2019

Preliminary Assessment of Ferrate Treatment of Metals in Acid Mine Drainage

Joseph E. Goodwill  
*University of Rhode Island, goodwill@uri.edu*

Julie LaBar

Debbie Slovikosky

William H.J. Strosnider

Follow this and additional works at: [https://digitalcommons.uri.edu/cve_facpubs](https://digitalcommons.uri.edu/cve_facpubs)

**Citation/Publisher Attribution**


Available at: [http://dx.doi.org/10.2134/jeq2019.02.0079](http://dx.doi.org/10.2134/jeq2019.02.0079)

This Article is brought to you by the University of Rhode Island. It has been accepted for inclusion in Civil & Environmental Engineering Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact digitalcommons-group@uri.edu. For permission to reuse copyrighted content, contact the author directly.
Preliminary Assessment of Ferrate Treatment of Metals in Acid Mine Drainage

Joseph E. Goodwill\textsuperscript{1}
Julie LaBar\textsuperscript{2}
Debbie Slovikosky\textsuperscript{3}
William H. J. Strosnider\textsuperscript{4,5}

\textsuperscript{1} Department of Civil and Environmental Engineering, University of Rhode Island, Kingston, RI
\textsuperscript{2} Science Department, Centenary University, Hackettstown, NJ
\textsuperscript{3} Environmental Engineering Program, Saint Francis University, Loretto, PA
\textsuperscript{4} Center for Watershed Research and Service, Saint Francis University, Loretto, PA
\textsuperscript{5} Baruch Marine Field Laboratory, University of South Carolina, Georgetown, SC

ABBREVIATIONS

AMD, acid mine drainage; DS, dissolved; LP, large particles; NP, nanoparticles; PZC, point of zero charge; SP, small particles; UF, ultra-filtration; XPS, x-ray photoelectron spectroscopy

CORE IDEAS

- Ferrate likely a viable option for acid mine drainage treatment
- Oxidation of manganese with NaOH co-addition near stoichiometric requirement
- Resultant particles may challenge downstream clarification
ABSTRACT

We report a preliminary assessment of ferrate (Fe(VI)) for the treatment of net-acidic mine drainage (AMD), focused on precipitation of metals (i.e. iron and manganese) and subsequent removal. Two dosing approaches were studied to simulate the two commercially viable forms of ferrate production: Fe(VI) only, and Fe(VI) with sodium hydroxide (NaOH). Subsequent metal speciation was assessed via filter fractionation. When only Fe(VI) was added, the pH remained < 3.6, and the precipitation of Mn and Fe was < 30% and < 70% at the highest, stoichiometrically excessive, Fe(VI) dose. When NaOH and Fe(VI) were added simultaneously, precipitation of Mn was much more complete, at doses near the predicted oxidation stoichiometric requirement. The optimal dosage of Fe(VI) for Mn treatment was 25 µM. The formation of Mn(VII) was noted at Fe(VI) dosages above the stoichiometric requirement, which would be problematic in full-scale AMD treatment systems. Precipitation of Fe was > 99% when only NaOH was added, indicating oxidation by Fe(VI) did not play a significant role when added. Fe(III) and Al(III) particles were relatively large, suggesting probable success in subsequent removal through sedimentation. Resultant Mn-oxide particles were relatively small, indicating that additional particle destabilization may be required to meet Mn effluent goals. Fe(VI) seems viable for the treatment of AMD especially when sourced through on-site generation due to the coexistence of NaOH in the product stream. More research in the use of Fe(VI) for AMD treatment is required to answer extant questions.

INTRODUCTION

Abandoned mine drainage (AMD) is a global environmental issue (Wolkersdorfer et al., 2004a-c; Sun et al., 2013; Strosnider et al., 2014). AMD commonly contains elevated metals
(particularly Fe, Al, and Mn), acidity, and sulfate concentrations (Younger et al., 2002). There are two common and effective approaches for AMD treatment: active and passive. Passive treatment employs unrefined materials (e.g., limestone, compost) under gravity flow conditions in engineered basins (e.g., ponds, limestone beds, wetlands, bioreactors). Active treatment employs chemical dosing (e.g., NaOH, CaOH) and ongoing energy inputs (e.g., electricity for aeration/mixing) in traditional wastewater treatment unit processes (e.g., clarifiers, aeration basins). Hybrid systems also exist that combine passive and active approaches within the same treatment train. Spontaneous removal of Fe and Al through oxidation (for Fe(II)) and precipitation is a relatively straightforward process. However, rapid abiotic Mn removal requires pH > 9, which is not achievable in passive treatment systems and relatively expensive in active treatment systems (Younger et al., 2002; Skousen et al., 2017). Thus, the abiotic oxidation of reduced Mn is a common concern in AMD treatment, both from passive and active perspectives.

