SPECIFIC CONDUCTANCE REDUCTION IN VALLEY FILL RUNOFF USING THE COST-EFFECTIVE SULFATE REMOVAL PROCESS¹

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Abstract: In recent years, the 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 $\mu\text{S}/\text{cm}$, the Appalachian Research Initiative for Environmental Science (ARIES) Center at Virginia Tech requested that testing be conducted 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. The primary contributing ions were determined to be Na^+ , Mg^{2+} , Ca^{2+} , and SO_4^{2-} . Once characterized, the sample water was treated using a two-step precipitation method called the Cost-Effective Sulfate Removal (CESR) process. Study results indicate that source water with an SC of 1,500-2,500 $\mu\text{S}/\text{cm}$ could be successfully reduced below the proposed EPA limit of 500 $\mu\text{S}/\text{cm}$ when the second step of the CESR process lasted 18 hours and the reagent dose was 1.25x the source water sulfate concentration. The success of this process was due to its ability to remove more than 85% of the Ca, Mg, and SO_4^{2-} from the water, which together accounted for more than 90% of ions in the source water.

Additional Key Words: Electrical Conductivity, Appalachia, CESR

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Introduction

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 (Pond et al., 2014; Timpano et al., 2010). 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. The goal of this study was to reduce the concentration of the primary ions of concern in waters from two surface mining sites in Southwest Virginia, Office Fill (OF) and Barton Hollow (BH), using an engineered precipitation technique.

The CESR process, which targets sulfate as well as Ca and Mg, was developed in the 1990's by European engineers (Reinsel, 2015a). 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 application of the CESR process using sample water from Berkeley Pit, an acid mine site in Butte, Montana, water with an initial sulfate concentration of 8,700 mg/L was reduced to an effluent concentration of 56 mg/L. The average cost of this process was determined to be \$0.79/m³ of treated water when removing 1,500 mg/L of SO_4^{2-} . The estimated upper level cost of treatment was found to be \$1.58/m³ (Lorax, 2003). The process was also used to treat waters at a copper mine with an initial SO_4^{2-} concentration of 3,350 mg/L; the effluent sulfate concentration was 360 mg/L (Water Online, 2016).

The CESR process is a two-stage precipitation method for waters containing Na, Ca, and SO_4^{2-} . In Stage I, the goal is to precipitate gypsum (CaSO_4) to its lowest solubility limit of 2,000 mg/L. This is done by increasing the pH of the water to 10.5 with a slurry of CaO and water and stirring the mixture for 40 minutes at 100 rpm in a jar stirrer (Reinsel, 2015b).

After the mixture has been stirred for 40 mins, the jar stirrer should then be adjusted to 20 rpm and 2 mg/L of polymer should be 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 for dewatering before continuing with Stage II because any

remaining gypsum will react with the Stage II reagent and prevent optimal SO_4^{2-} precipitation (Reinsel, 2015b).

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 stabilizes, further treatment of the water will not result in additional sulfate removal. At this point, 2 ppm of the polymer flocculent Magnafloc 155 should be added to the reactor and the water should be stirred in for a minimum of five minutes, after which the stirrer should be turned off and the jar should be allowed to settle. The water should be removed and re-carbonated to a neutral pH before discharge. The precipitate should be dewatered and prepared for disposal. (Reinsel, 2015b). A schematic of the CESR process is shown in Fig. 1.

Figure 1. CESR Process Diagram¹

¹ Due to the complexity of this process, it is suggested that any implementation on site be fully automated.

The precipitate from the CESR process is ettringite, a unique calcium-alumina-sulfate compound with the formula $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot3\text{H}_2\text{O}$ (PCA, 2001). Ettringite has a polishing effect on the water and has been shown to bring concentrations for metals such as Cr, As, and Se down below their detection limits. Up to a third of dissolved Cl^- and NO_3^- in source water may also be removed during precipitation of this mineral. Ettringite can also be disposed of as non-hazardous waste; however, sludge disposal is still a key consideration of the process. Large amounts of ettringite precipitate are produced during Stage II of the process, approximately 45 lbs/per 1,000 gallons of water treated (Water Online, 2016). Sludge tested in the lab showed that precipitate was 80%-85% water; dewatering sludge on site may substantially reduce disposal costs.

