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Laboratory assessment of ferrate for drinking water treatment

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ABSTRACT

A laboratory assessment of ferrate (Fe(VI)) for drinking water treatment was conducted, including batch and continuous flow experiments on natural water samples. In batch experiments, ferrate preoxidation enhanced the removal of ultraviolet light absorbing compounds (UV254) by subsequent coagulation in some water samples, while some samples showed no improvement. Ferrate oxidation was not found to have negative impacts on subsequent coagulation. In continuous flow experiments, ferrate preoxidation improved finished water turbidity, UV254 absorbance and disinfection by-product formation as compared to no preoxidation and to preoxidation with
Mn(VII). However, improvements were similar in magnitude to those achieved by adding the same mass of Fe(III) in place of Fe(VI) prior to a formal coagulation step, in one study water. Particulate iron resulting from Fe(VI) reduction was effectively destabilized and removed via coagulation and filtration. Ferrate may be a viable technology for drinking water treatment depending on raw water quality and treatment goals.

**Keywords:** ferrate, organic carbon, coagulation, drinking water treatment, disinfection by-products, preoxidation

**INTRODUCTION**

Ferrate (Fe(VI)) has been proposed as a viable alternative to other strong oxidants such as chlorine dioxide, ozone and permanganate in drinking water treatment (DWT) (Jiang and Lloyd, 2002; Sharma et al., 2005). As a strong oxidant, there has been much published research on the oxidation of various inorganic and organic contaminants by Fe(VI). Generally, Fe(VI) effectively and rapidly oxidizes contaminants germane to water treatment, relative to typical dosages of iron (Fe) and process time-scales. Additionally, ferrate has been evaluated as a coagulant with respect to removal of turbidity (Ma and Liu, 2002), formation of flocs (Graham et al., 2010), and interactions with natural organic matter (Jiang and Wang, 2003; Lim and Kim, 2009), as compared to traditional coagulants (e.g. salts of iron and aluminum). Contradiction in the literature exists, with some researchers concluding ferrate improved the removal of organics during coagulation (Jiang and Lloyd, 2002), and others finding varied or minimal impact (Graham et al., 2010). Fundamental processes have not been discussed in great detail. Ferrate has been demonstrated to inactivate various pathogens (Gombos et al., 2012; Hu et al., 2008; Sharma, 2007) at exposure
values that appear achievable in water treatment (Jiang et al., 2015b). Ferrate has not been shown to form common hazardous byproducts (DeLuca et al., 1983; Sharma et al., 2005). However, ferrate was found to oxidize bromide depending on several water quality factors (Jiang et al., Submitted).

Ferrate can be produced by several methods including oxidation by chlorine in an alkaline solution (e.g., wet oxidation method) (Ockerman and Schreyer, 1951), and electrochemically (Alsheyab et al., 2009). Following production via wet oxidation or electrochemical methods, the product can be refined through a process involving potassium hydroxide, precipitation and drying, ultimately yielding >95% purity potassium ferrate (K$_2$FeO$_4$) (Thompson et al., 1951). A version of these processes has been commercialized by the Battelle Memorial Institute (Monzyk et al., 2013). Also, a version of the wet oxidation method has been commercialized by Ferrate Treatment Technologies (Ciampi and Daly, 2009). This technology currently produces ferrate that has been used successfully in several applications including the treatment of industrial wastewater and ship ballast water. Due to the use of chlorine in the wet-oxidation method, chlorine may be present in the final ferrate product, potentially leading to the formation of chlorinated byproducts in treated water especially in the case of preoxidation (e.g., the addition of an oxidant to raw water, before clarification). Quantifying the concentration of chlorine in the presence of other strong oxidants is not possible by typically used methods (e.g., iodometric, amperometric, or DPD methods) due to interference (APHA et al., 2005). Therefore, to avoid the potential formation of disinfection byproducts (DBPs), it is possible that dosing the potassium ferrate salt (K$_2$FeO$_4$) will be a more common ferrate adaptation source specifically for drinking water treatment. Issues related to using K$_2$FeO$_4$ include shipping and dosing of a solid product. K$_2$FeO$_4$ was used for all batch and continuous flow experiments in this work. Controls in the wet-oxidation process may be used to
reduce the risk of chlorine residual in the final ferrate product, and ferrate produced by the wet-oxidation method may also be used in drinking water treatment, assuming very low chlorine residuals in the final product are achievable. Currently, there is very limited publicly available cost information in a drinking water treatment context for either production method.

