

5-2014

Comparing Ferrous Chloride and Ferrous Sulfate as Secondary Coagulants at the Beaver Water District Drinking Water Treatment Plant

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Comparing Ferrous Chloride and Ferrous Sulfate as Secondary Coagulants at the Beaver Water
District Drinking Water Treatment Plant

Comparing Ferrous Chloride and Ferrous Sulfate as Secondary Coagulants at the Beaver Water
District Drinking Water Treatment Plant

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Civil Engineering

by

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University of Arkansas
Bachelor of Science in Civil Engineering, 2012

May 2014
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This thesis is approved for recommendation to the Graduate Council.

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Abstract

In November 2012, the Beaver Water District (BWD) switched primary oxidants from free chlorine to chlorine dioxide (ClO_2) to curb formation of trihalomethanes, a regulated group of organic disinfection byproducts (DBPs). Because ClO_2 is reduced to chlorite (ClO_2^-), a regulated inorganic DBP, BWD incorporated ferrous salt into their coagulation regime to quench chlorite to chloride. In this study, two ferrous salts – ferrous chloride (FC) and ferrous sulfate (FS) – were compared as secondary coagulants in combination with alum, the primary coagulant. Ferrous salts were dosed stoichiometrically to reduce chlorite and alum was dosed at percentages (0-100%) relative to a typical alum dose at the BWD, 30 mg/L as alum. Settled water turbidity, dissolved organic carbon (DOC), chloride to sulfate mass ratio (CSMR), solids settleability, and water filterability were assessed in laboratory scale bench tests and pilot plant studies as a function of percent alum dose reduction (ADR). Results from bench scale jar tests and pilot plant study showed that settled water turbidity and DOC were not compromised up to ~40% ADR (18 mg/L as alum) and were indifferent to the type of ferrous salt added. As expected, CSMR, a corrosion surrogate, increased with increasing ADR (or decreasing sulfate addition) and was higher for the FC-treated waters compared to the FS-treated waters. However, CSMR remained below the suggested threshold of 0.6 for ADR values up to 60%, indicating both ferrous salts were viable options for chlorite quenching at BWD. Notably, the headloss rate during filtration in the pilot plant study was lower for the FS-treated waters at all values of ADR tested, and thus is the recommended secondary coagulant for the BWD.

Acknowledgments

I would like to thank Bill Hagenburger and all the employees at Beaver Water District who added so much to my education and personal experience over the past two years. My time spent with you has been invaluable. I would like to thank Dr. Julian Fairey for his counsel and insightful review throughout my graduate studies. I would like to thank my peers from the Water Research Laboratory for all your instruction and encouragement. I thank my friends, family and trivia team for all the help in maintaining balance and perspective. Finally, I must thank Matthew Harvey for your patience, support, and cooking skills.

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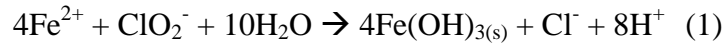
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1. Introduction and Motivation

Rook (1974) discovered that hypochlorous acid, the most common drinking water disinfectant used worldwide, reacts with natural organic matter (NOM) in water to form halogenated disinfection byproducts (DBPs), such as trihalomethanes and haloacetic acids. Chronic exposure to DBPs has been linked to adverse reproductive outcomes (i.e., low birth weight), bladder cancer, and rectal cancer (Morris et al., 1992; Boorman et al., 1999; Nieuwenhuijsen et al., 2000; Villanueva et al., 2004). In 2006, the United States Environmental Protection Agency (USEPA) promulgated the Stage 2 Disinfectants/DBPs Rule which requires compliance based on “worst case” locations in the distribution system for a running annual average of the 11 regulated DBPs – four trihalomethanes, five haloacetic acids, chlorite and bromate. In November 2012, facing enforcement of the Stage 2 Rule, the Beaver Water District (BWD, Lowell AR) switched primary disinfectants from gaseous chlorine (i.e., free chlorine or hypochlorous acid) to chlorine dioxide (ClO_2) in an attempt to curb formation of DBPs.

ClO_2 has gained favor at drinking water treatment plants (DWTPs) because it is a strong oxidant (i.e., a good disinfectant) and does not react with NOM to form halogenated DBPs (Werdehoff and Singer, 1987). However, ClO_2 forms inorganic DBPs, chlorite and chlorate. Chlorite is a constituent of concern as it is regulated by the USEPA at 1 mg/L as ClO_2^- and has been linked to anemia and delayed neurodevelopment (Taylor et al., 2002). At the BWD, approximately 70% of ClO_2 applied is reduced to chlorite, a yield that is at the upper end of the range (30-70%) reported in previous studies (Werdehoff and Singer, 1987; Baribeau et al., 2002; Alam et al., 2008). Chlorite formation, without substantial changes at the DWTP, put a practical limit of 1.4 mg/L on the ClO_2 dose in order to achieve chlorite compliance. Further, BWD’s goal is to maintain the chlorite residual at no more than 20% of the regulatory limit, or 0.2 mg/L as

ClO_2^- . While chlorite can be reduced by sulfite ion, ferrous ion, or granular activated carbon (Griese et al., 1991; Henderson et al., 2001), ferrous ion is favored by the BWD and reacts with chlorite as shown in Equation 1.



Here, ferrous ion reduces chlorite ion to chloride (Katz and Narkis, 2001) with the stoichiometric ratio of 4 moles of Fe (55.6 g/mole) to 1 mole of ClO_2^- (67.5 g/mole), requiring 3.3 g of Fe^{2+} to reduce 1 g of ClO_2^- . Chlorite ion reduction to chloride by ferrous ion occurs rapidly (5-15 sec) at pH 5-7 and the resultant precipitate – $\text{Fe}(\text{OH})_{3(\text{s})}$ – does not adversely affect alum coagulation (Iatrou and Knocke, 1992). It has also been shown that ferrous iron is effective at pH 8-10 given a 10-20% increase in dose above the stoichiometric requirements (Hurst and Knocke, 1997).

Ferrous ion can be added at the BWD DWTP as ferrous chloride (FC) or ferrous sulfate (FS) in combination with aluminum sulfate (alum). Both ferrous salts have the same stoichiometric chlorite quenching capacity, but commercially available FC is more cost effective given its higher iron content per unit volume (i.e., the FC stock is ~15% Fe at \$0.344 per kg compared to the FS stock which is ~5% Fe for \$0.336 per kg). Further, the ferrous iron content, indicated by a bright green color, as opposed to the reddish-brown color of oxidized ferric ion (Fe^{3+}), which does not reduce chlorite, is retained longer in FC stock solutions compared to FS. This has been observed in the BWD pilot plant facility and by others (Rittmann, 2003), suggesting that FC could further reduce chemical costs by remaining viable for longer periods of time at the DWTP. For these reasons, FC is a more attractive option compared to FS, which is currently being fed in combination with alum at the BWD DWTP. However, it is unknown how turbidity, dissolved organic carbon (DOC, a NOM surrogate), and filter headloss will be

impacted by the use of FC instead of FS as a secondary coagulant. While ferrous (Fe^{2+}) is oxidized to ferric ion (Fe^{3+}), a common coagulant, the cost of ferrous addition is justified principally for chlorite reduction, but has the potential to also improve coagulation.

Another regulation to be considered when changing the disinfection regime is the 1991 USEPA Lead and Copper Rule. Action levels of 0.015 mg/L Pb and 1.3 mg/L Cu must be met, based on the 90th percentile level of tap water samples. Exceeding either action level does not constitute a violation, but does necessitate additional monitoring, corrosion control measures, public education and notification, and possibly lead service line replacements (US EPA, 2008). The chloride to sulfate mass ratio (CSMR) has been shown to be a useful corrosion surrogate (Edwards, 2007; Nguyen et al., 2011; Cartier et al., 2012), with a threshold of 0.6 constituting the upper bound, above which detailed corrosion testing is warranted. By adding more chloride to the water, coagulation with FC increases CSMR, whereas coagulation with FS would decrease CSMR by increasing the sulfate content.

Sulfate reacts with lead to form relatively insoluble and stable PbSO_4 solids, which subsequently act as a protective scale. Chloride develops soluble complexes with lead, such as PbCl^+ , which inhibits the protective scale formation and increases the galvanic current (Nguyen et al., 2010). Therefore, as chloride increases relative to sulfate, the amount of soluble lead leaching into the bulk water may also increase. This reaction is only pertinent when iron pipe is connected to copper pipe, and will not occur in solid lead pipes. In five case studies evaluating the impact of CSMR on lead leaching due to changes in the coagulation regime, soluble lead release generally increased with increasing CSMR (Nguyen et al., 2010). However, it is important to note that lead release is difficult to predict and can be affected by a broad range of variables, including the pipe age and water chemistry history (Schock et al., 1995).

The primary goal of this study is to determine the impact of adding a ferrous-based coagulant at a dose sufficient to quench chlorite on settled water turbidity and DOC. FC and FS will be compared as secondary coagulants in bench scale and pilot plant experiments over a range of alum doses. CSMR will be calculated to assess the potential for lead corrosion and the solids formed will be characterized to assess settleability and filterability of the waters generated using the various coagulation regimes. The findings of this study will form the basis of a recommendation for the optimal coagulant scheme at the BWD.

2. Methods and Materials

2.1 Sample Site and Collection for Bench Scale Testing

Sample waters for this study were collected from Beaver Lake at the southern intake structure of the BWD DWTP. Beaver Lake was created by the United States Army Corps of Engineers between 1960-1966 by damming the White River and contains 2.04×10^9 m³ of water at normal pool elevation (USGS, 2000). The contributing watersheds include the White River, Beaver Lake, and the Illinois River. BWD treats Beaver Lake water and distributes drinking water to the cities of Fayetteville, Springdale, Rogers, and Bentonville. These four customer cities then sell water to 14 surrounding municipalities. In total, BWD serves approximately 320,000 people in Northwest Arkansas (Corps of Engineers, 2013).

For the jar test experiments, 63 L of Beaver Lake water was collected on February 17, 2014 at a depth of 3 m below the water surface using a 6 L horizontal water sampler (Wildco, Model 1960-H65, Yulee, FL). This sample water was transferred to pre-cleaned 9 L HDPE carboys with screw top lids and transported to the University of Arkansas in a chilled cooler and stored at 4°C until use.

2.2 Reagent Preparation and Washing Procedures

Milli-Q water (18.2 MΩ-cm) was used for preparation of all stock solutions, dilutions, and analyses, and was generated using a Millipore Integral 3 Milli-Q water system (Billerica, MA). All chemicals used were ACS-grade supplied by VWR. The sample water was vacuum filtered using 0.45 μm polyethersulfone membranes, which were rinsed with 500 mL of Milli-Q water prior to use. To minimize organic carbon adsorption and leaching by the filter, the first 25 mL of sample through the filter was wasted (Karanfil et al., 2003).

Glassware was cleaned by soaking and scrubbing individual pieces in an Alconox detergent and tap water bath, followed by a rinsing regime. This consisted of a triple rinse in tap water, triple rinse in deionized (DI) water, and triple rinse with Milli-Q water. Amber glassware and glassware used in analyses with organic solvents were baked in a muffle furnace at 400°C for 30 minutes. Other glassware and lids were dried in a desiccator oven at 45°C for at least 8 hours. Plastic dishware and precision glassware (i.e., volumetric flasks) were washed and rinsed following the procedure described previously and dried at room temperature.

2.3 Chlorine dioxide synthesis and dosing

ClO₂ was synthesized following established procedures in the Water Research Laboratory (WRL) (Granderson et al., 2013). In summary, the stock ClO₂ was generated by combining solutions of sodium chlorite and potassium persulfate in a 500 mL gas-washing bottle (Wilmad-Labglass, Vineland, NJ). Nitrogen gas flowed through the combined solution in the gas-washing bottle at approximately 250 mL per minute for 45 minutes, protected from light infiltration with a cardboard box. The stock ClO₂ was transferred to a beaker of 500 mL of chilled Milli-Q water, insulated with chilled ice packs, by means of a submerged fritted disk. Stock ClO₂ was immediately transferred by a 100 mL gas tight syringe (SGE, Australia) into clean 20 mL amber vials with PTFE lined screw top lids. The vials of ClO₂ stock were stored at 4°C and protected from light until use. Despite quality control efforts, the concentration of the stock may vary due to age, filling technique and other factors. As such, immediately before use, the concentration of ClO₂ in each vial was determined by diluting a sample of the stock in Milli-Q water to achieve less than 1.0 Abs. at 360 nm on the Shimadzu UV-Vis 2450 (Kyoto, Japan) spectrophotometer, applying an assumed molar absorptivity of 1225 cm⁻¹ M⁻¹.

2.4 Jar Test Procedures and Solids Characterizations

A suite of jar tests, intended to resemble conventional drinking water treatment processes, were completed with alum and either FC or FS. The initial alum dose of 30 mg/L as alum was decreased by increments of ten percent while the ferrous salt dose was held constant at 2.31 mg/L as Fe. As the collected sample water turbidity was low – 7.5 NTU relative to the average of 17 NTU (Avery, 2013) – kaolin, a powdered clay, was added to amend the turbidity to nearly 25 NTU. The amended sample water was then oxidized with 1 mg/L ClO_2 as ClO_2 in 1 L amber glass jars and held for 24 hours in the dark at ambient temperature. Half a liter of oxidized water was added to each rectangular jar. For all coagulant doses studied (Table A1), three individual jar tests were performed for triplicate analyses. For each alum dose, the ferrous chloride and ferrous sulfate combinations were tested on the same day from the same oxidized water batch. Coagulant stock solutions were made daily as needed and simultaneously added to jar testers with disposable plastic syringes. The coagulants mixed with the oxidized sample water at a high rate (~200 RPM) for 30 seconds, low rate (~40 RPM) for 30 minutes, and settled quiescently for 30 minutes. Approximately 250 mL of the settled water was decanted for water quality tests, as described in Section 2.5, and the remaining settled solids from each dose was combined and stored at 4°C for settleability tests.

