



OSMRE National Technology Transfer Team (NTTT), **Applied Science Final Report***
U.S. Department of the Interior, OFFICE OF SURFACE MINING RECLAMATION AND ENFORCEMENT

Co-treatment of Acid Mine Drainage in Municipal Wastewater Plants for Sustainable Design in Reclamation

OSMRE Cooperative Agreement Number:
S21AC10059-00

Final Report

Reporting Period 02/28/2023 – 02/28/2023

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Date Report was Issued June 30, 2023

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Abstract

Environmental issues related to nutrient pollution have led to stringent PO₄ discharge limits for wastewater treatment plants (WWTPs). Many WWTPs are struggling to meet these demands due to cost or site limitations. An alternative, low-cost solution to facilitate PO₄ removal could utilize locally available mine drainage (MD) in existing WWTPs. MD is a persistent source of metals pollution in coal and metal mining regions worldwide. The alkalinity innate to most WW may be sufficient to neutralize the acidity of MD when mixed in appropriate ratios, elevating pH and correspondingly decreasing concentrations of dissolved metals. Additionally, PO₄ in WW interacts with Fe and Al in MD and is removed from solution, reducing the need for enhanced biological treatment or chemical precipitation techniques for PO₄ removal in WW treatment systems. However, the potential for reduced treatment efficiency of the WW treatment system during cotreatment with MD is a concern that should be addressed. Herein, two separate studies were performed to determine the PO₄ removal and the treatment efficiency of WW treatment when MD was added to a batch treatment stage (primary clarifier) or a sequencing-batch reactor (SBR) with periodic aeration and settling.

For batch treatment in the primary clarifier, the extent of metals and PO₄ removal and the rate of BOD oxidation were quantified for mixtures of WW and three different MD sources having different dissolved concentrations of Fe and Al (pH of raw MD ranged from 3.13 – 4.58) at 10% and 40% MD ratios. The pH remained circumneutral 2 hours after WW was mixed with MD, ranging from 7.44-8.27 for 10% MD and 6.66-7.36 for 40% MD. BOD oxidation rate was not affected by MD addition, with first-order kinetic rates (*k*) ranging from 0.50-0.77 day⁻¹ for raw WW, 0.54-0.97 day⁻¹ for 10% MD, and 0.45-0.95 day⁻¹ for 40% MD. PO₄ removal increased linearly with $([Fe] + [Al])/[PO_4-P]$ molar ratio and reached 99% removal when the ratio was > 2. Observed PO₄ removal was attributed to both adsorption to metal oxides and precipitation as metal-phosphate minerals, with PO₄ removal being limited by equilibrium between metal oxides and metal-phosphate minerals. In addition, sweep coagulation was observed in several reactors with elevated Fe and Al concentrations, which decreased the ultimate BOD of the mixture by up to 40%, and could markedly reduce aeration requirements of the subsequent biological treatment process.

Continuous addition of MD to WW SBRs noted several key improvements to the existing conventional WW treatment process. Similar to batch treatment, >90% removal of PO₄ was noted. Co-treatment alone resulted in 1.5-log inactivation of pathogens, without the addition of any disinfectant chemical. Addition of AMD further decreased both BOD and TSS, key effluent parameters under the US Secondary Treatment Standards. Co-treatment also had appreciable impacts to solids train. Most notable improved settleability of sludge during clarification. Some minor adverse process effects were observed during co-treatment, but are unlinked to totally inhibit adaptation of co-treatment. Inhibitions to treatment performance included an increased effluent metal loading (i.e., Fe), a slightly decreased effluent pH (~0.5 pH unit decrease), and resultant sludge was ~25% less volatile.

Co-treatment of MD in WWTPs is an economically viable solution to solve two environmental concerns in historically mined regions where population is declining, rate payer utility costs are increasing, and WW treatment requirements for PO₄ are becoming more stringent. Continuous co-treatment at full-scale is especially most-feasible at lower acidity-loadings in order to maximizing treatment improvements while minimizing impacts on existing processes.

Introduction

Project Background

Mine drainage (MD) is a persistent and extensive source of water pollution and environmental degradation throughout the United States. Under the Surface Mining Control and Reclamation Act (1977), there are funds set aside for remediating abandoned mine drainage discharges (i.e., Title IV) and regulations for preventing new acid mine drainage discharges to the environment (i.e., Title V). Numerous passive and active treatment technologies exist for treating MD but they are often expensive and require new infrastructure. One option for treatment that has not been adequately explored is the possibility of treating MD using existing infrastructure at conventional wastewater treatment plants (WWTPs). Conventional WWTPs treat net-alkaline municipal wastewater (MWW) in a series of clarifiers and aerobic/anaerobic biological reactors. Adding moderate-to-low volumes (<50%) of MD to these WWTPs would likely have little impact on the biological treatment and could enhance tertiary treatment (i.e., phosphorus (P) removal) while also removing dissolved metals and acidity from the MD. This co-treatment option could be used to address both Title IV and Title V MD discharges. Approximately, 15% of the MD discharges, 22% of the underground mines, and 16% of the surface mines in Pennsylvania are within two miles of a WWTP. The passive co-treatment of acid mine drainage (MD) and MWW in systems other than conventional WWTPs has been proven feasible relatively recently (Strosnider et al., 2014, 2013, 2011a, 2011b; Strosnider and Nairn, 2010).

However, while passive co-treatment has been demonstrated to be a very promising option, it does not have the advantage of utilizing existing MWW treatment infrastructure. The prior co-treatment studies all required construction of new co-treatment infrastructure (e.g., wetlands, digesters, etc.) to meet treatment objectives. Only one study has looked at the effectiveness of MD and MWW co-treatment in a lab-scale conventional activated sludge system in Ireland where several different options for co-treatment were simulated, including the addition of raw (untreated) MD to aeration tanks, the pretreatment of MD by mixing with digested sewage sludge followed by sedimentation and then mixing in the aeration tank, and the pre-treatment of MD by mixing with screened MWW prior to treatment in the aeration tank (Hughes and Gray, 2013). Co-treatment with MWW was effective at removing metals and COD in the activated sludge reactors. MD addition could also improve coagulation and settling in activated sludge systems. It is well known that MD has high Fe^{3+} and Al^{3+} concentrations that could improve coagulation and settling in MWW, working as effective as commercial coagulants (i.e., FeCl_3) for removing turbidity (Rao et al., 1992). MD addition to activated sludge systems can also improve nutrient removal from the combined waste streams (Hughes and Gray, 2013; Ruihua et al., 2011).

Successful co-treatment of MD and MWW in conventional activated sludge treatment facilities requires that the activated sludge process is not impacted by acidity, metals, and SO_4 from the combined wastewaters. Hughes and Gray (2012) studied how various mixing percentages of synthetic MD in activated sludge reactors influenced the microbial diversity and metabolic activity. The microbes were able to withstand up to 19 to 52% MD by volume without having decreased metabolic activity. When the MD was added to sequencing batch reactors mimicking activated sludge reactors, the OUR also remained relatively constant at approximately 55 to 70 mg O_2 /liter-hour regardless of the percent of MD in the reactor (5, 10, or 25%) or the time (0- 24 days) that the activated sludge was in contact with the MD. All reactors saw a decrease in the abundance of sessile protozoa and increase in crawling and free-swimming protozoa, suggesting that the microbial community had acclimated to the increased metal and acidity loads. Overall, it does not appear that MD additions to activated sludge reactors would reduce COD removal from MWW or have a significant impact on the metabolic activity of microbes. However, further experimentation with coal mine MD is necessary to confirm and expand upon these findings before systems can be designed. Additionally, there is no existing data regarding the disposal of co-treated sludge leaving many operational questions.

Research Objectives

Current unknowns related to MD impacts on WWTPs prohibit full-scale adaptation. Therefore, the scope and approach of this research will be focused on evaluating the major hypotheses associated with co-treating MD and MWW in existing WWTPs. Specifically, the four primary objectives are to: 1) determine what types of MD chemistries can be treated with MWW at WWTPs and to identify the appropriate MD/MWW mixing ratios for optimal MD and MWW treatment; 2) demonstrate that adding MD to WWTPs will effectively treat the MD without impacting microbial activity and impairing MWW treatment performance; 3) illustrate that co-treatment will not complicate sludge handling and disposal processes at WWTPs; and 4) demonstrate that MD can be added to an existing conventional WWTP at minimal cost. Two separate experiments were conducted for this proposal based on the way MD is introduced to an existing WWTP: 1) Bench-scale batch-addition of MD to a WWTP primary clarifier; and 2) continuous addition of MD directly into the biological treatment aeration basin of a bench-scale sequencing batch reactor (SBR) WWTP.

Experimental

Batch Primary Clarification Methods

Sample collection

Primary influent municipal WW (downstream of a comminutor) was collected from the Saint Francis University (SFU) Sewage Treatment Plant between 9-10am on the day of co-treatment experiments. MD was collected from three discharges located nearby the SFU campus within 24 hours prior to co-treatment experiments: 1) Hughes Borehole (Fe+Al MD) is located in Portage, PA (40.408808°, -78.654778°) and contains elevated concentrations of Fe (~10 mg/L) and Al (~10 mg/L) with a median pH of 3.23; 2) Squatter Falls (Fe MD) is located in Logan Township, PA (40.505319°, -78.515256°) and contains elevated concentrations of Fe (~60 mg/L) and low Al (< 0.5 mg/L) with a median pH of 4.51; and Spaghetti Hole (Al MD) is located in Logan Township, PA (40.517268°, -78.514889°) and contains no detectable Fe (< 0.02 mg/L) and elevated concentrations of Al (~4 mg/L) with a median pH of 4.02. These three MD sources were chosen due to their representative Fe and Al concentrations, which are the two of the most common metals found in coal MD (Cravotta, 2008), and of most interest regarding coprecipitation with PO₄ in WW.

Co-treatment experiment setup

WW was combined with the three MD samples (at 10% and 40% MD mixing ratios) in 2 L Phipps & Bird Jar Testers (120x120x150 mm) and mixed using a 7790-910 Six-Paddle Stirrer (Phipps & Bird, Inc., Richmond, VA) within 1 h of collecting the WW. WW was also mixed with distilled water (DI) in 10% and 40% DI ratios as control experiments to observe dilution effects, in addition to a control reactor containing only raw WW with no dilution. The reactors were gently mixed (50 rpm, G = 40-50 s⁻¹) for 2 min and allowed to settle for 2 h after mixing, simulating primary clarification in WWTPs. After settling, supernatant and settled solids samples were collected for analysis.

Water quality analyses

Before and after mixing and settling in each reactor, the pH of the raw WW, raw MD, and co-treated mixtures were measured using a Mettler Toledo FiveEasy pH/mV reader equipped with an LE438 pH probe (Mettler Toledo, Columbus, OH). Dissolved oxygen was also measured using a YSI Professional Plus meter equipped with a YSI Pro-BOD probe (YSI, Yellow Springs, OH). Alkalinity was measured by acidification with H₂SO₄ to pH 4.5 using a Hach Titration kit (Hach Company, Loveland, CO). Chemical oxygen demand (COD) was measured using high-range Hach COD vials. After mixing and settling in the Phipps & Bird reactors, supernatant was collected and filtered using 0.45- μ m nylon syringe filters. The filtered supernatants were diluted 1:20 with DI water before being analyzed for PO₄

using the ascorbic acid method (APHA, 2017) on a Hach DR 6000 spectrophotometer. A subset of the filtered samples was acidified to pH < 2 using nitric acid, diluted 1:10 with 2% nitric acid, and analyzed for metal concentrations using an ICP-OES (Perkin Elmer Optima 3300 DV, PerkinElmer, Waltham, MA). Ferrous and total iron in the raw MD were determined with a Hach colorimeter using the 1,10-phenanthroline method (Hach method 8146) and the USEPA FerroVer method (Hach method 8008), respectively (APHA, 2017).

Solids analysis

Solids collected after co-treatment were concentrated using graduated cylinders and freeze dried using a Labconco FreeZone lyophilizer (Labconco, Kansas City, MO) at 0.2 mBar and -50°C for 48 hours. After freeze drying, the samples were ignited at 550°C for 2 hours in a muffle furnace (KSL-1100X, MTI Corporation, Pleasant Prairie, WI) to remove organic material. The ignited solids were analyzed by X-ray diffraction (XRD) at the Penn State Materials Research Institute. Powders were front loaded into a silicon zero background holder and diffraction data were collected from 5 to 85° 2θ using a Malvern Panalytical Empyrean® instrument fitted with a cobalt (Kα1-2 = 1.789010/1.792900 Angstrom) long-fine-focus X-ray tube operated at 40 kV and 40 mA. The incident beam path included a BBHD optic fitted with 1/8° divergence slit, 0.04 radian Soller slits, a 10 mm beam mask, and a fixed 1/2° anti-scatter slit. The diffracted beam path included a 1/4° programmable anti-scatter slit, 0.04 radian Soller slits, and an X'Celerator® detector used in scanning line (1D) mode with an active length of 2.1223° 2θ and a nominal step size of 0.0334° 2θ. Phase ID was carried out using Jade® software (version 8.7) from Materials Data Inc. (MDI) and the International Centre for Diffraction Data (ICDD) database (PDF4).

