Regeneration Solution for Experiments 2A,3</b>	<b>g/L</b>	<b>M</b>
<b>Mg</b>	4.49	0.1849
<b>Ca</b>	14.82	0.3698
<b>Ba</b>	0.51	0.0037
<b>K</b>	1.45	0.0370
<b>Na</b>	39.46	1.7164
<b>Cl</b>	101.76	2.8701

<b>Anion Regenerant Solution for Experiments 2A,3</b>	<b>g/L</b>	<b>M</b>
<b>SO4</b>	26.43	0.2752
<b>CO3</b>	16.51	0.2752
<b>NO3</b>	4.27	0.0688
<b>F</b>	0.05	0.0028
<b>Na</b>	66.29	2.8833
<b>Cl</b>	60.80	1.7151

<b>Cation Regenerant Solution for Experiments 4-7</b>	<b>g/L</b>	<b>M</b>
<b>Mg</b>	6.20	0.2549
<b>Ca</b>	20.44	0.5099
<b>Ba</b>	0.07	0.0005
<b>K</b>	5.98	0.1530
<b>Na</b>	40.51	1.7621
<b>Cl</b>	120.36	3.3948

Anion Regenerant Solution for Experiments 4-7	g/L	M
SO <sub>4</sub>	26.43	0.2752
CO <sub>3</sub>	16.51	0.2752
NO <sub>3</sub>	4.27	0.0688
F	0.05	0.0028
Na	66.29	2.8833
Cl	60.80	1.7151

Table 24: Experimental Matrix for Phase 3

Experiment Number	<sup>‡</sup> V <sub>Cation</sub>	<sup>‡</sup> V <sub>Anion</sub>	pH
2A	100	100	not adjusted
3	100	100	2.43, 9.84, 11.07
4	100	100	not adjusted
5	50	70	2.99, 7.5, 10.19
6	100	100	4.5,10.04
7	100	100	5.06,10.03

<sup>‡</sup>V<sub>Cation</sub> - Volume (mL) Cation Solution, V<sub>Anion</sub> - Volume (mL) Anion Solution

Table 25: Samples Collected from Phase 3 Experiments

Experiment Number	Samples Taken From Each Experiment
2A	Liquid: Initial solutions, Supernatant Solid: Final Precipitate
3	Liquid: Initial solutions, At pH=2.43, At pH=9.84, At pH=11.07, After heat Solid: At pH=2.43, At pH=9.84, After heat
4	Liquid: Initial solutions, Supernatant Solid: Final Precipitate

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<b>5</b>	Liquid: Initial solutions, At pH=2.99, At pH=7.5, At pH=10.19 Solid: At pH=2.43, At pH=7.5, At pH=10.19
<b>6</b>	Liquid: Initial solutions, At pH=4.5, At pH=10.04 Solid: At pH=4.5, At pH=10.04
<b>7</b>	Liquid: None Solid: At pH=5.06, At pH=10.03

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**Table 26: Notes for Phase 3 Experiments**

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<b>Experiment Number</b>	<b>Notes</b>
<b>2A</b>	Used same concentration factor for cation and anion solutions, added cation solution to anion solution
<b>3</b>	Reduced pH of anion solution to 2.43, added cation solution, raised pH to 9.84, then to 11.07
<b>4</b>	Used greater concentration factor for cation than anion solutions due to different exchange capacities
<b>5</b>	Lowered pH of anion solution to 2.99, mixed in cation solution, settled precipitate, increased pH to 7.5 by adding 20mL of anion solution, filtered solution, increased pH to 10.19, centrifuged to separate precipitate
<b>6</b>	Lowered pH of anion solution to 4.26, mixed in cation solution, settled precipitate after 10 min, increased pH 10.04, centrifuged to separate precipitate
<b>7</b>	Repeat of Experiment #6, expect solids were rinsed prior to drying.

---

At the end of each experiment, solids were separated from the supernatant by filtration using a vacuum flask and a cellulose fiber pad (Gelman Sciences 47mm Pure Cellulose Fiber Filter Pads #66025) or centrifuged to separate liquid and solid materials. Both liquid and solid samples were analyzed to determine the characteristics of the salt precipitation from each experiment. Concentrations of ions in liquid samples were



measured by AAS and IC. Solid samples were dried and then examined using SEM and XRD. One challenge of working with SEM and XRD is that samples must be dried prior to examination. The most common form of calcium sulfate is gypsum, ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), but it can be converted to anhydrite ( $\text{CaSO}_4$ ) by heating to above  $200^\circ\text{C}$ . The common forms of calcium carbonate are all anhydrous. Limited mineralogical changes are expected to occur at  $104^\circ\text{C}$ , the temperature at which solid samples were dried in the laboratory oven. The SEM was also equipped with EDS, which can identify elemental composition of a sample and provide a semi-quantitative analysis. Through the combination of these analyses, it was possible to speculate about the character of the precipitate from completed Phase 3 experiments

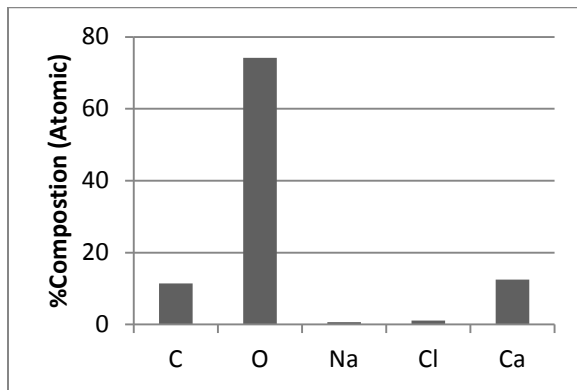
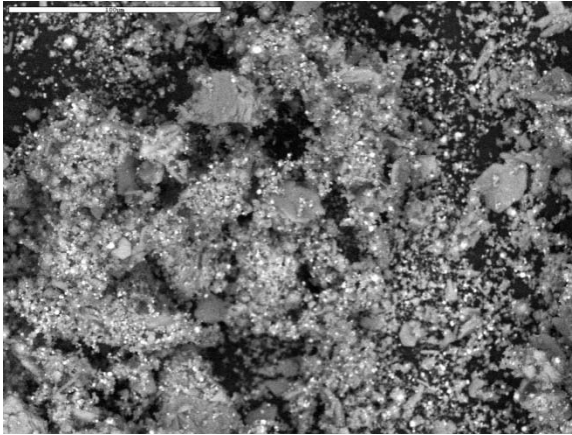
## 5.4 Results

There were three different conditions under which salts were precipitated from a mixture of anion and cation regeneration solutions. In the first, no pH adjustments were made. This occurred in experiments 2A and 4. SEM images and EDS spectra were taken of precipitates from both experiments, and an XRD spectrum was taken of precipitate from experiment 2. As can be seen in SEM images in Figure 43, these precipitates are similar. The images show a heterogeneous collection of solids of different sizes and shapes. The difference in brightness between particles indicates differences in atomic weight. Lighter shades indicate heavier elements. EDS spectra from different portions of each image (Figure 43) indicate that most of the precipitate from both experiments consists of calcium, oxygen, carbon, sodium, and chloride, although small amounts of magnesium, sulfur, and barium were also detected. The presence of sodium and chloride are most likely due to the fact that precipitates were not rinsed before drying in the oven. For this reason, ions that were still in solution at the end of the experiment may have precipitated during the drying process. It is likely that any sodium or chloride salts present in the samples precipitated in this fashion because they are generally soluble. In later precipitation experiments (#7 from this phase and Phase 4), all precipitates were thoroughly rinsed before drying. Figure 44 shows the XRD spectrum taken of precipitate from experiment 2 which shows the presence of several different salts including sodium

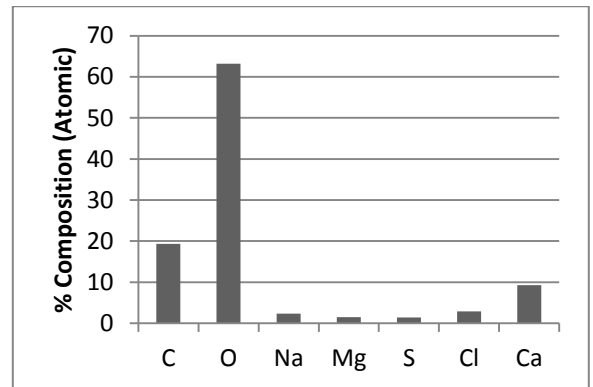
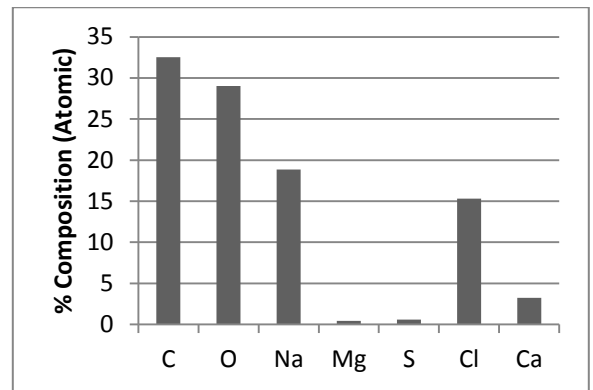
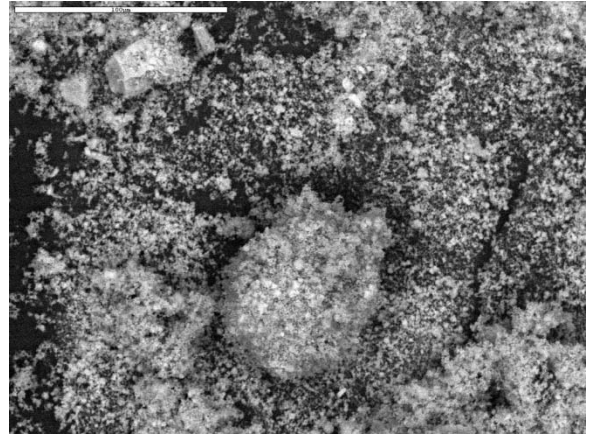
chloride (NaCl), bassanite ( $\text{Ca}(\text{SO}_4)(\text{H}_2\text{O})_{0.5}$ ), bassirite ( $\text{Ca}(\text{SO}_4)(\text{H}_2\text{O})_{0.8}$ ), bischofite ( $\text{MgCl}_2(\text{H}_2\text{O})_6$ ), and, calcium carbonate ( $\text{CaCO}_3$ ).

Figure 43: SEM Image and EDS Data from Experiment 2A and 4

Experiment 2A



Experiment 4



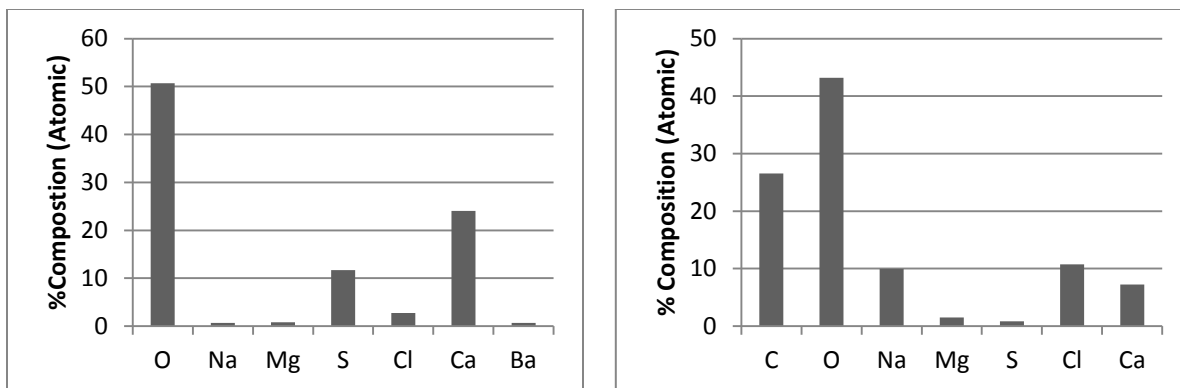
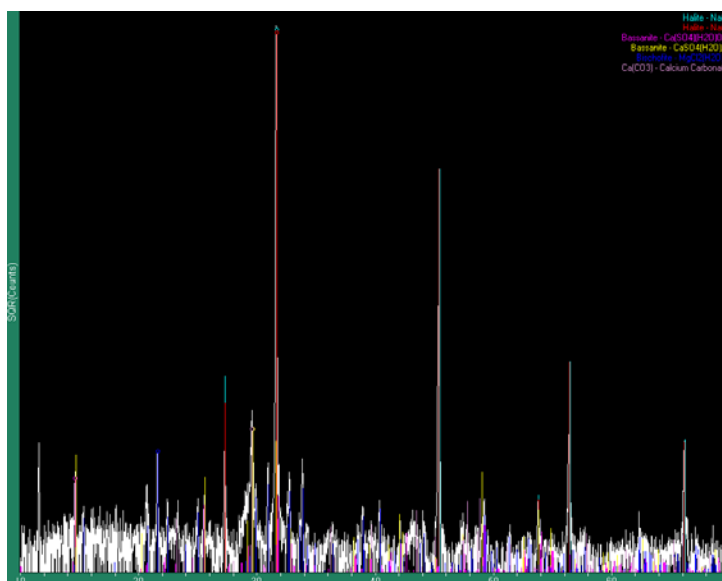


Figure 44: XRD Spectrum from Experiment 2A

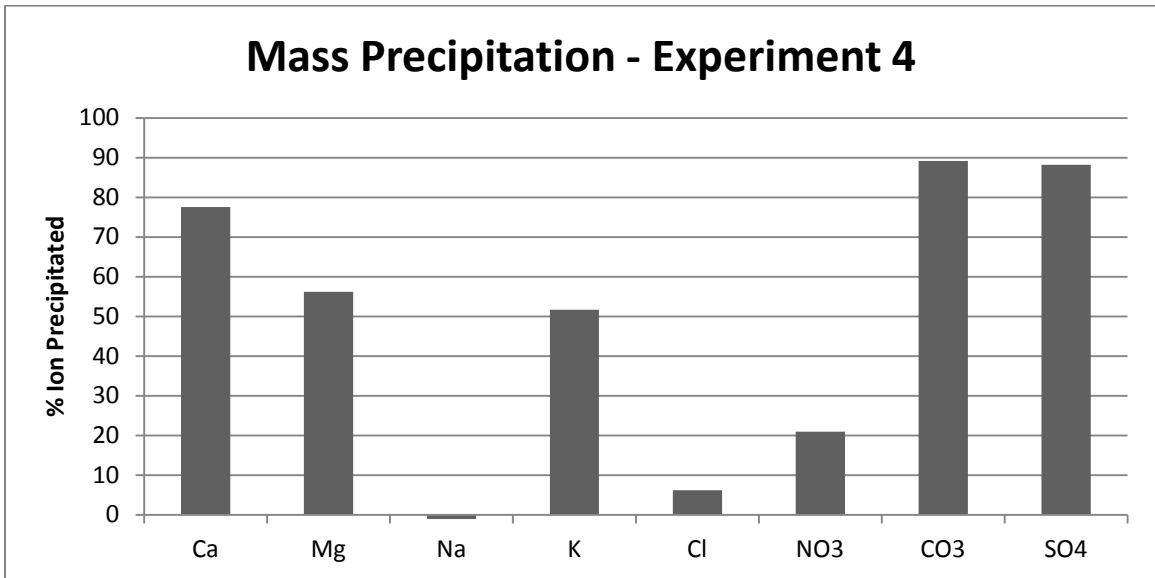
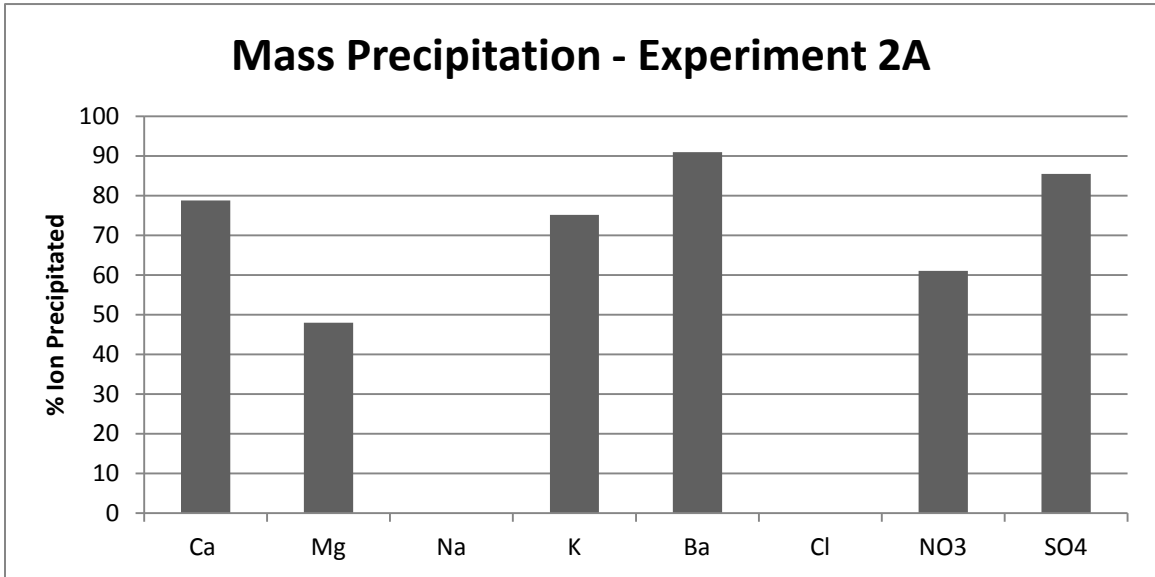


It must be noted that the EDS data does not include nitrogen in its analysis. EDS in general is not a good method for measuring nitrogen because K-alpha X-rays are strongly absorbed by carbon bearing materials, the material of which the detector window is made. It may be possible to analyze the samples using a wavelength dispersive spectrometer (WDS) at a later time.

An analysis of the ion concentrations in the supernatant compared to those in the regeneration solutions was also conducted to determine the extent of precipitation for each ion. The liquid analysis shows that all the cations and anions except sodium and chloride have left the solution in significant amounts (see Figure 45). From these data, it

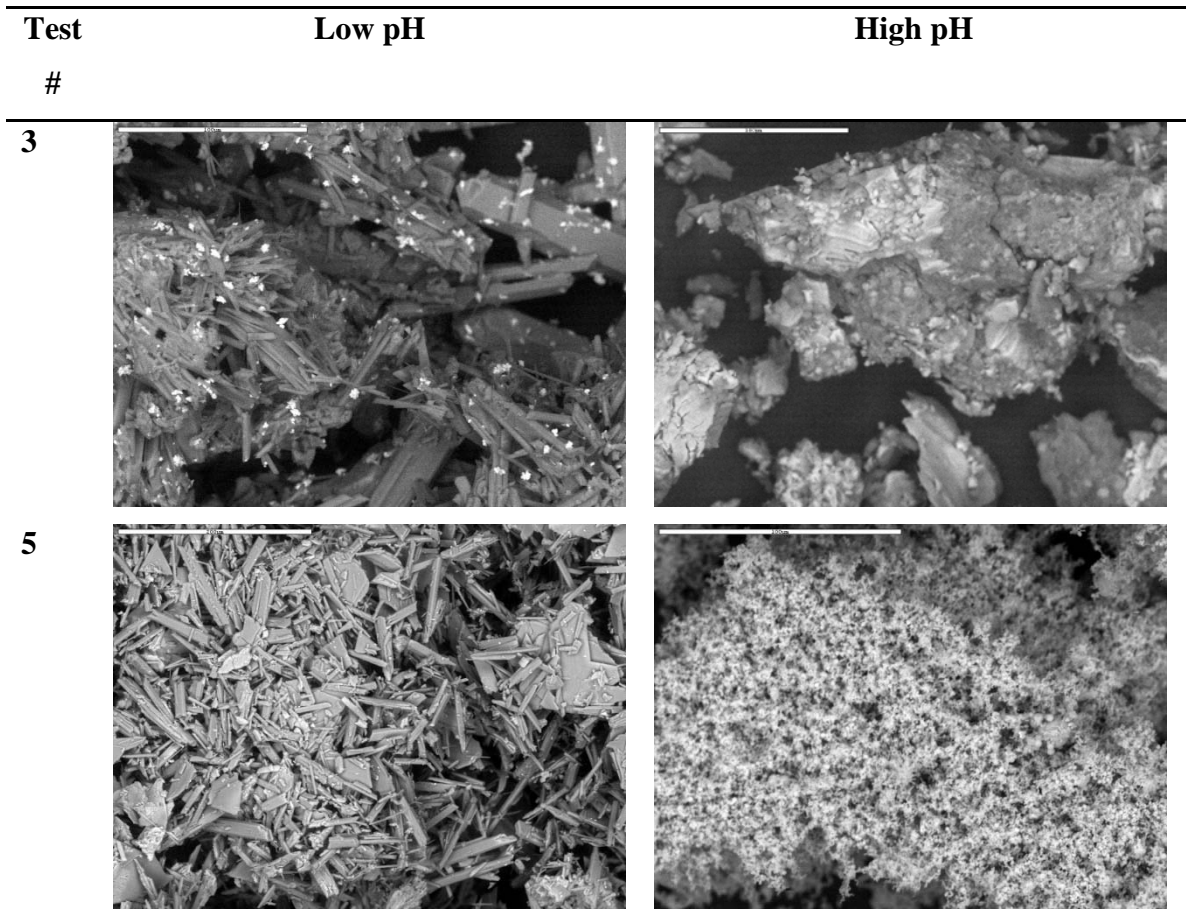
can be concluded that mixing the solutions without any pH adjustment results in a mixed precipitate. Mixing cation and anion regeneration solutions results in significant salt precipitation, however, it is unclear whether the recovered mixed salts have are sufficient in purity to have any beneficial uses.

Figure 45: Results from Liquid Analysis of Experiment 2A and 4



The next two types of precipitate result from experiments in which the pH was adjusted. This occurred in experiments 3-7. The sequence in these experiments was: 1) reduce pH of anion regeneration solution using HCl and mix solutions together, 2) separate precipitate from supernatant, 3) increase pH of supernatant and capture additional precipitate. In this way, two types of precipitate were formed during each experiment. SEM images of precipitates from low and high pH conditions are shown in Figure 46. In all of these images, a clear difference in morphology can be seen between the two corresponding images for each test. In most of the images of precipitate formed at high pH, the most abundant shapes are small spheres which are a common shape for calcium carbonate. The images of precipitates formed at low pH of precipitate are more homogenous and contain either hexagonal needles or flat flakes which are associated with calcium sulfate phases such as selenite and gypsum.

Figure 46: SEM Images from Experiments 3 and 5-7



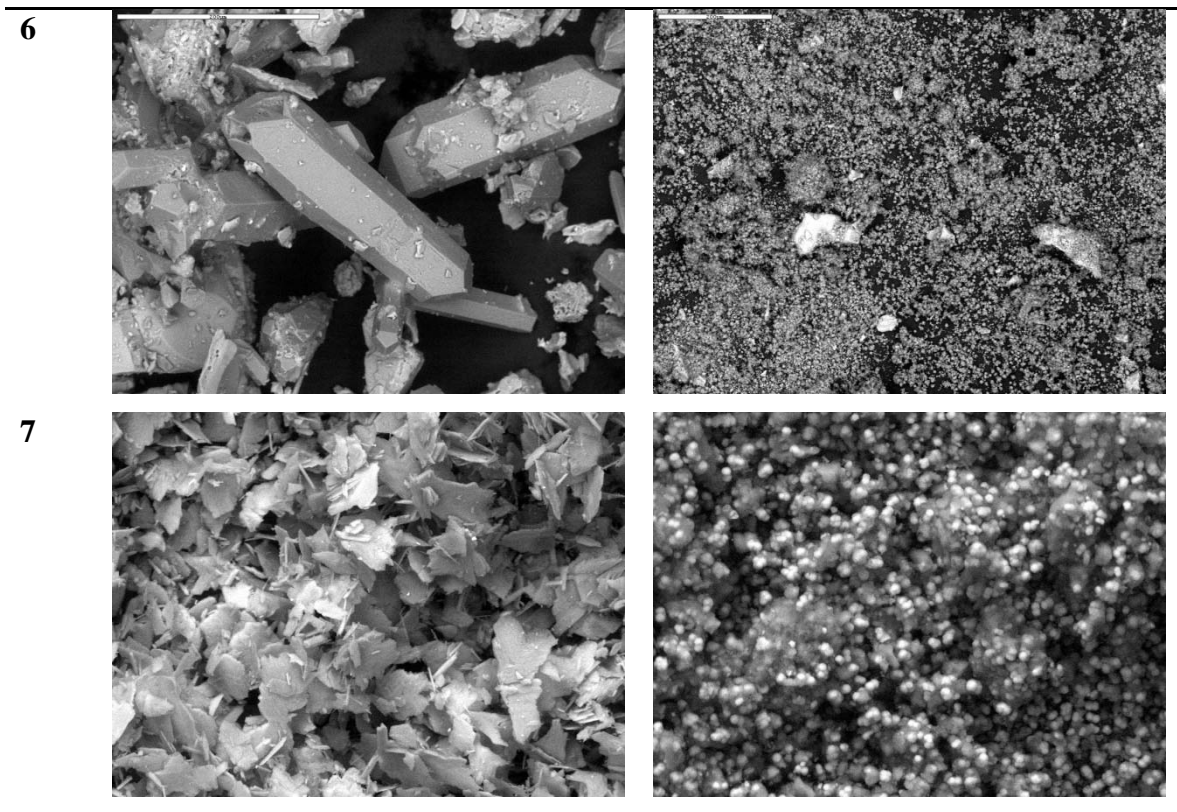
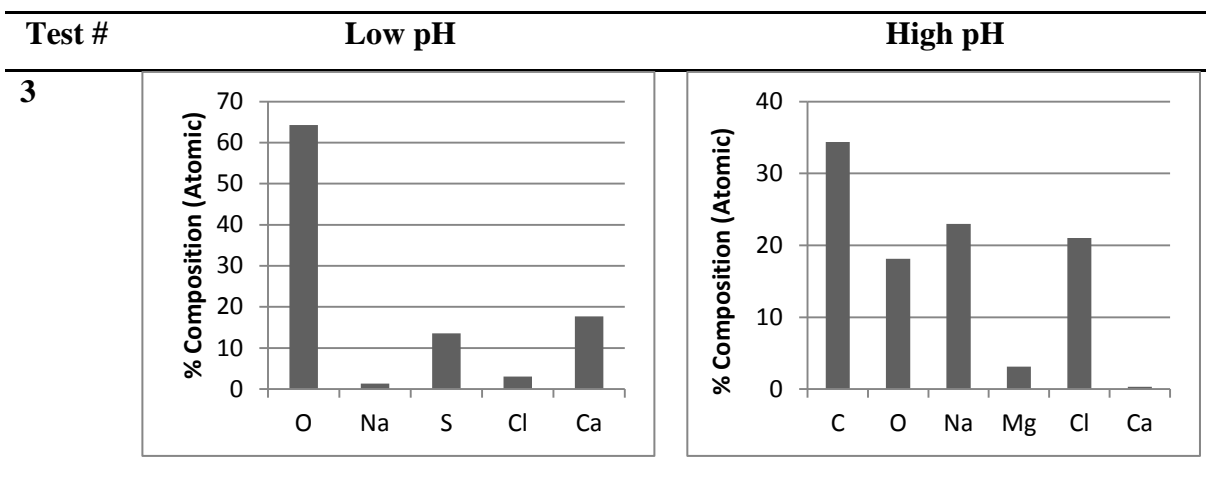
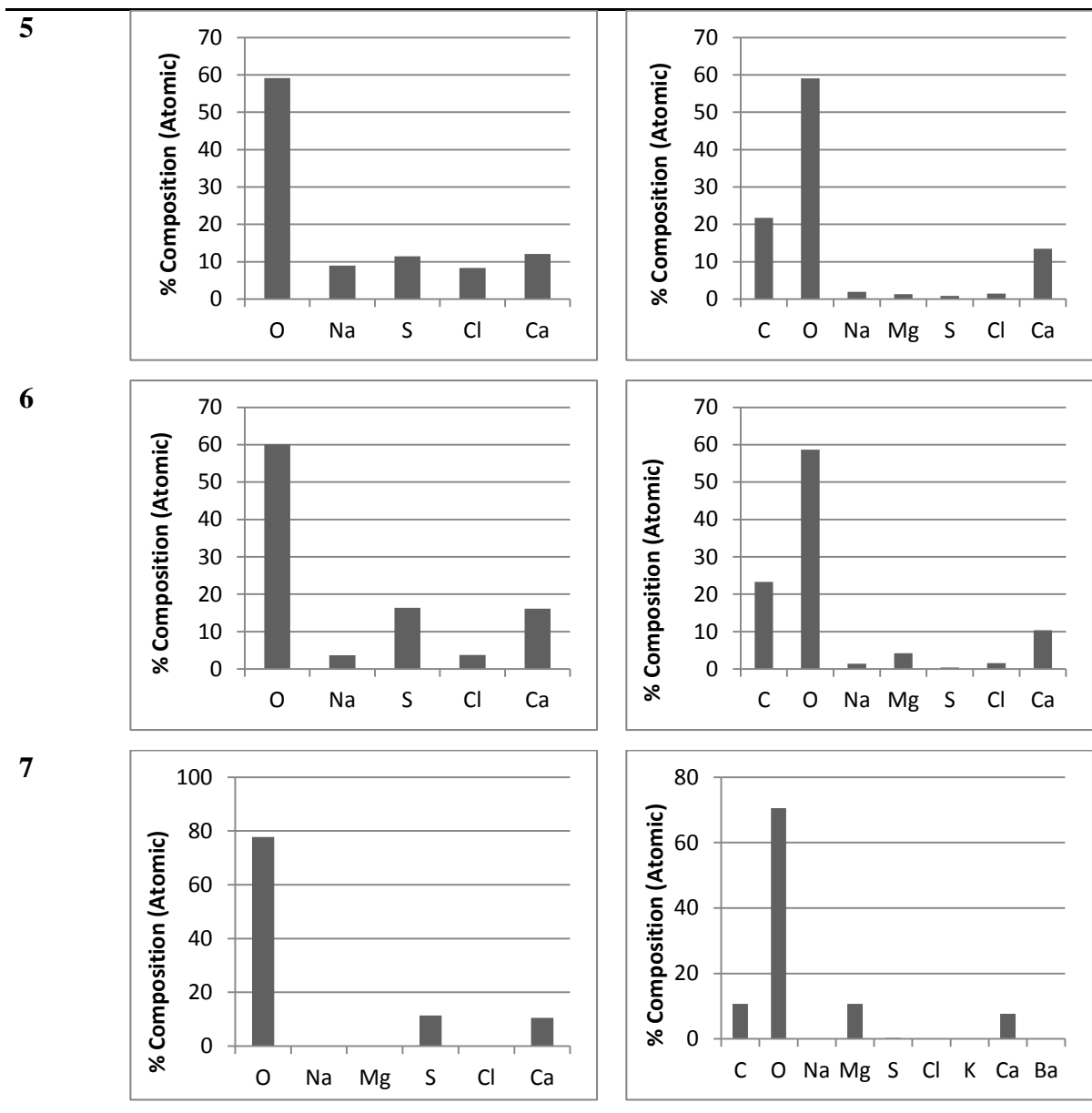


Figure 47: EDS Data from Experiments 3 and 5-7

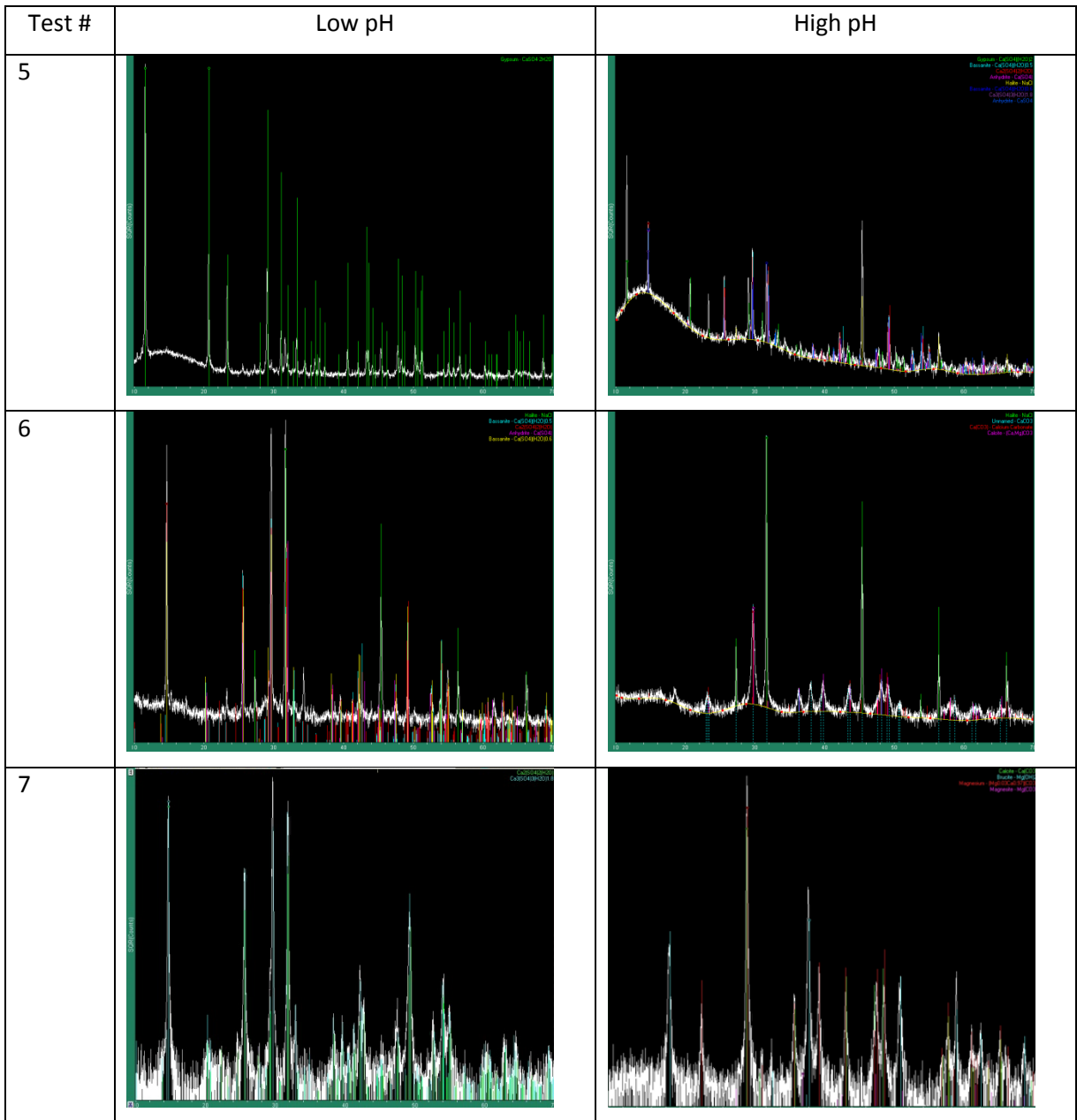




EDS data show that the precipitate formed at low pH consisted mostly of calcium, sulfate, oxygen, sodium, and chloride. In test 7, in which the precipitate was rinsed with DI water before drying, no sodium or chloride was detected by EDS. This indicates that their presence in the other low pH precipitates was probably due to the evaporation of the supernatant in the oven. The atomic ratio of these elements indicates matches that of calcium sulfate. The EDS spectra of precipitates formed at high pH show the presence of calcium, sodium, magnesium, oxygen, carbon, and chloride. Just as in the low pH test, sodium and calcium were not detected in precipitate from experiment 7. Based on the

combination of elements detected by EDS, these precipitates are mostly likely at mixture of calcium and magnesium carbonate.