Ferrate (Fe(VI)) is an oxidant of increasing focus in environmental research (Sharma et al., 2016), that may have advantages in AMD. For example, Fe(VI) has a high oxidation potential at low pH (Sharma et al., 2016), rapidly oxidizes of Mn (Goodwill et al., 2016), and leads to the in situ formation of Fe oxides (Goodwill et al., 2015; Zheng and Deng, 2016) that may support coagulation (Lv et al., 2018). Fe(VI) has also been shown to not directly produce halogenated byproducts in common natural water matrices (DeLuca et al., 1983; Huang et al., 2016; Jiang et al., 2016), although the formation of brominated byproducts has been noted (Huang et al., 2016; Jiang et al., 2016). Fe(VI) exists as FeO$_4^{2-}$(aq), and has equilibria between several protonated forms, as shown in Equations 1 through 3 (Carr, 2008; Rush et al., 1996; Sharma, 2002).
Fe(VI) can be produced electrochemically utilizing an iron-based sacrificial anode in a strong NaOH or KOH solution (Alsheyab et al., 2009; Dubrawski et al., 2018; Stanford et al., 2010). Fe(VI) can also be made using a wet-oxidation approach, which includes oxidation of ferric iron (commonly sourced as commercially available ferric sulfate or ferric chloride coagulants) by sodium hypochlorite (NaOCl) in a concentrated solution of NaOH (Ockerman and Schreyer, 1951). A version of the wet-oxidation method has been commercialized (Ciampi and Daly, 2009), with viable applications to industrial wastes. The Fe(VI) product resulting from either of these production methods co-exists in a strongly alkaline solution, with positive and negative implications of resulting pH changes of dosed waters depending on specific application and water quality.

The Fe(VI) product resulting from either production method can be further refined, leading to a high purity (>95%) potassium ferrate (K₂FeO₄) solid (Thompson et al., 1951). This additional refinement step requires additional cost and complexity, but removes concerns of very alkaline dosed solutions and the possibility of unreacted NaOCl, and allows for off-site production and shipment of a relatively stable, solid-phase product. Innovation has occurred with respect to electrochemical production and subsequent refinement (Monzyk et al., 2013), with K₂FeO₄ product now commercially available.
Unrefined Fe(VI) product (e.g. Fe(VI) in solution with high concentrations of NaOH) may be uniquely advantageous to the treatment of AMD, where increasing the pH is a primary concern. Fe(VI) produced on-site may meet multiple treatment objectives in a single step including increasing pH, oxidizing reduced metals, and increasing aggregation of resultant metal-oxide particles. This may lend an operational simplicity that AMD managers in more rural areas find attractive. Alternatively, utilization of solid K$_2$FeO$_4$ product may be preferred in some situations, due to the off-site production and corresponding lack of chemical inputs.

Despite these potential advantages there has not been a direct examination of Fe(VI) treatment of AMD. Most prior work has focused on ferrate applications in drinking water (Goodwill et al., 2016; Sharma, 2002; Song et al., 2016) and wastewater (Lee et al., 2009; Waite and Gray, 1984; Yates et al., 2014). There have been several studies examining ferrate treatment of solid phase mine tailings via heterogenous oxidation reactions (Murshed et al., 2003; Yu et al., 2013), in an attempt to decrease subsequent acidic discharges (Singer and Stumm, 1970). Murshed et al. (2003) found ferrate mitigates acid production by oxidizing sulfide to sulfates in heterogenous reactions between ferrate and a mine tailings slurry. The oxidation of H$_2$S by ferrate in homogenous aqueous phase reactions in laboratory and municipal wastewater matrices (pH ranged 7 to 12) has also been demonstrated (Sharma et al., 1997). Yu et al. (2013) examined the oxidation of several solid phase metal-sulfides at pH 9.0 and also noted the generation of sulfate. However, prior work on ferrate mitigation of mining wastes has focused on the oxidation of mine tailings, and not the drainage that results from the tailings. Thus, it is uncertain how ferrate may perform in the inherently complex matrix of AMD. Fe(VI) has been proposed as a solution to
challenging Mn(II) removal from mine drainage (Neculita and Rosa, 2019), yet no published data exist.