BOD removal rate

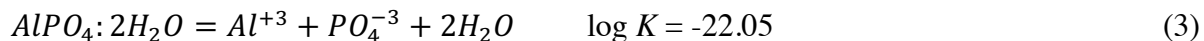
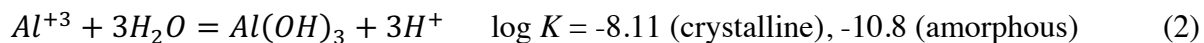
BOD removal rates were determined using Hach BOD Trak II respirometers by adding 95 mL of supernatant from each Phipps & Bird reactor into 300 mL BOD respirometer bottles containing 0.05 g of nitrification inhibitor (formula 2533; added to inhibit ammonia oxidation, which occurs days later than BOD oxidation and does not allow for a first-order model to be applied to the data). BOD consumption was recorded for 5-7 d and the rate of BOD removal (*k*) was determined using a first-order kinetic BOD model (eq. 1). The least squares method was used to minimize the difference between the measured data and model output. The *k* values from each reactor set were analyzed for normality and compared using a one-way ANOVA in RStudio.

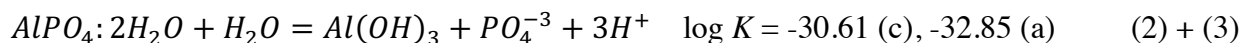
$$BOD_t = UBOD * (1 - e^{-kt}) \quad (1)$$

where BOD_{*t*} is the BOD at time *t* (mg/L), UBOD is the ultimate BOD (mg/L), *k* is the first-order reaction rate (d⁻¹), and *t* is time (d).

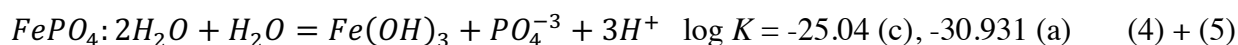
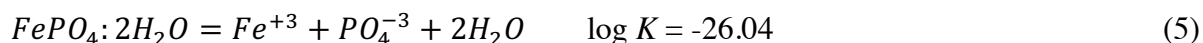
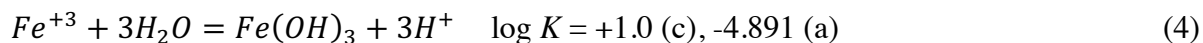
Coprecipitation modeling

PHREEQC 3.7.3 (<https://www.usgs.gov/software/phreeqc-version-3>) was used to determine speciation of the WW and MD mixtures using the equilibrium constants compiled from multiple sources (citations) and assuming that Fe- and Al-PO₄ minerals were in equilibrium with Fe(OH)₃ and Al(OH)₃ using the following conditions:





For modeling efforts, an intermediate $\log K = -9.455$ was used for $Al(OH)_3$



For modeling efforts, an intermediate $\log K = -2.9455$ was used for $Fe(OH)_3$

For samples containing constituents with concentrations below detection of the analytical technique, one-half of the minimum detection limit (MDL) was considered for data analysis (Fe, Al, and PO4-P MDL = 0.02 mg/L).

Continuous SBR Treatment Methods

SBR Design and Operation

The continuous co-treatment of AMD and MWW was examined in a bench-scale, continuous-flow treatment system which replicated a sequencing batch reactor (SBR) treatment plant, including biological and physical treatment processes traditionally applied in full scale WWTPs (Figure 1). The SBR system had two identical treatment trains in parallel (“SBR-1” and “SBR-2”), each with a single 2-L rectangular acrylic reactor (B-KER²®, Phipps & Bird) allowing for simultaneous analysis of two conditions, as described below. Influent and effluent flow was controlled by Masterflex (Avantor, Inc., Radnor, PA) peristaltic pumps plumbed with Masterflex L/S 3.1mm diameter tubing. Aeration was supplied to the reactors with variable-speed air pumps and stone diffusers (Unicliffe Co., Denver, CO) while reactors were mixed by a deep-vortex cross magnetic stirrer. Dissolved oxygen (DO) was continuously monitored in each reactor with optical, luminescence-based dissolved oxygen sensors (Vernier, Beaverton, OR) to maintain DO above 3 mg/L during aeration. SBR operating cycles (Figure S1) were controlled using BN-LINK (El Monte, CA) digital programmable outlet timers.

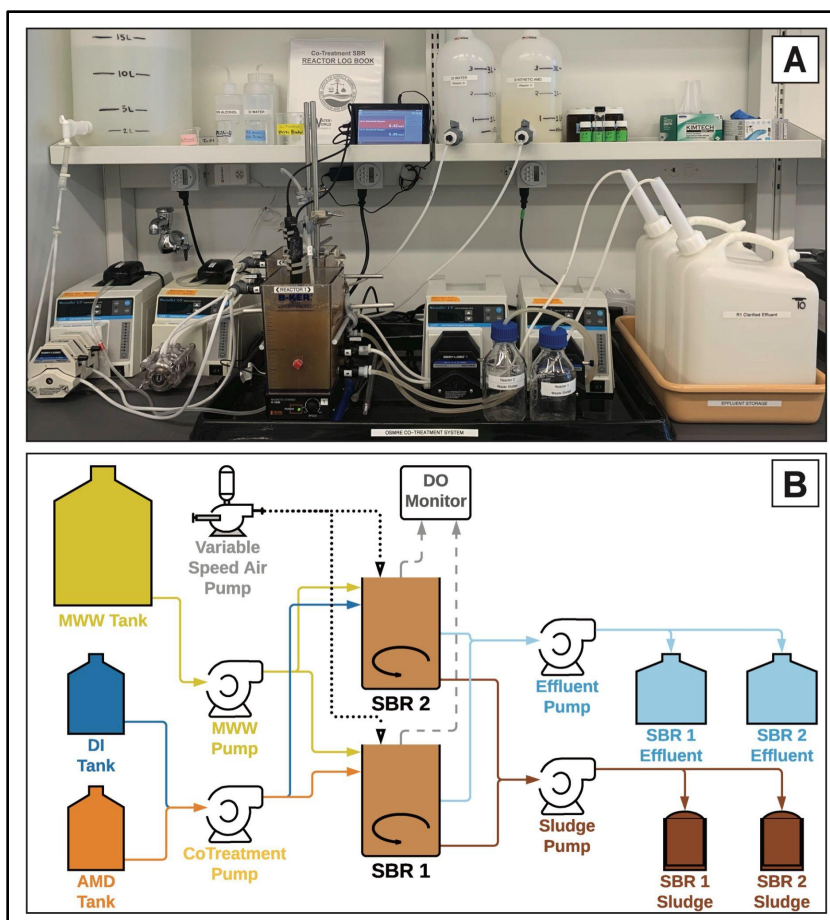


Figure 1: (A) Image of the complete and operating SBR system with SBR-1 in the foreground and SBR-2 behind. (B) Flow diagram of SBR system representing “Phase I” co-treatment.

Reactors were fed synthetic MWW replicating a primary MWW effluent (i.e., passed through screens and primary clarification) with average water quality presented in Table S1. At startup, each 2-L SBR was initially inoculated with 300mL of mixed-liquor suspended solids (MLSS) collected from the Warwick Sewer Authority WWTP (Warwick, RI) and mixed with 1.7 L synthetic MWW influent. Reactors established a stable microbial community over 45 days while acclimating to the experimental operating environment prior to any co-treatment experiments. SBR MLSS was controlled by periodic, manual sludge wasting, with a target biomass of 2,500 mg/L (± 300) based on SBR MLSS recommendations (EPA, 1999) and known full scale SBR MLSS concentrations in mining regions (e.g., Ebensburg (PA) Municipal Authority). MLSS was measured three times per week by Standard Method 2540D (American Public Health Association, American Water Works Association, & Water Environment Federation, 2017).

Following reactor stabilization, three different scenarios were examined with the SBRs. First, the “MWW” baseline (no co-treatment) condition of both reactors was monitored for 14 days to represent conventional treatment. After monitoring baseline conditions, reactors began two phases of co-treatment each with a different AMD chemistry (see SI Table S3): a relatively-weak AMD with 91 mg/L as CaCO_3 acidity (i.e., “weak”) and a relatively-strong 720 mg/L acidity AMD (i.e., “strong”). 42-day “Phase I” co-treatment fed SBR-1 with 10% (v/v) weak AMD (acidity 91 mg/L as CaCO_3) and SBR-2 receiving 10% deionized water to serve as a dilution control. A co-treatment ratio of 10% was selected as prior studies demonstrated the effectiveness in this range, and it is likely the most-feasible maximum at scale (Spellman Jr, Tasker, Strosnider, & Goodwill, 2020). Co-treatment occurred (i.e., addition of AMD/DI) after the aeration sequence but before settling (see Figure S1). Upon completion of Phase I co-treatment,

both reactors were co-treated with 10% strong AMD (acidity: 720 mg/L as CaCO₃) for “Phase II” which also lasted for 42 days. In Phase II, SBR-1 represents a microbial community already acclimated to weaker-acidity AMD while SBR-2 represents an unacclimated system.

SBR Treatment Performance Monitoring

Various characteristics of reactor effluent and settled sludge were examined during baseline monitoring and both co-treatment phases. Effluent turbidity was measured with a Hach (Loveland, CO) benchtop TL2300 turbidimeter. Wastewater “nutrients” (i.e., NH₃-N, NO₃-N, NO₂-N, and reactive PO₄-P) were all quantified photometrically with U.S. EPA-approved Hach TNTplus® vials. Total alkalinity (as CaCO₃) was also quantified by the Hach TNTplus® method. Total Fe and SO₄ were measured colorimetrically by Hach powder-pillow FerroVer (Standard Method 3500B) and SulfaVer (Standard Method 4500E) methods, respectively (APHA, 2012). Periodic metals grab samples were acidified with trace-metal grade HNO₃ and stored at 4 °C until time of analysis by an inductively coupled plasma (ICP) optical emission spectrophotometer (PerkinElmer, Inc., Waltham, MA). Dissolved (0.45µm nylon filter) samples were similarly preserved. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were 0.45µm filtered and measured with a TOC-L/TNM-L (Shimadzu, Kyoto, Japan) using the infrared catalytic oxidation combustion method (Sugimura and Suzuki, 1988). COD was determined by the reactor digestion method following Hach Method 8000. BOD was measured with the standard 5-day carbonaceous-BOD test (Standard Methods 5210B) performed at 20 °C (APHA, 2012). Total coliforms (colony forming units (CFU) per mL) were counted following Official Agricultural Chemists Standard Method 991.14 using Petrifilm™ Coliform Count Plates (3M, Saint Paul, MN). Total suspended solids (TSS) were measured gravimetrically by Standard Method 2540D (APHA, 2012). Settled sludge total and volatile solids (g/L and %) were also quantified gravimetrically according to Standard Method 2540G (APHA, 2012). Micrographs of dried sludge samples were collected using a Zeiss (Jena, Germany) Sigma VP field emission scanning electron microscope (SEM).

Results and Discussion

Batch Primary Clarification Performance

Fe and Al coprecipitation with PO₄ in the primary clarifier

After mixing and settling for 2 h, all WW and MD mixtures had Fe, Al, and PO₄-P concentrations below what would be expected from conservative mixing without reactions, indicating their removal from solution by adsorption or precipitation (**Table 1; complete data set provided in Table S1-S3**). Ca was also analyzed, but concentrations followed conservative mixing, indicating that Ca did not extensively precipitate with PO₄, likely due to the elevated pH > 9 required for Ca-PO₄ mineral formation at the concentrations observed during cotreatment (Stumm & Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 1995). The average % removal of PO₄ was greater at 40% MD compared to the corresponding 10% MD, suggesting that PO₄ removal is enhanced by higher concentrations of metals. The final concentrations of PO₄-P in cotreated mixtures varied based on MD site and mixing ratio, with concentrations <0.1 mg PO₄-P/L occurring in all 40% Fe MD samples. Average % Fe and Al removals were high (> 74%) in both 10% and 40% MD mixtures, which is largely attributed to the rapid formation and precipitation of Fe- and Al- oxyhydroxides. Fe and Al concentrations of the cotreated mixtures were below the standard regulatory limit of 1.5 mg Fe/L and 0.5 mg Al/L (Commonwealth of Pennsylvania, 2020) in 88% of the cotreated mixtures analyzed, indicating that cotreatment in the primary clarifier of WWTPs is sufficient for decreasing dissolved metals in MD to permissible discharge limits. In conventional wastewater treatment, subsequent treatment stages that include oxidation and sedimentation basins (i.e., secondary treatment) would present an opportunity for remaining metals in solution to precipitate.