The most commonly considered application of ferrate in drinking water treatment is as a preoxidant; i.e., occurring before clarification. This is because of the formation of Fe(III) solids that results from Fe(VI) reduction, and the expectation that these particles are best formed prior to particle destabilization and separation (i.e., clarification and/or filtration) processes. A general DWT schematic is shown in Figure 1, including ferrate preoxidation.

In the absence of specific oxidant demands, ferrate undergoes automatic decomposition (i.e., auto decay) that includes the oxidation of water, and the formation of Fe(III) solids and hydrogen peroxide (Carr, 2008; Lee et al., 2014). In a natural water matrix, natural organic matter (NOM) or buffer systems (e.g., carbonate) may serve to stabilize ferrate decomposition, likely through complexation with Fe(III) solids that would otherwise catalyze Fe(VI) decay (Jiang et al., 2015b). Natural sources of drinking water may also contain discrete oxidant demands such as reduced metals, organic contaminants, and pathogens. Thus, ferrate is likely to react through multiple simultaneous pathways when added to raw water as a preoxidant, with the oxidized constituents potentially playing a role in subsequent treatment processes. A summary of common possible ferrate reaction pathways is shown in Figure 2.

As shown in Figure 2, the possible impacts of adding ferrate to a raw water are multiple and complex. Very few studies have focused on the impacts of adding ferrate for drinking water treatment in a manner that accounts for multiple possible outcomes. Also, very few studies have been published on the use of ferrate in continuous flow (e.g., pilot) experiments in a drinking water
context, and the impact of adding ferrate, both on water quality and downstream physical-chemical processes is not fully known. Therefore, the objectives of this study are: (1) conduct batch experiments to evaluate the impact of adding ferrate as a preoxidant on subsequent coagulation (2) conduct continuous flow experiments to evaluate the impact of adding ferrate as a preoxidant on downstream physical and chemical water treatment processes, and water quality; (3) comment on the general benefits and feasibility of using ferrate in drinking water treatment as compared to other treatment chemicals such as permanganate (MnO₄⁻) and ferric chloride (FeCl₃).

MATERIALS AND METHODS

Batch Experiments. The batch experiment protocol is shown in Figure 3. Raw water of various sources was buffered with 10 mM borate, and ferrate was added as a preoxidant directly as a K₂FeO₄ salt, under rapid mixing (G ~ 200 sec⁻¹) at room temperature (21 deg C). Buffers have been commonly used in similar ferrate batch experiments (Sharma, 2010; Waite and Gray, 1984), and borate was chosen because it has been demonstrated to affect the rate of ferrate decay less than other buffer systems (Jiang et al., 2015b). Ferrate concentrations were measured using an indirect indicator spectrophotometric method (Lee et al., 2005). Two ferrate dosing conditions were utilized: a lower dose of 25 μM and a higher dose of 50 μM, which were chosen based on preliminary experiments (Goodwill et al., 2014). Fe(VI) preoxidation was conducted at two pH values, 6.2 and 7.5, to span the range of pH values commonly encountered in drinking water treatment. Following at least 45 minutes of reaction time, a portion of the resultant solution was analyzed for various parameters, while the remainder was subjected to coagulation with FeCl₃. A reaction time of > 45 minutes was chosen based on previously published studies ofdecay of ferrate in natural water matrices (Jiang et al., 2015b).
Coagulation was executed based on a common jar test procedure (Hudson and Wagner, 1981). Jar tests were executed using a programmable flocculator (Kemwater, Kemira). Six samples (e.g. jars) were dosed with various amounts of ferric chloride under rapid mixing ($G \sim 200 \text{ sec}^{-1}$), followed by 10 minutes of slower mixing ($G \sim 50 \text{ sec}^{-1}$). The pH was controlled at 5.5 by drop wise addition of 1 M NaOH or 1M HCl, as required. The solution was then allowed to settle under quiescent conditions for 30 minutes. Following coagulation, flocculation and sedimentation, a 20 mL sample was taken from the reactor and filtered using a fine glass fiber filter (Whatman GF/F) with an effective size exclusion of 0.7 μm. The UV254 absorbance of each jar test sample was measured, and the Fe(III) dose that yielded the lowest value of UV254 absorbance was defined as the optimum ferric dose (OFD). If ferric coagulant dosages yielded the same (e.g. < 5% difference) UV254 absorbance, then the lower of the two dosages was defined as the OFD. Optimal coagulation was defined by UV254 absorbance based on the nature of the raw waters (e.g., surface waters, relatively low turbidity, relatively high UV254 absorbance), consistent with typical practice of coagulation controlled by organic demand (Edzwald, 1993; Edzwald and Tobiason, 1999). UV254 absorbance was chosen as the primary measurement parameter because it is an excellent surrogate parameter for estimating concentrations of organic carbon in natural water (Edzwald et al., 1985).