An integral component for successful implementation of the CESR process is determining the ideal Stage II reagent dose. Although the reagent (Luminite MG-4) is inexpensive (approximately \$0.40/lb in 2016), it contains Al, which may be present in effluent 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 which is an inability of the animal to regulate osmosis (USEPA, 2016; Rosseland, 1990). Furthermore, it is possible that Al could enter the food chain through plants' nutrient uptake from the soil (Rosseland, 1990). Aluminum is least soluble at a neutral pH, between 6.5 and 9.0, has a chronic toxicity value of 748 $\mu\text{g/L}$, and an acute toxicity value of 1,496 $\mu\text{g/L}$ for freshwater organisms (USEPA, 1988). Due to the low toxicity values for aluminum, it is imperative to maintain low aluminum concentrations in CESR effluent.

The objectives of the experiments were to determine:

1. The effect of the CESR process on effluent SC and the ionic composition of source water.
2. The quantity of sludge produced by chemical softening and the CESR process.
3. The appropriate dose of the reagent, Luminite MG-4, necessary for optimal sulfate removal in Stage II of the CESR process.
4. An average treatment time for CESR Stage II precipitation.
5. Any challenges or limitations of implementing each process at a site.

Methods

Analysis of Samples

The cations measured in this study were Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . These cations and silicon (Si) were measured using an ICP-MS instrument (X Series ICP-MS, Thermo Electron Corporation). The anions, SO_4^{2-} , NO_3^- , and Cl^- , were measured using an ion chromatograph (Dionex ICS-1600, Thermo Electron Corporation). An Omega CDH-SD1 conductivity meter was used to measure temperature and specific conductance. 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 CaO, which becomes hydrated lime in water, and Luminite MG-4.

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 1, 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.

$$\% \text{ Moisture} = \frac{WW - DW}{WW} * 100\% \quad \text{Eq. 1}$$

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

Sample waters were collected at two surface mining sites: Office Fill (OF, Coordinates 37.066, -82.152) and Barton Hollow (BH, Coordinates 37.069, -82.135).

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 water was clarified. Precipitate formed in this step was dense and settled quickly.

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 reactor jar at a height for which 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 (1.0001g precision). The reagent was added to achieve a concentration that was 1.0-1.5 times the influent sulfate concentration. After adding the reagent, the pH decreased and a precipitate formed, presumably ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot3\text{H}_2\text{O}$) (PCA, 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 SO_4^{2-} 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. During bench testing, 10 minutes of flocculation was found to produce larger, faster settling sludge than the 5 minutes of flocculation that had been sufficient in Stage I. 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 a sticky sludge that cannot be easily removed. 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

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 (USEPA, 2011; Clark, 2016; Timpano, 2010; Pond et al., 2014). Office Fill had the higher SC of the two sites, with an initial SC value of 2,500 $\mu\text{S}/\text{cm}$, as compared to 1,500 $\mu\text{S}/\text{cm}$ 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. Total Dissolved Solids in mg/L for these sites was 0.8-0.9 of the SC in $\mu\text{S}/\text{cm}$ (Kemak, 2016). Table 1 provides additional information regarding the source waters.

Table 1. pH, SC, TDS, TSS, alkalinity and turbidity of Office Fill and Barton Hollow source water

Site	pH	SC $\mu\text{S}/\text{cm}$	TDS mg/L	TSS mg/L	Alkalinity mg/L CaCO_3	Turbidity 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 2 and 3 show the concentration of ions in the sample water and a cation-anion balance for each site's water. TDS at both sites, and therefore SC, was dominated by three key ions: Ca^{+2} , Mg^{+2} , and SO_4^{2-} . 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. Calcium and Mg were again 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. As at OF, the SO_4^{2-} 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 10% 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 2. Cation-anion balance for source water from Office Fill.

