Physicochemical Treatment Options for High-Conductivity Coal Mining Runoff

Catherine Vyvian Grey

Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science

In

Environmental Engineering

Gregory D. Boardman, Co-Chair
Peter J. Vikesland, Co-Chair
Jeffrey L. Parks

17 February, 2017

Blacksburg, VA

Physicochemical Treatment Options for High-Conductivity Coal Mining Runoff

Catherine Vyvian Grey

Academic Abstract

In recent years, the excessive specific conductance (SC) of Appalachian coal mining runoff waters has become a parameter of concern with the EPA due to its negative effect on aquatic life and water quality. In order to comply with the EPA guidance suggesting an effluent SC of 500 µS/cm, the Appalachian Research Initiative for Environmental Science (ARIES) Center at Virginia Tech requested that testing be done to determine the most effective technologies for reduction of SC. Runoff water was collected from two sites in southwestern Virginia and characterized to determine the source of SC in the water. The main contributing ions were determined to be Na^+, Mg^{2+}, Ca^{2+}, and SO_4^{2-}. Testing was performed to assess the possibility of using the speciation software, MINEQL+, with a set of empirical equations which predict SC using ionic composition for natural waters with a low to medium SC.

The physicochemical treatment methods tested were ion exchange, excess lime-soda softening, and the Cost Effective Sulfate Removal (CESR) process. Both cation (H^+ exchanger) and anion (Cl^- exchanger) exchange media were tested separately in batch reactors, which resulted in a higher effluent SC than initial SC. The softening method investigated, excess lime-soda softening, also resulted in increased SC levels because non-carbonate hardness levels were high and carbonate concentrations were low. The CESR process successfully lowered SC from 1,500-2,500 µS/cm to below the proposed EPA limit of 500 µS/cm. The success of this process was due to its ability to remove more than 85% of the calcium, magnesium, and sulfate from the water, which together accounted for more than 90% of ions in the source water.

Physicochemical Treatment Options for High-Conductivity Coal Mining Runoff

Catherine Vyvian Grey

Abstract for the General Public

In recent years, mining activities have generated large amounts of unweathered rock from blasting. This rock, which is often stored in valleys near the blasting sites, releases salts into water that passes over the rocks when it rains. The salty water flows into nearby streams populated with freshwater fish and other organisms that suffer when their environmental conditions are changed. The Appalachian Research Initiative for Environmental Science (ARIES) Center at Virginia Tech requested that testing be done to determine which engineering techniques would be most effective for reduction of these salts. The amount of salt in the water is measured by specific conductance (SC), which measures how well the water conducts electricity. Testing was also done to determine which types of salts were in the water; the results showed that the largest contributors were sodium, magnesium, calcium, and sulfate ions.

Three engineering techniques were investigated for removal of the contributing ions: ion exchange, softening, and the Cost Effective Sulfate Removal (CESR) process. Two types of ions exchange, one that targeted the positive ions (cation exchange) and one that targeted the negative ions (anion exchange), were tested. Both forms of ions exchange raised the SC to a higher concentration than the original water. Softening had a similar effect because one of the chemicals added during the process released additional sodium ions into the water. Finally, the CESR process was able to successfully reduce the SC below the limit proposed by the EPA as safe for stream life. This was due to the large reduction of three of the four major ions that was achieved during the CESR process.

Dedication and Acknowledgements

I would like to thank my committee for their support and guidance during the time I spent both researching and writing. I would not have been able to complete this thesis without their assistance and will always appreciate the effort they put into making me a better engineer.

I would especially like to thank my advisor, Dr. Greg Boardman, for helping me through every step of my thesis. Words cannot express how glad I am that I was able to join the research group of such an exceptionally kind, patient, and knowledgeable professor. I will always be grateful for the opportunity I had to work with such a wonderful advisor.

I would also like to thank all of the people who helped me in the lab: my committee member, Dr. Jeff Parks, who provided assistance with ICP analysis as well as SC modeling; Julie Petruska, who made sure the labs were safe and helped me set up my experiments; Jody Smiley, who helped with IC analysis and always brought in snacks for the department; and Beth Lucas, who assisted with administrative work and always brightened my day.

To my research partner Zach Kemak—I am so glad you joined the team. I never would have been able to characterize our water, set up my experiments, or make it home from those remote mining sites without you.

Finally, I would like to thank my family and friends for all their support during the course of my master's degree. I'd like to thank Cali Lewis for making it hard to leave for the lab every day and Anurag Mantha, Julia Byrd, Maddie Brouse, and Pam Rusinko for making it fun to come to Durham. I'd also like to thank my parents for encouraging me every step of the way.

Table of Contents

List of Tables and Figures

Chapter 1: Introduction

In 2011, the EPA issued a guidance intended to reduce the impact of surface mining activities on receiving streams in the central Appalachian region, which includes Kentucky, Tennessee, Virginia, and West Virginia (Griffith et al. 2012; EPA, 2011b). Within this document, a new guidance was recommended for specific conductance (SC), which has been found to be an accurate surrogate for total dissolved solids (TDS) (Clark, 2016; Daniels, 2016; Visconti, 2004). The guidance limits the SC of discharged waters to between 300-500 μS/cm to protect benthic macroinvertebrates and was most applicable to surface mining sites where rock debris is deposited on-site in valleys, referred to as valley fills (Pond et al., 2014; EPA, 2011a). The runoff water from these valley fills typically has TDS composed mostly of sulfate (SO_4^{2-}), calcium (Ca^{2+}), magnesium (Mg^{2+}) and a carbonate species (HCO_3^-) (EPA, 2011a, b; Clark, 2015; Timpano, 2015).

It has been well documented that valley fills and the associated increase in TDS is detrimental to stream health. Streams in the central Appalachian region naturally have an SC less than 200 μS/cm (Evans, 2014), but valley fill runoff increases the SC of receiving streams, often to levels above 1,000 μS/cm during and after active mining operations (Daniels, 2016). Affected streams may continue to be impaired up to 30 years after mining activity has ceased (Pond et al., 2014). This has resulted in a pervasive problem for benthic organisms and overall stream health in the twelve million acres of land devoted to surface mining in Central Appalachia (EPA, 2011a; Zipper, 2011).

In 2012, McCleskey published a set of empirical equations that might be used to predict the SC contribution from ions, ion pairs, and trace metals commonly found in natural waters. The equations accurately predicted the SC within 7.5% in 99% of the cases for a wide variety of raw waters, including seawater, pristine mountain water, acid mine drainage, and rivers affected by municipal wastewater. Speciation of chemicals in the water was determined through the use of the software, WATEQ4F. To test the robustness of the equations and compatibility with another popular software package for chemical speciation, MINEQL+ was considered in this study. In Chapter 2, the SC predicted from

these empirical equations with MINEQL+ is compared to the results published in the original study that were produced using WATEQ4F. (McCleskey, 2012)

Three different water treatment methods for SC removal are discussed in Chapter 3. The first treatment technique used was ion exchange. Cation and anion exchange media were chosen based on their selectivity for calcium and magnesium (cation exchange) or sulfate (anion exchange). This is due to the caveat in the EPA guidance that would allow sites to reduce concentrations of these ions in the water if the overall SC limit could not be reached (EPA, 2011b). The stoichiometric amount (SA) of ion exchange media needed for each water was determined using a cation-anion balance. The second technology tested was chemical softening. Excess lime-soda softening was chosen because there was not enough initial alkalinity in the water to precipitate all dissolved and added calcium (from lime) as $CaCO_3$, necessitating the addition of greater amounts of soda ash.

The final process investigated for SC reduction was the Cost Effective Sulfate Removal (CESR) process. This is a two stage process. During Stage I, the pH of source water is increased to 10.5 in a batch reactor to precipitate gypsum ($CaSO_4$) to its lower solubility limit of 2,000 mg/L as SO_4^{2-}. In Stage II, the pH is raised to and maintained at 11.3 using a pH control system. After the pH is adjusted, the reagent, Luminite MG-4, is added to the water at a dose of 1.0-1.5 times the water's sulfate concentration. This reagent combines with sulfate to form a calcium alumina-sulfate compound called ettringite. As ettringite precipitates, the pH will decrease. If the pH is below 11.0, the reaction will slow or stop. If the pH increases above 12.0, the reaction will not work. During the experiments conducted with the CESR process, four conditions were tested to enhance the performance of stage II operations. (Reinsel, 2015)

Literature Cited

Clark EV, Greer BM, Zipper, CE, Hester, ET. 2016. *Specific conductance–stage relationships in Appalachian valley fill streams.* Environ Earth Sci 75:1222.

Daniels WL, Zipper CE, Orndorff CW, Skousen JG, Barton CD, McDonald L, Beck M. 2016. *Predicting total dissolved solids release from central Appalachian coal mine spoils*. Environ Pollut 216:371–379

EPA. 2011a. *The effects of mountaintop mines and valley fills on aquatic ecosystems of the central Appalachian coalfields*. U.S. Environmental Protection Agency, Washington, DC, EPA/ 600/R-09/138F.

EPA. 2011b. *A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams (Final Report)*. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-10/023F.

Griffith, MB; Norton, SB; Alexander, SC; Pollard, AI; and LeDuc, SC. 2012. *The effects of mountaintop mines and valley fills on the physicochemical quality of stream ecosystems in the central Appalachians: A review*. JScience of the Total Environment. 417-418 (2012) 1-12.

McCleskey, RB; Nordstrom, DK; Ryan, JN; Ball, JW. 2012. *A new method of calculating electrical conductivity with applications to natural waters*. Geochimica et Cosmochimica Acta 77 (2012) 369-382.

Pond GJ, Passmore ME, Pointon ND, Felbinger JK, Walker CA, Krock KJ, Fulton JB, Nash WL. 2014. *Long-term impacts on macroinvertebrates downstream of reclaimed mountaintop mining valley fills in central Appalachia*. Environ Manag 54:919–933.

Reinsel, M. personal communication, Nov. 20. 2015.

Timpano AJ, Schoenholtz SH, Soucek DJ, Zipper CE. 2015. *Salinity as a limiting factor for biological condition in mining-influenced Central Appalachian headwater streams*. J Am Water Resour Assoc 51:240–250.

Visconti Reluy, F; de Paz Bécares, JM; Zapata Hernández, RD; and Sánchez Díaz, J. 2004. *Development of an equation to relate electrical conductivity to soil and water salinity in a Mediterranean agricultural environment*. Australian Journal of Soil Research, 2004, 42, 381-388.

Zipper CE, Burger JA, McGrath JM, Rodrigue JA, Holtzman GI. 2011. *Forest restoration potentials of coal-mined lands in the eastern United States*. J Environ Qual 40:1567–1577.

Chapter 2: Literature Review

Regulations and the Effect of Specific Conductance on Stream Life

In 2011, the EPA issued a guidance intended to reduce the impact of surface mining activities on receiving streams in central Appalachia (Figure 2.1, Modified from Griffith et al., 2012). Within this document, a new guidance was recommended for specific conductance (SC), which has been found to be an accurate surrogate for TDS (Clark, 2016; Daniels, 2016; Visconti, 2004) with an established relationship of 0.5 to 1 unit of SC per unit of TDS in mountain streams (Singh, et al, 1974). The new EPA guidance states that effluent SC should be below 500 µS/cm to protect sensitive benthic macroinvertebrates (EPA, 2011b).
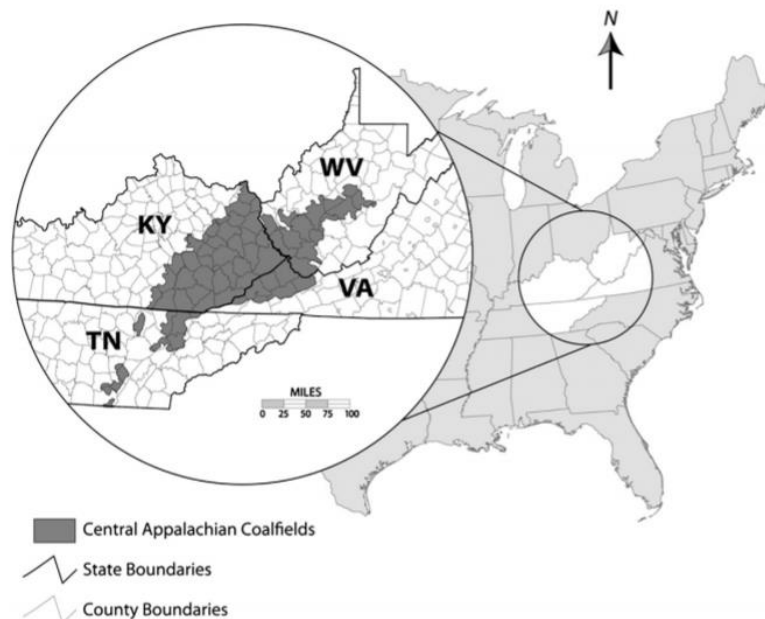
Figure 2.1: Regions Affected by EPA Guidance (Modified from Griffith et al., 2012)

Surface mines in Appalachia often dispose of their mining spoils in valley fills, where large quantities of unweathered rock are stored in valleys or hollows adjacent to a mining site (Pond, 2014; EPA, 2011a). In mines where blasting occurs, rocks are often

5

small and have a large surface area, magnifying the release of TDS during weathering (Evans, 2014). When a precipitation event occurs, water and atmospheric oxygen interact with the newly exposed rock and the valley fills become a source of high-TDS leachate that affects nearby surface water (Clark, 2015; Evans, 2014). These activities affect approximately 12 million acres of land in Virginia, West Virginia, Kentucky, and Tennessee, causing elevated concentrations of ions downstream of the fills and lowered water quality for aquatic life (EPA, 2011a; Zipper, 2011). In the central Appalachian region affected by the EPA guidance, the primary components of the TDS are SO_4^{2-}, HCO_3^-, Ca^{2+}, and Mg^{2+} (EPA, 2011a, b; Clark, 2015; Timpano, 2015; Pond et al. 2008).

It has been well documented that valley fills and the associated increase in TDS is detrimental to stream health. Streams in the central Appalachian region generally have an SC less than 200 µS/cm (Evans, 2014). Runoff water from newly exposed rock increases the SC of receiving streams, often to levels above 1,000 µS/cm during and soon after active operations (Daniels, 2016). These streams continue to be impaired, even 10-30 years after the fills were put in place (Pond et al., 2014). This problem is magnified because valley fills full of freshly eroded rock alter hydrological flowpaths, often becoming the headwaters of a stream and affecting communities downstream during and after mining activities (Bohme et al., 2015). This, combined with the large volume of land affected by mountaintop mining in the central Appalachian region, results in a large scale problem for benthic organisms and overall stream health across the region.

A true SC threshold is difficult to quantify because of variability between biota, temporal changes, and ionic composition of water, but it has been demonstrated that elevated salinity in freshwater streams is damaging to stream life, even when other parameters such as pH and dissolved oxygen remain within a healthy range (EPA 2011a, Timpano et al., 2015; Boehme et al., 2015). The pre-mining SC of the stream has a great effect on the repercussions of increased SC and TDS. For example, a stream with a baseline SC of 100 µS/cm will begin to suffer at an SC of around 300 µS/cm, but streams with a higher reference SC are able to withstand greater SC increases (Cormier et al., 2013). The effect of individual ions on stream health depends on the species used for testing and its

sensitivity to certain ions; for this reason, some sites may be able to satisfy the SC regulation by targeting specific ions if they are unable to meet the overall conductivity standard (EPA 2011b).

Components of Conductivity Removal

The relationship between total dissolved solids (TDS) and specific conductance (SC) has been studied for many years. As long ago as the 1930's, researchers have attempted to quantify this relationship, but have also recognized the challenges of creating a broadly applicable set of equations to model the TDS-SC relationship, even for the same type of water with different ionic concentrations (Gustafson and Behrman, 1939). Earlier models designed to relate SC and TDS measured each parameter separately for a site, determined a tailored conversion factor, and would then use the empirically derived constant as a multiplier to determine TDS from the more easily measured SC (Visconti, 2004). Later models were more sophisticated, moving away from predicting TDS from SC, and instead aiming to predict SC from TDS using the ionic strength of the solution (Ponnamperuma, 1966; Griffin and Jurinak, 1973). The equation for ionic strength is given in Equation 2.1 (McCleskey, 2012; Visconti, 2004).

$$I = \frac{1}{2} \sum_i |z|_i^2 C_i \qquad\qquad \text{Eq. 2.1}$$

In the late 1900's, researchers began using a theoretical model for SC prediction that used ion transport theory as a component of SC prediction (Visconti, 2004). In 1998, a model of this type was developed that summed the contribution of individual ions to the overall electrical conductance (EC), which could then be corrected for temperature to $25^{\circ}C$ to find the SC (Bockris and Reddy, 1998). Equation 2.2 is used to find the EC of an individual ion, with F being the Faraday's constant and u_i being the limiting equivalent ionic mobility ($mS\text{-}cm^2\text{-}mol/(eq\text{-}C)$).

$$\sigma_i = 10^{-6}|z|_i F C_i u_i \qquad \text{Eq. 2.2}$$

The overall EC could then be found using Equation 2.3.

$$EC = \sum_i \sigma_i \qquad \text{Eq. 2.3}$$

Simplifying, Equation 2.2 could be substituted into Equation 2.3 in order to calculate the EC more directly (Equation 2.4).

$$EC = 10^{-6}F \sum_i |z|_i C_i u_i \qquad \text{Eq. 2.4}$$

Finally, the EC could be corrected to 25°C to determine the SC.

The early models for SC modeling were the groundwork for the equations used in this study; however, the earlier predictive models did not successfully model SC for dissimilar waters and waters with different ionic strengths. This is due to the dependence of early models on correction factors for speciation that were tailor-made for the water being studied (USGS, 1988). This inability to model waters with ion pairs was a serious limitation for widespread use of the models (Visconti, 2004).

Another challenge with the equations historically used was that they did not successfully model SC from ionic composition in waters with low to medium SC (McCleskey, 2012). Many equations were best suited for modeling higher ionic strength waters, such as brackish and saline waters or industrial effluent. (McCleskey, 2012; USGS, 1988). Additionally, there was a lack of information regarding the conductivity data for electrolytes typically found in natural systems. Information was lacking in regards to the variety of ions, ion pairs, and trace metals found in the literature and with respect to ranges of pH, temperature, and ionic strength (McCleskey, 2011; Pawlowicz, 2008).

In 2012, a set of empirical equations was published by R. B. McCleskey that were used to predict the SC contribution from ions, ion pairs, and trace metals commonly found in natural waters of interest to environmental regulators (McCleskey, 2012). The model was supported by newly performed conductivity measurements of electrolyte solutions for which the SC had been measured over 5 to 90°C, concentrations from 10^{-4} to 1 mol/kg, and a pH range of 1.02 to 12.4 (McCleskey, 2011). The difference between measured and predicted SC for individual electrolytes used in this study was 0.1%, an improvement over previously used conductivity measurements that had a difference of 0.2% (McCleskey, 2011). The new method also overcame the previous limitation of correction factors for speciation by using speciation software, WATEQ4F, to provide information regarding concentrations of specific compounds and ions present in the water (McCleskey, 2012).

McCleskey's predictive equations have been tested for a wide variety of raw waters, including seawater, pristine mountain water, acid mine drainage, and rivers affected by municipal wastewater, accurately predicting the SC within 7.5% in 99% of instances (McCleskey, 2012). The wide range of potential applications for these equations makes it important to consider their compatibility with other modeling software.

Ion Exchange

Ion exchange is a well-established treatment technique during which an undesirable contaminant is removed from water and replaced with another, less objectionable ion (NHDES, 2009). Although ion exchange does not necessarily reduce TDS, it is possible that ion exchange could be used to reduce specific conductance because each ion contributes to the overall conductivity differently (McCleskey, 2012). Additionally, the selectivity of this technology would allow for mining sites to target specific ions (Wang, 2005), allowing them to meet discharge limits for individual ions that have been shown to negatively impact stream life, even if the overall SC limit could not be attained (EPA, 2011b).

To regenerate a cation exchange resin, the resin, which has negative functional groups built into its structure, is submerged into a regenerant solution containing a high concentration of weak positive ions, most often hydrogen or sodium. The inherent negative charge of the resin attracts the weak positive ions from the solution, and keeps them there in order to achieve a net charge of zero within the resin. The inverse is true for anion exchangers, which have a positively charged resin that has been exposed to a weak negative ion, most often hydroxide or chloride. When fresh resin is exposed to feed water, the stronger ions in the feed water replace the weaker ions already on the media. The initial exchange of ions occurs at the surface of the beads; however, the ions on the surface will eventually diffuse toward the center of the resin beads. After all the regenerant ions are replaced, the resin is "spent" and must be regenerated again (Bowell 2004). The regeneration process is shown in Equations 2.5 and 2.6.

Cation Softening Resin
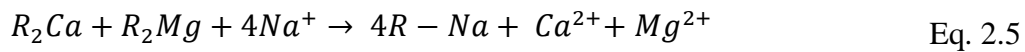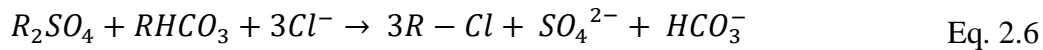
$$R_2Ca + R_2Mg + 4Na^+ \rightarrow 4R - Na + Ca^{2+} + Mg^{2+} \qquad \text{Eq. 2.5}$$

Anion Softening Resin

$$R_2SO_4 + RHCO_3 + 3Cl^- \rightarrow 3R - Cl + SO_4^{2-} + HCO_3^- \qquad \text{Eq. 2.6}$$

In these examples, the ions on the resin (R) that had been removed from the feed water are replaced by either sodium or chloride.

Ion exchange has been used in a wide variety of situations, such as desalination of brackish waters (Pless, 2006; Prajapati, 1985), treatment of nanofiltration and RO concentrates (Comstock, 2011), and softening of very hard water (Apell and Boyer, 2010; Comstock, 2011). Although ion exchange is typically installed as a fixed column (Apell and Boyer, 2010; NHDES, 2009), batch reactors are well suited to small water volumes, are able to equilibrate quickly, and provide more consistent results than fixed columns (Li and Yang, 2015; Wang, 2005). In a study investigating nitrite adsorption, uptake occurred

quickly, with equilibrium being reached in a batch reactor after only 40 minutes (Li and Yang, 2015). Another study targeting more similar contaminants to sites in central Appalachia more conservative, allowed batch reactors to equilibrate over the course of two days on a shaker table. This study later determined that equilibrium occurred in less than 24 hours (Indarawis and Boyer, 2013).