**Continuous Flow Experiments.** The treatment processes were developed to replicate full-scale DWT systems. The full-scale facilities chosen for this study used a packaged water treatment plant developed by WesTech (Trident®). The major characteristics of the Trident System include the use of an up-flow roughing filter, known as an adsorption clarifier (AC), filled with relatively coarse, low-density plastic media in place of a more conventional gravity based clarifier. The continuous flow system was constructed using PVC pipe, NSF 61 certified for use with potable
water. Prior to coagulation and clarification, Fe(VI) was dosed as a concentrated (1 mM) solution, proceeded by approximately 40 minutes of ferrate contact time through a series of two continuous flow stirred tank reactors. The Fe(VI) stock solution was made by dissolving K₂FeO₄ of 97% purity (Battelle Corporation) in deionized water. The concentration of the Fe(VI) stock solution was continuously monitored via absorbance at 510 nm, assuming a molar absorptivity of 1100 M⁻¹ cm⁻¹ (Rush et al., 1996). The pH of the Fe(VI) stock solution was also monitored and found to be 9.2 ± 0.15. In this pH range, concentrated solutions of Fe(VI) are relatively stable (Lee and Gai, 1993). The ferrate stock solution was replaced if the solution strength decreased by more than 10%. The experiment was designed so that fresh ferrate stock solutions were required approximately every hour. The ferrate feed was adjusted as needed to account for minor changes in stock concentration, ensuring a consistent, known ferrate dose.

Following this preoxidation step, coagulants and pH control chemicals were added to replicate full-scale systems immediately prior to an in-line static mixer (see details in Table 2). Water then flowed to the up-flow AC and then down through a conventional anthracite (15 inches) over sand (9 inches) dual-media filter. Filter media were collected from a full scale treatment facility using the Trident Package Plant system in a manner explained elsewhere (Islam et al., 2010; Soucie et al., 2003). The hydraulic loading rates of the AC and media filter were 20 and 10 m/hr, respectively. Headloss was monitored across the dual media filter. Turbidity and UV254 measurements were taken every minute following filtration using on-line flow through instrumentation. pH was also measured at various points across the treatment systems and was adjusted as necessary following preoxidation to replicate full scale conditions (see Table 2).

Two experiments were conducted for each source water, one without ferrate, replicating full-scale conditions (i.e., coagulant type, coagulation pH, etc.) and a second with ferrate, keeping
other factors the same. This allowed for a direct evaluation of the impact of adding ferrate to the treatment process.

In a subset of continuous flow experiments, preoxidation with Fe(VI) was compared to preoxidation using Mn(VII), and to the addition of Fe(III) as FeCl₃ prior to the primary coagulation step. In the case of Mn(VII), a dose was chosen to reflect the dose used at the full-scale facility. The FeCl₃ dose was chosen to yield the same concentration of iron as the K₂FeO₄ dose (~3 mg/L as Fe). FeCl₃ was added in the same location as the preoxidants. Following the contact tank, pH was adjusted using NaOH to replicate the pH of coagulation of the full-scale treatment systems prior to rapid mixing.

**Analytical Methods—Batch Experiments.** UV254 absorbance was measured using an ultraviolet and visible light spectrophotometer with forward optics (Genesys 10S, Thermo Scientific). All samples for UV254 absorbance measurement were filtered with a GF/F filter prior to analysis. Turbidity was measured using a laboratory turbidimeter that met the reporting requirements of EPA Method 180.1 (2100N, HACH). Iron, chlorine, and manganese concentrations were measured using adapted colorimetric methods (APHA et al., 2005), and a colorimeter (DR2400, HACH). Alkalinity was also measured colorimetrically via titration (APHA et al., 2005).