Table 1: Average % removal of PO₄, Fe, and Al relative to the initial (conservative) mixture of MD and WW in 10% and 40% MD mixing ratios (n=4 per MD sample).

MD sample	Average % removed relative to conservative mixture		
	PO ₄	Fe	Al
Fe+Al MD			
10%	24 ± 8.3	86 ± 19	86 ± 16
40%	79 ± 18	80 ± 22	91 ± 17
Fe MD			
10%	35 ± 13	85 ± 25	ND
40%	99 ± 0.2	93 ± 8.8	ND
Al MD			
10%	3.0 ± 1.1	ND	74 ± 45
40%	12 ± 7.0	ND	77 ± 37

ND: Not determined due to low concentrations in the raw MD

The extent of PO₄-P removal by coprecipitation with Fe and Al was dictated by the initial molar ratio of ([Fe]+[Al])/[PO₄-P] in the conservative mixture of WW and MD, where the % PO₄-P removal increased with an increasing molar ratio, and >99% PO₄-P removal was observed at molar ratios > 2.0 (**Figure 2**). At similar ([Fe]+[Al])/[PO₄-P] molar ratios, the % PO₄-P removals were greater for mixtures containing Fe than Al-only mixtures, indicating that Fe may outperform Al in terms of PO₄ removal.

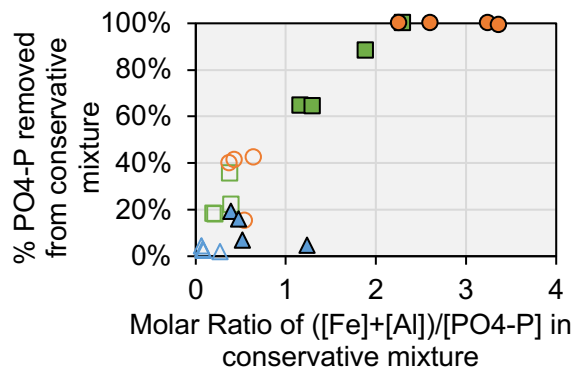


Figure 2: % $PO_4\text{-P}$ removed from the conservative mixture of WW and MD based on the molar ratio of $([Fe]+[Al])/[PO_4\text{-P}]$ of conservative mixtures of WW and 10% (○) and 40% (●) MD from three sites: Fe+Al MD (■), Fe MD (●), and Al MD (▲).

The mechanism for PO_4 removal is attributed to either 1) adsorption to Fe- and Al-oxides and/or 2) formation of Fe- and Al- PO_4 minerals. To gain insight into the mechanisms, equilibrium conditions between Fe- and Al-oxides and Fe- and Al- PO_4 minerals were plotted for amorphous and crystalline oxides, providing a range where equilibrium may occur (solubility limits shown in **Figure 3**). Samples containing only Fe were consistently under-saturated and plot below the equilibrium lines for amorphous and crystalline Fe-oxides, suggesting that adsorption of PO_4 to Fe-oxides is a major contributor to PO_4 removal. On the contrary, samples containing only Al plotted between the amorphous and crystalline equilibrium lines, suggesting that precipitation of the $AlPO_4$ solids is a viable attenuation mechanism and that adsorption to Al-oxides is not contributing to PO_4 removal. This could explain the less effective removal of $PO_4\text{-P}$ observed in the Al-only mixtures (**Figure 2**). Moreover, it is established that Fe- and Al-oxides form rapidly at circumneutral pH present during cotreatment, while Fe- and Al- PO_4 minerals can take hours to form under standard conditions (Wang, et al., 2022; Lagno & Demopoulos, 2005). Thus, during cotreatment of WW and MD, the initial oxide formation removes PO_4 from solution by adsorption and the remaining dissolved metal is available for PO_4 mineral formation, consistent with reactions (2-5). The kinetics of these mineral formations under conditions found during cotreatment should be further investigated to determine the possibility of additional PO_4 removal with increased retention times. XRD of the solids formed during cotreatment identified a broad range of minerals (metal oxides, phosphate minerals, and carbonate minerals; **Figure S1-S4**) with large uncertainty and was thus not informative in terms of removal mechanism. Future work investigating P removal in cotreatment settings could use synthetic solutions with precise compositions to remove uncertainty in mineral identification due to the complexity of raw MD and WW.

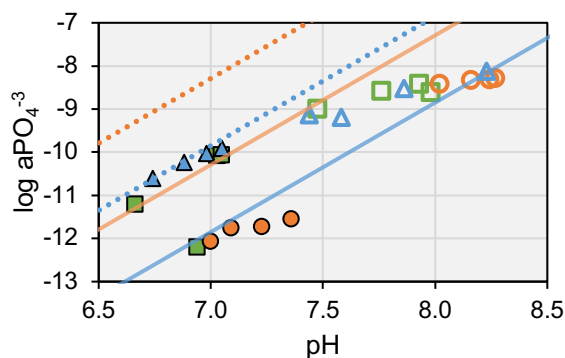


Figure 3: activity of PO_4^{3-} versus pH of measured values after cotreatment of WW and Fe+Al MD (■), Fe MD (●), and Al MD (▲) in 10% (○) and 40% (●) MD ratios. Solid lines represent the equilibrium conditions for crystalline Fe- (—) and Al- (—) phosphates ($FePO_4$ log $K = -26.4$; $AlPO_4$ log $K = -22.05$) and dotted lines represent

amorphous phosphates ($(\text{FePO}_4 \log K = -24.4; \text{AlPO}_4 \log K = -20.05)$ for equilibrium between MePO_4 and $\text{Me}(\text{OH})_3$: $\text{MePO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O} = \text{Me}(\text{OH})_3 + \text{PO}_4^{3-} + 3\text{H}^+$.

BOD removal after mixing and settling in the primary clarifier

The first-order rates of BOD removal (k) for 10% and 40% MD mixtures were not statistically different from raw WW (**Figure 4**; p value = 0.759 \gg 0.05). The pH remained circumneutral for all MD and WW mixtures at both mixing ratios (10% MD: 7.44 < pH < 8.27, 40% MD: 6.66 < pH < 7.36). The WW used in this study had elevated alkalinity (334 ± 17.5 mg CaCO_3/L) and a median pH of 8.25, which was sufficient to neutralize the acidity of the MD at 10 and 40% MD mixtures. The microbial consortia that are responsible for conventional activated sludge WW treatment are impacted by pH and k rates have been reported to change by $\sim 50\%$ over a 6.0-8.0 pH range. Although not apparent in this study, likely due to the water quality variability that is common for WW, previous work has shown that the magnitude of k is at a maximum in the acidic region (e.g., $6.0 < \text{pH} < 6.9$), decreases with increasing pH, is at a minimum in the neutral zone (e.g., pH 7.2 to 7.4), and again increases when the pH is > 7.6 (Mukherjee, Chatterji, & Saraswat, 1968). This “ k valley” is attributed to the fact that different reaction mechanisms prevail in the acidic and alkaline regions that may act as a catalyst for the microbial metabolism responsible for removing BOD from WW. In this experiment, the 40% MD reactors were commonly near the pH 7.0 “ k valley” noted by Mukherjee et al. (Mukherjee, Chatterji, & Saraswat, 1968), but did not exhibit a significantly lower k value, indicating that WW treatment facilities can accept relatively high ratios of MD without impacting treatment performance. However, alkalinity and acidity of WW and MD of interest should be considered to find an appropriate MD to WW mixing ratio that will result in a desired pH, which can be estimated using simple mixing trials. In addition, the bacteria responsible for removing nitrogen in WW treatment facilities are very sensitive to pH: ammonia oxidation is performed by nitrifying bacteria *Nitrosomonas*, which have an ideal pH range of 7.0-8.0, and, subsequently, nitrate reduction is performed by denitrifying bacteria *Nitrobacter*, which have an ideal pH range of 7.5-8.0 (Grady Jr, Daigger, Love, & Filipe, 2011). In previous work, rapid acidification of the activated sludge process to a pH of 6.5 decreased nitrification, changed microfauna populations, and presented issues with sludge handling (Kokina, et al., 2022). Thus, introduction of MD into a WWTP should be incrementally increased to allow for microorganism populations to acclimate to the changing conditions. However, it is possible that even if cotreatment inhibits N removal, the benefit of removing P without increasing the complexity of the entire process may warrant adding a tertiary system to remove N, which is generally less expensive to remove than P (average cost of N removal in conventional BNR = \$15/kg N removed (Vineyard, Hicks, Karthikeyan, & Barak, 2020); average cost of P removal in conventional BNR = \$110/kg P removed (Bashar, Gungor, Karthikeyan, & Barak, 2018)). Moreover, finding a mixing ratio to produce conditions that are appropriate for the treatment requirements of a specific WWTP is vital to the success of WW and MD cotreatment.

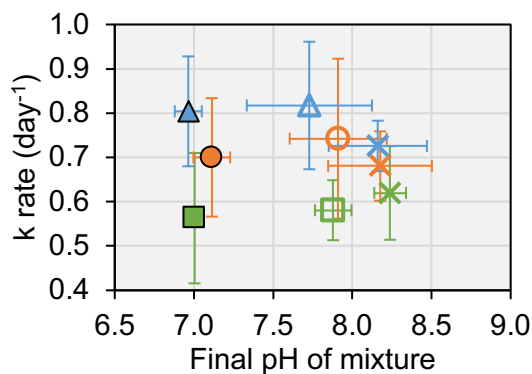


Figure 4: Average k rates and pH of raw WW (X) and WW mixed with 10% (○) and 40% (●) MD from three sites: Fe+Al MD (■), Fe MD (●), and Al MD (▲). Error bars represent one standard deviation ($n=3$ per MD site).

An additional benefit was observed in the 40% Fe+Al MD mixtures which consistently produced an

ultimate BOD that was 35-45% lower than the 40% DI controls (**Figure S1.A**). This reduced ultimate BOD was attributed to *sweep coagulation* – at pH 6.0-9.0 and 0.01 – 1.0 mM Fe and Al concentrations, the metal precipitates tend to adsorb colloids that become enmeshed in the resulting solid (Viessman Jr, Hammer, Perez, & Chadik, 2009; Johnson & Amirtharajah, 1983). As these solids settle from solution, they adsorb organic material from the water column that will settle with the precipitates (i.e., sweep), thereby decreasing solution BOD. Interestingly, this did not occur in the 40% Fe MD samples ($[\text{Fe}] = 0.46 \pm 0.07$ mM), even though the total amount of $[\text{Fe}] + [\text{Al}]$ was greater than the Fe+Al MD samples ($[\text{Fe}] + [\text{Al}] = 0.29 \pm 0.04$ mM) and fell within the region where sweep coagulation is expected to occur (**Figure S1.B**). To further investigate this phenomenon, an additional experiment was conducted where stock solutions containing only Fe, only Al, and both Fe and Al were mixed with WW and COD was measured before and after mixing and settling for 2 h. At concentrations ≥ 0.5 mM $[\text{Fe}] + [\text{Al}]$, all mixtures had a decreased COD, and % COD removal increased with increasing metals concentrations up to 30-40% at $[\text{Fe}] + [\text{Al}] = 1.0$ mM. However, consistent with the original cotreatment experiments, the solution containing Fe and Al removed 10-15% more COD than the Fe- and Al-only solutions at a concentration of 0.5 mM $[\text{Fe}] + [\text{Al}]$ (**Figure S1.C**). Overall, this result indicated that metal oxyhydroxides formed in the primary clarifier can remove organic material through sweep coagulation, thus markedly decreasing the oxygen demand entering the activated sludge process.

Environmental, social, and economic implications

Co-treating MD and WW could improve BOD and PO_4 removal in the primary clarifier of WWTPs, providing incentives for co-treatment. Advanced biological nutrient removal for PO_4 removal requires the WW to be cycled through various treatment stages and increases the complexity and operational costs of WWTPs. Additionally, aeration required for the activated sludge process typically accounts for >50% of the total energy costs of a WWTP (Metcalf & Eddy, 2014). Thus, removing PO_4 and BOD in the primary clarifier could decrease the aeration demand and therefore cost and energy requirements. It should be noted that if an MD is dominated by ferrous Fe, it will exhibit an oxygen demand for oxidation to ferric Fe, which could require additional aeration and should be considered when cotreatment is an option. Additionally, Fe and Al from MD will increase the sludge production rate, but it could also improve sludge dewatering, which could have potential economic benefits or drawbacks (Spellman Jr, Tasker, Goodwill, & Strosnider, 2020). Sludge collected from WW treatment facilities is often composted with lime and used as biosolids for land application (Wong & Fang, 2000). Further investigations concerning the impacts of varying MD chemistries on the characteristics of WW sludge should be conducted to determine if sludge handling procedures would alter, which could also have environmental and economic implications (e.g., cost of landfilling sludge vs. profit from selling biosolids) (Spellman Jr, Tasker, Goodwill, & Strosnider, 2020). The trade-off between decreased aeration needs and increased sludge production should be investigated to determine the potential economic benefits of adding MD to WW treatment facilities. In addition, the results presented here suggest that cotreatment of MD in existing WWTPs is feasible at full-scale, assuming appropriate mixing ratios. The potential cost savings from the elimination of constructing and maintaining standalone MD treatment systems could be substantial in the many regions with persistent MD issues. Government agencies responsible for the funding of MD treatment systems should consider these potential cost savings and be able to compensate WWTPs treating MD with savings from building and maintaining stand-alone MD treatment facilities. These savings could alleviate the increasing costs ratepayers are experiencing within shrinking mining economies.