If treatment of influent water is meant to remove both cations and anions with ion exchange, reactors are traditionally configured in series, with the effluent of a cation removal column becoming the influent of an anion exchange column or vice versa (Pless, 2006; Wang 2005). In a study using brackish water, one simulated (TDS = 2,222 mg/L) and one natural (TDS = 11,000 mg/L), it was possible to decrease the TDS of both waters below 1,00 mg/L. In this instance, the natural water TDS was 600 mg/L post-treatment and the simulated water was reduced to a TDS of 25 mg/L; however, the effluent pH was acidic (pH = 5.7) and treatment times were slow, taking 25 minutes to treat 100 mL of sample water. Treatment in these reactors was also augmented with lime as a pretreatment to remove scaling minerals that could clog the ion exchange media, although this was ineffective when the water hardness was associated with Cl^- and SO_4^{2-} instead of carbonate (Pless, 2006)

A concern specific to the water considered in this study is that high calcium, magnesium, and sulfate concentrations will exhaust the resins very quickly. It has been demonstrated that using ion exchange for water with high levels of TDS retains ions more poorly than when treating lower TDS waters (Comstock, 2011; Prajapati, 1985). Figure 2.2 shows leakage of cations from ion exchange media vs TDS of influent water. The flow rate of both experimental series in Figure 2.2 is 30 L/hour and the media used exchanges hydrogen ions. The TDS of influent water in both Series A and Series B is 750 mg/L; however, Series A has sodium as 30% of total influent cations and Series B has sodium as 40% of the total influent cations. The increase in leakage with higher sodium concentrations is likely due to the low affinity of most ion exchange media for sodium.
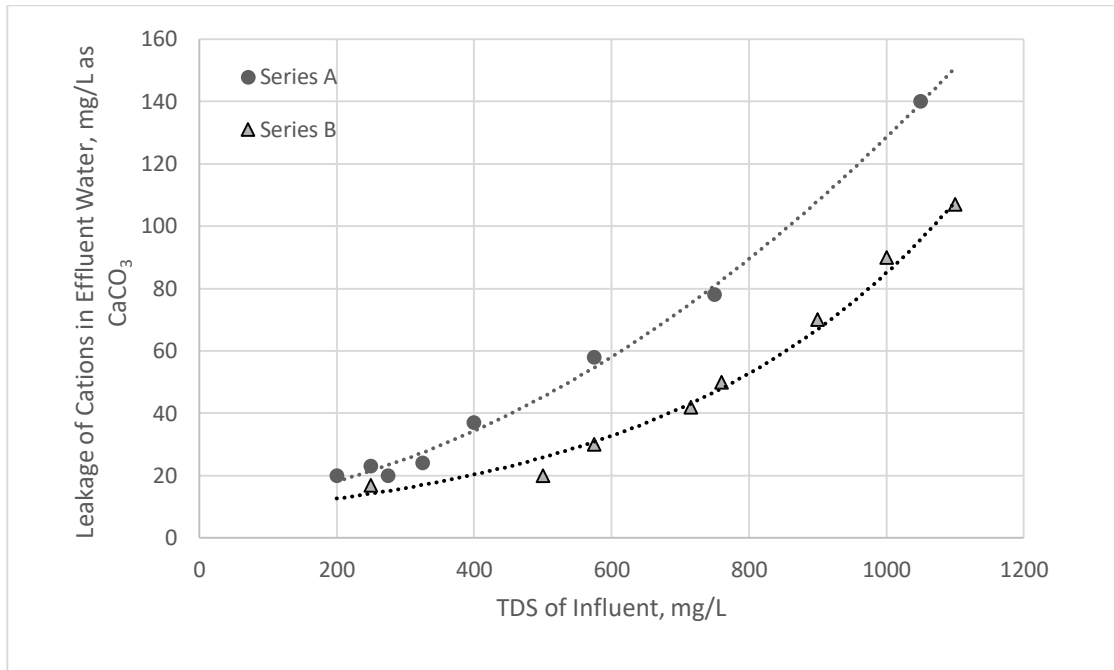
Figure 2.2: Effect of TDS on Cation retention (Modified from Prajapati, 1985)

Pretreatment, such as filtration, may be necessary after precipitation events to prolong the life of ion exchange resins and reduce head loss and fouling (NHDES, 2009; EPA, 2014). Clogged resins are very difficult to clean due to their small pore size and generally must be replaced, because that is the simplest and most economical way to remedy a clogged resin (EPA, 2014). The increased maintenance and cost associated with backwashing a pretreatment step would pose a significant inconvenience at remote mining sites.

A more recently studied option for ion exchange is combined treatment, during which cation and anion exchange resins are mixed within the same reactor (Apell and Boyer, 2010; Indarawis and Boyer, 2013). Combining ion exchange media within one reactor allows for a smaller footprint, as well as reduced need for regenerant solution and disposal (Apell and Boyer, 2010). In a study investigating the removal of HCO_3^-, SO_4^{2-}. Ca^{2+}, and Mg^{2+}, combined treatment was shown to be as, or more, effective than treatment

in series. This was potentially aided by the reduced precipitation of $CaCO_3$ and scaling of media seen in combined reactors due to the simultaneous removal of calcium and bicarbonate (Indarawis and Boyer, 2013).

Chemical Softening

Hardness, or the concentration of dissolved multivalent cations in water, usually calcium and magnesium, is typically viewed as an exclusively aesthetic issue for water quality (NHDES, 2008; USGS, 2016; Wang, 2005). In the case of valley fill runoff waters, however, these components are present in very high concentrations and are major components of the overall SC (EPA, 2011a, b; Clark, 2015; Timpano, 2015; Pond et al. 2008). For example, calcium and bicarbonate, which can be removed by softening, account for 39% of the TDS in affected Appalachian streams (Timpano et al. 2010).

Chemical softening is a highly effective treatment process for the removal of calcium and magnesium from hard waters (Mohammadesmaeili, 2010; Wang, 2005). The most appropriate softening process for the affected streams is excess lime-soda softening because calcium and magnesium concentrations are both high, but carbonate hardness is relatively low (Comstock, 2011; Mohammadesmaeili, 2010; Timpano et al., 2010; Edzwald, 2011). Addition of soda ash (Na_2CO_3) is necessary for the waters being treated because of the high proportion of non-carbonate anions in the runoff water (Davis and Cornwell, 2013).

Excess lime is often used in treatment plants for two reasons: to ensure that precipitation occurs expeditiously (Davis and Cornwell, 2013), as well as to raise the pH above 11 for magnesium removal (Jones, 2005). Two stage softening was determined to be most promising for SC reduction because it encourages additional precipitation of $CaCO_3$ (Wang et al, 2005). Figure 2.3 shows a schematic of the process for excess lime-soda softening with two stage recarbonation (Edzwald, 2011). Two stage recarbonation allows for additional recovery of $CaCO_3$, which ultimately translates into a lower effluent TDS (Edzwald, 2011; Wang, 2005).
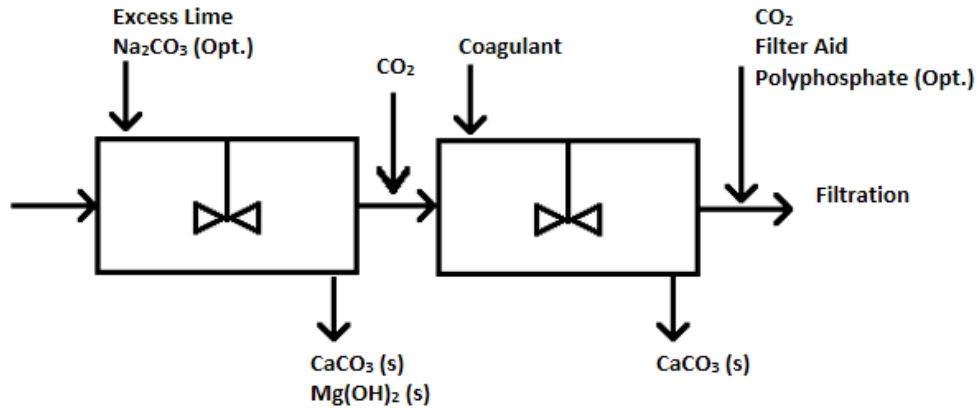
Figure 2.3: Excess Lime-Soda Softening, modified from Edzwald 2011

Chemical dosing for excess lime-soda softening has four primary components: calcium carbonate hardness (CCH), calcium non-carbonate hardness (CNCH), magnesium carbonate hardness (MCH), and magnesium non-carbonate hardness (MNCH). CCH is equivalent to the alkalinity in most cases; if the concentration of alkalinity exceeds that of the calcium and there is magnesium in the water, there will also be MCH. If there is more calcium than alkalinity, the water will have CNCH, which will be the concentration of calcium minus the alkalinity in the water. In the case that there is no MCH, the MNCH will simply be the concentration of magnesium in the water. If there is MCH, the MNCH is the magnesium concentration minus the MCH. If there is CNCH, the water will only have MNCH and no MCH because alkalinity precipitates as $CaCO_3$ with calcium. Lime dosing is related to CCH and MNCH, while soda addition is related to CNCH and MNCH. To determine chemical doses, one meq of chemical should be added per meq of target ion (CNCH, CCH, MNCH), with an additional 1.25 meq/L of lime added to expedite precipitation. (Davis and Cornwall, 2013).

As a process, softening is known for producing a significant amount of sludge, at volumes of 10% to 15% of the treated water volume (Wang, 2005). Sludge collection, storage, and dewatering may pose a challenge for mining sites with receiving streams in remote locations. Softening sludge compacts easily and is typically between 15% and 25%

14

solids (Wang, 2005). Flocculation and dewatering with lime-soda softening is also known to be a challenge due to the presence of $Mg(OH)_2$ in the precipitate (Corrigan et al., 2005). Magnesium hydroxide floc is extremely hydrophilic, tends to be gelatinous, and also tends to be difficult to flocculate due to its positive electromobility (Black and Christman, 1961). These factors make settling and dewatering of sludge containing $Mg(OH)_2$ more difficult than the disposal of $CaCO_3$ alone.

Softening has been used as an effective treatment for waters with higher TDS than those typically found in valley fill runoff, such as concentrates from RO (Comstock, 2011; Gabelich, 2011; Mohammadesmaeili, 2010). Lime softening successfully reduced Ca^{2+} by 69-74% a RO concentrate with a low alkalinity. It also reduced SO_4^{2-} concentrations by 0%-14%, and Mg^{2+} by 67%-98%, with higher Mg^{2+} removals occurring at a pH above 11 (Comstock, 2011). Calcium removal was greatly increased (93-99%) by lime-soda softening in the same study (Comstock 2011).

In another study focusing on high TDS waters treated with lime-soda softening, Mg^{2+} was decreased to below detection limits, while Ca^{2+} concentrations were reduced by approximately 99%, to only 5 mg/L. During that portion of the study, sulfate data were also provided. As expected, it showed that traditional lime-soda softening did not affect sulfate concentrations. Traditional lime-soda softening for high sulfate waters was also investigated in the study; a high sulfate concentration did not affect the precipitation of $CaCO_3$ or $Mg(OH)_2$ during softening. (Mohammadesmaeili, 2010)

The Cost Effective Sulfate Removal (CESR) Process

The CESR process, which targets sulfate as well as calcium and magnesium, was developed in the 1990's by European engineers (Reinsel, 2015). The process has been used in over twenty, full-scale treatment plants in Europe, but has not yet achieved widespread use in the United States (APEX Engineering, 2016; Lorax, 2003). This innovative process can achieve effluent sulfate levels of less than 100 mg/L, and unlike conventionally used

processes such as RO and ion exchange, does not create large volumes of liquid waste (i.e. regenerant, RO concentrate) that require disposal (Water Online, 2016).

In one case study for the CESR process at Berkeley Pit, an acid mine site in Butte, Montana, the process successfully reduced sulfate from a concentration of 8,700 mg/L to an effluent concentration of 56 mg/L. The average cost was determined to be $0.79/m^3 of treated water to remove 1,500 mg/L of SO_4^{2-}, with an upper cost of $1.58/m^3 (Lorax, 2003). In another case study, the CESR process was used to treat a copper mine wastewater with an initial sulfate concentration of 3,350 mg/L. The retention time in each reactor during this case study was short, so the effluent from this mine had a sulfate concentration of 360 mg/L (Water Online, 2016).

In Stage I of the CESR Process, gypsum ($CaSO_4$) precipitates to its solubility limit of 2,000 mg/L. This is done by raising the pH of the water to 10.5 with hydrated lime and stirring the mixture for 40 minutes at 100 rpm in a jar stirrer (Reinsel, 2015). Equation 2.7 shows the $CaSO_4$ precipitation process.
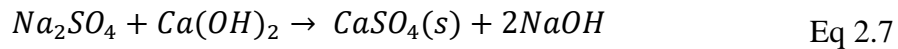
$$Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4(s) + 2NaOH$$
Eq 2.7

The jar stirrer is then adjusted to 20 rpm, and 2 mg/L polymer is added. This rate of stirring is continued for a minimum of five minutes to promote flocculation. The stirrer is then turned off and the precipitate is allowed to settle. The gypsum precipitate is removed before Stage II because the reagent in Stage II will not work if gypsum is present in the water (Reinsel, 2015)

After removing the gypsum in Stage I, additional lime is added to the water to increase the pH to 11.3. The reagent, Luminite MG-4, is then added at a concentration of 1.0-1.5 times the concentration of sulfate in the water. During the process, the pH will decrease as sulfate precipitates, and it is necessary to ensure the pH remains near 11.3. If the pH decreases below 11.0, the reaction will stop; however, if the pH is above 12, the reaction may reverse. When the pH stops decreasing, the removal of sulfate has been

reached and Stage II is complete. As in Stage I, 2 ppm of the polymer, Magnafloc 155, is added to the reactor and stirred for a minimum of five minutes. Following this step, the water is separated from the floc, recarbonated to a neutral pH, and ready for discharge. A schematic of the overall CESR Process may be found in Figure 2.4. (Reinsel, 2015)
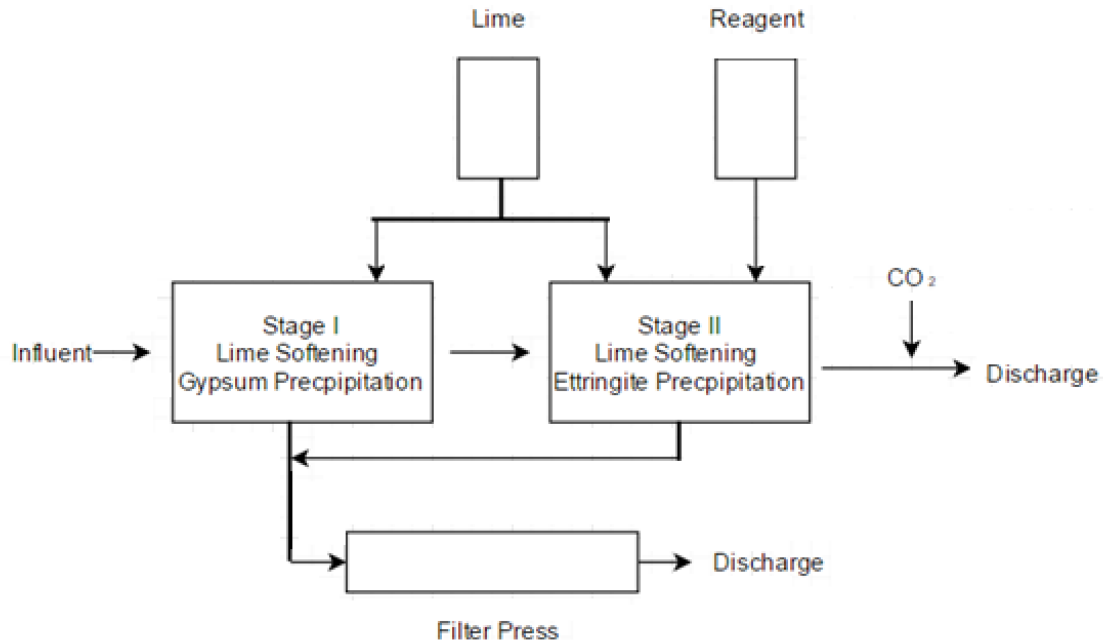
Figure 2.4: CESR Process Diagram

The precipitate from the CESR process is a unique calcium-alumina-sulfate compound known as ettringite ($3CaO•Al_2O_3•3CaSO_4•3H_2O$) (PSA, 2001). Ettringite has a polishing effect on the water, reducing concentrations of metals such as chromium, arsenic, and selenium, as well as removing up to a third of the chloride and nitrate in the water. Furthermore, ettringite can be disposed of as non-hazardous waste. A disadvantage of the ettringite is that large amounts of ettringite sludge are produced in Stage II, approximately 45 lbs. of dry sludge per 1,000 gallons of water treated (Water Online, 2016)

It is important to dose the water in Stage II with an appropriate amount of reagent. Although the reagent (Luminite MG-4) is inexpensive and costs approximately \$0.40/lb, it contains aluminum (Robert, 2016), which would be discharged with the process effluent if

excess reagent is added to the reactor. The discharge of aluminum should be avoided because aluminum can cause pulmonary and developmental problems in fish and benthic organisms that breathe using gills. The most notable sign of aluminum toxicity is an inability of the animal to regulate osmosis (EPA, 2016; Rosseland, 1990). Although aluminum is insoluble in water (Cornell, 1999), its solubility increases as pH decreases or increases, creating a greater likelihood that toxicity will occur at a lower pH (EPA, 2016). Furthermore, aluminum that has precipitated into the soil can enter the food chain through plants (Rosseland, 1990), so a treatment train component should be included during or following recarbonation to avoid the discharge of precipitated aluminum into the environment.

Literature Cited

Apell, JN. 2010. *Combined Ion Exchange Treatment for removal of dissolved organic matter and hardness.* Water Research 44 (2010) 2419-2430.

APEX Engineering. 2016. *CESR Process for Sulfate Removal*. Available online at http://www.apexengineering.us/CESR-Sulfate-Removal.html; Last accessed Jan. 17, 2017.

Black, A.P. and Christman, R.F. Jour. AWWA, 1961, 53:737

Bockris, JO'M and Reddy, AKN. 1998. *Modern Electrochemistry Vol. 1: Ionics.* Plenum Press: New York.

Boehme EA, Zipper CE, Schoenholtz SH, Soucek DJ, Timpano AJ. 2016. *Temporal dynamics of benthic macroinvertebrate communities and their response to elevated specific conductance in Appalachian coalfield headwater streams.* Ecol Indic 64:171–180.

Bowell, RJ. 2004. *A review of sulphate removal options for mine waters*. Proc., International Mine Water Association Symposium. Newcastle upon Tyne, England.

Ciaccio, L. *Water and Water Pollution Handbook*. Marcel Dekker, Inc. New York, 1971.

Clark EV, Greer BM, Zipper, CE, Hester, ET. 2016. *Specific conductance–stage relationships in Appalachian valley fill streams.* Environ Earth Sci 75:1222.

Comstock, S.E.H.; Boyer, T.H.; Graf, K.C. 2011. *Treatment of nanofiltration and reverse osmosis concentrates: comparison of precipitative softening, coagulation, and anion exchange.* Water Research 45 (2011) 4855–4865.

Cormier, SM; Suter, GW; and Zheng, L. 2013. *Derivation of a Benchmark for Freshwater Ionic Strength*. Environmental Toxicology and Chemistry, Vol. 32, No. 2, pp. 263-271.

Daniels WL, Zipper CE, Orndorff CW, Skousen JG, Barton CD, McDonald L, Beck M. 2016. *Predicting total dissolved solids release from central Appalachian coal mine spoils*. Environ Pollut 216:371–379

Davis and Cornwell. *Introduction to Environmental Engineering, Fifth Edition.* McGraw-Hill: New York. 2013.

Edzwald, J.K. 2011. *Water Quality and Treatment: A handbook on Drinking Water* (Sixth

Edition). American Water Works Association, American Society of Civil Engineers, McGraw-Hill: New York.

EPA, Region 5. 2016. *Ecological Toxicity Information*. Available online at https://archive.epa.gov/reg5sfun/ecology/web/html/toxprofiles.html; Last accessed Jan. 17, 2017.

EPA. 2014. Reference Guide to Treatment Technologies for Mining-Influenced Wastewater. EPA 542-R-14-001. Available from: www2.epa.gov/sites/production/files/2015-08/documents/reference_guide_to_treatment_technologies_for_miw.pdf (September, 2015).

EPA. 2011a. *The effects of mountaintop mines and valley fills on aquatic ecosystems of the central Appalachian coalfields*. U.S. Environmental Protection Agency, Washington, DC, EPA/ 600/R-09/138F.

EPA. 2011b. *A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams (Final Report)*. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-10/023F.

EPA. 2000. Wastewater Technology Factsheet – Chemical Precipitation. EPA 832-F-00-018. Available from: http://permanent.access.gpo.gov/websites/epagov/www.epa.gov/OWM/mtb/chemical_precipitation.pdf (September, 2015).

Evans, DM; Zipper, CE; Donovan, PF; and Daniels, WL. 2014. *Long Term Trends of Specific Conductance in Waters Discharged By Coal-Mine Valley Fills in Central Appalachia, USA*. Journal of the American Water Resources Association. Vol. 50, No. 6.

Faust, S.D. and Aly, O.M., 1998. Chemistry of Water Treatment. Ann Arbor Press, Chelsea, MI, p. 329.

Gabelich, CJ; Rahrdianto, A; Northrup, CR; Yun, TI; and Cohen, Y. 2011. *Process Evaluation of intermediate chemical demineralization for water recovery enhancement in production-scale brackish water desalting.* Desalination 272 (2011) 36-45.

Gottlieb, MC 2005. Chapter 12: Ion Exchange Applications in Water Treatment Plant

Design, 4th ed. New York: McGraw Hill

Griffith, RA and Jurinak, JJ. 1973. *Estimation of Activity Coefficients from the Electrical Conductivity of natural aquatic systems and soil extracts.* Soil Science 116, 26-30.

Griffith, MB; Norton, SB; Alexander, SC; Pollard, AI; and LeDuc, SC. 2012. *The effects of mountaintop mines and valley fills on the physicochemical quality of stream ecosystems in the central Appalachians: A review.* JScience of the Total Environment. 417-418 (2012) 1-12.

Gustafson, H and Behrman, S. 1939. *Determination of Total Dissolved Solids in water by electrical conductivity.* Ind Eng Chem Anal Ed. 11, 355

Jones, CS; Corrigan, TP; Graham, DB, and McMullen, LD. 2005. *Reduced Lime Feeds: Effects on Operational Costs and Water Quality.* Des Moines Water Works; Available online at: http://www.dmww.com/upl/documents/water-quality/lab-reports/lab-studies/reduced-lime-feeds-effects-on-operational-costs-and-water-quality.pdf. Last Accessed Jan 25, 2017.

Indarawis, KA and Boyer, TH. 2013. *Superposition of Anion and cation exchange for removal of natural water ions.* Separation and Purification Technology 118 (2013) 112-119.

Li, Haigang and Yang, Chuanfang. 2015. *Nitrite removal using ion exchange resin: Batch vs. Fixed bed performance.* Separation Science and Technology, 50:11, 1721-1730, DOI: 10.1080/01496395.2014.990099.

McCleskey, RB; Nordstrom, DK; Ryan, JN; Ball, JW. 2012. *A new method of calculating electrical conductivity with applications to natural waters.* Geochimica et Cosmochimica Acta 77 (2012) 369-382.

Miller, RL; Bradford, WL; and Peters, NE. 1988. *Specific Conductance: Theoretical Considerations and Application to Analytical Quality Control.* U.S. Geological Survey Water-Supply Paper 2311. Available online at: https://pubs.usgs.gov/wsp/2311/report.pdf; Accessed Jan. 20 2017.

Mohammadesmaeili, F., Badr, M.K., Abbaszadegan, M., Fox, P., 2010. Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment. Water Environment Research 82, 342e350.

NHDES (New Hampshire Department of Environmental Services). 2009. *Environmental*

Fact Sheet: Ion Exchange Treatment of Drinking Water. Available from: http://www.des.nh.gov/organization/commissioner/pip/factsheets/dwgb/documents/dwgb-2-12.pdf. (September, 2009).

NHDES (New Hampshire Department of Environmental Services). 2008. *Environmental Fact Sheet: Hardness in Drinking Water.* Available from: http://www.des.nh.gov/organization/commissioner/pip/factsheets/dwgb/documents/dwgb-3-6.pdf. (October, 2008).

Pawlowicz, R. 2008. *Calculating the conductivity of natural waters.* Limnol Oceanogr Meth 6, 489-501.

Ponnamperuma, FN; Tianco, EM and Loy, TA. 1966. *Ionic Strengths of the solutions of flooded soils and other natural aqueous solutions from Specific Conductance.* Soil Science 102, 408-413.

Pond GJ, Passmore ME, Pointon ND, Felbinger JK, Walker CA, Krock KJ, Fulton JB, Nash WL. 2014. *Long-term impacts on macroinvertebrates downstream of reclaimed mountaintop mining valley fills in central Appalachia.* Environ Manag 54:919–933.