Composite solids generated from the three jar tests of each combined coagulant dose were evaluated using an Imhoff cone, labeled with graduated markings of volume. When ambient temperature was reached, the initial volume of available sample was measured with a graduated cylinder. The turbidity and solids volume at the bottom of the Imhoff cone were recorded at times 0, 15, 30, 45, 60, 90 and 120 minutes. Turbidity was measured from a 20 mL sample collected from the center of the cone with a pipette, approximately one inch below the

water line. At 60 minutes, the sides of the cone were scraped with a thin metal rod to release solids attached to the sidewalls.

2.5 Water Quality Tests

Sample pH was measured with an Orion 8272 electrode (Thermo Orion, Waltham, MA), calibrated daily with pH standards of 4, 7 and 10. Conductivity was measured with an Accumet (Fisher Scientific, Hampton, NH) conductivity probe. Both conductivity and pH probes were connected to an Accumet XL60 dual channel meter. Turbidity was measured in Nephelometric Turbidity Units (NTU) with an HF Instruments Model DRT 100 turbidimeter. DOC, dissolved inorganic carbon (DIC), and total dissolved carbon were measured with a Sievers 5310C Portable TOC Analyzer (Sievers, Boulder, CO).

Dissolved aluminum residuals were analyzed using Hach AluVer 3 powder packets (Loveland, CO). Aluminum standards were made from aluminum sulfate hydrate. The five point standard curve, ranging from 0 to 0.2 mg/L as Al, had a $r^2 > 0.999$. One AluVer 3 packet was added to 25 mL of filtered sample combined with 25 mL of Milli-Q water and allowed to mix continuously for 3 minutes. The sample was then scanned at 535 nm through a 1 cm quartz cuvette on the spectrophotometer. The cuvette and glassware were rinsed with a 1:1 sulfuric acid solution and triple rinsed with Milli-Q water to avoid residual accumulation between samples.

Anions were analyzed with a Metrohm Professional Ion Chromatograph, Model 850.3040 (Riverview, FL) with 3.6 mM sodium bicarbonate eluent. Calibration standards of 0.1, 0.2, 0.5, 1.0, and 5.0 mg/L were formulated from Metrohm stock standards (REAIC1035, REAIC1013, REAIC1014) containing fluoride, chloride, chlorite, nitrite, bromide, chlorate, nitrate, phosphate, and sulfate. Each analyte standard curve had an r^2 value of 0.999 or higher. A check standard of

0.5 mg/L was run every 18 samples and had a deviation from the standard curve of $\pm 4\%$. A new standard curve was run for every new batch of eluent, or about every 120 samples.

2.6 Pilot Plant Study

The pilot plant at the BWD was used to complement the laboratory-scale jar tests. The pilot plant facility is located on site and includes two identical parallel treatment trains, each intended to mimic the full-scale DWTP.

2.7 Pilot Plant Facility

The flow rate of each train was 20.8 L per minute, pumped directly from the intake pipes that fed the full-scale plant. Therefore, the pilot plant received the same water as the full-scale plant at any given time. Pre-oxidant can be added to the influent water, followed by a 60 minute contact time through PVC barrels, which mimics the contact time from the intake structure on Beaver Lake to the treatment plant. Rapid mix of coagulant chemicals was accomplished with an inline mixer. Slow mixing consisted of four equal-sized flocculation chambers with paddle mixers rotating sequentially at 70, 60, 40 and 30 RPM, and had a total detention time of 40 minutes. Non-ionic polymer can be added in the second flocculation basin, but was not in this study. Settling was achieved with a plate settler and the sludge cleared from the sedimentation tank floor with a chain and flight system on a timed cycle: 120 seconds of accumulation followed by a 5 second flush from the lowest point of the tank. Lime basins allowed for lime slurry to be added for pH adjustment directly after settling. Each train featured two 3-meter tall, 20.3 cm diameter filter columns, designed to mimic the two configurations of full-scale filters at BWD. The DWTP has two facilities, Croxton and Steele, which have similar treatment trains with the exception of filtration. Croxton filters were loaded at $2.6 \text{ L/m}^2\text{-s}$ and had a deeper media profile

with 122 cm of anthracite, 31 cm of sand, 10 cm garnet, and 30 cm of torpedo sand. The Steele filters were operated at $2.2 \text{ L/m}^2\text{-s}$ and had a shallower media profile with 42 cm of anthracite, 23 cm of sand, 11 cm of garnet, and 30 cm of gravel. In the pilot plant, filters were typically run in parallel, which provides combined filtered water for analysis, but can be isolated if needed. The pilot facility is capable of feeding sodium hydroxide, also known as caustic soda, for final pH adjustment and free chlorine for residual at the top and/or the bottom of the filters to achieve finished water with pH of 9.0 and a chlorine residual of 1.5 mg/L as Cl_2 (Black & Veatch, 2010).

Progressive cavity pumps, manufactured by Moyno, Inc (Springfield, OH), were used to pump the influent water, provide inline mixing, and lift the water to the top of the filter columns. All other hydraulic movement was achieved by gravity flow. Chemicals were fed using Watson Marlow (Falmouth, Cornwall, UK) peristaltic pumps. Chlorine dioxide was pumped into the system using C-flex tubing and lime slurry was pumped with neoprene tubing. All other chemicals were fed using 1.6 mm marprene tubing.

Alum, caustic soda, FS, lime, and non-ionic polymer are acquired directly from stock at the DWTP as needed. FC was supplied from Kemira (Helsinki, Finland) and free chlorine was derived from a Chlorox bleach solution. ClO_2 was generated in a Siemens Diox A3/10 by combining 7.5% sodium chlorite and 9% hydrochloric acid (Washington, D.C.). All chemicals were batched to respective concentrations with tap water in designated, rinsed 20 L HDPE carboys with screw top lids.

2.8 Alum Reduction Pilot Study

Similar to the laboratory-scale jar tests (Section 2.4), the pilot plant was used to assess the impact of a reduction in the alum dose on particle removal when FC or FS was added. The

initial alum dose of 30 mg/L as alum was reduced by increments of twenty percent, up to 60% reduction, while the ferrous salt dose was held constant. Influent water was treated with ClO_2 at 0.6 mg/L as ClO_2 , added near the intake structure of the full-scale DWTP. As the water had been partially oxidized prior to reaching the pilot plant, the influent water was piped directly to the rapid mix basin where FC and alum were added to Train 1 and FS and alum were added to Train 2. FC and FS were held constant at 1.65 mg/L as Fe and dosed to completely quench the average influent chlorite concentration of 0.54 mg/L as ClO_2^- . Lime was added at 5.5 mg/L as CaO. Filter performance was monitored by head loss through the column, measured in real time on an IDP10 differential pressure meter (Invensys Foxboro, Houston, TX). After samples were taken for a given dosing parameter, the filters were backwashed for ten minutes. Finished water pH and chlorine residual were not monitored for this study.

This pilot plant study occurred in March 2014 over 5 consecutive days. At this time, Beaver Lake was experiencing elevated turbidity levels (between 30 and 45 NTU) as a result of runoff due to a rainstorm event in the area which produced 5.8 cm of precipitation on March 17 as recorded by Station 032444 (NOAA, 2014). Each coagulant dose (Table A5) was run for at least 18 hours to reach steady state within the system. After operational samples were tested to confirm acceptable performance, samples were collected in amber glassware to be transported to the University of Arkansas in a chilled cooler to be stored at 4°C until use. Water samples were taken at the influent, after settling, and after filtration in triplicate at ten minute intervals.

2.9 Operational Samples

The pilot plant facility at BWD is complemented with a wet chemistry laboratory to monitor operational parameters such as turbidity, pH, and oxidant residual. Turbidity is

measured on a Hach 2100N Turbidimeter, which is calibrated monthly by a trained BWD laboratory staff member. The pH is measured with an Orion 81022BNGWP Ross Ultra electrode on an Orion 3Star meter, calibrated daily to pH 7, 8, and 10. The operator can monitor chlorine dioxide residual, chlorite concentration, and chlorine residual on the Hach AutoCAT 9000, an automatic amperometric titrator and an EPA approved method to determine chlorine dioxide concentration. The operational data during the pilot plant study can be seen in Table A6a and Table A6b.

3. Results and Discussion

3.1 Bench Scale Water Quality Parameters

Table A1 shows the average water quality parameters for the raw water and those following kaolin amendment and ClO₂ oxidization (referred to herein as sample waters). As a result of kaolin addition, the turbidity increased from an average of 7.5 NTU in raw water to an average of 30 NTU (range of 24.8-34.0 NTU) for the sample waters. Water pH decreased from an average of 7.91 in the raw water to 7.80 (range of 7.71-7.83) in the sample waters. Average conductivity (range of 171.1-185.4 μS/cm) and DOC (range of 2.75-3.13 mg/L as C) of the sample waters was within 1% and 3% of their average raw water values, respectively; indicating these parameters were unaffected by kaolin amendment and ClO₂ oxidation.

Figure 1 shows the water quality parameters of the sample waters before and after coagulation with FC and FS as a function of percent alum dose reduction (ADR). Waters coagulated with alum only at 30 mg/L served as a baseline for comparison. The average turbidity of the settled water samples was between 1.9 and 2.7 NTU (Figure 1a and Table A2) through 50% ADR for both FC and FS, but increased thereafter to ~20 NTU by 100% ADR (no alum addition). On average, the FC- and FS-treated waters had turbidities within 8% of one another. The ferrous salts, dosed only to quench chlorite formation as secondary coagulant (i.e. 100% ADR) removed ~30% of the initial turbidity. Figure 1b shows the impact of ADR on sample pH. The average pH of the sample waters prior to jar testing was between 7.71 and 7.83 (Table A1). Following coagulation, the average pH was similar through 20% ADR but increased thereafter from ~7.00 to ~7.50 (Figure 1b). Increasing pH with increasing ADR (i.e. decreasing alum dose) was an expected result given alum is an acid. No differences in pH were apparent between the

FC and FS coagulants, as indicated by an average 0.4% difference in $[H^+]$. At the BWD DWTP, the post-sedimentation water has a pH between 7.0 and 7.1. While the settled water pH increased as ADR increased, BWD is accustomed to operating with settled pH levels near that of the 0-40% ADR (pH 7.03 ± 0.07). As such, operation at a higher ADR (in excess of 40%) may require less lime addition for adequate pH control compared to adding alum as the sole coagulant. Figure 1c shows the conductivity of the sample waters increased after coagulation across the range of ADR, between 171.1-193.4 $\mu\text{S}/\text{cm}$. However, no correlations were apparent with respect to ADR. Figure 1d shows DOC as a function of ADR before and after coagulation. After jar testing, the average DOC was between 1.83-2.29 mg/L as C, with the higher values (or less DOC removal) corresponding to ADRs in excess of 70%. From 0-60% ADR, DOC was removed between 27-40% (33% on average) relative to the initial value. DOC values for the FC- and FS-treated samples showed an average 0.3% difference, indicating DOC removal was insensitive to the type of ferrous salt.

Figure 2 shows the dissolved aluminum concentration as a function of ADR. At higher ADR (60-100%), dissolved aluminum was not detectable with the exception of the FS 90% ADR sample (0.15 mg/L as Al). When dosed with the maximum amount of alum (alum only, 0% FC and 0% FS), the results varied. Alum only and 0% FC had no dissolved Al, but 0% FS had 0.14 mg/L as Al. There were no correlations between the residual dissolved Al and ADR in regards to ferrous salt type. Values ranged between 0.00-0.18 mg/L as Al (average of 0.13 mg/L as Al for 0-50% ADR). Aluminum is not regulated by the USEPA, but has a secondary maximum contaminant level of 0.05-0.2 mg/L (US EPA, 2013). Above these levels, drinking water may develop color noticeable to the consumer. More testing should be completed before making any ADR recommendations on the basis of dissolved aluminum.

3.2 Bench Scale Settleability Test

Given that turbidity was a function of ADR (Figure 1a), various settling characteristics of the solids formed in the coagulation experiments were examined. Figure 3 shows the settled-solids turbidity decreased as a function of settling time for the FC- (Figure 3a) and FS-coagulated samples (Figure 3b). The settled-solids turbidity was independent of coagulant type, with only a 1.5% difference between the FC- and FS-treated waters. For example, a 30 min settling time decreased the initial solids turbidity by an average of $57\% \pm 7\%$ for both ferrous salts. Similarly, after 120 min of settling time, the initial solids turbidity decreased by an average of $89\% \pm 3\%$ for both ferrous salts.

Decreasing the amount of coagulant added should decrease the sludge production. As expected, the solids accumulation (defined as mL of solids collected at the bottom of Imhoff cone divided by the total volume of sample in L) decreased with increasing ADR from ~ 9 mL/L to ~ 1 mL/L (Figure 4). Similar to previous findings, the solids accumulation was insensitive to the type of ferrous salt added, which differed by 9% on average. In comparison to alum only, values of ADR less than 50% accumulated as many or more solids, in agreement with the settled water turbidity results (Figure 1a).

3.3 Bench Scale CSMR

When dosed with alum only, the resulting CSMR was 0.20 (Figure 5 and Table A3). For the FS-treated waters, CSMR increased with ADR from 0.19 to 0.38. The increasing trend in CSMR for the FS-treated samples was expected because the amount of sulfate added decreased with increasing ADR (or decreasing alum addition). Coagulation with FC resulted in greater CSMR values than alum alone or FS-coagulated waters regardless of ADR, as expected

(Rittmann, 2003). Similar to the FS results, CSMR for the FC-treated waters increased over the range of ADR, albeit at higher values – from 0.36 to 0.83. However, for FC-treated water, the average CSMR values did not exceed the corrosion potential threshold of 0.60, as discussed in the Introduction, until the ADR was 80% or higher. As CSMR values above 0.60 have been associated with increased lead leaching from premise plumbing in water distribution systems (Edwards, 2007), it can be concluded that FS at any ADR or FC from 0-70% ADR are suitable coagulant regimes for chlorite reduction.