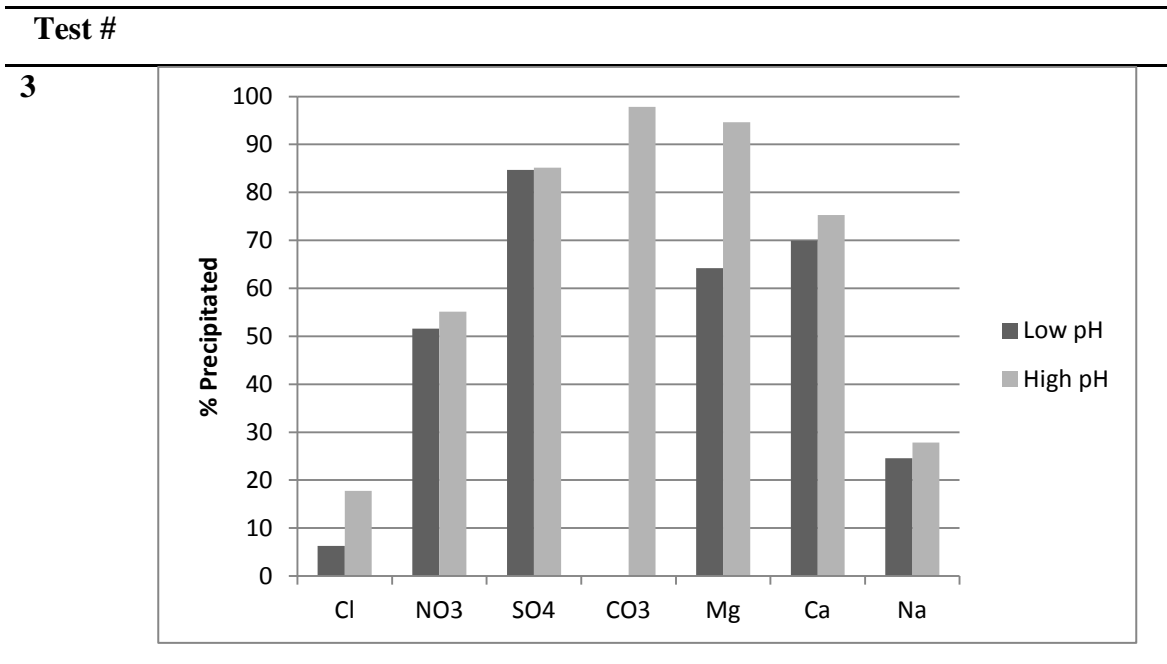
Figure 48: Figure 37: XRD Spectra from Experiments 3 and 5-7



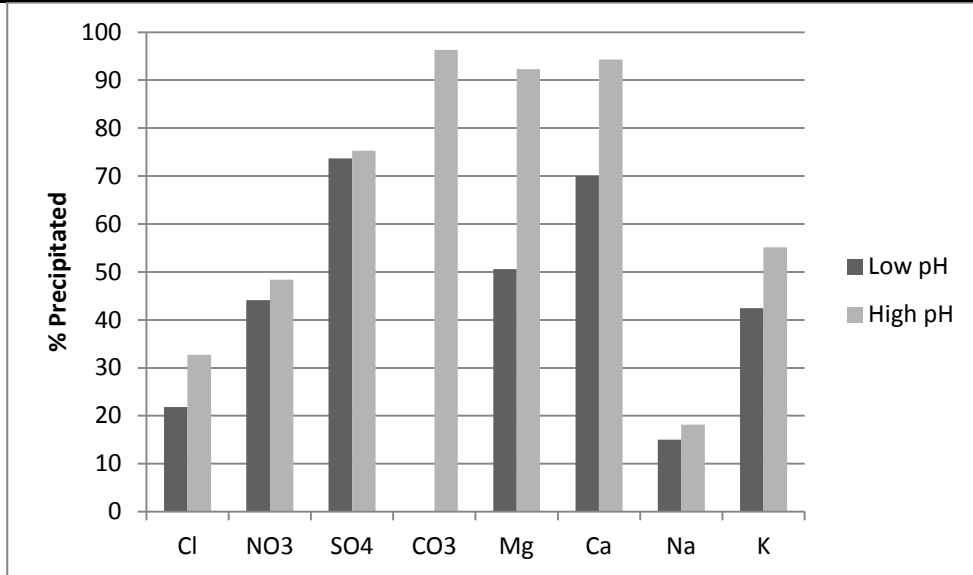
XRD analysis was performed on precipitate from high and low pH conditions from test 5, 6, and 7. The only crystals phases identified in precipitate formed at low pH were gypsum and halite. Precipitates formed at high pH contained calcite, halite, brucite,



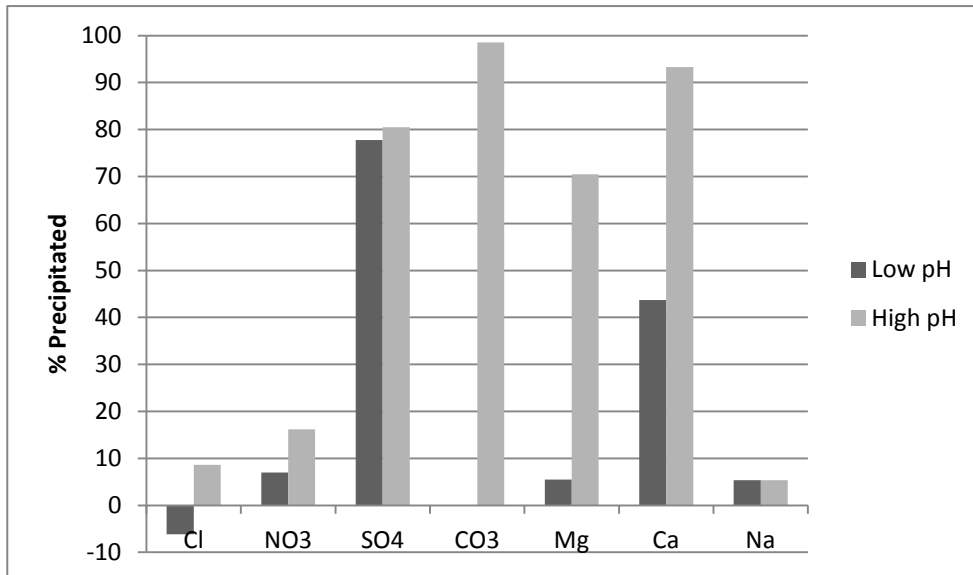
magnesite, and a magnesium carbonate. Analysis of ion concentrations in solution before and after precipitation under high and low pH conditions was done for tests 3, 5, and 6. Results show that a large fraction of the sulfate and nitrate precipitation occurred during low pH conditions and that they precipitated with calcium and magnesium. These results also show that some sodium and chloride precipitated prior to drying in the oven although some error is built into sodium and chloride measurements because of the very high dilution required to measure them. Low pH precipitation is limited by the amount of sulfate and nitrate in these solutions and by the solubility of sulfate and nitrate phases. When these ions are consumed, the remaining calcium and magnesium stay in solution. When the pH increases, most of the remaining calcium and magnesium precipitate with carbonate.



5



6



Results from Phase 3 experiments showed that it is possible to recover calcium sulfate from a mixed solution of cations and anions if the pH is reduced below 4.4. Depending on the purity of this salt, it may be suitable for commercial use. The carbonate salt that is produced during the high pH precipitation contains both calcium and magnesium. The ionic strength of the concentrate does not significantly inhibit precipitation of supersaturated salts. The recovery of other salts will require further concentration of the ions in solution, which may be economically feasible depending on the value of the salts and their particular properties in terms of solubility.

## CHAPTER 6

### PHASE 4 – PILOT SCALE PROCESS TESTING IN BRIGHTON, CO

The pilot study was conducted in conjunction with CDM at the East Cherry Creek Valley Water and Sanitation District's Brine Minimization Pilot located in Brighton, CO. The pilot study was intended to test the efficiency of the treatment process designed to recover salts from reverse osmosis concentrate using inter-stage, sequential ion exchange columns. The following are the major objectives of the pilot study:

1. Determine the consistency of the mass and purity of the recovered salt products.
  - Anion and cation regenerant fluids were mixed under high and low pH conditions to spontaneously precipitate supersaturated salts. Lab results have shown that gypsum and mixed carbonate salts can be recovered.
2. Determine the best fraction of the regenerant solution to use for salt recovery.
  - For example, if the first and last quarter of the regeneration process yield low ion concentrations, it may be more useful to collect only the fluid from the middle portion of the process in order to increase the solubility index and precipitate a greater salt quantity.
3. Determine the effect of anti-scalant addition on the resin capacity.
  - An anionic anti-scalant may foul the anion exchange column and result in a capacity decrease. A fouling resistant anion resin has been selected to decrease this likelihood.
4. Optimize the operation cycle length to maximize ion concentrations in regeneration solutions and minimize unused cation exchange capacity.
  - The cation exchange resin has a higher exchange capacity than the anion exchange resins, so normal operation cycles are limited by the anion exchange capacity. This leaves some unused cation exchange capacity. A breakthrough curve was measured during Week 3, and the operation cycle was extended during Weeks 5 and 6.

5. Determine if pilot effluent recycle affects the performance of the 2nd stage RO system.
  - o Pressure, temperature, and permeate were be measured during the 2nd stage RO system operation.

## 6.1 Pilot Design

The pilot system featured two ion exchange columns in series, the first containing Purolite SST65, a SAC resin and the second containing Purolite A850, a SBA resin. The feed water was the concentrate from a pilot scale RO unit operated by CDM. Feed water chemistry is listed in Table 27. The system was designed with solenoid valves and a timer for automatic operation and regeneration.

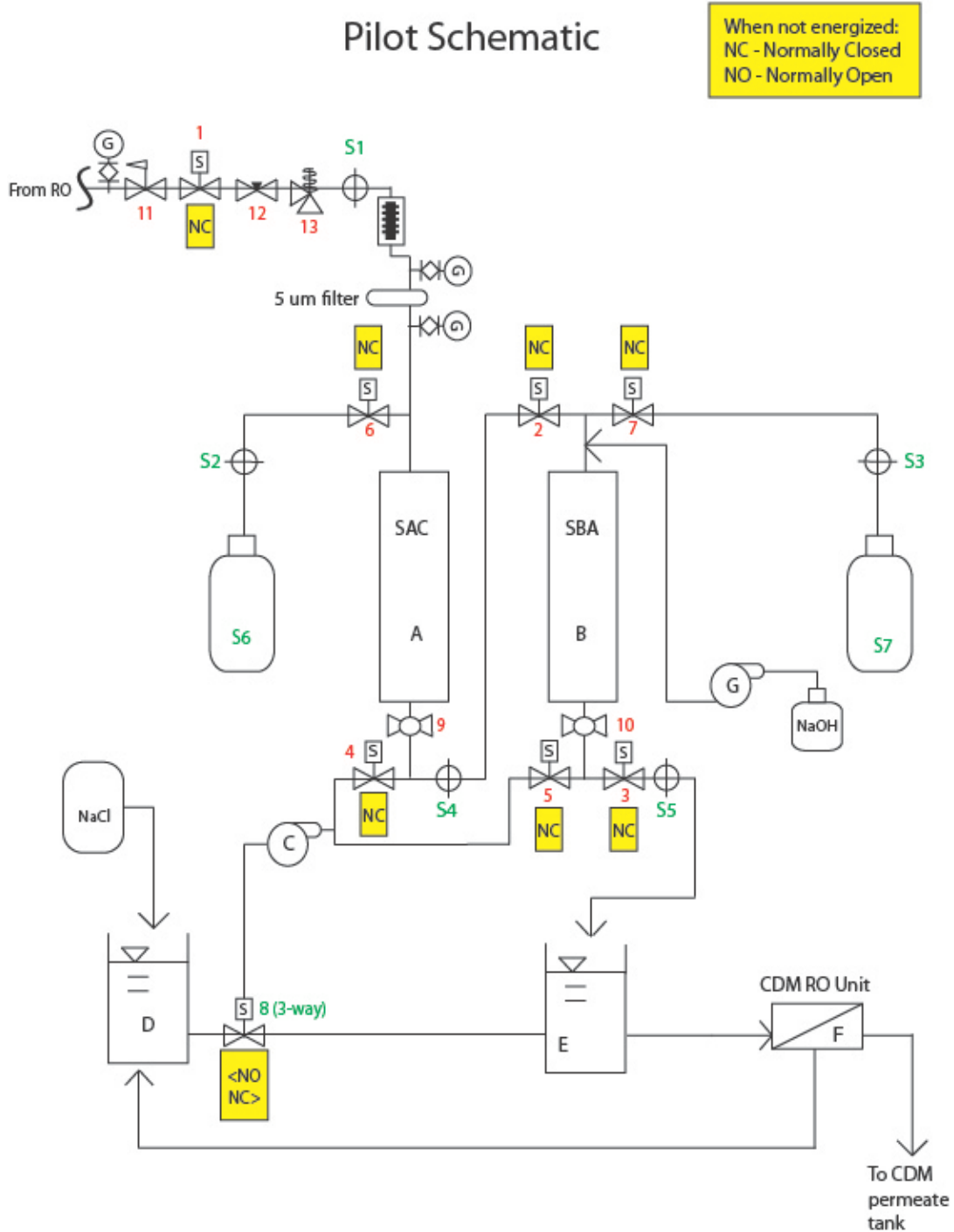
**Table 27: Pilot Feed Water Ion Concentrations**

	mg/L	M
<b>Ca</b>	460	
<b>Mg</b>	190	
<b>K</b>	20	
<b>Na</b>	570	
<b>Cl</b>	610	
<b>SO4</b>	690	
<b>TDS</b>	4450	
<b>CO3</b>		0.0274

The normal service cycle of the IX process was 2 hours at 0.44 gpm. Effluent from the pilot was sent to single stage RO unit until enough concentrate was produced for daily regeneration requirements. Sodium chloride was added to the RO concentrate until the target concentration (10%) was reached. The rest of the pilot effluent was saved for column rinsing or wasted. The normal counter-current regeneration cycle lasted 52.5 minutes at 0.0870 gpm. For the first 23 minutes of the regeneration cycle , 10% NaCl solution was pumped through the columns. This was followed by 30 minutes of rinsing with pilot effluent. Regeneration and rinse fluids from each column were collected during selected regeneration cycles. The fluids from the SAC and SBA columns were mixed to precipitate supersaturated salts. The total normal cycle time including

operation, regeneration, and rinse was 2.875 hours. The pilot was located on the I-76 Frontage Rd directly south of the E 160<sup>th</sup> St exit. The pilot system design is shown in Figure 49, and the legend and operations information are shown in Table 28.

Figure 49: Pilot Schematic



**Table 28: Legend for Schematic Diagram**

<b>A</b>	<b>Strong Acid Cation Exchange Column</b>
<b>B</b>	Strong Base Anion Exchange Column
<b>C</b>	Strong Acid Cation Regeneration Pump
<b>D</b>	IX Regenerant/Brine
<b>E</b>	Tank IX Effluent/Stage 2 RO Feed Tank
<b>F</b>	Stage 2 RO Unit
<b>G</b>	NaOH metering pump
<b>S=Sample</b>	
<b>Port</b>	
<b>S1</b>	Feed
<b>S2</b>	Cation Regeneration Fluid
<b>S3</b>	Anion Regeneration Fluid
<b>S4</b>	Cation Effluent/Regenerant Feed
<b>S5</b>	Anion Effluent/Regenerant Feed
<b>S6</b>	Mixed Cation Regeneration Fluid
<b>S7</b>	Mixed Anion Regeneration Fluid
<b>Valves</b>	
<b>1-7</b>	2-way Solenoid Valves
<b>8</b>	3-way Solenoid Valves
<b>9-10</b>	Manual, Ball
<b>11</b>	Pressure Reducing Valve
<b>12</b>	Needle Valve (for throttling)
<b>13</b>	Pressure Relief Valve

Pilot Operations:

<b>Valve Operation</b>	<b>x=energized</b>			
<b>Valve</b>	Service	Regen	Rinse	
<b>1-3, circuit 1</b>	x			
<b>4-7, circuit 2</b>		x		
<b>8, circuit 3</b>			x	
<b>Time (min)</b>	120 (regular), 165 (optimized)	23	30	
<b>Control Sequence</b>		<b>Time (min)</b>		
<b>1</b>	energize circuit	120 or 165		
<b>2</b>	energize circuit 2, pump C	52.5		
<b>3</b>	energize circuit 3	22.5		
<b>4</b>	Start over	0		
	English		Metric	
		Unit		Unit
<b>Column Diameter</b>	4	inches	10.16	cm
<b>Resin Depth</b>	4	ft	1.22	m
<b>Column Area</b>	0.0873	ft <sup>2</sup>	81.1	cm <sup>2</sup>
<b>Resin Volume</b>	0.35	ft <sup>3</sup>	9.88	L
<b>Service Rate</b>	10	BV/hr		
<b>Service Cycle</b>	20	BV		
<b>Operating Time</b>	2	h		
<b>Flow Rate</b>	0.44	gpm	1.65	L/min
<b>Velocity</b>	4.99	gpm/ft <sup>2</sup>	12.19	m/h
		Unit		Unit

<b>Regen salt</b>	NaCl			
<b>Regen mode</b>	Counter-current			
<b>NaCl Concentration</b>	10	%	10	%
<b>Regen volume</b>	0.75	BV	0.75	BV
<b>Regen rate</b>	2	BV/h	2	BV/h
<b>Regen time</b>	0.375	h		
<b>Flow rate</b>	0.0870	gpm	0.33	L/min
<b>Velocity</b>	0.997	gpm/ft <sup>2</sup>	2.4	m/h
<b>Regen sol'n density</b>	66.8		1.07	kg/L
<b>NaCl conc in regen solution</b>	6.68	lb/ft <sup>3</sup>	0.107	kg/L
<b>NaCl mass</b>	1.75	lb	0.793	kg
<b>NaCl dose</b>	5.0	lb/ft <sup>3</sup>	0.080	kg/L
		Unit		Unit
<b>Rinse volume</b>	1	BV	1	BV
<b>Rinse rate</b>	2	BV/h	2	BV/h
<b>Rinse time</b>	0.5	h		
<b>Flow rate</b>	0.0870	gpm	0.33	L/min
<b>Velocity</b>	0.997	gpm/ft <sup>2</sup>	2.4	m/h
<b>Summary</b>				
<b>SAC Resin</b>	Purolite SST65			
<b>SBA Resin</b>	Purolite A850			
<b>Total Cycle Time</b>	2.875	h		
<b>Cycles/Day</b>	8.35			
<b>Volume treated/day</b>	436.0	gal		
<b>SAC Regen/day</b>	16.3	gal		



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<b>SBA Regen/day</b>	16.3	gal
<b>SAC Rinse/day</b>	21.8	gal
<b>SBA Rinse/day</b>	21.8	gal
<b>Total regen/rinse</b>	76.3	gal
<b>net IX recovery</b>	82.5	%
<b>total salt/day</b>	29.2	lb

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Pictures of the pilot equipment are presented in Figure 50, Figure 51, Figure 52, Figure 53, and Figure 54.

**Figure 50: Pilot Equipment on Site**



Figure 51: Pilot Equipment including timer (far left), power supply (middle), titration setup (front), and regeneration pump (far right)

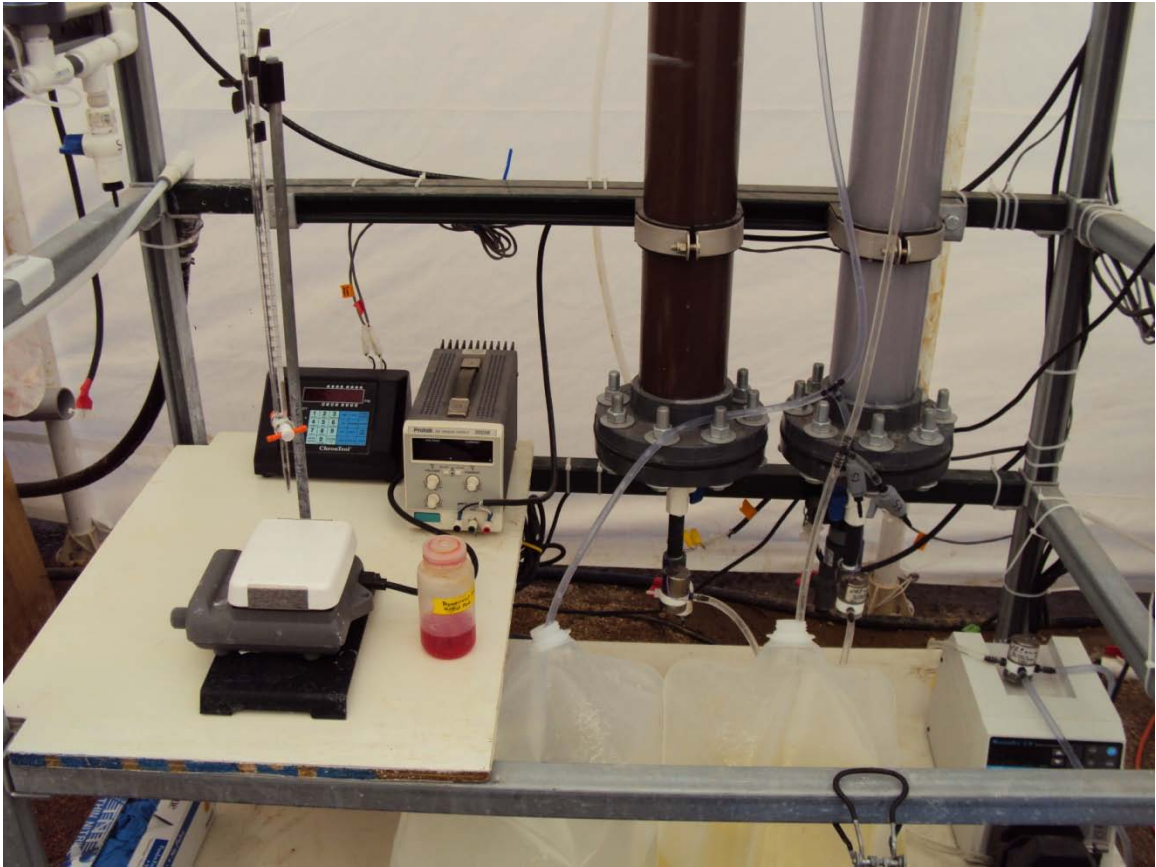


Figure 52: Solenoid Valves at top of Columns

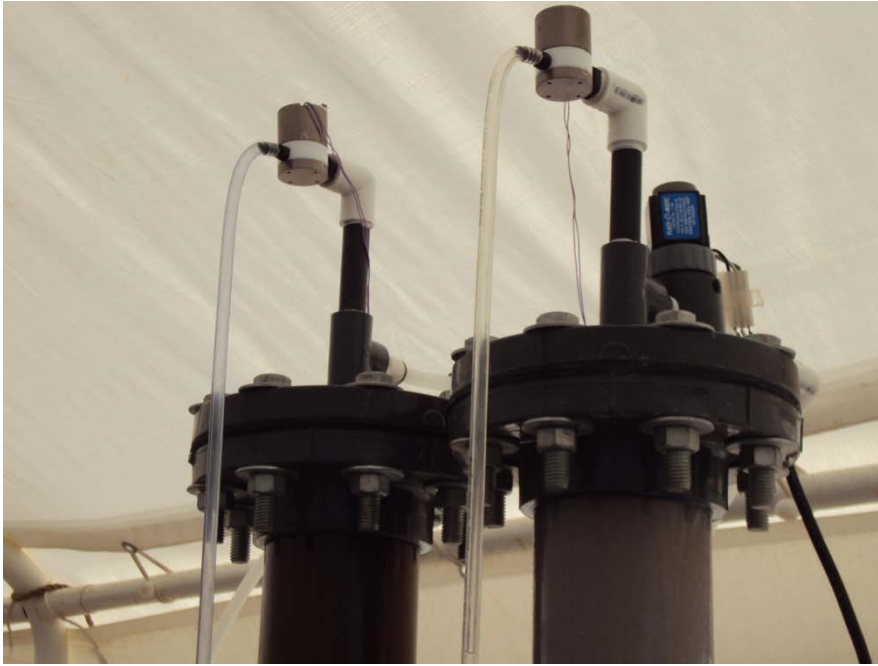


Figure 53: Solenoid Valves at Bottom of Columns



Figure 54: Control Sequence at Pilot Input including Pressure Reducer, Solenoid Valve, Pressure Gauge, Needle Valve, and Pressure Relief Valve



#### Daily Operations:

The following tasks were performed on a daily basis to maintain the pilot system and verify system operation. These tasks are also listed on the Parameter Checklist Form located in the Appendix 4. The pilot project schedule is shown in Figure 55.

#### Parameter checklist

- Flow – verify feed flow (on flow meter) twice per day (morning and evening)
- pH – verify feed pH twice per day (morning and evening)
- Conductivity – verify feed conductivity twice per day (morning and evening)
- Pressure – record pressure from each of three pressure gauges twice per day (morning and evening)
- Make regeneration brine (once per day)

- Approximately 40 gallons of regeneration brine is required per day
- The amount of pilot effluent necessary to feed the second stage RO system will depend on the recovery.
- Pilot effluent was directed to holding tank (Tank E). When enough is collected, the second stage RO system was run (as daily batch) to generate concentrate effluent.
- Two regeneration fluid tanks were used, so system operations did not have to be stopped to generate regeneration fluid.
- Pilot effluent was directed to Tank E and used as rinse water.
- When 40 gallons of concentrate were generated, sodium chloride was added until 10% solution was achieved. The amount of sodium chloride needed was determined based on the correlation between conductivity and % solution.

Figure 55: Pilot Project Schedule

Tasks	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7
	June 6-10	June 13-17	June 20-24	June 27-Jul 1	July 4-8	July 11-15	July 18-22
Setup	██████████						
Objective 1	██████████	██████████			██████████		
High and Low pH precipitation	██████████	██████████			██████████		
Objective 2		██████████	██████████	██████████	██████████		
Characterize elution curves		██████████	██████████	██████████	██████████		
Precipitate w/ best fraction			██████████	██████████		██████████	
Objective 3		██████████	██████████	██████████			
Measure Change in Capacity		██████████	██████████	██████████			
Objective 4			██████████	██████████	██████████	██████████	██████████
Breakthrough Curve			██████████	██████████	██████████	██████████	██████████
Increase Operation Cycle Length					██████████	██████████	██████████
Breakdown							██████████

Week 1:

Pilot was assembled and set up for automatic operation and regeneration. Flow meter will was calibrated for RO concentrate which is denser than water. Sample taps were installed, and all working parameters were verified. Data was collected for Objective 1, and high and low pH salt precipitation commenced.

Week 2:

Data collection and precipitation for Objective 1 continued. In addition, samples were taken to create elution curves to be used for Objective 2. Resin samples were also taken at the end of service cycles to measure exchange capacity for Objective 3.

Weeks 3 and 4:

Resin samples continued to be taken at the end of service cycles to measure exchange capacity for Objective 3. For Objective 2, salts were precipitated using the same procedure described for Objective 1 using the most concentrated fractions of regeneration fluids determined from measurements taken during week 2. Measurement of the column breakthrough curve was done during Week 3 to determine the optimum length for the operation cycle to be implemented during Week 5.