Constituent	mg/L	meq/L	Sum [meq/L]
Ca ²⁺	346.0	17.26	39.43
Mg ²⁺	247.1	20.34	
K ⁺	10.5	0.27	
Na ⁺	36.0	1.57	
HCO ₃ ⁻	241.6	3.96	36.90
SO ₄ ²⁻	1,531.0	31.86	
NO ₃ ⁻ as N	3.5	0.25	
Cl ⁻	29.3	0.83	

Table 3. Cation-anion balance for source water from Barton Hollow.

Constituent	mg/L	meq/L	Sum [meq/L]
Ca ²⁺	181.4	9.04	17.94
Mg ²⁺	93.6	7.70	
K ⁺	7.7	0.20	
Na ⁺	22.8	0.99	
HCO ₃ ⁻	96.39	1.58	17.84
SO ₄ ²⁻	775.8	16.15	
NO ₃ ⁻ as N	4.0	0.11	
Cl ⁻	4.1	0.58	

Silicon, which is often found in the Si⁴⁺ 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.

CESR Process Effluent

Two initial tests were performed by dosing the water with Luminite MG-4 at 1.5 times (x) the SO₄²⁻ concentration and allowing the reaction to occur for eight hours in Stage II. Although the SC was reduced under these conditions (Table 4) by an average of 55% for OF waters and 44% at

BH, the ICP analysis (Table 5) revealed that there was far more potential for the removal of SO_4^{2-} . Aluminum and SO_4^{2-} concentrations were both high in the test water effluent, 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. Water treated with the CESR process has been shown to have effluent sulfate concentrations below 100 mg/L; this information, coupled with the high concentration of reagent remaining, made it clear that the reaction time was not long enough. An additional takeaway from the high effluent Al concentration was that reagent dosing was too high for the source water's composition.

Table 4. SC of clarified water and sludge produced from CESR process using a reagent concentration of 1.5 x the SO_4^{2-} concentration and an 8-hour reaction time.

	OF Stage 1		OF Stage 2		BH Stage 1		BH Stage 2	
	Avg	COV	Avg	COV	Avg	COV	Avg	COV
SC, $\mu\text{S}/\text{cm}^*$	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%

*Two replicates per site were performed for this trial

Table 5. Ionic composition of CESR process effluent water: reagent concentration of 1.5 x the SO_4^{2-} concentration and an 8-hour reaction time

Replicate	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 Rep 1	21	972	418	6	24	8	17
OF Rep 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 Rep 1	36	194	117	3	18	7	3
BH Rep 2	41	492	250	0	18	9	4

*Source water values included for reference

A reagent dose of 1.0x the sulfate concentration and a 12-hour reaction time were chosen for the second set of trials to allow a longer window for precipitation to occur. SC reduction under

these conditions was similar, but slightly more successful than the reduction achieved in the first set of trials, with a 58% reduction of SC at OF and 61% reduction at BH (Table 6). Comparison with the ICP results (Table 7) 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, though in this trial Al concentrations were low, around 2 mg/L at both sites. It appeared that a 12-hour reaction time was sufficient for the reagent dose in the second trial, so the next set of trials were conducted using the same reaction time.

Table 6. SC of clarified water and sludge produced from CESR process using a reagent concentration of 1.0 x the SO_4^{2-} concentration and a 12-hour reaction time.

	OF Stage 1		OF Stage 2		BH Stage 1		BH Stage 2	
	Avg	COV	Avg	COV	Avg	COV	Avg	COV
SC, $\mu\text{S}/\text{cm}^*$	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%

*Two replicates per site were performed for this trial

Table 7. Ionic composition of CESR process effluent water: reagent concentration of 1.0 x the SO_4^{2-} concentration and a 12-hour reaction time

Replicate	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 Rep 1	3	990	393	16	22	8	17
OF Rep 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 Rep 1	3	541	172	40	17	7	3
BH Rep 2	0	441	232	0	19	8	46

*Source water values included for reference

The third set of trials occurred with a reagent dose that was 1.25 x the SO_4^{2-} concentration and using a reaction time of 12 hours. These conditions resulted in an SC reduction of about 50% for

both BH and OF (Table 8). ICP results from Table 9 showed that Al concentrations in Stage II effluent were approximately 16 mg/L for both sites, while SO_4^{2-} concentrations were well above 100 mg/L (585 mg/L at OF, 300 mg/L at BH). The presence of both high Al and SO_4^{2-} concentrations in the water indicated that the dosing could feasibly be correct, but the reaction time was too short.