**Analytical Methods—Continuous Flow Experiments.** UV254 absorbance at the media filter effluent was measured using a flow through, online spectrometer (Spectrolyzer, S::CAN) at two minute increments. Turbidity was measured using a laboratory turbidimeter (Ratio XR, HACH) with a flow through cell apparatus. Headloss across the dual media filter was recorded using pressure transducers (Series 200, Noshok). The pH meters, turbidimeter, and pressure transducers were connected to a 14-bit analog to USB data acquisition device (USB-1408FS,
Measurement Computing), which logged results to a computer every 30 seconds. Particle counts were measured in four predefined size channels using a light blockage instrument (2400PS, Chemtrac), operated in flow through mode (100 mL/min). Particle count data were streamed directly to a computer with measurements recorded every 30 seconds.

**Analytical Methods—Organic Carbon and DBPs.** For samples from both the batch and continuous flow experiments, organic carbon was quantified through measurements of non-purgeable organic carbon (NPOC) with a Shimadzu TOC-VCPH carbon analyzer. A hydrogen phthalate standard (10 mg/L) was used to calibrate the instrument. All samples were acidified with 6 N HCl and purged with nitrogen prior to analysis. OC measurements conformed to Standard Methods Section 5310B (APHA et al., 2005).

Measurement of disinfection byproduct formation potential (DBPFP) was initiated by chlorinating buffered (pH = 7.0, 10 mM phosphate) samples in 300 mL chlorine demand free, headspace free bottles, and incubated at 20 deg C for 72 hours. Chlorine dosages were as required to yield a residual between 3 and 5 mg/L as Cl₂ following the incubation period. After incubation, the samples were analyzed for four trihalomethanes (THMs) and nine haloacetic acids (HAAs). THMs were measured by liquid/liquid extraction with pentane followed by gas chromatography (GC) with electron capture detection (ECD), and conformed to USEPA Method 551.1. HAAs were measured by liquid/liquid extraction with methyl-tertiary-butyl-ether (MTBE), derivatization with acidic methanol and analysis by GC-ECD. The HAAs analysis method conformed to USEPA Method 552.2.

**Source Waters.** Waters used in the batch scale experiments were collected from eleven different surface water sources across New England. In general, the water collected was typical of surface waters in the northeastern part of the United States: low hardness, low turbidity, with
moderate to high amounts of dissolved organic matter. None of the studied water sources had appreciable concentrations of inorganic contaminants such as iron, manganese or arsenic. Thus, the focus of preoxidation was on the removal of organic matter and minimizing DBPs. Table 1 includes water quality information for the studied waters.

Two water sources were selected from the set of waters used in the batch experiments for continuous flow experiments: Atkins and South Deerfield. More information about the treatment parameters for these two waters is included in Table 2.

RESULTS

The results for UV254 absorbance following coagulation at the OFD with and without ferrate preoxidation at various dosage and pH values are shown in Figure 4. In four cases, ferrate preoxidation yielded lower UV254 absorbance following coagulation than coagulation alone (Holton, Readsboro, South Deerfield and Stockbridge). In general, this benefit was more pronounced when preoxidation occurred at a pH of 6.2 than at 7.5. However, for the majority of studied waters, coagulation with Fe(VI) preoxidation did not have an appreciable positive impact on removal of UV254 absorbance as compared to only coagulation with FeCl₃. A similar effect has been noted for assessing the impact of ferrate peroxidation on the formation of disinfection byproducts following chlorination (Jiang et al., 2015a). Ferrate preoxidation did not change the OFD of some waters following ferrate preoxidation, as shown in Table 3. For the Catamount, Northampton and Stockbridge waters, however, the OFD decreased 16%, 40% and 33%, respectively. No pattern of appreciable negative impacts on coagulation as a result of ferrate preoxidation was noted in the results.
The impact of ferrate preoxidation on UV254 absorbance removal by downstream processes was examined using continuous flow experiments. Dual media filter effluent UV254 absorbance was monitored in parallel with turbidity and filter headloss, with results shown in Figure 5. Turbidity for both studied waters show decreasing trends initially that can be attributed to filter ripening. Following establishment of steady performance, the UV254 absorbance for the Atkins water without and with Fe(VI) preoxidation was approximately 0.050 and 0.045 cm⁻¹, respectively, indicating approximately a 10% decrease in UV254 absorbance as a result of preoxidation as compared to no preoxidation. Likewise, for South Deerfield, the UV254 absorbance without and with Fe(VI) preoxidation was approximately 0.028 and 0.022 cm⁻¹, respectively, approximately a 20% decrease as a result of preoxidation.

The continuous flow experimental results for turbidity show a similar pattern as UV254 absorbance, with lower turbidities resulting from ferrate preoxidation. For the Atkins water, turbidity without and with ferrate preoxidation was 0.22 and 0.12 NTU, respectively, and for South Deerfield, turbidity without and with ferrate preoxidation was 0.09 and 0.08 NTU, respectively. The relative improvement in turbidity was more significant for the Atkins water.