Continuous SBR Treatment Performance

General SBR Treatment Performance

Figure 5 presents the general treatment efficiency (e.g., percent of pollutant removed) under each test condition for major pollutants. The treatment system similarly removed both BOD and DOC at >96% under all conditions. COD was generally removed at >85% with little influence from co-treatment, which

is in agreement with existing literature (Spellman Jr, Tasker, Strosnider, & Goodwill, 2020). The COD removals in this study are also similar to the COD removal rates (87-90%) seen with Cu-mine drainage co-treatment (Hughes & Gray, Co-treatment of acid mine drainage with municipal wastewater: performance evaluation, 2013). While BOD, COD, and DOC were relatively unimpacted by co-treatment, several key treatment parameters, including nutrients, were. Baseline operation removed only 29% of reactive $\text{PO}_4\text{-P}$ influx, while co-treatment with weak AMD more than doubled PO_4 removal to 69%. Strong AMD co-treatment further increased PO_4 removal to 93%, with over half of samples below or approaching the method limit of detection (0.1 mg-P/L). However, co-treatment conversely impacted nitrogen removal. While the treatment system removed 60% of total dissolved nitrogen (TDN) under normal operating conditions, removal decreased to 48% and 51% in the weak and strong conditions, respectively. The most notable change in effluent quality during co-treatment was $\text{NH}_3\text{-N}$ removal. NH_3 was consistently removed below detection (<1 mg/L) in both the baseline and weak AMD co-treatment scenarios, but removal dropped to only 18% under strong AMD co-treatment conditions. Further discussion of effluent nutrients, including likely mechanisms and implications, are provided later in this document.

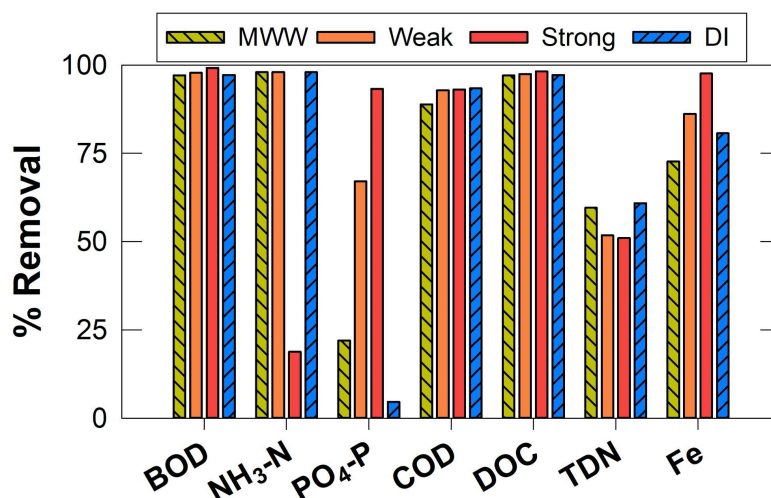


Figure 5: Average removal of select pollutants by treatment system with no co-treatment (MWW), weak AMD co-treatment, strong AMD co-treatment, and DI dilution control. Removals relate average effluent concentrations to influent mixed concentrations and accounted for dilution effects.

All public WWTPs in the United States must, at minimum, meet effluent criteria given in the Secondary Treatment Standards (40-CFR-133), which sets monthly average limits of pH (6-8), BOD (<30 mg/L), and TSS (<30 mg/L). Average effluent quality during all experimental conditions met 40-CFR-133 treatment standards, with BOD values < 5 mg/L (Figure 6A), TSS < 20 mg/L (Figure 6B), and pH averaging between 6.5-7.5 (Figure 6C). Although BOD was relatively low under all conditions (Metcalf & Eddy, et al., 2013), BOD during weak AMD co-treatment was slightly lower, but statistically similar ($p = 0.05$), to that of the baseline treatment. BOD values trended downward with increasing AMD strength, with strong AMD co-treatment averaging only 0.8 mg/L BOD, significantly less ($p = 0.05$) than MWW effluent BOD. The demonstrated minimal impacts on BOD removal are comparable to those found when co-treating a circumneutral (pH = 6.1) mine drainage (Spellman Jr, Tasker, Strosnider, & Goodwill, 2020). The noted decrease in BOD with strong AMD is likely due to either adsorption of biomaterial onto metals or microbial-mediated bioflocculation of organics (Choo & Kang, 2003; Spellman Jr, Tasker, Strosnider, & Goodwill, 2020).

TSS trends were similar to BOD, being below the targeted regulatory limit during all conditions while trending downward with increased AMD strength (Figure 6B). Although the average effluent TSS was not statistically different between the two AMD strengths, co-treatment did significantly ($p = 0.05$)

decrease effluent TSS. MWW samples averaged 18 mg/L while weak and strong AMD co-treatment averaged 10 and 9 mg/L, respectively, suggesting co-treatment likely improves suspended solids removal. Improved TSS removal and sludge settling is likely a result of enhanced particle aggregation caused by the hydrolysis of Fe and Al in the reactors during co-treatment (Figure S3). Elevated Fe from AMD under both conditions would have encouraged particle aggregation by sweep flocculation (see Figure S3A) as described by Johnson and Amirtharajah, 1983 and previously suggested for co-treatment scenarios by Spellman et al., (2020). Aggregation mechanisms varied for Al more than Fe, where strong AMD co-treatment Al would have also encouraged sweep flocculation while aggregation during weak AMD co-treatment was most likely a combination of both sweep flocculation and particle destabilization mechanisms (see Figure S3B). TSS results are in parallel with sludge settling results (Figure S2), which showed slightly improved settling (i.e., lower sludge blanket height) during co-treatment.

Although co-treatment did decrease system pH, it was not detrimental to effluent quality. Effluent pH averaged 7.10 during baseline treatment and subsequently decreased with weak and strong AMD co-treatment to 6.97 and 6.53, respectively (Figure 3C). Even with the elevated acidity loading during strong AMD co-treatment, the alkaline reactors consistently neutralized most acidity with 60% of all pH measurements exceeding 6.50 and only two measurements below 6.00 during the 42 days of monitoring (pH 5.9 on days 3 and 4). Prior studies similarly demonstrated that effluent pH can be maintained above 6.0 while co-treating relatively strong AMD, even at high mixing ratios (Hughes & Gray, Co-treatment of acid mine drainage with municipal wastewater: performance evaluation, 2013). Effluent alkalinity also remained sufficient during co-treatment, averaging 80 mg/L as CaCO₃ for both conditions, down from baseline MWW effluent alkalinity of 109 mg/L as CaCO₃. Although pH and alkalinity did not drop into ranges that would compromise MWW treatment in this study, facilities implementing co-treatment should examine the need for alkaline dosing capabilities onsite (e.g., caustic soda, lime, etc.). However, pH considerations will likely not be operationally prohibitive, as pH adjustment is relatively commonplace in many WWTPs for various processes including sludge stabilization, biological nutrient removal, coagulation, and odor management (Metcalf & Eddy, 2014).

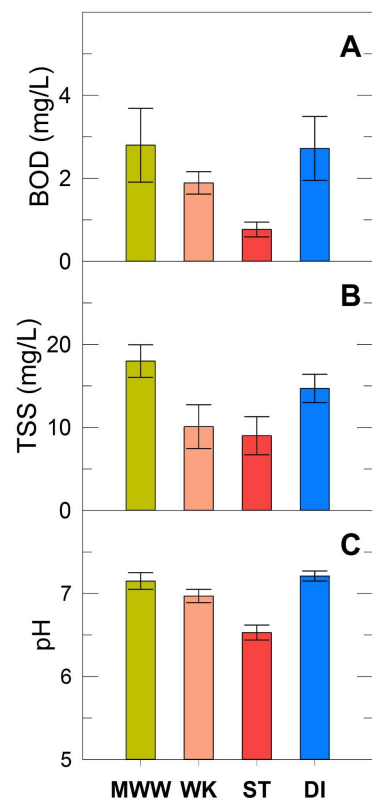


Figure 6: Average effluent values for the three characteristics regulated by the U.S. Secondary Treatment

Regulation (40-CFR-133). Regulations require that the 30-day average effluent value must not exceed 30 mg/L for BOD (A) or TSS (B), and pH (C) must be maintained between 6 and 9. Error bars represent the 95% confidence interval for each treatment condition.

Pathogen removal is a key consideration in MWW treatment for protection of public health. Figure 7 shows the average count of indicator fecal coliform bacteria in non-chlorinated reactor effluents. Baseline operating effluents averaged 4,390 CFU/mL, not atypical for unchlorinated MWW effluents and very similar to the average noted in the DI-dilution co-treatment effluent (4,350 CFU/mL). However, the concentration of indicator bacteria drastically decreased with increased AMD strength. Average weak AMD co-treatment indicator bacteria concentrations were 2,000 CFU/mL, half of the baseline condition counts. The average counts further decreased with strong AMD co-treatment to only 200 CFU/mL, an order of magnitude decrease from baseline MWW treatment. Untreated AMD is known to decrease indicator bacteria concentrations when discharged into receiving waters (Keating, Clements, Ostrowski, & Hanlon, 1996; Kruse, Reber, & Imhoff, 2019), with similar effects seen in the controlled treatment environment of this study. The decrease in indicator bacteria is likely due to chemical inactivation of bacteria by acidity and metals (Keating, Clements, Ostrowski, & Hanlon, 1996), as well as physical removal by Fe- and Al-driven coagulation (Edzwald & Tobiason, 1999). Potential impacts of these mechanisms on beneficial treatment microorganisms are discussed in Section 3.3. The reduced pathogen loading in secondary effluents from co-treatment could decrease WWTP overall chemical and energy demands for disinfection compared to conventional operation. Furthermore, removal of pathogens and AMD by co-treatment may have impacts beyond operations and the environment, potentially facilitating community-level socioeconomic impacts. For example, co-treatment may help reclaim surface waters degraded by AMD acidity and MWW pathogens that otherwise limit recreational opportunities (Mishra, Hitzhusen, & Guldmann, 2012; Dorevitch, Pratap, & Scheff, 2012), which have been an engine for socioeconomic rebound in historic mining regions (Gottfried, 1976; Maples & Bradley, 2021).

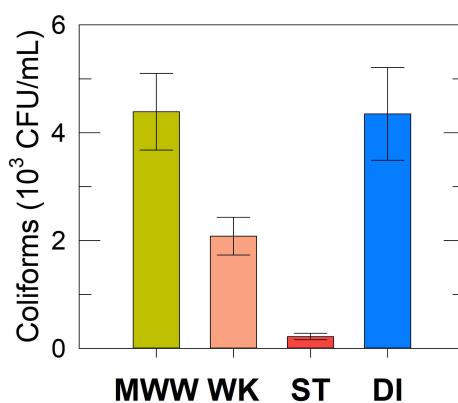


Figure 7: Fecal coliform colony forming units (CFU) in non-chlorinated effluent samples with 95% confidence interval error bars

Nutrients and metals

Removing excess nutrients is paramount for WWTP's regardless of receiving water. Nutrient-induced eutrophication is common in many US watersheds that are also impacted by mining (e.g., Upper Colorado River, Chesapeake Bay, etc.) (Kemp et al., 2005; Carlson and Carlson, 1982). Concentrations of inorganic nitrogen (NO_3 , NO_2 , and NH_3) and reactive PO_4 in SBR effluents are presented in Figure 8. Average effluent total inorganic nitrogen concentrations (Figure 8A) were similar under all conditions. Baseline effluent averaged 11.7 mg-N/L while weak and strong AMD co-treatment averaged 10.2 and 12.6 mg-N/L, respectively, neither being statistically different from the baseline ($p = 0.05$). Baseline operation generally achieved complete nitrification with 92% of effluent nitrogen being NO_3 and <1% of effluent nitrogen as NO_2 . During weak AMD co-treatment, nitrification was slightly impeded with only

81% of effluent nitrogen as NO_3 and 10% as NO_2 . Complete denitrification to N_2 was not necessarily anticipated as the SBR biological treatment phase was, for operational simplicity, exclusively aerobic while denitrification is generally favorable under anoxic conditions (Cooper et al., 1992). While NH_3 accounted for < 9% during both MWW and weak AMD co-treatment conditions, nitrification was inhibited by strong AMD co-treatment where NH_3 accounted for 83% of effluent nitrogen. Elevated NH_3 concentrations in effluents could pose serious toxicity to aquatic organisms (Fan et al., 2021; Thurston et al., 1984), with chronic toxicity occurring at just 1.9 mg-N/L (EPA, 2013), and must be addressed for successful co-treatment.