The overarching objective of this work was a preliminary examination of ferrate oxidation of AMD, and a general assessment of the feasibility of ferrate oxidation for active or hybrid AMD treatment systems. More specifically, the study focused on the stoichiometry, products and qualitative kinetics of the reactions between Fe(VI) and several dissolved metals within an AMD matrix. Special attention was paid to Mn, as some abiotic passive systems have struggled to decrease Mn concentrations to treatment goals (LaBar et al., 2011). A secondary objective was to inform which Fe(VI) production method—onsite production of Fe(VI) in a NaOH liquid stream, or off-site production of K$_2$FeO$_4$ solid—may be most appropriate for AMD treatment.

**MATERIALS AND METHODS**

AMD studied in this work came from the Puritan discharge in Portage, Pennsylvania (PA) within the Appalachian coal basin. The discharge is from an abandoned underground partially-flooded and freely-draining coal mine. Water quality at the site has been monitored extensively over the last decade. The mean pH of the discharge is 3.2, with no alkalinity, and average acidity of 134 mg/L as CaCO$_3$. Mean concentrations of Fe, Al and Mn are 9.4 mg/L, 11.2 mg/L, and 1.9 mg/L, respectively. A simple Fe speciation model was developed in Geochemist Workbench (Bethke, 2008) for the Puritan AMD. Model results showed essentially all Fe was likely in the +3 oxidation state.
Since 2012, the discharge has been partially treated using a baffled limestone bed. Treated effluent has a mean pH of 7.1 and an alkalinity of 106 mg/L; however, the system only removes approximately 78%, 63%, and 33% of the total Fe, Al, and Mn, respectively. This particular discharge qualifies for exemption from effluent discharge limits; however, typical limits from the Pennsylvania Department of Environmental Protection include 3.0 mg/L and 2.0 mg/L for total Fe and Mn, respectively. Similar requirements for Al do not exist. Organic carbon has not been quantified, but is expected to be in trace amounts, as is typical of coal mine drainage in the Appalachian Basin (Watzlaf et al., 2004).

Samples of AMD were collected directly at the outfall of the Puritan discharge, Collapsible containers sealed with Parafilm were used to ensure no oxygen was entrained during sample collection and transport. All experiments were executed within 48 hours of sample collection. The turbidity and pH of collected samples was monitored to ensure no significant changes in water quality between sampling and experimentation.

The oxidation experiments were executed by an adapted jar test procedure (Ma and Liu, 2002) involving 1 L of AMD. The square reaction vessels (e.g. “jars”, B-Ker, Phipps & Bird) had the following dimensions: length = 4.5 in, width = 4.5 in, and height to water surface = 3 in. Two sets of experiments were done: one adding Fe(VI) only, and the other adding Fe(VI) with a 50% NaOH solution, replicating the expected matrix of on-site generated solutions. NaOH solution dose was set as the amount required to increase solution pH to approximately 5.25, and determined in preliminary titration experiments to be 6.8 mL. Subsequently, 6.8 mL of 50% NaOH solution was added simultaneously with Fe(VI) in the set of experiments including NaOH.
co-addition. Fe(VI) was added by making a concentrated (2 mM) solution from DI water and
K$_2$FeO$_4$ (Battelle Memorial Institute/Element 26) with an unbuffered pH of 9.2. The
concentration of Fe(VI) dosing solution was confirmed via direct spectrophotometric
measurement at 510 nm immediately prior to addition (Carr, 2006). Chemicals were dosed to the
reaction vessels under intense mixing (G ~ 350 sec$^{-1}$). Mixing was then decreased (G ~ 75 sec$^{-1}$)
for a total time of 30 minutes, although reactions were observed to proceed more rapidly.
Duplicate experiments were conducted for each scenario, and preliminary metal concentrations
were initially measured using colorimetric methods (Eaton et al., 2005) adapted for use via
commerically available units (i.e. Hach reagents and spectrometer), in order to provide rapid
assessment, and adjustment of subsequent Fe(VI) dosages. The applicable colorimetric methods
for each metal are as follows: Hach FerroVer, #8008 (Iron), Hach Low Range (LR) Mn Method,
#8145 (Manganese) and Hach AluVer, #8012 (Aluminum). Samples were collected from each
experimental condition, acidified to 1% nitric acid, and then final metal concentrations were
measured using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). ICP-
AES-generated concentrations were used for reporting. Means and standard deviations were
calculated, with reported error bars representing one standard deviation. ICP-AES analysis was
not available for an experimental control condition (with 50% NaOH solution, and Fe(VI) = 0
µM), and thus those data were generated only from colorimetric measurements.

Turbidity samples were drawn after 60 minutes of settling (e.g. no mixing) that succeeded the 30
minutes of slow mixing. Samples were drawn from a tap in the reactor vessel positioned
equidistant from the water surface elevation and the reactor bottom. Samples were drawn
quiescently, to minimize perturbation of the particle suspension. Turbidity was measured with an
USEPA Method 180.1 compliant turbidimeter (HACH 2100).