3.4 Pilot Plant Water Quality Parameters

Influent water to the pilot facility had been dosed with 0.60 mg/L ClO_2 and, as shown in Figure 6, contained an average chlorite concentration of 0.54 mg/L as ClO_2^- . As such, the chlorite yield was 90% of the ClO_2 dose, which was higher than the average 70% chlorite yield at BWD, possibly due to variability in water characteristics or ClO_2 feed-rate at the DWTP. All coagulant combinations, including both ferrous salts dosed at 1.65 mg/L as Fe, completely quenched chlorite ion. In contrast, alum only coagulated water had an average chlorite of 0.45 mg/L as ClO_2^- in the filtered water, indicating partial chlorite removal (~16%) within the treatment process.

Little variation in the water quality parameters between the two pilot plant treatment trains was observed when operated at a coagulant dose of 30 mg/L as alum (Table A4, March 24 sampling date). Trains 1 and 2 had similar (i.e., within 1 standard deviation or less than 3% difference) average turbidities for the settled and filtered waters, pH, conductivity and DOC. This result indicates that subsequent differences in these water quality parameters could most likely be attributed to the type of ferrous salt added.

Average water quality parameters at the pilot plant are shown in Figure 7. Over the five-day alum reduction study, the influent turbidity ranged from 33-43 NTU (Figure 7a and Table A4). Settled water turbidities increased with ADR from 4.2-24.5 NTU for FC treated waters and from 3.7-35 NTU for FS treated waters. FC- and FS-coagulated waters at 0% ADR had lower settled turbidities than the alum only coagulated waters by 2.5 and 4.8 NTU for FC- and FS-waters, respectively, indicating coagulation was enhanced with the addition of ferrous salt in combination with alum. At 0% and 20% ADR, the FC- and FS-treated trains had similar turbidities (less than 15% difference), but at higher ADR values, the FC-train produced lower settled turbidities than the FS-train by 3.9 NTU at 40% ADR and 10.5 NTU at 60% ADR; indicating FC was the more effective coagulant for particle removal over the range of ADRs tested. Filtered water turbidities were lower than their corresponding settled water turbidities for all coagulation regimes, and followed similar trends as described for the settled waters with respect to ADR and ferrous salt type. However, differences in the pH of coagulation may explain the measured differences in turbidity between FC and FS.

The settled and filtered water pH as a function of ADR is shown in Figure 7b. The average influent pH to the pilot facility was 7.82 ± 0.01 (Table A4). For all ADR values tested for the settled waters, coagulation with FC produced an average pH of 6.90 ± 0.04 , whereas FS produced an average pH of 7.08 ± 0.11 , a 34% difference in $[H^+]$. Filtered water pH had been amended with lime slurry to increase pH and mimic water properties at the BWD DWTP entering filtration. For all ADR values tested, FC produced an average filtered water pH of 7.45 ± 0.15 and FS produced an average settled water pH of 7.77 ± 0.19 , a 52% difference in $[H^+]$. As such, for the pilot plant samples, the lower turbidities of the FC-coagulated waters compared to FS (Figure 7a) may have been due to the lower pH of coagulation, similar to the findings of

numerous other coagulation studies (Amirtharajah and Mills, 1982; Edzwald and Tobiason, 1999; Chow et al., 2009).

While conductivity measurements in the bench scale tests showed no apparent correlations with ADR (Figure 1c), the pilot plant data showed decreased conductivity with increasing ADR in both settled and filtered water samples (Figure 7c). This result indicates that alum dose was a primary factor in controlling conductivity at the pilot plant. On average, the influent conductivity ranged from 188.2-193.7 $\mu\text{S}/\text{cm}$ (Table A4). Waters treated with FS generally had lower conductivities than those treated with FC, indicating less dissolved species in the FS-coagulated waters.

Figure 7d shows filtered water DOC as a function of ADR. Influent DOC ranged from 3.3-4.0 mg/L as C (Table A4). Coagulation with alum only resulted in a DOC of 2.0-2.1 mg/L as C. As expected, DOC increased with increasing ADR from ~ 1.8 to ~ 2.5 mg/L as C, with FC-coagulated waters containing less DOC than FS-coagulated waters by as much as ~ 0.2 mg/L as C. Similar to the turbidity results (Figure 7a), the lower pH of FC coagulation (Figure 7b) was the likely cause of the increased DOC removal. As such, for the pilot plant facility, coagulation with FC was more effective than with FS, because of the lower pH of FC coagulation.

3.5 Pilot Plant Headloss Rate

Headloss rates through the filters increased with increasing ADR, as shown in Figure 8. Although differences in the performance between the Croxton and Steele filters may have existed from previous pilot plant experiments, the headloss rates for the alum only condition were similar (between 1-2 cm/hr). Croxton filter columns experienced headloss at 1.2- and 1.3 cm/hr for Train 1 (FC fed) and Train 2 (FS fed), respectively; Steele filter columns experienced

headloss at 1.5- and 1.7 cm/hr for Train 1 and Train 2, respectively. For 0% ADR, the FS-treated waters had lower average headloss rates (0.99 ± 0.10 cm/hr) compared to waters treated with alum only (1.46 ± 0.20 cm/hr), indicating FS addition during alum coagulation improved filter operation. However, the FC-coagulated waters (Train 1) had higher headloss rates at 0% ADR, at values of 2.2- and 3.2 cm/hr, for the Croxton and Steele filters, respectively. The FC-treated water headloss rate peaked at 60% ADR at 8.3 cm/hr in the Croxton filter and 11.2 cm/hr in the Steele filter, indicating FC negatively impacted filter operation. Headloss rates were similar for the 0% and 20% ADR FS values, increased by ~1 cm/hr for 40% ADR, and by another ~6 cm/hr for 60% ADR. However, at 60% ADR, the headloss through all filters was in excess of 8 cm/hr, over four times greater compared to the alum only condition, and impractically high for filter operation. Additionally, the filter backwash was visually different after 60% ADR (results not shown), requiring multiple flushes with air to separate the media and release the amassed solids.

The FC-treated water, despite having lower settled turbidity and DOC compared to FS-treated waters, experienced higher rates of headloss accumulation. Perhaps additional, unaccounted for, settling occurred in the lime basins. It is also possible that the particles remaining in the FC-treated water interacted with the filter media in such a way as to exacerbate the rate of headloss increase. A previous study noted that enhanced coagulation can produce less-dense and fragile floc which can impact filter runtimes and performance (Carlson et al., 2000).

3.6 Pilot Plant CSMR

CSMR in the filtered sample waters from the pilot scale study are shown in Figure 9 and Table A5 as a function of ADR. During the 5-day study period, CSMR values of the influent ranged from 0.58 to 0.64. Feeding alum only at 30 mg/L in both trains resulted in CSMR values

of 0.26-0.27, which was attributed to an increase in sulfate alone (Table A5). CSMR of FS-treated waters increased from 0.25 to 0.36 as ADR increased from 0 to 60%, respectively, again primarily due to decreased sulfate. CSMR of FC-treated waters were higher, with an average of 0.50 ± 0.08 , due to higher chloride. As the propensity for lead corrosion in water distribution systems may increase with CSMR, especially for values above 0.6 (Edwards, 2007), supplementing the coagulation regime with FS as opposed to FC may decrease the potential for lead corrosion.

3.7 Comparisons of Bench Scale and Pilot Plant Experiments

In terms of settled water turbidity and DOC, the bench scale and pilot plant experiments showed similar trends, both increasing with increasing ADR. Significant increases in these bulk water quality parameters were apparent at ADR values in excess of ~40-60%. Both bench scale and pilot plant results indicated combined coagulation at 0% ADR can improve treatment relative to alum only coagulation. In terms of the effect of ferrous salt type on settled water turbidity and DOC, no significant differences were observed in the bench scale tests, whereas lower turbidities and DOC values for coagulation with FC at the pilot plant was attributed to lower pH of coagulation as compared to FS. This result indicates that adding FS as a secondary coagulant would require additional pH adjustment prior to coagulation to achieve similar turbidity and DOC as adding FC. Removal of chlorite at the pilot plant was equally as effective with FC and FS.

Solids settleability could not directly be compared between the bench scale and pilot plant experiments. The settleability tests at the bench scale revealed no performance difference in the two ferrous salts, but did show ADR, through 50%, produce as many or more solids than

alum only coagulation. The headloss rate measurements (Figure 8) at the pilot plant indicated that FS was superior to FC (i.e., had lower headloss rates) for all ADR values tested. As such, from an operational standpoint, the results indicate FS was preferable to FC.

CSMR values from the bench scale and pilot plant experiments followed similar trends. As expected, CSMR generally increased with increasing ADR (or decreasing sulfate addition) and was higher for the FC-coagulated samples. Dosed only for chlorite quenching in conjunction with alum as the primary coagulant, FS addition did not change the CSMR value relative to that of alum only. CSMR values above the lead corrosion threshold, assumed to be ~ 0.6 in this study, was only exceeded for FC-coagulated samples at ADR values above 60%, an impractically low alum dose with regard to achieving adequate turbidity, DOC, and headloss rate accumulation. Overall, comparison of the bench scale and pilot plant experiments indicate that both ferrous salts are capable of achieving adequate CSMR values. Other parameters, such as headloss rate, turbidity or DOC removal should control selection of the secondary coagulant for chlorite removal.

Lastly, it is worth noting that the few differences that did exist between the bench scale and pilot plant results may also be attributed to differences in reagent quality and dosing. At the WRL, bench scale tests were performed under controlled circumstances with regards to glassware cleanliness, chemical grade, exposure to elements, and dosing accuracy. In contrast, the pilot facility uses many chemicals from the full-scale DWTP, which may have partially degraded (i.e., hydrated) due to age and exposure to air or light. Further, chemical dosing was tightly controlled at bench scale using micropipettes, but pilot scale dosing required the use of peristaltic pumps with tubing that can fluctuate over time, causing the feed rates to vary.

Conclusions and Future Work

Bench scale jar tests with Beaver Lake water and pilot plant studies at the BWD were completed to compare the relative effectiveness of two secondary coagulants – ferrous chloride (FC) and ferrous sulfate (FS) – in terms of settled water turbidity, DOC, chlorite reduction, CSMR, solids settleability, and water filterability. In both sets of experiments, alum was used as the primary coagulant, and was added with FC or FS at alum dose reduction (ADR) percentages varying from 0-100% (with 0% ADR corresponding to 30 mg/L as alum). Based on these experiments, the following conclusions were made:

- For the bench scale jar tests, settled water turbidity and DOC was independent of the type of ferrous salt added and unaffected at ADR values up to ~50% (15 mg/L as alum). Pilot plant data showed increased settled water turbidity and DOC with increasing ADR for all values tested, but experienced low filtered water turbidities (i.e., less than 5 NTU) up to 40% ADR (18 mg/L as alum). Further, turbidity and DOC values were lower with FC as a secondary coagulant, likely due to the lower pH (by ~0.2 log units) of coagulation relative to FS.
- For the pilot plant experiments, both FC and FS completely quenched chlorite (initial concentration ~0.54 mg/L as ClO_2^-) for all values of ADR tested (0-60%).
- At 0% ADR (or 30 mg/L as alum), ferrous salt addition decreased turbidity and DOC relative to alum only, indicating a dose of FC or FS sufficient to quench chlorite improved the settled water quality.
- CSMR data from the bench scale jar tests and pilot plant experiments showed similar trends. As expected, CSMR was higher for FC-coagulated waters compared to FS-coagulated waters and increased with increasing ADR (i.e., decreasing sulfate); however,

CSMR was below the corrosion threshold on 0.6 for ADR values up to 60%, regardless of the type of ferrous salt added.

- In the pilot plant study, coagulation with FC resulted in higher filter headloss rates than that with FS, favoring FS for selection as the secondary coagulant at BWD.
- Results from the bench scale studies followed similar trends as the pilot plant results, indicating that well-designed bench scale studies can be a valuable tool to help interpret less controlled pilot plant experiments.

In this study, sampling for the bench scale experiments took place in February 2014 and pilot plant experiments in March 2014. As source water quality at BWD is known to vary seasonally (Pifer and Fairey, 2012), future research could repeat the experimental protocol used in this study seasonally. Additionally, as DOC is a crude DBP surrogate, formation potential tests (Pifer et al., 2011; Pifer and Fairey, 2012) could be done on raw and settled waters to assess the impact of the coagulation regime (i.e., ferrous salt type and alum dose) on trihalomethane- and nitrosamine precursor removal. Similarly, CSMR is only a surrogate of galvanic corrosion and, as such, quantitative analyses of lead and copper corrosion could advance the findings presented in this thesis. Here, dunk tests with copper couplings containing a 50:50 lead-tin solder inlay are submerged in sample water (i.e., settled water from bench scale and pilot plant studies) for 24-72 hours before measuring dissolved lead and copper (Nguyen et al., 2011). Further, the pilot plant could be used to feed a simulated drinking water distribution system, equipped with copper couplings with lead-tin solder to help understand the effects of hydrodynamics and water chemistry on lead corrosion. In addition to dissolved lead and copper, the solid precipitates formed on the couplings could be analyzed by x-ray diffraction, which can provide insight as to the composition and structure of the solids (Connolly, 2012).