The loss of nitrification efficiency is likely a negative consequence of AMD acidity as nitrification kinetics are heavily influenced by pH (Shammas, 1986). The optimal pH for maximum biological NH_3 oxidation is believed to be between pH 8.0-9.3 (Shammas, 1986), with biological oxidation rate decreasing exponentially with decreasing pH. Limited oxidation is observed between pH 6.3 and 6.7 and no NH_3 oxidation below pH 5.5 (Painter, 1970). The impact of decreased pH on reaction kinetics may explain the insufficient NH_3 removal seen in the strong AMD co-treatment trial (effluent pH 6.53). Furthermore, the biological oxidation of NO_2 to NO_3 during nitrification is also inhibited by low pH, likely to a greater extent than NH_3 oxidation, with optimal oxidation rate at pH ~8.5 and < 50% of maximum oxidation at pH 7.0 (Wild et al., 1971). This may explain the slight decrease in nitrification observed in weak AMD co-treatment where acidity from the weak AMD did not inhibit the oxidation of NH_3 but did inhibit the subsequent oxidation of NO_2 . As previously discussed, co-treatment WWTPs may also need to implement pH adjustment systems in order to optimize the biological treatment process and meet effluent objectives.

Removing PO_4 is of similar importance, as WWTPs in regions where co-treatment may be feasible (i.e., mining regions) generally discharge into freshwater receiving bodies which are often phosphorus-limited (Spellman et al., 2022; Dodds and Smith, 2016). Average effluent reactive PO_4 -P concentrations are shown in Figure 8B. Baseline MWW operation produced effluents exceeding 3.1 mg-P/L, < 30% removal of influent P (i.e., Figure 8). Converse to the nitrogen observations, co-treatment positively influenced PO_4 removal. Effluent concentration dropped to 1.1 mg-P/L with weak AMD co-treatment and < 0.3 mg-P/L during strong AMD co-treatment. The primary mechanisms for PO_4 removal during co-treatment are hypothesized to be PO_4 adsorption onto hydrolyzed Fe (Spellman et al., 2020; Wei et al., 2008) and co-precipitation with Al (Spellman et al., 2022). These results suggest co-treatment is an efficient tertiary treatment technology for the removal of PO_4 , as previously suggested in co-treatment studies (Spellman et al., 2020; Wei et al., 2008; Ruihua et al., 2011). Co-treatment would decrease PO_4 loading on receiving waters which would limit P-induced eutrophication. The laboratory SBR systems decreased effluent PO_4 loading by 2.5 and 3.3 fold with weak and strong AMD co-treatment, respectively. A full-scale co-treatment WWTP (e.g., ~19,000 m^3 /day) with similar influent concentrations and operating efficiency could theoretically decrease PO_4 loading in its receiving water by as much as 55 kg/day compared to conventional MWW treatment. This would be a major reduction in nutrient pollution that is needed in many mining-region watersheds.

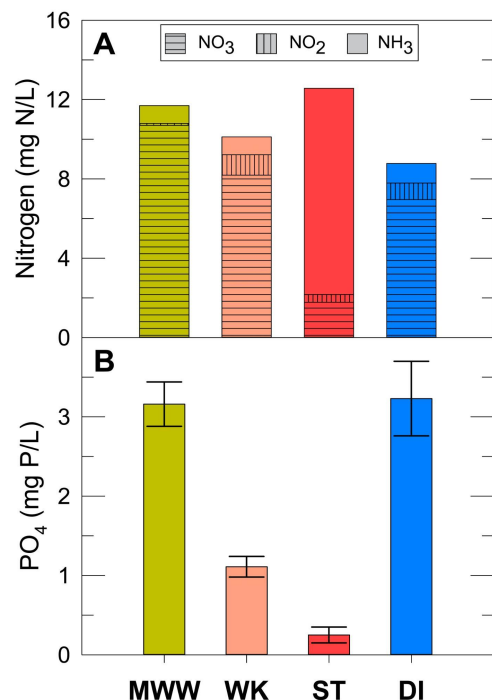


Figure 8: (A) Effluent inorganic nitrogen species NH_3 (solid), NO_3 (horizontal stripe), and NO_2 (vertical stripe) as mg-N/L and (B) average effluent orthophosphate concentration (as mg-P/L) with 95% confidence interval error bars.

Temporal changes in effluent total Fe are shown in Figure 9A. Minimal fluctuation in effluent total Fe was observed during conventional treatment, with the dotted line in Figure 9A representing the average concentration of 0.25 mg/L. Co-treatment had a varying impact on effluent Fe. Weak AMD co-treatment averaged 1.29 mg/L Fe in effluent with a maximum of 1.93 mg/L, generally trending upward (linear $R^2 = 0.69$) at a rate of approximately $0.05 \text{ mgL}^{-1}\text{day}^{-1}$. Effluent Fe concentrations during strong AMD co-treatment were more viable, averaging 0.98 mg/L Fe and reaching a 1.49 mg/L maximum with no apparent linear or logarithmic trend ($R^2 < 0.05$).

Effluent average metals concentrations are presented in Figure 9B. By mass, Fe was the most abundant metal amongst measured constituents, with average concentrations more than double that of Al and an order of magnitude higher than Mn. In general, the majority of measured metals (>85%) were defined as particulate (> $0.45\mu\text{m}$). Both weak and strong co-treatment significantly ($p < 0.05$) increased average effluent Fe from baseline treatment conditions (0.28 mg/L). Weak AMD co-treatment effluent averaged slightly more Fe than strong AMD co-treatment (1.29 and 0.98 mg/L, respectively), effluent Fe concentrations were not significantly different between co-treatment trials ($p > 0.05$). Similar to Fe results, both co-treatment trials significantly ($p < 0.05$) increased effluent Al concentration over MWW baseline effluent which averaged only 0.10 mg/L Al. Both co-treatment scenarios produced similar ($p > 0.05$) effluent Al concentrations of 0.38 and 0.44 for weak and strong AMD co-treatment, respectively. While Fe and Al notably increased during co-treatment, all effluent Mn concentration were $< 0.20 \text{ mg/L}$ and did not vary significantly across all trials, including during both co-treatment scenarios.

The metals results observed in both experimental conditions holds key implications for co-treatment feasibility. Although strong AMD introduced nearly an order of magnitude more Fe than weak AMD co-treatment, strong effluent produced Fe concentrations generally lower than weak AMD co-treatment with no statistical difference between effluent concentrations. Major temporal increases in effluent Fe concentrations were also generally not observed. However, relatively minor increases in effluent Fe could still become problematic for WWTPs depending on discharge permits, as Fe can be chronically toxic to aquatic organisms at $>1.0 \text{ mg/L}$ (U.S. Environmental Protection Agency, 1986).

Effective Fe removal generally relies on hydrolysis, where particulate oxyhydroxides can be removed via sedimentation. In the case of weak AMD co-treatment, the majority (85%) of Fe was Fe(II) (Watzlaf et al., 2004) prior to contacting MWW. During co-treatment, Fe(II) likely precipitates as oxyhydroxides through two mechanisms, either (i) direct Fe(II) hydrolysis (Wells and Salam, 1965) or (ii) oxidation to Fe(III) followed by hydrolysis of Fe(III) (Watzlaf et al., 2004). It has been noted that FeOOH precipitates formed by direct Fe(II) hydrolysis in the presence of elevated organic matter are less crystalline and have less active surface area with higher electrostatic repulsion than those from Fe(III) hydrolysis (Li et al., 2020). This suggests that hydroxides formed during weak AMD co-treatment may have been weakly-bound to sludge floc and more likely to resuspend during aeration and mixing, leading to slow increases in effluent Fe concentrations. Conversely, strong AMD co-treatment would have directly added Fe(III) to the reactors (>5% Fe(II) in strong AMD), which could have immediately undergone hydrolysis and formed stronger flocs with sludge. The Fe(II) oxidation-hydrolysis mechanism is likely less favorable in co-treatment than direct hydrolysis. The oxidation of Fe(II) is the rate-limiting step (Singer and Stumm, 1970) which proceeds by both chemical oxygenation and microbially-mediated oxidation, and the contributions of these reactions vary depending on reactor pH and nature of the microbial community (Kirby et al., 1999). Although the O₂ oxygenation of Fe(II) to Fe(III) is fast ($k = 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$, Stumm and Lee, 1961), the microbial community actively competes for O₂ at uptake rates as fast as 30-40 mg-O₂ L⁻¹hr⁻¹ (Young, 1999; Suescun et al., 1998) which would inhibit the rate of direct Fe(II) oxygenation to Fe(III).

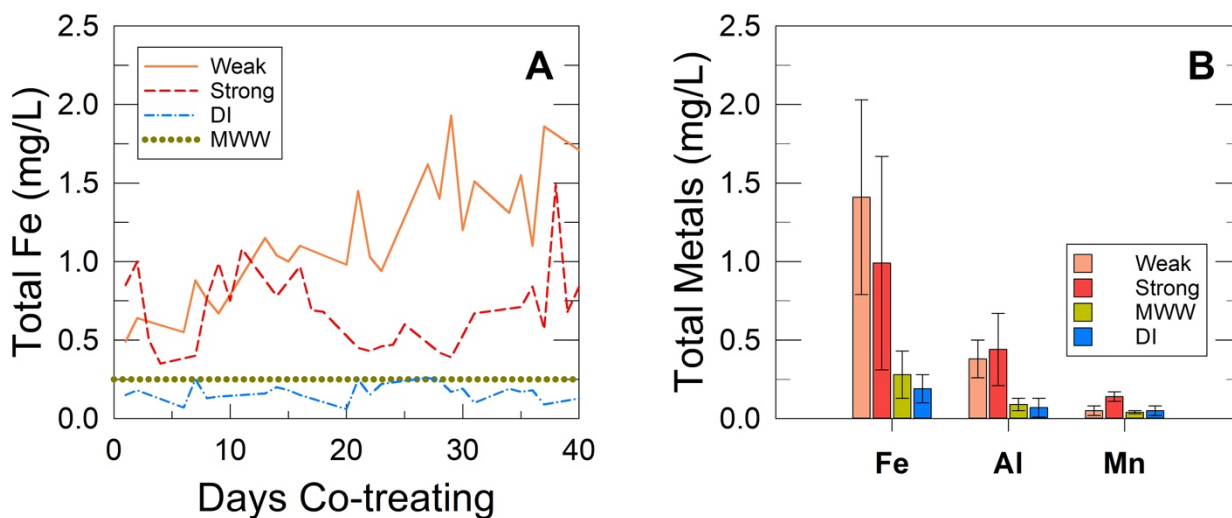


Figure 9: (A) Trend of effluent total Fe for 40 days of co-treating. Horizontal dotted line indicated average effluent total Fe for the baseline MWW condition. (B) 30-day average Total Fe, Al, and Mn concentrations in effluent with 95% confidence interval error bars.

Impacts to Sludge

Figure 10A and B present the total concentration and volatile fraction of dry sludge solids produced under all conditions. The total concentration of solids (i.e., absent of water) in sludge and its volatility play key roles in how sludge is processed (Metcalf & Eddy, 2014). Weak and strong AMD co-treatment both increased the total solids from 12.3 g/L at baseline to 17.3 and 15.5 g/L, respectively. While the increases during both co-treatment scenarios relative to the MWW baseline were significant ($p < 0.05$), the solids concentration between weak and strong AMD co-treatment were statistically similar ($p > 0.05$). The increase in concentrations were accompanied by an increase in sludge solids percent (w/w) from 1.01% at baseline to 1.65% and 1.63% for weak and strong AMD co-treatment, respectively. These experimental findings agree with prior work which theoretically hypothesized co-treatment sludge would have a lower bound water content (i.e., increased solids) (Spellman Jr, Tasker, Goodwill, & Strosnider,

2020). The dry solids content (%) from all three scenarios was within the range typically seen in conventional activated sludge facilities (Water Environment Federation, 2010; Metcalf & Eddy, et al., 2013). While elevated solids % generally indicates a lower energy input required for sufficient dewatering (Katsiris & Kouzeli-Katsiri, 1987), the subsequent increase in total dewatered solids could complicate certain disposal considerations (i.e., landfilling) due to the significant increase in dry solids mass. Co-treatment resulted in more pronounced changes to volatility of dry sludge. Baseline treatment produced sludge that was primarily (~85%) volatile while co-treatment substantially decreased solids volatility to 77% and 63% with weak and strong AMD, respectively. The decrease in volatility is due to the metals (Figure 10C) which remain in sludge after ignition (APHA, 2012).