Week 5: The length of the operation cycle was increased based on data from a breakthrough curve measured during Week 3. Samples were also taken to generate elution curves for Objective 2 and salts were precipitated under high and low pH conditions for Objective 1.

Week 6:

Salts were precipitated under high and low pH conditions using the best fractions of regeneration fluids determined from measurements taken during week 5. for Objective 2.

Week 7:

The pilot was disassembled and transported back to UNM.

At the end of each week during the pilot testing program, samples were transported to UNM for analysis.

## **6.12 Pilot Methods**

Methods/Procedure:

Objective 1: Quantify the consistency of the recovered salt products in terms of mass and purity.

The purity of the recovered salts was measured. Data was collected to satisfy this objective during weeks 1, 2, and 5. During weeks 1 and 2, a 20 bed volume operation

cycle was implemented. During week 5, the operation cycle increased to 28 bed volumes. Salts were be precipitated and analyzed for 2 cycles in week 1, 3 cycles in week 2, and 3 cycles in week 5. A total of 8 cycles were analyzed, and 3 of occurred during week 5 with the extended operation cycle.

Objective 2: Determine the most concentrated fraction of the regeneration solution to use for salt recovery.

The objective of the process was to maximize the quality and quantity of salt products that can be recovered by mixing cation and anion regeneration fluids. The regeneration process includes 0.75 bed volumes of 10% NaCl regeneration solution followed by 1.0 bed volumes of rinse water (effluent from pilot). So, each column generates 1.75 bed volumes of regeneration fluid per cycle. Earlier research showed that the maximum concentration of calcium and sulfate during regeneration occurs at approximately 1 bed volume into the regeneration process. By capturing the most concentrated effluent, it may be possible to generate a greater quality and quantity of salt product. To evaluate this hypothesis, elution curves were constructed from samples taken at different times during the regeneration process. Based on these curves, the most concentrated fraction of the regeneration fluid was for salt precipitation. Data showed that the maximum cation and anion concentrations occurred at the same points in the regeneration cycle, so the same fractions were captured during cation and anion regeneration cycles. The collected fractions were mixed and allowed to precipitate using the procedure described previously for salt precipitation.

Data to create the elution curves were collected during weeks 2 and 5 and analyzed during the following weekends so salts could be precipitated using the optimum fraction of the regeneration solutions during weeks 3 and 6.

Procedure (Analysis of Salt Products for Objectives 1 and 2):

1. Collect feed water from sample tap S1 at the beginning of the service cycle.
  - a. Measure pH, conductivity, temperature, and total carbonate (on-site).
  - b. Fill a 250 mL Nalgene bottle and store for analysis of cations and anions at UNM during the following weekend.

- c. At UNM, analyze for calcium, magnesium, sodium, and potassium concentrations using the AA spectrometer.
  - d. At UNM, analyze for chloride, nitrate, fluoride, and sulfate using the ion chromatograph.
2. Collect SAC regeneration waste from regeneration in a 5-gal cubitainer. During weeks 1, 2, and 5, entire regeneration was collected. During weeks, 3, 4, and 6, a predetermined fraction of the regeneration cycle was collected (determined by elution experiments during Week 2).
  - a. After ensuring that contents of the cubitainer are well-mixed, measure pH, conductivity, temperature, and total carbonate.
  - b. Label cubitainer and store for analysis of ions and precipitation at UNM during the following weekend (ion analysis is identical to Steps 1.b to 1.d).
3. Collect SBA regeneration waste in a 5-gal cubitainer. Procedure is identical to Step 2 for SAC regeneration waste.
4. Precipitation at ambient pH (at UNM):
  - a. Mix 100 mL of SAC regeneration solution with 100 mL of SBA regeneration solution in a tared Erlenmeyer flask.
  - b. Allow precipitates to form and settle for 36 hours.
  - c. Collect a sample of supernatant and conduct all analyses for feed water in Step 1.
  - d. Transferred to four 50 mL centrifuge vials and centrifuged to separate liquid and solid.
  - e. Decant approximately  $\frac{3}{4}$  of the liquid from each vial and combine the remaining mixture from the four vials into one vial. Centrifuge again.
  - f. Decant  $\frac{3}{4}$  of the liquid again and replace with DI water. Centrifuge again. Repeat the process three times.
  - g. Decant most of the DI water and return the remaining mixture was to the tared Erlenmeyer flask.
  - h. Dry in the lab oven at 104°C for 24 hours.
  - i. Remove flasks from oven, allow them to equilibrate to room temperature, and weigh them.



- j. The difference between the tared mass and the mass after drying is assumed to be the total precipitated mass, although it is possible that a small amount of precipitate re-dissolved upon contact with DI water.
  - k. Analyze precipitated solid by SEM, EDS, XRD, and XRF.
5. Precipitation at low pH:
- a. Collect 100 mL of SBA regeneration solution and reduce pH to 4.5 using hydrochloric acid.
  - b. Mix the pH-adjusted SBA regeneration waste with 100 mL of SAC regeneration solution in a tared Erlenmeyer flask. Continue all analyses listed in Step 4.

Procedure (Development of Elution Curve – weeks 2 and 5 only):

1. Collect approximately 250 mL of regeneration fluid from sample taps S2 and S3 in clean Nalgene bottles at 15, 20, 25, 30, 35, 40 and 45 minutes into the regeneration process.
  - a. Measure pH, conductivity, temperature, and total carbonate (on-site).
  - b. Store the Nalgene bottle and for analysis of cations and anions at UNM during the following weekend.
  - c. At UNM, analyze for calcium, magnesium, sodium, and potassium concentrations using the AA spectrometer.
  - d. At UNM, analyze for chloride, nitrate, fluoride, and sulfate using the ion chromatograph.
2. Elution curves were generated based on the data analyzed at UNM, and the times at which the most concentrated fractions of the regeneration process were selected for use during precipitation experiments.

**Table 29: Sampling and Analysis Plan (Objective 1):**

Sample Location	Sample Type	Frequency	Analyses
<b>S1</b>	Feed Water	2 cycles – week 1	calcium, magnesium,
		3 cycles – week 2	sodium, potassium,

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			carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>S6, S7</b>	Regeneration	2 cycles – week 1	calcium, magnesium,
	Fluids	3 cycles – week 2	sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket after precipitation– no pH adjustment</b>	Supernatant	2 cycles – week 1 3 cycles – week 2	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket after precipitation– no pH adjustment</b>	Solid	2 cycles – week 1 3 cycles – week 2	SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass
<b>Precipitation bucket after precipitation - low pH condition</b>	Supernatant	2 cycles – week 1 3 cycles – week 2	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket after precipitation - low pH condition</b>	Solid	2 cycles – week 1 3 cycles – week 2	SEM, EDS (relative elemental composition), XRD

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<b>Precipitation bucket after precipitation - high pH condition</b>	Supernatant	2 cycles – week 1 3 cycles – week 2	(presence of known crystal phases), mass calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket after precipitation - high pH condition</b>	Solid	2 cycles – week 1 3 cycles – week 2	SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass

**Table 30: Sampling and Analysis Plan (Objective 2):**

Sample Location	Sample Type	Frequency	Analyses
<b>S2, S3</b>	Regeneration fluids	At 15, 20, 25, 30, 35, 40 and 45 into the regen cycle 2 cycles – week 2 2 cycles – week 5	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>S6, S7</b>	Regeneration Fluids	3 cycles – week 3 3 cycles – week 6	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket</b>	Supernatant	3 cycles – week 3	

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<b>after precipitation– no pH adjustment</b>		3 cycles – week 6	
<b>Precipitation bucket after precipitation– no pH adjustment</b>	Solid	3 cycles – week 3	SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass
		3 cycles – week 6	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket after precipitation - low pH condition</b>	Supernatant	3 cycles – week 3	SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass
		3 cycles – week 6	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket after precipitation - low pH condition</b>	Solid	3 cycles – week 3	SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass
		3 cycles – week 6	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket after precipitation - high pH condition</b>	Supernatant	3 cycles – week 3	SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass
		3 cycles – week 6	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH
<b>Precipitation bucket after precipitation - high pH condition</b>	Solid	3 cycles – week 3	SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass
		3 cycles – week 6	calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and pH

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### Objective 3: Determination of Anti-Scalant Effect on Resin Capacity

Anionic anti-scalants can potentially foul anion exchange resins, lowering their exchange capacity. Purolite A850 was designed to reduce organic fouling, so it is particularly suited for treating water containing organic anti-scalants. However, it is important to quantify any capacity reduction and determine the extent of organic fouling due to anti-scalant addition. SBA resin capacity was determined by analysis of a resin sample taken from a column at the end of the service cycle. Resin samples were submerged in 2N sodium hydroxide and the ions in the resulting liquid were analyzed for carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate using IC and titration. Fouling was indicated by the presence or absence of organic carbon in the liquid sample which was measured using the TOC analyzer.

#### Procedure:

1. At the end of the service cycle, pilot operation was halted and a resin sample of approximately 5g was removed from the top of the SBA column and stored in a sealed container.
2. During the following weekend, the resin sample was rinsed with DI water until all non-adsorbed ions are removed.
3. The resin sample was divided into three, 1g amounts (for triplicate analysis) using an analytical balance and placed into 50mL of 2N NaOH to strip off the adsorbed ions and the TOC (if any).
4. Liquid samples were analyzed by IC, titration, and the TOC analyzer to measure carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and TOC.
5. Data from each cycle was compared to determine if capacity decreased and if it can be correlated to the amount of organic carbon present on the resin.

**Table 31: Sampling and Analysis Plan (Objective 3)**

Sample Location	Sample Type	Frequency	Analyses
<b>Resin from top of the</b>	Resin	2 cycles – week 2	Strip with NaOH, then

<b>SBA column</b>	sample	2 cycles – week 3	measure carbonate,
		2 cycles – week 4	bicarbonate using titration, measure chloride, nitrate, fluoride, sulfate using the IC, and measure organic carbon using the TOC analyzer

Objective 4: Optimize the operation cycle to increase run length before regeneration is necessary.

One measure of process efficiency is the ratio of the operation cycle volume to the regeneration cycle volume. A conservative estimate was used to determine the operation cycle for the first four weeks of the experiment, but it is important to determine the limits of efficiency. A breakthrough curve was measured during the third week to determine the capacity of the ion exchange columns with respect to the major ions of interest: calcium, magnesium, and sulfate. Based on these data, an extended cycle was implemented. The cation column has a higher capacity than the anion column because the cation resin has approximately three times more capacity than the anion resin. In a full scale system, it might have been possible to equalize the anion and cation removal capacity by having different cation and anion resin volumes, but constraints on the current system did not allow it for this project. Equal resin volumes were simulated by running the cation column to its full capacity even though the capacity of the anion column was exceeded. When the anion exchange capacity was reached, the effluent was diverted from the feed tank so it would not be treated by the second stage RO unit. That way, both columns could be run to capacity. Regeneration solutions from the extended cycle were mixed to precipitate salts, and during Week 6 only the most concentrated fractions of the regeneration solutions were used.

**Table 32: Sampling and Analysis Plan (Breakthrough Curve for Week 3)**

Objective	Sample	Sample Type	Frequency	Analyses
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Location				
<b>1</b>	S4 at 120, 132, 144, 156, 168, 180, 192. 204, 216, and 228 min after normal cycle	Regeneration Fluids	1 cycles – week 3	calcium, magnesium, sodium, potassium, and conductivity
<b>2</b>	S5 at 120, 132, 144, 156, 168, 180, 192. 204, 216, and 228 min after normal cycle	Regeneration Fluids	1 cycles – week 3	carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, and conductivity

Objective 5: Determine if pilot effluent affects the performance of the 2<sup>nd</sup> stage RO system.

If ion leakage occurs during pilot operations, it is possible that membrane fouling could occur in the 2<sup>nd</sup> stage RO system. To determine if this occurred, several parameters related to RO operations were recorded on a daily basis including feed pressure, concentrate pressure, feed temperature, and permeate flow. These values were entered into ROData.xls, a spreadsheet provided by Hydranautics, which calculated normalized permeate flow. Pressure and flow was read directly from gauges and meters located on RO unit operations panel. Temperature was measured using a handheld meter. A form for recording data from the RO unit is located in the appendix.

**Table 33: Sampling and Analysis Plan for Objective 5**

Sample Location	Frequency	Data to be measured/read
<b>2<sup>nd</sup> stage RO Unit</b>	Daily, during RO operation	feed pressure, concentrate pressure, feed temperature, and permeate flow

Sampling forms for each week, for daily operations, and for RO unit data (Table 34) are saved as PDF files and can be found in Appendix 3.

**Table 34: Data Forms and File Names Located in Appendix 4**

<b>File Type</b>	<b>Filename</b>
<b>Data Form – Week 1</b>	Week 1 Form.pdf
<b>Data Form – Week 2</b>	Week 2 Form.pdf
<b>Data Form – Week 3</b>	Week 3 Form.pdf
<b>Data Form – Week 4</b>	Week 4 Form.pdf
<b>Data Form – Week 5</b>	Week 5 Form.pdf
<b>Data Form – Week 6</b>	Week 6 Form.pdf
<b>Daily Operations Form</b>	DailyOps.pdf
<b>RO Data Form</b>	ROData.pdf

## **6.2 Pilot Results**

### **6.21 Mass Analysis**

The first objective of the pilot project was to measure the mass and purity of recovered salts. The composition of precipitated salts was examined using three methods. First, precipitated salts were viewed using SEM. They were then analyzed by EDS to determine elemental composition and XRD to identify mineral phases. The solutions relevant to the mass analysis were the anion and cation regeneration solutions and the supernatants from the high and ambient pH precipitation tests. Solutions were analyzed using AA and IC to measure the concentrations of common ions including calcium, magnesium, potassium, sodium, chloride, and sulfate. Acid titrations to measure total carbonate were also performed on anion and cation regeneration solutions. Results from the liquid analysis of the cation and anion regenerant solutions are shown in Table 35 and Table 36 (-- indicates no data is available). Samples from three different regeneration cycles were taken every week, and the average ion concentration is an average of ion concentration measurements from those three samples.



**Table 35: Average Ion Concentrations in the Cation Regeneration Solution**

	<b>Ca</b>	<b>Mg</b>	<b>K</b>	<b>Na</b>	<b>Cl</b>	<b>SO4</b>	<b>CO3</b>
<b>Week</b>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	M
<b>1</b>	5154	1306	2	6132	24188	460	--
<b>2</b>	5096	1919	--	8064	27510	394	0.03
<b>3</b>	11855	5600	206	10411	51871	255	0.04
<b>4</b>	13679	5824	180	6221	49765	175	0.04
<b>5</b>	5798	1708	83	3702	21297	460	0.03
<b>6</b>	12546	3703	163	6663	46180	301	0.05

**Table 36: Average Ion Concentrations in the Anion Regeneration Solution**

	<b>Ca</b>	<b>Mg</b>	<b>K</b>	<b>Na</b>	<b>Cl</b>	<b>SO4</b>	<b>CO3</b>
<b>Week</b>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	M
<b>1</b>	62	28	2	13604	12992	8224	--
<b>2</b>	--	--	--	--	13042	10236	0.20
<b>3</b>	--	--	80	25662	26324	17012	0.20
<b>4</b>	38	31	--	22989	16292	26998	0.22
<b>5</b>	179	122	44	10178	5021	17673	0.13
<b>6</b>	129	133	103	10389	5266	48167	0.25

Operation cycles in Weeks 1-4 were 20 bed volumes, and the volume of the regeneration and rinse cycle was 1.75 bed volumes. If all ions that entered the column during the operation cycle were exchanged onto the resin, and if they were removed from the resin during regeneration, the ion concentration factor (ratio of ion concentration in the regeneration solution to ion concentration in the feed solution) would be equal to the ratio of the number of bed volumes of operation to the number of bed volumes of regeneration. For Weeks 1-4, this ratio was equal to 11.43. In Weeks 5 and 6, when the operation cycle was increased to 28 bed volumes, the ratio became 16.00. Table 37 shows the actual concentration factors for ions in each cycle for each week. Week 1 was excluded because only one cycle was taken that week, and the pilot was still experiencing

some startup problems. With an operation cycle of 20 bed volumes, no divalent cation should break through, so their concentration factors should be equal to the ratio of the number of bed volumes of operation to the number of bed volumes of regeneration. Potassium may break through the column before the operation cycle is complete and therefore have a lower concentration factor. The same is true for divalent and monovalent ions in the anion column. Sulfate should have the highest possible concentration factor while bicarbonate, the dominant form of dissolved CO<sub>2</sub> at moderate pH values, may break through before the operation cycle is complete. In Week 2, concentration factors follow expected patterns. In Week 5, when the operation cycle was extended, calcium and magnesium appear to break through before the end of the cycle.

**Table 37: Concentration Factors for Each Ion for Weeks in which the Entire Regeneration Cycle was Captured**

	Cycle	Ca	Mg	K	SO4	TOTCO3
<b>Week 2</b>	1	9.8	10.3	10.1	11.8	7.2
	2	11.2	10.2	--	11.6	7.7
	3	10.4	7.9	--	10.2	6.3
	2a	10.1	12.7	--	11.9	7.7
<b>Week 5</b>	1	13.5	8.9	5.4	18.2	--
	2	13.5	8.1	5.3	17.9	4.5
	3	13.2	8.7	5.0	17.4	5.0

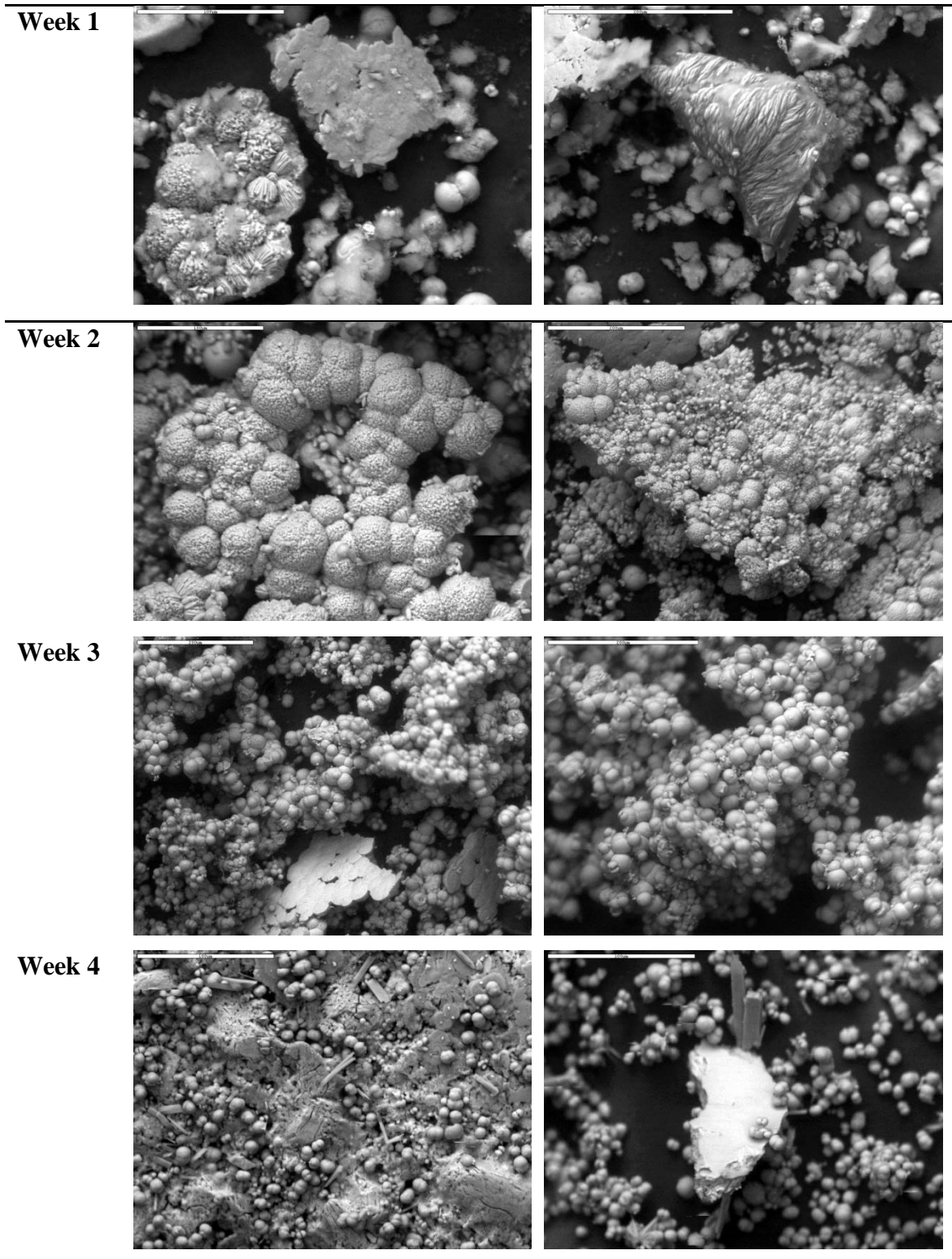
Using concentrations listed in Table 35 and Table 36, it was possible to calculate the total mass of each ion present when equal volumes of the solutions were mixed. In cases where the pH of the anion regeneration solution was reduced, the additional chloride mass from the added HCl was calculated using a combined mass and charge balance and was added to the total chloride mass present in the mixed solution. The calculation of additional HCl was done according the following technique. The charge of the anion regenerant solution was calculated based only upon the pH and the resulting carbonate speciation (the total carbonate was known). Then, the charge of the pH adjusted solution was calculated based upon the new pH, the new carbonate speciation, and a variable amount of chloride. Using Goal Seek in Excel, the charge of the pH

adjusted solution was matched to the original solution by changing the concentration of chloride. Each solution (50 mL) required about 3 mL of HCl to reduce the pH to the desired amount, but acid concentrations varied. The additional mass of chloride was calculated by multiplying the molar concentration of chloride obtained in the equation by the volume of the solution (50 mL + 3 mL) and then multiplying by the molar mass. Chloride could not be adjusted for Week 1, Cycle 1 because carbonate measurements were not made.

Inspection of precipitates from each week and pH condition was performed with an SEM, and it was possible to develop a preliminary identification of the salts based on characteristic shape. These identifications were corroborated by EDS and XRD analyses. SEM images of precipitate from each week and pH condition are shown in Figure 56 and Figure 57. The most commonly observed shapes in these images are smooth spheres, textured spheres, and needles.

EDS spectra were taken on several instances of each of these shapes to identify them in terms of elemental composition. According to the semi-quantitative integration of the EDS spectra, smooth and textured spheres consist mainly of calcium carbonate. Figure 58 shows the elemental percent composition of several examples of these spheres from different samples compared with the atomic composition of pure calcium carbonate, shown at the top of the figure. Each example displays the signature 20% calcium and carbon and the 60% oxygen characteristic of calcium carbonate. All of the samples that precipitated under ambient pH conditions contain these spheres. EDS spectra of the needle like shapes that occurred in several samples. Figure 59 shows several examples of the needle-like structures with associated semi-quantitative atomic composition with the atomic percent composition for reference. These samples were analyzed under a low pressure vacuum, which can make carbon measure difficult due to interference from carbon molecules in the air. What is notable in this analysis is that calcium and sulfur occur in the characteristic 1 to 1 ratio. When carbon measurements are deleted from the analysis, the percent compositions match up very to those of pure calcium sulfate.

Figure 56: SEM Images of Precipitate from Ambient pH Conditions



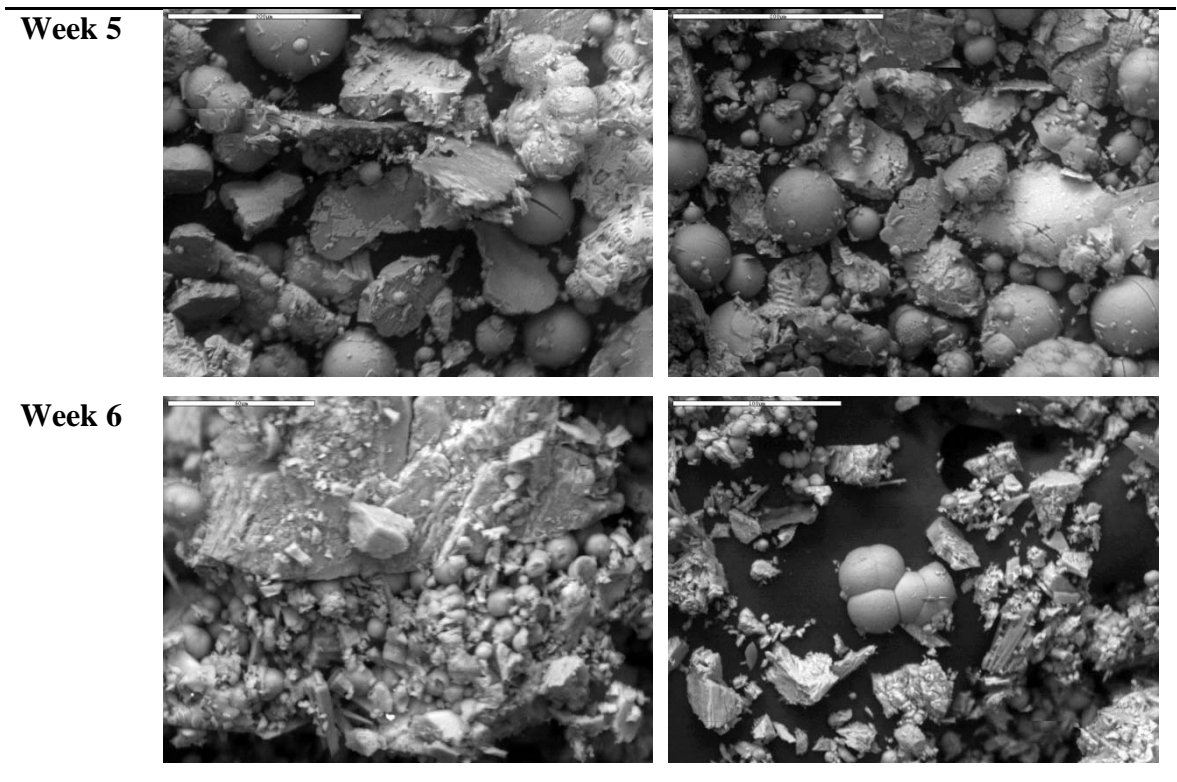
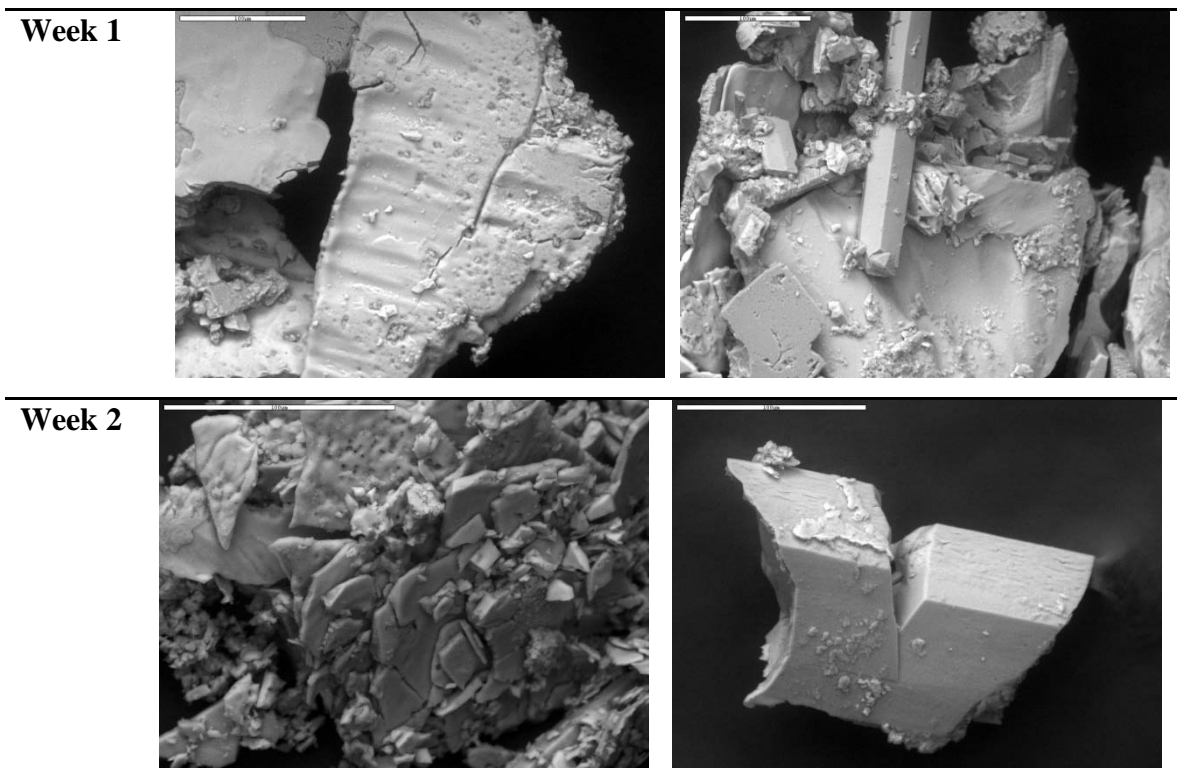
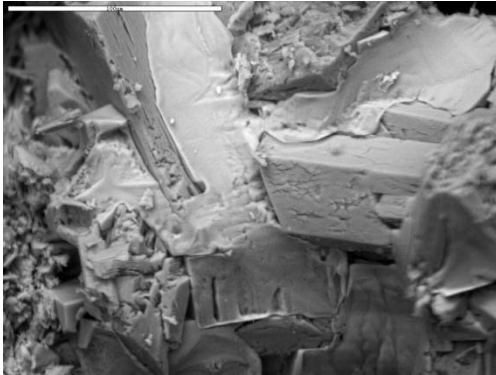
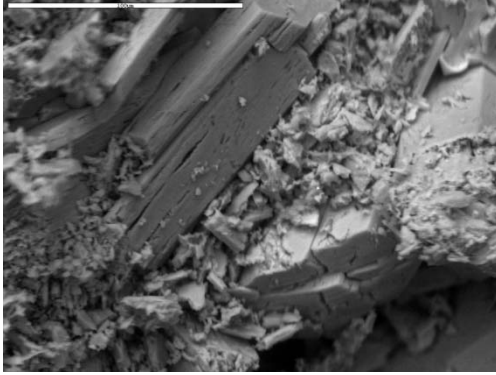


Figure 57: SEM Images of Precipitate from Low pH Conditions

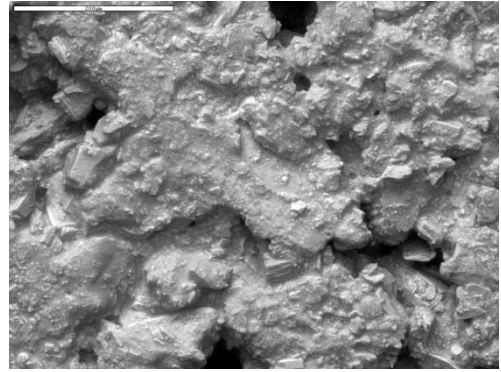
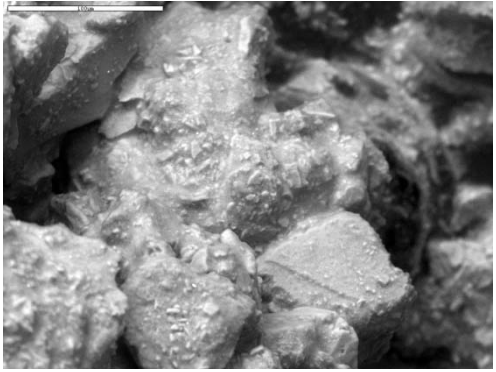