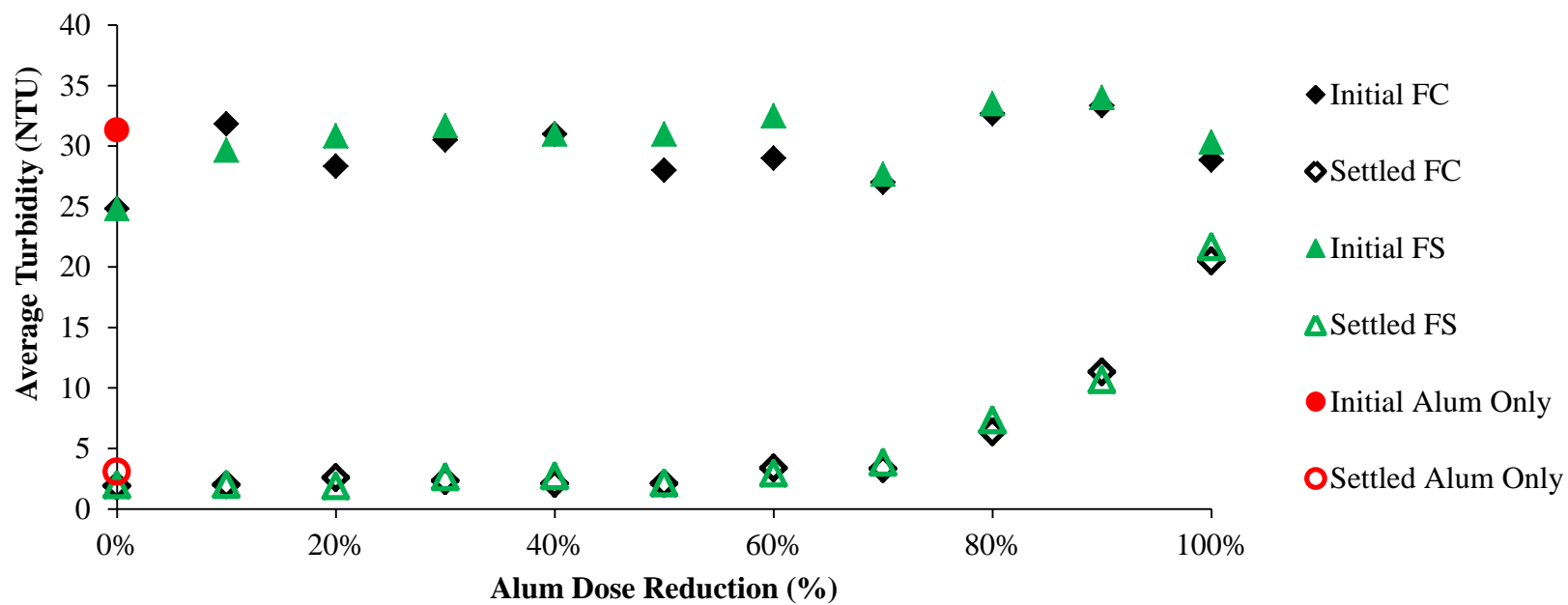


Figure 1. (a) Turbidity as a function of alum dose reduction. Samples were produced at the University of Arkansas Water Research Laboratory by jar tests which combined ferrous chloride (FC) and ferrous sulfate (FS) at 2.31 mg/L as Fe with varying doses of alum. Original alum dose (0%) set at 30 mg/L as alum. Initial parameters measured from water which had been amended with kaolin and oxidized with 1 mg/L ClO_2 as ClO_2 for 24 hours prior to jar testing.

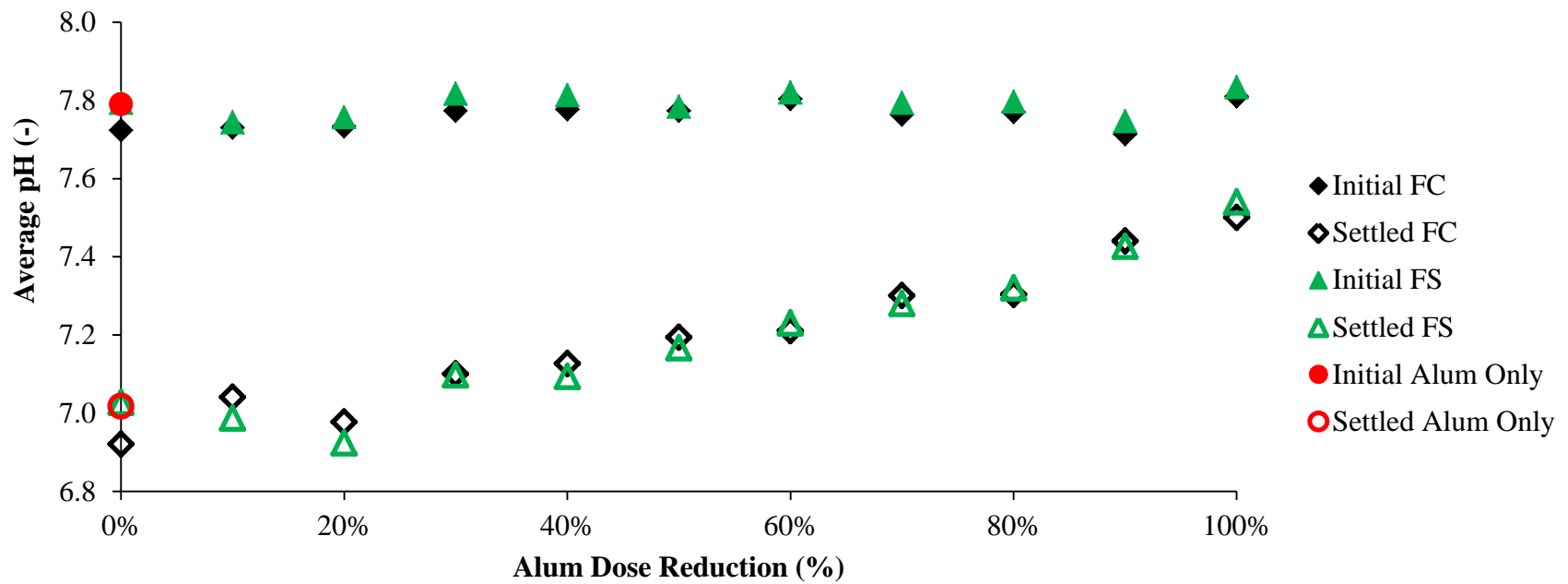


Figure. 1 (b) pH as a function of alum dose reduction. Samples were produced at the University of Arkansas Water Research Laboratory by jar tests which combined ferrous chloride (FC) and ferrous sulfate (FS) at 2.31 mg/L as Fe with varying doses of alum. Original alum dose (0%) set at 30 mg/L as alum. Initial parameters measured from water which had been amended with kaolin and oxidized with 1 mg/L ClO_2 as ClO_2 for 24 hours prior to jar testing.

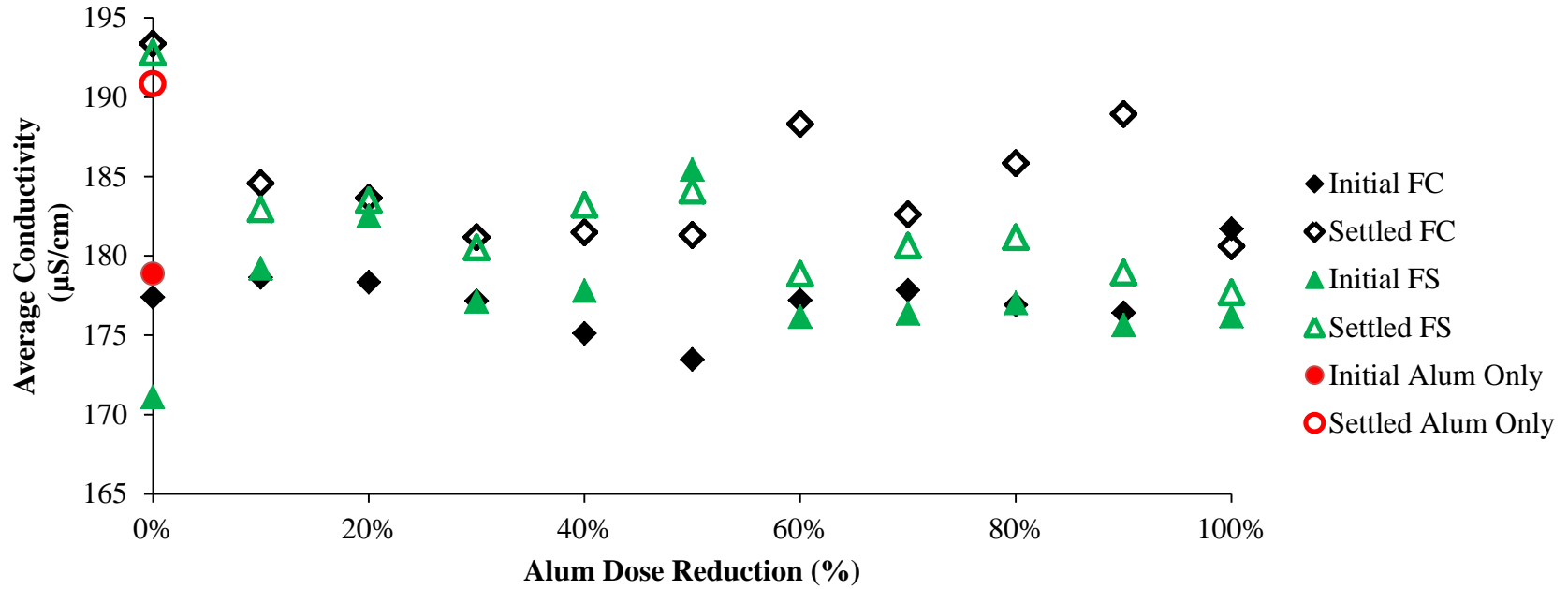


Figure. 1 (c) Conductivity as a function of alum dose reduction. Samples were produced at the University of Arkansas Water Research Laboratory by jar tests which combined ferrous chloride (FC) and ferrous sulfate (FS) at 2.31 mg/L as Fe with varying doses of alum. Original alum dose (0%) set at 30 mg/L as alum. Initial parameters measured from water which had been amended with kaolin and oxidized with 1 mg/L ClO_2 as ClO_2 for 24 hours prior to jar testing.

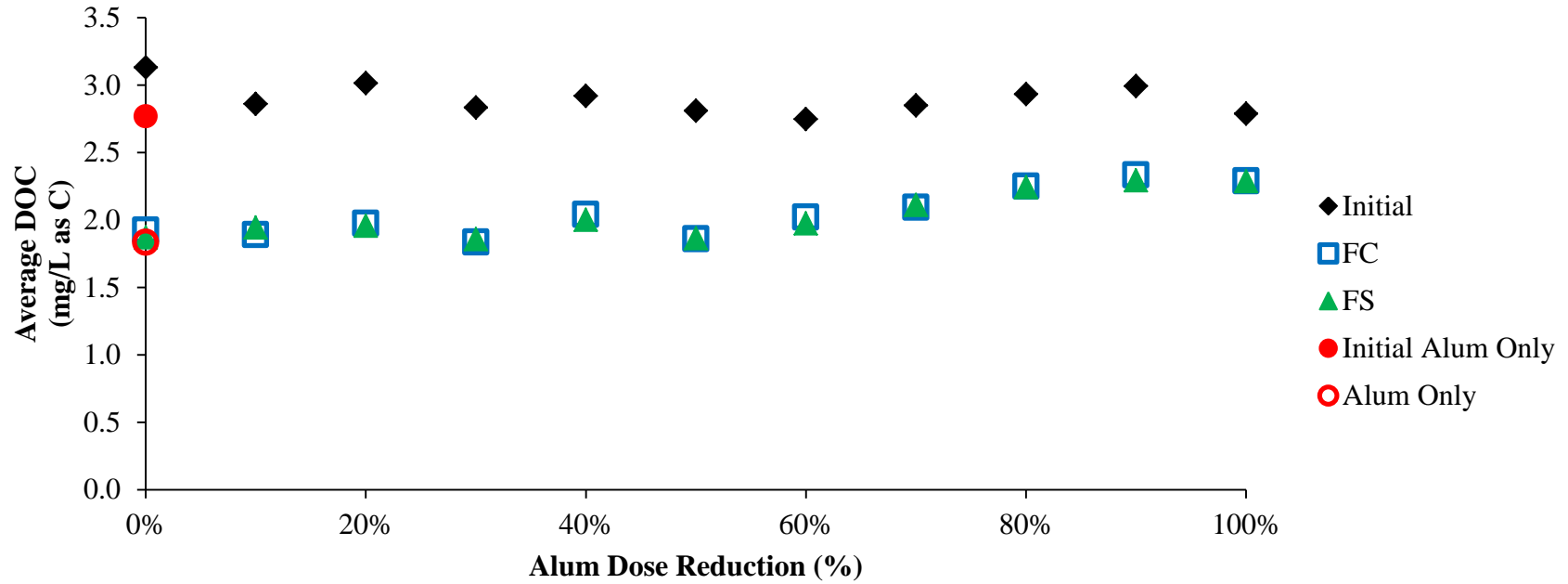


Figure 1. (d) Dissolved organic carbon as a function of alum dose reduction. Samples were produced at the University of Arkansas Water Research Laboratory by jar tests which combined ferrous chloride (FC) and ferrous sulfate (FS) at 2.31 mg/L as Fe with varying doses of alum. Original alum dose (0%) set at 30 mg/L as alum. Initial parameters measured from water which had been amended with kaolin and oxidized with 1 mg/L ClO₂ as ClO₂ for 24 hours prior to jar testing.