Portland Cement Association (PSA). 2001. *Concrete information: Ettringite Formation and the Performance of Concrete.* Available online at http://www.cement.org/docs/default-source/fc_concrete_technology/is417-ettringite-formation-and-the-performance-of-concrete.pdf?sfvrsn=2; Last accessed Jan. 20, 2017.

Prajapati, MN; Gaur, PM; and Dasare, BD. 1985. *Brackish water desalination by a continuous counter-current ion-exchange technique.* Desalination, 52 (1985) 317-326.

Reinsel, M. personal communication, Nov. 20. 2015.

Reinsel, M. 2015. *Sulfate Removal Technologies: A Review.* Available online at http://www.wateronline.com/doc/sulfate-removal-technologies-a-review-0001; Last accessed Jan. 17, 2017.

S.E.H. Comstock, T.H. Boyer, K.C. Graf. 2011. *Treatment of nanofiltration and reverse osmosis concentrates: comparison of precipitative softening, coagulation, and anion exchange.* Water Research 45 (2011) 4855–4865.

Singh, T and Kalra, YP. 1974. *Specific Conductance Method for In Situ Estimation of Total*

Dissolved Solids. American Water Works Association. Available online at http://www.jstor.org.ezproxy.lib.vt.edu/stable/pdf/41268134.pdf; Last accessed online Jan. 20, 2017.

Stacy, Robert, personal communication, Feb. 18, 2016.

Timpano AJ, Schoenholtz SH, Zipper CE, Soucek DJ (2010) *Isolating effects of total dissolved solids on aquatic life in central Appalachian coalfield streams*. In: Proceedings, national meeting of the American society of mining and reclamation, Pittsburgh, PA, pp 1284–1302.

Timpano AJ, Schoenholtz SH, Soucek DJ, Zipper CE. 2015. *Salinity as a limiting factor for biological condition in mining-influenced Central Appalachian headwater streams*. J Am Water Resour Assoc 51:240–250.

USGS (United States Geological Survey). 2016. *The USGS Water Science School: Water Hardness.* Available at https://water.usgs.gov/edu/hardness.html. Last Accessed Jan 20, 2017.

Visconti Reluy, F; de Paz Bécares, JM; Zapata Hernández, RD; and Sánchez Díaz, J. 2004. *Development of an equation to relate electrical conductivity to soil and water salinity in a Mediterranean agricultural environment.* Australian Journal of Soil Research, 2004, 42, 381-388.

Wang, LK; Hung, YT; and Shammas, NK. 2005. *Phisiochemical Treatment Processes.* Handbook of Environmental Engineering Volume 3. Humana Press: New Jersey.

Water Online. 2016. *A New Process For Sulfate Removal From Industrial Waters*. Available online at http://www.wateronline.com/doc/a-new-process-for-sulfate-removal-from-indust-0001; Last accessed Jan. 17, 2017.

Zipper CE, Burger JA, McGrath JM, Rodrigue JA, Holtzman GI. 2011. *Forest restoration potentials of coal-mined lands in the eastern United States*. J Environ Qual 40:1567–1577.

Chapter 3: MINEQL+ for Conductivity Modeling

Authors: Catherine Grey, Gregory Boardman, Jeffrey Parks, and Zachary Kemak

<u>Introduction</u>

For decades, researchers have struggled to accurately model the relationship between total dissolved solids (TDS) and specific conductance (SC) (Gustafson and Behrman, 1939). In early attempts, investigators measured each water quality parameter separately, determined a tailored conversion factor, and then used the empirically derived constant as a multiplier to determine TDS from the more easily measured SC (Visconti, 2004). Later models became more sophisticated, moving away from predicting TDS from SC, and instead predicted SC from TDS using the ionic strength of the solution (Ponnamperuma, 1966; Griffin and Jurinak, 1973). The equation for ionic strength is given in Equation 3.1 (McCleskey, 2012; Visconti, 2004).

$$I = \frac{1}{2}\sum_i |z|_i^2 C_i \qquad \text{Eq. 3.1}$$

Near the turn of the century, researchers turned to a theoretical model using ion transport theory as a component of SC prediction (Visconti, 2004). In 1998, a model of this type was developed that summed the contribution of individual ions to the overall electrical conductance (EC), which could then be corrected for temperature to 25 ºC to find the SC (Bockris and Reddy, 1998). Equation 3.2 is used to find the EC of an individual ion, with F being the Faraday's constant and u_i being the limiting equivalent ionic mobility (mS-cm^2-mol/(eq-C)).

$$\sigma_i = 10^{-6}|z|_i F C_i u_i \qquad \text{Eq. 3.2}$$

The overall EC could then be found using Equation 2.3.

$$EC = \sum_i \sigma_i \qquad \text{Eq. 3.3}$$

Simplifying, Equation 3.2 could be substituted into Equation 3.3 in order to calculate the EC more directly (Equation 3.4).

$$EC = 10^{-6}F \sum_i |z|_i C_i u_i$$

<div align="right">Eq. 3.4</div>

Finally, the EC could be corrected to 25°C using a linear, temperature-based correction factor to determine the SC.

The early models for SC modeling laid the groundwork for the equations used in this study but struggled to model SC successfully for dissimilar waters and waters with different ionic strengths. This is due to the dependence of early models on correction factors for speciation that were tailor-made for the water being studied (USGS, 1988). This inability to model waters with ion pairs, or a pair of oppositely charged ions held together by Coulombic attraction instead of a covalent bond, was a serious limitation for widespread use of the models (Visconti, 2004).

Another challenge with the equations historically used was that they did not successfully model SC in low to medium SC waters (McCleskey, 2012). Most models developed before the McCleskey equations were published in 2012 were best suited for modeling waters with a higher ionic strength, such as brackish and saline waters or industrial effluent. (McCleskey, 2012; USGS, 1988). There was also a lack of information regarding the conductivity data for electrolytes typically found in natural systems, in regards to the variety of ions, ion pairs, and trace metals, and with respect to ranges of pH, temperature, and ionic strength (McCleskey, 2011; Pawlowicz, 2008).

In 2012, a set of empirical equations (Table 3.1) was published by R. B. McCleskey that predicted the SC contribution from ions, ion pairs, and trace metals commonly found in natural waters (McCleskey, 2012). The model was supported by conductivity measurements of electrolyte solutions for which the SC had been measured over 5 to 90 °C, concentrations from 10^{-4} to 1 mol/kg, and a pH range of 1.02 to 12.4 (McCleskey,

2011). The difference between measured and predicted SC for individual electrolytes used in this study was 0.1%, an improvement over previously used conductivity measurements that had a difference of 0.2% (McCleskey, 2011). The new method also overcame the previous limitation of correction factors for speciation by using the software, WATEQ4F, to provide information regarding concentrations of specific compounds and ions present in the water (McCleskey, 2012).

McCleskey's predictive equations have been tested for a wide variety of raw waters, including seawater, pristine mountain water, acid mine drainage, and rivers affected by municipal wastewater. The equations accurately predicted the SC within 7.5%, in 99% of the cases (McCleskey, 2012). Due to the wide range of potential applications for these equations, it important to understand if they can be used with other chemical modeling software. With this in mind, the objectives of this study were to:

1. Verify use of McCleskey's equations over the range of ionic strength seen in the waters of this project.
2. **Determine the ability of MINEQL+ to be used with McCleskey's equations through a comparison of predicted and measured SC.**

Methods and Materials

Analysis of Samples

Temperature and specific conductance measurements were made with an Omega meter (CDH-SD1 Meter). A pH meter (Oakton, pH 110 series with RS 232) was used to measure pH. Mass of chemicals was measured using an Entris Analytical scale (Sartorius Corp).

Principles of McCleskey's Prediction Model

To use McCleskey's equations, four parameters are needed from the sample water: pH, water temperature, and concentrations of all dissolved elements. These data are entered into speciation software, which will generate the types and concentrations of every ion and ion pair present in the water. With the knowledge of which dissolved compounds are present in the water, the user may calculate the individual SC of each solution. This can be done using a set of empirical equations generated by McCleskey for each ion or ion pair, found in Table 3.1. It is necessary to calculate three values to find the individual conductivity for any ion or compound in the water: $\lambda^0(T)$, A(T), and B(T).

Table 3.1: SC Modeling Equations (Modified from McCleskey, 2012)

Ion	λ^0	A	B
K^+	$0.003046T^2 + 1.261\ T + 40.70$	$0.00535T^2 + 0.9316T + 22.59$	1.5
Na^+	$0.003763T^2 + 0.8770\ T + 26.23$	$0.00027T^2 + 1.141T + 32.07$	1.7
H+	$-0.01414T^2 + 5.355T + 224.2$	$-0.000918T^2 + 1.842 + 39.23$	0.3
Ca^{2+}	$0.009645T^2 + 1.984T + 62.28$	$0.03174T^2 + 2.334\ T + 132.3$	2.8
Mg^{2+}	$0.01068T^2 + 1.695T + 57.16$	$0.02453T^2 + 1.915T + 80.50$	2.1
SO_4^{2-}	$0.01037T^2 + 2.838T + 82.37$	$0.03324T^2 + 5.889T + 193.5$	2.6
CO_3^{2-}	$-0.000326T^2 + 2.998T + 64.03$	$-0.00181T^2 + 5.542T + 120.2$	2.3
HCO_3^-	$0.000614T^2 + 0.9048T + 21.14$	$-0.00503T^2 + 0.8957T + 10.97$	0.1
NO_3^-	$0.001925T^2 + 1.214T + 39.90$	$0.00118T^2 + 0.5045T + 23.31$	0.1
OH^-	$0.003396T^2 + 2.925T + 121.3$	$0.00933T^2 + 0.1086T + 35.90$	0.0
$NaSO_4^-$	$0.002309T^2 + 5.459T + 219.2$	$0.01454T^2 + 5.193T + 253.6$	0.5
HSO_4^-	$0.000927T^2 + 0.8337T + 29.56$	$0.02887T^2 + 0.8730T + 36.25$	7.0
$NaCO_3^-$	$0.00336T^2 + 3.845T + 89.51$	$0.00061T^2 + 6.38T + 141.7$	2.0

After calculating the values for $\lambda^0(T)$, A(T), and B(T), as well as the overall ionic strength, the SC of an individual component may be found using Equation 2.5 (McCleskey, 2012).

$$\lambda_i = \lambda^o(T) - \frac{A(T)I^{1/2}}{1 + B\,I^{1/2}}$$

Eq. 3.5

When all λ_i values are known, the overall SC of the solution may be predicted by summing the product of the SC of individual components (λ_i) and the concentration of each compound (m_i), which was generated in step one using the speciation software. Equation 3.6 shows this process of finding SC_P, the predicted SC of the solution.

$$SC_P = \sum_i \lambda_i \, m_i$$

Eq. 3.6

McCleskey's model may be used for ionic strengths between 0.0004 and 0.7 mol/kg (m), temperatures between 0 °C and 95 °C, pH between 1.0 and 10.0, and an SC between 30 and 70,000 µS/cm. The upper limit of ionic strength here is the ionic strength of seawater, which is also 0.7 m (Murray, 2004). In the original study, the relationship between the measured SC (SC_M) and the SC_P results generated using m_i values from WATEQ4F was excellent. The R^2 values for all solutions were above 0.88, and 98% of the R^2 values were greater than 0.92 (McCleskey, 2012).

Experimental Setup

Synthetic waters were generated with eight compounds: sodium bicarbonate ($NaHCO_3$), potassium nitrate (KNO_3), magnesium sulfate ($MgSO_4$), potassium sulfate (K_2SO_4), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), sodium sulfate (Na_2SO_4), potassium chloride (KCl), and sodium chloride (NaCl). A solution for each compound was generated at six molalities (m): 0.0001, 0.001, 0.01, 0.1, 0.2, and 0.5 m. Molality was used in the original experiments and therefore was also used during these experiments. The temperature, pH, and SC_M of each solution was measured. Masses of dry chemicals for each molecule were weighed and then added to 1 L of nanopure water to create a solution at each molality.

After measuring all necessary parameters, the speciation information for each solution was generated using MINEQL+. Information from MINEQL+, regarding the composition of dissolved substances in the water, was used to calculate $\lambda^0(T)$, A(T), and

B(T), which were then used along with the calculated ionic strength to find the λ_i for each species in solution. The λ_i for each compound was multiplied by the m_i value generated by MINEQL+ and all values were summed to determine the SC_P. This value was compared to the SC_M, and the percent difference was determined.

Statistical Analysis

The percent difference between SC_M and SC_P was the primary method of assessing the effectiveness of MINEQL+ in modeling SC for the predictive equations. The percent difference was calculated using Equation 3.7.

$$\%_{diff} = \left(\frac{SC_M - SC_P}{SC_M}\right) * 100\%$$

Eq. 3.7

A percent difference of 5% or below was desired, but a difference of 10%-15% may be acceptable depending on the desired application.

Results

For all waters tested, the temperature was approximately 22 °C. The pH of five solutions (KNO_3, K_2SO_4, $CaCl_2 \cdot 2H_2O$, KCl, and $NaCl$) was in the range of 4.5 to 4.7 for the lowest molality (0.0001 m), and 5.7 for the highest molality (0.5 m). Three compounds behaved differently: $MgSO_4$ and $NaHCO_3$ solutions both had a pH around 6 for the lowest m and pH of 9 and 8, respectively, at the highest m; Na_2SO_4 had a pH of 5 at the lowest m and 8 at the highest m. The initial specific conductance of the waters is shown in Table 3.2. SC increased with m for all ions, with SC for the 10^{-4} m solutions being in the range of 10-30 µS/cm. The SC for the 10^{-3} m solutions increased to approximately 100-250 µS/cm. Solutions with molalities in the range of 0.01-0.5 m had SC values that were much higher, ranging from 1,000 to 30,000-70,000 µS/cm. Higher SC could not necessarily be related to the valence of ions in solution; the highest SC of 70,000 µS/cm was associated with $CaCl_2$, while the two lowest SC values were associated with $MgSO_4$ and $NaHCO_3$.

Table 3.2: Measured SC of Synthetic Waters

**Measured SC of Synthetic Waters [µS/cm]**								
Molality	**Na$_2$SO$_4$**	**KNO$_3$**	**CaCl$_2$**	**MgSO$_4$**	**NaHCO$_3$**	**KCl**	**NaCl**	**K$_2$SO$_4$**
0.0001	24	14	19	15	9	16	13	31
0.001	238	147	219	195	89	149	123	277
0.01	2,020	1,361	2,070	1,463	869	1,415	1,180	2,390
0.1	15,360	11,540	17,790	8,940	7,200	12,340	10,220	18,830
0.2	27,300	21,500	33,400	15,300	13,280	23,900	19,140	35,000
0.5	52,100	47,400	69,500	30,500	28,800	55,500	44,100	58,000

The predicted SC for each water is shown in Table 3.3. These values were calculated using the equations in Table 3.1, Eq. 3.5, and Eq. 3.6.

Table 3.3: Predicted SC of Synthetic Waters

**Predicted SC of Synthetic Waters [µS/cm]**								
Molality	**Na$_2$SO$_4$**	**KNO$_3$**	**CaCl$_2$**	**MgSO$_4$**	**NaHCO$_3$**	**KCl**	**NaCl**	**K$_2$SO$_4$**
0.0001	28	26	35	24	7	23	28	31
0.001	222	134	249	197	78	136	123	273
0.01	1,984	1,259	2,217	1,046	776	1,295	1,113	2,390
0.1	18,137	11,311	18,636	3,600	6,315	11,828	9,827	19,849
0.2	33,607	21,325	35,067	6,307	11,248	22,725	18,608	37,029
0.5	87,774	53,312	81,041	10,571	22,174	53,519	42,857	82,500

Using the information from these two tables, it was possible to calculate the percent difference between measured and calculated SC values (Table 3.4).

Molality	Na₂SO₄	KNO₃	CaCl₂	MgSO₄	NaHCO₃	KCl	NaCl	K₂SO₄
0.0001	13%	88%	82%	64%	16%	42%	121%	2%
0.001	7%	9%	14%	1%	12%	8%	0%	2%
0.01	2%	7%	7%	29%	11%	8%	6%	0%
0.1	18%	2%	5%	60%	12%	4%	4%	5%
0.2	23%	1%	5%	59%	15%	5%	3%	6%
0.5	68%	12%	17%	65%	23%	4%	3%	42%

Discussion

Overall, the percent difference values for SC_M and SC_P were very different for each solution. One of the most striking errors is seen in the row of Table 3.4 for 10^{-4} m, where five of the eight percent differences were greater than 20%. It is likely that the cause of this error was that the solution's ionic strength was outside the recommended ionic strength range recommended by McCleskey. Those solutions with a low m and high error had an ionic strength of 0.0001 m, while the lower threshold of ionic strength tested by McCleskey was 0.0004 m. Similarly, for the 0.5 molality solutions, four of the percent difference values were above 20%. This can be attributed to an ionic strength above the recommended limit of 0.7 m for two ion pairs: Na_2SO_4 had an ionic strength of 0.732 m and K_2SO_4 had an ionic strength of 0.695 m. For $NaHCO_3$ ($I = 0.399$ m), the cause of the disparity is unknown, although the percent difference for that compound was 23%, the lowest of any compound in that row. The $MgSO_4$ solution ($I = 0.287$ m) had a percent difference of 65% at that concentration; however, the percent differences for that compound were high in all instances.

Another trend shown in Table 3.4 is that percent differences tended to be smaller for ion pairs that included less elements and lower valences. For example, percent differences for NaCl and KCl were below 10% for all molalities measured, whereas the

31

percent difference for chemicals including more elements such as Na_2SO_4, $NaHCO_3$, and most notably, $MgSO_4$, were all much higher. The compound with the largest percent difference was $MgSO_4$, for which every percent difference, but one, was above 20%. Most were near 60%. It was at first hypothesized that the cause of this disparity was the tendency of $MgSO_4$ to absorb water from the air (UCLA, 2017). If not considered during preparation of the solution, the true concentration of $MgSO_4$ in the water would have been less than intended. However, the SC_P was far less than the SC_M for every measurement taken, indicating that the concentration in the water was higher than intended. The difference in SC_M and SC_P was seen even when the hydrated form of $MgSO_4$ was used.

There were limitations in this study, including the fact that replicates were not tested and not all of the ranges in pH, temperature, and chemical complexes of the original study were reproduced herein. However, the work does serve as a foundation for additional research and may reveal some issues with the robustness of the equations and/or the use of alternative chemical modeling software.

Conclusion

The results of this study demonstrated that use of McCleskey's equations with MINEQL+ did not totally replicate the percent differences between SC_P and SC_M seen by McCleskey when he used WATEQ4F. Certain percent differences were probably high in this study because solutions were not within the recommended ionic strengths; however, the overall percent differences within the recommended ionic strength range were higher than the 0.1% difference reported by McCleskey (2011) for synthetic waters. When compared to McCleskey's work in 2012 with more complex waters, the SC of certain waters synthesized for this study were within the accuracy of 12% achieved in his study, though several differences were above 20%. The highest percent differences of solutions within the ionic strength range of McCleskey's empirical equations were seen at 0.5 m and in tests with $MgSO_4$.

It is recommended that work be continued in this area to better evaluate how well MINEQL+ can be used in conjunction with McCleskey's equations. It may be necessary to make some adjustments in the equations when using different chemical modeling software. It is also important to understand why magnesium sulfate behaved differently than expected. Being able to predict SC based on an elemental analysis is certainly an important tool that will have widespread application in selecting treatment operations and will lead to an enhanced understanding of environmental impacts.

Acknowledgements

Literature Cited

Bockris, JO'M and Reddy, AKN. 1998. *Modern Electrochemistry Vol. 1: Ionics.* Plenum Press: New York.

Griffith, RA and Jurinak, JJ. 1973. *Estimation of Activity Coefficients from the Electrical Conductivity of natural aquatic systems and soil extracts.* Soil Science 116, 26-30.

Gustafson, H and Behrman, S. 1939. *Determination of Total Dissolved Solids in water by electrical conductivity.* Ind Eng Chem Anal Ed. 11, 355

McCleskey, RB; Nordstrom, DK; Ryan, JN; Ball, JW. 2012. *A new method of calculating electrical conductivity with applications to natural waters.* Geochimica et Cosmochimica Acta 77 (2012) 369-382.

Miller, RL; Bradford, WL; and Peters, NE. 1988. *Specific Conductance: Theoretical Considerations and Application to Analytical Quality Control.* U.S. Geological Survey Water-Supply Paper 2311. Available online at: https://pubs.usgs.gov/wsp/2311/report.pdf; Accessed Jan. 20 2017.

Murray, J.W. *Activity Scales and Activity Corrections.* University of Washington, Published October 2004.

Pawlowicz, R. 2008. *Calculating the conductivity of natural waters.* Limnol Oceanogr Meth 6, 489-501.

Ponnamperuma, FN; Tianco, EM and Loy, TA. 1966. *Ionic Strengths of the solutions of flooded soils and other natural aqueous solutions from Specific Conductance.* Soil Science 102, 408-413.

UCLA. 2017. *Drying Agents.* Available online at: http://www.chem.ucla.edu/~bacher/Specialtopics/Drying%20Agents.html. Last Accessed February 21, 2017.

Visconti Reluy, F; de Paz Bécares, JM; Zapata Hernández, RD; and Sánchez Díaz, J. 2004. *Development of an equation to relate electrical conductivity to soil and water salinity in a Mediterranean agricultural environment.* Australian Journal of Soil Research, 2004, 42, 381-388.

Chapter 4: Physicochemical Treatment Methods

Ion Exchange, Chemical Softening, and the Cost Effective Sulfate Removal Process for Specific Conductance Reduction

Authors: Catherine Grey, Gregory Boardman, Jeffrey Parks, and Zachary Kemak

Abstract

Coal mines in central Appalachia that dispose of mining spoils in valley fills have been identified as a contributor to elevated specific conductance (SC) in receiving streams. Runoff waters from these areas, which contain elevated levels of Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-}, have been shown to significantly impact the benthic organisms in receiving streams. Three physicochemical methods were used in this study to reduce the concentration of the primary ions of concern in waters from two strip mining sites in Southwest Virginia, Office Fill (OF) and Barton Hollow (BH). In experiments with ion exchange, the effluent SC from both cation and anion exchange reactors was higher than initial specific conductance. The SC of cation exchange effluent was approximately 2.5 times higher than initial values for both BH and OF, while the SC of anion exchange effluent was only about 20% - 40% higher than the initial SC for both sites. These results, in conjunction with the non-ideal conditions at many mining sites for use of ion exchange, would suggest that ion exchange not be used as a standalone treatment technique for SC reduction.

Excess lime-soda softening was also used to remove calcium and magnesium from the mining waters. The post-treatment SC was higher than the initial value, despite the greatly decreased calcium and magnesium concentrations, due to the increased sodium concentrations in the water from soda ash addition. This was attributed to the very low (<5%) carbonate hardness present in the source water. However, for sites with higher carbonate hardness, it may be possible to reduce SC using lime softening, alone. Sludge volumes from the process were about 15%-20% of the process water volume treated. In future studies, the feasibility of drying the sludge on-site, selling it as a soil amendment to raise alkalinity, and/or utilizing it on-site for land reclamation should be investigated.

The Cost Effective Sulfate Removal (CESR) Process was evaluated for use in reducing sulfate, calcium, and magnesium concentrations, which accounted for about 90% of the ions in water from the two sample sites. The process was shown to reduce SC from 2,500 and 1,500 µS/cm to or below the proposed EPA limit of 500 µS/cm. Under the best conditions tested, concentrations of sulfate, calcium, and magnesium, were reduced by 93%, 87%, and 99.9%, respectively, at OF, and 80%, 61%, and 99.7%, respectively, at BH.