The resulting metal (hydro)oxides were fractionated using a series of filters with progressively
smaller effective/pore sizes in a method previously developed for determining the size and
oxidation state of Mn particles (Carlson et al., 1997). The filters included a fine glass fiber
(GF/F) (effective size = 0.7 µm), a microfiltration (MF) membrane (pore size = 0.2 µm), and an
ultrafiltration (UF) membrane (molecular weight cut-off = 30 KDa). Particles retained on the
GF/F were defined as large particles (LP). Particles passing the GF/F but retained on the MF
were called small particles (SP). Particles passing the MF but retained on the UF were called
nanoparticles (NP). Any material passing the 30 KDa UF was operationally defined as dissolved
(DS) (Tobiason et al., 2008).

RESULTS AND DISCUSSION

Impact on pH and Dissolved Metals
Figure 1 includes the resulting pH and dissolved metal concentrations following the two Fe(VI)
dosing regimes as a function of Fe(VI) dose. pH did not increase appreciably in the no NaOH
condition when dosed Fe(VI) was 100 µM or less. Even at the highest Fe(VI) dose, there was
only a small increase in pH from 3.2 to 3.6. The pH in the condition with NaOH ranged from
5.25 to 6.8, at the lowest and highest Fe(VI) dosages, respectively.

The (lack of) impact on pH by Fe(VI) in the no NaOH condition can be explained by considering
the acidity of the AMD and alkalinity of Fe(VI). Fe(VI) primarily exists as FeO₄⁻² in an aqueous
solution at pH 9.2 used for dosing (see Equation 3), and can be considered the conjugate base of
the other protonated forms (Equations 1 and 2). As such, the alkalinity of an FeO$_{4}^{-2}$ dose can be
calculated with respect to calcium carbonate (CaCO$_{3}$), based on their equivalent weights (Eaton
et al., 2005). In this way, a 300 µM FeO$_{4}^{-2}$ dose yields approximately 30 mg/L alkalinity as
CaCO$_{3}$. The final mixed pH can be estimated at 3.8 based on the of the acidity of the AMD and
alkalinity equivalent of 300 µM FeO$_{4}^{-2}$ dose, assuming a system open to the atmosphere (Stumm
and Morgan, 2012), which is in general agreement with measurements. Clearly, it would take
considerably more FeO$_{4}^{-2}$ to raise the pH of the AMD near a typical treatment goal of > 6.0
(Johnson and Hallberg, 2005). Thus, results support the conclusion that FeO$_{4}^{-2}$ alone is likely
inadequate as a single treatment approach to AMDs of similar or greater acidity. A combination
of NaOH and Fe(VI) was adequate to increase the resulting pH to circumneutral values. Results
indicate that the combination of Fe(VI) in a high strength NaOH solution—similar to that
generated from on-site electrochemical of wet-oxidation methods—may yield significantly less
acidic pH values. Methods for producing Fe(VI) in a KOH solution also exist, and it is
anticipated that impact on pH would be the same to that of NaOH, assuming similar molar
dosages.
Fig 1. Metal concentrations after 30 kDa membrane ultrafiltration (UF) and pH following ferrate oxidation of acid mine drainage with and without NaOH co-addition.

Figure 1 also includes operationally-defined dissolved metal concentrations following Fe(VI) addition with and without co-addition of NaOH. The extent of metals precipitation clearly
depended on the co-addition of NaOH. When NaOH was not added and the pH was relatively low, precipitation of Fe, Mn, and Al was incomplete. 74%, 29%, and 21% of the Fe, Mn and Al were separated by the UF membrane, respectively, at the highest Fe(VI) dose of 300 µM.

Precipitation of metals was more complete with NaOH and Fe(VI) co-addition. In a control condition, where only NaOH was added (e.g. Fe(VI) dose = 0 mg/L), almost all Fe and Al did not pass the UF membrane. This indicates that Fe(VI) oxidation did not play a significant role in changing the oxidation and/or particulate state of Fe or Al in the AMD. However, the majority of Mn still passed the UF membrane, until Fe(VI) was included with the NaOH.