The removal of more turbidity and UV254 absorbance did not correlate with an increase in headloss across the dual media filter. Results shown in Figure 5 have been referenced to the initial clean bead headloss, and are in units of inches of H₂O. In general, headloss development across the dual media filters for both waters with and without ferrate was very low due to the prior clarification process. No lasting impact of ferrate preoxidation was noted; however, headloss in both waters during preoxidation increase fairly quickly over the first hour of operation, and then much more gradually as operation continued. Ultimately, headloss results for both waters and preoxidation conditions were very similar. The addition of ferrate preoxidation did not negatively
affect the ability of the AC or dual media filter to successfully operate for the desired filter run length.

The impact of Fe(VI) on filter performance was also assessed through particle counts in the filter effluent, with results shown in Figure 6. Particle count measurements were only made during the South Deerfield experiment. In general, particle counts with and without ferrate were low and within typical treatment goals. Ferrate preoxidation resulted in 3-5 particles per mL, while no preoxidation yielded filter effluent particle counts of approximately 30 per mL. Particle counts generally agree with turbidity results in Figure 5. Results indicate no negative impacts of ferrate preoxidation in terms of particles in filter effluent. It should be noted that the minimum detectable particle diameter of the light blockage counting instrument was 2 μm, and the maximum detectable diameter is 100 μm. Attempts at measuring particles number concentrations using dynamic light scattering (DLS) were not successful, likely due to insufficient particle concentration in the filtered effluent.

The primary source of particles from ferrate addition is reduction of Fe(VI) to Fe(III). The fate of iron contributed by ferrate was examined across the treatment system with results shown in Figure 7. Figure 7 shows the increase in iron concentration as a result of ferrate addition. In the inlet of the oxidant contact tank (CT), the iron concentration was approximately 2.9 mg/L, with approximately 90% of the iron defined as dissolved, on a mass of metal basis. Following coagulation and rapid mixing, almost all iron was particulate, with a total iron concentration of 2.5 mg/L. Approximately 90% of iron was removed across the AC. Following filtration, the iron concentration was < 0.1 mg/L, well below the United States Environmental Protection Agency (USEPA) Secondary Maximum Contaminant Level (SMCL) of 0.3 mg/L.
Results of disinfection byproduct formation potential analysis following filtration and chlorination for continuous flow experiments are shown in Figure 8. Also included are results for DBPFP after previously un-chlorinated finished water from the full-scale facilities was subjected to the previously described chlorination procedure. Results from DBPFP at the full scale are similar to results for the respective continuous flow experiments. Concentrations of THMFP and HAAFP for the experiments using Atkins water were higher than those for the South Deerfield water. This coincides with results of UV254 absorbance for the continuous flow experiments, which showed greater UV254 absorbance remaining in Atkins water than in the South Deerfield water. For the Atkins water, THMFP and HAAFP levels decreased as a result of preoxidation with ferrate from approximately 105 µg/L to 90 µg/L. A decrease in DBPFP was also noted for the South Deerfield samples, but to a lesser extent, even though the dose of Fe(VI) was two-times that used for the Atkins water (25 µM versus 50 µM). Variations in Fe(VI) impact on DBPFP across variations in water quality has also been noted in batch experiments (Jiang et al., 2015a).

Continuous flow experiments were repeated twice on South Deerfield water, once using Mn(VII) peroxidation, and once using Fe(III) addition to allow for direct comparisons to ferrate preoxidation, with results for UV254 absorbance and turbidity shown in Figure 9. Ferrate preoxidation yielded lower turbidity and UV254 values compared to no preoxidation (e.g., polymer only), or preoxidation with Mn(VII). However, results for UV254 absorbance and turbidity were very similar for Fe(III) addition and Fe(VI) preoxidation. The Fe(III) and Fe(VI) dosages were both approximately 3 mg/L as Fe. Thus, results indicate that the benefits of lower turbidity and UV254 absorbance following clarification and filtration are likely a function of ferric iron, and not due to the oxidative effect of Fe(VI).
The performance in continuous flow experiments for Fe(VI), Fe(III) and Mn(VII) were also compared with respect to DBPFP with results shown in Figure 10. Results in Figure 11 support UV254 absorbance and turbidity results, with water treated with Fe(VI) and Fe(III) having similar levels of THMFP and HAAFP, which were both lower than THMFP and HAAFP in water treated with Mn(VII) or without any preoxidation. For the no preoxidation and preoxidation with Mn(VII) cases, the THMFP was approximately 50 µg/L and the HAAFP ranged from 55 to 60 µg/L. For the Fe(III) and preoxidation with Fe(VI) case, the THMFP was approximately 40 µg/L. Fe(III) treatment produced 39 µg/L of HAAFP while Fe(VI) preoxidation produced 50 µg/L.