Introduction

In 2011, the EPA issued a memorandum announcing new restrictions on specific conductance (SC) of runoff waters from surface mining sites in central Appalachia, most notably those using valley fills to dispose of waste rock from blasting (EPA, 2011a; EPA, 2011b). These rocks, which were often unweathered and small, have a high surface area that allows runoff water to strip select minerals from the rock, during and after a precipitation event (Clark, 2015; Evans, 2014). The high-conductivity runoff then enters receiving streams and reduces the number of benthic macroinvertebrates over time, disrupting the food chain (Boehme et al., 2015; Timpano et al., 2011; EPA 2011a). Effects of this runoff have been shown to continue, even 20-30 years after mining activities have ceased (Pond et al., 2014), creating a persistent problem for streams in over 12 million acres of land in Kentucky, Tennessee, Virginia, and West Virginia (EPA, 2011a; Zipper, 2011). The primary components of this runoff are SO_4^{2-}, HCO_3^-, Ca^{2+}, and Mg^{2+} (EPA, 2011a, b; Clark, 2015; Timpano, 2015; Pond et al. 2008). In this study, the effectiveness of three physicochemical operations to reduce SC in waters at two mining sites was explored: Ion exchange, Chemical Softening, and the Cost Effective Sulfate Removal (CESR) process.

Ion Exchange

Ion exchange is a well-established treatment technique during which an undesirable contaminant is removed from water and replaced with another, less objectionable ion (NHDES, 2009). Although ion exchange does not necessarily reduce Total Dissolved Solids (TDS), it is possible that ion exchange could be used to reduce specific conductance because each ion contributes to the overall conductivity differently (McCleskey, 2012). Additionally, the selectivity of this technology would allow for mining sites to target specific ions (Wang, 2005), allowing them to meet discharge limits for individual ions that have been shown to negatively impact stream life, even if the overall SC limit could not be attained (EPA, 2011b).

To regenerate a cation exchange resin, the resin, which has negative functional groups built into its structure, is submerged into a regenerant solution containing a high concentration of weak positive ions, most often hydrogen or sodium. The inherent negative charge of the resin attracts the weak positive ions from the solution, and keeps them there in order to achieve a net charge of zero within the resin. The inverse is true for anion exchangers, which have a positively charged resin that has been exposed to a weak negative ion, most often hydroxide or chloride. When fresh resin is exposed to feed water, the stronger ions in the feed water replace the weaker ions already on the media. The initial exchange of ions occurs at the surface of the beads; however, the ions on the surface will eventually diffuse toward the center of the resin beads. After all the regenerant ions are replaced, the resin is "spent" and must be regenerated again (Bowell 2004). The regeneration process is shown in Equations 4.1 and 4.2.

Cation Softening Resin
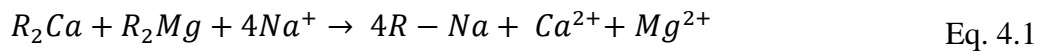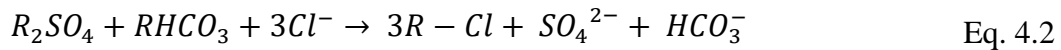
$$R_2Ca + R_2Mg + 4Na^+ \rightarrow 4R - Na + Ca^{2+} + Mg^{2+}$$
Eq. 4.1

Anion Softening Resin

$$R_2SO_4 + RHCO_3 + 3Cl^- \rightarrow 3R - Cl + SO_4^{2-} + HCO_3^-$$
Eq. 4.2

In these examples, the ions on the resin (R) that had been removed from the feed water are replaced by either sodium or chloride.

Ion exchange has been used for a wide variety of TDS reduction efforts, such as desalination of brackish waters (Pless, 2006; Prajapati, 1985), nanofiltration and RO concentrates (Comstock, 2011), and treatment of very hard water (Apell and Boyer, 2010; Comstock, 2011). Although ion exchange is typically installed as a fixed column (Apell and Boyer, 2010; NHDES, 2009), batch reactors are well suited to small water volumes, are able to equilibrate quickly, and provide more consistent results than fixed columns (Li and Yang, 2015; Wang, 2005). In a study investigating nitrite adsorption, uptake occurred

quickly, with equilibrium being reached in a batch reactor after only 40 minutes (Li and Yang, 2015). In another study, which targeted contaminants similar to those of this study, batch reactors were allowed to equilibrate over the course of two days on a shaker table. It was later determined that equilibrium occurred in less than 24 hours (Indarawis and Boyer, 2013).

If treatment of influent water is meant to remove both cations and anions with ion exchange, reactors are traditionally configured in series, with the effluent of a cation removal column immediately becoming the influent of an anion exchange column, or vice versa (Pless, 2006; Wang 2005). In a study with brackish water, one simulated (TDS = 2,222) and one natural (TDS = 11,000), Pless (2006) demonstrated that it was possible to bring the TDS of both waters to below the suggested limit for potable water of 500 mg/L. In this case, the natural water TDS was 600 ppm post-treatment, and the simulated water was reduced to a TDS of 25 ppm. However, the effluent pH was acidic (pH = 5.7) and treatment times were slow, taking 25 minutes to treat 100 mL of sample water. Treatment in the reactors was also augmented by adding lime softening as a pretreatment to remove scaling minerals that could clog the ion exchange media, although this was ineffective when the water hardness was associated with Cl^- and SO_4^{2-} instead of carbonate (Pless, 2006).

Chemical Softening

Hardness, or the concentration of dissolved multivalent cations in water, usually calcium and magnesium, is typically viewed as an exclusively aesthetic issue for water quality (NHDES, 2008; USGS, 2016; Wang, 2005). In the case of valley fill runoff water, however, these components are present in very high concentrations and are major components of the overall SC (EPA, 2011a, b; Clark, 2015; Timpano, 2015; Pond et al. 2008). For example, calcium and bicarbonate, which can be removed by softening, account for 39% of the Total Dissolved Solids (TDS) in affected Appalachian streams (Timpano et al. 2010).

Chemical softening is a highly effective treatment process for the removal of calcium, magnesium, and carbonate species from hard waters (Mohammadesmaeili, 2010; Wang, 2005). The most appropriate softening process for the affected streams is excess lime-soda softening because calcium and magnesium concentrations are both high, but carbonate hardness is relatively low (Comstock, 2011; Mohammadesmaeili, 2010; Timpano et al., 2010; Edzwald, 2011). Addition of soda ash (Na_2CO_3) is necessary for the waters being treated because of the high proportion of non-carbonate anions in the runoff waters (Davis and Cornwell, 2013).

Excess lime is often used in treatment plants for two reasons: to ensure that precipitation occurs expeditiously (Davis and Cornwell, 2013), as well as to raise the pH above 11 for magnesium removal (Jones, 2005). Two stage softening was determined to be the most promising for SC reduction because it encourages additional precipitation of $CaCO_3$ (Wang et al, 2005). Figure 4.1 shows a schematic of the process for excess lime-soda softening with two stage recarbonation (Edzwald, 2011). Two stage recarbonation allows for additional recovery of $CaCO_3$, which ultimately translates into a lower effluent TDS (Edzwald, 2011; Wang, 2005).
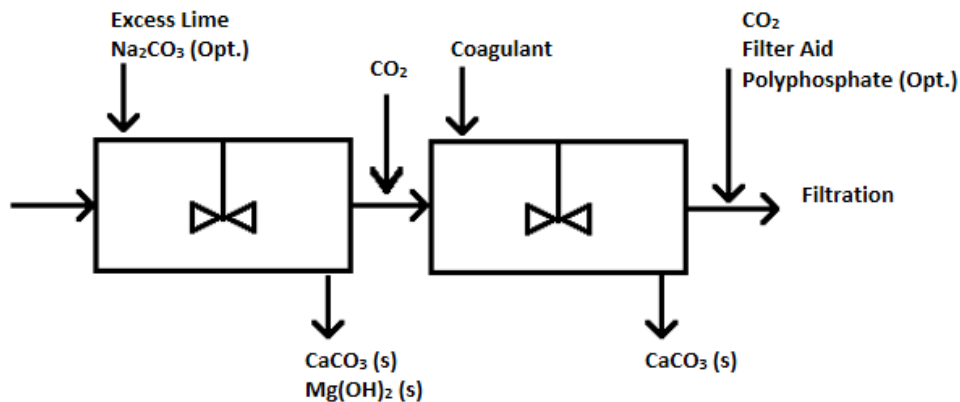
Figure 4.1: Excess Lime-Soda Softening, modified from Edzwald, 2011

Chemical dosing for excess lime-soda softening has four primary components: calcium carbonate hardness (CCH), calcium non-carbonate hardness (CNCH), magnesium carbonate hardness (MCH), and magnesium non-carbonate hardness (MNCH). CCH is equivalent to the alkalinity in most cases. If the concentration of alkalinity exceeds that of the calcium, there will also be MCH. If there is more calcium than alkalinity, the water will have CNCH, which will be the concentration of calcium minus the alkalinity in the water. In the case that there is no MCH, the MNCH will simply be the concentration of magnesium in the water. If there is MCH, the MNCH is the magnesium concentration minus the MCH. If there is CNCH, the water will only have MNCH and no MCH because alkalinity precipitates as $CaCO_3$ with calcium. Lime dosing is related to CCH and MNCH, while soda addition is related to CNCH and MNCH. To determine chemical doses, one meq of chemical should be added per meq of target ion (CNCH, CCH, MNCH), with an additional 1.25 meq/L of lime added to expedite precipitation. (Davis and Cornwell, 2013).

As a process, softening is known for producing a significant amount of sludge, at volumes of 10% to 15% of the treated water volume (Wang, 2005). Sludge collection, storage, and dewatering may pose a challenge for mining sites with receiving streams in remote locations. Softening sludge compacts easily and is typically between 15% and 25% solids (Wang, 2005). Flocculation and dewatering with lime soda softening is also known to be a challenge due to the presence of $Mg(OH)_2$ in the precipitate (Corrigan et al., 2005). Magnesium hydroxide floc is extremely hydrophilic, tends to be gelatinous, and is difficult to flocculate due to its positive electromobility (Black and Christman, 1961). These factors make settling and dewatering of sludge containing $Mg(OH)_2$ more difficult than the disposal of $CaCO_3$ alone.

Softening has been used as an effective treatment for waters with higher TDS than those typically found in valley fill runoff, such as concentrates from reverse osmosis (RO) (Comstock, 2011; Gabelich, 2011; Mohammadesmaeili, 2010). Lime softening successfully reduced Ca^{2+} by 69-74% in one study of RO concentrate with a low alkalinity. It also reduced SO_4^{2-} concentrations by 0%-14% and Mg^{2+} by 67%-98%, with higher Mg^{2+}

removals occurring at a pH above 11 (Comstock, 2011). Calcium removal was greatly increased (93-99%) by lime-soda softening in the same study (Comstock 2011).

In another study focusing on high TDS waters, Mohammadesmaeili (2010) found that during lime-soda treatment, it is possible to greatly reduce both Ca^{2+} and Mg^{2+} concentrations. Mg^{2+} was decreased to below detection limits, while Ca^{2+} concentrations were reduced by approximately 99%, to only 5 mg/L. During that portion of the study, sulfate data were also provided and, as expected, it showed that traditional lime-soda softening did not have a significant effect on sulfate concentrations. The author also investigated traditional lime-soda softening of high sulfate waters, revealing that a high sulfate concentration did not act as a notable deterrent on the on the softening process. (Mohammadesmaeili, 2010)

CESR Process

The Cost Effective Sulfate Removal (CESR) process, which targets sulfate as well as calcium and magnesium, was developed in the 1990's by European engineers (Reinsel, 2015). The process has been used in over twenty full-scale treatment plants in Europe, but has not yet achieved widespread use in the United States (APEX Engineering, 2016; Lorax, 2003). This innovative process can achieve effluent sulfate levels of less than 100 mg/L, for a much lower cost than conventionally used processes like reverse osmosis (RO) and ion exchange (Water Online, 2016).

In one case study of the CESR process at Berkeley Pit, an acid mine site in Butte, Montana, investigators found that the process could successfully reduce sulfate from a concentration of 8,700 mg/L to an effluent concentration of 56 mg/L. The average cost of this process was determined to be $0.79/$m^3$ of treated water to remove 1,500 mg/L of SO_4^{2-}, with an upper cost of $1.58/$m^3$ (Lorax, 2003). The process was also used to treat waters at a copper mine with an initial sulfate concentration of 3,350 mg/L. The effluent had a sulfate concentration of 360 mg/L (Water Online, 2016).

In Stage I of the CESR Process, gypsum ($CaSO_4$) precipitates to its solubility limit of 2,000 mg/L. This is done by increasing the pH of the water to 10.5 with hydrated lime and stirring the mixture for 40 minutes at 100 rpm in a jar stirrer (Reinsel, 2015). Calcium sulfate precipitation is shown in Equation 4.3.
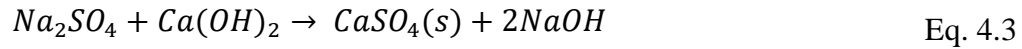
$$Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4(s) + 2NaOH$$ Eq. 4.3

The jar stirrer is then adjusted to 20 rpm, and 2 mg/L polymer is added. This rate of stirring is continued for a minimum of five minutes to promote flocculation. The stirrer is then turned off and the precipitate is allowed to settle. The gypsum is removed before continuing with Stage II because any remaining gypsum will react with the reagent to prevent further sulfate precipitation (Reinsel, 2015). A schematic of the overall CESR process may be found in Figure 4.2.
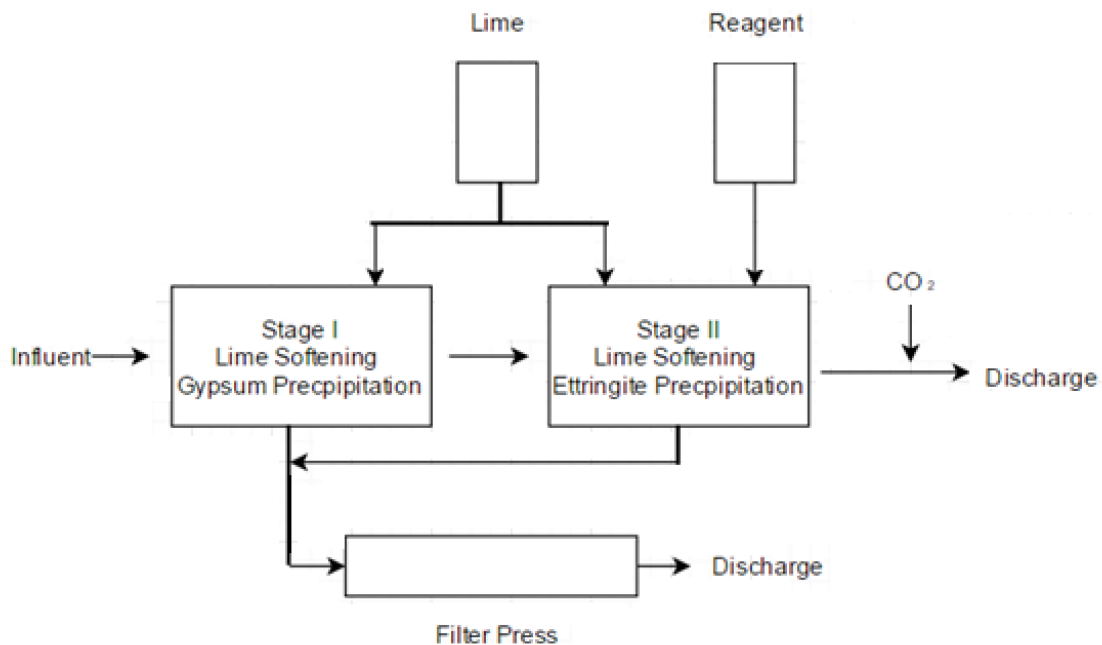
Figure 4.2: CESR Process Diagram

After removing the gypsum in Stage I, additional lime is added to the water to raise the pH to 11.3. The reagent, Luminite MG-4, is then added at a concentration of 1.0-1.5 times the concentration of sulfate in the water. During the process, the pH will decrease as sulfate precipitates, and it is necessary to ensure the pH remains near 11.3. If the pH decreases below 11.0, the reaction will stop; however, if the pH is above 12, the reaction may reverse. When the pH stops decreasing, the removal of sulfate has been reached and Stage II is completed. As in Stage I, 2 ppm of the polymer flocculent Magnafloc 155 is added to the reactor and stirred in for a minimum of five minutes. Following this step, the water is separated from the floc, recarbonated to a neutral pH, and ready for discharge. (Reinsel, 2015)

The precipitate from the CESR process is a unique calcium-alumina-sulfate compound, known as ettringite, with the formula, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 3H_2O$ (PSA, 2001). Ettringite has a polishing effect on the water, bringing metals such as chromium, arsenic, and selenium down below their detection limits, as well as removing up to a third of the chloride and nitrate in the water. Furthermore, ettringite can be disposed of as non-hazardous waste. A disadvantage of the ettringite is that large amounts of ettringite sludge are produced in Stage II, approximately 45 lbs per 1,000 gallons of water treated (Water Online, 2016)

It is important to dose the water in Stage II with an appropriate amount of reagent. Although the reagent (Luminite MG-4) is inexpensive approx. (approximately \$0.40/lb in 2016), it contains aluminum (Robert, 2016), which is discharged in process effluents if excess reagent is added to the reactor. Aluminum can cause pulmonary and developmental problems in fish and benthic organisms that breathe using gills; the most notable sign of toxicity is an inability of the animal to regulate osmosis (EPA, 2016; Rosseland, 1990). Although aluminum is insoluble in water (Cornell, 1999), its solubility increases as pH decreases, which increases the likelihood that toxicity will occur at a lower pH (EPA, 2016). Furthermore, it is possible that aluminum could enter the food chain through plants and nutrient uptake from the soil (Rosseland, 1990), so safeguards against aluminum discharge should be considered, during or following recarbonation.

44

<u>Objectives</u>

The objectives of the experiments were to determine:

1. The effect that ion exchange, chemical softening, and the CESR process had on effluent SC

2. The effect that each process had on the ionic composition of the source water

3. The quantity of sludge produced by chemical softening and the CESR process

4. The appropriate dose of the reagent, Luminite MG-4, necessary for optimal sulfate removal in Stage II of the CESR process.

5. An average treatment time for CESR Stage II precipitation.

6. Any challenges or limitations of implementing each process at a site

Methods and Materials

<u>Analysis of Samples</u>

The cations measured in this study were calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+). These cations and silicone (Si) were measured using an ICP-MS instrument (X Series ICP-MS, Thermo Electron Corporation). The anions, sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-), were measured using an ion chromatograph (Dionex ICS-1600, Thermo Electron Corporation). To measure temperature and specific conductance, a specific conductance meter (CDH-SD1 Meter, Omega) was used. A pH Controller (DL125 Black Box Series, Milwaukee Instruments) was used to measure and control the pH of reactors during Stage II of the CESR process. Alkalinity, Total Dissolved Solids (TDS), and Total Suspended Solids (TSS) were measured in accordance with Standard Methods (APHA, 2012; method numbers 2320B, 2540B, and 2540 D, respectively). Turbidity was measured using a Turbidimeter (Digital Direct-Reading Turbidimeter, Orbeco-Hellige).

The chemicals used in these softening experiments were calcium oxide (CaO), which becomes hydrated lime in water, and soda ash (Na_2CO_3). Both compounds were obtained from Fisher Scientific.

Capillary Suction Times (CST) were performed according to Standard Methods (APHA, 2012; Method Number 2710 G) to determine dewatering times for the CESR sludge. Percent moisture was determined using Equation 4.4, where WW is the wet weight of sludge, and DW is the dry weight of sludge after being dried at 103-105°C for one hour.

$$\% \, Moisture = \frac{WW - DW}{WW} * 100\%$$

Eq. 4.4

Statistical Analysis

The coefficient of variations (COV) was used to determine how variable results of an experiment were with respect to the mean value. The COV was calculated by dividing the sample standard deviation by the average (Fisher, 1950).

Experimental Materials and Conditions

Ion Exchange

Ion exchange resins were chosen from the DOW chemical website based on each media's selectivity for certain ions. The cation exchange media selected, DOWEX Marathon C, H^+ form, has a preference for calcium and magnesium ions. The capacity of this ion exchange media is 1.4 eq/L and it is regenerated using H_2SO_4 or HCl. Amberlite PWA 15 anion exchange media, also a DOW product, was chosen because of its ability to remove sulfate, the most prominent anion in the mining waters. This resin also functions best at a neutral pH, has an exchange capacity of 1.40 eq/L, and may be regenerated with NaCl.

To test the media, 100 mL of sample water was placed in a 250 mL Erlenmeyer flask along with a predetermined amount of ion exchange media. It was necessary to leave headspace in the flask to ensure even distribution and suspension of the ion exchange media in the reactor.

Six different doses of ion exchange media were used in each replicate to determine the optimal treatment concentration. The stoichiometric amount (SA) of media needed for a given water was determined from the ion composition and the removal capacity of the ion exchange media given in its Safety Data Sheet (1.40 eq/L for both the cation and anion exchange media). Ion removals at media doses of 50%, 75%, 100%, 125%, 150%, and 200% of the SA were then measured. Although the literature indicated that equilibrium could be reached in less than 24 hours (Li and Yang, 2015; Indarawis and Boyer, 2013), the reactors were placed on a shaker table at 60 rpm for 24 hours. After 24 hours, samples were filtered through a 0.45 μm Whatman membrane filter (47 mm diameter, Sigma-Aldrich) using a vacuum pump, and then SC, pH, and ionic composition were measured.

Chemical Softening

To begin these tests, 500 mL of raw water was poured into 1,000 mL Gator jars, which served as the batch reactors for these experiments. In Stage I, lime and soda ash associated with CCH and CNCH were added to the water, as well as excess lime. The goal of this was to precipitate all calcium in the water as $CaCO_3$. Soda ash was added to the reactor to increase the carbonate species concentration in the water, thereby providing carbonate for the calcium present in the source water and lime added in Stages I and II. Lime was added to the jars to increase the pH of the water to 10.3. After chemical addition, the reactors were mixed rapidly for five minutes at 100 rpm in a Phipps and Bird jar stirrer, and then flocculated for 25 minutes at 20 rpm. No flocculent was added to the reactors, and after turning off the mixer, the flocs were allowed to settle for 10 minutes.

After settling, water was decanted from the first reactor and the second stage began. The full 500 mL of water was transferred to a clean 1000 mL Gator jar and additional lime, which was associated with MNCH, was added to raise the pH to 11.0. The reactor was stirred for five minutes at 100 rpm, followed by 25 minutes of flocculation at 20 rpm. The floc was allowed to settle for 10 minutes. The supernatant was collected for recarbonation to a pH of 10.3 to allow for additional recovery of $CaCO_3$ before recarbonating the effluent a final time to its original pH of 7.6.

CESR Process

For Stage I, 600 mL of raw water was added to 1,000 mL Gator jars, which served as the reactors for these experiments. The pH of the water was increased to 10.5 by pumping a solution of 15% hydrated lime into the water using a pH controller (DL125 Black Box pH Controller, Milwaukee Instruments). The instrument measured and maintained the pH. The solution was stirred at 100 rpm for 40 minutes. After 40 minutes, 2 mg/L of Magnafloc 155 (BASF, Tucson, AZ) was added, and the mixture was stirred at 20 rpm for 5 minutes. The reactor was allowed to settle for 10 minutes or more, until the precipitate had settled. Precipitate formed in this step was dense and settled quickly.