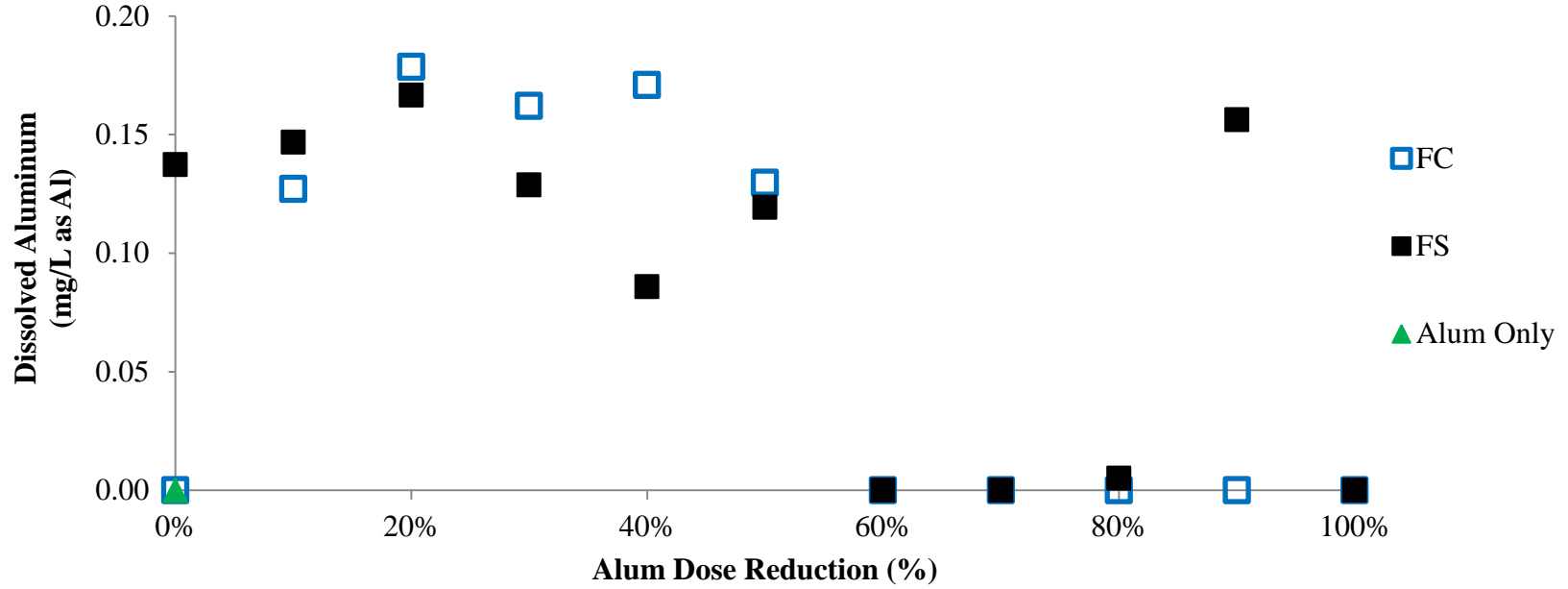


Figure 2. Dissolved aluminum as a function of percent alum reduction. Samples were produced following jar tests and measured at the University of Arkansas Water Research Laboratory. Sample waters were dosed with ferrous chloride (FC) and alum, ferrous sulfate (FS) and alum, and only alum. Both ferrous chloride and ferrous sulfate were dosed at 2.31 mg/L as Fe and the initial alum dose was 30 mg/L as alum.

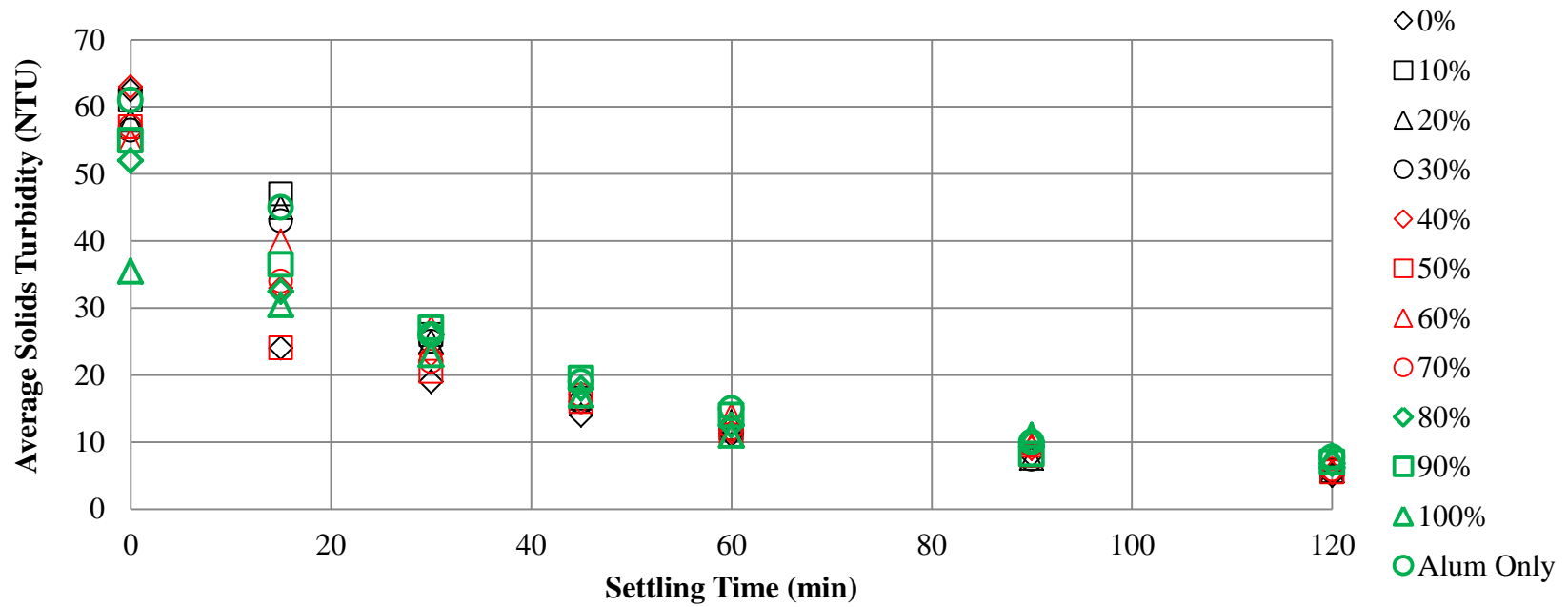


Figure 3. (a) Imhoff cone settled turbidity as a function of settling time. Sample solids were produced by waters treated with ferrous chloride, dosed at 2.31 mg/L as Fe, and reduced percentages of alum as specified, originally dosed at 30 mg/L as alum (0%). Turbidity samples were taken from one inch below the water line in the center of the Imhoff cone.

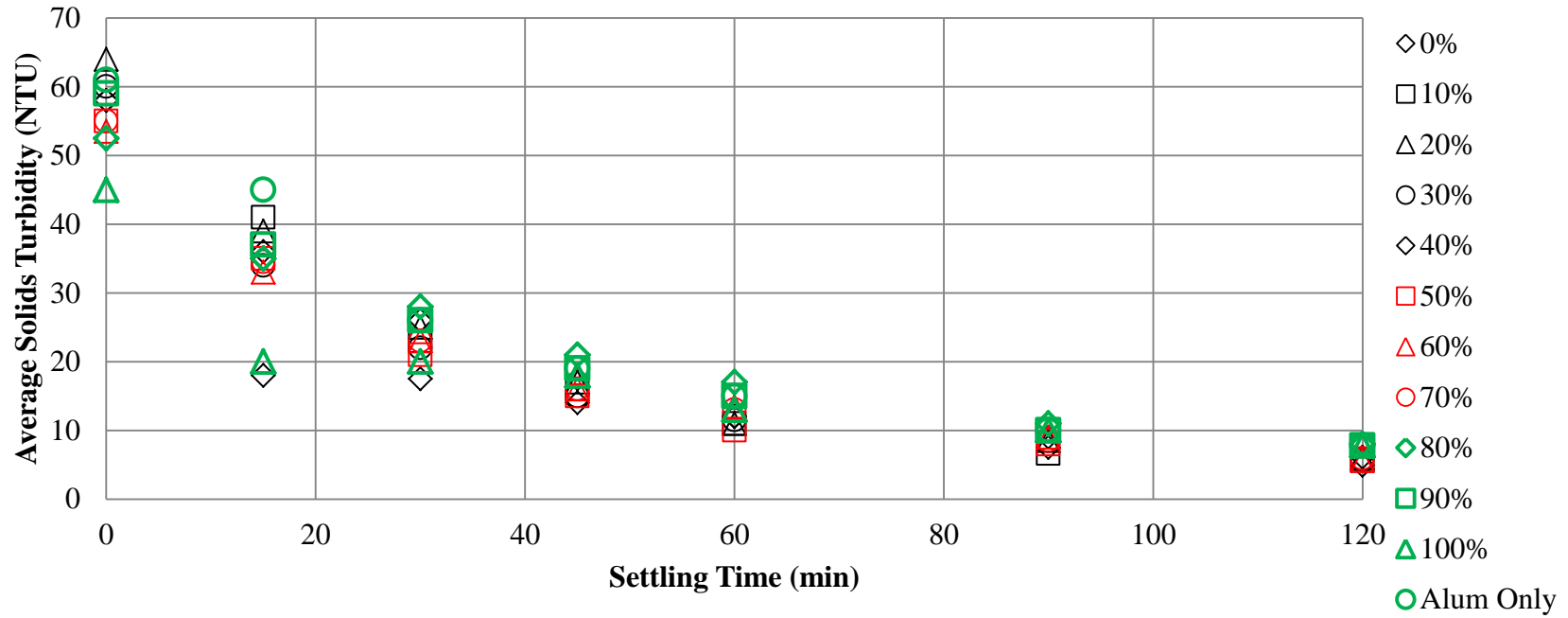


Figure 3. (b) Imhoff cone settled turbidity as a function of settling time. Sample solids were produced by waters treated with ferrous sulfate, dosed at 2.31 mg/L as Fe, and reduced percentages of alum as specified, originally dosed at 30 mg/L as alum (0%). Turbidity samples were taken from one inch below the water line in the center of the Imhoff cone.

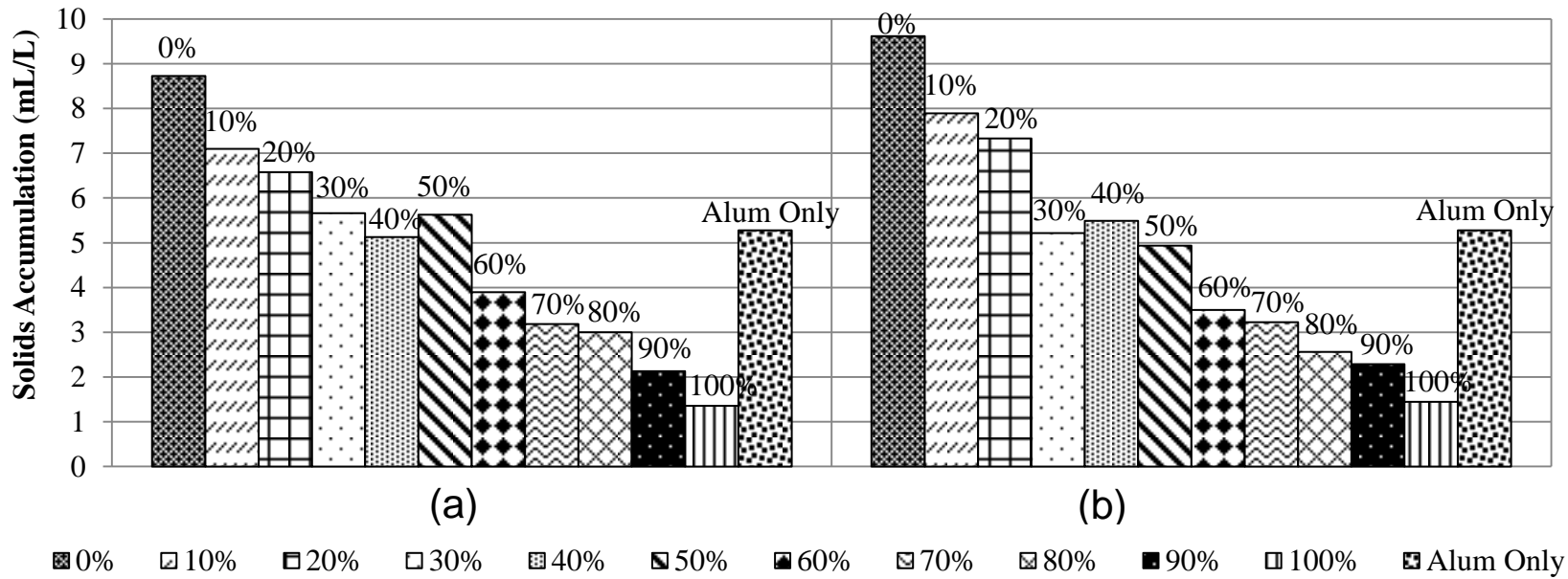


Figure 4. Imhoff cone accumulated solids volume (mL) per total sample volume (L) for (a) ferrous chloride and reduced percentages of alum and (b) ferrous sulfate and reduced percentages alum with the initial alum dose at 30 mg/L. Both ferrous chloride and ferrous sulfate dosed at 2.31 mg/L as Fe.

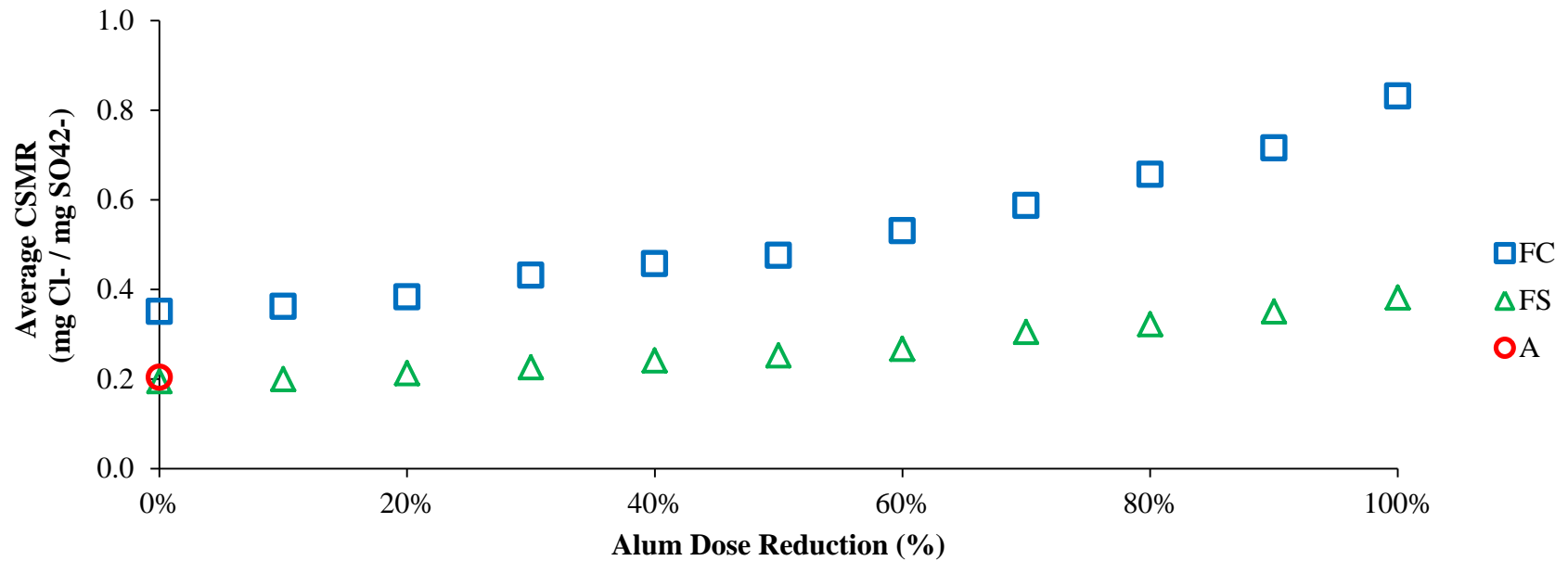


Figure 5. Chloride to sulfate mass ratio (CSMR) following jar tests at the University of Arkansas Water Research Laboratory as a function of percent alum reduction. Sample waters were dosed with ferrous chloride (FC) and alum, ferrous sulfate (FS) and alum, and only alum (A). Both ferrous chloride and ferrous sulfate were dosed at 2.31 mg/L as Fe and the initial alum dose was 30 mg/L as alum.