Table 8. SC of clarified water and sludge produced from CESR process using a reagent concentration of 1.25 x the SO_4^{2-} concentration and a 12-hour reaction time

	OF Stage 1		OF Stage 2		BH Stage 1		BH Stage 2	
	Avg	COV	Avg	COV	Avg	COV	Avg	COV
SC, $\mu\text{S}/\text{cm}^*$	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%

*Three replicates per site were performed for this trial

Table 9. Ionic composition of CESR process effluent water: reagent concentration of 1.25 x the SO_4^{2-} concentration and a 12-hour reaction time.

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 Rep 1	43	201	109	0	27	16	26
OF Rep 2	1	1,046	465	1	39	16	29
OF Rep 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 Rep 1	0	640	203	37	19	7	3
BH Rep 2	26	230	106	0	23	10	8
BH Rep 3	22	31	45	0	19	10	7

*Source water values included for reference

In the final set of trials, reagent was added at a concentration of 1.25 x the SO_4^{2-} concentration with a Stage II reaction time of eighteen hours. Under these conditions, the Stage II effluent water had a final SC near or below the proposed EPA limit of 500 $\mu\text{S}/\text{cm}$.

The average effluent SC in OF Stage II was 442 $\mu\text{S}/\text{cm}$, an 82% reduction from the initial SC value of 2,510 $\mu\text{S}/\text{cm}$. The effluent SC for BH was similar at 456 $\mu\text{S}/\text{cm}$, a 70% reduction from the initial value of 1,534 $\mu\text{S}/\text{cm}$ (Table 10). 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 11). The Ca 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.

The effluent water from all four trials had a pH above 11.0 when the CESR process was complete. It was lab verified that re-carbonation could return the pH to a neutral value. Re-carbonation did not noticeably change the SC of any waters tested.

Table 10. SC of clarified water and sludge produced from CESR process using a reagent concentration of 1.25 x the SO_4^{2-} concentration and an 18-hour reaction time

	OF Stage 1		OF Stage 2		BH Stage 1		BH Stage 2	
	Avg	COV	Avg	COV	Avg	COV	Avg	COV
SC, $\mu\text{S}/\text{cm}^*$	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%

*Three replicates per site were performed for this trial

Table 11. Ionic composition of CESR process effluent water: reagent concentration of 1.25 x the SO_4^{2-} concentration and a 18-hour reaction time.

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 Rep 1	10	92	38	0	25	9	26
OF Rep 2	14	120	53	0	22	8	22
OF Rep 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 Rep 1	17	177	81	0	18	9	5
BH Rep 2	36	90	82	2	17	7	11
BH Rep 3	13.6	128.9	61.0	0.1	22.9	11.2	3.2

*Source water values included for reference

Sludge Characterization

A known limitation of the CESR process is that a high volume of sludge is produced, especially during Stage II. A small amount of dense precipitate is produced in Stage I; sludge volume produced from Stage I averaged 0.2% - 1.0% of the volume of water treated. Sludge production in Stage II is much higher, but the variety and quantity of sludge produced depends on a number of factors, including reagent dosing. The sludge volume produced for the Trial 4 reactor conditions averaged 30% of the process volume before dewatering. Figures 2 and 3 show how the sludge produced from treatment of the BH and OF waters settled.

Figure 2. Office Fill sludge settling time.

Figure 3. Barton Hollow sludge settling time.