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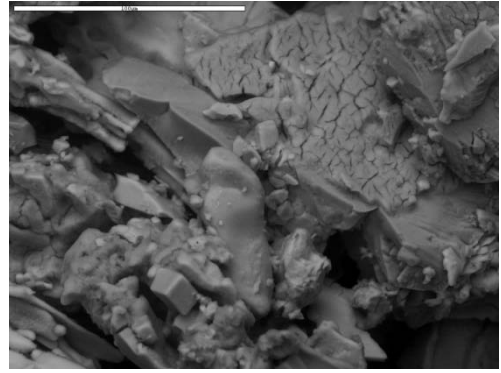
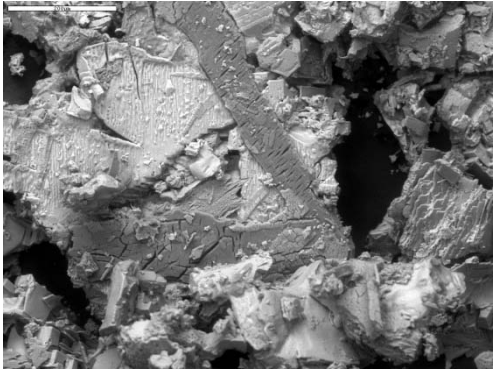
**Week 3**



**Week 4**



**Week 5**



Week 6

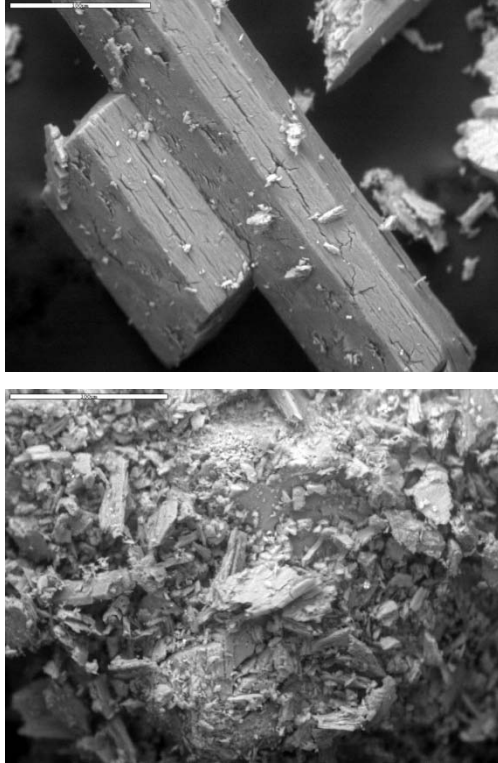
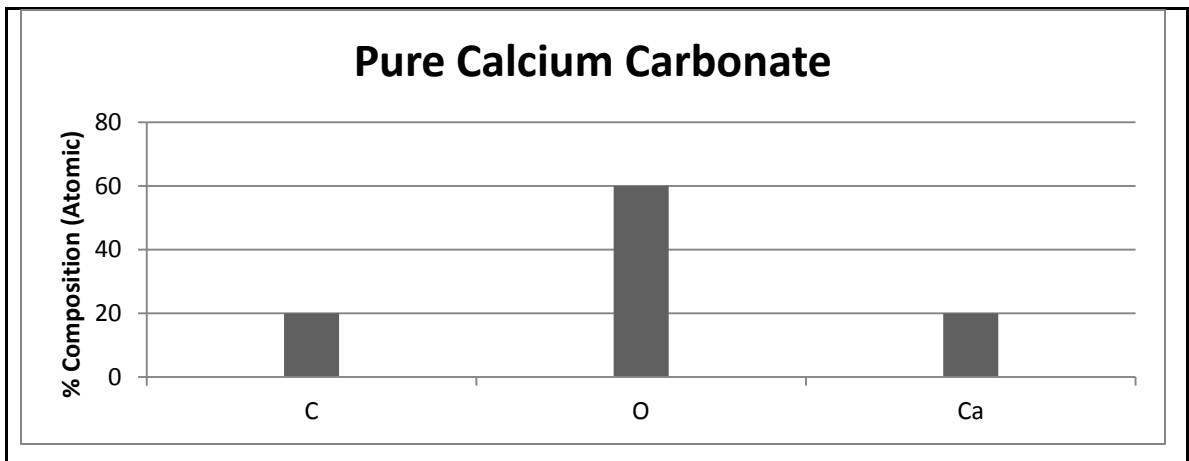


Figure 58: Semi Quantification of EDS Spectra Showing % Composition of Spheres Identified by SEM



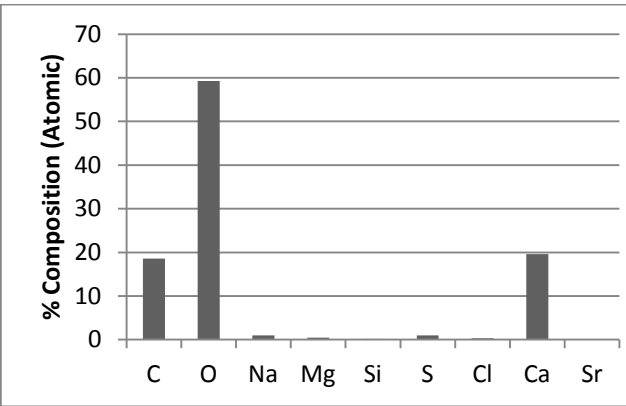
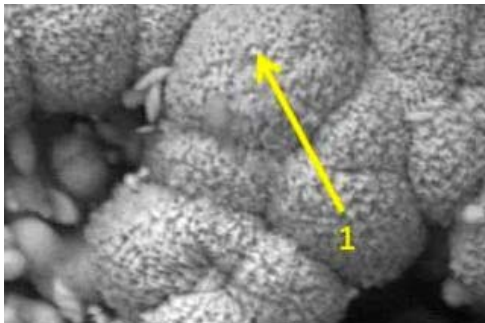
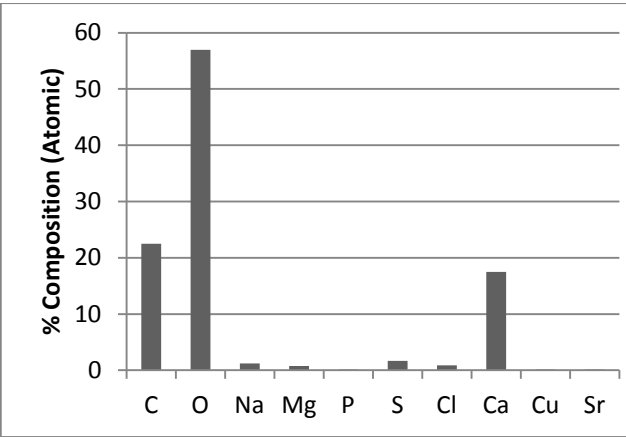
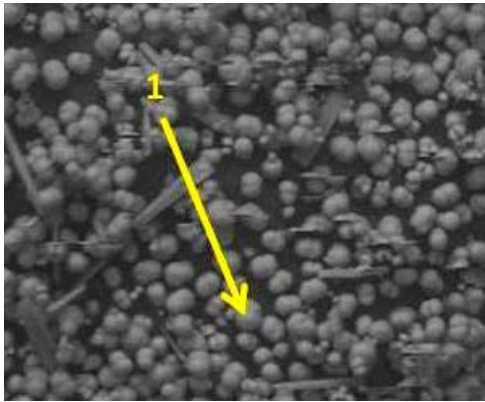
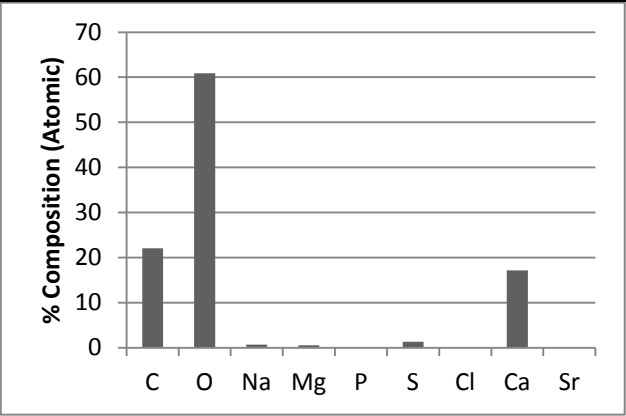
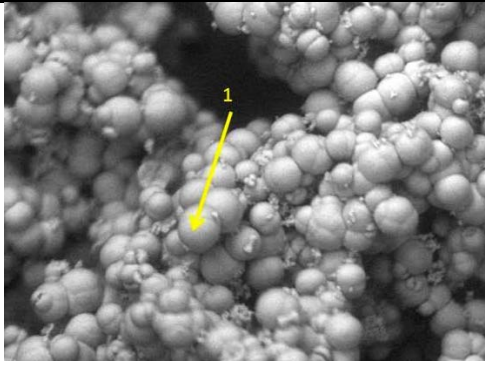
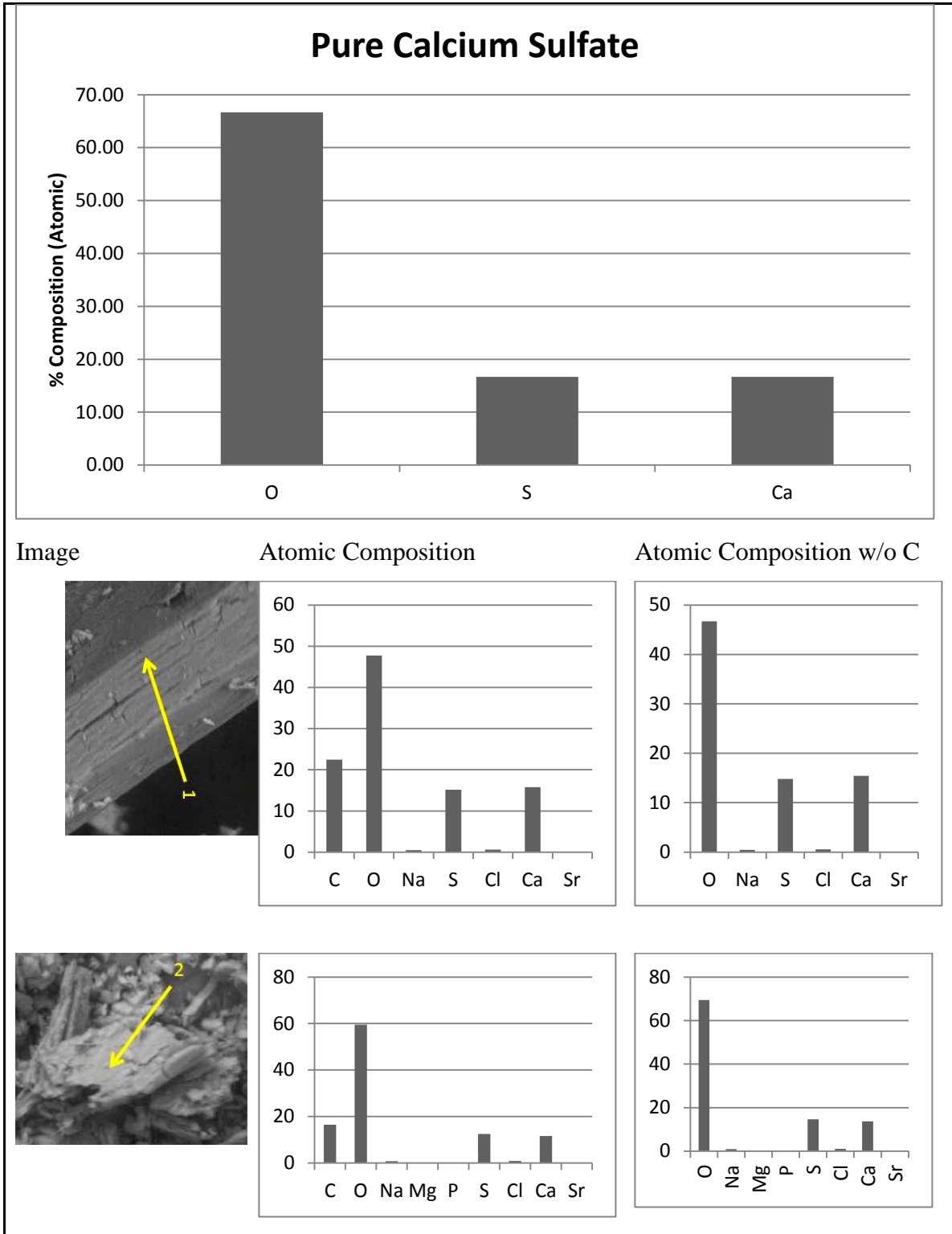
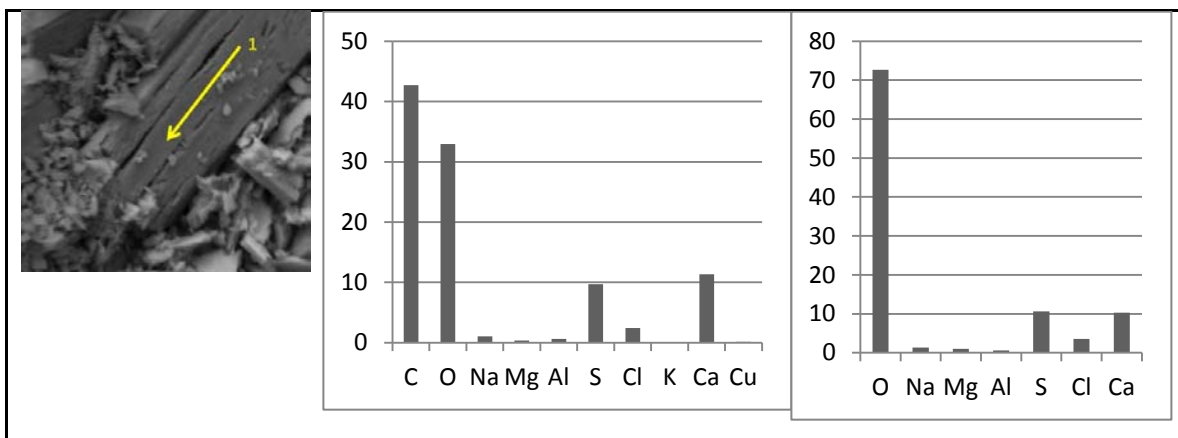




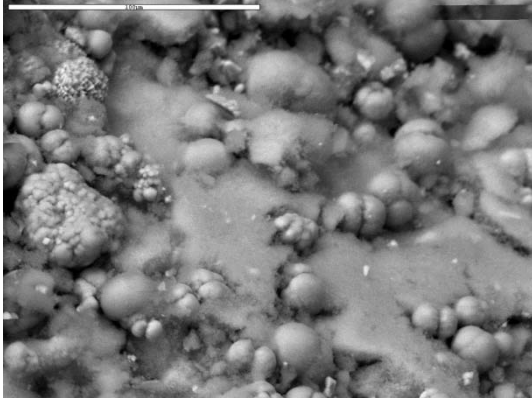
Figure 59: Semi Quantification of EDS Spectra Showing % Composition of Needles Identified by SEM





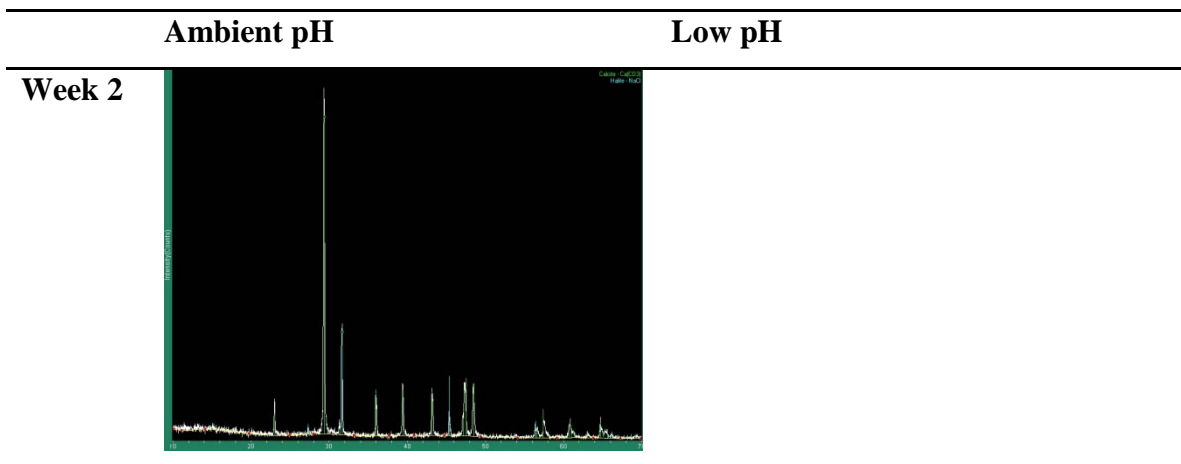
XRD was used to characterize the precipitates from each week. XRD will only detect phases that have regular crystalline structure. Amorphous phases do not produce a diffraction pattern. Based on visual inspection by SEM, it can be seen that the vast majority of the precipitate are in crystalline form. However, there is one image taken from a precipitate formed under ambient pH conditions in Week 1 that appears to contain some amorphous material (see Figure 60), but it may be instrument focus issue because this was not seen in any other images from this sample nor was it seen in images from any other sample. There XRD equipment available for use required more than 0.5 g of mass in order to obtain a spectrum, so mixing conditions that did not produce at least this amount of mass were not included in the analysis. Sufficient mass was produced in ambient pH mixing conditions for Weeks 2, 3, 4 and 6 and in low pH mixing conditions for Weeks 3, 4, and 6. XRD results are shown in Figure 61.

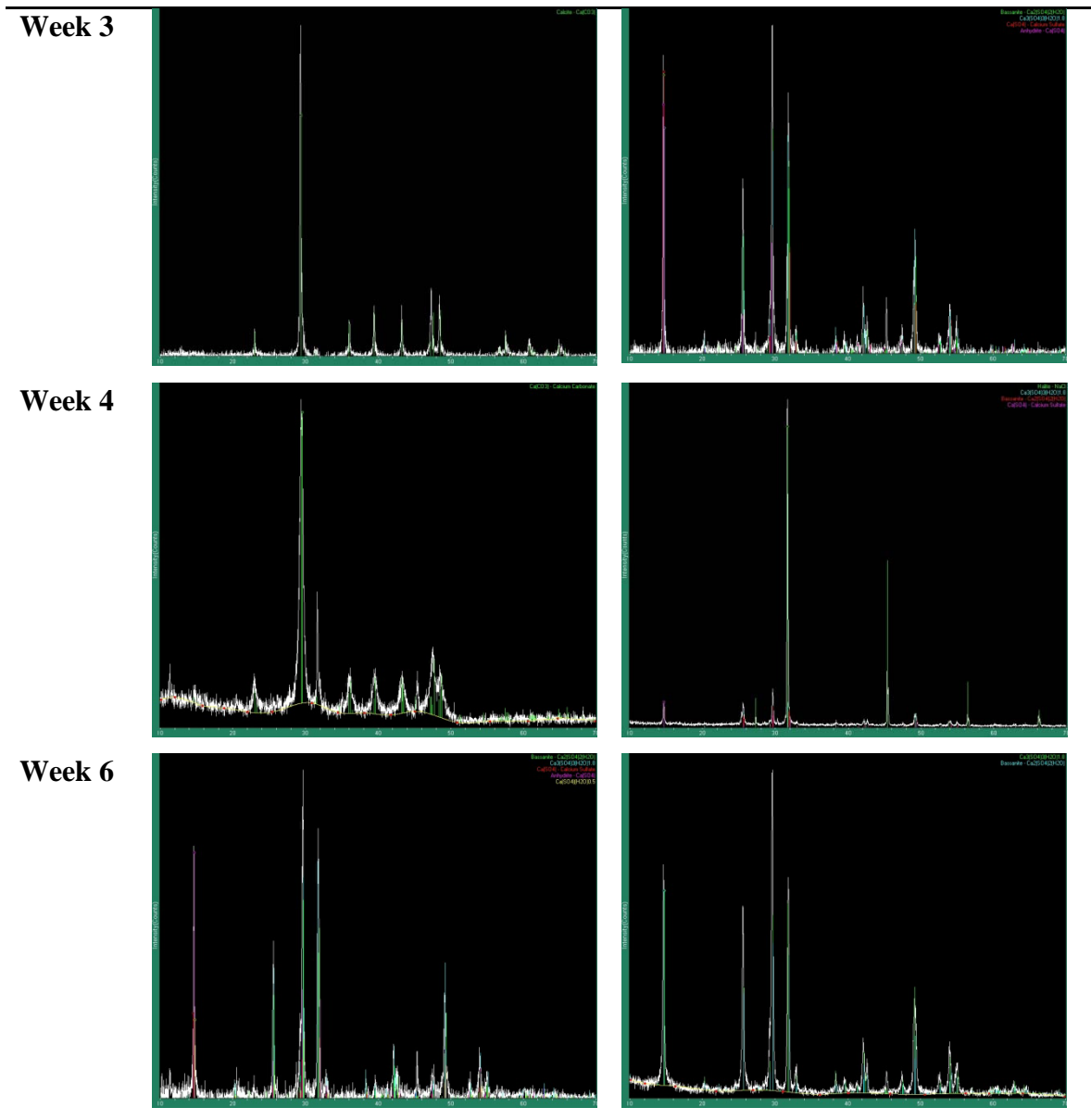
Figure 60: SEM Image Showing Possible Amorphous Material



Jade 9.1 (Materials Data Incorporated) was used to analyze the XRD spectra. Results from the XRD analysis shows the major constituent of the precipitate that formed at ambient pH conditions in all weeks but Week 6 is calcium carbonate. Calcium carbonate was identified as calcite or generic calcium carbonate, but the spectra are very similar for all calcium carbonate crystals, so it is difficult to pinpoint the crystal phase. XRD spectra show that the bulk constituent of the precipitate that formed under low pH mixing conditions for Weeks 3 and 6 was calcium sulfate. Several crystal phases were identified in the XRD crystal library including bassanite, anhydrite, and generic calcium sulfate displaying a few different levels of hydration.

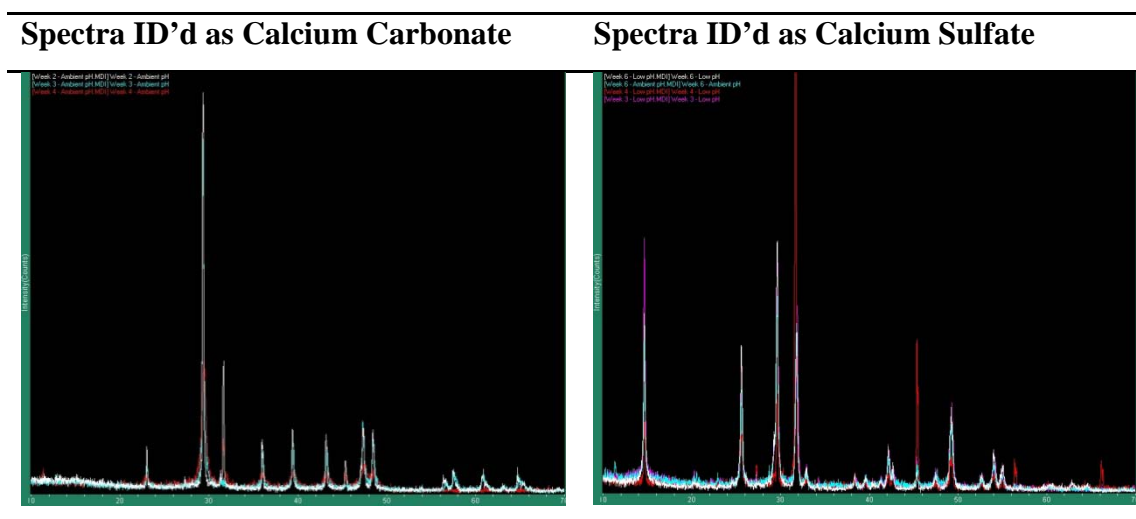
Figure 61: XRD Spectra of Precipitate Samples





Using Jade 9.1, it is possible to overlay spectra to determine their similarities. This produces as a qualitative measure of spectra similarities. Two overlays were created to compare spectra. Those identified as mainly calcium carbonate were overlain, and the similarity index between them was calculated to be 90%. The spectra identified mainly as calcium sulfate were also overlain, and the software calculated a similarity index of 91%. These overlays are shown in Figure 62.

Figure 62: Overlaid Spectra from XRD Analysis



## 6.22 Mass Determination

Precipitate mass was quantified according the following procedure outlined in the previous section. One cycle was chosen from each week for mass analysis (see Table 38). Results from this analysis are reported in Table 38.

Table 38: Precipitate Mass from Each Week from Ambient and Low pH Techniques

Week	Cycle	pH Condition	Initial pH of Anion Regen Solution	Final pH of Anion Regen Solution	Precipitate Mass (g)
1	1	Ambient	N/A	N/A	0.4565
2	2	Ambient	N/A	N/A	0.6403
3	2	Ambient	N/A	N/A	2.1022
4	2	Ambient	N/A	N/A	1.2904
5	2	Ambient	N/A	N/A	0.1998
6	2	Ambient	N/A	N/A	2.3512
1	1	Low	8.33	2.17	0.1443
2	2	Low	8.39	2.52	-0.0408
3	2	Low	8.34	2.57	1.8152

<b>4</b>	2	Low	8.67	3.15	1.0366
<b>5</b>	2	Low	8.45	2.59	0.1592
<b>6</b>	2	Low	8.64	2.86	2.4508

During weeks 3, 4, and 6 of the pilot test, regeneration solution was only collected between minutes 15 and 35 of the 53 minute regeneration cycle, in order to obtain the most concentrated fraction and to increase the mass of spontaneous precipitate. During these weeks a total of 13.2 L of regeneration solution (cation plus anion) was collected per cycle as opposed to the 34.98 L obtained when the entire cycle was collected during Weeks 1, 2, and 5. For Weeks 1-4, using a 20 bed volume operation cycle, there were 8.35 regeneration cycles per day, so the flow rate for collected regeneration solution during Weeks 1 and 2 was 292.08 L/day, opposed to 110.22 L/day during Weeks 3 and 4. For Weeks 5 and 6, using a 28 bed volume operation cycle, there were 8.00 regeneration cycles per day, so the flow rate for collected regeneration solution during Weeks 5 was 231.22 L/day, opposed to 87.25 L/day during Week 6. The amount of precipitate that could be produced per cubic meter of RO concentrate for each week and pH condition was calculated and is show in Figure 63 and Figure 64.

**Figure 63: Calculated Salt Yield per Cubic Meter of RO Concentrate for each Week at Ambient pH**

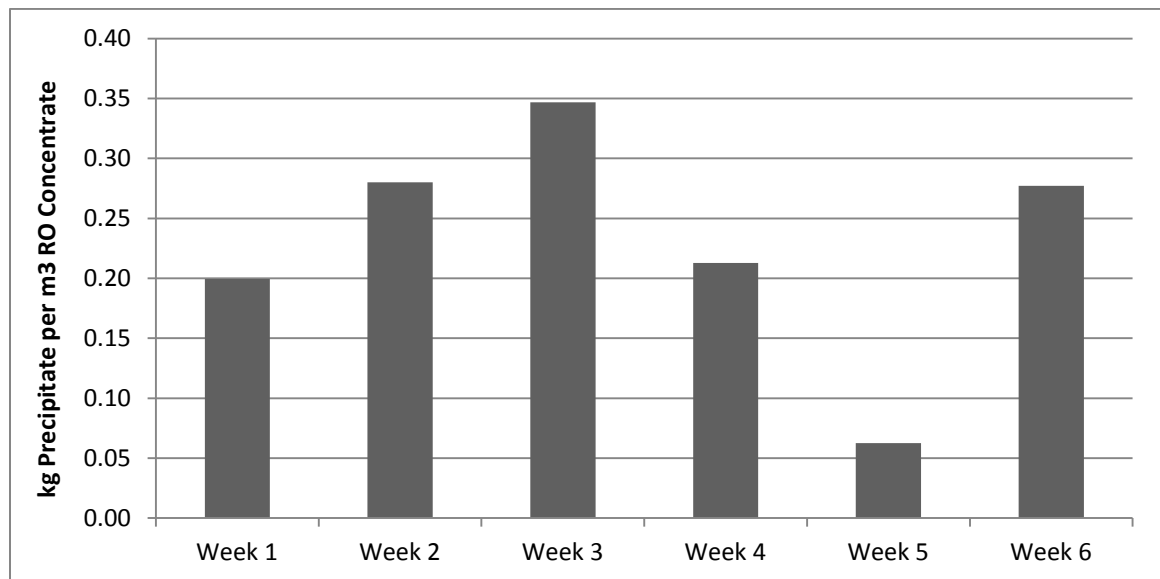


Figure 64: Calculated Salt Yield per Cubic Meter of RO Concentrate for each Week at Low pH

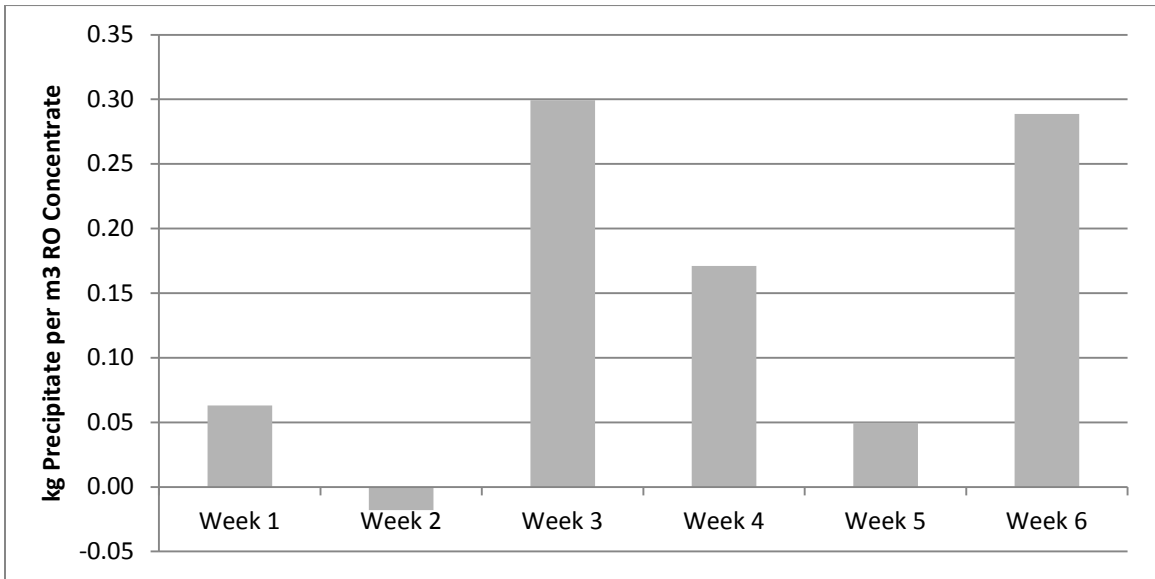
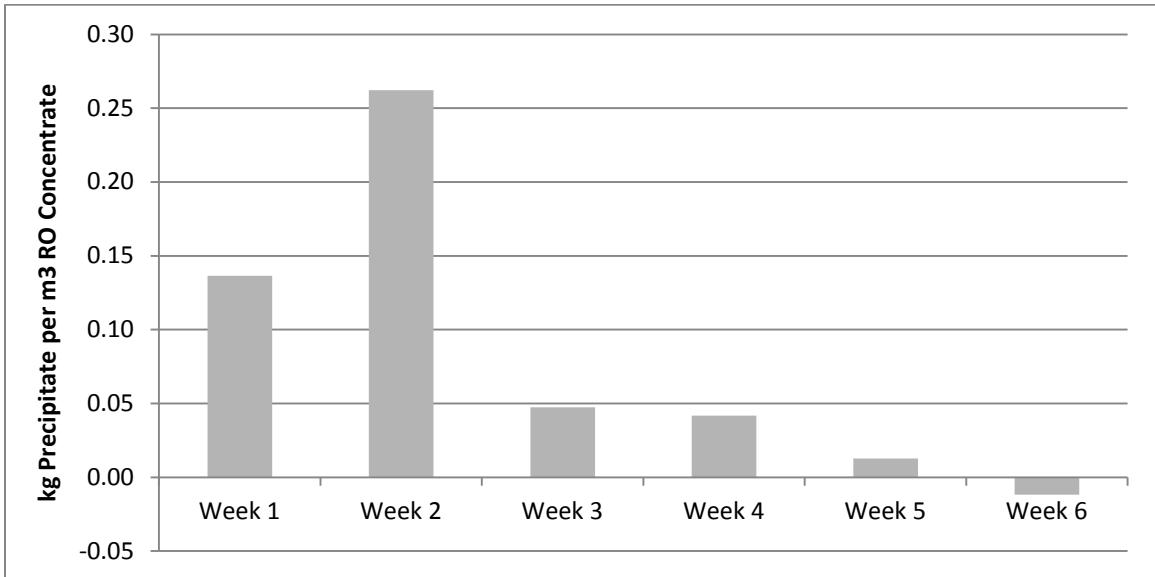


Figure 65: Difference in Yield between Precipitation at Ambient and Low pH Conditions



According to the pilot design, regeneration solution was only collected from the most concentrated portion of the regeneration cycle during Weeks 3, 4, and 6. The entire cycle was collected during Weeks 1, 2, and 5. During Weeks 5 and 6, the operation cycle was extended by 8 bed volumes. These changes to the pilot operation and collection methods caused changes to salt production rate and the salt character. In Weeks 1 and 2,

ambient pH conditions produced a much greater amount of salt precipitation than low pH conditions. This was most likely the result of increased solubility of calcium carbonate by the low pH. In ambient pH mixing conditions, calcium carbonate precipitated immediately, consuming the available calcium that would otherwise have been able to precipitate with sulfate. However, sulfate concentrations were low in these solutions, so even in low pH conditions, only a small amount of calcium sulfate precipitated. During Week 5, in which the operation cycle was extended, sulfate concentrations increased relative to carbonate concentrations, and there was also a small increase in calcium concentrations. In ambient pH conditions, less precipitate formed compared to the same test from Weeks 1 and 2. This was likely due to the decrease in carbonate concentration. Due to the increase in sulfate concentration, more precipitate formed under low pH conditions in Week 5 than during Weeks 1 and 2. This can also be seen when comparing the difference in mass precipitation at ambient and low pH conditions between Weeks 1 and 2 and Week 5 (see Figure 65). During the weeks in which the most concentrated portion of the regeneration cycle was collected, all resulted in increased precipitate mass yield compared to their full regeneration cycle counterparts. Sulfate concentrations during these weeks were 2-3 times higher than weeks in which full regeneration cycles were collected. This resulted in calcium sulfate precipitation regardless of pH mixing conditions. Regeneration solution in Week 6 was higher in sulfate concentration than that in Weeks 3 and 4, due to increased operational cycle. Precipitate produced under ambient pH mixing conditions in Weeks 3 and 4 was mainly calcium carbonate although a very small amount of calcium sulfate also precipitated in Week 4. Mixing regeneration solutions at low pH during Weeks 3 and 4 produced calcium sulfate precipitate at a lower salt yield than that which occurred at ambient pH mixing conditions. In Week 6, sulfate concentrations were higher than in any other week due to the combination of increased operational cycle and collection of the most concentrated portion of the regeneration cycle. Sulfate was so abundant that it consumed all the available calcium to form calcium sulfate under both ambient and low pH conditions at the same yield. No calcium carbonate was detected in these samples.