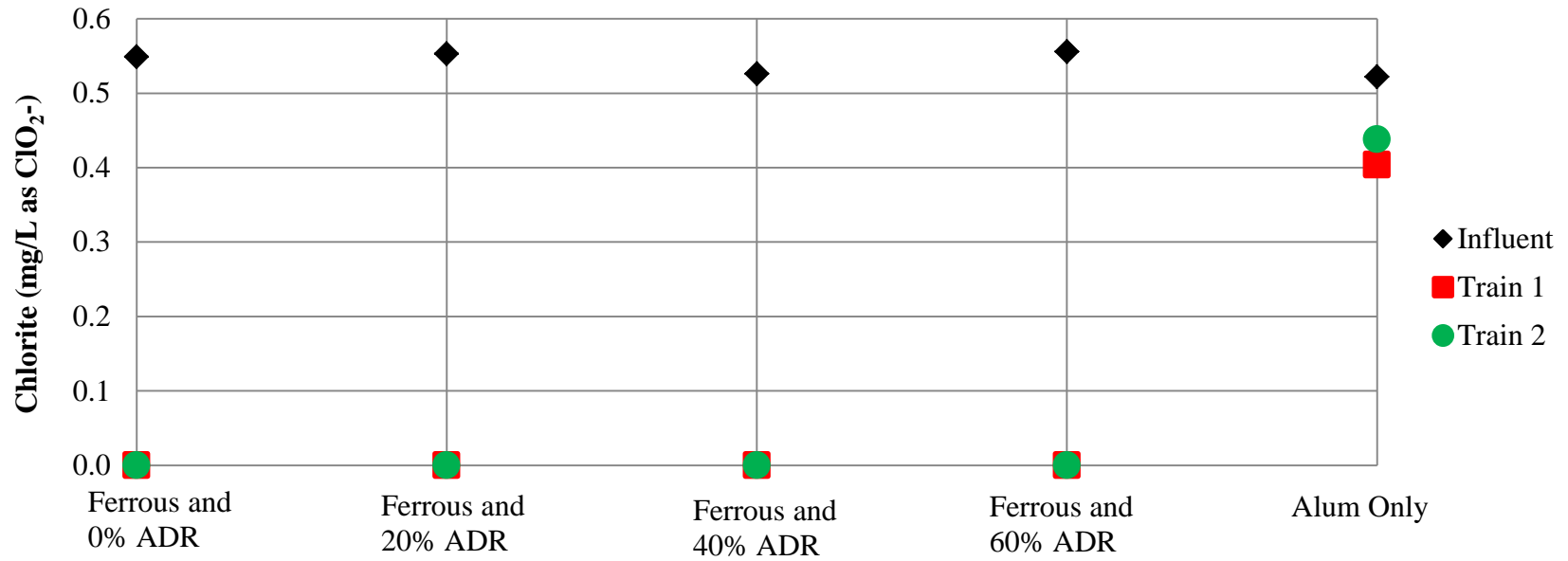


Figure 6. Influent and filtered water chlorite residual as a function of coagulant dosing scheme as generated at the Beaver Water District pilot plant. Ferrous chloride (Train 1) and ferrous sulfate (Train 2) were dose at 1.65 mg/L as Fe. ADR is alum dose reduction. Original alum dose was 30 mg/L as alum.

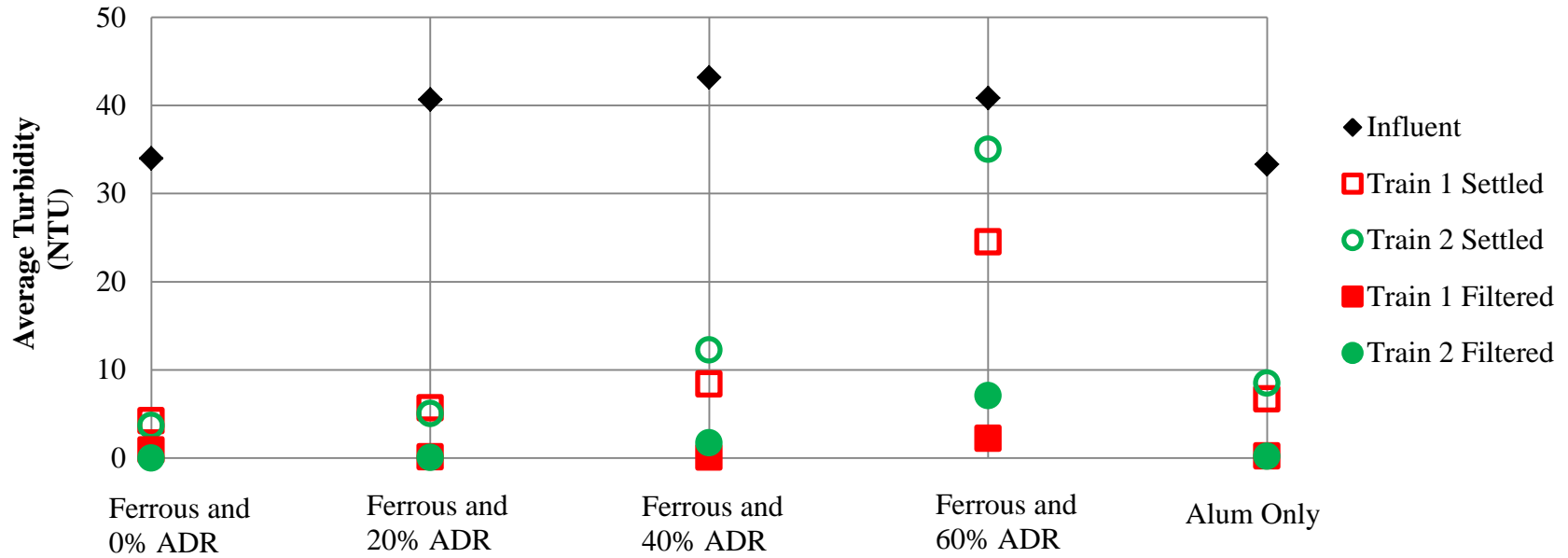


Figure 7. (a) Turbidity as a function of coagulant dose scheme. Samples generated by the pilot plant facility at Beaver Water District and parameters measured at the University of Arkansas Water Research Laboratory. Ferrous chloride (Train 1) and ferrous sulfate (Train 2) were dosed at 1.65 mg/L as Fe. ADR is alum dose reduction. Original alum dose was 30 mg/L as alum.

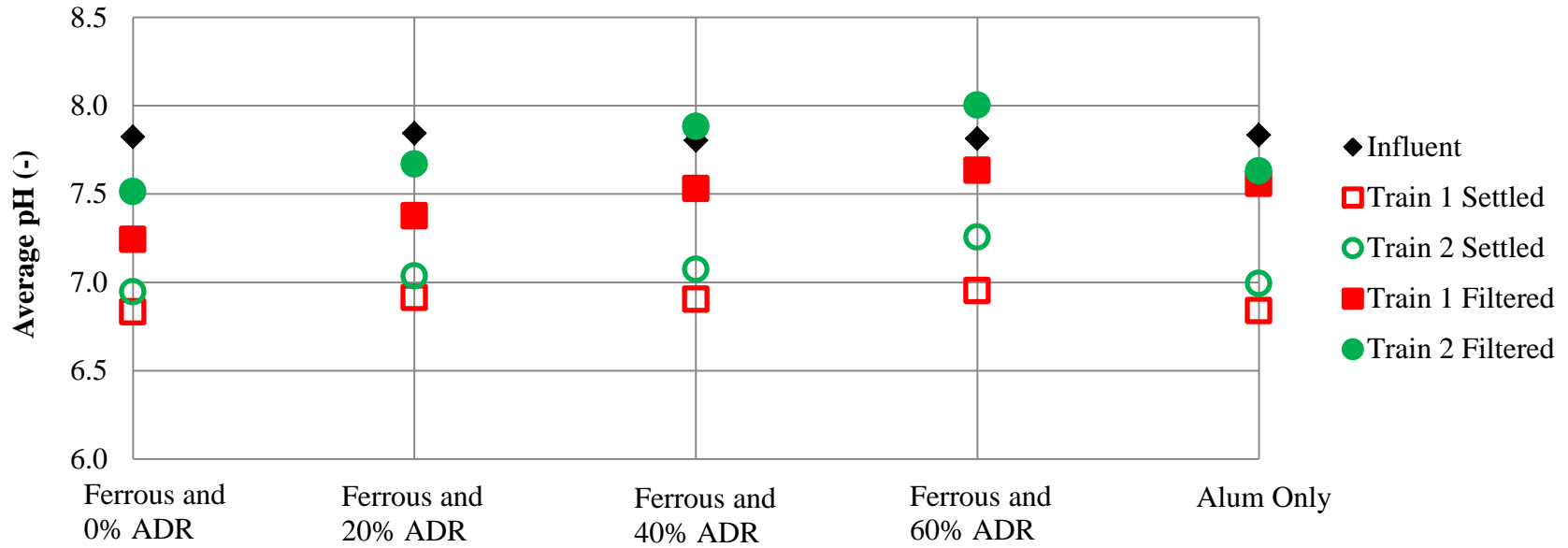


Figure 7. (b) pH as a function of coagulant dose scheme. Samples generated by the pilot plant facility at Beaver Water District and parameters measured at the University of Arkansas Water Research Laboratory. Ferrous chloride (Train 1) and ferrous sulfate (Train 2) were dosed at 1.65 mg/L as Fe. ADR is alum dose reduction. Original alum dose was 30 mg/L as alum.

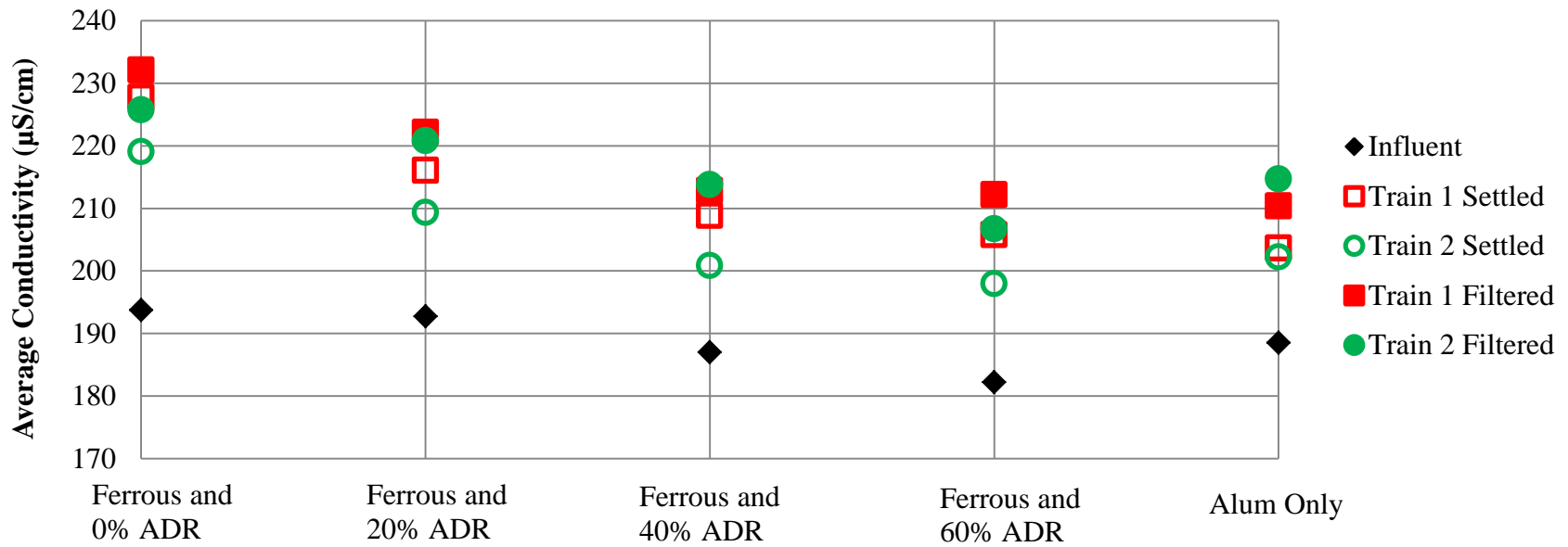


Figure 7. (c) Conductivity as a function of coagulant dose scheme. Samples generated by the pilot plant facility at Beaver Water District and parameters measured at the University of Arkansas Water Research Laboratory. Ferrous chloride (Train 1) and ferrous sulfate (Train 2) were dosed at 1.65 mg/L as Fe. ADR is alum dose reduction. Original alum dose was 30 mg/L as alum.