Both co-treatment trials had notable impacts on settled sludge metals content. Sludge Fe increased from 28 mg/L under baseline operation to 142 mg/L and 233 mg/L after weak and strong AMD co-treatment, respectively (Figure 10C). This represents a 5x increase after weak AMD co-treatment and nearly an order of magnitude increase after strong AMD co-treatment. While final sludge Fe concentrations were significantly elevated from baseline, on a dry-weight basis neither weak or strong AMD co-treatment (8,200 and 13,700 mg/kg, respectively) increased Fe outside the range of 1,575-299,000 mg/kg reported for typical wasted activated sludge (EPA, 2009). The accumulation rate of Fe in sludge varied in each co-treatment phase (Figure 10C). During weak AMD co-treatment, Fe accumulation was 4.8 mgL⁻¹day⁻¹ for the first 15 days but then decreased to 2.9 mgL⁻¹day⁻¹. While the two-step accumulation rate during weak AMD co-treatment can be noted, the accumulation rate can be averaged to 3.9 mgL⁻¹day⁻¹ with strong spatial linearity ($R^2 = 0.98$) throughout the entirety of Phase I. Fe accumulation during Strong AMD co-treatment, however, was less linear ($R^2 = 0.90$) and appeared to follow a more logarithmic accumulation. Fe accumulated over the first 15 days at 11.2 mgL⁻¹day⁻¹ but then slowing by more than half to 5.3 mgL⁻¹day⁻¹ for the next 8 days. Notably, there was no additional accumulation over the final period of Phase II. The leveling-out noted in sludge Fe may indicate an equilibrium of sludge Fe, which may have . The Al content in sludge showed similar increases and accumulation, with sludge containing 14 mg/L and 95 mg/L of Al after weak and strong AMD co-treatment, respectively (Figure S4). Mn did not show substantial temporal accumulation in sludge and varied < 0.5 mg/L during all phases. While Fe and Al content in sludge did increase, neither metal is regulated as a contaminant under U.S. biosolids laws (i.e., US Code of Federal Regulations Title 40, Part 503) and may have numerous benefits, such as improvements to dewaterability, as previously summarized in Spellman et al. (2020b) Table 1. However, if significant metals accumulation is of concern, these concerns could be mitigated operationally by either (i) decreasing the co-treatment mixing ratio to subsequently decrease the metals loading to the system and/or (ii) increasing the sludge wasting rate to remove more total solids and slow metals accumulation.

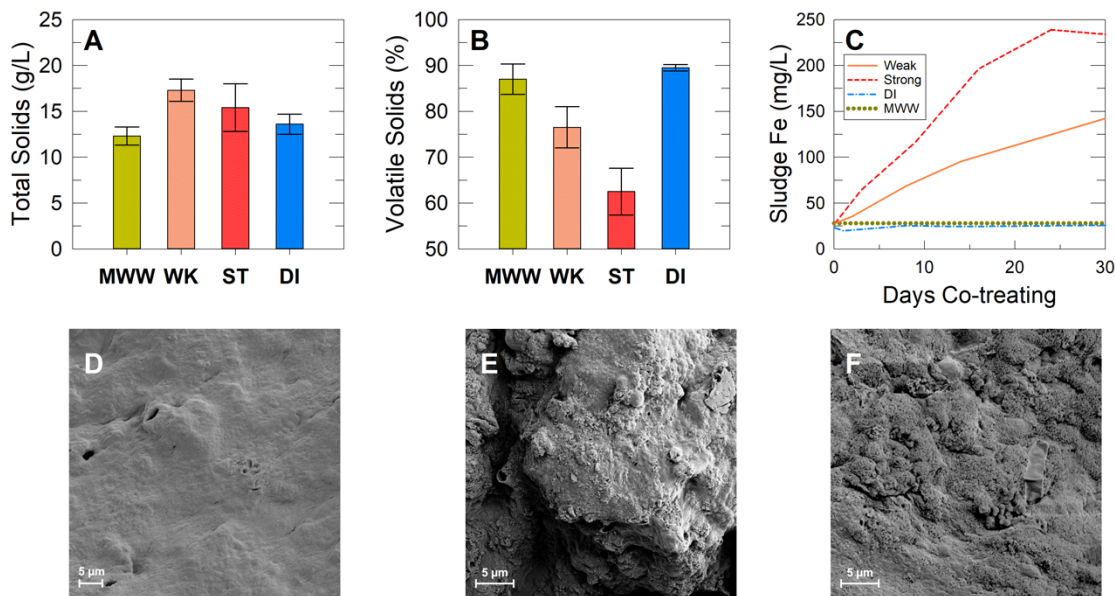


Figure 10: Characteristics of settled sludge including (A) total dry solids, (B) percent volatile solids, and (C) bound Fe content. SEM micrographs of dry sludge from MWW (D), Weak (E), and Strong (F) conditions.

The sludge solids results present several operational implications for co-treatment sludge processing. Facilities that use gravity thickening (separate from main process clarifiers) could see some improvements in resultant sludge solids due to increased density and larger sludge flocs formed by aforementioned metal-driven coagulation mechanisms. This implies co-treatment sludges would likely require decreased chemical input (e.g., polymer) to achieve desired thickening. WWTPs that use sludge digestion for reduction of volatile solids might also expect improvement as it would seem having fewer volatile solids entering the digester could increase overall efficiency. However, Gossett et al. (1978) demonstrated that addition of Al and Fe (from aluminum sulfate and ferric chloride) negatively impacted digester efficiency, specifically significant decreases in biogas production and volatile solids reduction, which is attributed to a loss of sludge biodegradability from metals. Facilities using “advanced thermal oxidation” (i.e., incineration) would likely see an increase in ash production which would need subsequent storage/disposal. However, as highlighted by Spellman et al. (2020b), the ash theoretically may have a significant amount of extractable P which could lead to potential beneficial uses (e.g., agricultural land application).

Resultant sludge morphology was examined by collecting SEM micrographs of dry sludge at each condition, which are also presented in Figure 10. Micrographs of baseline MWW sludge (Figure 10D) showed surfaces to be smooth and relatively featureless. These observations appear similar to discussion of MWW sludge micrographs in other, unrelated studies (Mahon, O’Connell, Healy, & Morrison, 2017). Co-treatment did result in visual morphological changes to sludge (Figure 10E & F). Micrographs from both co-treatment conditions appeared more textured and geometric compared to the MWW baseline sludge. The texture of both co-treatment sludges appear similar to micrographs of sludges treated with alum and/or ferric chloride (Rashed, El Daim El Taher, & Fadlalla, 2016), suggesting increased crystallinity derived from the AMD metals.

Conclusions

- Batch cotreatment of MD and WW (in the primary clarifier) removes substantial PO₄ via coprecipitation with metals or from adsorption to metal-oxides.
- The extent of PO₄ removal was related to the molar ratio of $([Fe]+[Al])/[PO_4-P]$, where >99% removal was consistently observed at $([Fe]+[Al])/[PO_4-P] > 2.0$.
- PO₄ is initially removed by adsorption to rapidly-forming metal oxides and the remaining dissolved metal is available for PO₄ mineral formation, but kinetics of metal-phosphate minerals should be investigated further.
- The rate of BOD removal was not impacted up to 40% MD addition.
- For MD containing moderate-to-high levels of Fe and Al, sweep coagulation was observed in the primary clarifier, which has the potential to reduce BOD leaving the primary clarifier by 40-50%.
- Process improvements were noted during continuous addition of MD including >90% PO₄ removal, 1.5-log inactivation of pathogens, decreased BOD & TSS, and improved sludge settling
- However, some adverse effects were observed such as Increased effluent Fe, Decreased effluent pH, and Less volatile sludge
- Continuous co-treatment at lower acidity-loadings appears feasible, especially for PO₄ limited facilities

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Table S3. Al removal from batch (primary clarifier) treatment

MD Sample	Al (mg/L)							
	raw		conservative mixture		measured		% removed from conservative mixture	
	WW	MD	10%MD	40%MD	10%MD	40%MD	10%MD	40%MD
Fe+Al 1	<0.02	12.36	1.24	4.94	0.46	1.68	63.1%	66.1%
Fe+Al 2	0.01	14.67	1.47	5.87	0.08	0.02	94.6%	99.7%
Fe+Al 3	<0.02	13.82	1.38	5.53	<0.02	<0.02	99.3%	99.8%
Fe+Al 4	0.58	17.52	2.27	7.36	0.33	0.07	85.5%	99.0%
Fe 1	<0.02	0.35	0.04	0.14	<0.02	<0.02	77.3%	93.2%
Fe 2	<0.02	0.34	0.03	0.14	<0.02	<0.02	76.7%	93.0%
Fe 3	<0.02	0.43	0.04	0.17	0.05	<0.02	3.8%	94.4%
Fe 4	0.58	0.50	0.57	0.55	0.08	0.04	86.0%	92.7%
Al 1	0.17	5.28	0.68	2.22	0.64	1.72	6.0%	22.3%
Al 2	<0.02	3.53	0.35	1.41	0.01	0.10	97.2%	92.9%
Al 3	<0.02	3.56	0.36	1.42	<0.02	0.02	97.3%	98.6%
Al 4	<0.02	3.32	0.33	1.33	0.02	0.07	94.1%	94.8%

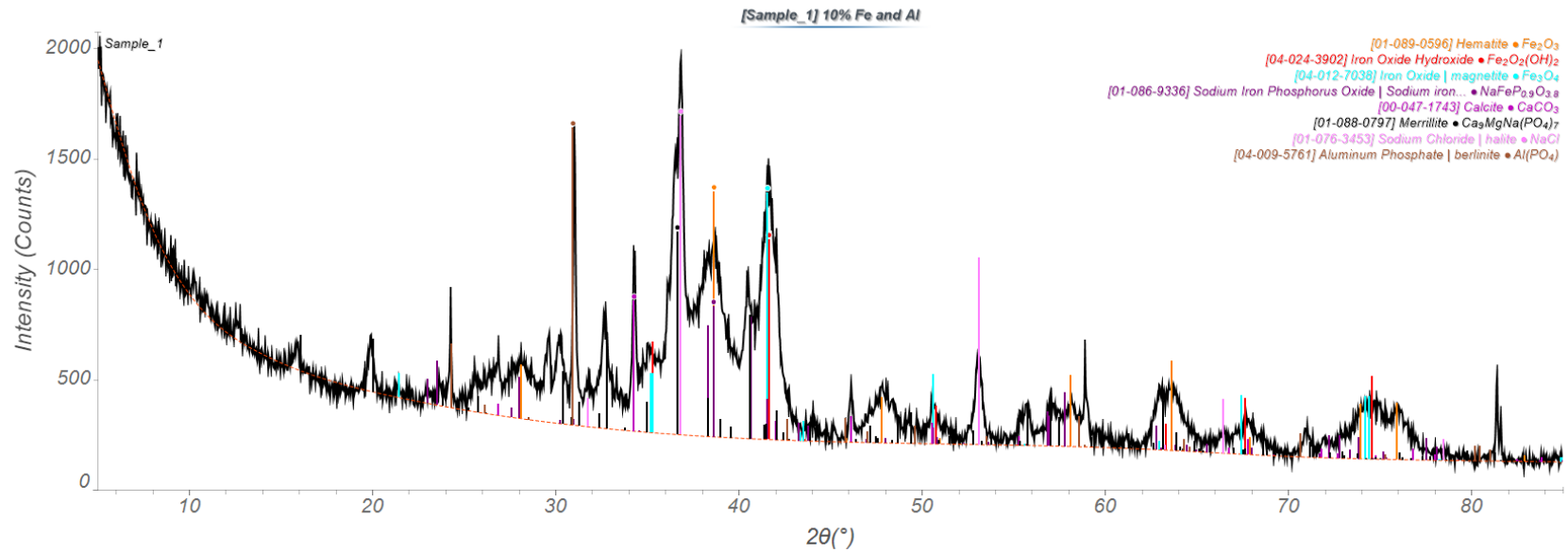


Figure S1. XRD interpretation of solids formed during cotreatment of WW and Fe+Al MD at 10% MD mixing ratio from batch (primary clarifier) treatment.