## 6.23 Conclusions from Investigation of Precipitate

A few general conclusions can be drawn from the combination of data from SEM, EDS, and XRD. First, calcium sulfate and calcium carbonate can be precipitated separately by controlling the pH when mixing cation and anion regeneration solutions. For all weeks except Week 6, mixing at ambient pH conditions resulted in a calcium carbonate precipitate. The carbonate consumed the available calcium, and only negligible amounts of calcium sulfate precipitated. Analyses of cations in solution, which were somewhat unreliable, showed that some magnesium precipitated as well. If that happened, it would most likely be in the form of a calcium magnesium carbonate such as dolomite, but it was neither observed under the SEM nor identified by XRD. EDS did indicate a very low percentage (less than 1.5% in all cases) of magnesium precipitation, but that is close to the limit of the instrument's accuracy. In Week 6, the precipitate from both ambient and low mixing conditions was mainly calcium sulfate although a small amount of calcium carbonate was identified visually in the SEM images from that sample. XRD identified both samples as calcium sulfate. All samples that precipitated under low pH conditions consisted mostly of calcium sulfate. This was observed visually through the SEM and was confirmed by EDS and XRD. This data show that calcium carbonate precipitation can be controlled by reducing the pH to less than 4 during mixing. If sufficient sulfate exists to consume the available calcium, pH adjustment is not needed to suppress calcium carbonate precipitation.

One of the concerns that arose when considering precipitation of salts by mixing cation and anion regeneration solutions was the high ionic strength of the mixture and the presence of phosphonate based anti-scalants. Phosphonates are highly water soluble salts and ester of phosphonic acid,  $\text{HPO}(\text{OH})_2$ . The inhibition action of phosphonates is significantly better towards calcium carbonate, magnesium hydroxide, and barium sulfate than toward calcium sulfate precipitation [33]. They are able to suppress precipitation of both calcium sulfate and calcium carbonate at high levels of supersaturation [34]. The effect of phosphonate based anti-scalant on precipitation in simulated RO concentrate from the a brackish water system was studied by Greenlee et al [35]. It was found that solution pH is major factor in anti-scalant effectiveness. Significant calcite precipitation occurred at a pH of 10.5 in the presence of anti-scalant (as opposed to pH 8 in solutions

without anti-scalant). PreTreat Plus 100 is only weakly attracted to the anion resin and easily eluted during regeneration, according to King Lee, the manufacturer. For this reason, it will not be concentrated by the anion exchange process. It is not likely that to significantly suppress precipitation at low concentrations, but it may have some effect on the size and morphology of precipitated crystals [35].

In addition to the high concentrations of divalent ions, there are also high concentrations of sodium and chloride because the columns are regenerated with a 10% sodium chloride solution. The ionic strength of the cation and anion regeneration solutions, calculated only from the measured ions, ranged from 0.6 M to 2.5 M. Although, the decreased activity of divalent ions may decrease the salt yield, salts precipitated spontaneously when the regeneration solutions were mixed. The feed flow rate to the RO system producing concentrate for the pilot was approximately 1.75 gpm. From the mass quantification section, it was estimated that during Week 6, it was possible to precipitate about 12 kg of salt per cubic meter of regeneration solution. If the RO system was treating 5 million gallons per day (MGD) of RO concentrate, the salt yield would be approximately 6 tons/day. Using this process, it is possible to recover approximately 45% of the calcium and approximately 28% of the sulfate from the mixed regeneration solution. That is equal to an overall recovery of approximately 15% of the total gypsum in the RO concentrate.

## **6.24 Determination of Most Concentrated Regeneration Solution Fraction**

The second objective of this phase of the project was to determine which portion of the regeneration cycle yielded the highest concentrations of ions and to compare precipitation using only that fraction with precipitation using the regeneration solution from an entire regeneration cycle. Comparison of salt yield from concentrated fractions versus standard cycles was discussed previously, so this section will focus only on the determination of the most concentrated fraction.

Elution curves were taken in Week 2 and Week 5 to capture any changes due to extension of the operation cycle. Figure 66, Figure 67, Figure 68, and Figure 69 show the

concentration of ions eluting from the column, the total carbonate of the solutions, and the conductivity of the solutions, throughout the cycle.

Figure 66: Elution Curve for Week 2

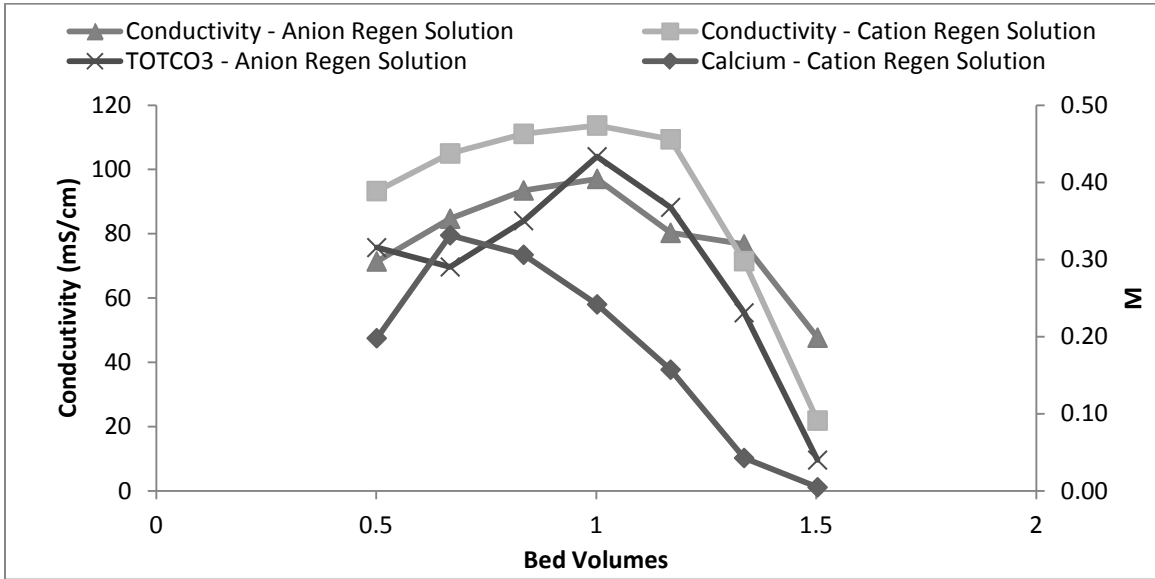


Figure 67: Normalized Elution Curve for Week 2

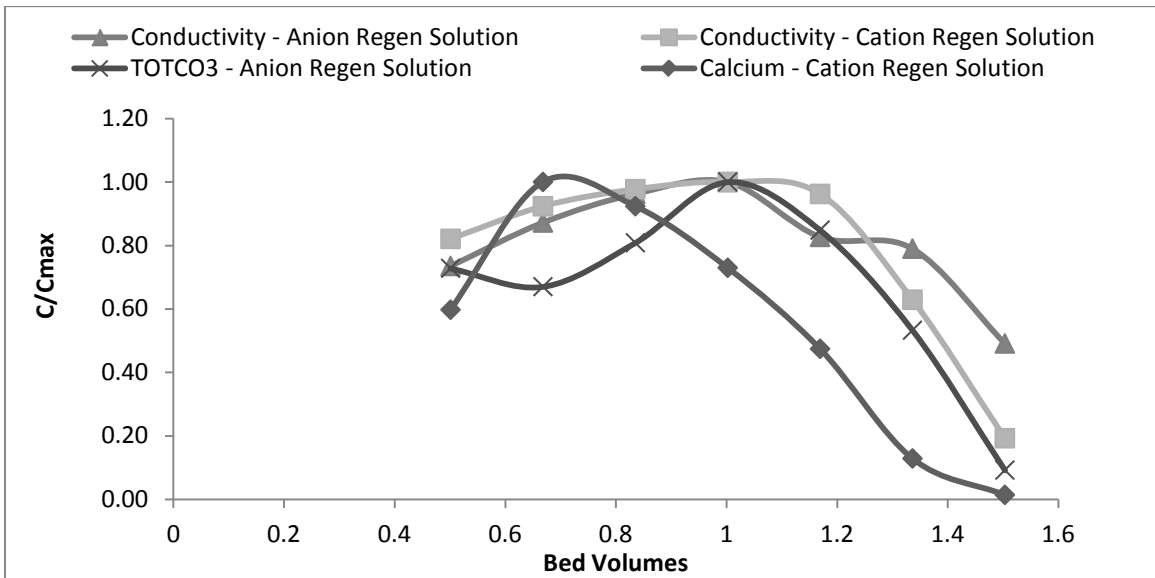


Figure 68: Elution Curve for Week 5

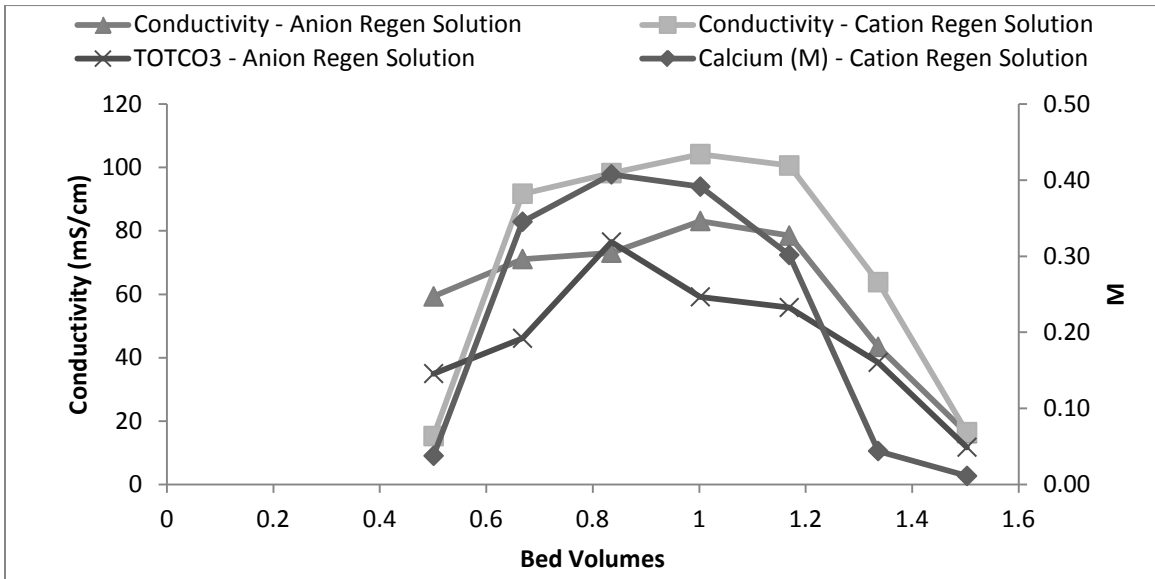
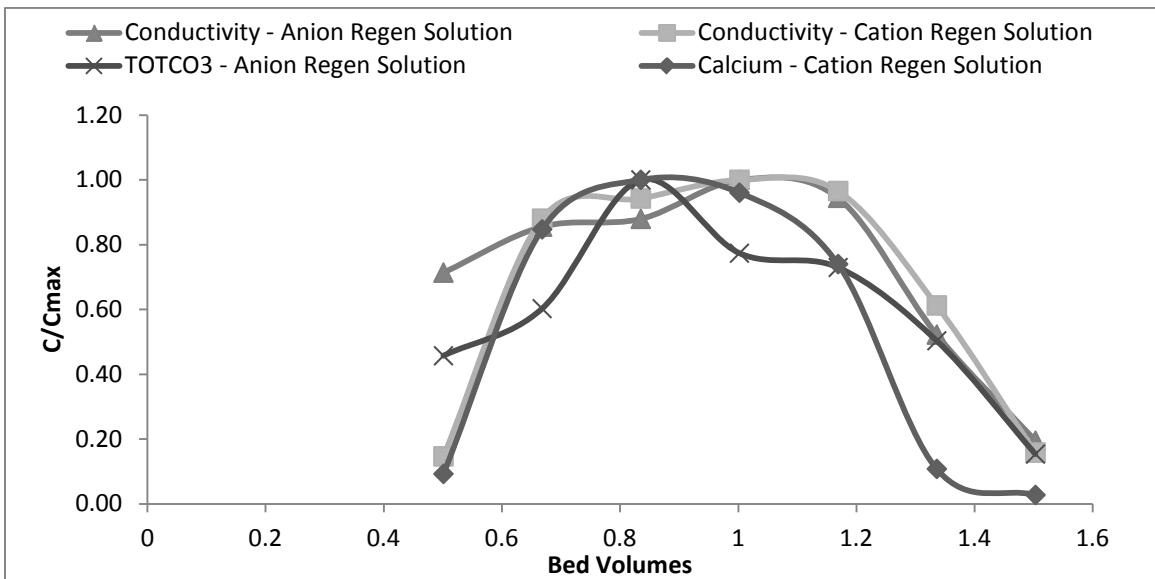


Figure 69: Normalized Elution Curve for Week 5



Time constraints during pilot operation prevented the measurement of calcium concentration at the time the elution curves were taken. The calcium concentration appears on the elution curves although it was measured later and did not impact the determination of the most concentrated portion of the cycle. Electrical conductivity was measured in the field while calcium concentration was measured in the laboratory.

Conductivity and total carbonate both peaked at about 1 bed volume into the regeneration cycle, so the most concentrated portion of the cycle was determined to occur between 0.67 and 1.17 bed volumes or between 15 and 35 minutes into the regeneration cycle. As is evident from the elution curves, calcium concentration peaked slightly earlier in the regeneration cycle than the conductivity and the carbonate concentration. In retrospect, it may have been more useful to collect the fraction between about 0.60 and 1.10 bed volumes instead. The concentrations of ions in the regeneration solutions are shown in Table 35 and Table 36.

One factor that should not be overlooked when considering this data is that there may have been variations in the sodium chloride regeneration solution concentration that affected the elution curve. Regeneration solution was prepared using a conductivity meter, salt pellets used for home water softening, and a scale with a .02 lb precision. The amount of salt that needed to be added was calculated by taking a conductivity reading from a tank containing approximately 40 gallons of secondary RO concentrate, referring to a chart that related conductivity to concentration in lb/gallon, subtracting the current concentration of salt from 0.89 lb/gallon (10% solution), and multiplying by 40. The desired amount was weighed on the scale, poured into the tank, and mixed until it was dissolved as much as possible. Complete dissolution of the salt pellets was difficult to achieve. This method was fairly crude and likely resulted in a range of solution concentrations. Given that consideration, the elution curves from the two different weeks are quite similar. The main difference between the two is that the calcium curve is broader and peaks a bit later in the elution from Week 5. The conductivity of the cation regeneration solution is higher in Week 2, which may account for the earlier calcium peak.

During pilot design, it was difficult to predict the necessary number of bed volumes to completely regenerate the columns, but elution curves show that the majority of ions were displaced from the column during the 1.75 bed volume regeneration cycle. In standard practice, the number of bed volumes used for regeneration and rinsing is much higher. In this application, however, it makes sense to use the smallest volume of regeneration solution possible in order to maintain the highest possible concentration of ions. The elution curves show that the majority of ions are removed from the column

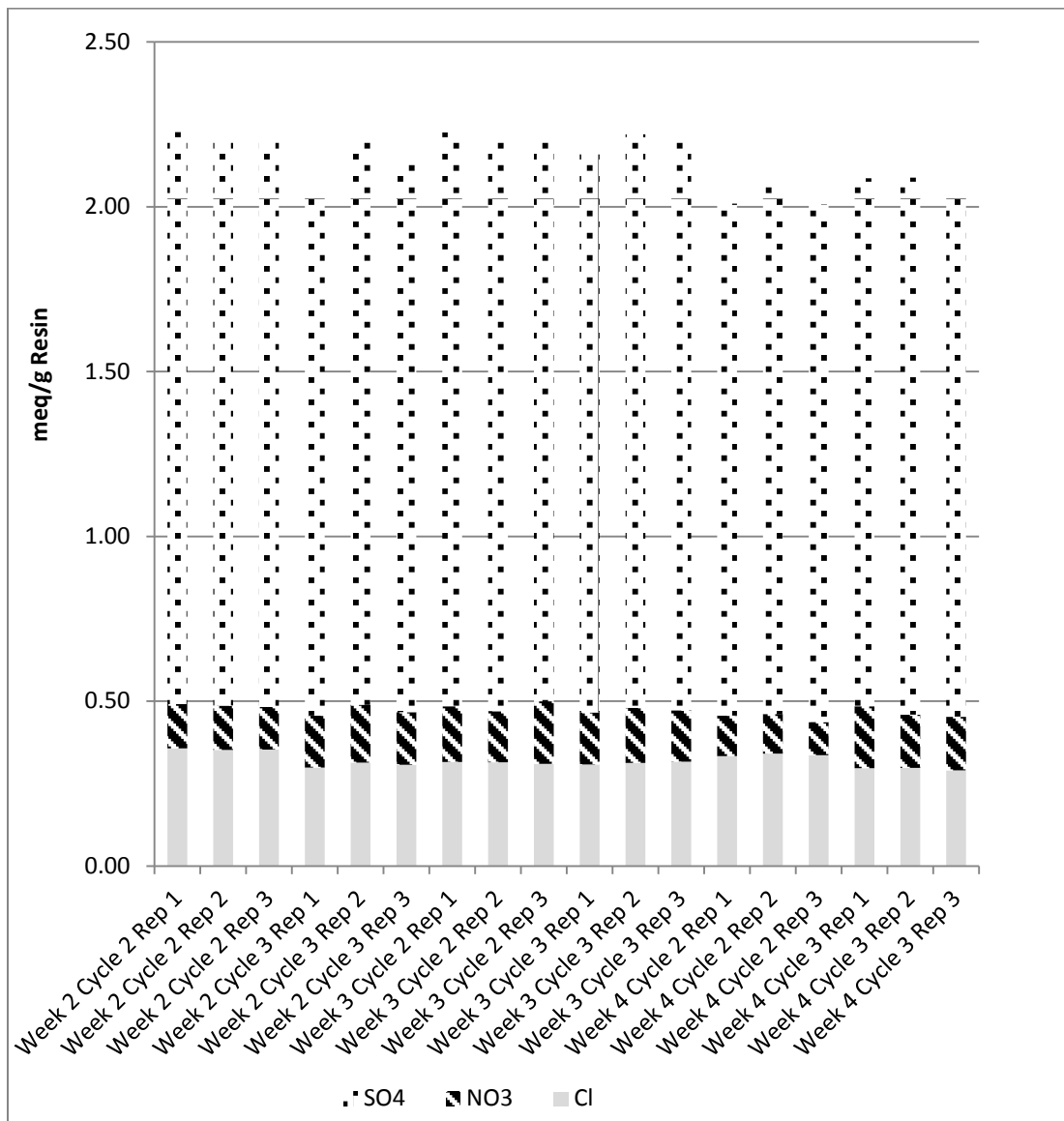
before 1.75 bed volumes and that it may be possible to reduce the rinsing time by a few minutes without compromising column efficiency.

## **6.25 Effect of Anti-Scalant on Resin Capacity**

Fouling of the anion exchange resin by organic anti-scalant was a potential problem identified at the beginning of the study. The feed water to the primary RO system was treated with King Lee Pretreat Plus 100 which is a phosphonate based anti-scalant that works as a chelating agent to complex the metals and prevent precipitation. According to chemists at King Lee, phosphonate is weakly attracted to the anion resin and easily eluted during regeneration. In order to confirm that the resin was not fouled over time, regardless of the cause, resin samples were taken from the top of the anion exchange column at the end of the operation cycles during Weeks 2, 3, and 4. Resin samples washed, dried, weighted, and then stripped using 1N NaOH and allowed to equilibrate. Liquids were then analyzed for sulfate, chloride, nitrate, and total organic carbon (TOC). Based on results of the liquid analysis, the total number of equivalents of ions on the resin per gram was calculated. The amount of TOC (in ppm C) per resin gram was also calculated, but the ratio between ppm C and equivalents is unknown, so it could not be added to the sum of equivalents from the ions. Specification sheets from Purolite list 1.25 eq/L as the minimum capacity of A850 resin. Laboratory measurements of dry resin show that it has a density of 0.73238 g/mL, indicating that dried resin should have a minimum capacity 1.7 eq/g. A total of 18 samples were analyzed. Two resin samples were collected per week, and each was separated into 3, 1 g masses for analysis. Mass concentrations of ions were measured, converted to equivalents, multiplied by the solution volume, and then divided by the exact mass measurement (close to 1 g) to find the amount of eq/g on the resin for each ion. Results from this analysis are shown in Figure 70 and Table 39. Carbonate titrations were not done for these samples due to the extremely high pH of the solution used to strip the resins. However, there is no reason to expect that ratio of ions on the resin would change over time, so even if the total capacity including the carbonate is a little higher, the trend of total capacity of time should still be valid. The total concentration of ions on the resin displays a slight decrease in in Week 4 compared to Weeks 2 and 3, but this is not necessarily due to fouling by the anti-scalant.

There are several factors that could potentially lead to a decrease in anion exchange capacity. Other organic compounds in the feed water could foul the resin or the decrease in exchange capacity could be due to the buildup of higher capacity ions that were not measured in the laboratory. Although the cause of the decrease in capacity is unknown, the effect of it on the overall operation of the pilot was very minor. The anion exchange column operated without a problem throughout the duration of the pilot and there was no measured decrease in sulfate exchange.

Figure 70: Concentration of Cl, NO<sub>3</sub>, and SO<sub>4</sub> on Resin Stripped (meq/g)



**Table 39: Amount of meq/g of Cl, NO3, and SO4 on Resin Stripped with NaOH**

	<b>Resin</b>	<b>Cl</b>	<b>NO3</b>	<b>SO4</b>	<b>Total</b>
	<b>g</b>	<b>meq/g</b>	<b>meq/g</b>	<b>meq/g</b>	<b>meq/g</b>
<b>Week 2 Cycle 2 Rep 1</b>	1.0003	0.36	0.13	1.74	2.23
<b>Week 2 Cycle 2 Rep 2</b>	1.0004	0.36	0.13	1.71	2.20
<b>Week 2 Cycle 2 Rep 3</b>	1.0008	0.36	0.13	1.72	2.20
<b>Week 2 Cycle 3 Rep 1</b>	1.0005	0.30	0.16	1.58	2.04
<b>Week 2 Cycle 3 Rep 2</b>	1.0001	0.32	0.18	1.71	2.20
<b>Week 2 Cycle 3 Rep 3</b>	1.0001	0.31	0.16	1.67	2.14
<b>Week 3 Cycle 2 Rep 1</b>	1.0002	0.32	0.17	1.74	2.23
<b>Week 3 Cycle 2 Rep 2</b>	0.9994	0.32	0.15	1.74	2.21
<b>Week 3 Cycle 2 Rep 3</b>	0.9998	0.31	0.19	1.71	2.21
<b>Week 3 Cycle 3 Rep 1</b>	1.0003	0.31	0.16	1.69	2.16
<b>Week 3 Cycle 3 Rep 2</b>	1.0003	0.32	0.17	1.74	2.22
<b>Week 3 Cycle 3 Rep 3</b>	0.9996	0.32	0.16	1.73	2.20
<b>Week 4 Cycle 2 Rep 1</b>	1.0001	0.34	0.12	1.55	2.01
<b>Week 4 Cycle 2 Rep 2</b>	1.0002	0.35	0.12	1.61	2.07
<b>Week 4 Cycle 2 Rep 3</b>	1.0005	0.34	0.10	1.57	2.01
<b>Week 4 Cycle 3 Rep 1</b>	1.0000	0.30	0.19	1.60	2.09
<b>Week 4 Cycle 3 Rep 2</b>	1.0000	0.30	0.16	1.63	2.09
<b>Week 4 Cycle 3 Rep 3</b>	0.9997	0.29	0.16	1.58	2.03

Solutions containing the constituents stripped from the resin were also analyzed for TOC. The TOC concentration on the resin ranged from 11.16 ppm C/g to 8.45 parts per million (ppm) C/g. TOC concentrations are compared to total concentration (meq/g) of ions in Figure 71. There does not appear to any correlation between the besides a general decrease in both values over time. The same values, normalized to the maximum concentrations of each are shown in Figure 72. In the case of each constituent, the decrease is slight compared to the maximum value and did not impact column performance. To verify trends and understand long term impacts, it would be necessary to obtain performance for a series of months.