The concentration of all metals reached a minimum at a Fe(VI) dose of 25 µM, which includes a decrease in operationally-defined dissolved Fe, Mn and Al concentration by 98%, 93% and 97%, respectively. Fe(VI) dosages greater than 25 µM did not further decrease metal concentrations despite additional increases in pH, therefore 25 µM represents the optimal dosage in this case. However, dissolved Mn concentrations did increase at Fe(VI) dosages above 25 µM. A persistent pink color was observed in these situations, which was confirmed to be Mn(VII) via an assessment of visible light absorbance, featuring two distinct peaks at 526 and 546 nm (data not shown) (Den Boef et al., 1958). The in-situ formation of Mn(VII) from the oxidation of Mn(II) by Fe(VI) has been previously noted in a laboratory drinking water matrix (Goodwill et al., 2016). Results here demonstrate the potential for this to occur in an AMD water matrix under simultaneous addition of Fe(VI) and NaOH. The in-situ formation of Mn(VII) during AMD treatment could present ecological and aesthetic concerns to receiving water bodies. Attention should be paid to the potential for optimal Fe(VI) based on theoretical stoichiometry.
Metal Oxidation Stoichiometry

Figure 2 includes the results from experiments up to the previously described optimal Fe(VI) dose of 25 µM, in terms Fe and Mn precipitated on a molar basis. Figure 2 also includes the theoretical stoichiometry of the oxidation reaction between Fe(II) and Fe(VI) (Lee et al., 2014), and Mn(II) and Fe(VI) (Goodwill et al., 2016), respectively. Lee et al. (2014) demonstrated a 3:1 stoichiometry in an N₂ purged, circumneutral pH solution with 5 mM carbonate buffer (see Figure SI-14 in that work), summarized as Equation 4. Goodwill et al. (2016) demonstrated a 2:3 stoichiometry at pH 6.2 and 7.5 in a 1 mM carbonate buffered water, summarized as Equation 5, with final oxidation states confirmed via x-ray photoelectron spectroscopy (XPS). In that work, Mn was sourced as a manganous salt, and known to be in the +2 (e.g. reduced) oxidization state. Both equations are net, and do not show potential intermediate steps including Fe(V) or Fe(IV).

\[
3Fe(II) + Fe(VI) \rightarrow 4Fe(III)
\]  
(Equation 4)

\[
3Mn(II) + 2Fe(VI) \rightarrow 3Mn(IV) + 2Fe(III)
\]  
(Equation 5)

In Figure 2, data points falling to the right of the theoretical stoichiometric ratio represent dosages of Fe(VI) that caused precipitation less than the expected oxidation of Fe(II) or Mn(II). Similarly, points to the left represent precipitation beyond reduced metal oxidation expectations for the respective Fe(VI) dose. Both Fe and Mn precipitation were well below stoichiometric expectations when no NaOH was added. This suggests Fe(VI) auto-decay (e.g. oxidation of water) competes with other redox pathways, or that the Fe and Mn were already in an oxidized state prior to Fe(VI) addition. The apparent rate constant \(k_{app}\) of Fe(VI) auto-decay has been
quantified by Lee et al. (2014), and ranges from $\sim 5 \times 10^4 \text{M}^{-1}\text{s}^{-1}$ at pH 3.0 to $\sim 1 \times 10^4 \text{M}^{-1}\text{s}^{-1}$ at pH 3.5. However, Lee et al. utilized phosphate buffers to sequester Fe(III) iron particles, which retards the rate of Fe(VI) decay (Jiang et al., 2015). Thus, the actual Fe(VI) auto-decay in an AMD matrix may be greater. Lee et al. (2014) estimated a second-order rate constant ($k_2$) of $\gg 5 \times 10^6 \text{M}^{-1}\text{s}^{-1}$ for Fe(II) oxidation by Fe(VI) at pH 5.0.

Similarly, Goodwill et al. (2016) estimated a $k_2$ for Mn(II) oxidation by Fe(VI) of $> 5 \times 10^4 \text{M}^{-1}\text{s}^{-1}$ when pH $< 8.0$ in carbonate buffered water. This prior work suggests oxidation of Fe(II) and Mn(II) by Fe(VI) in acid environments proceeds as fast or faster than Fe(VI) auto-decay in a phosphate buffered laboratory water matrix. Alternative kinetic explanation may be found in the potential speciation differences in the metal hydroxides as a function of pH not included in the prior estimations. For example, the estimate of $k_2$ by Goodwill et al. does not account for speciation differences between Mn$^{+2}$, and Mn(OH)$^{+1(aq)}$ as a function of pH. In general, the kinetics of Mn oxidation with various oxidants decreases as pH decrease due to increased fractions of Mn$^{+2}$ versus Mn(OH)$^{+1}$ ($pK = 10.6$) (Allard et al., 2013; Knocke et al., 1987; Morgan and Stumm, 1964). It is also possible that Fe and Mn formed very small ($< 20 \text{ nm}$) particles that were operationally defined as dissolved. The oxidation-reduction pathways of Fe(VI) in the presence of acid are complex and an active area of research, including the “activation” of ferrate by accelerating decay to oxidize recalcitrant organics by increasing formation of reactive iron-species (Feng et al., 2018).
Fig 2. Molar concentrations of precipitated Fe and Mn for a given Fe(VI) dose in both with and without 6.8 mL of 50% NaOH solution conditions. Expected Fe oxidation stoichiometry of 3Fe(II):Fe(VI) from Lee et al., 2014. Expected Mn oxidation stoichiometry of 3Mn(II):2Fe(VI) from Goodwill et al., 2016.