DISCUSSION

**Ferrate and coagulation—batch experiments.** The UV254 absorbance results for the batch experiments indicate that Fe(VI) preoxidation had a variable beneficial impact on subsequent coagulation aimed at the removal of humic substances when compared to coagulation with FeCl₃ without any preoxidation. In some instances, preoxidation with Fe(VI) improved removal of UV254 absorbance, but in other instances it did not. Preoxidation with ferrate also lead to significant decreases in OFD in some of the studied water samples. The variability in Fe(VI) effect is likely attributable to variations in the natural organic matter properties, as pH and mixing conditions were held constant across all batch experiments. The variable effect of ferrate on coagulation has been noted by other researchers, and has been attributed to the oxidation effects of ferrate on organic matter, including the cleaving of more humic macromolecular structures into more hydrophilic structures (Graham et al., 2010). The cleaving of organic structures has also been understood to occur following preoxidation with ozone, which could have negative impacts on
subsequent coagulation (Edwards et al., 1994; O’Melia et al., 1999). However, no significant negative impacts of ferrate on coagulation were noted.

In the batch experiments, when Fe(VI) did improve UV254 absorbance removal after subsequent coagulation, the benefit was generally greater when preoxidation occurred at pH 6.2 versus 7.5. However, ferrate decay in natural water is highly dependent on pH, with the rate of decay decreasing as pH increases (Jiang et al., 2015b). Therefore, UV254 absorbance removal increased even as ferrate exposure (i.e., dose × time) decreased. One possible explanation is the increase in oxidation potential of Fe(VI) as pH decreases (Carr et al., 1984). Alternatively, results point to a more complex relationship between Fe(VI) and reduction byproducts Fe(V) and Fe(IV) that are known to form from ferrate decay (Lee et al., 2014; Sharma et al., 2005). Ferryl(IV) and perferryl(V) are potentially reactive with numerous oxidant demands (Sharma, 2010, 2002; Sharma et al., 2005), and half-lives of the two species are very short, making spectrophotometric measurement difficult (Lee et al., 2005). It is possible that Fe(V) and Fe(IV) play an important role in NOM removal through preoxidation and subsequent coagulation, which would be independent of pH, and more pronounced as Fe(VI) decays into more reduced forms of iron.

**Ferrate and filtered water quality—continuous flow experiments.** For the two continuous flow experiments conducted on Atkins and South Deerfield water, preoxidation with ferrate generally improved finished water quality as compared to no preoxidation. Results indicate that, for both treatment systems, finished water quality resulting from full-scale treatment simulation could be improved by the addition of Fe(VI). Preoxidation with Fe(VI) lead to lower filtered water turbidities and UV254 absorbance values, without impacting filter run times. Fe(VI) preoxidation also lead to decreases in DBP formation potential.
The successful coagulation and ultimate removal of particulate iron is noteworthy, as previous studies had indicated that Fe(VI) reduction in natural water leads to large fractions of stable nanoscale particles that could challenge downstream particle removal processes (Goodwill et al., 2015). Results from this study demonstrate successful destabilization of particles resulting from ferrate reduction by coagulation with subsequent removal via clarification and dual media filtration. Lower turbidities resulting from ferrate preoxidation followed by coagulation have also been previously noted (Ma and Liu, 2002).