Figure 71: Change in Concentration of Ions and TOC on Anion Exchange Resin over Time

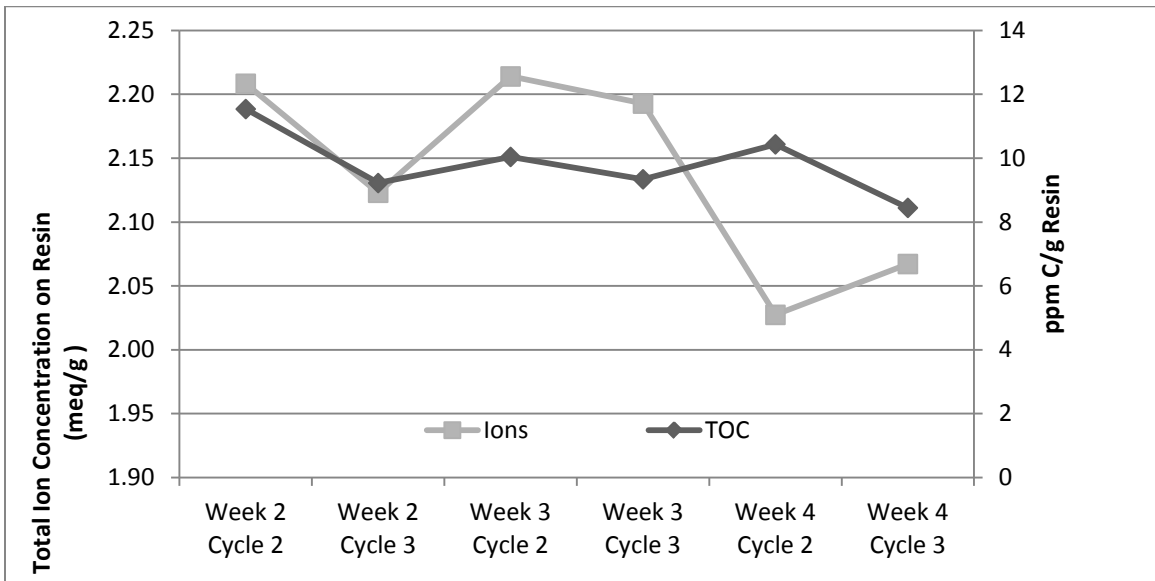
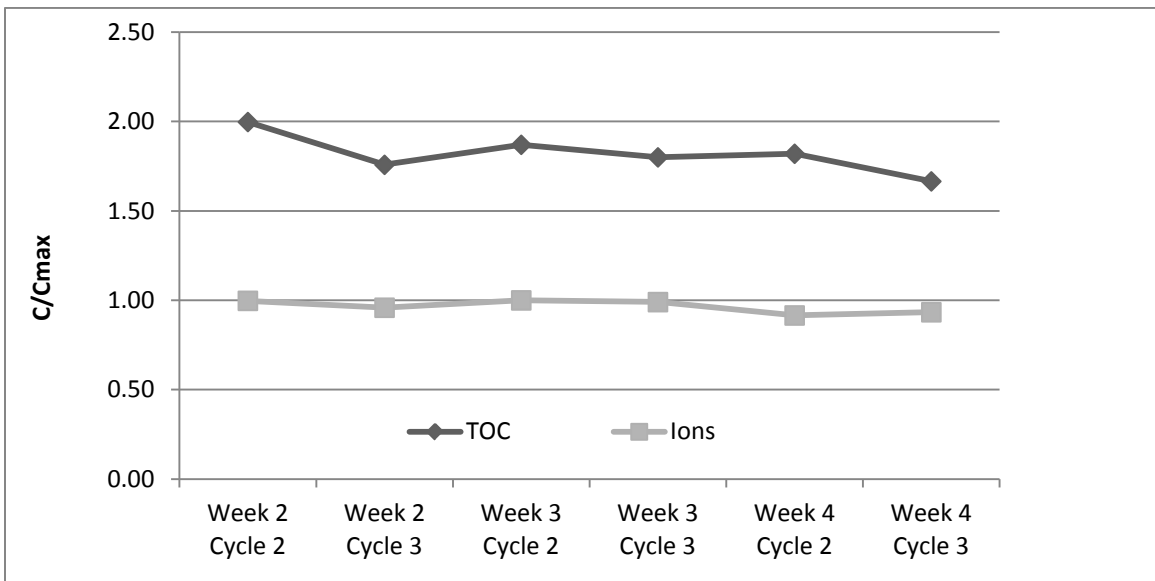


Figure 72: Change in Normalized Concentration of Ions and TOC on Anion Exchange Resin over Time

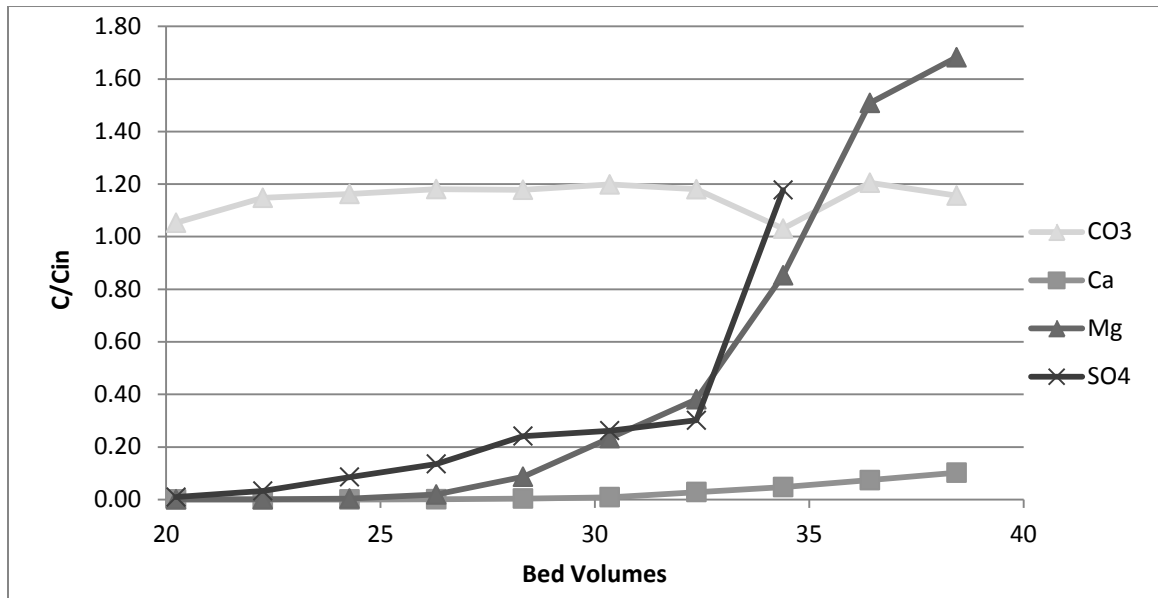


## 6.26 Optimization of Operation Cycle Length

One of the difficulties in performing sequential cation and anion exchange is that most cation resins have higher exchange capacities than anion resins. For the purposes of this pilot, identical columns were used for both resins to simplify the

hydraulics, but this resulted in wasted exchange capacity in the cation exchange column. The design operation cycle length was based on the estimated anion exchange capacity, but the actual capacity of both columns was unknown. In order to optimize the length of the operation cycle, it was necessary to generate a breakthrough curve to map the concentration of cations and anions in the effluent. During week 3, an operation cycle was extended by 108 minutes (18.44 bed volumes), and samples were taken every 12 minutes. The samples were analyzed by AA, IC, and acid titration to measure calcium, magnesium, sulfate, and total carbonate. The resulting breakthrough curves are shown in Figure 73.

**Figure 73: Breakthrough Curve from Extended Operation Cycle in Week 3**



The figure shows that effluent carbonate concentration had already reached the influent concentration at the end of the standard operation cycle, indicating that it was present in the effluent that was stored and treated by a secondary RO system to produce regeneration solution. The regeneration solution, therefore, contained even more carbonate, and this could potentially cause problems if any cations leaked into the effluent or if carbonate concentrations became high enough to cause precipitation in the

cation exchange column. Precipitation can occur in the cation column during regeneration if sulfate and carbonate are present in sufficient quantities.

The breakthrough curves shows that the sulfate begins to break through the anion exchange column at about 22 bed volumes, so the operational cycle based on this column was already close to being fully optimized with regards to sulfate. At 20 bed volumes, the entire resin capacity for carbonate appears to be exhausted, and the fact that the effluent concentration is greater than influent concentration indicates that it is being displaced from the resin by higher selectivity ions, such as sulfate (i.e. chromatographic peaking). That phenomenon explains why sulfate concentrations in the anion regenerations solution were so much higher in Week 6 compared to Weeks 3 and 4.

Breakthrough of calcium began at about 32 bed volumes, but magnesium appeared in the effluent at about 28 bed volumes. Magnesium exceeded the influent concentration at 34 bed volumes, at the same time that the calcium concentration began to increase. This represents the displacement of magnesium from the resin by calcium, which has a higher selectivity. If samples had been taken beyond 38 bed volumes, the magnesium concentration would eventually approach the influent concentration as the resin in the column equilibrated to the influent concentrations. Some displacement of magnesium by calcium occurred in during the 8 bed volume extension of the operation cycle, and this can be seen in the comparison of the average calcium to magnesium ratio in the cation regenerant solution between the normal and extended cycles (see Table 40). When the operation cycle was extended, the ratio of calcium to magnesium on the resin increased. This phenomenon could be optimized to increase calcium concentrations in the regeneration by increasing the size of the anion exchange column relative to the cation exchange column.

**Table 40: Average Concentrations Ratio (eq) between Calcium and Magnesium**

	<b>Ca:Mg (eq)</b>	<b>Std Dev</b>
<b>Normal Cycle (2-4)</b>	1.44	0.164
<b>Extended Cycle (5-6)</b>	2.06	0.003

To avoid possible precipitation of magnesium salts, the operation cycle was extended to 28 bed volumes. The last 8 bed volumes of effluent were diverted away from the second stage RO system to prevent sulfate precipitation from occurring on the membrane or having them build up in the secondary concentrate being used to regenerate the columns. Extending the operation cycle also greatly increased the sulfate concentration on the anion exchange resin. By extending the operation cycle and capturing the most concentrated fraction of the regeneration solution, it was possible to precipitate calcium sulfate without adjusting the pH during mixing, due to the high concentration of sulfates in the anion regeneration solution. In a full scale system, this could represent a large savings in terms of process simplification, safety, and costs related to acid.

### **6.27 RO System Performance While Treating Pilot Effluent**

For the duration of pilot testing, effluent from the sequential ion exchange process was stored and treated by a single element RO system to produce more water and to produce concentrate to use as the ion exchange regeneration solution. Several parameters recorded on regular basis to keep track of system performance over time. These parameters included feed pressure, concentrate pressure, concentrate flow, permeate flow, feed temperature, feed conductivity, feed pH, concentrate temperature, concentrate conductivity, and concentrate pH. The RO system was not run continuously because only a small amount of secondary concentrate was needed to regenerate the columns on a daily basis. On most days, the system was only run for a few hours, and occasionally enough secondary concentrate was produced so that the system did not have to be run at all on certain days. In particular, extra concentrate was produced on Fridays to prevent someone from having to run the RO system over the weekend. Effluent that was not treated by secondary RO was stored and used for rinsing at the end of the regeneration cycle.

Although data was recorded on a regular basis (see Table 41) when the RO system was in use, frequent system shutdowns make it difficult to interpret. There were significant changes in ambient temperature during the system operation which often occurred between 7:30AM and 11:00AM. One incident that may have damaged the membrane occurred during the first weekend (June 10-11) when the backpressure in the

feed line prevented the feed valve from closing during the regeneration cycle. As a result, the columns were unable to regenerate, and effluent full of divalent ions were sent to the effluent storage tank and subsequently to the secondary RO system before the problem was realized. Within an hour, the RO system was shut down, and a short auto-flushing sequence was run. However, some scaling may have occurred at that time. During Week 3 (June 19-25), an algal growth problem was noticed in the effluent storage tank that fed the RO system. Although it was realized during Week 4, further inspection of the cartridge filters on the pilot system and the RO system revealed it had been occurring unnoticed before that time. The tank was emptied and washed with chlorine bleach. The membrane was removed from the RO system and a chlorine flush was performed. System performance deteriorated at the end of June, and the membrane was replaced on June 29<sup>th</sup>. It is unclear which of the issues that occurred caused the decline in performance. The fouled membrane was retained and remains in cold storage, and a membrane autopsy may be performed as part of an adjoining study.

Hydranautics ESPA-2 membranes were used in the RO system. Recorded data was entered in the ROData spreadsheet provided by Hydranautics which contains the specific membrane information needed to normalize the data. Figure 74, showing, normalized permeate flow, was generated by the ROData spreadsheet. As can be seen on this chart, membrane performance declined steadily over time between June 16<sup>th</sup> and June 28<sup>th</sup> (Weeks 3 and 4), and then improved upon membrane replacement on June 29<sup>th</sup>. It is unclear whether the decline was due to the scaling from treating the pilot effluent of fouling from algal growth.

Figure 74: Normalized Permeate Flow (from Hydranautics spreadsheet)

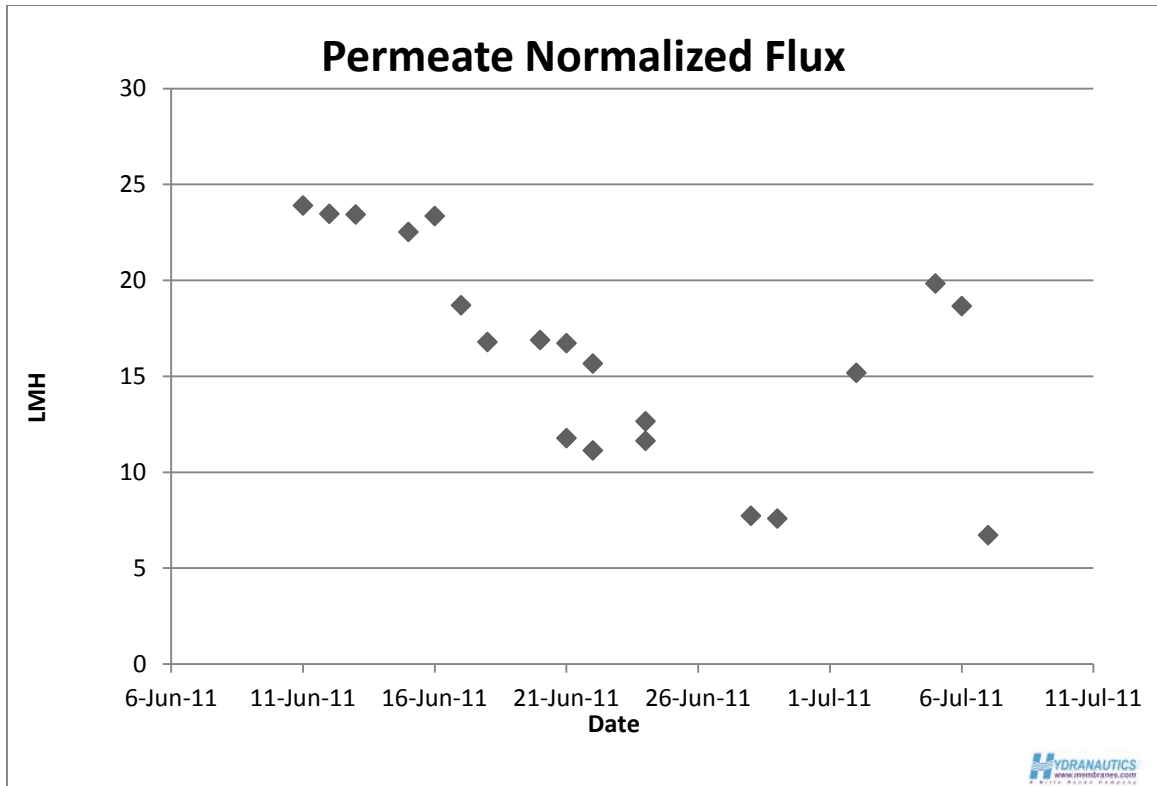


Table 41: RO Data Recorded During System Operation

Date/Time	Feed Pressure	Concentrate Pressure	Concentrate Flow	Permeate Flow	Permeate Flow	Feed Temp
	psi	psi	gpm	gpm	m3/d	°C
6/10/11 8:05 AM	260	245	0.2	0.65	3.54	15.8
6/11/11 7:30 AM	258	245	0.175	0.7	3.82	17.7
6/12/11 9:00 AM	261	255	0.175	0.75	4.09	20.1
6/13/11 7:30 PM	265	255	0.15	0.8	4.36	22.8
6/14/11 7:59 AM	270	260	0.18	0.85	4.63	19.1
6/15/11 1:26 PM	260	252	0.2	0.75	4.09	23.9
6/16/11 8:41 AM	265	255	0.2	0.7	3.82	19.5
6/17/11 8:40 AM	265	255	0.2	0.6	3.27	20.7
6/18/01 9:20 AM	265	259	0.15	0.5	2.73	19
6/20/11 8:24 AM	265	255	0.15	0.48	2.62	17.5

6/21/11 8:42 AM	265	260	0.2	0.5	2.73	17.4
6/21/11 11:26 AM	262	255	0.2	0.4	2.18	21.2
6/22/11 7:55 AM	270	260	0.2	0.5	2.73	18.8
6/22/11 10:13 AM	260	255	0.2	0.38	2.07	21.8
6/24/11 7:43 AM	270	265	0.2	0.45	2.45	21.7
6/24/11 9:58 AM	260	252	0.2	0.4	2.18	22.6
6/28/11 9:05 AM	262	253	0.2	0.27	1.47	20.6
6/29/11 10:01 AM	261	252	0.18	0.3	1.64	25.8
7/2/11 6:00 PM	265	260	0.18	0.55	3.00	
7/5/11 4:34 PM	258	249	0.2	0.69	3.76	25.1
7/6/11 9:37 AM	250	235	0.2	0.6	3.27	24
7/7/11 11:09 AM	261	252	0.2	0.25	1.36	22.5

Date/Time	Feed Conductivity mS/cm	Feed pH	Concentrate Temp °C	Concentrate Conductivity mS/cm	Concentrate pH
6/10/11 8:05 AM			22.8		
6/11/11 7:30 AM	6.1		23	24	7.7
6/12/11 9:00 AM	6.05				
6/13/11 7:30 PM	6		26.9	26.4	7.7
6/14/11 7:59 AM			25.1	24.3	7.68
6/15/11 1:26 PM	6.99		30.7	25.2	7.75
6/16/11 8:41 AM	7.13	7.42	26.3	24.7	7.73
6/17/11 8:40 AM	7.01	7.53	28.1	24.1	7.83
6/18/01 9:20 AM	7.26	7.73	26.4	22.4	7.74
6/20/11 8:24 AM	7.22	7.6	25.5	20.9	7.83
6/21/11 8:42 AM	7.14	7.5	25.6	17.81	7.76
6/21/11 11:26 AM	7.01	7.62	29.9	18.03	7.81
6/22/11 7:55 AM	7	7.54	25.8	15.44	7.74
6/22/11 10:13 AM	7.22	7.43	31.7	19.14	7.77
6/24/11 7:43 AM	7.07	7.44	26.7	16.47	7.65

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<b>6/24/11 9:58 AM</b>	7.24	7.44	32.2	18.6	7.69
<b>6/28/11 9:05 AM</b>	6.78	7.34	33.3	15.1	7.61
<b>6/29/11 10:01 AM</b>	6.87	7.41	36.9	15.8	7.62
<b>7/2/11 6:00 PM</b>	7.21	7	34	26.7	7.64
<b>7/5/11 4:34 PM</b>	6.87	7.75	31.4	24.5	7.38
<b>7/6/11 9:37 AM</b>	6.88	7.69	29.9	19.92	7.6
<b>7/7/11 11:09 AM</b>	6.68	7.6	34.1	14.01	7.51

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## CHAPTER 7

### DISCUSSION AND CONCLUSIONS

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#### 7.1 Conclusions

##### 7.11 Ions of Interest can be recovered from Higher Ionic Strength Solutions using Ion Exchange

Ion exchange is traditionally used to treat low ionic strength solutions, and resin selectivity towards multivalent ions is known to decrease with increasing ionic strength. The prediction of selectivity becomes more difficult with increasing solution concentration because of the formation of complexes, decreased ion activity, specific ion interactions, and incomplete hydration [4]. Results from this research indicate that the decrease in calcium and sulfate selectivity occurring with ionic strength solutions up to 0.3 M is not prohibitive to the salt recovery process. Feed solution to the pilot system had an ionic strength of 0.27 M, and significant salt was recovered by mixing cation and anion regeneration solutions. As seen from regression relationship between calcium selectivity, ionic strength, and ionic fraction, calcium selectivity decreases more rapidly with ionic strength than with ionic fraction. Solutions with high ionic fractions of calcium can be treated provided that the ionic strength remains below 0.35 M (see Figure 75). For sulfate, selectivity is correlated with ionic strength by a power relationship. No data was measured for solutions with higher ionic strength than 0.35, so it is difficult to speculate about their effect on sulfate selectivity. However, for solutions with ionic strength less than or equal to 0.35 M, selectivity is sufficient for sulfate recovery and salt precipitation.

Figure 75: Regression Relationship for Calcium Selectivity with Ionic Fraction and Ionic Strength

		Equivalent Fraction of Calcium																		
		0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.55	0.6	0.65	0.7	0.75	0.8	0.85	0.9	0.95
Ionic Strength	0.05	61.94	48.80	42.45	38.45	35.61	33.44	31.71	30.29	29.09	28.05	27.15	26.35	25.63	24.99	24.40	23.86	23.37	22.92	22.49
	0.1	33.54	26.42	22.98	20.82	19.28	18.11	17.17	16.40	15.75	15.19	14.70	14.27	13.88	13.53	13.21	12.92	12.66	12.41	12.18
	0.15	23.43	18.46	16.05	14.54	13.47	12.65	11.99	11.46	11.00	10.61	10.27	9.96	9.69	9.45	9.23	9.03	8.84	8.67	8.51
	0.2	18.16	14.31	12.45	11.27	10.44	9.81	9.30	8.88	8.53	8.23	7.96	7.73	7.52	7.33	7.15	7.00	6.85	6.72	6.60
	0.25	14.91	11.74	10.22	9.25	8.57	8.05	7.63	7.29	7.00	6.75	6.53	6.34	6.17	6.01	5.87	5.74	5.62	5.52	5.41
	0.3	12.69	9.99	8.69	7.87	7.29	6.85	6.50	6.20	5.96	5.75	5.56	5.40	5.25	5.12	5.00	4.89	4.79	4.69	4.61
	0.35	11.07	8.72	7.58	6.87	6.36	5.98	5.67	5.41	5.20	5.01	4.85	4.71	4.58	4.46	4.36	4.26	4.18	4.09	4.02
	0.4	9.83	7.75	6.74	6.10	5.65	5.31	5.04	4.81	4.62	4.45	4.31	4.18	4.07	3.97	3.87	3.79	3.71	3.64	3.57
	0.45	8.86	6.98	6.07	5.50	5.09	4.78	4.54	4.33	4.16	4.01	3.88	3.77	3.67	3.57	3.49	3.41	3.34	3.28	3.22
	0.5	8.07	6.36	5.53	5.01	4.64	4.36	4.13	3.95	3.79	3.66	3.54	3.43	3.34	3.26	3.18	3.11	3.05	2.99	2.93
	0.55	7.42	5.84	5.08	4.60	4.26	4.01	3.80	3.63	3.48	3.36	3.25	3.16	3.07	2.99	2.92	2.86	2.80	2.74	2.69
	0.6	6.87	5.41	4.71	4.26	3.95	3.71	3.52	3.36	3.23	3.11	3.01	2.92	2.84	2.77	2.71	2.65	2.59	2.54	2.49
	0.65	6.40	5.04	4.39	3.97	3.68	3.45	3.28	3.13	3.01	2.90	2.80	2.72	2.65	2.58	2.52	2.47	2.41	2.37	2.32
	0.7	5.99	4.72	4.11	3.72	3.45	3.24	3.07	2.93	2.81	2.71	2.63	2.55	2.48	2.42	2.36	2.31	2.26	2.22	2.18
	0.75	5.64	4.44	3.86	3.50	3.24	3.04	2.89	2.76	2.65	2.55	2.47	2.40	2.33	2.27	2.22	2.17	2.13	2.09	2.05
	0.8	5.33	4.20	3.65	3.31	3.06	2.87	2.73	2.60	2.50	2.41	2.33	2.27	2.20	2.15	2.10	2.05	2.01	1.97	1.93
	0.85	5.05	3.98	3.46	3.13	2.90	2.72	2.58	2.47	2.37	2.29	2.21	2.15	2.09	2.04	1.99	1.94	1.90	1.87	1.83
	0.9	4.80	3.78	3.29	2.98	2.76	2.59	2.46	2.35	2.25	2.17	2.10	2.04	1.99	1.94	1.89	1.85	1.81	1.78	1.74
	0.95	4.57	3.60	3.13	2.84	2.63	2.47	2.34	2.24	2.15	2.07	2.00	1.95	1.89	1.85	1.80	1.76	1.73	1.69	1.66
	1	4.37	3.44	3.00	2.71	2.51	2.36	2.24	2.14	2.05	1.98	1.92	1.86	1.81	1.76	1.72	1.68	1.65	1.62	1.59

## 7.12 Breakthrough Curves can be Predicted Using Separation Factor Regression Relationships and Modeling

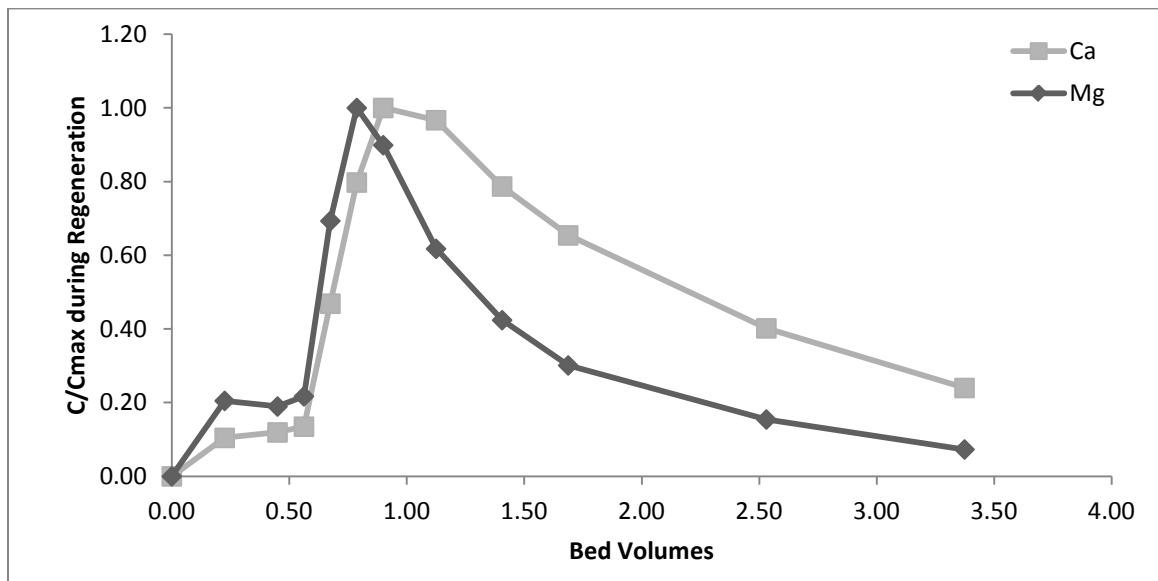
The ion exchange column model was an equilibrium model that worked by discretizing the column into a number of equal volume segments in which resin and solution phase ions concentrations were calculated using user entered separation factors. The numerical dispersion that occurred based on the number of segments in which the column was divided was used to model physical dispersion of ions in the column. Because dispersion is modeled by varying the number of column segments, the number of segments used in the model must be empirically calibrated to the behavior of a specific column. The separation factors were generated using the regressions discussed previously. Column efficiency was defined as the fraction of the column that was in equilibrium with the influent solution at breakthrough, and a correlation was found between modeled column efficiency and separation factor. Time to breakthrough was calculated using the model based upon the correlations between influent solution ion concentrations, separation factors, and column efficiency. Calculated results were verified by column tests in the lab. These tools that were developed (MATLAB model and regression relationships) can be used in the future to predict breakthrough curves and

resin phase concentration for any solution falling within the parameters used to create the regressions.

### 7.13 Calcium and Magnesium Selectivity is too similar for Ion Separation by Regeneration

In theory, ions exit the column in the order of reverse selectivity during regeneration with the least selective ion exiting the column first. Measurements of ions concentrations taken during regeneration of the laboratory scale columns showed that although the peak concentration of magnesium occurred prior the peak concentration of calcium, the concentration curves overlapped almost entirely (see Figure 76). Overlapping peaks are caused by mixing within the column and by the fact the calcium and magnesium have similar separation factors with respect to sodium. All tests in which regeneration conditions were altered by changing flow rate, flow direction, and sodium chloride concentration showed little change in peak characteristics.

Figure 76: Overlapping Concentration Curves of Calcium an Magnesium During Regeneration



During loading, ions are through to distribute within the column in ion rich zones, with lower selectivity ions near the bottom of the column and higher selectivity ions near

the inlet. This occurs because when the feed solution initially contacts the resin, there are many open active sites available, and even lower selectivity ions will exchange. As more high selectivity ions arrive in the fresh solution, they displace the lower selectivity ions. Over the length of column, a series of ions rich zones develop based on selectivity. In theory, it may be possible to elute these accumulation zones separately by isolating them in a partially loaded column. Resin phase ion concentrations were measured by taking resin samples from a column with ports along its length. It was found that the calcium and magnesium zones overlapped to such a degree that they could not be separated efficiently. A resin phase accumulation of magnesium was seen, but it was not very large. When the bottom of the column was regenerated separately, a marked decrease in the ratio of calcium to magnesium was observed, but this technique was not successful in recovering a solution with only one cation.

#### **7.14 Gypsum can be Recovered from a Mixture of Cation and Anion Regeneration Solutions**

Results from mixing simulated and pilot generated cation and anion regeneration solutions showed that by controlling the pH at the time mixing, carbonate salt precipitation can be suppressed. This allows gypsum to be precipitated separately. During the pilot testing, the columns were run to breakthrough of sulfate and near to breakthrough of calcium (Week 6) to maximize the amounts of calcium and sulfate on the resin. The resulting regeneration solution contained more calcium and sulfate than those from the previous weeks. When the most concentrated 30% of the regeneration solutions were mixed at ambient pH conditions, only gypsum precipitated because of the increased amount of sulfate in solution. Maximizing calcium and sulfate concentrations can be done by equalizing the cation and anion exchange capacities. This can be achieved by increasing the volume of the anion exchange column relative to the cation exchange column. Results from mixing the most concentrated pilot generated cation and anion regeneration solutions shows that it is possible to recover 0.29 kg of gypsum per cubic meter of treated RO concentrate.

## 7.2 Discussion

A novel method of concentrate reduction has been proposed and tested. The impacts of improving the management and treatment of RO concentrate could be very powerful. They include: driving down the total cost of water production, allowing desalination to be utilized in areas where concentrate management is the limiting factor, increasing total water recovery, and saving energy. The scope of these impacts is wide because water scarce inland regions can be found across the United States and around the world.

The efficiency of sequential ion exchange for reduction of RO concentrate increases with the ratio of the length of the operation cycle is to the length of the regeneration cycle. This research has shown that most exchanging ions can be eluted from the column using 0.75 bed volumes of regeneration solution and 1.00 bed volumes of rinse water. The length of the operation cycle is limited by the influent ion solution concentrations, the dispersion, and the separation factor of the exchanging ion. The efficiency of a specific system can be modeled using the MATLAB equilibrium model and the separation factor regression relationships.

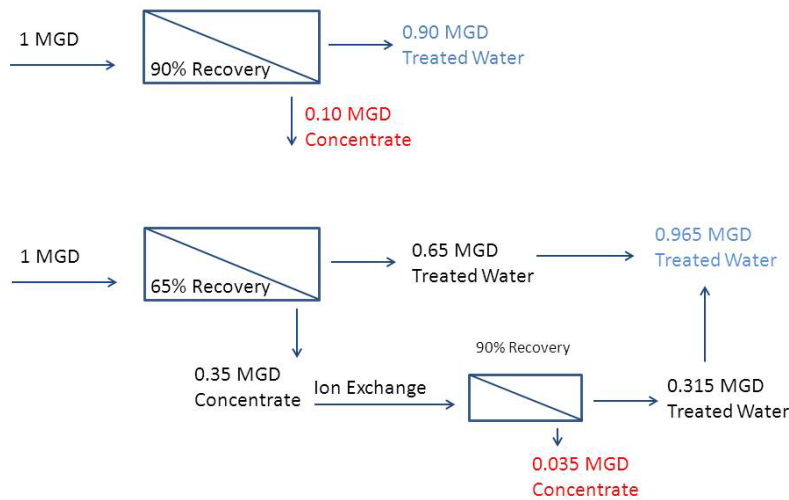
Salt recovery is optimized by increasing column efficiency in the term of the length of the MTZ and the reduction of unused column capacity. Since anion and cation exchange resins generally have different capacities, the system should be optimized to use the full capacity of each column. In the pilot test, this was done by extending the operation cycle past sulfate breakthrough and diverting the extra effluent to waste. It can also be achieved by using increasing the volume of anion exchange column relative to the cation exchange column until the total capacities are equal.

Modeling breakthrough curves is useful in deciding whether the ion exchange process is applicable to a particular solution. The highest possible concentration factor of the regeneration solution relative to the feed solution is the number of bed volumes of operation divided by the number of bed volumes required for regeneration. The concentration factor for a particular ion decreases as the concentration of that ion the feed solution increases. It will also decrease with increased dispersion and with decreasing separation factor. Model results will indicate the extent of ion recovery if the separation factors and amount of dispersion is known. The resin capacity of most common strong

acid cation exchange resins is approximately 2.5 eq/L. To maintain a concentration factor greater than 10, the RO concentrate to be treated cannot contain more than 0.25 eq/L of exchanging ion. That corresponds to about 5000 mg/L of calcium. In reality, separation factors are reduced due to high ionic strength and other ions are also exchanging to the resin, so the upper limit is slightly lower. If the RO system recovery were at 75%, the raw water could not contain more than 1250 mg/L of calcium. This falls within the range of calcium concentrations for most brackish water sources.