Fe and Mn may exist in numerous species, depending on pH, concentration (i.e. relative saturation) and oxidization-reduction potential (ORP) of solution. For example, in acidic environments, Fe may exist as Fe(III) and remain in a dissolved form, such as Fe$^{3+}_{(aq)}$ or
Fe(OH)$_2^{+2}$(aq). In the pH range 3 – 4 even minor changes in pH and/or ORP will impact this speciation. If soluble forms of Fe(III) or Mn(III/IV) resulted from AMD oxidation by ferrate without NaOH co-addition, then they would have been operationally defined as dissolved, and thus fall to the right of the theoretical stoichiometry in Figure 2. Results from Fe speciation modeling show the overwhelming majority of Fe was already as Fe(III). Deeper exploration of AMD metal speciation following Fe(VI) addition without additional pH control is required to more fully understand this system; however, it seems unlikely that this treatment regime would warrant serious consideration for full-scale adaptation.

Much more precipitation of Fe and Mn occurred as a function of Fe(VI) dose when NaOH was added simultaneously. For Fe, precipitation far exceeded the assumed oxidization reaction stoichiometry between Fe(II) and Fe(VI) as shown in Equation 5. This includes the control situation where only NaOH was added, and the Fe(VI) dose was zero—essentially all Fe was defined as particulate. Coupled with the model prediction of primarily Fe(III) existing in the untreated AMD, this result supports the conclusion that Fe(VI) played an insignificant role, and changes in pH from NaOH addition decreased the solubility of Fe(III), without changes in oxidation state. Alternatively, an electrophile other than those attributed to Fe(VI) participated in a redox reaction with Fe when the pH ≥ 5.5 (see Figure 1 for resulting pH values for all experiments). It is likely that dissolved oxygen (O$_2^{aq}$) was present during the reaction, as the reaction was open to the atmosphere under a turbulent mixing regime. Also, self-decay of Fe(VI), leads to the in-situ production of O$_2$, with molar yields of approximately 60% (Lee et al., 2014). Additional oxidation experiments in controlled anoxic conditions would be required to
fully confirm this; however, it is anticipated that full-scale AMD treatment with Fe(VI) would also be open to the atmosphere.

Precipitation of Mn was also more complete with NaOH and Fe(VI) co-addition, and approached the expected theoretical stoichiometry as shown in Equation 6. Also, results from the NaOH-only control showed a small amount (~20%) of Mn was defined as particulate. There are several important implications of this result. First, this supports the conclusion that Fe(VI) oxidized dissolved Mn(II), and Mn(IV) and Fe(III) were the final products from the reaction (see Equation 5), as the existence and/or formation of other Mn oxidation states would have led to a different stoichiometric relationship, and a divergence from the theoretical line included in Figure 2. The oxidation kinetics of Mn(II) and O$_2$ are very slow ($k_2 \sim 10^{-9}$, at pH = 6.0) (Pankhow and Morgan, 1981). Secondly, it seems almost all Fe(VI) reacted with Mn(II) and did not proceed via other oxidation-reduction pathways or Fe(VI) self-decay. Comparative kinetics supports this conclusion, based on the previously discussed respective estimated $k_2$ values for Fe(VI) oxidation of Mn(II) and Fe(VI) auto-decay at near-neutral pH values. More study is required to fully elucidate the redox reactions between Mn(II) and Fe(VI) in the relatively complex AMD matrix; however, results in Figure 2 indicate Fe(VI) addition to AMD may support Mn treatment goals at dosages near the theoretical stoichiometric requirement. This selectivity has also been noted with respect to organic carbon in prior studies. The presence of organic carbon at levels much higher than what is typical in Appalachian coal mine AMD did not significantly increase the amount of Fe(VI) required for complete Mn(II) oxidation (Goodwill et al., 2016).
Adsorption of aqueous phase metals onto metal oxide surfaces may have taken place at the experimental conditions in our study. The methods utilized do not enable the differentiation between adsorbed species and the particle metal, which require surface techniques such as XPS (Cerrato et al., 2011), or similar. Adsorbed aqueous metals would have been operationally defined as either LP, SP or NP, (depending on the size of the adsorbent particle) and served to shift points in Figure 2 vertically. Figure 2 supports limited adsorption of Mn(II) based on results being proximate to expected stoichiometry. Adsorption of Mn(II) onto metal oxides is proportional to pH, with limited adsorption expected when pH < 6.0 (Morgan and Stumm, 1964), as was the case in most all of the Fe(VI) dosages reported in Figure 2.