During Stage II, 500 mL of the water was decanted and its pH was maintained at 11.3 using the pH controller. The probe of the pH controller was attached to the side of the gator jar at an appropriate height so that the sensor of the probe was entirely immersed. The jar stirrer was set to 100 rpm and the reagent, Luminite MG-4, was added to the reactor after being weighed in its dry powder form on an Entris Sartorius scale. After adding the reagent, sulfate would begin to precipitate out in the form of ettringite ($3CaO•Al_2O_3•3CaSO_4•3H_2O$), and the pH would decrease (PSA, 2011). When the pH decreased below 11.3, the pH controller would activate the pump, which pumped the 15% hydrated lime into the water until the pH was once again above 11.3. Because it was difficult to assess when sulfate precipitation ceased, reaction times of 8, 12, and 18 hours were tested. After the allotted amount of time, the stirrer was decreased to 20 rpm and 2 mg/L of the polymer flocculent, Magnafloc 155, was added. After flocculent addition, the

reactor was stirred at 20 rpm for 10 minutes, and the floc was allowed to settle for 30 minutes. It was discovered that 10 minutes of flocculation was necessary to produce larger, faster settling sludge. After settling, the SC and ionic composition of the water were tested, and the dewatering times and water content of the sludge were determined.

Proper maintenance of the pH control system is one of the most important aspects of sulfate removal in Stage II. To prevent damage to the pH probe in both stages, it should be removed from the water before the flocculent is added. If not removed, the probe will be coated in sticky, difficult-to-remove sludge. In addition, the probe needed to be regularly cleaned in an acidic solution to remove scaling caused by the high level of water hardness in the mining waters.

Results

Study Site Characteristics

Sample waters were collected at two strip mining sites in Southwest Virginia's Dickinson County, Office Fill (OF) and Barton Hollow (BH). At both sites, mining spoils were placed in valleys (valley fills). Water samples collected from OF and BH were similar in composition to other sites in central Appalachia (EPA, 2011a, b; Clark, 2015; Timpano, 2015; Pond et al. 2008). OF had the higher SC of the two sites, with an initial SC value of 2,500 μS/cm, as compared to 1,500 μS/cm at BH. The water from both sites was clear, with turbidities less than 10 NTU. The TSS concentration was 12 mg/L at OF and 16 mg/L at BH. Water at both sites had a neutral pH and high TDS. TDS in mg/L was 0.8-0.9 of the SC in μS/cm (Kemak, 2016). Table 4.1 provides additional information regarding the source waters.

Table 4.1: Source Water Quality Information

Site	pH	SC	TDS	TSS	Alkalinity	Turbidity
		µS/cm	mg/L	mg/L	mg/L CaCO$_3$	NTU
Office Fill	7.61	2,510	2,265	12	198	9.9
Barton Hollow	7.44	1,532	1,200	16	79	8.1

Tables 4.2 and 4.3 show the concentration of ions in the sample water and a cation-anion balance for each site's water. TDS, and therefore SC, at both sites was dominated by three key ions: calcium, magnesium, and sulfate. At OF, the water was very hard, with a Ca concentration of 350 mg/L and a Mg concentration of 250 mg/L. Sulfate and bicarbonate were the prominent anions, with the sulfate concentration near 1,500 mg/L and a bicarbonate concentration of 240 mg/L. Even at the high bicarbonate concentration, sulfate still accounted for approximately 85% of the anions (in equivalents) at OF.

At BH, concentrations of all ions were significantly lower, as was the SC, of course. Ca and Mg were still the dominant cations, at concentrations of 180 mg/L and 95 mg/L, respectively. Sulfate concentrations at BH were about 775 mg/L, about half the concentration of OF water, and bicarbonate concentrations were around 100 mg/L. Like at OF, the sulfate concentration at BH accounted for about 85% of the total anions in the sample water.

The cation-anion balance had a percent difference of less than 5% for both sites, indicating that the composition of the water was reasonably characterized. Office Fill cations summed to 39.4 meq/L, and anions summed to 36.9, creating a percent difference of 6.4%. At BH, the total cation concentration was 17.94 meq/L with an anion concentration of 17.84 meq/L, a percent difference of 0.5%.

Table 4.2: Office Fill Cation-Anion Balance

Constituent	mg/L	meq/L	Sum [meq/L]
Ca^{2+}	346.0	17.26	
Mg^{2+}	247.1	20.34	39.43
K^+	10.5	0.27	
Na^+	36.0	1.57	
HCO_3^-	241.6	3.96	
SO_4^{2-}	1,531.0	31.86	36.90
NO_3^- as N	3.5	0.25	
Cl^-	29.3	0.83	

Table 4.3: Barton Hollow Cation-Anion Balance

Constituent	mg/L	meq/L	Sum [meq/L]
Ca^{2+}	181.4	9.04	
Mg^{2+}	93.6	7.70	17.94
K^+	7.7	0.20	
Na^+	22.8	0.99	
HCO_3^-	96.39	1.58	
SO_4^{2-}	775.8	16.15	17.84
NO_3^- as N	4.0	0.11	
Cl^-	4.1	0.58	

Silicone, which is often found in the Si^{4-} form in natural waters, was also measured at these sites. The concentration at OF was 0.64 meq/L and at BH was 0.58 meq/L.

Cation Exchange

The doses and results of cation exchange treatment on the effluent specific conductance and pH are shown in Tables 3.4 and 3.5. In these tables, "SA" refers to the stoichiometric amount of media that would theoretically satisfy the demand of ions in the water. At OF, the SA dose was 2.69 g/100 mL and at BH, the SA was 1.23 g/100 mL. The percent given in each column heading of Tables 4.4 and 4.5 represents a percent of the SA.

Table 4.4: Effect of Cation Exchange Treatment on Effluent SC for OF

% of SA	50%	75%	100% (SA)	125%	150%	200%
Dose (g/100 mL)	1.35	2.02	2.69	3.36	4.04	5.38
SC	8,053	8,760	7,923	8,808	9,023	8,753
pH	1.87	1.835	1.64	1.58	1.545	1.54

Table 4.5: Effect of Cation Exchange Treatment on Effluent SC for BH

% of SA	50%	75%	100% (SA)	125%	150%	200%
Dose (g/100 mL)	0.62	0.92	1.23	1.54	1.85	2.46
SC	4,670	5,235	5,370	5,383	5,400	5,415
pH	2.02	1.93	1.88	1.85	1.85	1.83

The results of cation exchange treatment on the effluent ionic composition for each media dose are shown in Tables 4.6 and 4.7.

Table 4.6: Effect of Cation Exchange Treatment on OF Ions

Sample	Concentration [mg/L]					
	Na	Mg	SO$_4$	Cl	K	Ca
Untreated Water	36.0	247.1	1,500.0	0.0	10.5	346.0
50% SA	15.9	18.9	1,465.0	25.3	3.3	15.0
75% SA	11.2	2.0	1,451.0	24.1	1.6	1.6
SA	9.3	1.0	1,471.0	26.2	1.2	2.5
125% SA	8.9	1.6	1,424.5	20.6	1.2	39.3
150% SA	10.2	1.2	1,397.0	21.5	1.5	0.9
200% SA	14.4	8.5	1,421.0	21.8	2.7	13.4

Table 4.7: Effect of Cation Exchange Treatment on BH Ions

Sample	Concentration [mg/L]					
	Na	Mg	SO$_4$	Cl	K	Ca
Untreated Water	22.8	93.6	775.8	0.0	7.7	181.4
50% SA	19.0	13.2	808.3	6.4	4.7	11.1
75% SA	12.3	1.2	813.4	4.7	2.3	0.8
SA	8.2	0.4	806.9	3.6	1.3	-0.1
125% SA	6.2	0.3	798.1	3.3	0.9	0.4
150% SA	5.0	0.2	796.1	3.2	0.7	0.5
200% SA	3.6	0.5	794.8	3.0	0.5	1.3

Anion Exchange

The doses and results of anion exchange treatment on the effluent specific conductance and pH are shown in Tables 4.8 and 4.9. As above, "SA" refers to the stoichiometric amount of media that would theoretically satisfy the demand of ions in the water. At OF, the SA dose was 1.92 g/100 mL and at BH, the SA was 1.75 g/100 mL. The percent given in each column heading of Tables 4.8 and 4.9 represents a percent of the SA.

Table 4.8: Effect of Anion Exchange Treatment on Effluent SC for OF

% of SA	50%	75%	100% (SA)	125%	150%	200%
Dose (g/100 mL)	0.96	1.44	1.92	2.40	2.88	3.84
SC	2,955	3,185	3,325	3,415	3,500	3,550
pH	7.73	7.67	7.65	7.775	7.7	7.735

Table 4.9: Effect of Anion Exchange Treatment on Effluent SC for BH

% of SA	50%	75%	100% (SA)	125%	150%	200%
Dose (g/100 mL)	0.88	1.31	1.75	2.19	2.63	3.50
SC	1,902	1,963	2,015	2,040	2,040	2,080
pH	8.03	7.93	7.84	7.85	7.85	7.82

The results of anion exchange treatment on the effluent ionic composition for each media dose are shown in Tables 4.10 and 4.11.

Table 4.10: Effect of Anion Exchange Treatment on OF Ions

Sample	Concentration [mg/L]					
	Na	Mg	SO_4	Cl	K	Ca
Untreated Water	36.0	247.1	1,079	0.0	10.5	346.0
50% SA	34.7	238.6	812.4	579.5	10.1	315.4
75% SA	34.8	240.9	461.2	962.1	10.2	326.4
SA	35.6	246.6	385.4	1,082.0	10.4	336.7
125% SA	36.4	252.5	350.5	1,150.5	10.6	344.5
150% SA	35.4	245.5	380.1	1,103.9	10.6	331.1
200% SA	34.9	242.5	431.4	1,088.0	10.2	325.9

Table 4.11: Effect of Anion Exchange Treatment on BH Ions

Sample	Concentration [mg/L]					
	Na	Mg	SO₄	Cl	K	Ca
Untreated Water	22.8	93.6	775.8	0.0	7.7	181.4
50% SA	24.0	101.0	456.2	277.1	8.1	179.5
75% SA	14.2	62.6	102.2	332.2	4.8	118.8
SA	25.4	110.7	85.2	670.4	8.5	196.7
125% SA	25.4	110.8	51.7	708.3	8.5	195.3
150% SA	24.8	107.0	36.9	663.7	8.0	183.7
200% SA	29.0	125.5	40.5	842.3	9.4	217.5

Chemical Softening

The chemical doses for each site were calculated using the cation-anion balances in Tables 4.2 and 4.3. For OF, the CCH was simply the alkalinity, 3.96 meq/L. This value was subtracted from the overall calcium concentration of 17.26 meq/L, yielding a CNCH value of 13.30 meq/L. All of the alkalinity was associated with calcium, so the MCH was zero and the MNCH was the magnesium concentration, 20.34 meq/L. The calculations for BH were completed in a similar fashion. CCH was equal to the alkalinity at 1.58 meq/L, while CNCH was 7.46 meq/L. There was no MCH, and MNCH was 7.70 meq/L. The lime dose, associated with CCH and MNCH was 1.42 g/L after the inclusion of excess lime at OF, and was 0.59 g/L at BH. Soda ash, associated with the noncarbonate hardness, amounted to 1.78 g/L at OF and 0.80 g/L at BH. Doses used at OF are shown in Table 4.12, while those used at BH are shown in Table 4.13.

Table 4.12: Office Fill Excess Lime-Soda Softening Doses

Concentration, meq/L		Lime, meq	Soda Ash, meq	Lime, mg/L	Soda Ash, mg/L
CCH	3.96	3.96	-	147	0
MCH	0.00	-	-	0	0
MNCH	20.34	20.34	20.34	753	1,078
CNCH	13.30	-	13.30	0	705
Excess Lime		**1.25**	**-**	46	-
Total (g/L)				1.42	1.78
Total (g/500 mL)				0.71	0.89

Table 4.13: Barton Hollow Excess Lime-Soda Softening Dosing

Concentration, meq/L		Lime, meq	Soda Ash, meq	Lime, mg/L	Soda Ash, mg/L
CCH	1.58	1.58	-	59	0
MCH	0.00	-	-	0	0
MNCH	7.70	7.70	7.70	285	408
CNCH	7.46	-	7.46	0	396
Excess Lime		**1.25**	**-**	46	-
Total (g/L)				0.59	0.80
Total (g/500 mL)				0.29	0.40

Table 4.14 provides SC, pH, and sludge volumes for each stage of the softening process. The initial SC increased by 58% after Stage I treatment, then slightly increased an additional 11% between Stages I and II. Effluent SC, after softening the OF waters, was 4,250 μS/cm. The values for BH followed the same trend to a lesser extent, with the largest increase of 48% after Stage I treatment, followed by an SC decrease of 16% after Stage II treatment for an effluent SC of 2,025 μS/cm. The pH of both waters was initially 7.5-7.6, about 10.4 after Stage I (i.e., OF I and BH I), and at approximately 11 after Stage II. After recarbonation, the SC of the water was within 1% of SC at the end of Stage II for either site's water, so it was not reported.

Table 4.14: SC, pH, and Sludge Volumes for Lime Soda Softening

	SC, μS/cm		pH		Sludge, mL	
Stage	**Avg**	**COV**	**Avg**	**COV**	**Avg**	**COV**
OF Raw	2,510	-	7.62	-	-	-
OF I	3,960	0.36%	10.44	0.27%	50	0.0%
OF II	4,250	1.7%	10.99	0.51%	21	6.7%
BH Raw	1,534	-	7.53	-	-	-
BH I	2,270	8.1%	10.43	1.29%	10	0.0%
BH II	2,025	1.0%	10.95	0.52%	25	5.7%

The ionic composition of the waters from each site is shown in Tables 4.15 and 4.16. At OF, the calcium concentration in the water was reduced by 67% at the end of Stage I, and by 77% after lime addition in Stage II. Following recarbonation, calcium was ultimately reduced to 8% of its original value. At BH, the % calcium reduction after Stage I was 71%, following Stage II was 84%, and after recarbonation was 85%. The lower limit for calcium concentrations at both sites was 27 mg/L. Magnesium removal, another target ion of excess lime-soda softening, was more successfully achieved at BH than OF. BH magnesium reduction was 7% after Stage I, 93% after Stage II, and 96% after recarbonation. For OF water, % magnesium reduction was 20% following Stage I, 71% after Stage II, and 73% after recarbonation. The average minimum concentration of

magnesium at OF was 65.5 mg/L. At both sites, sulfate remained within 5% of its initial value, indicating that, as expected, it was unaffected by the softening process. The final ion that changed notably was sodium, which increased by 2,000% at OF and by 1,500% at BH. The initial concentration of sodium at OF was 36 mg/L, but increased to 775 mg/L due to soda ash addition. The BH sodium concentration, initially 23 mg/L, increased to 365 mg/L following soda ash addition. As expected, sodium concentrations stayed fairly consistent between treatment stages, with a COV of only 0.9% for OF and 1.5% for BH.

Table 4.15: Ionic Composition of Office Fill Waters

Sample	Concentration, mg/L						
	Ca	Mg	SO$_4$	Na	K	Cl	Si
Untreated Water	346.0	247.1	1,500.0	36.0	10.5	0.0	4.5
OF Stage I	114.0	197.6	1,407.0	767.8	9.3	21.0	3.8
OF Stage II	79.1	70.5	1,445.0	776.9	9.6	21.3	2.1
Recarbonation	26.9	65.6	1,497.0	764.8	9.6	22.4	1.8

Table 4.16: Ionic Composition of Barton Hollow Waters

Sample	Concentration, mg/L						
	Ca	Mg	SO$_4$	Na	K	Cl	Si
Untreated Water	181.4	93.6	775.8	22.8	7.7	0.0	4.1
BH Stage I	52.5	87.2	801.1	357.3	7.6	2.1	4.2
BH Stage II	29.3	6.4	815.2	365.4	8.2	2.4	2.4
Recarbonation	27.6	3.6	818.4	366.9	7.9	2.2	2.2

Sludge volumes for the 500 mL reactors used in this study may be found in Table 4.17. Final sludge quantities for the entire softening process were 14% of the volume of OF water treated and 7% of the BH treated water volume. This falls within the range of 10% to 15% solids per unit water treated noted in the literature (Wang, 2005). The COV is close to zero for the production of sludge in Stage I for both sites, but is slightly above 5% for Stage II. The COV for OF was 6.7% and the COV at BH was 5.7% COV, both of which were acceptably low.

Table 4.17: Softened Water Sludge Production

Stage	Office Fill		Barton Hollow	
	Avg [mL]	COV	Avg [mL]	COV
Initial	-	-	-	-
I	50	0.0%	10	0.0%
II	21	6.7%	25	5.7%

CESR Process

Two initial tests were performed by dosing the water with Luminite MG-4 at 1.5 times (x) the sulfate concentration and allowing the reaction to occur for eight hours in Stage II. Although the SC was reduced slightly under these conditions (Table 4.18), by an average of 55% for OF waters and 44% at BH, the ICP analysis (Table 4.19) revealed that there was far more potential for the removal of sulfate. Aluminum and sulfate concentrations were both high in the test waters, with an average concentration of 39 mg/L Al and 620 mg/L SO_4^{2-} in the OF effluent, and 38 mg/L Al and 343 mg/L SO_4^{2-} in the BH effluent. The CESR process is capable of reducing sulfate concentrations below 100 mg/L, so it is clear that the reaction time was not long enough. Additionally, the high aluminum concentration in the effluent water suggested that reagent dosing was too high under these conditions, so in the next set of trials the reagent dose was equal to (1.0x) the sulfate concentration.

Table 4.18: SC and Sludge of CESR- 1.5x Reagent, 8 Hour Reaction

CESR: 1.5x Reagent, 8 Hours							
	OF Stage 1		OF Stage 2		BH Stage 1		BH Stage 2	
	Avg	COV	Avg	COV	Avg	COV	Avg	COV
SC, µS/cm	2,065	30%	1,137	54%	1,409	17%	862	28%
Sludge, % of water volume	0.33%	71%	8.3%	97%	0.25%	47%	10.9%	110%

Table 4.19: Ionic Composition CESR Stage II- 1.5x Reagent, 8 Hour Reaction

	Concentration [mg/L]						
Replicate	Al	S	Ca	Mg	Na	K	Cl
OF Source	0	1,500.0	346.0	247.1	36.0	10.5	0.0
OF 1	21	972	418	6	24	8	17
OF 2	57	269	158	0	21	8	15
BH Source	0.0	775.8	181.4	93.6	22.8	7.7	0.0
BH 1	36	194	117	3	18	7	3
BH 2	41	492	250	0	18	9	4

A 12-hour reaction time was chosen for this set of trials to allow a longer window for precipitation to occur. SC reduction under these conditions was similar, but slightly higher than those achieved in the first set of trials, with a 58% reduction of SC at OF and 61% reduction at BH (Table 4.20). Comparison with the ICP results (Table 4.21) showed that sulfate concentrations at both sites (OF = 715 mg/L; BH = 341 mg/L) were still far greater than the potential limit of 100 mg/L, while aluminum concentrations were still low, around 2 mg/L at both sites. For this reagent dose, it appeared that a 12-hour reaction time was sufficient, so the next set of trials were conducted at the same reaction time.

Table 4.20: SC and Sludge of CESR- 1.0x Reagent, 12 Hour Reaction

	OF Stage 1		OF Stage 2		BH Stage 1		BH Stage 2	
	Avg	COV	Avg	COV	Avg	COV	Avg	COV
SC, μS/cm	2,190	2%	1,569	2%	1,431	16%	893	25%
Sludge, % of water volume	0.80%	112%	10.4%	103%	0.63%	104%	15.6%	121%

Table 4.21: Ionic Composition CESR Stage II - 1.0x Reagent, 12 Hour Reaction

	Concentration [mg/L]						
Replicate	Al	S	Ca	Mg	Na	K	Cl
OF Source	0	1,500.0	346.0	247.1	36.0	10.5	0.0
OF 1	3	990	393	16	22	8	17
OF 2	0	441	232	0	19	8	46
BH Source	0.0	775.8	181.4	93.6	22.8	7.7	0.0
BH 1	3	541	172	40	17	7	3
BH 2	0	441	232	0	19	8	46

The third set of trials occurred with a reagent dose that was 1.25x the sulfate concentration and at a reaction time of 12 hours. This resulted in an SC reduction of about 50% for both BH and OF (Table 4.22). ICP results from Table 4.23 showed that aluminum concentrations in Stage II effluent were approximately 16 mg/L for both sites, while sulfate concentrations were well above 100 mg/L (585 mg/L at OF, 300 mg/L at BH). The presence of both aluminum and sulfate concentrations in the water indicated that the dosing could feasibly be correct, but the reaction time was too short.

Table 4.22: SC and Sludge of CESR- 1.25x Reagent, 12 Hour Reaction

Parameter	OF Stage 1		OF Stage 2		BH Stage 1		BH Stage 2	
	Avg	COV	Avg	COV	Avg	COV	Avg	COV
SC, µS/cm	2,307	23%	1,224	43%	1,454	21%	783	40%
Sludge, % of water volume	0.70%	90%	13.3%	43%	0.95%	57%	5.9%	72%

Table 4.23: Ionic Composition of CESR Stage II- 1.25x Reagent, 12 Hour Reaction

Sample	Concentration [mg/L]						
	Al	S	Ca	Mg	Na	K	Cl
OF Source	0	1,500.0	346.0	247.1	36.0	10.5	0.0
OF 1	43	201	109	0	27	16	26
OF 2	1	1,046	465	1	39	16	29
OF 3	4	508	212	0	27	11	33
BH Source	0.0	775.8	181.4	93.6	22.8	7.7	0.0
BH 1	0	640	203	37	19	7	3
BH 2	26	230	106	0	23	10	8
BH 3	22	31	45	0	19	10	7

In the final set of trials, reagent was added at a concentration of 1.25x the sulfate concentration with a Stage II reaction time of eighteen hours. Under these conditions, the CESR process was able to decrease the final SC of the water to near or below the proposed EPA limit of 500 µS/cm. For this reason, this trial will be referred to as the "best tested" (BT) trial.

The average effluent SC in OF Stage II was 442 µS/cm, an 82% reduction from the initial SC value of 2,510 µS/cm. The effluent SC for BH was similar at 456 µS/cm, a 70% reduction from the initial value of 1,534 µS/cm (Table 4.24). The Stage II effluent sulfate concentration at both sites was near 100 mg/L, with an average concentration of 119 mg/L at OF and 132 mg/L at BH (Table 4.25). The calcium in the water was also reduced substantially, with an 81% reduction at OF and a 59% reduction at BH. Magnesium at both sites was reduced below detection limits.