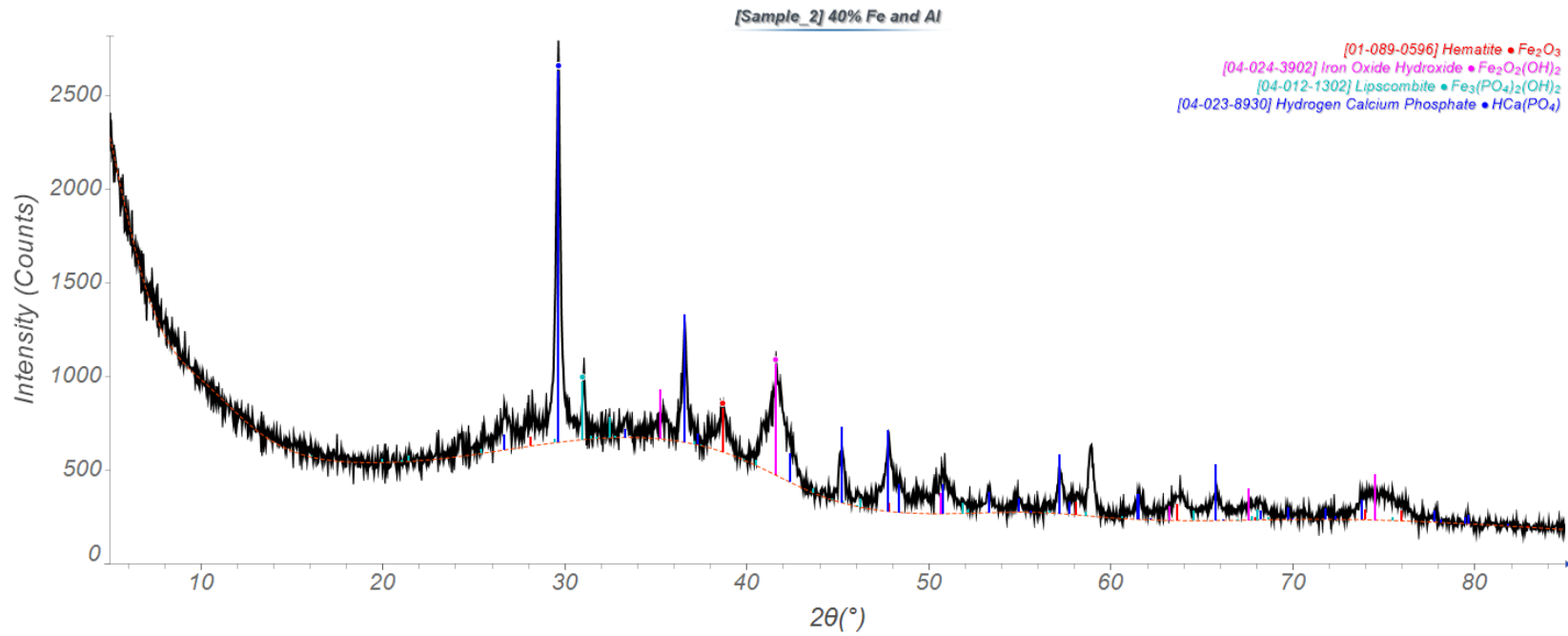


Figure S2. XRD interpretation of solids formed during cotreatment of WW and Fe+Al MD at 40% MD mixing ratio from batch (primary clarifier) treatment.

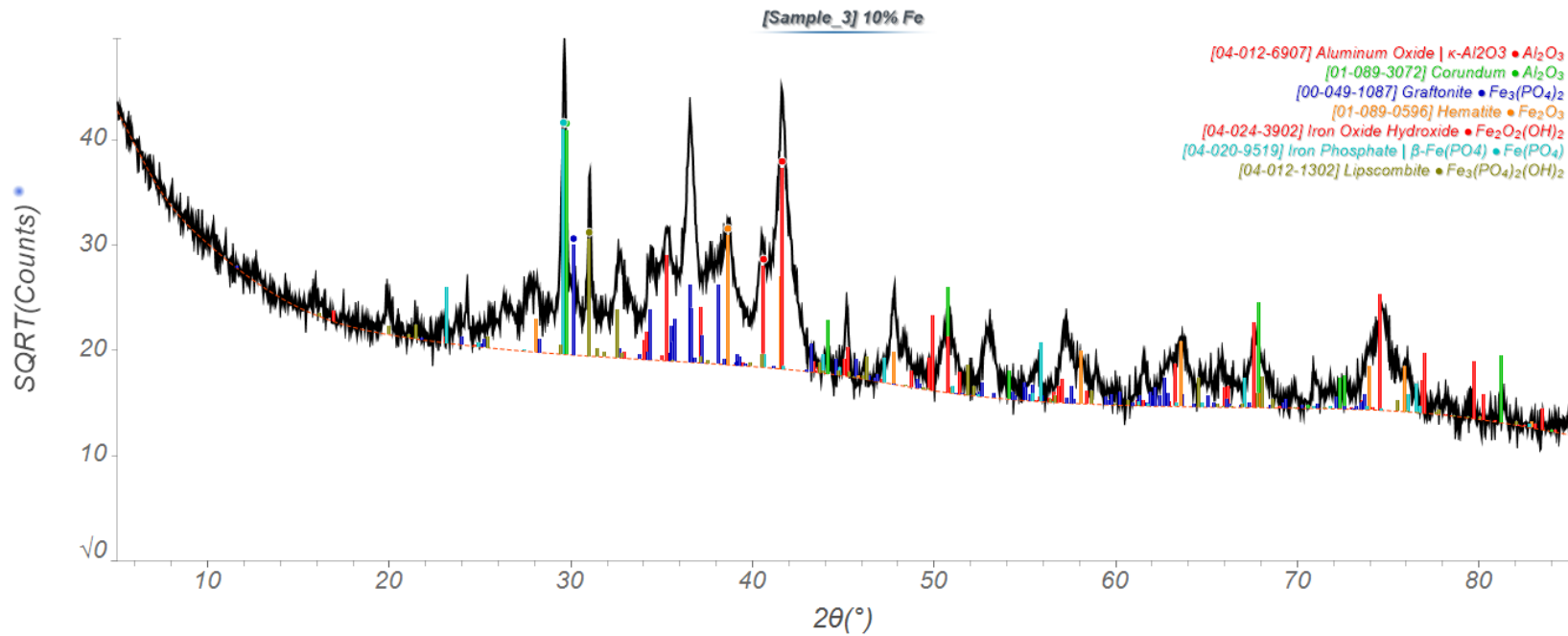


Figure S3. XRD interpretation of solids formed during cotreatment of WW and Fe MD at 10% MD mixing ratio from batch (primary clarifier) treatment.

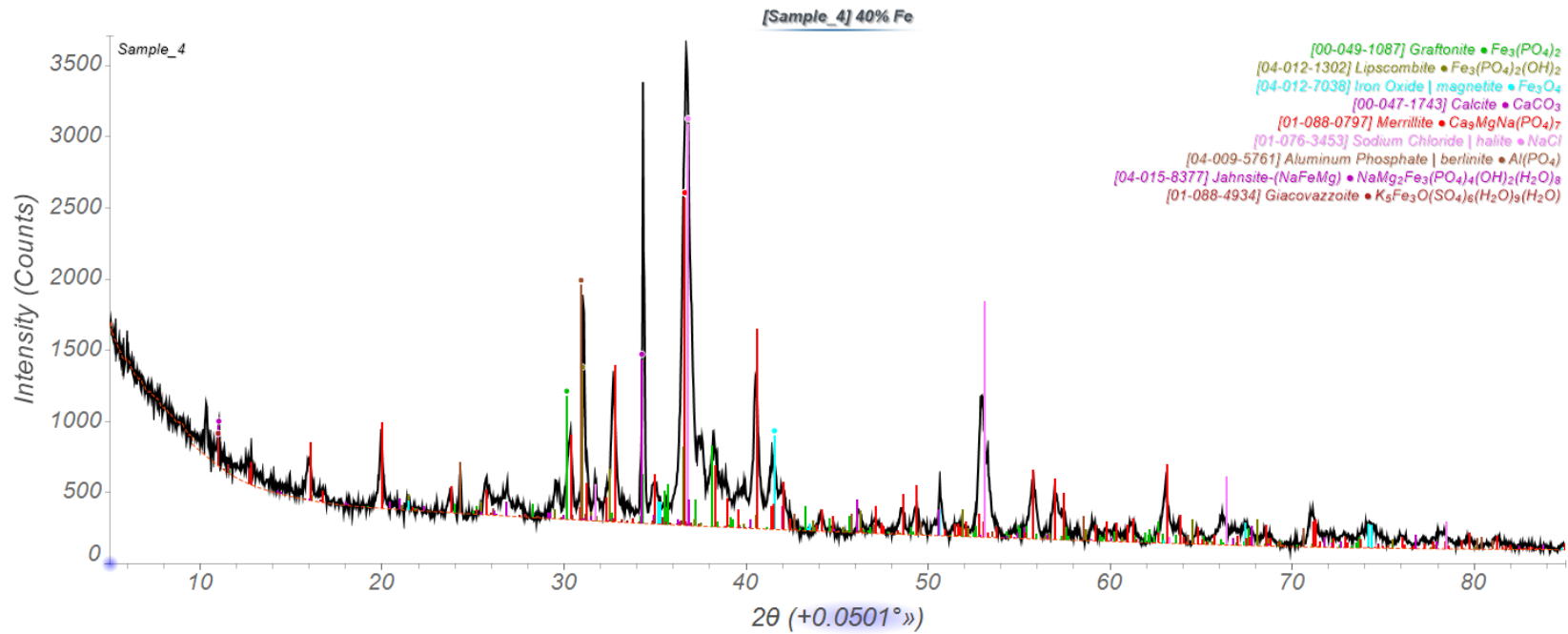
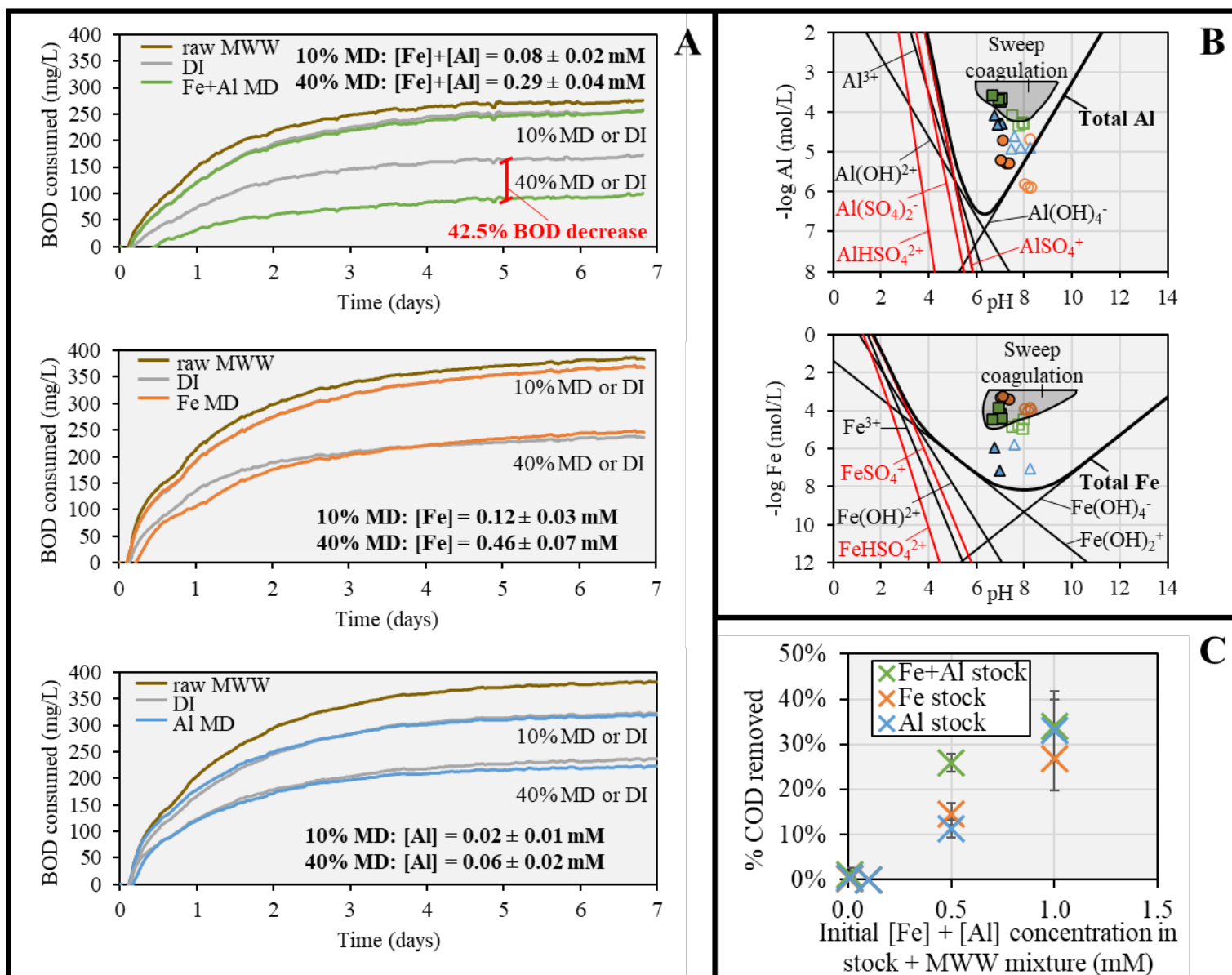


Figure S4. XRD interpretation of solids formed during cotreatment of WW and Fe MD at 40% MD mixing ratio from batch (primary clarifier) treatment.



decreased in Fe+Al MD samples by an average of 42.5%, despite the total mass of [Fe] + [Al] being lower than in the Fe MD samples. **B)** Fe and Al pC-pH diagrams for cotreatment mixtures with the region where sweep coagulation is expected to occur highlighted (adapted from Amirtharajah and Mills, 1982; equilibrium constants from Ball & Nordstrom, 1991). **C)** % COD removed from MWW mixed with stock solutions of Fe, Al, and equal parts Fe + Al.