The Capillary Suction Time (CST) of sludge from the Stage 4 trials are shown in Tables 12 and 13. 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 or 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 12. 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 13. 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. 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

The three most important factors for success using the CESR process are reagent dose, reaction time, and consistent maintenance of pH during Stage II. These factors are far 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 Al and SO_4^{2-} concentrations of water, post treatment. If Al is low and SO_4^{2-} is high, too little reagent was added to the water. If SO_4^{2-} is low and Al is high, the opposite is true. If Al and SO_4^{2-} concentrations are both high, not enough time was provided for the precipitate to form. Finally, if both Al and SO_4^{2-} are high and Ca concentrations are higher than expected or higher than the initial Ca concentration, this is an indication that pH was not controlled in the correct range or the controller has overdosed 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 1.25 x the SO_4^{2-} 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 SO_4^{2-} concentration.

The first three trials of the CESR experiments (1.5 x reagent, 8-hour reaction; 1.0 x reagent, 12-hour reaction; and 1.25 x 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 was the discharge SC of 500 $\mu\text{S}/\text{cm}$ met. The key differences between these trials was revealed in the ICP data. In the first trial, effluent Al concentrations were around 40 mg/L for both waters, SO_4^{2-} reductions were near 60%, and Ca removals were low (< 20% for both BH and OF). Magnesium removal was near 99% for both waters in this trial due to the Mg precipitation that occurs at a pH of 11. In the second trial, effluent Al was a low (2 mg/L), but removal percentages for SO_4^{2-} were only 52% at OF and 56% at BH. Calcium removal was only 10% for OF and 36% for BH; Mg removal was similar to that of the first trial.

In the third and fourth trials, a reagent dose of 1.25 x the SO_4^{2-} concentration was used. The third trial was performed using a Stage II reaction time of 12 hours, while the fourth trial had an 18-hour reaction time. In trial 3, the concentration of Al in the effluent of both site waters was 16 mg/L. Sulfate concentrations for trial 3 were reduced by about 60% at both sites, and Ca had

been reduced by 25% at OF and 35% at BH. The presence of notable amounts of both SO_4^{2-} and Al 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 Al and a SO_4^{2-} 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% SO_4^{2-} removal at BH were complemented by 81% Ca removal at OF and 59% Ca removal at BH. Magnesium concentrations in both instances were below the detection limit. The presence of additional Al in the effluent indicated that a lower reagent dose than the one used in the fourth trial, perhaps a dose of 1.20 times the SO_4^{2-} concentration, might further improve the effluent water quality, lower the final SC, and reduce effluent Al.

It is possible to use the CESR process to achieve reduction of SC when, on a field scale, the primary contributors to SC are SO_4^{2-} , Ca, and Mg. 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 Ca and Mg that 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 film from forming on the probe.

To generate consistent results during Stage II, it is also imperative to ensure that lime dosing 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 consider in instances where the pumping system has not been used in some time. During testing, scaling was seen to occur within pH controller tubing 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 and potentially bringing the Stage II reactor pH above 12. At this pH, SO_4^{2-} will no longer precipitate, the CESR process will reverse or stop, and the effluent SC may be higher than the initial SC due to excessive Ca 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 the original guidelines used for testing stated that five minutes of flocculation would be sufficient, it was determined in the lab that floc was larger and settled more quickly with ten minutes of gentle 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. Capillary Suction Time (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 also being acceptable for heavier sludge (Sawalha and Scholz, 2007). When compared to these values, the CESR sludge is reasonably near an acceptable dewatering time for most wastewater residuals even before any further polymer addition or modification.

The goal in coagulation-flocculation operations is to produce large, fluffy floc that settles well. In the CESR process, when lime dosing is inconsistent, flocs may be very large and settle poorly, taking up 50%-80% of the reactor volume even after an extensive settling time. An alternative parameter found in the lab is that 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 at a remote site near a mine that should be noted. The first is that collection of runoff waters and prediction of runoff volume is a challenge around many mining sites. Some streams used in this study were present throughout the year, but others 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 SO_4^{2-} , would create difficulties for proper chemical dosing, most notably the dosing of the Al 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 SO_4^{2-} , and to prevent overdosing of Luminite MG 4 in Stage II operations.