Table 4.24: SC and Sludge of CESR- 1.25x Reagent, 18 Hour Reaction

	OF Stage 1		OF Stage 2		BH Stage 1		BH Stage 2	
	Avg	COV	Avg	COV	Avg	COV	Avg	COV
SC, µS/cm	2,210	4%	442	19%	1,450	2%	456	8%
Sludge, % of water volume	0.83%	0%	21.8%	9%	0.28%	69%	29.7%	34%

Table 4.25: Ionic Composition of CESR Stage II- 1.25x Reagent, 18 Hour Reaction

	Concentration [mg/L]						
Sample	Al	S	Ca	Mg	Na	K	Cl
OF Source	0	1,500.0	346.0	247.1	36.0	10.5	0.0
OF 1	10	92	38	0	25	9	26
OF 2	14	120	53	0	22	8	22
OF 3	18.5	144.2	101.8	0.3	15.1	6.4	2.5
BH Source	0.0	775.8	181.4	93.6	22.8	7.7	0.0
BH 1	17	177	81	0	18	9	5
BH 2	36	90	82	2	17	7	11
BH 3	13.6	128.9	61.0	0.1	22.9	11.2	3.2

Characterization of CESR Sludge

A known limitation of the CESR process is that Stage II produces a significant amount of sludge. Stage I produces a small amount of dense precipitate; sludge volume produced from Stage I averaged 0.2% - 1.0% of the volume of water treated. However, Stage II produces much more sludge, the variety and quantity of which depends on the dosing. The sludge volume produced for the BT reactor conditions averaged 30% of the process volume before dewatering. Figures 4.3 and 4.4 show how the sludge produced from treatment of the BH and OF waters settled.
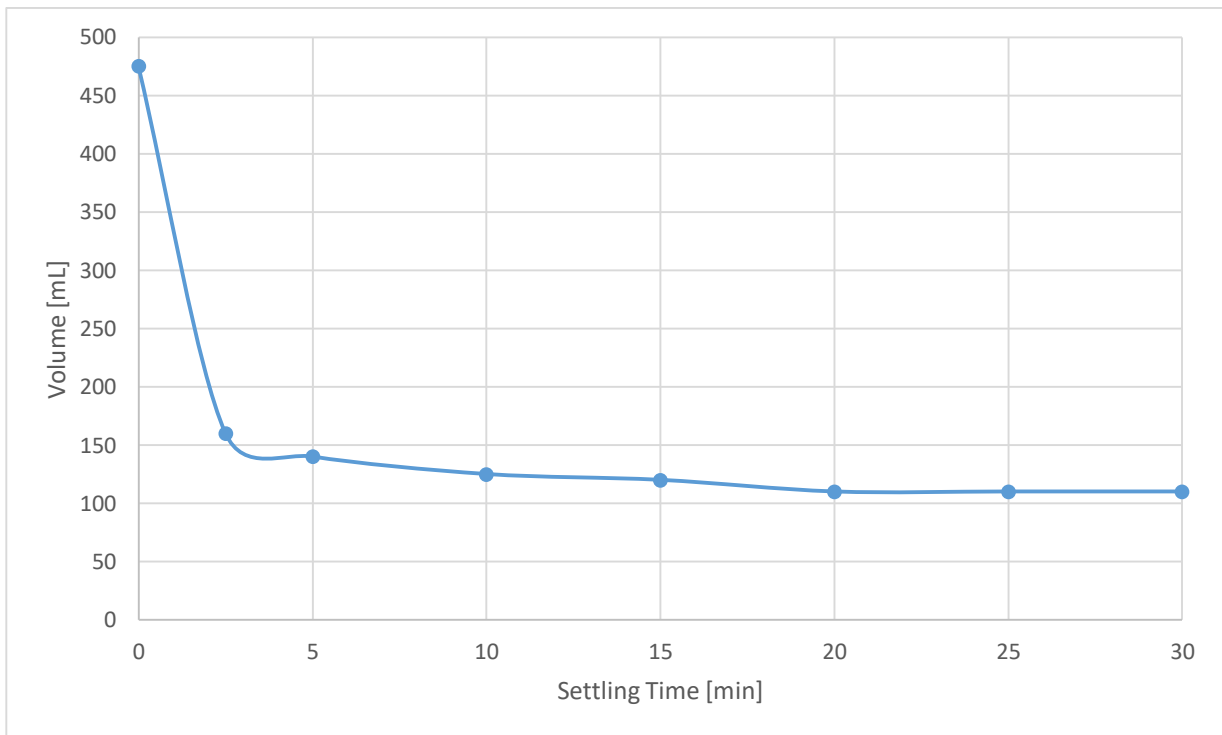
Figure 4.3: Office Fill Sludge Settling Time
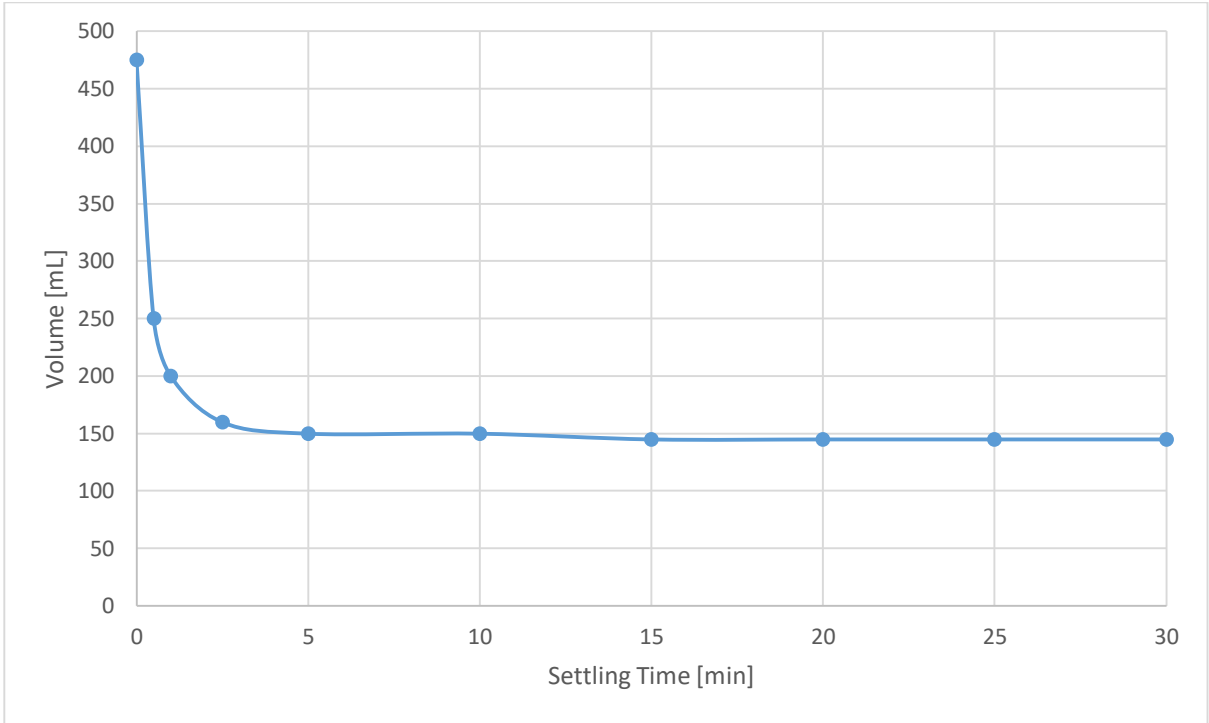
Figure 4.4: Barton Hollow Sludge Settling Time

The Capillary Suction Time (CST) of sludge from the BT trials are shown in Tables 4.26 and 4.27. The average CST for OF sludge was 34 seconds, while the average for BH was 20.6 seconds. A CST of 20 seconds is often the goal for wastewater sludge (Vesilind, 1988), though times of 50 seconds of higher have been used as acceptable dewatering times for heavy wastewater sludge (Sawalha and Scholz, 2007). The CST of the CESR sludge is well within this range and can be dewatered without further modification.

Table 4.26: Office Fill Sludge Capillary Suction Time

Replicate	Time, Seconds		
	OF A	**OF B**	**OF C**
1	26.6	40.6	41.3
2	31.1	31.7	28.2
3	21.2	33.9	38.8
4	36.8	38.7	34.6
5	38.7	39.1	28.3
Avg	30.9	36.8	34.2
COV	23.4%	10.3%	17.4%

Table 4.27: Barton Hollow Capillary Suction Time

Replicate	Time, Seconds		
	BH A	**BH B**	**BH C**
1	29.1	14.4	29.4
2	16.5	20.4	19.1
3	24.4	12.9	21.5
4	27.0	16.1	27.8
5	16.8	12.4	21.0
Avg	22.8	15.2	23.8
COV	25.6%	21.2%	19.1%

Testing was also done to determine the percent moisture of sludge from both sites (Appendix D, Tables D.5 and D.6). The percent moisture of OF sludge was 80.7%, while the percent moisture of BH sludge was 85.7%. The COV for both percent moisture values was below 5%.

Discussion

Ion Exchange

It is evident from the data that the ion exchange media selected for this study will not reduce the SC of the waters, despite having removed large portions of the dominant ions present. For OF, waters that underwent cation exchange treatment experienced a very large increase in effluent SC, with the increase not following any discernable trend related to ion exchange dosing. The increase in SC was the most extreme of any series of experiments, with increases ranging from 315% to 350% and a peak SC of more than 9,000 µS/cm. At the same time, concentrations of the major cations, Ca and Mg, were reduced by 98%. The increase in SC can be directly related to the extremely low pH values of the effluent water, which ranged from 1.87 to 1.54, and (Table 4.4 and 4.5) tended to decrease with higher ion exchange doses. The BH SC values also increased dramatically, although unlike at OF, the increase in SC was proportional to the ion exchange dose. The BH SC peaked at 5,400 µS/cm, with its lowest value being 4,670 µS/cm. Like at OF, the concentrations of major cations at BH were reduced by about 98% during treatment. Increases in SC were a result of hydrogen ion addition to the water. Effluent pH for BH was also low, with a pH range of 2.02 to 1.83. With the exception of one outlier, the COV for the cation exchange data was below 3% for each dose, which was below the conventionally accepted standard of 5%.

Increases in SC in the reactors with anion exchange media were far less than for the cation exchange reactors. Increases in SC were also predictable and corresponded well with the dose of ion exchange media present in the reactor. In the OF effluent, SC increased from an initial value of 2,500 µS/cm to final values ranging from 2,950 µS/cm to 3,550 µS/cm. The SC increase can be attributed in this case to elevated Cl^- concentrations, which initially had a concentration below detection limits and increased to 580-1,150 mg/L in the treated waters. Sulfate was the primary anion affected by the anion exchange media, with reductions of 50% - 75%, from 1,100 mg/L in raw water to approximately 400 mg/L in treated water. The BH reactors behaved similarly, with a pre-treatment SC of approximately 1,450 µS/cm and a post-treatment SC range of 1,900 - 2,100 µS/cm. The SC also tended to increase with ion exchange dose, although it did not increase in a

predictable way due to the SA dose of ion exchange being exceeded in the higher-dose reactors. Cl⁻ concentrations, which initially were below detection limits, increased to 275-850 mg/L in effluent waters. Sulfate reductions spanned a range of 40% to 95%, with an initial concentration of 775 mg/L and effluent concentrations below 100 mg/L in reactors with higher than SA ion exchange doses. No COV for the anion exchange treated waters exceeded 3%.

A potential solution to the limitations posed by the ion exchange media used in this study would be to use cation and anion exchange media that use H^+ and OH^-, respectively, as the ions exchanged. This solution has potential to mitigate the problems caused by pH increases or decreases from using each type of ion exchange individually.

One of the most common concerns with ion exchange is that the regenerant solution sometimes requires special treatment for disposal. Strong acids or bases are used as regenerants, resulting in the generation of a hazardous waste (EPA 2014). Ion exchange media are also subject to physical degradation from the multitude of reactions that occur within the resins. Cracking, the most common form of physical degradation, greatly reduces an ion exchange system's efficiency. In a column setup, cracked resins will decrease average bead size, reduce void volume, and increase head loss. Oxidation is another process of concern because it targets the links between polymers, resulting in over-hydration and swelling of the beads. Precipitates can also cause problems; anion exchange resins are especially vulnerable to damage from precipitates, which either coat the beads or fill in voids (Gottlieb 2005).

Another limitation in treating waters with high TDS is that resins are exhausted after treating a small volume of water. The TDS of both BH and OF waters are much higher than those typically found in municipal waters and will quickly exhaust a large volume of resin. Even before a resin is exhausted, waters with a high TDS will cause leakage and poorer retention of target ions than waters with lower TDS, as shown in Figure 4.5. (Comstock, 2011; Prajapati, 1985). The flow rate of both experimental series in Figure 4.5 is 30 L/hour and the media used exchanges hydrogen ions. The TDS of influent water in

both series is 750 mg/L; however, Series A has sodium as 30% of total influent cations and Series B has sodium as 40% of the total influent cations. The increase in leakage with higher sodium concentrations is likely due to the low affinity of most ion exchange media for sodium.
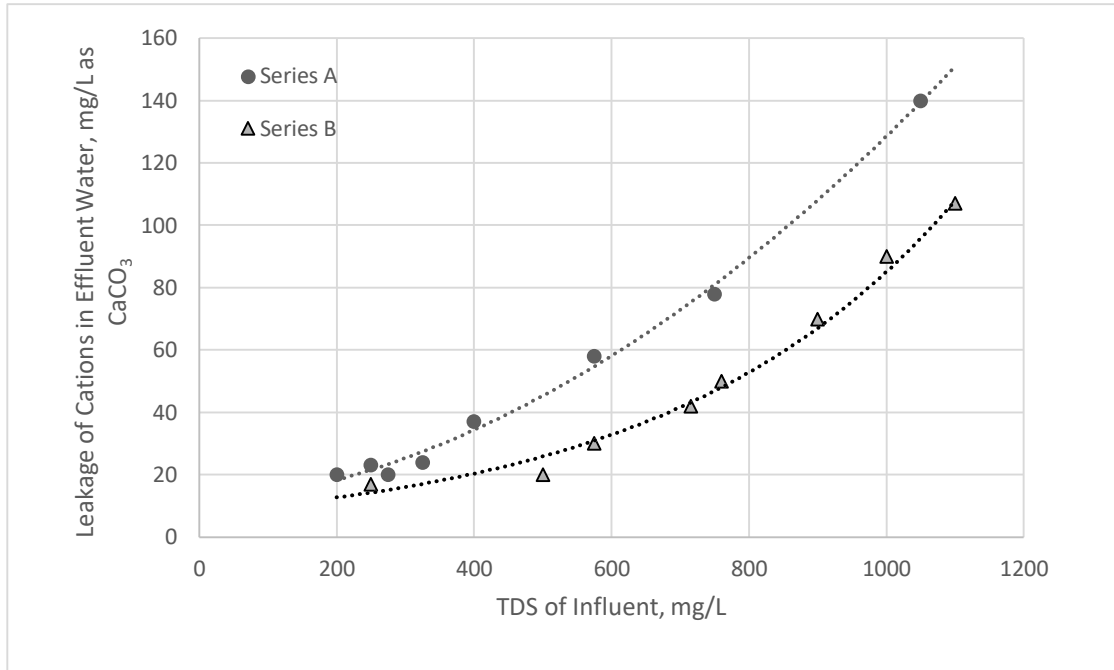
Figure 4.5: Effect of TDS on Cation retention (Modified from Prajapati, 1985)

Another factor to consider is that ion exchange media tend to be very sensitive to clogging. Pretreatment methods, such as filtration, may be necessary after precipitation events to prolong the life of ion exchange resins and to reduce head loss and fouling (NHDES, 2009; EPA, 2014). Clogged resins are very difficult to clean due to their small pore size and generally must be replaced because that is the simplest and most economical way to remedy a clogged resin (EPA, 2014).

A final concern related to the implementation of ion exchange is that buying and maintaining an ion exchange treatment system is a fairly expensive and laborious process. The media itself is fairly sophisticated, costing on average much more than precipitation technologies that would accomplish similar treatment (i.e., chemical softening). The cation exchange media used in this study cost $8,800/m^3$, while the anion exchange media was $10,600/m^3$ (DWPA a, 2017; DWPS b, 2017). Additional costs and maintenance are due to the need for backwashing the media to prevent clogging, regenerating media after it is "spent," and purchasing expensive regenerant solutions that must often be carefully disposed of as hazardous waste if very acidic or basic.

Chemical Softening

From the results of this study, it is clear that excess lime-soda softening, despite being the most appropriate type of softening for this water (high hardness, low alkalinity), is not an acceptable technology for SC reduction at the sites studied. The primary reason for the inability of this process to reduce SC is the need for soda ash addition, which caused a 70% increase in the effluent SC at OF and a 32% increase in SC at BH. Calcium concentrations were reduced during this process by 92% at OF and 85% at BH. Magnesium was reduced at OF by 73% and by 96% at BH. The reductions in SC caused by removal of the major cations present in the influent were negated by the addition of sodium ions. Sodium concentrations increased by 2,000% at OF and by 1,500% at BH.

The disparity in effluent SC values between BH and OF is directly related to the amount of soda ash required. About 1.25 times more soda ash was added to the OF water than BH, resulting in a higher concentration of Na^+ ions in the OF effluent (765 mg/L at OF as opposed to 360 mg/L at BH). The SC increase at BH was only 32%, while the OF SC increased by 70%. A relationship could be developed between the percent increase in SC and the added concentration of $NaCO_3$ in the softening reactors. For example, the increase in SC at BH during softening was 491 µS/cm, which was an SC percent increase of 32%. The concentration of soda ash added to the water was 0.805 g/L. When the percent increase in SC is divided by the concentration of soda ash added, the value is 39.8% for

BH. When the same calculation is performed at OF, the SC/SA concentration is 38.9%. The COV between these two values is only 1.9%, indicating that the ratio of SC and SA mass added is very similar between the two sites and that it may be possible to predict the SC increase that will occur when soda ash is added to the water.

Alkalinity at these sites accounted for only about 10% of anions in the water at each site, so other mines affected by this regulation with a higher alkalinity may be able to utilize softening as a SC reduction method. The possibility of using lime softening for SC reduction would depend on the alkalinity and initial SC of the water. If a high proportion of the cations are calcium and magnesium and the anions include a high percentage of carbonate, it may be possible to reduce SC using lime softening alone. Further testing should be performed on waters with a higher alkalinity to develop further recommendations for the conditions under which lime softening might be useful.

There is also the challenge of ensuring the consistency and reliability of effluent water quality at sites affected by the proposed regulation. Streams at sites are significantly affected by precipitation events. Some streams only appear during or after a precipitation event, and often have high concentrations of ions due to the contact of runoff waters with newly deposited rocks. Larger receiving streams are not immune to the effects of this high-TDS runoff, and can experience major fluctuations in ionic composition and flow rates during storm events. The inconsistency of the runoff and stream composition would make testing a stream's water composition after a precipitation event an important priority for chemical dosing and success of the softening process. The fluctuation in flow rate would also make the inclusion of a holding basin at the beginning of the treatment train a key component of any design.

A potential area for further investigation would be the use of softening in series with other treatment techniques. For example, excess lime-soda softening may be a useful pretreatment operation to couple with ion exchange to reduce the presence of ions in the water that would exhaust or clog the ion exchange media. In this instance, an ion exchange

system that exchanges H^+ ions to replace the Na^+ added during softening may be a viable option because it reduces both pH and Na^+ concentrations. It may also be possible to reduce the overall SC using cation and anion exchangers in series, using H^+ and OH^- as the ions exchanged.

As a process, softening is known for producing a significant amount of sludge, at volumes of 10% to 15% of the treated water volume (Wang, 2005). The sludge produced in this process was within this range, with OF waters producing sludge at a volume of 15% of the treated water volume and BH producing 7%. Softening sludge is typically between 15% and 25% solids (Wang, 2005). Flocculation and dewatering with lime soda softening is also known to be a challenge due to the presence of $Mg(OH)_2$ in the precipitate (Corrigan et al., 2005).

An additional challenge related to sludge in this process comes from the variability of streams subject to these regulations. If stream fluctuations are not taken into account, it is possible that variations in flow could agitate the settled sludge in each basin of the process, damaging the floc in a basin with turbulence or disturbing settled sludge so that some escapes with the effluent. Providing a location for sludge storage on-site that protects residuals from being washed away during a rain event would also be a key component of the process design.

A benefit of the softening process is that softening sludge is not classified as hazardous and is frequently sold to farms due to its valuable alkaline properties. The sale of sludge from the softening process can be a profitable supplement to the cost of implementing the process. In the mining industry, sites that have large amounts of open land available may also be able to lessen dewatering and transport expenses by spreading the process residuals out to dry, instead of purchasing expensive dewatering equipment. With proper protection of the sludge, transportation and sale of the sludge could also be limited to once a year, allowing site owners to wait until the beginning of the growing season to sell sludge to farmers and prevent additional costs for residual storage during the year. In addition, and perhaps most importantly, the sludge might be used on-site where companies are attempting to reclaim the land by planting trees and grasses.

CESR Process

The data from this study clearly show that the three most important factors in properly using the CESR process are reagent dose, reaction time, and consistent maintenance of pH during Stage II. These factors are, of course, easier to control in the lab than on-site where runoff water is inconsistent in composition. Success in dosing and reaction time can be measured by comparing the aluminum and sulfate concentrations of water, post treatment. If aluminum is low and sulfate is high, too little reagent was added to the water. If sulfate is low and aluminum is high, the opposite is, of course, true. If aluminum and sulfate concentrations are both high, not enough time was provided for the precipitate to form. Finally, if both aluminum and sulfate are high and calcium concentrations are higher than expected or higher than the initial calcium concentration, this is an indication that pH was not controlled in the correct range or has been overdosing the water with lime. In this case, the pH probe should be cleaned in an acidic solution to remove scaling and recalibrated. For the waters used in this study, the best reaction time and dose of reagent were, respectively, 18 hours and 1.25x the sulfate concentration. This dose and time may change based on water composition, but the reagent dose will always be in the range of 1.0x-1.5x the sulfate concentration.

The first three trials of the CESR experiments (1.5x reagent, 8-hour reaction; 1.0x reagent, 12-hour reaction; and 1.25x reagent, 12-hour reaction) superficially yielded very similar results when looking at SC reduction alone. All three trials resulted in SC reductions of 45%-60% for waters at both sites, though in none of the trials would the discharge SC of 500 μS/cm be met. The key differences between these trials was revealed in the ICP data. In the first trial, effluent aluminum concentrations were around 40 mg/L for both waters, sulfate reductions were near 60%, and calcium removals were low (< 20% for both BH and OF). Magnesium removal was near 99% for both waters in this trial due to the precipitation that occurs at a pH of 11. In the second trial, effluent aluminum was a low (2 mg/L), but removal percentages for sulfate were only 52% at OF and 56% at BH. Calcium removal was only 10% for OF and 36% for BH; magnesium removal was similar to that of the first trial.

In the third and fourth (BT was trial four) trials, a reagent dose of 1.25x the sulfate concentration was used, although in the third and BT trials, the reaction times were 12 hrs and 18 hrs, respectively. In trial 3, the concentration of aluminum in the effluent of both site waters was 16 mg/L. Sulfate concentrations for trial 3were reduced by about 60% at both sites, and calcium had been reduced by 25% at OF and 35% at BH. The presence of notable amounts of both sulfate and aluminum indicated the need for a longer reaction time, which was tested in trial 4. The effluent in trial 4 had an average of 18 mg/L of aluminum and a sulfate concentration near the expected removal limit for CESR (119 mg/L at OF, 132 mg/L at BH). The 92% sulfate removal at OF and 83% sulfate removal at BH were complimented by 81% calcium removal at OF and 59% calcium removal at BH. Magnesium concentrations in both instances were below the detection limit. The presence of additional aluminum in the effluent indicated that a lower reagent dose than the one used in the BT trial, perhaps a dose of 1.20 times the sulfate concentration, might further improve the effluent water quality, lower the final SC, and reduce effluent aluminum.

This work demonstrated that it is possible to use the CESR process for significant reduction of SC when the primary contributors to SC are sulfate, calcium, and magnesium. The key components in ensuring the process is successful are correctly dosing the reagent in Stage II and making sure that the pH can be correctly measured and controlled at all times. Properly maintaining the pH probe is a challenge in the CESR reactor, especially in Stage II, because the probe is submerged in water with high concentrations of calcium and magnesium, which often form a scale on exposed surfaces. In order to prevent clogging and eventual destruction of the pH probe, the sensor should be rinsed well and submerged in an acidic solution after use. The probe should also be removed from the reactors in both Stage I and II before the flocculent is added to prevent a gummy, difficult-to-remove film from forming on the probe.

To generate consistent results during Stage II, it is also imperative to ensure the lime dosing portion of the pH controller is consistent throughout the operation. If too much lime is in solution, scaling will occur in any tubes or pipes. This is especially important to take into account in instances where the pumping system has not been used in some time. Scaling was seen to occur in as little as four days. In this situation, water may build up behind the precipitate until it is forced out, causing an overdose of lime, which can increase the pH to above 12. At this level, sulfate will no longer precipitate and the effluent SC may even be higher than the initial SC due to excessive calcium concentrations.