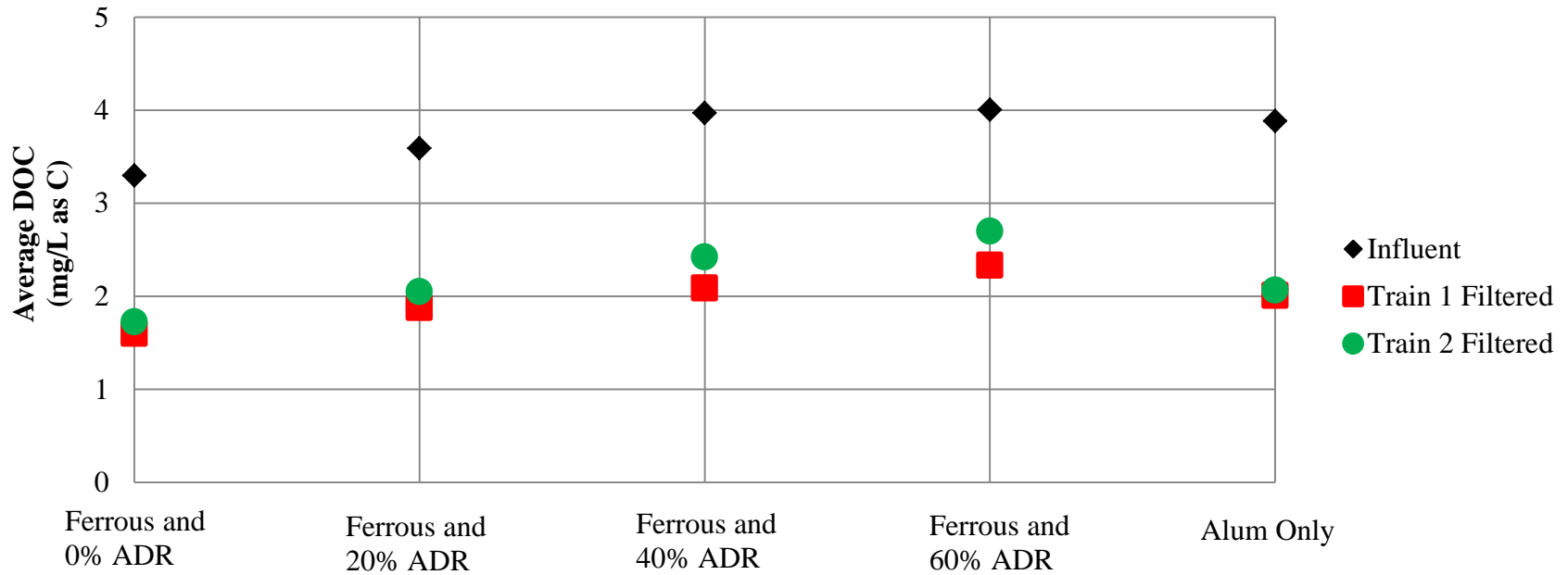


Figure 7. (d) Dissolved organic carbon as a function of coagulant dose scheme. Samples generated by the pilot plant facility at Beaver Water District and parameters measured at the University of Arkansas Water Research Laboratory. Ferrous chloride (Train 1) and ferrous sulfate (Train 2) were dosed at 1.65 mg/L as Fe. ADR is alum dose reduction. Original alum dose was 30 mg/L as alum.

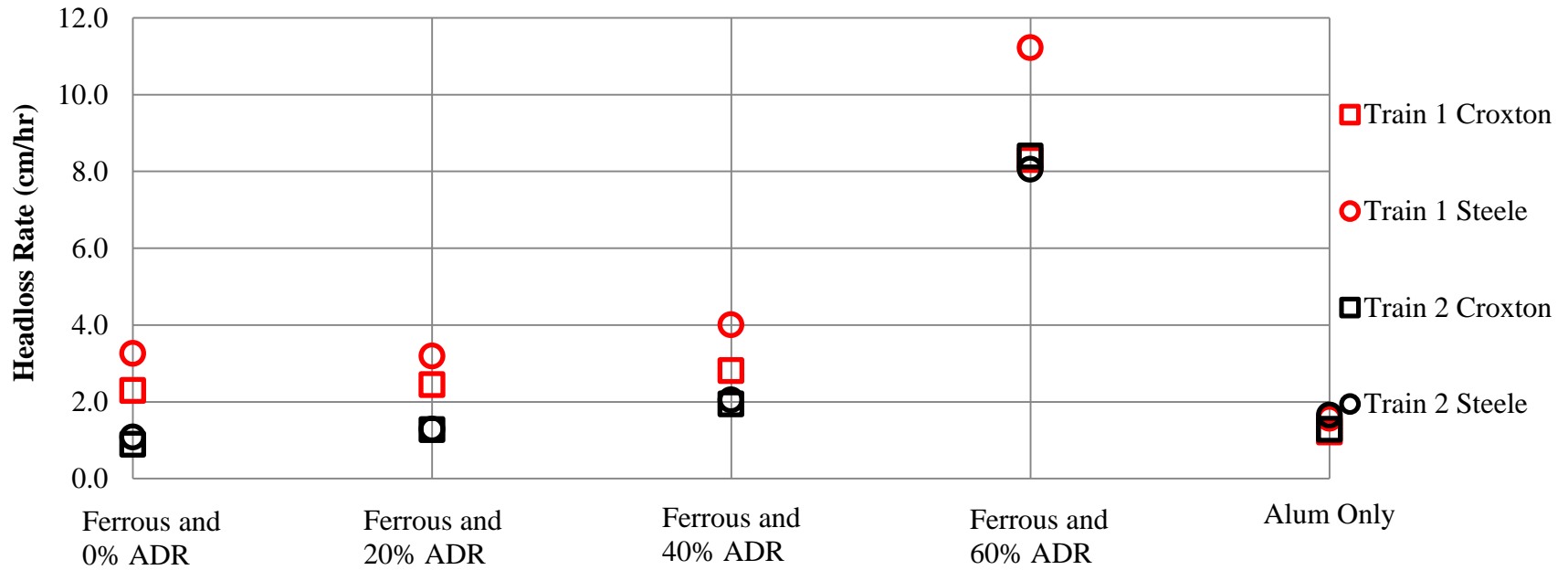


Figure 8. Filter accumulated headloss rate (cm/hr) as a function of coagulant dose scheme. Samples generated by the pilot plant facility at Beaver Water District and parameters measured at the University of Arkansas Water Research Laboratory. Ferrous chloride (Train 1) and ferrous sulfate (Train 2) were dosed at 1.65 mg/L as Fe. ADR is alum dose reduction. Original alum dose was 30 mg/L as alum. Croxton filters loaded at 2.6 mm/sec and Steele filters loaded at 2.2 mm/sec.

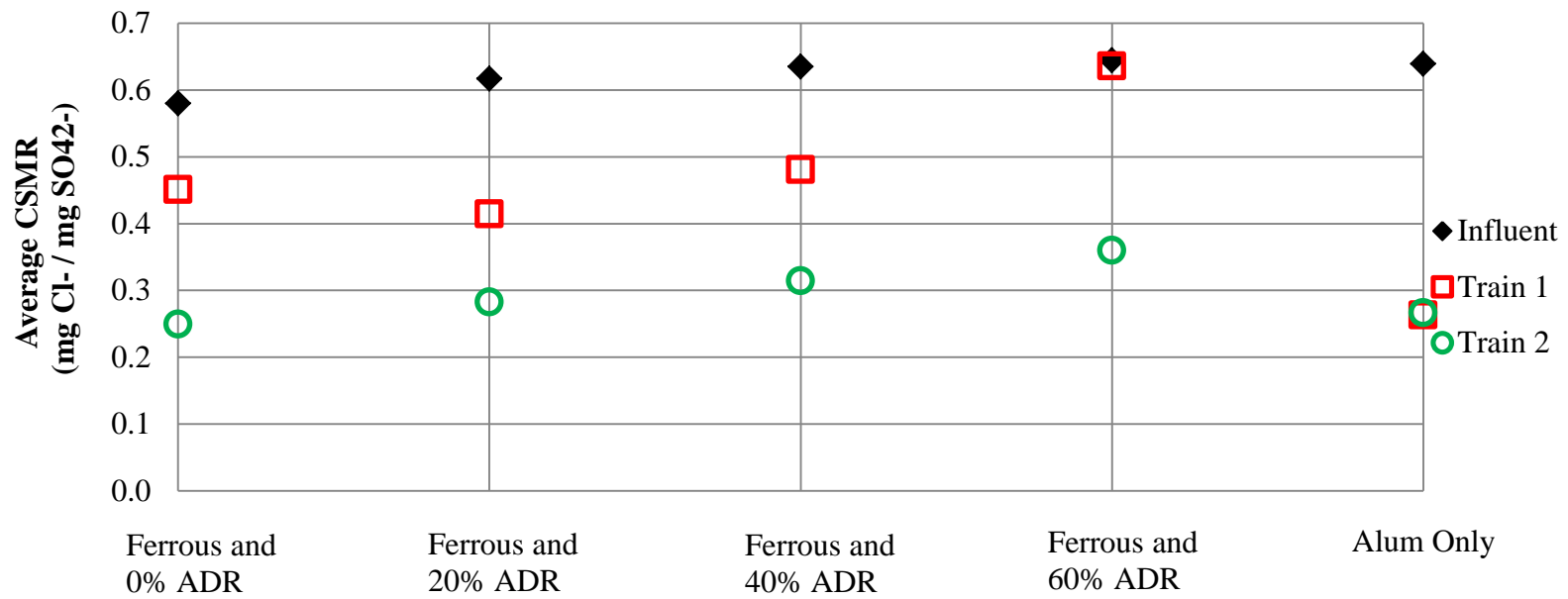


Figure 9. Chloride to sulfate mass ratio (CSMR) of filtered water as a function of coagulant dose scheme. Samples generated by the pilot plant facility at BWD and parameters measured at the University of Arkansas Water Research Laboratory. Ferrous chloride (Train 1) and ferrous sulfate (Train 2) were dosed at 1.65 mg/L as Fe. ADR is alum dose reduction. Original alum dose was 30 mg/L as alum.

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Appendix

Table A1. Water quality parameters after oxidation with chlorine dioxide at a dose of 1 mg/L as ClO₂, but prior to jar testing as determined at the University of Arkansas Water Research Laboratory.

Alum Reduction	Alum Dose (mg/L as Alum)	FC Dose (mg/L as Fe)	FS Dose (mg/L as Fe)	Turbidity (NTU)	Conductivity (μS/cm)	pH	DOC (mg/L as C)
Raw ^a	-	-	-	7.5 ± 0.0	175.3 ± 0.5	7.91 ± 0.02	2.99 ± 0.02
0%	30	2.31	-	24.8 ± 0.2	177.4 ± 4.8	7.72 ± 0.01	3.13 ± 0.04
		-	2.31	24.8 ± 0.8	171.1 ± 7.0	7.79 ± 0.02	
10%	27	2.31	-	31.8 ± 1.0	178.6 ± 2.6	7.73 ± 0.03	2.86 ± 0.01
		-	2.31	29.7 ± 1.2	179.2 ± 1.7	7.74 ± 0.02	
20%	24	2.31	-	28.3 ± 1.7	178.3 ± 1.7	7.73 ± 0.02	3.01 ± 0.06
		-	2.31	30.8 ± 2.2	182.5 ± 2.6	7.76 ± 0.01	
30%	21	2.31	-	30.5 ± 1.9	177.2 ± 3.3	7.77 ± 0.04	2.83 ± 0.06
		-	2.31	31.7 ± 1.2	177.1 ± 2.3	7.82 ± 0.00	
40%	18	2.31	-	31.0 ± 2.4	175.1 ± 0.9	7.78 ± 0.02	2.92 ± 0.04
		-	2.31	31.0 ± 0.8	177.8 ± 0.8	7.81 ± 0.00	
50%	15	2.31	-	28.0 ± 2.2	173.5 ± 2.2	7.77 ± 0.01	2.81 ± 0.02
		-	2.31	31.0 ± 0.8	185.4 ± 2.6	7.78 ± 0.00	
60%	12	2.31	-	29.0 ± 0.8	177.2 ± 3.8	7.80 ± 0.01	2.75 ± 0.02
		-	2.31	32.5 ± 0.4	176.2 ± 2.7	7.82 ± 0.02	
70%	9	2.31	-	27.0 ± 2.2	177.8 ± 2.1	7.76 ± 0.02	2.85 ± 0.03
		-	2.31	27.7 ± 1.2	176.4 ± 2.6	7.79 ± 0.01	
80%	6	2.31	-	32.7 ± 1.9	176.9 ± 1.7	7.77 ± 0.00	2.93 ± 0.02
		-	2.31	33.5 ± 1.9	177.0 ± 0.6	7.80 ± 0.02	
90%	3	2.31	-	33.3 ± 2.1	176.4 ± 2.1	7.71 ± 0.02	2.99 ± 0.03
		-	2.31	34.0 ± 0.8	175.6 ± 1.0	7.75 ± 0.02	
100%	0	2.31	-	28.8 ± 1.0	181.7 ± 1.9	7.81 ± 0.01	2.79 ± 0.06
		-	2.31	30.3 ± 0.9	176.2 ± 0.9	7.83 ± 0.01	
-	30	-	-	31.3 ± 2.5	178.9 ± 1.7	7.79 ± 0.03	2.77 ± 0.06

^a Denotes unamended raw water sample with no oxidation. Values are averages ± standard deviation. FC is ferrous chloride. FS is ferrous sulfate. DOC is dissolved organic carbon.

Table A2. Water quality parameters after jar tests as determined at the University of Arkansas Water Research Laboratory.