Although it may seem counter-intuitive, overall recovery of a system including RO and sequential ion exchange may increase if the RO recovery is reduced to maintain a suitable concentrate for the ion exchange system. If the recovery were reduced to 65%, the raw water could contain up to 1750 mg/L of calcium. A comparison between an RO system at high recovery and a RO system at lower recovery with inter-stage sequential ion exchange is shown in Figure 75. Lower recovery RO systems also require less energy and less anti-scalant. In addition to increased water recovery, there is the added benefit of salt production.

Figure 77: Comparison between RO System at High Recovery and RO at Lower Recovery Combined with IX



Gypsum and carbonate salts can be spontaneously precipitated from regeneration solutions from a sequential ion exchange system. When the process is optimized, pH adjustment is not necessary for spontaneous precipitation of gypsum. Pilot tests showed that approximately 45% of the calcium and 28% of the sulfate was recovered.

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## APPENDIX 1 – NOTATION

Symbol	Units	Description
$q_B$ or $[R\_B]$	mol/g	concentration of counter-ion resin phase,
$C_A$ or $[B]$	M	concentration of co-ion solution phase,
$q_A$ or $[R\_A]$	mol/g	concentration of counter-ion resin phase,
$C_B$ or $[B]$	M	concentration of counter-ion in solution phase
$z$	--	valence of ion
$\alpha_A^B$	--	separation factor for ion B over ion A
$X_i$		Equivalent fraction in phase (r, resin and s, solution)
$k_A^B$	--	selectivity coefficient for ion B over ion A
$\Delta G^\circ$	J/mol	change in standard Gibbs free energy
$R$	J/mol·K	universal gas constan
$T$	K	temperature
$K^T$	--	thermodynamic selectivity coefficient
$\bar{\mu}^-$	J/mol	standard chemical potential of ion in resin phase
$\mu^\circ$	J/mol	standard chemical potential of ion in solution phase
$\mu$	J/mol	chemical potential of ion in solution phase
$a$	--	activity of ion in solution phase
$\bar{x}$	--	resin phase equivalent fraction
$\bar{\mu}^{-E}$	J/mol	partial molar excess free energy of ion in resin phase e
$\Delta \bar{G}^E$	J/mol	excess free energy of system
$g_{0,1}$	--	free energy interaction parameters
$\Delta \bar{G}_r$	J/mol	change in Gibbs free energy for precipitation or dissolution
$K_{SO}$	--	solubility constant

## APPENDIX 2 – UTILITY SURVEY

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This survey was administered to facilities that currently operate or were planning to operate RO systems. Only 9 responses were received. Because the sample size was so small, data analysis was not possible. Completed surveys are available upon request.

### 1. Operating an RO facility?

CDM and the University of New Mexico are researching methods to selectively recover salts and minerals from the waste stream from desalination facilities. The research is sponsored by the WaterReuse Foundation. Separation of salts from the waste stream would also increase water recovery. As part of this project, we are interested in finding out the level of interest in salt recovery by utilities, what benefits might accrue, and what problems would need to be overcome. This survey should only take about 15-20 minutes.

In appreciation for completing this survey, the WaterReuse Foundation has agreed to provide respondents with an electronic copy of our final report (due in 2011).

1. Does your utility currently operate a treatment facility using any form of reverse osmosis (reverse osmosis, nanofiltration, membrane softening, etc)?

- Yes  
 No

### 2. Background (operating facilities)

1. What is the name of your utility?

2. What is the name and location of your treatment facility?

3. What membrane process is being used?

- Reverse Osmosis  
 Nanofiltration

4. What is source water?

- Seawater
- Brackish Surface Water
- Brackish Ground Water
- Hard Groundwater
- Other (please specify)

5. What is the plant capacity (mgd)?

6. What is the source water TDS (mg/L)?

**3. Concentrate management (operating facilities)**

1. What is your concentrate flowrate?

2. What is your concentrate TDS (in mg/L)? (Whole number between 0 and 100000)

3. How does your facility dispose of concentrate?

- Discharge to surface water
- Discharge to ocean
- Discharge to sewer/WWTP
- Deep well injection
- Evaporation pond
- Other (please specify)

4. Was your current disposal method the only option considered during design?

- Yes
- No

6. Why was the chosen concentrate disposal option selected?

7. Does your concentrate quality vary – seasonally or on any cycle?

Yes

No

If yes, please describe briefly.

8. What is the total capital cost of your facility? (estimate total worth in today's dollars)

9. What percentage of capital costs were dedicated to concentrate management and disposal facilities? (Enter a whole number percentage)

10. What percentage of operating costs are dedicated to concentrate management and disposal issues? (Enter a whole number percentage)

11. What percentage of operator time is dedicated to concentrate management and disposal issues? (Enter a whole number percentage)

#### 4. Planning or designing an RO facility?

1. Is your utility currently planning or designing a treatment facility using any form of reverse osmosis (reverse osmosis, nanofiltration, membrane softening, etc)?

Yes

No

#### 5. Background (planning/design)

1. What is the name of your utility?

2. What is the name and location of the treatment facility?

3. What membrane process(es) is being planned? (Check all that apply)

- Reverse Osmosis
- Nanofiltration
- Softening
- Other (please specify)

4. What is source water?

- Seawater
- Brackish Goundwater
- Brackish Surface Water
- Hard Groundwater
- Other (please specify)

5. What is the source water TDS (in mg/L)?

6. What is the projected plant capacity (mgd)?

7. What is the projected capital cost of your facility?

## 6. Concentrate management (planning/design)

1. What concentrate management and disposal options are being considered (check all that apply)?

- Discharge to surface water
- Discharge to ocean
- Discharge to sewer/WWTP
- Deep well injection
- Evaporation pond
- Other (please specify)

2. Why was the chosen concentrate management option selected?

3. What is your concentrate flowrate?

4. What is your concentrate TDS (in mg/L)? (Enter a whole number between 0 and 100000)

## 7. Selective recovery and beneficial use

1. Rank the following factors in order of importance with regard to concentrate management and disposal:

	Very important	Important	Slightly important	Not important at all
Capital Cost	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Operating Cost	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Minimizing Volume	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Minimizing Land Use	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Minimizing Chemical Use	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Regulatory Restrictions	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Environmental Concerns	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Ease of Permitting	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Sustainability/longevity of Method	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>

2. What other factors are important with regard to concentrate management and disposal?

3. If technology was available to recovery salts from the concentrate stream that could be sold (and simultaneously recover more water), how much would you be willing to spend on this technology as a percentage of your total facility cost?

- None
- < 5%
- 5-15%
- 15-25%
- 25-50%
- > 50%

Additional Comments

## **APPENDIX 3 – MARKET ANALYSIS (BY CDM)**

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FINAL

**University of New Mexico**  
RO Salt Market Analysis Report

University of New Mexico

October 2011

**CDM**

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# Section 1

## Desalination Concentrate Market Analysis

### 1.1 Introduction

Desalination technologies have been the focus of significant research and treatment evaluations in the United States and worldwide in recent years due to the increasing scarcity of water as an essential resource. Reverse osmosis (RO) membrane, ion exchange, and electrodialysis technologies have been the preferred technical option to create potable water from brackish and saline water sources which contain more than 1,000 milligrams per liter (mg/L) total dissolved solids (TDS). RO, ion exchange, and electrodialysis desalination processes generate significant quantities of concentrate in the range of 10 to 30 percent of total water treated. The concentrate contains high concentrations of TDS, which are almost exclusively inorganic salts and metals. Concentrate disposal is becoming problematic especially in the desert southwest where the TDS associated with the concentrate stream can have a significant impact on the limited surface water supplies as well as groundwater supplies. The limited capacity of existing surface and alluvial groundwater supplies to handle RO concentrate disposal has resulted in many desalination plants not being built due to a lack of a cost-effective concentrate disposal solution (Mickley, 2006).

Concentrate disposal is also becoming an increasing concern for the planning, management, and operation of water resources due to the increasing cost for permitting and disposal. Consequently, the beneficial use of concentrate is being considered as a possible option to offset some of these economic factors. Access to existing and future salt markets may provide operators of desalination facilities with revenue sources that might compensate for the high operating, transportation, and market access costs.

The purpose of this market analysis is to:

1. Identify the primary salts generated from brackish water supplies using RO processes.
2. Evaluate the market potential of these salts in select industries that currently use salt products in the production of other goods.
3. Provide a guide for possible uses of recoverable salts to a utility operating a desalination plant that could offset the cost of RO concentrate disposal.

## Section 2

# Concentrate Disposal and Management

Currently, typical brackish water RO membranes achieve greater than 98 percent rejection of all ions, so the concentrate contains a mixture of all the available salts. Using a variety of existing and new technologies, it is technically feasible that RO concentrate brine could potentially be segregated into different types of salts and as either a liquid or a dried product. Previous studies have shown that a range of salts could be obtained from RO concentrate brine (Ahuja and Howe, 2007) depending on the composition of the brackish water supply. Use of these salts would depend largely on the presence of a local or regional market for salt products and meeting the purity requirements for the potential end users.

Currently there are no brackish water RO systems that separate one or several specific salts for beneficial use and in all cases the composite concentrate is disposed as a waste product. The selection of a disposal method involves selecting the most economical means of brine disposal. There are a number of methods that are currently used for brine and salt disposal which are discussed in the following section.

### 2.1 Current Options for Concentrate Disposal

One of the most significant challenges in both the design and operation of desalination plant is how to dispose of the brine discharge or salt concentrate waste that is generated in the treatment process. Table 1 presents current methods of concentrate disposal and minimization.

**Table 1 Existing Concentrate Disposal/Minimization Methods**

Surface Water Discharge
Sewer Discharge
Deep Well Injection
Evaporation Ponds
Wetlands Developments
Thermal Mechanical Evaporation Near Zero Liquid Discharge
Spray Dryers and Crystallizers Zero Liquid Discharge



discharge) for disposal in a landfill. These processes consist of thermal evaporators, crystallizers, and spray dryers. The capital operations and maintenance costs of these processes are significantly influenced by the energy required to operate the process, and typically the capital cost is increased to add heat exchangers and multiple effects to reduce the amount of energy required. ZLD processes have mainly been used in industrial applications and generally have not been used at the scale of a municipal water treatment plant (CDM, 2009). The primary purpose of ZLD has been to reduce the volume of concentrate and increase water recovery. While it is possible to extract some commercially usable salts from ZLD processes, a much more complicated ZLD process is required to eliminate the impurities that affect the marketability of the salts (CDM, 2009).

A ZLD processing scheme developed by Geo-Processors USA, Inc. has been successfully pilot tested outside the United States to recover commercial grade salts from many different waters. This technology involves a series of volume reduction steps followed by a salt recovery step. The results of their testing are proprietary and the commercial viability has not been demonstrated in the United States (Mickley, 2008).

ZLD processes as well as other processes (RO, nano-filtration, and ion exchange) that concentrate waste solutions and isolate salts are important for selective salt recovery. Treatment steps such as pH adjustment, chemical addition, thickening, and washing may also be required. A selective salt recovery process would involve a series of concentration and treatment steps to obtain an individual salt in its desired form. If multiple salts were recovered, the process may involve a series of concentration and treatment steps that would recover the salts sequentially from the lowest to the highest solubility. However, a discussion of the composition of RO concentrate, the major ions found in brackish groundwater, and the solubility of the recoverable salts is essential to understand the process and limitations of obtaining usable salts from RO concentrate.

## 2.2 Characteristics of RO Concentrate

RO concentrate has similar constituents to those of the raw feed water except that much of the water has been removed. Thus the concentrations of the constituents in concentrate from a typical RO process are four to six times greater than in the feed water. In seawater desalination, sodium chloride is the primary salt and in brackish water desalination, a mixture of calcium, magnesium, sulfates, and carbonates are concentrated along sodium chloride along with trace elements.

Typical TDS concentrations in RO feed water and in concentrate are presented in Table 3.

**Table 3 Typical RO Feedwater and Concentrate TDS<sup>1</sup>**

Process	Feedwater TDS (mg/L)	Concentrate TDS (mg/L)	Concentration Factor
Seawater RO	32,000-45,000	50,000-80,000	1.7-2.5
Brackish Water RO	1,000-10,000	3,000-40,000	2.9-6.7

1 - Adapted from Jordahl, 2006

The amount of concentrate generated by an RO plant can vary throughout the year. Concentrate production generally peaks in the summertime when water demand and production is high and is much less in the winter when water demands are lower. The seasonal fluctuations in concentrate production are a significant factor in the marketability of recoverable salts.

## 2.3 Water Quality from Representative Aquifers

Ahuja and Howe (2007) compared water quality data from ten representative aquifers located around the United States with that of ocean water. This comparison is presented in Table 4.



Table 4 Water Quality Comparison - Ocean Water and Ten Brackish Groundwater Sources in the United States<sup>1</sup>

State		Alabama	Arizona	California	Colorado	Florida	New Mexico	New York	Ohio	Texas	Wyoming
County		Montgomery	Maricopa	Orange	Mesa	Palm Beach	Tularosa Basin	Niagra	Tuscarawas	Bexar	Carbon
Source	Ocean Water	Single Well	Median	Median	Median	Median	Single Well	Single Well	n/a	Median	Single Well
Parameter (mg/L)											
Sodium	10,500	230	210	717	935.5	1010	125	1010	12.4	455	1260
Potassium	380	2.0	5.6	5.19	10.65	36	85	30.9	11	26.9	2.26
Calcium	400	520	340	282	285.5	124	650	643	374	543	40.3
Magnesium	1350	4.4	90	116	272	131	120	192	201	195	27.4
Strontium	8	n/a	2.7	2.09	n/a	13.6	n/a	n/a	3	n/a	0.94
Barium	0.03	0.03	0.1	0.045	0.016	n/a	0.13	n/a	n/a	6	0.006
Chloride	19,000	110	650	349	473	1760	180	1470	2.6	874.5	118
Sulfate	2700	1100	380	1180	2830	350	1350	2180	2210	1710	2580
Carbonate	140	430	390	1130	507.5	152	350	506	60.5	283.5	134
Fluoride	1.3	0.7	0.4	0.4	0.85	0.8	1.53	n/a	0.2	2.7	0.18
Nitrate	1.8	0.1	13	0.05	n/a	n/a	0	n/a	0.05	n/a	0.004
Silica	3	26	63.1	23.5	19.25	14	15	n/a	13.2	18.8	9.32
Alkalinity	n/a	350	320	929	416	152	350	506	60.5	240	134
TDS	33,484	2400	2138	3805	5334	3591	2877	6032	2887	4115	4172

1 – Ahuja and Howe (2007)  
n/a - data not available

As shown in Table 4, the predominant cation in ocean water is sodium and the predominant anion is chloride such that 85 percent of the salinity of ocean water is made up of sodium chloride. Brackish groundwater contains other major and minor cations and anions in addition to sodium chloride which are listed in Table 5.

**Table 5 Major Cations and Anions in Brackish Groundwater**

Cations	Anions
Sodium	Sulfate
Calcium	Chloride
Magnesium	Carbonate

It is important to note that of these major anions, carbonate can be present as bicarbonate or carbonate. However, bicarbonate is the main carbonate species in virtually all natural waters. Sulfate can be more common in groundwater than chloride (Ahuja and Howe, 2007).

There are also minor cations in brackish groundwater such as ferrous iron and manganese and minor anions such as fluoride, phosphate, and nitrate. These ions account for less than one percent of the ions in water and are of minimal interest since the focus of this study is the recovery of commercial quantity of salts that may have significant value.

## 2.4 Salt Solubility

The solubility of salts associated with the major and minor cations is an important consideration in the beneficial use of RO concentrate. Solubility is a measure of how difficult it is to recover a specific salt. Generally a salt with a low solubility is easier to recover than a salt with a high solubility when using a fractioning process. This may not be the case when using a membrane separation process, since the selectivity of the membrane controls the fractionization process. Ahuja and Howe (2007) evaluated the solubility of major cation and anion salts and found that chloride salts and sodium salts are highly soluble and calcium and magnesium salts that do not contain chloride, are considerably less soluble. The same study also noted that the solubility of carbonate and hydroxide species is pH dependent. Solubility increases as pH decreases and calcium carbonate and magnesium hydroxide precipitate at high pH.

The solubility of the salts produced in the RO process is important as salts precipitate in sequence to their solubility. The RO process is affected by the precipitation of sparingly soluble salts. Thermal brine concentrators, which can be used to process concentrate, are affected by moderately soluble salts such as sodium carbonate and sodium sulfate. Crystallizers precipitate sodium carbonate, sodium sulfate, and sodium chloride, but have a waste stream for highly soluble salts such as calcium chloride and magnesium chloride (Mickley, 2008). A general sequence of salt precipitation in the RO process is presented in Table 6.

**Table 6 General Salt Precipitation Sequence**

Solubility Level	Salt
Low soluble salts	Calcium carbonate, calcium sulfate
Moderately soluble salts	Sodium carbonate, sodium sulfate
Soluble salts	Sodium chloride
Highly soluble salts	Calcium chloride, magnesium chloride

Ahuja and Howe (2007) identified four candidate salts for removal and recovery for beneficial use based on their solubility. Two additional salts from that study, calcium chloride and sodium carbonate have been added to this report as potentially marketable salts. These salts and their solubility, and factors regarding their recovery are presented in Table 7.

**Table 7 Solubility of Candidate Salts for Removal and Recovery**

Salt	Solubility (mg/L)	Factors Regarding Recovery
Calcium Carbonate	6.6	Sparingly soluble. Removal could be controlled by raising the pH, targets carbonate in RO concentrate.
Calcium Sulfate	2050	Sparingly insoluble. Solubility not dependent on pH. May be possible to control separation of calcium sulfate from other carbonate and hydroxide compounds if separation occurred at low pH.
Sodium Sulfate	281,000 (28 percent solution)	Moderately soluble. In some waters the amount of calcium is insufficient to remove the sulfate. Sodium sulfate would need to be removed in these waters to adequately remove sulfate present in the concentrate.
Sodium Carbonate	307,000 (30 percent solution)	Moderately soluble. May be difficult to precipitate sodium carbonate as a dry salt.
Sodium Chloride	360,000 (36 percent solution)	Very soluble. May be difficult to concentrate RO concentrate to precipitate sodium chloride as a dry salt. If substantial amounts of sulfate and carbonate are removed with calcium then chloride would remain for pairing with sodium.
Calcium Chloride	813,000 (81 percent solution)	Extremely soluble. May be difficult to concentrate RO concentrate to precipitate calcium chloride as a dry salt.

Ahuja and Howe (2007) suggest that by focusing on these calcium and sodium salts, 85 to 95 percent of the mass of dissolved solids in the concentrate could potentially be separated and marketed. The uses of these recoverable salts are presented in the following section.

## 2.5 Concentrate Products Uses

### 2.5.1 Calcium Carbonate

Calcium carbonate exists in three polymorphic crystalline forms: calcite, aragonite, and vaterite. Calcite is by far the most abundant of these forms and is one of the most abundant minerals on earth making up about 4 percent of the earth's crust. It is also the most stable form of calcium carbonate. The main source of calcium carbonate is the mining of limestone and is currently mined in all regions of the US.

Calcium carbonate is commercially available as ground calcium carbonate (GCC) or as precipitated calcium carbonate (PCC). GCC is processed natural calcium carbonate and has impurities that result in a lower brightness. PCC is a white powder that is typically 99 percent pure and is produced using mechanical segregating processes to remove impurities followed by one of three chemical processes: the Solvay process, a byproduct of caustic soda production, and through the re-carbonizing process. Out of the 15 million tons of calcium carbonate produced in 2005, almost 75 percent was GCC and the remaining 25 percent was PCC (Ahuja and Howe, 2007). In 2006, almost 90 percent of the PCC produced was used by the paper industry.

Significant end-uses and industrial applications for calcium carbonate include:

- Pulp and paper
- Building construction (marble floors, roof materials, and roads)
- Glass (improves chemical durability)
- Rubber (mainly PCC)
- Paint (extend resin and polymers and control texture)
- Plastic (PVC pipe, mainly GCC)
- Dietary supplement (antacids)
- Water treatment (pH control, softening)

### 2.5.2 Calcium Sulfate

Calcium sulfate can exist in three crystalline forms:  $\text{CaSO}_4$  (anhydrite),  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  (hemihydrate or basanite), and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (dihydrate or gypsum). Calcium sulfate is obtained through the mining of gypsum. Gypsum is mined in 29 states with 77 percent of the production taking place in 8 states: Oklahoma, Arkansas, Iowa, California, Nevada, Texas, Indiana, and Michigan (Kostick, 2008).

Gypsum is processed (calcined or uncalcined) depending on its final use. Most gypsum that is produced (about 75 percent) is calcined before use and the remaining 25 percent remains uncalcined. The calcination process involves grinding gypsum to no less than 100 mesh and then heating it to drive off excess water. Calcination produces the hemihydrate form of calcium sulfate,

which is then mixed with other ingredients to make wallboard and plaster. Uncalcined gypsum is used in cement and in agriculture.

In 2009, 95 percent of the gypsum consumed in the US was used for wallboard plaster products and cement. The remaining 5 percent was used for agricultural uses and a small amount of high purity gypsum was used for industrial processes (glass making and smelting). Gypsum waste generated by wallboard manufacturing, installation, and building demolition can be recycled and used for agricultural uses and to manufacture new wallboard. Other potential markets for recycled wallboard include athletic field marking, cement production as a stucco additive, grease adsorption, sludge drying, and water treatment (Crangle, 2010).

Synthetic calcium sulfate is also manufactured from a process called flue gas desulfurization, which removes sulfur dioxide from power plant emissions to prevent acid rain. Flue gas desulfurization is a wet scrubbing process that produces calcium sulfite. A subsequent oxidation process converts calcium sulfite into calcium sulfate (synthetic gypsum) that can then be sold to wallboard manufacturing facilities.

### 2.5.3 Sodium Sulfate

Sodium sulfate has two common crystalline forms, anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ). It can also be produced from natural deposits or synthetically manufactured. Natural sodium sulfate is produced in the US by two production facilities, one in California and one in Texas. Natural sodium sulfate is mined from deposits of dry lake beds or directly from brine lakes. Synthetic sodium sulfate is produced by using waste products from other chemical manufacturing processes such as battery reclamation and cellulose production (Kostick, 2010).

According to Kostick (2010) the primary use of sodium sulfate is powdered detergents with 35 percent of the sodium sulfate produced in 2009 being used for this purpose. The remaining uses are:

- Glass (18 percent)
- Pulp and paper (15 percent)
- Textiles (4 percent)
- Carpet freshener (4 percent)
- Miscellaneous (24 percent)

### 2.5.4 Sodium Carbonate

Sodium carbonate, or “soda ash” is produced either by mining or is synthesized similarly to calcium chloride as another product in the Solvay process. Over 85 percent of soda ash comes from Wyoming with the remaining 15 percent coming from the Searles Valley, California.

According to Kostick (2010) the main uses of soda ash are:

- Glass production (48 percent)

- Chemicals (29 percent)
- Soap and detergents (10 percent)
- Pulp and paper (2 percent)
- Water treatment (2 percent)
- Flue gas desulfurization (2 percent)

### 2.5.5 Sodium Chloride

Sodium chloride is one of the most widely used inorganic feedstocks in chemical manufacturing and has many uses. Sodium chloride in all of its chemical permutations is used in over 14,000 applications. The major uses of sodium chloride in 2009 information provided by Kostick (2010) are:

- Roadway deicing (43 percent)
- Chemical industry (35 percent)
- Distributors (8 percent)
- Agriculture and Food (3 percent each)
- Water Treatment (3 percent)

It should be noted that salt in brine form represented 90 percent of the salt used for feedstock in the chemical industry (Kostick, 2010).

Sodium chloride is produced by four methods:

1. Surface or underground mining of rock salt
2. Solar evaporation of seawater or brines
3. Mechanical evaporation of purified brine feedstock
4. Production of salt brine by solution mining of underground halite deposits

Sodium chloride is available in a dry form (rock salt or flake salt) and in brine form. Salt obtained from underground mining, solar evaporation, and mechanical evaporation produces a dry salt. Salt produced by solution mining is used in a brine form and is not evaporated to form a dry salt. Brine obtained from solution mining is used in the chlor-alkali industry which produces chlorine and sodium hydroxide. Domestic sources of rock salt and salt from brine are located in the northeast, western, and southern gulf states.

An average of 40 percent of sodium chloride used in the US is used for road deicing. Approximately 18 million tons of rock salt and brine is used annually by municipalities to prepare roads for motor traffic. The demand is heavily driven by weather conditions and has also recently been affected by the reduced financial resources of many cities and towns. Geographically, most

of the demand is generated in the northeast and midwest US, the Great Lakes area, and the state of Alaska. However, it is also used in the colder climates and higher elevations of the western US where snow and winter road conditions are common.

### 2.5.6 Calcium Chloride

Calcium chloride is a white crystalline salt and is very soluble in water. It is produced by refining naturally occurring brine, by neutralizing hydrochloric acid with limestone, and as a by-product of the Solvay process used to produce synthetic sodium carbonate (soda ash). Extremely pure calcium chloride products can be produced using the limestone-hydrochloric acid process if the hydrochloric acid purity is sufficient. In the US, production of calcium chloride is utilized by concentrating and purifying brines from salt lakes. Calcium chloride produced from natural brine lakes is not as pure as calcium chloride produced from the Solvay process or from the limestone-hydrochloric acid process. Calcium chloride produced as a by-product of the Solvay process is a 10 to 15 percent solution that contains a percentage of sodium chloride. This stream is then purified using the methods used for natural brines.

Commercial products are supplied in dry form as powders, flakes, and pellets and in liquid form as a 30 to 45 percent solution. The main uses of calcium chloride are:

- Deicing/road stabilization
- Dust control
- Oil extraction and completion fluids
- Accelerator in concrete
- Industrial processing
- Plastics manufacturing

## Section 3

# Market Trends and Analysis

This section presents a description of the existing markets for the concentrate salts discussed in Section 2. This section also presents purity requirements for use, a matrix of regional markets, and an analysis of the marketability of the salts.

### 3.1 Market Descriptions and Trends

This section presents a market analysis for each of the six salts discussed in Section 2. The market analysis contains production information, pricing, uses, and a discussion of the market trends and issues associated with each of the salts.

#### 3.1.1 Calcium Carbonate

Information on the domestic production and consumption and the average price of calcium carbonate in five year increments for the period 1999 to 2009 was not available from USGS Mineral Commodity Summaries. Extensive research into price trends and production and consumption trends indicated that prices and production of calcium carbonate are proprietary and cannot be obtained without subscribing to a reporting service. However, pricing information from 2005 was available from a Water Reuse Foundation study (Jordahl, 2006) and is presented in Table 8.

**Table 8 Calcium Carbonate Pricing 2005**

Type	Price (\$/Ton)
Ground, Dry Coarse	\$60-\$65
Ground, Dry Medium	\$95-\$100
Ground, Dry Fine	\$230-\$280
Precipitated	\$264-\$350



### 3.1.2 Calcium Sulfate (Gypsum)

Domestic calcium sulfate (gypsum) production and demand and price history in five year increments for the period 1999 to 2009 are presented in Table 9.

**Table 9 Domestic Calcium Sulfate Production and Pricing 1999 to 2009<sup>1</sup>**

	1999	2004	2009
<b>Production (thousand tons)</b>			
Crude	21,400	19,800	10,400
Synthetic	3,600	12,100	8,500
Calcined	22,700	28,100	15,400
<b>Consumption (thousand tons)</b>	<b>35,000</b>	<b>43,000</b>	<b>23,100</b>
<b>Average Price (per ton)</b>			
Crude	\$6.92	\$6.90	\$7.71
Calcined	\$17.02	\$20.00	\$36.29

1-(Crangle, 2000, 2005, 2010)

**Market trends** – Demand for gypsum depends on the strength of the construction industry since almost 95 percent of the gypsum consumed is for construction products such as wallboard, plasters, and cement. Wallboard plants that use synthetic gypsum will reduce the use of natural gypsum. The US has adequate domestic resources but they are unevenly distributed, resulting in imports from Canada and Mexico. Synthetic gypsum generated by industrial processes is an important substitute for mined gypsum and in 2009 synthetic gypsum made up 57 percent of the total domestic supply (Crangle, 2010).

### 3.1.3 Sodium Sulfate

Domestic sodium sulfate production and demand and price history in five year increments for the period 1999 to 2009 is presented below in Table 10.

**Table 10 Domestic Sodium Sulfate Production and Pricing 1999 to 2009<sup>1</sup>**

	1999	2004	2009
Production (thousand tons)	650	470	330
Consumption (thousand tons)	580	360	310
Average Price (per ton)	\$114	\$114	\$127

1-(Kostick, 2000, 2005, 2010)

**Market trends** – The primary market for sodium sulfate is powdered detergents where it serves as low cost inert white filler. However, the market is increasing toward liquid laundry detergents that do not contain sodium sulfate. The major market for powdered detergents containing sodium sulfate is in Asia and Latin America. Sodium sulfate use in the textile industry has also been decreasing due to imports of less expensive textile products.

Sodium sulfate resources are adequate to last hundreds of years at the rate of current consumption. Sodium sulfate can also be obtained as a by-product of battery recycling and the production of chemicals such as boric acid, chromium chemicals, rayon, and cellulose. Sodium hydroxide and emulsified sulfur can be substituted for sodium sulfate in the pulp and paper industry (Kostick, 2010).

### 3.1.4 Sodium Carbonate (Soda Ash)

Domestic sodium carbonate (soda ash) production and demand and price history in five year increments for the period 1999 to 2009 is presented in Table 11.

**Table 11 Domestic Sodium Carbonate Production and Use 1999 to 2009<sup>1</sup>**

	1999	2004	2009
Production (thousand tons)	11,100	11,900	12,000
Consumption (thousand tons)	7,300	6,900	6,700
Average Price (per ton)	\$117.50	\$117.50	\$272.50

1-(Kostick, 2000, 2005, 2010)

**Market Trends**– The soda ash industry suffered in 2009 due to the recession. The two main suppliers in the US reduced outputs for most of the year, mostly due to increased competition from China. However, overall worldwide demand is expected to grow 1.5 to 2 percent per year over the next several years.

There appears to be adequate reserves of soda ash in the Green River and Searles Lake mines to last for many years. There are also many other sources in the world that have yet to be quantified. It is possible to manufacturer synthetic soda ash from salt and limestone but it is more costly to produce and creates hazardous wastes (Kostick, 2010).

### 3.1.5 Sodium Chloride

Domestic sodium chloride production and demand in five year increments for the period 1999 to 2009 is presented in Table 12.

**Table 12 Domestic Sodium Chloride Production and Use 1999 to 2009<sup>1</sup>**

	1999	2004	2009
<b>Production</b> (thousand tons)	45,600	49,700	50,700
<b>Consumption</b> (thousand tons)	53,900	59,400	62,700
<b>Average Price Dry salt, bulk, \$/ton</b>			
Vacuum	\$110	\$122	\$165
Solar	\$40	\$55	\$67
Rock	\$19	\$24	\$35
Brine	\$6	\$7	\$8

1-(Kostick, 2000, 2005, 2010)

**Market Trends**– Table 12 indicates that more salt is consumed than is produced. The balance is made up from imports which make up 19 percent of the salt consumed. The market for road salt has been impacted by state and local budget constraints due to the recession. This may affect the availability and consumption of rock salt for deicing in 2010.

World salt resources are practically unlimited and salt from the oceans is inexhaustible. Sources of rock salt and salt from brine are in the Northeast, Central Western, and Gulf Coast states and saline lakes and solar evaporation facilities are located near populated regions in the western US. There are no economic substitutes for sodium chloride. Calcium chloride, calcium magnesium acetate, and potassium chloride can be used for deicing and in other processes but at a higher cost (Kostick, 2010).