Although field scale studies are needed, when reagent doses and reactor times are within a certain range, it seems possible this process could reduce SC in mining runoff waters to below the proposed EPA limit of 500 $\mu\text{S}/\text{cm}$. The best reagent dose and reaction time for mining waters in this study were, respectively, 1.25 times the SO_4^{2-} 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 SO_4^{2-} , Ca, and Mg, 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 SO_4^{2-} concentration to ensure the reagent dose is appropriate and excess Al 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.

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Literature Cited

- APEX Engineering. 2016. CESR Process for Sulfate Removal. Accessed on Jan 17, 2017 from <http://www.apexengineering.us/CESR-Sulfate-Removal.html>.
- American Public Health Association (APHA). 2012. Standard Methods for the Examination of Water and Wastewater, 22nd Edition. American Public Health Association. Washington DC.
- Clark, E.V., B.M. Greer, C.E. Zipper, and E.T. Hester. 2016. Specific conductance–stage relationships in Appalachian valley fill streams. *Environmental Earth Sciences* 75:1222. <https://link.springer.com/article/10.1007%2Fs12665-016-6026-2>.
- Fisher, R.A. 1950. Statistical methods for Research Workers. London: Oliver and Boyd.
- 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.
- Lorax Environmental. 2003. Treatment of Sulphate in Mine Effluents. International Network for Acid Prevention.
- Pond, G.J., M.E. Passmore, N.D. Pointon, J.K. Felbinger, C.A. Walker, K.J. Krock, J.B. Fulton, and W.L. Nash. 2014. Long-term impacts on macroinvertebrates downstream of reclaimed mountaintop mining valley fills in central Appalachia. *Environ Manag* 54:919–933. <https://doi.org/10.1007/s00267-014-0319-6>.
- Portland Cement Association (PCA). 2001. Concrete information: Ettringite Formation and the Performance of Concrete. Accessed on Jan 20, 2017 from http://www.cement.org/docs/default-source/fc_concrete_technology/is417-ettringite-formation-and-the-performance-of-concrete.pdf?sfvrsn=2.
- Reinsel, M. 2015a. Sulfate Removal Technologies: A Review. Accessed on Jan 17, 2017 from <http://www.wateronline.com/doc/sulfate-removal-technologies-a-review-0001>.
- Reinsel, M. personal communication, Nov. 20. 2015b.
- Rosseland, B.O., T.D. Eldhuset, and M. Staurnes. 1990. Environmental Effects of Aluminum. *Environmental Geochemistry and Health*, 12 (1-2): 17-27. <https://doi.org/10.1007/BF01734045>

- Sawalha, O. and M. Scholz. 2007. Assessment of Capillary Suction Time (CST) Test Methodologies. *Environmental Technology*, Vol. 28, Iss. 12. 2007.
<https://doi.org/10.1080/09593332808618898>
- Timpano, A.J., S.H. Schoenholtz, C.E. Zipper, and D.J Soucek. 2010. Isolating effects of total dissolved solids on aquatic life in central Appalachian coalfield streams. *Proceedings, national meeting of the American Society of Mining and Reclamation*, Pittsburgh, PA, pp 1284–1302. <http://dx.doi.org/10.21000/JASMR10011284>
- United States Environmental Protection Agency (USEPA). 1988. Ambient Water Quality Criteria for Aluminum. Accessed on May 12, 2018 from
<https://nepis.epa.gov/Exe/ZyPDF.cgi/2000M5FC.PDF?Dockkey=2000M5FC.PDF>. Last accessed May 12, 2018.
- United States Environmental Protection Agency (USEPA). 2011. 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.
- United States Environmental Protection Agency (USEPA). 2016. Ecological Toxicity Information. Accessed on Jan 17, 2017 from
<https://archive.epa.gov/reg5sfun/ecology/web/html/toxprofiles.html>.
- 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.
- Water Online. 2016. A New Process for Sulfate Removal from Industrial Waters. Accessed on Jan 17, 2017 from <http://www.wateronline.com/doc/a-new-process-for-sulfate-removal-from-indust-0001>.