Alum Reduction (%)	Ferrous Type	Turbidity (NTU)	Conductivity ($\mu\text{S}/\text{cm}$)	pH	DOC (mg/L as C)
0%	FeCl ₂	1.9 \pm 0.1	193.4 \pm 1.8	6.92 \pm 0.06	1.92 \pm 0.09
	FeSO ₄	2.0 \pm 0.4	192.8 \pm 0.2	7.03 \pm 0.05	1.87 \pm 0.06
10%	FeCl ₂	2.0 \pm 0.6	184.6 \pm 3.0	7.04 \pm 0.04	1.89 \pm 0.02
	FeSO ₄	2.0 \pm 0.1	182.9 \pm 0.8	6.99 \pm 0.03	1.94 \pm 0.01
20%	FeCl ₂	2.6 \pm 0.3	183.6 \pm 0.6	6.98 \pm 0.01	1.97 \pm 0.04
	FeSO ₄	1.9 \pm 0.1	183.5 \pm 0.2	6.92 \pm 0.02	1.96 \pm 0.02
30%	FeCl ₂	2.3 \pm 0.3	181.2 \pm 1.9	7.10 \pm 0.01	1.84 \pm 0.02
	FeSO ₄	2.6 \pm 0.2	180.5 \pm 2.0	7.10 \pm 0.01	1.86 \pm 0.00
40%	FeCl ₂	2.1 \pm 0.1	181.5 \pm 1.0	7.13 \pm 0.01	2.04 \pm 0.07
	FeSO ₄	2.7 \pm 0.9	183.2 \pm 1.8	7.09 \pm 0.02	2.00 \pm 0.03
50%	FeCl ₂	2.1 \pm 0.3	181.3 \pm 0.4	7.19 \pm 0.01	1.86 \pm 0.02
	FeSO ₄	2.1 \pm 0.2	184.1 \pm 2.2	7.17 \pm 0.00	1.86 \pm 0.00
60%	FeCl ₂	3.4 \pm 0.7	188.3 \pm 0.5	7.21 \pm 0.01	2.02 \pm 0.07
	FeSO ₄	2.9 \pm 0.2	178.9 \pm 1.4	7.23 \pm 0.01	1.97 \pm 0.01
70%	FeCl ₂	3.3 \pm 0.3	182.6 \pm 2.6	7.30 \pm 0.01	2.09 \pm 0.03
	FeSO ₄	3.8 \pm 0.8	180.6 \pm 1.0	7.28 \pm 0.01	2.11 \pm 0.03
80%	FeCl ₂	6.4 \pm 0.4	185.8 \pm 2.9	7.30 \pm 0.02	2.25 \pm 0.02
	FeSO ₄	7.3 \pm 0.4	181.2 \pm 2.5	7.32 \pm 0.01	2.24 \pm 0.03
90%	FeCl ₂	11.3 \pm 0.5	188.9 \pm 7.3	7.44 \pm 0.02	2.33 \pm 0.06
	FeSO ₄	10.7 \pm 0.2	178.9 \pm 2.1	7.43 \pm 0.04	2.29 \pm 0.08
100%	FeCl ₂	20.5 \pm 1.1	180.6 \pm 2.1	7.50 \pm 0.05	2.29 \pm 0.02
	FeSO ₄	21.7 \pm 0.5	177.7 \pm 1.5	7.54 \pm 0.02	2.29 \pm 0.02
Alum Only	-	3.1 \pm 0.2	190.8 \pm 3.0	7.02 \pm 0.01	1.83 \pm 0.01

Values are averages \pm standard deviation. Dosing scheme denoted by percent alum reduction and ferrous salt type. Ferrous dosed at 2.31 mg/L as Fe and original alum dose was 30 mg/L as alum. DOC is dissolved organic carbon.

Table A3. Anion concentrations after oxidation with chlorine dioxide at a dose of 1 mg/L as ClO₂ and jar testing as determined at the University of Arkansas Water Research Laboratory.

Alum Reduction (%)	Ferrous Type	Chloride (mg/L as Cl ⁻)	Sulfate (mg/L as SO ₄ ²⁻)	CSMR (-)
0%	FeCl ₂	8.17 ± 0.09	23.30 ± 0.35	0.35
	FeSO ₄	5.39 ± 0.04	27.65 ± 0.36	0.19
10%	FeCl ₂	8.22 ± 0.06	22.73 ± 0.09	0.36
	FeSO ₄	5.42 ± 0.04	27.17 ± 0.24	0.20
20%	FeCl ₂	8.47 ± 0.11	22.12 ± 1.01	0.38
	FeSO ₄	5.61 ± 0.04	26.35 ± 0.91	0.21
30%	FeCl ₂	8.09 ± 0.01	18.77 ± 0.05	0.43
	FeSO ₄	5.31 ± 0.04	23.50 ± 0.24	0.23
40%	FeCl ₂	8.05 ± 0.14	17.59 ± 0.50	0.46
	FeSO ₄	5.33 ± 0.08	22.07 ± 0.67	0.24
50%	FeCl ₂	8.00 ± 0.11	16.81 ± 0.36	0.48
	FeSO ₄	5.27 ± 0.07	20.88 ± 0.12	0.25
60%	FeCl ₂	7.92 ± 0.09	14.92 ± 0.24	0.53
	FeSO ₄	5.16 ± 0.06	19.33 ± 0.33	0.27
70%	FeCl ₂	8.09 ± 0.07	13.78 ± 0.30	0.59
	FeSO ₄	5.36 ± 0.11	17.59 ± 0.19	0.30
80%	FeCl ₂	8.12 ± 0.13	12.36 ± 0.20	0.66
	FeSO ₄	5.31 ± 0.07	16.49 ± 0.22	0.32
90%	FeCl ₂	8.18 ± 0.07	11.44 ± 0.17	0.72
	FeSO ₄	5.39 ± 0.03	15.39 ± 0.12	0.35
100%	FeCl ₂	8.06 ± 0.13	9.69 ± 0.16	0.83
	FeSO ₄	5.13 ± 0.03	13.44 ± 0.11	0.38
Alum Only	-	4.87 ± 0.05	23.93 ± 0.49	0.20

Values are averages ± standard deviation. Dosing scheme denoted by percent alum reduction and ferrous salt type. Ferrous salt dosed at 2.31 mg/L as Fe. Original alum dose (0% reduction) was 30 mg/L as alum. CSMR defined as chloride to sulfate mass ratio, based on mean values

. **Table A4.** Water quality parameters generated from samples of the BWD pilot facility.

Date (2014)	Alum Dose (mg/L as Alum)	Ferrous Dose (mg/L as Fe)	Sample Location	Turbidity (NTU)	Conductivity ($\mu\text{S/cm}$)	pH	DOC (mg/L as C)
March 20	30	1.65	Influent	34.0 \pm 0.0	193.7 \pm 0.7	7.82 \pm 0.02	3.30 \pm 0.05
			FeCl ₂ Settled	4.2 \pm 0.2	227.7 \pm 0.3	6.83 \pm 0.05	
			FeSO ₄ Settled	3.7 \pm 0.4	219.1 \pm 3.4	6.95 \pm 0.03	
			FeCl ₂ Filtered	0.9 \pm 0.2	232.1 \pm 1.0	7.24 \pm 0.01	1.60 \pm 0.02
			FeSO ₄ Filtered	0.0 \pm 0.0	225.8 \pm 0.1	7.51 \pm 0.00	1.72 \pm 0.04
March 21	24	1.65	Influent	40.7 \pm 0.5	192.8 \pm 0.7	7.84 \pm 0.02	3.59 \pm 0.07
			FeCl ₂ Settled	5.7 \pm 0.6	216.1 \pm 2.6	6.91 \pm 0.03	
			FeSO ₄ Settled	5.0 \pm 0.3	209.3 \pm 0.1	7.04 \pm 0.02	
			FeCl ₂ Filtered	0.1 \pm 0.1	222.1 \pm 1.8	7.38 \pm 0.02	1.88 \pm 0.02
			FeSO ₄ Filtered	0.1 \pm 0.1	220.8 \pm 0.7	7.67 \pm 0.01	2.05 \pm 0.02
March 22	18	1.65	Influent	43.2 \pm 0.6	187.0 \pm 1.5	7.80 \pm 0.05	3.97 \pm 0.05
			FeCl ₂ Settled	8.4 \pm 0.2	208.9 \pm 0.5	6.90 \pm 0.01	
			FeSO ₄ Settled	12.3 \pm 0.2	200.9 \pm 1.8	7.07 \pm 0.04	
			FeCl ₂ Filtered	0.1 \pm 0.0	212.9 \pm 1.1	7.53 \pm 0.02	2.09 \pm 0.04
			FeSO ₄ Filtered	1.7 \pm 0.1	213.8 \pm 1.8	7.88 \pm 0.01	2.42 \pm 0.04
March 23	12	1.65	Influent	40.8 \pm 0.9	182.2 \pm 0.6	7.81 \pm 0.03	4.01 \pm 0.03
			FeCl ₂ Settled	24.5 \pm 2.7	205.8 \pm 1.4	6.95 \pm 0.04	
			FeSO ₄ Settled	35.0 \pm 0.8	198.0 \pm 0.3	7.26 \pm 0.11	
			FeCl ₂ Filtered	2.2 \pm 0.1	212.2 \pm 1.5	7.63 \pm 0.02	2.33 \pm 0.01
			FeSO ₄ Filtered	7.1 \pm 0.5	206.7 \pm 0.5	8.00 \pm 0.01	2.70 \pm 0.04
March 24	30	0	Influent	33.3 \pm 0.9	188.5 \pm 2.5	7.83 \pm 0.02	3.88 \pm 0.02
			T-1 Alum Settled	6.7 \pm 0.5	203.6 \pm 0.6	6.84 \pm 0.02	
			T-2 Alum Settled	8.5 \pm 3.5	202.2 \pm 0.3	6.99 \pm 0.06	
			T-1 Alum Filtered	0.2 \pm 0.0	210.4 \pm 0.9	7.56 \pm 0.02	2.01 \pm 0.00
			T-2 Alum Filtered	0.2 \pm 0.0	214.7 \pm 2.2	7.63 \pm 0.02	2.07 \pm 0.02

Values are averages \pm standard deviation. All measurements were made at the University of Arkansas Water Research laboratory. T-1 and T-2 indicate Train 1 and Train 2, respectively.

Table A5. Water quality parameters generated by the pilot plant facility and measured at the University of Arkansas Water Research Laboratory.

Date (2014)	Alum Dose (mg/L as Alum)	Ferrous Dose (mg/L as Fe)	Sample Location	Chloride (mg/L as Cl ⁻)	Sulfate (mg/L as SO ₄ ²⁻)	CSMR (-)
March 20	30	1.65	Influent	7.21 ± 0.04	12.43 ± 0.17	0.58
			FeCl ₂ Filtered	12.41 ± 0.07	27.52 ± 0.11	0.45
			FeSO ₄ Filtered	7.57 ± 0.07	30.33 ± 0.26	0.25
March 21	24	1.65	Influent	7.13 ± 0.03	11.56 ± 0.08	0.62
			FeCl ₂ Filtered	10.01 ± 0.08	24.15 ± 0.41	0.41
			FeSO ₄ Filtered	7.29 ± 0.08	25.81 ± 0.01	0.28
March 22	18	1.65	Influent	6.76 ± 0.02	10.65 ± 0.12	0.63
			FeCl ₂ Filtered	10.52 ± 0.15	21.89 ± 2.07	0.48
			FeSO ₄ Filtered	7.00 ± 0.07	22.26 ± 0.39	0.31
March 23	12	1.65	Influent	6.23 ± 0.65	9.68 ± 1.13	0.64
			FeCl ₂ Filtered	10.78 ± 0.01	16.95 ± 0.05	0.64
			FeSO ₄ Filtered	7.04 ± 0.08	19.57 ± 0.33	0.36
March 24	30	0	Influent	6.81 ± 0.03	10.66 ± 0.05	0.64
			T-1 Alum Only Filtered	6.81 ± 0.04	25.90 ± 0.32	0.26
			T-2 Alum Only Filtered	6.80 ± 0.01	25.54 ± 0.33	0.27

Values are averages ± standard deviation. CSMR defined as chloride to sulfate mass ratio. T-1 and T-2 indicate Train 1 and Train 2, respectively.

Table A6(a). Operational parameters as measured at the Beaver Water District Pilot Plant Laboratory for Train 1, which used ferrous chloride at a constant dose of 1.65 mg/L as Fe and alum reduction (AR) by percentage. The initial alum dose was 30 mg/L as alum.

		Influent			FeCl ₂ Settled			FeCl ₂ After Lime		FeCl ₂ Filtered	
Date	Dosing	Turbidity (NTU)	pH	Temperature (°C)	Turbidity (NTU)	pH	Temperature (°C)	pH	temp	pH	Temperature (°C)
Mar-19, 2014	Alum only	18.0	7.71	13.2	4.37	6.40	14.4	7.48	14.1	7.45	11.1
Mar-20, 2014	0% AR	32.0	7.65	13.4	5.28	6.82	15.5	7.14	13.2	7.13	14.7
Mar-21, 2014	20% AR	40.7	7.62	12.2	9.69	6.93	15.1	7.19	11.8	7.21	12.7
Mar-22, 2014	40% AR	44.3	7.57	11.7	14.2	7.02	14.5	7.43	12.1	7.45	12.4
Mar-23, 2014	60% AR	41.9	7.6	12.9	33.3	7.16	15.7	7.55	13.1	7.59	14.0
Ma-24, 2014	Alum only	35.0	7.63	12.7	12.0	7.03	14.7	7.47	14.2	7.45	13.9

Table A6(b). Operational parameters as measured at the Beaver Water District Pilot Plant Laboratory for Train 2, which used ferrous sulfate at a constant dose of 1.65 mg/L as Fe and alum reduction (AR) by percentage. The initial alum dose was 30 mg/L as alum.

Date	Dosing	Influent			FeSO ₄ Settled			FeSO ₄ After Lime		FeSO ₄ Filtered	
		Turbidity (NTU)	pH	Temperature (°C)	Turbidity (NTU)	pH	Temperature (°C)	pH	Temperature (°C)	pH	Temperature (°C)
Mar-19, 2014	Alum only	18.0	7.71	13.2	5.02	6.99	14.9	7.61	14.0	7.55	10.5
Mar-20, 2014	0% AR	32.0	7.65	13.4	5.39	6.97	16.2	7.33	13.5	7.35	12.6
Mar-21, 2014	20% AR	40.7	7.62	12.2	12.4	7.00	15.0	7.56	12.9	7.58	13.3
Mar-22, 2014	40% AR	44.3	7.57	11.7	18.6	7.12	15.1	7.78	12.4	7.79	12.6
Mar-23, 2014	60% AR	41.9	7.6	12.9	52.0	7.20	15.8	7.95	14.5	7.95	14.6
Mar-24, 2014	Alum only	35.0	7.63	12.7	16.3	7.04	18.0	7.51	14.5	7.54	13.2