S1. SBR Operation

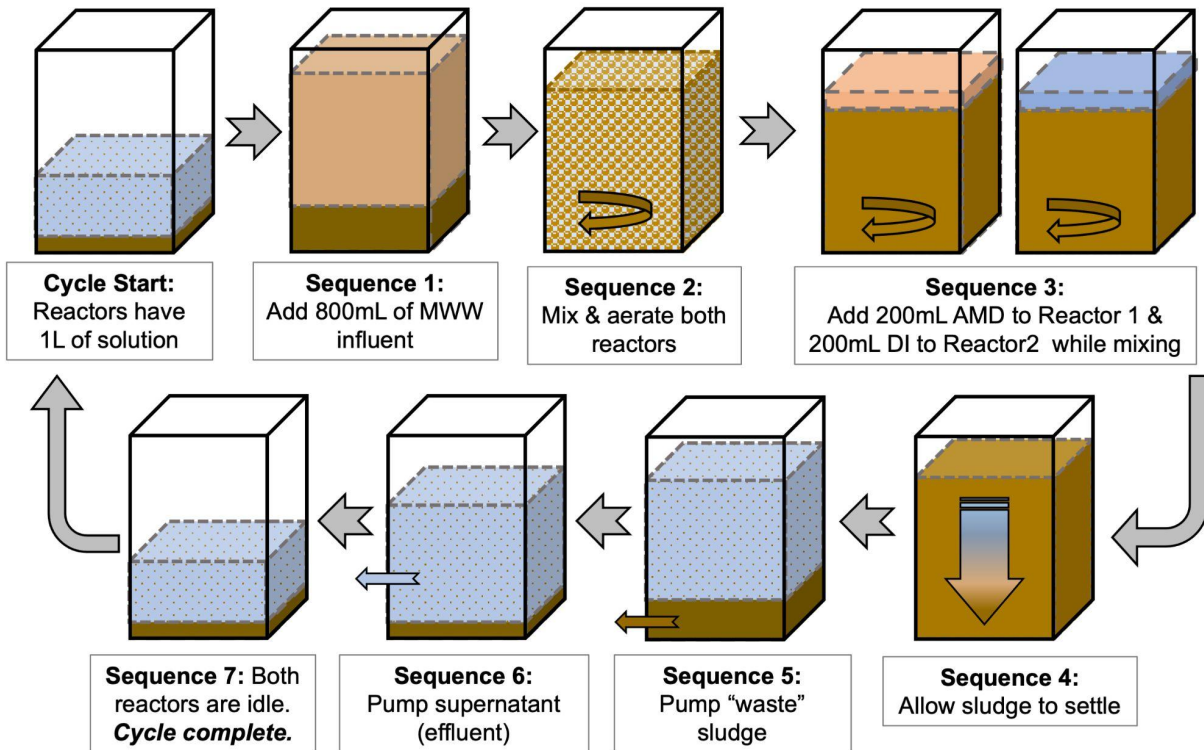


Figure S1: Sequences in each operating cycle. Sequence 3 shows conditions in only Phase I co-treatment with weak AMD and DI. Strong AMD was added to both reactors in Phase II.

S2. MWW Influent and AMD

Table S1: Average quality of synthetic MWW influent

<u>Parameter</u>	<u>Average Concentration</u>
pH	7.6
DOC	110 mg-C/L
TDN	25 mg-N/L
PO₄-P	4.5 mg-P/L
Alkalinity	180 mg/L as CaCO ₃
COD	270 mg/L
SO₄	39 mg/L
Total Fe	0.9 m/L

Table S3: Average chemistry of synthetic AMD. Calculated acidity determined by equation 2 in Watzlaf et. al 2004.

Compound	"Weak"	"Strong"
pH	4.0	2.7
mg/L Fe (II)	25.2	9.1
mg/L Fe (III)	4.3	152
mg/L Al	5.1	35
mg/L SO₄	104	725
Acidity (calc) as CaCO₃	91	720

S3. Sludge Settling

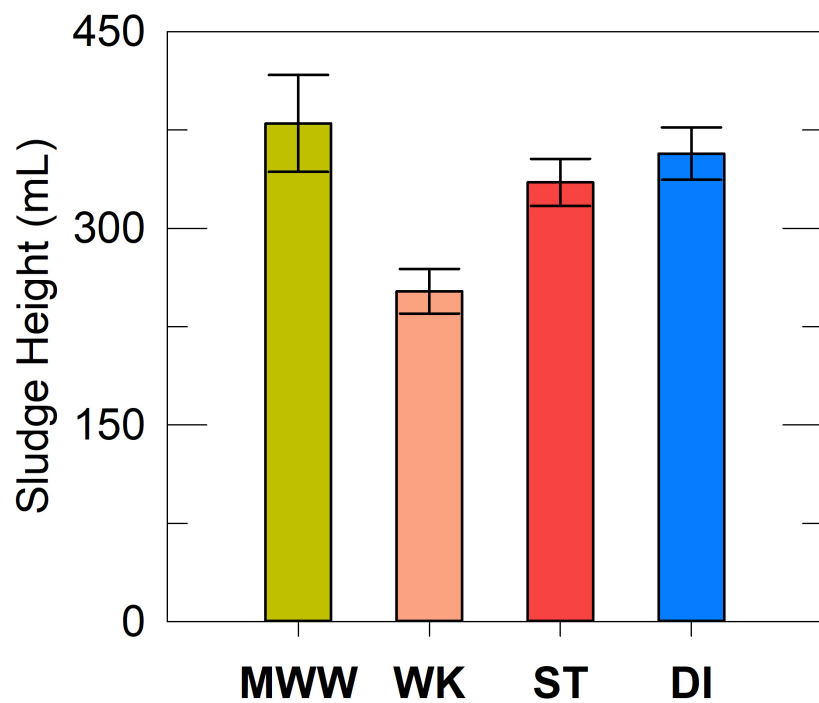


Figure S2: Average settled sludge blanket height

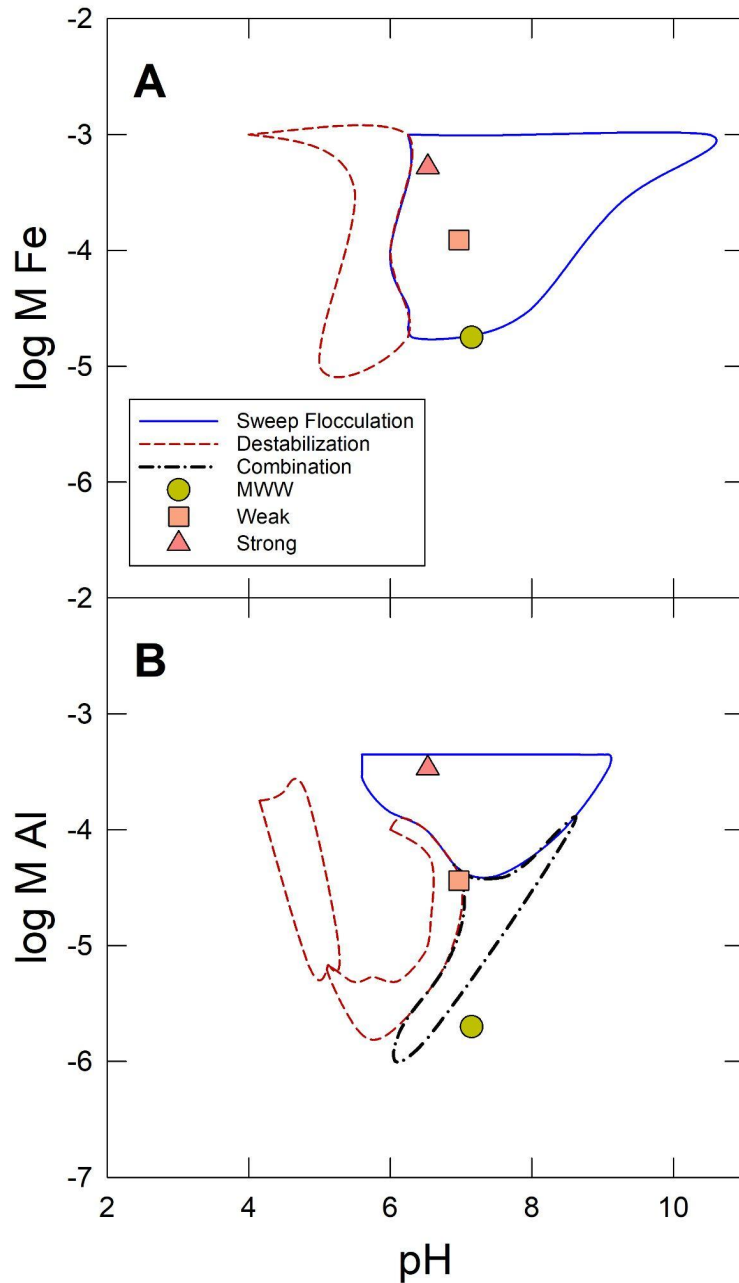


Figure S3: Likely particle aggregation mechanisms by (A) iron and (B) aluminum. Sweep flocculation and destabilization regions were approximated from those originally given in Johnson and Amirtharajah, 1983.

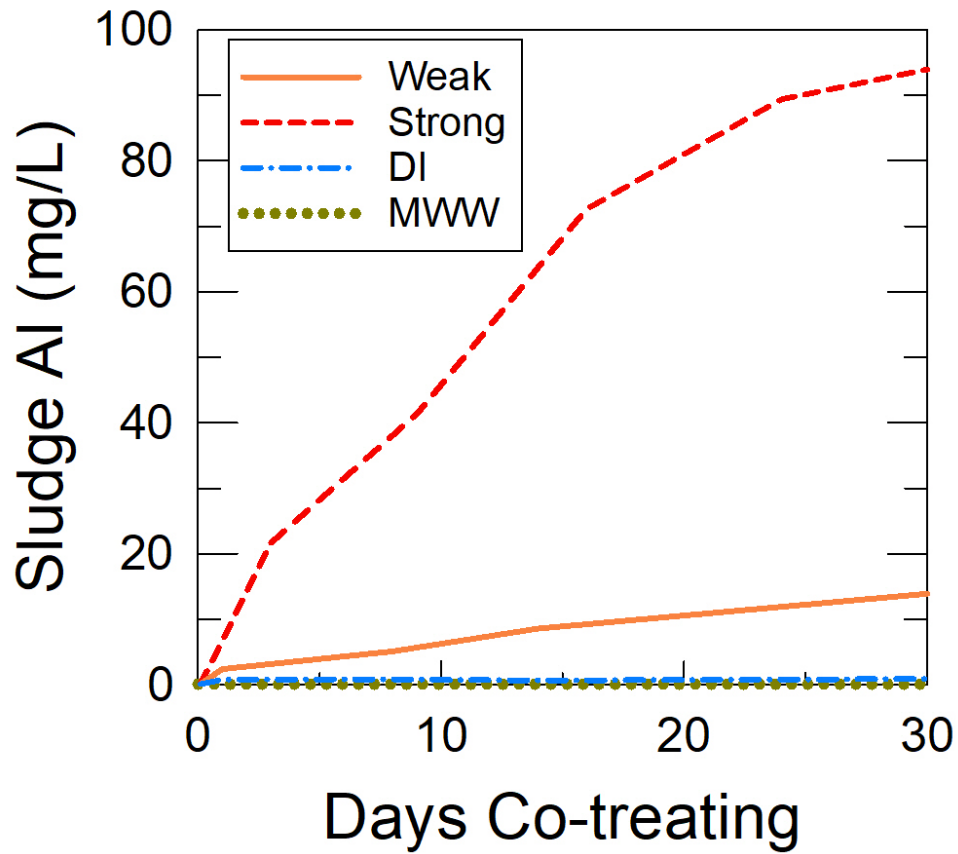
S4. Effluent Al

Figure S4: Trend of Al-content bound in sludge during all treatment phases.

SI References:

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