**Size Fractionation of Resulting Particles**

Figure 3 includes the metal fractionation results for selected Fe(VI) dosages, with and without NaOH. Most metals remained defined as dissolved following even the highest dose of Fe(VI) without NaOH co-addition. Again, results of the Fe speciation model indicate the most Fe was in the +3 oxidation state, even though it was found to pass the filtration steps in this study. Only 30% of total Mn and 65% of total Fe was in a particulate phase after a Fe(VI) dose of 100 µM (without NaOH); however, almost all the particles that did form were operationally defined as LP, indicating aggregation resulting from the low solution pH. Ferrate resultant Fe(III) particles have been found to have a point of zero charge (PZC) at pH 3.0 to 3.6 in natural water matrices with low dissolved organic carbon (Goodwill et al., 2015; Lv et al., 2018), suggesting optimal aggregation in that pH range. However, particle surface chemistry in the oxidized AMD matrix is expected to be complex due to the potential hydrolysis of Al and Fe (e.g. dual coagulation) (Johnson and Amirtharajah, 1983) leading to the formation of polymeric hydrolysis products.
(Duan and Gregory, 2003). The effect of mixing conditions on aluminum precipitation is also important (Clark et al., 1993), but not examined in the context of this preliminary study. More work on this topic is a focus of future research towards coagulation process optimization in an AMD treatment context.
Fig. 3. Size fractionation of metal particles resulting from the oxidation of acid mine drainage by ferrate, on a mass of metal basis, with and without the co-addition of 6.8 mL of 50% NaOH solution. (LP = Large Particles, SP = Small Particles, NP = Nanoparticles, DS = Dissolved).

Particle size distributions with NaOH differed with almost all Fe and Al in a particulate form in the only NaOH condition. However, most Mn remained dissolved until including a Fe(VI) dose of 25 µM. Therefore, the precipitation of Fe may be attributable to the increase in pH from NaOH alone, as supported by results in Figure 2. 83% of Mn resulting from oxidation was characterized as NP. Prior investigations have noted the formation of nanoscale (e.g. colloidal) Mn particles following exposure of Mn(II) to strong oxidants (Knocke et al., 1991; Reckhow et al., 1991; Tobiason et al., 2016). The PZC of Mn-oxide particles in a laboratory water matrix was found to occur below pH 3 (Morgan and Stumm, 1964), indicating the possibility of a stable Mn colloidal suspension in the pH ranges in this study with NaOH co-addition. The Mn particles formed without NaOH co-addition were significantly larger. Removing Mn NPs from solution may be challenging (Brandhuber et al., 2013; Islam et al., 2010), however, it may be possible to optimize particle aggregation by decreasing the amount of NaOH.

Approximately 75% and 98% of Al and Fe, respectively, were defined as LP following a ferrate dose of 25 µM with NaOH co-addition. At higher ferrate dosages nearly all Al and Fe was LP, on a mass basis. In these situations, the resulting pH ranged from 6.0 to 6.6 (see Figure 1), which is much higher than the PZCs for Al and Fe (hydr)oxides (Duan and Gregory, 2003; Faust and Aly, 1998; Stumm and O’Melia, 1968; Van Benschoten and Edzwald, 1990). Aggregation in this pH range may be suboptimal due to charge reversal and repulsive forces; however, the
opportunity for sweep flocculation exists due to the elevated range of total metal in the oxidized AMD, especially at the higher dosages of Fe(VI) (Davis and Edwards, 2014; Dentel, 1991). In this regime, enmeshment in metal precipitates with sufficient kinetic energy may overcome repulsive forces, leading to improved aggregation in a single or dual coagulation situation (Dentel, 1991; Graham et al., 2010; Johnson and Amirtharajah, 1983).

### Settling of Resultant Particles

**Fig 4.** Turbidity of AMD solutions following various ferrate dosages, with and without the co-addition of 6.8 mL of 50% NaOH solution.