In one comparative continuous flow experiment conducted on South Deerfield water, the improvement in finished water quality resulting from ferrate was also more significant than the impact of preoxidation with Mn(VII). However, Fe(VI) preoxidation did not improve finished water quality more than adding the same mass dose of Fe(III). The addition of Fe(III) lowered UV254 absorbance and turbidity to similar levels as compared to Fe(VI), and decreased the formation of HAAs approximately 15% more than for Fe(VI) preoxidation. These results are important as they imply that much of the benefit from adding Fe(VI) in the South Deerfield water could be realized simply by adding the same amount of Fe(III) prior to the existing coagulation process, in this specific case. It should be noted that no attempt was made to optimize the treatment process around the addition of ferrate or ferric chloride as was done in the batch experiments, and therefore the results only show the impact of adding either Fe(VI) or Fe(III) to the existing treatment system. While meaningful cost data do not exist for ferrate in full-scale drinking water treatment, it is very likely that ferric coagulants represent a lower cost treatment option than ferrate (ferric coagulants are one of the inputs for commercialized wet oxidation ferrate manufacturing systems). There are numerous other water quality objectives that were not explored under the scope of this work that are likely to be more conducive to preoxidation with ferrate than the addition of
FeCl₃ alone. Potential examples include the oxidation of dissolved manganese (Goodwill, 2015), inactivation of pathogens (Gilbert et al., 1976; Hu et al., 2008), and the oxidation of Microcystin (Jiang et al., 2014) and arsenic (Lee et al., 2003). It is also possible that Fe(VI) preoxidation would lead to different outcomes as compared to Fe(III) with water containing organic matter with different characteristics than the water in this study. Also, Fe(VI) was found not to have significant negative impacts on coagulation in any of the studied waters. This is noteworthy, as other water treatment objectives may be met with ferrate without decreasing effectiveness of coagulation, in contrast to findings that ozone can have negative impacts on coagulation (O’Melia et al., 1999).

**Engineering and operational considerations.** Evaluation of ferrate through continuous flow experiments also afforded the opportunity to assess possible engineering or operational issues that would arise from adding ferrate preoxidation to an existing drinking water treatment system. The addition of ferrate did not appreciably impact headloss across dual media filters following clarification by an upflow adsorption clarifier. Results from the iron profile indicate that the majority of iron resulting from ferrate reduction was removed by the clarification process prior to filtration. Headloss measurements across the AC were not made; however, during piloting of the South Deerfield and Atkins treatment facilities, headloss development across the AC was very low (e.g., inches of H₂O after several hours of operation). In general, headloss development across the dual media filters both with and without ferrate preoxidation in these continuous flow experiments followed the headloss development profile and magnitude of the respective pilot facilities (Dumais, 1990; Norgren et al., 1993).

Consistent ferrate dosing was achieved by dissolving K₂FeO₄ into DI water and dosing a concentrated solution. At larger scales, Fe(VI) can be added as a solution, or as a powder, perhaps in a manner similar to calcium hypochlorite. If Fe(VI) is added as a solution of K₂FeO₄, then ferrate
stability will need to be considered, and challenges may exist. In this study, ferrate was found to be relatively stable when a concentrated solution was made in DI water (pH ~ 9.2). At the full scale, it is likely that ferrate solutions will be made with finished water, due to economic considerations. Ferrate decay in this water matrix may be different than DI water, and should be evaluated prior to the use of ferrate at the full scale. Alternatively, ferrate can be produced on site via the wet oxidation method, assuming negligible residual chlorine is present in the final product, and the impacts of other produced solution constituents are acceptable. Successful generation of ferrate onsite would decrease concerns related to ferrate stability and shipping. There has also been piloting for in situ electrochemical production of Fe(VI) for wastewater treatment (Yates et al., 2014).

Ferrate exists in several protonated states in aqueous solutions (Sharma, 2011) and thus increases the pH of an aqueous solution when added as a potassium salt of the conjugate base. In the continuous flow experiments, pH was found to increase following the addition of ferrate, and the addition of acid during coagulation was needed to achieve the desired operating pH representative of existing full-scale conditions. In some situations, the possibility of pH control will be a factor to consider for ferrate in drinking water treatment, especially if the ferrate solution generated is a very alkaline solution.

CONCLUSION

In batch experiments involving numerous raw water samples, preoxidation by Fe(VI) was found to have varied impact on UV254 absorbance removal with subsequent coagulation. In the minority of instances, preoxidation with Fe(VI) improved UV254 absorbance removal. In other instances, the impact was negligible compared to coagulation without any preoxidation. In
continuous flow experiments, the addition of a Fe(VI) preoxidation step was found to improve UV254 absorbance, turbidity and DBP levels in finished water, as compared to treatment without preoxidation, without other negative water quality or operational impacts. However, for one source water, when FeCl₃ was added prior to polymer coagulation, the beneficial impact on water quality was essentially the same, indicating that interactions between Fe(III) and NOM, not oxidation of NOM by Fe(VI) were the major contributing processes, in that specific situation. The combination of optimized ferric coagulation and ferrate preoxidation may have provided additional benefits. Additional Fe(VI) preoxidation can support other water treatment objectives such as disinfection, and oxidation of specific inorganic and organic contaminants, not achievable by coagulation alone. The lack of a negative impact on coagulation suggests ferrate preoxidation has advantages over ozone preoxidation.