Sludge production is an important factor to consider when designing a precipitation reactor. Stage I sludge production was less than 1% of treated water volume for both BH and OF in all trials. Stage II sludge produced under the first three trials was 10% - 20% of treated water volume. The sludge in the fourth trial was about 20% of treated water volume at OF and 30% of the treated water volume at BH. Although instructions stated that five minutes of flocculation would be sufficient, it was determined through testing that floc was larger and settled more quickly with ten minutes of stirring. After addition of the flocculent and stirring for 10 minutes at 20 rpm, sludge from waters at both sites settled to its final volume in approximately 30 minutes. The moisture content of the sludge was similar to typical, dewatered wastewater treatment plant sludge (80% - 85% moisture). It should also be noted that the sludge is not categorized as hazardous. CST values for the sludge, as determined using Standard Methods, were 34 seconds for OF and 20.6 seconds for BH. A commonly used CST value for wastewater sludge is 20 seconds (Vesilind, 1988), with CST values above 50 seconds for heavier sludge being commonly used (Sawalha and Scholz, 2007). When compared to these values, the CESR sludge is reasonably near an acceptable dewatering time for most wastewater residuals without any further polymer addition or modification.

The goal in coagulation-flocculation operations is to produce rather large flocs that settle well. In the CESR process, when lime dosing is inconsistent, flocs may be very large and not settle well, taking up 50%-80% of the reactor volume even after extensive settling. Alternatively, extremely small diameter floc that accounts for less than 5% of treated water volume and settles quickly is an indicator that the process has failed. In either of these situations, the CESR process effluent will likely have a high SC and should not be discharged to the environment. Both situations can be avoided with proper care and maintenance of the pH controller.

There are several challenges for implementing the CESR process that should be noted. The first is that collection of runoff waters and prediction of runoff volume is a challenge at many mining sites. Some streams used in this study were present throughout the year, but other would appear only during and after precipitation events. Those hoping to implement the CESR process on site would need to develop collection systems or know where runoff water collects after storm events. The inconsistency in presence and composition of valley fill runoff waters also means that many sites would be unable to use continuously stirred tank reactors (CSTR's) as a treatment option for two reasons: 1) Inconsistent flow rates would make continuous treatment difficult, and 2) Changes in major ion concentrations, especially sulfate, would create difficulties for proper chemical dosing, most notably the dosing of the aluminum reagent in Stage II. For the sites in this study, it might be possible to use batch reactors. Using this technique, it is possible to know the initial concentrations of important parameters, such as sulfate, and to prevent overdosing of Luminite MG 4 in Stage II operations.

Conclusion

The ion exchange media used in this study, which was chosen because of its high selectivity for the target ions, calcium, magnesium, and sulfate, was unable to reduce specific conductance to acceptable concentrations in the effluent water. The media used in this study instead increased the effluent SC. Cation exchange treatment of the Office Fill water resulted in the highest SC increase, with effluent values more than three times higher than influent values. Use of anion exchange media for Barton Hollow waster increased the effluent SC the least, by only 500 μS/cm on average. Although the SC increased during treatment, the target ions of calcium and magnesium were greatly reduced by cation exchange treatment (96% and 98%, respectively, at OF; 99% and 97%, respectively, at BH), and sulfate was significantly reduced by anion exchange treatment (56% at OF; 83% at BH).

There are several important limitations to consider before implementing ion exchange technology at a remote mining site. Streams on these sites are subject to fluctuations in flow and ionic composition as the water flows through and around the mining spoils. Precipitation also readily increases stream turbidity, which can clog and damage an ion exchange column. Ion exchange is rather expensive, at $10,600/m^3 for the anion exchange media used in this study, and $8,800/m^3 for the cation exchange media. Additionally, costs will be increased by maintenance procedures that can include, for waters with high TDS, frequent backwashing and regeneration. Also of concern is that the regenerant from the process might be categorized as a hazardous waste, dependent upon the raw water composition. The ion exchange media used in this study are therefore not recommended as a primary method for specific conductance reduction in waters at strip mining sites. However, such media might be used as a polishing step that targets specific ions to meet discharge standards.

Chemical softening remains a very effective method for reducing calcium and magnesium concentrations in water. However, in waters such as these with insufficient levels of carbonate hardness, softening will not reduce the overall specific conductance and may, in fact, cause effluent conductivity to increase. ICP-MS analysis demonstrated that the target ions, calcium and magnesium, were effectively removed from the water during softening, but sodium concentrations increased by 1,500% to 2,000% due to the addition of Na_2CO_3, negating the positive effects of the softening process. In this study, softening caused an appreciable increase in the SC of the effluent water.

Due to the nature of the mining sites affected by the proposed regulation, it would be fairly difficult to implement softening operations on site. At a typical mining site, there are many small streams affected by valley fills that would ultimately affect the SC of receiving streams. Some of these streams appear only during and after precipitation events, making it more difficult to manage chemical additions. Sludge collection, dewatering, and storage also poses a significant problem. If a softening system could be implemented at a site, however, the sale or onsite use of softening residuals to increase soil alkalinity could be a valuable asset to companies. Sites with large amounts of open land could also reduce dewatering and transportation costs for residuals by allowing them to air dry.

Overall, excess lime-soda softening is not a recommended treatment technique for SC reduction in waters that have a high concentration of sulfate and high non-carbonate hardness. It is important to note that not all sites affected by the proposed regulation have the same composition as the waters selected for this study, so certain sites with higher-alkalinity waters may be able to benefit from SC reduction through softening.

It has been shown that when reagent doses and reactor times are within a certain range, it is possible to reduce SC in mining runoff waters to below the proposed EPA limit of 500 µS/cm, using the CESR Process. The best reagent dose and reaction time for mining waters in this study were, respectively, 1.25 times the sulfate concentration and 18 hours. However, the water at different sites should be individually tested to confirm the optimal reagent dose and reaction time. Under the right conditions, the CESR process reduces the

concentrations of sulfate, calcium, and magnesium, the three dominant ions in the source water, by 80%-90%, 59%-81%, and more than 99%, respectively. These three ions combined contributed to approximately 90% of the chemical equivalents present at both sites, so targeting these ions for removal in waters similar to those at OF and BH will yield fruitful results in SC reduction.

When implementing the CESR process, care should be taken in determining the water's initial sulfate concentration to ensure that the reagent dose is appropriate and excess aluminum is not released into the environment. In order to achieve consistent results with this process, it is also key to properly maintain and clean the pH control system. When the process is performed successfully, sludge volume will account for approximately 30% of the water volume after settling, with a moisture content of 80% to 85%. This sludge can be disposed of as a non-hazardous waste.

Literature Cited

Apell, JN. 2010. *Combined Ion Exchange Treatment for removal of dissolved organic matter and hardness.* Water Research 44 (2010) 2419-2430.

APEX Engineering. 2016. *CESR Process for Sulfate Removal*. Available online at: http://www.apexengineering.us/CESR-Sulfate-Removal.html; Last accessed Jan. 17, 2017.

APHA. 2012. *Standard Methods for the Examination of Water and Wastewater*. 22nd Edition. American Public Health Association. Washington DC.

Black, A.P. and Christman, R.F. Jour. AWWA, 1961, 53:737

Boehme EA, Zipper CE, Schoenholtz SH, Soucek DJ, Timpano AJ. 2016. *Temporal dynamics of benthic macroinvertebrate communities and their response to elevated specific conductance in Appalachian coalfield headwater streams.* Ecol Indic 64:171–180.

Bowell, RJ. 2004. *A review of sulphate removal options for mine waters*. Proc., International Mine
Water Association Symposium. Newcastle upon Tyne, England.

Ciaccio, L. *Water and Water Pollution Handbook*. Marcel Dekker, Inc. New York, 1971.

Clark EV, Greer BM, Zipper, CE, Hester, ET. 2016. *Specific conductance–stage relationships in Appalachian valley fill streams.* Environ Earth Sci 75:1222.

Comstock, SEH; Boyer, T.H.; Graf, K.C. 2011. *Treatment of nanofiltration and reverse osmosis concentrates: comparison of precipitative softening, coagulation, and anion exchange.* Water Research 45 (2011) 4855–4865.

Cornell Civil Engineering Department. 1999. *Aluminum Solubility*. Available online at: http://ceeserver.cee.cornell.edu/mw24/projects/SSF/alsol/aluminumsolubility.htm. Last accessed 12 February 2017.

Davis and Cornwell. *Introduction to Environmental Engineering, Fifth Edition.* McGraw-Hill: New York. 2013.

DWPSa. 2017. "Amberlite PWA 15" Order Page. Available Online at: https://dwps.octochemstore.com/amberlite/product/amberlite-pwa15-2/. Last accessed February 12, 2017.

DWPSb. 2017. "DOWEX Marathon C (H+)" Order Page. Available Online at:

https://dwps.octochemstore.com/dowex/product/dowex-marathon-c-h/. Last accessed February 12, 2017.

Edzwald, J.K. 2011. *Water Quality and Treatment: A handbook on Drinking Water* (Sixth Edition). American Water Works Association, American Society of Civil Engineers, McGraw-Hill: New York.

EPA. 2016. *Ecological Toxicity Information*. Available online at https://archive.epa.gov/reg5sfun/ecology/web/html/toxprofiles.html; Last accessed Jan. 17, 2017. EPA. 2014. Reference Guide to Treatment Technologies for Mining-Influenced Wastewater. EPA 542-R-14-001. Available from: www2.epa.gov/sites/production/files/2015-08/documents/reference_guide_to_treatment_technologies_for_miw.pdf (September, 2015).

EPA. 2011a. *A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams (Final Report)*. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-10/023F.

EPA. 2011b. *The effects of mountaintop mines and valley fills on aquatic ecosystems of the central Appalachian coalfields*. U.S. Environmental Protection Agency, Washington, DC, EPA/ 600/R-09/138F.

EPA. 2000. Wastewater Technology Factsheet – Chemical Precipitation. EPA 832-F-00-018. Available from: http://permanent.access.gpo.gov/websites/epagov/www.epa.gov/OWM/mtb/chemical_precipitation.pdf (September, 2015).

Evans, DM; Zipper, CE; Donovan, PF; and Daniels, WL. 2014. *Long Term Trends of Specific Conductance in Waters Discharged by Coal-Mine Valley Fills in Central Appalachia, USA*. Journal of the American Water Resources Association. Vol. 50, No. 6.

Faust, S.D. and Aly, O.M., 1998. Chemistry of Water Treatment. Ann Arbor Press, Chelsea, MI, p. 329.

Fisher, R.A. 1950. *Statistical methods for Research Workers*. London: Oliver and Boyd.

Gabelich, CJ; Rahrdianto, A; Northrup, CR; Yun, TI; and Cohen, Y. 2011. *Process Evaluation of intermediate chemical demineralization for water recovery enhancement in production-scale brackish water desalting*. Desalination 272 (2011) 36-45.

Gottlieb, MC 2005. Chapter 12: Ion Exchange Applications in Water Treatment Plant Design, 4th ed. New York: McGraw Hill

Indarawis, KA and Boyer, TH. 2013. *Superposition of Anion and cation exchange for removal of natural water ions.* Separation and Purification Technology 118 (2013) 112-119.

Jones, CS; Corrigan, TP; Graham, DB, and McMullen, LD. 2005. *Reduced Lime Feeds: Effects on Operational Costs and Water Quality*. Des Moines Water Works; Available online at: http://www.dmww.com/upl/documents/water-quality/lab-reports/lab-studies/reduced-lime-feeds-effects-on-operational-costs-and-water-quality.pdf. Last Accessed Jan 25, 2017.

Kemak, Zachary. 2016. *Biological and Membrane Treatment Applications for the Reduction of Specific Conductivity and Total Dissolved Solids in Coal Mining Waters*. Thesis submitted in partial fulfilment of the MS ENE degree. Virginia Tech. Blacksburg, Virginia.

Li, Haigang and Yang, Chuanfang. 2015. *Nitrite removal using ion exchange resin: Batch vs. Fixed bed performance.* Separation Science and Technology, 50:11, 1721-1730, DOI: 10.1080/01496395.2014.990099.

Lorax Environmental. 2003. *Treatment of Sulphate in Mine Effluents*. International Network for Acid Prevention.

M. Reinsel, personal communication, Nov. 20. 2015.

Mohammadesmaeili, F., Badr, M.K., Abbaszadegan, M., Fox, P., 2010. Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment. Water Environment Research 82, 342e350.

NHDES (New Hampshire Department of Environmental Services). 2009. *Environmental Fact Sheet: Ion Exchange Treatment of Drinking Water.* Available from: http://www.des.nh.gov//commissioner/pip/factsheets/dwgb/documents/dwgb-2-12.pdf. (September, 2009).

NHDES (New Hampshire Department of Environmental Services). 2008. *Environmental Fact Sheet: Hardness in Drinking Water.* Available from: http://www.des.nh.gov/organization/commissioner/pip/factsheets/dwgb/documents/dwgb-3-6.pdf. (October, 2008).

Pond GJ, Passmore ME, Pointon ND, Felbinger JK, Walker CA, Krock KJ, Fulton JB, Nash WL. 2014. *Long-term impacts on macroinvertebrates downstream of reclaimed mountaintop mining valley fills in central Appalachia.* Environ Manag 54:919–933.

Portland Cement Association (PSA). 2001. *Concrete information: Ettringite Formation and the Performance of Concrete.* Available online at http://www.cement.org/docs/default-source/fc_concrete_technology/is417-ettringite-formation-and-the-performance-of-concrete.pdf?sfvrsn=2; Last accessed Jan. 20, 2017.

Prajapati, MN; Gaur, PM; and Dasare, BD. 1985. *Brackish water desalination by a continuous counter-current ion-exchange technique.* Desalination, 52 (1985) 317-326.

Reinsel, M. 2015. *Sulfate Removal Technologies: A Review.* Available online at http://www.wateronline.com/doc/sulfate-removal-technologies-a-review-0001; Last accessed Jan. 17, 2017.

Rosseland, BO; Eldhuset, TD; Staurnes, M. 1990. *Environmental Effects of Aluminum.* Environmental Geochemistry and Health, 12 (1-2): 17-27. (1990).

Comstock, S.E.H.; Boyer, T.H.; Graf, K.C. 2011. *Treatment of nanofiltration and reverse osmosis concentrates: comparison of precipitative softening, coagulation, and anion exchange.* Water Research 45 (2011) 4855–4865.

Stacy, Robert, personal communication, Feb. 18, 2016.

Sawalha, O. and Scholz, M. 2007. *Assessment of Capillary Suction Time (CST) Test Methodologies.* Environmental Technology, Vol. 28, Iss. 12. 2007.

Timpano AJ, Schoenholtz SH, Zipper CE, Soucek DJ. 2011. *Isolating effects of total dissolved solids on aquatic life in central Appalachian coalfield streams.* In: Proceedings, national meeting of the American society of mining and reclamation, Pittsburgh, PA, pp 1284–1302.

USGS (United States Geological Survey). 2016. *The USGS Water Science School: Water Hardness.* Available at https://water.usgs.gov/edu/hardness.html. Last Accessed Jan 20, 2017.

Vesilind, PA. 1988. *Capillary Suction Time as a Measure of Sludge Dewaterability.*

Journal of the Water Pollution Control Federation, Vol. 60 (Feb, 1988). pp. 215-
220. Water Environment Federation.

Wang, LK; Hung, YT; and Shammas, NK. *Phisiochemical Treatment Processes.*
Handbook of Environmental Engineering Volume 3. Humana Press: New Jersey.
2005.

Water Online. 2016. *A New Process for Sulfate Removal from Industrial Waters*.
Available online at http://www.wateronline.com/doc/a-new-process-for-sulfate-
removal-from-indust-0001; Last accessed Jan. 17, 2017.

Zipper CE, Burger JA, McGrath JM, Rodrigue JA, Holtzman GI. 2011. *Forest restoration
potentials of coal-mined lands in the eastern United States*. J Environ Qual
40:1567–1577.

Chapter 5: Overall Conclusion and Engineering Significance

Coal mines in central Appalachia that dispose of mining spoils in valley fills have been identified as a contributor to the elevated specific conductance measured in receiving streams. Runoff waters at these sites extract ions from the spoils and can significantly affect the health of benthic organisms living in the streams. Thus, the overall goal of this study was to investigate the feasibility of possibly implementing three different physicochemical operations to treat the waters at mining sites.

To expand the accessibility of the specific conductance (SC) modeling equations published by McCleskey in 2012, the speciation software, MINEQL+, was tested for SC prediction with various concentrations of six compounds of environmental interest. Prediction of SC for certain species was within 5%, but many predictions exceeded a 20% difference from the measured SC. It is recommended that further work be conducted in this area to better understand the fundamental chemistry behind the larger errors seen in this study and the limitations of using MINEQL+ in conjunction with McCleskey's equations.

During ion exchange testing, both cation and anion exchange media were used to remove calcium, magnesium and sulfate. It was determined that the media used in the study increased SC. Final recommendations for ion exchange are to use cation and anion exchange in series, where H^+ and OH^- are the ions exchanged, or to use ion exchange only as a polishing step to meet specific discharge limits.

Excess lime-soda softening was selected as the most appropriate softening for the source waters being treated; however, the addition of soda ash to increase carbonate concentrations in the water also increased sodium concentrations and the SC. Softening is therefore not recommended for waters with a high hardness and low alkalinity. However, softening may have some promise for SC reduction in waters that have a higher alkalinity than those consider in this study. It is also important to note that companies might be able to recover some of the costs of softening operations by drying solids on-site and selling the residuals as soil amendments for farming, or using the residuals for on-site land reclamation.

The final treatment technique considered in this project was the Cost Effective Sulfate Removal (CESR) process. Several reagent dosing and reaction times were tested for Stage II of the process. The best results were achieved at a reagent dose of 1.25 times the sulfate concentration and an 18-hour reaction time. Under these conditions, the effluent SC was reduced to below the proposed limit of 500 µS/cm. Sulfate, calcium, and magnesium were reduced by 93%, 87%, and 99.9%, respectively, at OF, and 80%, 61%, and 99.7%, respectively, at BH. In this process, ettringite, a non-hazardous waste, is produced at a volume that is about 30% of the volume of water treated. Although further study is warranted to evaluate the practicability of this process at mining sites, the process appears to show promise either as a standalone or complementary treatment step.

Literature Cited

Apell, JN. 2010. *Combined Ion Exchange Treatment for removal of dissolved organic matter and hardness.* Water Research 44 (2010) 2419-2430.

APEX Engineering. 2016. *CESR Process for Sulfate Removal*. Available online at http://www.apexengineering.us/CESR-Sulfate-Removal.html; Last accessed Jan. 17, 2017.

Black, A.P. and Christman, R.F. Jour. AWWA, 1961, 53:737

Bockris, JO'M and Reddy, AKN. 1998. *Modern Electrochemistry Vol. 1: Ionics.* Plenum Press: New York.

Boehme EA, Zipper CE, Schoenholtz SH, Soucek DJ, Timpano AJ. 2016. *Temporal dynamics of benthic macroinvertebrate communities and their response to elevated specific conductance in Appalachian coalfield headwater streams.* Ecol Indic 64:171–180.

Bowell, RJ. 2004. *A review of sulphate removal options for mine waters*. Proc., International Mine Water Association Symposium. Newcastle upon Tyne, England.

Ciaccio, L. *Water and Water Pollution Handbook*. Marcel Dekker, Inc. New York, 1971.

Clark EV, Greer BM, Zipper, CE, Hester, ET. 2016. *Specific conductance–stage relationships in Appalachian valley fill streams.* Environ Earth Sci 75:1222.

Comstock, S.E.H.; Boyer, T.H.; Graf, K.C. 2011. *Treatment of nanofiltration and reverse osmosis concentrates: comparison of precipitative softening, coagulation, and anion exchange.* Water Research 45 (2011) 4855–4865.

Cormier, SM; Suter, GW; and Zheng, L. 2013. *Derivation of a Benchmark for Freshwater Ionic Strength*. Environmental Toxicology and Chemistry, Vol. 32, No. 2, pp. 263-271.

Daniels WL, Zipper CE, Orndorff CW, Skousen JG, Barton CD, McDonald L, Beck M. 2016. *Predicting total dissolved solids release from central Appalachian coal mine spoils*. Environ Pollut 216:371–379

Davis and Cornwell. *Introduction to Environmental Engineering, Fifth Edition.* McGraw-Hill: New York. 2013.

Edzwald, J.K. 2011. *Water Quality and Treatment: A handbook on Drinking Water* (Sixth

Edition). American Water Works Association, American Society of Civil Engineers, McGraw-Hill: New York.

EPA, Region 5. 2016. *Ecological Toxicity Information*. Available online at https://archive.epa.gov/reg5sfun/ecology/web/html/toxprofiles.html; Last accessed Jan. 17, 2017.

EPA. 2014. Reference Guide to Treatment Technologies for Mining-Influenced Wastewater. EPA 542-R-14-001. Available from: www2.epa.gov/sites/production/files/2015-08/documents/reference_guide_to_treatment_technologies_for_miw.pdf (September, 2015).

EPA. 2011a. *The effects of mountaintop mines and valley fills on aquatic ecosystems of the central Appalachian coalfields*. U.S. Environmental Protection Agency, Washington, DC, EPA/ 600/R-09/138F.

EPA. 2011b. *A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams (Final Report)*. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-10/023F.

EPA. 2000. Wastewater Technology Factsheet – Chemical Precipitation. EPA 832-F-00-018. Available from: http://permanent.access.gpo.gov/websites/epagov/www.epa.gov/OWM/mtb/chemical_precipitation.pdf (September, 2015).

Evans, DM; Zipper, CE; Donovan, PF; and Daniels, WL. 2014. *Long Term Trends of Specific Conductance in Waters Discharged By Coal-Mine Valley Fills in Central Appalachia, USA*. Journal of the American Water Resources Association. Vol. 50, No. 6.

Faust, S.D. and Aly, O.M., 1998. Chemistry of Water Treatment. Ann Arbor Press, Chelsea, MI, p. 329.

Gabelich, CJ; Rahrdianto, A; Northrup, CR; Yun, TI; and Cohen, Y. 2011. *Process Evaluation of intermediate chemical demineralization for water recovery enhancement in production-scale brackish water desalting.* Desalination 272 (2011) 36-45.

Gottlieb, MC 2005. Chapter 12: Ion Exchange Applications in Water Treatment Plant

Design, 4th ed. New York: McGraw Hill

Griffith, RA and Jurinak, JJ. 1973. *Estimation of Activity Coefficients from the Electrical Conductivity of natural aquatic systems and soil extracts.* Soil Science 116, 26-30.

Griffith, MB; Norton, SB; Alexander, SC; Pollard, AI; and LeDuc, SC. 2012. *The effects of mountaintop mines and valley fills on the physicochemical quality of stream ecosystems in the central Appalachians: A review.* JScience of the Total Environment. 417-418 (2012) 1-12.

Gustafson, H and Behrman, S. 1939. *Determination of Total Dissolved Solids in water by electrical conductivity.* Ind Eng Chem Anal Ed. 11, 355

Jones, CS; Corrigan, TP; Graham, DB, and McMullen, LD. 2005. *Reduced Lime Feeds: Effects on Operational Costs and Water Quality*. Des Moines Water Works; Available online at: http://www.dmww.com/upl/documents/water-quality/lab-reports/lab-studies/reduced-lime-feeds-effects-on-operational-costs-and-water-quality.pdf. Last Accessed Jan 25, 2017.

Indarawis, KA and Boyer, TH. 2013. *Superposition of Anion and cation exchange for removal of natural water ions.* Separation and Purification Technology 118 (2013) 112-119.

Li, Haigang and Yang, Chuanfang. 2015. *Nitrite removal using ion exchange resin: Batch vs. Fixed bed performance.* Separation Science and Technology, 50:11, 1721-1730, DOI: 10.1080/01496395.2014.990099.

McCleskey, RB; Nordstrom, DK; Ryan, JN; Ball, JW. 2012. *A new method of calculating electrical conductivity with applications to natural waters*. Geochimica et Cosmochimica Acta 77 (2012) 369-382.