### 3.1.6 Calcium Chloride

Information on the domestic production and consumption and the average price of calcium chloride in five year increments for the period 1999 to 2009 was not available from USGS Mineral Commodity Summaries. Extensive research into price trends and production and consumption trends indicated that prices and production of calcium chloride are proprietary and cannot be obtained without subscribing to a reporting service. However, pricing information from 2005 was available from (Jordahl, 2006) and is presented in Table 13.

**Table 13 Calcium Chloride Pricing 2005**

Type	Price (\$/Ton)
Conc. Reg 77-80%	\$200
Conc. Reg 77-80% flake	\$250-\$280
Anhydrous 94-97% bulk	\$275
Anhydrous 94-97% 50 lb	\$346-\$354
Liquid 35% basis	\$135-\$153
Liquid 45% basis	\$160-\$175

## 3.2 Purity Requirements and Obstacles for Use

### 3.2.1 Calcium Carbonate

#### Purity Requirements

Purity requirements for the uses of calcium carbonate vary depending on the use and whether it is GCC or PCC. Purity requirements for GCC and PCC used for industrial applications are listed below:

#### GCC<sup>11</sup>

- Purity as CaO<sub>3</sub> – Minimum 96 percent
- Calcium carbonate content – 96 percent
- Silica as SiO<sub>2</sub> – Maximum 0.3 percent by weight
- Magnesium Oxide (MgO) – Maximum 0.5 percent by weight
- Sulphate – Maximum 0.3 percent by weight
- Chloride – Maximum 0.1 percent by weight
- Iron, Aluminum, Phosphate – Maximum 0.5 percent by weight
- Sodium Oxide (Na<sub>2</sub>O) –Maximum 0.2 percent by weight

#### PCC<sup>1</sup>

- Purity as CaO<sub>3</sub> – Minimum 96 percent
- Calcium carbonate content – 96 percent
- Silica as SiO<sub>2</sub> – Maximum 0.3 percent by weight
- MgO – Maximum 0.5 percent by weight
- Sulfate – Maximum 0.3 percent by weight
- Chloride – Maximum 0.1 percent by weight
- Iron, Aluminum, Phosphate – Maximum 0.1 percent by weight
- Na<sub>2</sub>O –Maximum 0.2 percent by weight

#### Obstacles for Use

Calcium carbonate is mined and used in the dry state and opportunities for direct use of calcium carbonate brine appear to be limited and brine solutions are not expected to have widespread market applicability. However, calcium carbonate is very insoluble and can be precipitated from

<sup>1</sup> Adapted from <http://www.famousminerals.net>

RO concentrate by increasing the pH. It may be possible to precipitate calcium carbonate from the concentrate for use as a dry material. Precipitated calcium carbonate (PCC) from RO concentrate would have to meet the purity requirements for PCC that is currently obtained through the Solvay process.

### 3.2.2 Calcium Sulfate

#### Purity Requirements

- The ASTM standard for gypsum (ASTM C-22) requires that gypsum shall not contain less than 70 percent by weight of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Silica and sodium chloride should not be more than 6 percent and 0.01 percent by weight and it should also be free from clayey material.
- Gypsum with a purity of 75 to 85 percent is used in cement manufacturing but a minimum of 82 percent is preferred.
- Gypsum used for Plaster of Paris requires purity ranging from 80 to 97 percent.
- Gypsum of 75 percent purity and below is used as manure or sweet-lime.
- Gypsum used in wallboard is negatively affected by certain salts. The maximum content of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Mg}_2\text{O}$  in wallboard is 0.3 percent by weight and the maximum concentration of chloride in gypsum is 100 parts per million (ppm). (Ahuja & Howe, 2007).

#### Obstacles for Use

Calcium sulfate is mined and used in the dry state and opportunities for use of sodium sulfate brine appear to be limited. Calcium sulfate obtained by precipitation from a brine solution would have to meet the purity requirements for wallboard, which limit the amount of other salts, chlorides, and silica that can be present in the gypsum precipitate. In addition, the direct use of brine in the production of concrete would be severely limited by the presence of other ions in the brine. Chlorides in the brine may not be desirable and excess gypsum added to the cement could make the setting time excessively long.

A potential direct use of the brine would be direct irrigation to improve the quality of soil. Salt affected (sodic) soils in the southwest US have very low infiltration rates and surface crusting and do not support agriculture. This results in water loss to the local area as rain water does not enter groundwater pathways (Jordahl, 2006). Gypsum is currently used for remediation of sodic soils which suggests that calcium sulfate brine applied to the soil could be used to improve the quality of the soil. However, direct irrigation using RO concentrate presents a series of challenges as the volume of concentrate produced may exceed the available land and the cost to haul the concentrate to the application area may be high. Also, irrigation with RO concentrate would be subject to regulatory requirements and concerns about potential groundwater impacts.

### 3.2.3 Sodium Sulfate

#### Purity Requirements

The main use of sodium sulfate is in powdered laundry detergent. Purity requirements for sodium sulfate used for detergent and dye chemicals that had the following specifications<sup>2</sup>:

- Sodium Sulfate > 99 percent by weight
- Calcium, magnesium < 0.15 percent by weight
- Iron < 0.002 percent
- Moisture < 0.2 percent
- Water insoluble < 0.05 percent
- Whiteness > 85 percent

Purity requirements for other uses were not available.

#### Obstacles for Use

Sodium sulfate is highly soluble and is commonly used in a dry form. The major market for sodium sulfate for detergents is in Asia and Latin America which limits the potential domestic use of sodium sulfate produced from RO concentrate. In the pulp and paper industry, the use of sodium emulsified sulfur and caustic soda can replace sodium sulfate.

The market analysis presented in Section 3.1 indicated that there are more than adequate reserves of naturally occurring sodium sulfate that are expected to last for many years. Sodium sulfate can also be obtained by recycling car batteries and as a byproduct of other industrial products. Isolating and recovering sodium sulfate from RO concentrate may be difficult and costly and with plentiful supplies of lower cost sodium sulfate available, and a limited domestic marketplace, there does not appear to be a market for sodium sulfate produced from RO concentrate.

### 3.2.4 Sodium Carbonate (Soda Ash)

#### Purity Requirements

Soda ash is usually supplied in Grades A and B, which have are more than 99 percent pure. Soda ash with a bulk density greater than 0.8 percent is called dense soda ash. The purity requirements for Grades A and B natural soda ash produced in the United States are presented in Table 14.

<sup>2</sup> <http://made-in-china.com/showroom/shengongchem/product>

**Table 14 Soda Ash Quality<sup>2</sup>**

Composition	Grade A	Grade B
Na <sub>2</sub> CO <sub>3</sub>	99%	99.80%
NaHCO <sub>3</sub>	-	-
NaCl	0.03%	0.02%
Na <sub>2</sub> SO <sub>4</sub>	0.07%	0.02%
Fe <sub>2</sub> O <sub>3</sub>	0.0006%	0.0005%
NaF	0	0
H <sub>2</sub> O Insol	0	0

2- <http://www.ndctz.com/sodaash.html>

The main use of sodium carbonate is glass production. Glass production requires a dense pure soda ash that is free of chloride and iron impurities. Dense soda ash is also used in water treatment applications due to its handling characteristics. It has little dust and good flow characteristics. It is typically used to increase the pH in water treatment processes.

### Obstacles for Use

Sodium carbonate is more soluble than sodium sulfate and may be more difficult to obtain from RO concentrate than other salts because of the necessity to raise the pH to precipitate it. It is commonly used in the dry form which means that direct use of the brine is not possible. Extraction of sodium carbonate from concentrate is likely to be difficult and expensive and may not prove to be economical.

## 3.2.5 Sodium Chloride

### Purity Requirements

Brine is used in the chlor-alkali industry to produce chlorine and sodium hydroxide. Most salt brine is produced by the same companies that use it. However, some chlor-alkali producers purchase brine from independent supply companies and in some cases brine is produced by a chemical company that uses some of it and sells the rest to a neighboring chemical company (Kostick, January 2010).

The production processes used to generate chlorine and sodium hydroxide require brine free of sulfate, calcium, magnesium, barium, and metals that would affect the electrolytic process. Many of the processes used to generate chlorine and sodium hydroxide have a brine pre-treatment process to remove impurities before the electrolytic process. Brines used in these processes typically have low concentrations of calcium and magnesium, which allow for the use of an ion exchange pre-treatment process. Brackish water used for municipal water supplies typically has high concentrations of calcium and magnesium, which would require softening the concentrate before it is sent to a chlor-alkali plant.

Rock salt is used in on-site sodium hypochlorite generating systems. Rock salt used in this process must meet the following purity requirements<sup>3</sup>:

- Sodium chloride – 96 percent
- Calcium sulfate – 0.3 percent maximum
- Magnesium chloride – 0.06 percent
- Calcium chloride – 0.1 percent
- Magnesium sulfate – 0.02 percent maximum
- Insolubles – 0.1 percent maximum
- Metals (lead, copper, iron) – 0.007 percent maximum
- Fluoride – 0.002 percent maximum

ASTM D632 specifies a minimum sodium chloride content of 95 percent for sodium chloride used for road salt but does not specifically discuss impurities.

### **Obstacles for Use**

Sodium chloride has many uses and offers possibilities for extraction and/or use of the RO concentrate. On the other hand, it is extremely soluble, which increases the difficulty of concentrating the RO concentrate to precipitate sodium chloride as a dry salt. Dry salt is commonly extracted from brine through solar evaporation and mechanical evaporation of purified brine feedstock. These processes suggest that it is possible to obtain dry salts from RO concentrate/brine.

As previously discussed, brine is used directly in the production of chlorine and sodium hydroxide. However, both of these processes require brine with low concentrations of impurities, primarily other chlorides that prevent direct use of RO concentrate in these processes. In addition, nearly half of the brine used by chemical manufacturers is produced from brine wells owned by the manufacturer and is not purchased on the open market (Ahuja and Howe, 2007). This may limit the opportunities for RO concentrate use as a source of supply for a chemical manufacturer.

## **3.2.6 Calcium Chloride**

### **Purity Requirements**

ASTM Standard D98 provides purity requirements for both dry and liquid calcium chloride. Purity requirements limit the amount of impurities, primarily other chlorides such as alkali chlorides and magnesium chlorides. Other limits on impurities are specific to the purchaser and the end use and are generally proprietary.

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<sup>3</sup> Severn Trent Services, 2010



Dry calcium chloride is classified by grade which is related to the minimum calcium chloride concentration. Grade 1 requires a minimum 77 percent concentration, Grade 2 requires a 90 percent minimum concentration, and Grade 3 requires a minimum 94 percent concentration. Liquid calcium chloride is typically provided in concentrations of 28 to 42 percent to a purchaser.

### **Obstacles for Use**

Calcium chloride is extremely soluble and may be more difficult to obtain from RO concentrate than other salts. Calcium chloride obtained from RO concentrate would also have to meet the purity requirements of the potential end user, which could require additional refining steps to remove impurities. For example, calcium chloride used for dust control is hygroscopic, that is, it adsorbs moisture from the atmosphere. Brines high in sodium chlorides do not have this quality and would be of limited value for dust control.

Another issue is that some states do not allow the use of concentrates for dust control and deicing. Colorado prohibits the use of concentrates for dust control and deicing and California requires new products to undergo extensive health and environmental testing before it can be placed into use (Jordahl, 2006).

## **3.3 Regional Use of Concentrate Products**

Many of the salts found in RO concentrate have regional uses that may help with determining the potential marketability of the salt. For example, dry sodium chloride (rock salt) and calcium chloride are used extensively in cold climates for deicing and are not used in warmer climates, such as southern states and the desert southwest. Industrial uses of salts such as calcium carbonate in the paper and plastic industry and gypsum (calcium sulfate) may also have regional uses.

In an effort to correlate potential markets with locations of existing and future desalination plants, the following marketing regions were established and are described below.

### **Hot Arid Region**

The Hot Arid Region includes New Mexico, west Texas, Arizona, inland California, and Nevada. Based on data from Jordahl (2006), there were a total of 62 desalination plants in this region with the majority located in California and Texas.

This area is experiencing significant population growth and high water demand as well as scarce water resources. This region features high evaporation rates, low precipitation, and high annual average temperatures. The likelihood of inland desalination plants being constructed in this region is high due to limited supplies of potable water, frequent drought, and population growth. In addition, common concentrate disposal options such as deep well injection and evaporation ponds may be limited due to regulatory factors, geology, and cost and availability of land.

### **Cold Arid Region**

The Cold Arid Region includes the states of Colorado, Wyoming, Montana, Idaho, and Utah and also parts of North and South Dakota, western Nebraska, and Kansas. Based on data from Jordahl (2006), there were a total of 14 desalination plants in this region.

This region is defined by areas at higher latitudes that receive low annual rainfall and have higher evaporation rates than humid areas. The state of Colorado in particular is experiencing high population growth and water demands such that inland desalination plants are becoming a likely source of potable water. Concentrate disposal options in this region may also be limited due to low evaporation rates and restrictions on disposing to the sanitary sewer. Geology may also limit deep well injection.

### Warm and Humid Region

The Warm and Humid Region includes the gulf coast states, east Texas, Florida, Georgia, and North and South Carolina. This region has the largest concentration of existing desalination plants with the vast majority being located in Florida. However, communities in coastal Georgia and South Carolina where saltwater intrusion from the Atlantic Ocean is contaminating groundwater sources are also considering or have in place desalination plants for treatment of brackish water. This region receives a significant amount of rain during the year and has relatively low annual evaporation rates. This region has rapidly growing population centers which have resulted in the expansion of urban areas into rural areas that were sources of water for coastal communities.

### Other United States Regions

The remaining areas of the US include the Pacific Northwest, Appalachian states, and the Northeast/ New England states. These regions generally obtain water from surface sources or groundwater sources that are seen as plentiful. However, these areas have also experienced tremendous population growth in recent years, which has stressed existing water supplies.

## 3.4 Regional Markets

Marketing RO concentrate products will require an evaluation of potential markets within the proximity of the existing and/or future RO treatment facility to determine if any current or planned industries would have a need for salt product. To facilitate this evaluation, a matrix of potential uses of RO concentrate salts and the regions where they may be used is presented below in Table 15.

**Table 15 Regional Brine Market Matrix**

	Hot Arid Region	Cold Arid Region	Warm Humid Region	Other US Regions
Calcium carbonate	Paper Glass Building materials	Paper Glass Building materials	Paper Glass Building materials	Paper Glass Building materials
Calcium sulfate (gypsum)	Wallboard Building materials Cement production	Wallboard Building materials Cement production	Wallboard Building materials Cement production	Wallboard Building materials Cement production
Sodium sulfate	Glass Detergents	Glass Detergents	Glass Detergents Textiles	Glass Detergents
Sodium carbonate (soda ash)	Glass Chemicals	Glass Chemicals	Glass Chemicals	Glass Chemicals
Sodium chloride	Chlor-alkali industry	Road salt Chlor-alkali industry	Chlor-alkali industry	Chlor-alkali industry
Calcium chloride	Dust control	Road salt Dust control	Dust control	Dust control



## 3.6 Market Analysis

The 2009 domestic production of the six recoverable RO concentrate salts evaluated in this study is presented in Table 17.

**Table 17 Domestic Production of Selected Salts 2009**

Salt	Volume Produced (tons/year) <sup>1</sup>
Calcium Carbonate <sup>2</sup>	1,223,220,000
Calcium Sulfate	34,272,200
Sodium Sulfate	330,600
Sodium Carbonate	12,011,800
Sodium Chloride	50,692,000
Calcium Chloride <sup>3</sup>	1,700,000
<b>TOTAL</b>	<b>1,332,226,600</b>

1 – Volume converted from metric tons to short tons

2 – As limestone

3 – 2004 production data. More recent data was not available.

As shown in Table 17, the salt industry produced over a billion tons of potentially recoverable salts in 2009. While this quantity is partially skewed by the volume of calcium carbonate produced as limestone, the total quantity produced is still large. To put this quantity in perspective with the volume of salt produced by an RO plant, a 10 MGD RO plant using zero discharge technology (i.e., 100 percent recovery) treating water with a TDS of 5000 mg/L would generate approximately 80,000 tons per year of salt. This is less than one-tenth of one percent of the total volume of the salts listed in Table 17.

The comparatively small amount of salt produced in a year from a single treatment plant suggests that it would have a minimal impact if it was sold on the open market because there are plentiful supplies of these salts produced each year. It may be possible to find a local user of the salt, such as a municipality that uses road salt or calcium chloride for deicing, or a chemical plant that could use the brine in a chlor-alkali process.

A potential problem associated with a RO plant as a salt supplier is the plant may produce more salt than a municipality or industry can use. For instance, Colorado uses approximately 35,000 tons per year for deicing (CDM, 2009). This is less than half the salt produced by the 10 MGD plant discussed previously using a ZLD process. If the same plant was operating at 80 percent recovery, it would still generate more salt than the state could use in a year.

It should be noted that the types and concentrations of salts found in RO concentrate are dependent upon the concentrations of the constituents in the raw water stream and the treatment characteristics of the RO system and the ZLD system, if one is being used. It should also be noted that the ability to sell the salts at market price depends upon achieving the required purity in the recovery process.

Assuming a potential market or customer could be found for a recoverable salt; the potential revenue generated could offset disposal costs or be less than commonly used disposal methods such as evaporation ponds or deep well injection. Table 18 presents an estimate of the potential revenue that could be generated by recovering salts from the desalination plant described in the preceding paragraph assuming a market could be obtained for the salt. The assumed percentages of each salt in the concentrate are;

- Calcium Carbonate – 10%
- Calcium Sulfate – 20%
- Sodium Sulfate – 20%
- Sodium Carbonate – 10%
- Sodium Chloride – 30%
- Calcium Chloride – 10%

**Table 18 Potential Annual Revenue from the Sale of Recoverable Salts<sup>1</sup>**

Salt <sup>2</sup>	Annual Revenue <sup>3</sup>
Calcium Carbonate	\$494,650
Calcium Sulfate	\$129,370
Sodium Sulfate	\$1,932,940
Sodium Carbonate	\$2,073,725
Sodium Chloride	\$799,050
Calcium Chloride	\$1,522,000

1-Assumptions: 10 MGD Plant, 100 percent recovery(ZLD process), 5000 mg/L TDS feed water.

2-Dry form

3-Based on costs from 2009

As shown in Table 18, the recoverable salts with the greatest potential revenue in the dry form are sodium carbonate (soda ash), calcium chloride, and sodium sulfate (gypsum). It should be noted that sodium chloride brine has a very low market price of \$8 per ton which will reduce the potential revenue as the value of dry sodium chloride is greater than the brine. However, sodium chloride brine should be easier to produce than dry salt and potentially easier to market since it is used in the chlor-alkali industry and it is not uncommon for chlor-alkali producers to purchase brine from other sources for use.

A 10 MGD plant with a raw water TDS concentration of 5000 mg/L generates approximately 80,000 tons of solids per year. Assuming a landfill disposal cost of \$50.00 per ton, the annual cost of disposing these solids in a landfill would be \$4,000,000. Thus, if the utility was able to give the RO concentrate to an industrial partner at no cost, the avoided cost of landfill disposal would result in significant savings.

## 3.7 Case Studies

Two case studies of future RO plants in which selective salt recovery was considered in the design of the facility are presented in the following two sections. While neither plant has been constructed, the purpose of presenting the case studies is to illustrate the approaches to selective salt recovery that were considered for these future facilities. It is important to note that selective salt recovery was not the primary focus of these studies. However, data was obtained that can be used to give a utility an idea of the issues associated with planning a future plant with selective salt recovery.

In the case of Sandoval County, selective salt recovery using nano-filtration to recover sodium chloride brine was considered to offset the cost of operating the proposed 5 MGD treatment plant. The East Cherry Creek project evaluated two ZLD technologies that could recover a large portion of the concentrate from a brackish water RO treatment system. The ZLD processes generate a dry salt that can be landfilled or possibly marketed. It is important to note that the purpose of the study was not to determine budget costs for a standard ZLD project. The effectiveness of ZLD processes are site specific as the quality of the brackish water has a profound effect on the operating conditions of the membrane processes.

### 3.7.1 Case Study 1 - Sandoval County, New Mexico 5 MGD Desalination Treatment Facility

In 2009, a pilot test was conducted on a brackish groundwater aquifer in Sandoval County, New Mexico for potential use as source of potable water. The County planned to design and eventually construct a 5 MGD treatment plant to meet future water demands in the area. The brackish water aquifer was 4,000 feet below ground surface, was under artesian pressure and had a temperature of 150 degrees Fahrenheit. The brackish groundwater contained high concentrations of dissolved solids (12,000 mg/L), hardness, arsenic, and radionuclides, as well dissolved carbon dioxide and hydrogen sulfide gases. While the primary objective of pilot testing was to identify the treatment processes required for producing potable water, a secondary objective was to identify treatment processes so that salts could be selectively recovered from the concentrate to facilitate disposal and allow beneficial reuse.

The results of pilot testing recommended pretreatment with aeration for gas removal, combined coagulation/sedimentation for arsenic reduction, and warm lime softening. Granular media filtration would follow the softening step and a weak acid cation ion exchange process would serve as a polishing step before final treatment with RO. The numerous pretreatment processes before RO were necessary to remove arsenic and radionuclides as well as hardness and to prevent scaling of the RO membranes. The pretreatment processes also allowed for potential beneficial reuse of the RO concentrate by removing many of the contaminants that would restrict potential use.

Pilot test data on the RO concentrate was evaluated to identify the composition of the waste stream and the potential beneficial reuse of recoverable salts. The RO brine concentrate consisted primarily of sodium chloride blended and sodium sulfate. A nano-filtration process was evaluated to determine if the sodium chloride could be recovered at a reasonable purity. Computer projections using Dow NF270 membranes indicated that 98 percent pure sodium chloride brine

could be produced from a 5 MGD plant operating at 90 percent recovery. The sodium chloride brine would then be sent to a thermal brine concentrator and a crystallizer and possibly used in the treatment plant's sodium hypochlorite disinfection process, or possibly sold as road salt. The sodium sulfate waste stream was not evaluated to determine if a marketable product could be recovered from the waste brine stream.

The study concluded that the revenue generated by recovering and selling the sodium chloride and deep well injection of the sodium sulfate brine would be more economical than the annual cost of RO concentrate disposal by deep well injection (UAM and CDM, 2009).

### 3.7.2 Case Study 2 - East Cherry Creek Valley Water and Sanitation District Zero Liquid Discharge (ZLD) Pilot Study

In 2008, CDM conducted a pilot study on the concentrate stream from the Town of Lochbuie, Colorado low pressure reverse osmosis (LPRO) facility. Raw water being treated at the facility had a TDS concentration of 900 mg/L and the concentrate TDS was 3500 mg/L. The primary purpose of the pilot study was to evaluate the effectiveness of two ZLD treatment processes to increase water recovery: high recovery RO and Vibratory Shear Enhanced Process (VSEP). A secondary objective of the pilot test was to generate representative dry solids from concentrated brine wastes to determine the composition and ability to be landfilled or marketed as a usable product. Concentrate from the LPRO treatment plant was considered to be representative of many brackish RO projects with typical concentrations of calcium, magnesium, and sulfate and elevated levels of sodium, chloride, and silica.

Results of the pilot testing showed that the high recovery RO system consistently achieved 94 to 95 percent recovery. The VSEP process was capable of achieving recoveries of 94 to 97 percent but the process required continual permeate flushing and/or frequent chemical cleaning. The concentrated brine from both processes was sent to an evaporation basin. After the water was evaporated, the dried mixed salts from each process were analyzed to determine the mineral composition. The mineral composition of the salts generated from each ZLD process is:

- High Recovery RO – Primarily sodium carbonates but when fully dried converted to halite (sodium chloride) and thenardite (sodium sulfate).
- VSEP – The concentrate from this process was saturated with calcium sulfate (gypsum) and halite (NaCl).

It should be noted that the composition of the dry salts will vary based on the pretreatment process selected for the concentrate from an RO system.

It was concluded that the dried mixed salts had little commercial value due to the high percentage of sodium chloride in the mixture and the presence of many trace minerals. More complicated evaporation processes would possibly yield commercially valuable minerals; however, it is not likely that the cost of the additional processes would be offset by the value of value of the minerals recovered.

## Section 4

# Conclusions and Recommendations

The six recoverable salts discussed in this report are marketable as there are many uses as well as demand. Recovering dry salts and or/brine also has an economic benefit to the utility as it would reduce the costs of disposal. However, there are numerous challenges to overcome in marketing the salts. These challenges are:

- Existence and size of the local market
- Meeting purity requirements
- The volume of concentrate and/or salt produced at a RO plant may exceed market demand.
- Plentiful natural sources of salts that reduce the market for salts obtained from RO concentrate
- Treatment costs associated with producing and marketing salts from RO concentrate
- The salts with the greatest market value (calcium chloride and sodium carbonate) and the salt with the largest market for use (sodium chloride) are among the most soluble of the salts and will be the most difficult and costly to recover
- Potential conflict between producing water as a utility and producing salt and/or brine as a price variable commodity

Another challenge facing a utility that is considering recovering and selling salts from RO concentrate is the lack of an existing market. Most successful marketing ventures are based on creating a product that meets a need. In the case of an RO plant marketing concentrate, the product (concentrate) already exists and it is the market that needs creating. Also, many industries that use the salts are used to entering into long term contracts with suppliers. Potential industries/users may not be inclined to change their source of supply as there may be concerns with the form and purity of the salt and/or brine. A solution to the lack of an existing large scale market is to look for a local, site specific market close to the RO plant that may have a use for one or more of the salts or the brine.



Meeting purity requirements is also a significant challenge. Most existing RO plants have established methods of disposing concentrate (sanitary sewer, deep well injection, evaporation ponds) and would need to be modified to treat the concentrate to make it marketable. While this is certainly possible using a series of ZLD processes, the capital cost of modifying the existing treatment plant would outweigh the benefit of recovering the salts. Also, ZLD processes have not been proven at the scale of a municipal water treatment plant although it is anticipated that these processes will become more economical as demand for higher recoveries increases.

The possibility of incorporating ZLD technology and salt/brine recovery could be considered in the planning for a new RO plant similar to the case studies discussed at the end of Section 3. The possibility of recovering concentrate salts and/or brine could be evaluated to offset the operations and maintenance cost of operating the plant or as a by-product of a ZLD process incorporated into the design to recover as much water as possible from the plant. It is important to note that the feasibility of selective salt recovery is site specific as water quality varies from site to site, and a suitable market may not be available in the vicinity of the proposed treatment plant.

While there are a number of challenges to selective salt recovery in the short term, in the long term selective salt recovery will become more viable. With an increasing demand for potable water, more seawater and inland brackish water desalination plants will be required and the issue of concentrate disposal will have to be addressed. As ZLD technologies become more cost effective, the cost of processing the concentrate will also decrease, thus making selective salt recovery more viable. Selective salt recovery and maximizing water recovery is also a sustainable solution for concentrate disposal which is an issue facing every RO treatment plant.

## Section 5

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**APPENDIX 4 – FORMS USED FOR DATA COLLECTION DURING  
PILOTING**

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**Week 1**

	Date	Time Start
Cycle 1		

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 1**

	Date	Time Start
Cycle 2		

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 2**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 1				

Sample Location	Sample Type	Time	Time into cycle	pH	Constituents to measured at UNM	Initials
S1	Feed Water				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S6	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	



**Week 2**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 2				

Sample Location	Sample Type	Time	Time into cycle	pH	Constituents to measured at UNM	Initials
S1	Feed Water				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Top of SBA column	Resin Sample				carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, TOC	
S2	Regeneration Fluids		15 <input type="checkbox"/>			
			20 <input type="checkbox"/>			
			25 <input type="checkbox"/>			
			30 <input type="checkbox"/>			
			35 <input type="checkbox"/>			
			40 <input type="checkbox"/>			
			45 <input type="checkbox"/>			
S3	Regeneration Fluids		15 <input type="checkbox"/>			
			20 <input type="checkbox"/>			
			25 <input type="checkbox"/>			
			30 <input type="checkbox"/>			
			35 <input type="checkbox"/>			
			40 <input type="checkbox"/>			
			45 <input type="checkbox"/>			
S6	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 2**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 3				

Sample Location	Sample Type	Time	Time into cycle	pH	Constituents to measured at UNM	Initials
S1	Feed Water				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Top of SBA column	Resin Sample				carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, TOC	
S2	Regeneration Fluids		15 <input type="checkbox"/>			
			20 <input type="checkbox"/>			
			25 <input type="checkbox"/>			
			30 <input type="checkbox"/>			
			35 <input type="checkbox"/>			
			40 <input type="checkbox"/>			
			45 <input type="checkbox"/>			
S3	Regeneration Fluids		15 <input type="checkbox"/>			
			20 <input type="checkbox"/>			
			25 <input type="checkbox"/>			
			30 <input type="checkbox"/>			
			35 <input type="checkbox"/>			
			40 <input type="checkbox"/>			
			45 <input type="checkbox"/>			
S6	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 3**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 1				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Top of SBA column	Resin Sample			carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, TOC	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 3**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 2				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Top of SBA column	Resin Sample			carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, TOC	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 3**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 3				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Top of SBA column	Resin Sample			carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, TOC	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 4**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 1				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Top of SBA column	Resin Sample			carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, TOC	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 4**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 2				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Top of SBA column	Resin Sample			carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, TOC	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 4**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 3				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Top of SBA column	Resin Sample			carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate, TOC	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	



**Week 5**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 1				

Sample Location	Sample Type	Time	pH	Constituents to	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate,	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate,	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate,	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate,	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate,	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD	

**Week 5**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 2				

Sample Location	Sample Type	Time	Time into cycle	pH	Constituents to measured at UNM	Initials
S1	Feed Water				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S2	Regeneration Fluids		15 <input type="checkbox"/>			
			20 <input type="checkbox"/>			
			25 <input type="checkbox"/>			
			30 <input type="checkbox"/>			
			35 <input type="checkbox"/>			
			40 <input type="checkbox"/>			
S3	Regeneration Fluids		15 <input type="checkbox"/>			
			20 <input type="checkbox"/>			
			25 <input type="checkbox"/>			
			30 <input type="checkbox"/>			
			35 <input type="checkbox"/>			
			40 <input type="checkbox"/>			
S6	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 5**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 3				

Sample Location	Sample Type	Time	Time into cycle	pH	Constituents to measured at UNM	Initials
S1	Feed Water				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S2	Regeneration Fluids		15 <input type="checkbox"/>			
			20 <input type="checkbox"/>			
			25 <input type="checkbox"/>			
			30 <input type="checkbox"/>			
			35 <input type="checkbox"/>			
			40 <input type="checkbox"/>			
S3	Regeneration Fluids		15 <input type="checkbox"/>			
			20 <input type="checkbox"/>			
			25 <input type="checkbox"/>			
			30 <input type="checkbox"/>			
			35 <input type="checkbox"/>			
			40 <input type="checkbox"/>			
S6	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant				calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid				SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 6**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 1				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 6**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 2				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

**Week 6**

	Date	Time Start	Time - End of Op Cycle	Time - Regen Start
Cycle 3				

Sample Location	Sample Type	Time	pH	Constituents to measured at UNM	Initials
S1	Feed Water			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S6	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
S7	Regeneration Fluids			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation– no pH adjustment	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – low pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – low pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	
Precipitation bucket after precipitation – high pH condition	Supernatant			calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, nitrate, fluoride, sulfate	
Precipitation bucket after precipitation – high pH condition	Solid			SEM, EDS (relative elemental composition), XRD (presence of known crystal phases), mass	