ACKNOWLEDGEMENTS

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


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


**FIGURE 1** Scherratic of simplified water treatment process including ferrate preoxidation

[Diagram of water treatment process with stages: Ferrate → Coagulant → Chlorine, Preoxidation → Coagulation, Flocculation → Clarification → Filtration → Disinfection]
FIGURE 2  Schematic of common possible reaction pathways for ferrate preoxidation in drinking water treatment

FIGURE 3  Batch experimental method diagram
FIGURE 4  UV254 absorbance after coagulation at optimum ferric dose with and without ferrate preoxidation

coagulation pH = 5.5, 1 μM borate buffer
FIGURE 5  UV254 absorbance, turbidity, and headloss from continuous flow experiments

Atkins, No Fe(VI)  
- Atkins, 25 mM Fe(VI)  
S. Deerfield, No Fe(VI)  
- S. Deerfield, 50 mM Fe(VI)
FIGURE 6  Counts of particles from light-blockage instrument in filter effluent with and without ferrate preoxidation

![Graph showing particle counts over filter run time](image)

- **S. Deerfield, No Fe(VI)**
- **S. Deerfield, 50 μM Fe(VI)**

minimum detectable size = 2 μm
maximum detectable size = 100 μm
FIGURE 7  Iron concentration and fraction across continuous flow experiment on S. Deerfield water with ferrate preoxidation

CT = contact tank, AC = adsorption clarifier, Mix = following coagulant dose and pH control, Eff = filter effluent, Fe(VI) dose = 50 μM
FIGURE 8  Continuous flow and full DBPFP for Atkins and S. Deerfield water

Atkins: Fe(VI) = 25 μM
S. Deerfield: Fe(VI) = 50 μM
DBPFP = disinfection byproduct formation potential
FIGURE 9  UV254 absorbance and turbidity for continuous flow experiments on S. Deerfield water

Polymer Only
Fe(III) and Polymer
Fe(VI) and Polymer
Mn(VII) and Polymer

Polymer only = no preoxidation
Fe(III) = 3 mg/L as Fe
Fe(VI) = 50 μM (2.9 mg/L as Fe)
Mn(VII) = 10 μM
FIGURE 10  Disinfection byproduct formation potential results for continuous flow experiments on S. Deerfield water

Poly Only  Fe(VI)  Mn(VII)  Fe(III) Full Scale

Sample Treatment

THMs

HAAs

Poly = only polymer, no preoxidation
Polymer dose = 6 mg/L as product
Fe(VI) dose = 50 μM (2.9 mg/L as Fe)
Mn(VII) dose = 10 μM
Fe(III) dose = 3 mg/L as Fe

Continuous flow experiment apparatus
### TABLE 1  Water quality information for all batch experiment water

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>TOC—mg/L</th>
<th>DOC—mg/L</th>
<th>UV254 Abs—1/cm</th>
<th>SUVA—L/mg/m</th>
<th>OFD—mg/L as Fe</th>
<th>Raw pH</th>
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<tbody>
<tr>
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<td>1.8</td>
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<tr>
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<td>2.7</td>
<td>0.08</td>
<td>2.9</td>
<td>4</td>
<td>6.6</td>
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<tr>
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<td>6.5</td>
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<td>0.08</td>
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<td>7.0</td>
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</table>

OFD = optimal ferric dose  
SUVA = specific ultra-violet absorbance

### TABLE 2  Full scale and continuous flow experimental parameters

<table>
<thead>
<tr>
<th>Treatment Parameter</th>
<th>Atkins</th>
<th>S. Deerfield</th>
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<tbody>
<tr>
<td>Coag. Type</td>
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<td>Coag. Trade Name</td>
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<td>Coagulation pH</td>
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<td>Ferrate Dose—µM</td>
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<td>Filter Run Time—hours</td>
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### TABLE 3  Optimal ferric dose with and without ferrate preoxidant

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<thead>
<tr>
<th>Utility</th>
<th>Optimal Ferric Dose—<em>mg/L</em></th>
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<td>25 μM pH=7.5</td>
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<td>10</td>
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<td>Stockbridge</td>
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</table>

Coagulation pH = 5.5
Borate buffer = 1 mM