Figure 4 includes results for settled turbidity after Fe(VI) addition with and without NaOH co-addition. Turbidity was elevated following treatment in both conditions, and directly proportional to Fe(VI) dose. Turbidity was higher in most Fe(VI) dosages with the co-addition of
NaOH, likely due to lower solubility of Al and Fe and more complete oxidation of Mn (Sanchez 2007). Settling in both conditions was poor as determined by high residual turbidity. The poor settling of ferrate resultant particles has been noted previously in an advanced wastewater treatment context (Zheng and Deng, 2016).

The poor settling of other metal oxide particles may be attributable to the small extent of particle destabilization. Surface charge of resultant particle suspensions was not able to be quantified, as would likely be the case in isolated pseudo-passive systems. Attempts at optimization of dosing on settled water turbidity may be helpful. Both topics should be the focus of future research. A high turbidity discharge could create ecological and/or regulatory issues, especially in receiving waters with sensitive aquatic life. Subsequent passive (e.g., sedimentation ponds, wetlands) or active (e.g., clarifiers) may not be adequate for particle separation without enhanced coagulation and/or flocculation.

ACKNOWLEDGEMENTS

This is contribution number 1870 for the Belle W. Baruch Institute for Marine and Costal Sciences.

CONCLUSIONS

Fe(VI) is an interesting alternative treatment for AMD, and seems especially effective at oxidizing dissolved Mn within an AMD matrix, at dosages near the minimum stoichiometric requirement when pH > 5.0. The co-addition of Fe(VI) and NaOH seems to yield high performance and operational simplicity, and currently available commercial options for this
exist. The addition of Fe(VI) without NaOH proved inadequate and full-scale adaption of this approach seems unlikely. Further research is required to assess impacts on trace metals and the stability of the particle suspension resulting from Fe(VI) oxidation, appropriate clarification process steps, and to confirm the final speciation of metal oxides produced. Also, the dose of NaOH may be adjusted to optimize Fe(VI) oxidation effectiveness while minimizing negative surface charges.

REFERENCES


Den Boef, G., Van Der Beek, H.J., Braaf, T., 1958. Absorption spectra in the visible and UV region of potassium permanganate and potassium manganate in solution and their application to the analysis of mixtures of these compounds. Recl. des Trav. Chim. des Pays-Bas 77, 1064–1070.


Ockerman, L., Schreyer, J., 1951. Preparation of Sodium Ferrate(VI) 72, 5478.

Pennsylvania Department of Environmental Protection (PA DEP). Title 25 Environmental Protection. 1998. Chapter 87.102


impact the Rio Pilcomayo headwaters. Environ. Earth Sci. 71, 3223-3234. doi:
10.1007/s12665-013-2734-z

Stumm, W., Morgan, J.J., 2012. Aquatic Chemistry: Chemical Equilibria and Rates in Natural
Waters. John Wiley & Sons.

Stumm, W., O’Melia, C., 1968. Stoichiometry of Coagulation. J. Am. Water Works Assoc. 60,
514–539.

of streams with and without acid mine drainage impacts: a paired catchment study in karst

Thompson, G., Ockerman, L., Schreyer, J., 1951. Preparation and purification of Potassium
Ferrate VI. J. Am. Chem. Soc. 73, 1379–1381. doi:10.1021/ja01147a536


Characterization and Performance of Filter Media for Manganese Control. Water Research
Foundation, Denver, CO.

salts—I. Hydrolytic reactions of alum and polyaluminum chloride. Water Res. 24, 1519–
1526. doi:10.1016/0043-1354(90)90086-L


Watzlaf, G. Schroeder, K., Kleinmann, R., Kairies, C., Narin, R., 2004. The passive treatment of
cog coal mine drainage, Laboratory Report DOE/NETL-2004/1202, Pittsburgh, PA.


30
Fig 1. Metal concentrations after 30 kDa membrane ultrafiltration (UF) and pH following ferrate oxidation of acid mine drainage with and without NaOH co-addition.
Fig 2. Molar concentrations of precipitated Fe and Mn for a given Fe(VI) dose in both with and without 6.8 mL of 50% NaOH solution conditions. Expected Fe oxidation stoichiometry of 3Fe(II):Fe(VI) from Lee et al., 2014. Expected Mn oxidation stoichiometry of 3Mn(II):2Fe(VI) from Goodwill et al., 2016.
Fig. 3. Size fractionation of metal particles resulting from the oxidation of acid mine drainage by ferrate, on a mass of metal basis, with and without the co-addition of 6.8 mL of 50% NaOH solution. (LP = Large Particles, SP = Small Particles, NP = Nanoparticles, DS = Dissolved).

157x160mm (300 x 300 DPI)
Fig 4. Turbidity of AMD solutions following various ferrate dosages, with and without the co-addition of NaOH.