Miller, RL; Bradford, WL; and Peters, NE. 1988. *Specific Conductance: Theoretical Considerations and Application to Analytical Quality Control.* U.S. Geological Survey Water-Supply Paper 2311. Available online at: https://pubs.usgs.gov/wsp/2311/report.pdf; Accessed Jan. 20 2017.

Mohammadesmaeili, F., Badr, M.K., Abbaszadegan, M., Fox, P., 2010. Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment. Water Environment Research 82, 342e350.

Murray, J.W. *Activity Scales and Activity Corrections*. University of Washington,

Published October 2004.

NHDES (New Hampshire Department of Environmental Services). 2009. *Environmental Fact Sheet: Ion Exchange Treatment of Drinking Water.* Available from: http://www.des.nh.gov/organization/commissioner/pip/factsheets/dwgb/documents/dwgb-2-12.pdf. (September, 2009).

NHDES (New Hampshire Department of Environmental Services). 2008. *Environmental Fact Sheet: Hardness in Drinking Water.* Available from: http://www.des.nh.gov/organization/commissioner/pip/factsheets/dwgb/documents/dwgb-3-6.pdf. (October, 2008).

Pawlowicz, R. 2008. *Calculating the conductivity of natural waters.* Limnol Oceanogr Meth 6, 489-501.

Ponnamperuma, FN; Tianco, EM and Loy, TA. 1966. *Ionic Strengths of the solutions of flooded soils and other natural aqueous solutions from Specific Conductance.* Soil Science 102, 408-413.

Pond GJ, Passmore ME, Pointon ND, Felbinger JK, Walker CA, Krock KJ, Fulton JB, Nash WL. 2014. *Long-term impacts on macroinvertebrates downstream of reclaimed mountaintop mining valley fills in central Appalachia.* Environ Manag 54:919–933.

Portland Cement Association (PSA). 2001. *Concrete information: Ettringite Formation and the Performance of Concrete.* Available online at http://www.cement.org/docs/default-source/fc_concrete_technology/is417-ettringite-formation-and-the-performance-of-concrete.pdf?sfvrsn=2; Last accessed Jan. 20, 2017.

Prajapati, MN; Gaur, PM; and Dasare, BD. 1985. *Brackish water desalination by a continuous counter-current ion-exchange technique.* Desalination, 52 (1985) 317-326.

Reinsel, M. personal communication, Nov. 20. 2015.

Reinsel, M. 2015. *Sulfate Removal Technologies: A Review.* Available online at http://www.wateronline.com/doc/sulfate-removal-technologies-a-review-0001; Last accessed Jan. 17, 2017.

Sawalha, O. and Scholz, M. 2007. *Assessment of Capillary Suction Time (CST) Test Methodologies.* Environmental Technology, Vol. 28, Iss. 12. 2007.

Singh, T and Kalra, YP. 1974. *Specific Conductance Method for In Situ Estimation of Total*

Dissolved Solids. American Water Works Association. Available online at http://www.jstor.org.ezproxy.lib.vt.edu/stable/pdf/41268134.pdf; Last accessed online Jan. 20, 2017.

Stacy, Robert, personal communication, Feb. 18, 2016.

Timpano AJ, Schoenholtz SH, Zipper CE, Soucek DJ (2010) *Isolating effects of total dissolved solids on aquatic life in central Appalachian coalfield streams*. In: Proceedings, national meeting of the American society of mining and reclamation, Pittsburgh, PA, pp 1284–1302.

Timpano AJ, Schoenholtz SH, Soucek DJ, Zipper CE. 2015. *Salinity as a limiting factor for biological condition in mining-influenced Central Appalachian headwater streams*. J Am Water Resour Assoc 51:240–250.

USGS (United States Geological Survey). 2016. *The USGS Water Science School: Water Hardness.* Available at https://water.usgs.gov/edu/hardness.html. Last Accessed Jan 20, 2017.

Vesilind, PA. 1988. *Capillary Suction Time as a Measure of Sludge Dewaterability*. Journal of the Water Pollution Control Federation, Vol. 60 (Feb, 1988). pp. 215-220. Water Environment Federation.

Visconti Reluy, F; de Paz Bécares, JM; Zapata Hernández, RD; and Sánchez Díaz, J. 2004. *Development of an equation to relate electrical conductivity to soil and water salinity in a Mediterranean agricultural environment.* Australian Journal of Soil Research, 2004, 42, 381-388.

Wang, LK; Hung, YT; and Shammas, NK. 2005. *Phisiochemical Treatment Processes.* Handbook of Environmental Engineering Volume 3. Humana Press: New Jersey.

Water Online. 2016. *A New Process For Sulfate Removal From Industrial Waters*. Available online at http://www.wateronline.com/doc/a-new-process-for-sulfate-removal-from-indust-0001; Last accessed Jan. 17, 2017.

Zipper CE, Burger JA, McGrath JM, Rodrigue JA, Holtzman GI. 2011. *Forest restoration potentials of coal-mined lands in the eastern United States*. J Environ Qual 40:1567–1577.

Appendix A: MINEQL Modeling

Table A.1 Sodium Sulfate SC Prediction

Goal (mol/kg)	g/kg	mg/kg	pH	Temp (Deg C)	SC (uS/cm)	SC (uS/cm)	% error
0.0001	0.014204	14.204	4.88	20.9	24.4	27.6	13.0
0.001	0.14204	142.04	5.22	21.0	238	221.6	6.9
0.01	1.4204	1420.4	5.59	21.0	2,020	1,983.8	1.8
0.1	14.204	14204	6.16	21.2	15,360	18,137.1	18.1
0.2	28.408	28408	7.10	21.2	27,300	33,607.5	23.1
0.5	71.02	71020	8.36	21.3	52,100	87,773.7	68.5

Table A.2 Potassium Nitrate SC Prediction

Goal (mol/kg)	g/kg	mg/kg	pH	Temp (Deg C)	SC (uS/cm)	SC (uS/cm)	% error
0.0001	0.01011	10.11	4.41	20.3	13.8	25.9	87.7
0.001	0.101103	101.1	5.01	20.2	146.7	133.7	8.9
0.01	1.011032	1011	5.15	20.1	1,361	1,259.5	7.5
0.1	10.11032	10110	5.13	20.2	11,540	11,310.5	2.0
0.2	20.22064	20221	5.63	20.5	21,500	21,325.1	0.8
0.5	50.5516	50552	5.69	20.5	47,400	53,311.6	12.5

Table A.3 Calcium Chloride SC Prediction

Goal (mol/kg)	g/kg	mg/kg	pH	Temp (Deg C)	SC (uS/cm)	SC (uS/cm)	% error
0.0001	0.014701056	14.701056	4.56	21.9	19	34.5	81.6
0.001	0.14701056	147.01056	4.74	22.0	219	249.4	13.9
0.01	1.4701056	1470.1056	5.09	22.1	2,070	2,217.2	7.1
0.1	14.701056	14701.056	5.25	22.6	17,790	18,635.8	4.8
0.2	29.402112	29402.112	5.16	22.7	33,400	35,066.8	5.0
0.5	73.50528	73505.28	5.27	23.5	69,500	81,040.5	16.6

Table A.4 Magnesium Sulfate SC Prediction

Goal (mol/kg)	g/kg	mg/kg	pH	Temp (Deg C)	SC (uS/cm)	SC (uS/cm)	% error
0.0001	0.0120366	12.0366	6.18	21.7	14.7	24.1	-64.0
0.001	0.120366	120.366	5.97	21.8	194.8	197.5	-1.4
0.01	1.20366	1203.66	8.23	22.1	1,463	1,045.5	28.5
0.1	12.0366	12036.6	9.28	22.7	8,940	3,599.7	59.7
0.2	24.0732	24073.2	9.46	22.8	15,300	6,307.1	58.8
0.5	60.183	60183	9.36	23.7	30,500	10,570.8	65.3

Table A.5 Sodium Bicarbonate

Goal (mol/kg)	g/kg	mg/kg	pH	Temp (Deg C)	SC (uS/cm)	SC (uS/cm)	% error
0.0001	0.0084007	8.4007	6.65	20.5	8.6	7.2	16.4
0.001	0.084007	84.007	7.24	20.4	88.9	78.5	11.7
0.01	0.84007	840.07	8.13	20.5	869	776.1	10.7
0.1	8.4007	8400.7	8.13	20.3	7,200	6,314.5	12.3
0.2	16.8014	16801.4	8.22	20.5	13,280	11,248.4	15.3
0.5	42.0035	42003.5	8.14	20.5	28,800	22,174.1	23.0

Table A.6 Potassium Chloride SC Prediction

Goal (mol/kg)	g/kg	mg/kg	pH	Temp (Deg C)	SC (uS/cm)	SC (uS/cm)	% error
0.0001	0.00745513	7.45513	4.56	20.3	15.9	22.6	41.9
0.001	0.0745513	74.5513	5.21	20.2	148.8	136.3	8.4
0.01	0.745513	745.513	5.30	20.2	1,415	1,295.4	8.4
0.1	7.45513	7455.13	5.27	20.2	12,340	11,827.6	4.2
0.2	14.91026	14910.26	5.67	20.2	23,900	22,725.0	4.9
0.5	37.27565	37275.65	5.69	20.1	55,500	53,519.3	3.6

Table A.7 Sodium Chloride SC Prediction

Goal (mol/kg)	g/kg	mg/kg	pH	Temp (Deg C)	SC (uS/cm)	SC (uS/cm)	% error
0.0001	0.005844	5.844	4.31	22.0	12.8	28.3	121.0
0.001	0.05844	58.44	4.71	22.0	123.3	123.3	0.0
0.01	0.5844	584.4	5.16	22.0	1,180	1,112.5	5.7
0.1	5.844	5844	5.54	22.2	10,220	9,826.8	3.8
0.2	11.688	11688	5.42	22.5	19,140	18,608.0	2.8
0.5	29.22	29220	5.65	22.1	44,100	42,856.7	2.8

Table A.8 Potassium Sulfate SC Prediction

Goal (mol/kg)	g/kg	mg/kg	pH	Temp (Deg C)	SC (uS/cm)	SC (uS/cm)	% error
0.0001	0.0174259	17.4259	5.06	22.0	30.5	31.1	2.1
0.001	0.174259	174.259	4.94	22.2	277	272.6	1.6
0.01	1.74259	1742.59	5.25	22.1	2,390	2,389.9	0.0
0.1	17.4259	17425.9	5.83	22.0	18,830	19,849.1	5.4
0.2	34.8518	34851.8	5.84	22.2	35,000	37,028.7	5.8
0.5	87.1295	87129.5	6.15	21.2	58,000	82,500.4	42.2

Appendix B: Ion Exchange

Table B.1 Office Fill Anion Exchange SC and pH, Replicate 1

% of SA	50%	75%	SA	125%	150%	200%
Dose (g)	0.96	1.44	1.92	2.40	2.88	3.84
SC, µS/cm	3,000	3,160	3,300	3,420	3,490	3,540
pH	7.74	7.71	7.69	7.91	7.75	7.84

Table B.2 Office Fill Anion Exchange SC and pH, Replicate 2

% of SA	50%	75%	SA	125%	150%	200%
Dose (g)	0.96	1.44	1.92	2.40	2.88	3.84
SC, µS/cm	2,910	3,210	3,350	3,410	3,510	3,560
pH	7.72	7.63	7.61	7.64	7.65	7.63

Table B.3 Barton Hollow Anion Exchange SC and pH, Replicate 1

% of SA	50%	75%	SA	125%	150%	200%
Dose (g)	0.88	1.31	1.75	2.19	2.63	3.50
SC, µS/cm	1,878	1,930	2,000	2,000	2,010	2,040
pH	7.86	7.71	7.61	7.57	7.55	7.52

Table B.4 Barton Hollow Anion Exchange SC and pH, Replicate 2

% of SA	50%	75%	SA	125%	150%	200%
Dose (g)	0.88	1.31	1.75	2.19	2.63	3.50
SC, µS/cm	1,925	1,995	2,030	2,080	2,070	2,120
pH	8.19	8.14	8.07	8.12	8.14	8.12

Table B.5 Office Fill Cation Exchange SC and pH, Replicate 1

% of SA	50%	75%	SA	125%	150%	200%
Dose (g)	1.35	2.02	2.69	3.36	4.04	5.38
SC, µS/cm	7,610	8,790	9,070	9,070	9,030	9,030
pH	1.87	1.82	1.6	1.55	1.54	1.54

Table B.6 Office Fill Cation Exchange SC and pH, Replicate 2

% of SA	50%	75%	SA	125%	150%	200%
Dose (g)	1.35	2.02	2.69	3.36	4.04	5.38
SC, µS/cm	8,200	8,750	7,540	8,720	9,020	8,660
pH	1.87	1.85	1.68	1.61	1.55	1.54

Table B.7 Barton Hollow Cation Exchange SC and pH, Replicate 1

% of SA	50%	75%	SA	125%	150%	200%
Dose (g)	0.62	0.92	1.23	1.54	1.85	2.46
SC, µS/cm	4,400	5,100	5,340	5,360	5,370	5,370
pH	2.03	1.93	1.87	1.86	1.86	1.83

Table B.8 Barton Hollow Cation Exchange SC and pH, Replicate 2

% of SA	50%	75%	SA	125%	150%	200%
Dose (g)	0.62	0.92	1.23	1.54	1.85	2.46
SC, µS/cm	4,760	5,280	5,380	5,390	5,410	5,430
pH	2.01	1.92	1.89	1.84	1.83	1.83

Table B.9 OF Anion Exchange Ionic Composition, Replicate 1

	Concentration [mg/L]						
	Na	**Mg**	**Si**	**SO₄**	**Cl**	**K**	**Ca**
Untreated Water	**36.0**	**247.1**	**4.5**	**1,500.0**	**0.0**	**10.5**	**346.0**
50% SA	36.1	252.7	4.5	747.1	802.1	10.9	374.0
75% SA	37.8	264.3	4.8	545.9	1,088.0	11.2	394.5
SA	39.4	276.0	4.8	394.0	1,275.0	11.6	412.1
125% SA	37.3	262.4	4.7	271.8	1,330.0	11.7	391.8
150% SA	37.7	265.3	4.8	199.4	1,485.0	11.2	392.9
200% SA	37.7	266.2	4.9	128.8	1,577.0	11.3	396.1

Table B.10 OF Anion Exchange Ionic Composition, Replicate 2

	Concentration [mg/L]						
	Na	**Mg**	**Si**	**SO₄**	**Cl**	**K**	**Ca**
Untreated Water	**36.0**	**247.1**	**4.5**	**1,500.0**	**0.0**	**10.5**	**346.0**
50% SA	33.5	230.0	0.0	124.8	1,159.0	9.7	284.8
75% SA	33.5	229.1	0.1	175.3	1,122.0	9.6	278.8
SA	33.5	228.8	0.0	224.8	1,076.0	9.6	278.8
125% SA	33.4	229.0	0.0	306.9	1,026.0	9.6	276.8
150% SA	33.5	228.5	0.0	488.4	877.7	9.6	270.3
200% SA	32.1	219.6	0.0	663.4	691.0	9.2	258.8

Table B.11 BH Anion Exchange Ionic Composition, Replicate 1

	Concentration [mg/L]						
	Na	**Mg**	**Si**	**SO₄**	**Cl**	**K**	**Ca**
Untreated Water	**22.8**	**93.6**	**4.1**	**775.8**	**0.0**	**7.7**	**181.4**
50% SA	26.0	114.2	4.6	192.6	609.2	8.8	218.2
75% SA	25.6	113.1	4.5	93.3	714.7	8.7	215.1
SA	25.4	112.1	4.4	54.4	721.7	8.7	212.0
125% SA	23.2	101.6	4.1	44.7	669.7	7.0	181.9
150% SA	23.1	100.9	4.1	33.0	679.6	7.0	182.1
200% SA	26.5	116.5	4.5	24.9	820.0	9.1	222.5

Table B.12 BH Anion Exchange Ionic Composition, Replicate 2

	Concentration [mg/L]						
	Na	Mg	Si	SO$_4$	Cl	K	Ca
Untreated Water	**22.8**	**93.6**	**4.1**	**775.8**	**0.0**	**7.7**	**181.4**
50% SA	25.3	108.3	2.5	136.5	554.2	8.4	177.6
75% SA	2.5	11.0	0.2	11.8	55.3	0.8	19.4
SA	25.2	108.3	2.0	77.0	626.1	8.4	178.3
125% SA	25.4	109.5	2.5	48.9	694.8	8.4	178.6
150% SA	26.4	112.3	1.6	29.1	657.7	8.9	185.4
200% SA	35.0	150.0	0.1	48.1	1,005.0	11.7	252.8

Table B.13 OF Cation Exchange Ionic Composition, Replicate 1

	Concentration [mg/L]						
	Na	Mg	Si	SO$_4$	Cl	K	Ca
Untreated Water	**36.0**	**247.1**	**4.5**	**1,500.0**	**0.0**	**10.5**	**346.0**
50% SA	27.7	36.9	4.2	1,454.0	24.5	6.1	22.3
75% SA	16.9	3.4	4.1	1,423.0	24.7	2.6	2.0
SA	11.7	1.3	4.7	1,484.0	30.4	1.6	0.7
125% SA	8.3	0.7	3.9	1,308.0	20.7	1.1	0.4
150% SA	6.5	0.5	3.9	1,336.0	22.2	0.8	0.5
200% SA	4.6	0.3	4.0	1,368.0	22.6	0.6	0.1

Table B.14 Office Fill Cation Exchange Ionic Composition, Replicate 2

	Concentration [mg/L]						
	Na	**Mg**	**Si**	**SO$_4$**	**Cl**	**K**	**Ca**
Untreated Water	**36.0**	**247.1**	**4.5**	**1,500.0**	**0.0**	**10.5**	**346.0**
50% SA	4.1	0.9	15.7	1,476.0	26.2	0.5	7.7
75% SA	5.6	0.5	0.1	1,479.0	23.5	0.6	1.3
SA	6.9	0.8	13.7	1,458.0	22.0	0.9	4.3
125% SA	9.4	2.4	36.6	1,541.0	20.5	1.3	78.2
150% SA	14.0	2.0	0.1	1,458.0	20.8	2.1	1.3
200% SA	24.2	16.8	0.4	1,474.0	20.9	4.9	26.7

Table B.15 BH Cation Exchange Ionic Composition, Replicate 1

	Concentration [mg/L]						
	Na	**Mg**	**Si**	**SO$_4$**	**Cl**	**K**	**Ca**
Untreated Water	**22.8**	**93.6**	**4.1**	**775.8**	**0.0**	**7.7**	**181.4**
50% SA	20.9	24.2	3.8	775.4	3.0	5.8	20.5
75% SA	15.0	2.0	3.9	770.6	3.2	3.0	1.5
SA	9.9	0.6	4.1	764.2	3.0	1.6	0.5
125% SA	7.3	0.4	3.8	756.4	2.7	1.1	0.7
150% SA	6.0	0.3	3.8	749.4	2.8	0.9	0.9
200% SA	4.2	0.9	4.2	745.4	2.7	0.6	2.5

Table B.16 BH Cation Exchange Ionic Composition, Replicate 2

	Concentration [mg/L]						
	Na	**Mg**	**Si**	**SO$_4$**	**Cl**	**K**	**Ca**
Untreated Water	**22.8**	**93.6**	**4.1**	**775.8**	**0.0**	**7.7**	**181.4**
50% SA	17.1	2.2	0.0	841.2	9.7	3.6	1.7
75% SA	9.6	0.4	0.0	856.1	6.3	1.6	0.0
SA	6.5	0.2	0.0	849.5	4.2	1.0	-0.8
125% SA	5.0	0.1	0.0	839.8	4.0	0.7	0.2
150% SA	4.0	0.1	0.0	842.7	3.6	0.5	0.1
200% SA	2.9	0.1	0.0	844.2	3.3	0.4	0.1

Appendix C: Chemical Softening

Office Fill Softening Ionic Composition, Replicate 1

	Concentration [mg/L]						
	Ca	Mg	SO$_4$	Na	K	Cl	Si
Untreated Water	346.0	247.1	1,500.0	36.0	10.5	0.0	4.5
Stage I	103.1	192.6	1,407.0	760.2	9.1	21.2	3.8
Stage II	128.9	140.6	1,438.0	787.0	9.7	21.2	1.8
Recarbonation	18.0	130.1	1,528.0	772.9	9.6	23.3	1.0

Office Fill Softening Ionic Composition, Replicate 2

	Concentration [mg/L]						
	Ca	Mg	SO$_4$	Na	K	Cl	Si
Untreated Water	346.0	247.1	1,500.0	36.0	10.5	0.0	4.5
Stage I	124.9	202.5	1,407.0	775.4	9.4	20.8	3.9
Stage II	29.3	0.3	1,452.0	766.8	9.6	21.3	2.5
Recarbonation	35.8	1.1	1,466.0	756.7	9.5	21.6	2.5

Barton Hollow Softening Ionic Composition, Replicate 1

	Concentration [mg/L]						
	Ca	Mg	SO$_4$	Na	K	Cl	Si
Untreated Water	181.4	93.6	775.8	22.8	7.7	0.0	4.1
Stage I	48.9	87.6	800.5	356.2	7.6	2.1	3.9
Stage II	30.2	7.4	805.8	365.7	8.6	2.6	2.4
Recarbonation	28.2	3.7	826.0	363.4	7.9	2.2	2.1

Barton Hollow Softening Ionic Composition, Replicate 2

	Concentration [mg/L]						
	Ca	**Mg**	**SO$_4$**	**Na**	**K**	**Cl**	**Si**
Untreated Water	181.4	93.6	775.8	22.8	7.7	0.0	4.1
Stage I	56.1	86.8	801.7	358.4	7.5	2.0	4.5
Stage II	28.3	5.4	824.5	365.1	7.8	2.1	2.4
Recarbonation	27.0	3.4	810.7	370.4	8.0	2.1	2.3

Appendix D: CESR Process

Table D.1: Trial 1 SC Values and Overall Percent Reduction

	OF		BH	
Replicate	1	2	1	2
Start	2,510	2,510	1,534	1,534
Stage 1	1,910	2,220	1,402	1,416
Stage 2	1,574	699	689	1,034
% Red	37%	72%	55%	33%

Table D.2: Trial 2 SC Values and Overall Percent Reduction

	OF		BH	
Replicate	1	2	1	2
Start	2,510	2,510	1,534	1,534
Stage 1	2,140	2,240	1,437	1,425
Stage 2	1,543	1,595	1,054	732
% Red	39%	36%	31%	52%

Table D.3: Trial 3 SC Values and Overall Percent Reduction

	OF			BH		
Replicate	1	2	3	1	2	3
Start	2,510	2,510	2,510	1,534	1,534	1,534
Stage 1	2,340	2,340	2,240	1,385	1,488	1,488
Stage 2	673	1,718	1,280	1,138	658	552
% Red	73.2%	31.6%	49.0%	26%	57%	64%

Table D.4: Trial 4 SC Values and Overall Percent Reduction

	OF			BH		
Replicate	1	2	3	1	2	3
Start	2,510	2,510	2,510	1,534	1,534	1,534
Stage 1	2,220	2,220	2,190	1,454	1,438	1,458
Stage 2	374	419	533	497	435	437
% Red	85.1%	83.3%	78.8%	68%	72%	72%

Table D.5: Office Fill Sludge Percent Moisture

	OF A	**OF B**	**OF C**
Tray	1.2677	1.2425	1.2584
Before	2.4084	2.4309	2.0766
After	0.5720	0.4360	0.3350
Δ	1.8364	1.9949	1.7416
% H2O	76.2%	82.1%	83.9%

Table D.6: Barton Hollow Sludge Percent Moisture

	BH A	**BH B**	**BH C**
Tray	1.2645	1.2462	1.2592
Before	1.3408	1.5238	1.3703
After	0.1878	0.1875	0.2284
Δ	1.153	1.3363	1.1419
% H2O	86.0%	87.7%	83.3%