Use of Ferrate in Small Drinking Water Treatment Systems

Contents

Abstract

Funding Opportunity Title and Number: Research and Demonstration of Innovative Drinking Water Treatment Technologies in Small Systems; EPA-G2011-STAR-G1

Project Title: Use of Ferrate in Small Drinking Water Treatment Systems
Principal Investigators: David Reckhow (Lead PI), John Tobiason (Co-PI), Paula Rees (Co-PI)
Institution: University of Massachusetts, Amherst
Project Period and Location: January 1, 2012 to December 31, 2014, Amherst, MA
Project Cost: $497,078
Project Summary:

Many small drinking water systems are at a comparative disadvantage due to their size (e.g., limited financial and human resources), and sometimes due to their remote location. The challenge in meeting emerging regulations can be a formidable one. The objective of this project is to test the ability of ferrate oxidation to solve a wide range of water quality and treatment problems faced by small systems. The general working hypothesis is that ferrate is: (1) more effective and less detrimental than existing conventional oxidative technologies such as chlorination, chloramination, and permanganate oxidation, and that it is (2) comparable in performance to advanced technologies such as ozonation or chlorine dioxide oxidation that are more costly, more hazardous or require specialized expertise to operate.

This work will be conducted in laboratory-scale, pilot-scale and full-scale treatment systems. We will be using raw waters from 17 small drinking water systems representing a wide range of quality characteristics and treatment needs. These will be treated in the laboratory (either at UMass or Haskell Indian Nations University) using lab-scale versions of existing treatment processes, both with and without ferrate as a pre/intermediate or post oxidant, depending on the nature of the treatment train. In many cases we will add trace contaminants so as to challenge the system. Conditions (e.g., ferrate dose, pH, etc.) will be established to achieve a range of treatment goals. In 6 of these cases, we will establish small-scale continuous flow pilot plants using that same water and larger-scale treatment processes. This will allow us to collect more data on chemical performance while getting data on aspects that cannot be readily investigated at the bench scale (e.g., biological removal, sludge production, buildup of filter headloss. Finally, a large on-site pilot or full-scale until will be installed for final testing.

The proposed project will result in document providing guidance for the beneficial use of ferrate in small systems. We will highlight the ways it can be used to improve water quality, lower cost and provide a more sustainable treatment alternative to other technologies. We will also make use of the NIWR centers to help disseminate the information through workshops and various newsletters and publications.

Supplemental Keywords: oxidation, costs, NOM, DBPs, PPCPs

Research Plan

Background

Ferrate is a powerful oxidant and disinfectant that has been proposed for use in drinking water treatment in the US for more than a decade. In many ways, it can be considered a low-cost, simple alternative to ozonation, and thus it is well suited for use in small systems. Like ozone and chlorine dioxide, ferrate is a highly selective oxidant, but it does not lead to the formation of any know hazardous byproducts (e.g., no brominated or chlorinated DBPs, no bromate or chlorite). Despite its effectiveness and low cost, ferrate has only recently been used at full-scale for the first time in the US (a Florida groundwater plant). Until recently, a major impediment to its use has been the lack of availability of ferrate (e.g., Jiang & Lloyd, 2002). This obstacle seems to be rapidly disappearing, as several business ventures have been launched to fill this need. On such company is already offering full-scale units for on-site production and their officials cite a cost of only $0.06 per HCF[1], or about 2% of the average water charge in MA. There are competing technologies under development (e.g., electrochemical methods) and a flurry of US patent applications[2]. Now it appears that the biggest impediment is the lack of independent, unbiased information concerning ferrate's full impact on treatment systems and finished water quality. One of the objectives of this research is to provide such information so that regulators and water treatment managers can make informed decisions on this option.

Ferrate is considered to be a "green "chemical for use in water treatment (e.g., Ghernaout et al., 2011). This is partly because it doesn't produce any known toxic byproducts. The end product of ferrate oxidation is relatively benign ferric sludge and oxidized forms of water contaminants. Among the latter are oxygenated NOM molecules and compounds that are more readily removed by biodegradation. In addition, ferrate may be produced using standard chemicals that are often present in water treatment plants (i.e., ferric coagulants, caustic and in some technologies, chlorine), and its use is thought to reduce the subsequent need for these chemicals.

Ferrate is relatively unstable in the presence of moisture and therefore it is considered most practical to generate it on site near the point of use. There are three general methods used to generate ferrate, all from readily-available starting materials of good stability and all using alkaline conditions. These include: (1) the electrochemical method, (2) the high-temperature dry oxidation method, and (3) the ambient temperature wet oxidation method. The first and third methods are the ones considered most practical for drinking water applications. Electrochemical methods have been the subject of many recent publications in the open literature (e.g., Licht & Yu, 2005; Yu & Licht, 2008; Mácová et al., 2009; Jiang et al., 2009; Alsheyab et al., 2009; Alsheyab et al., 2010a; Alsheyab et al., 2010b; Sánchez-Carretero et al., 2011).

In contrast there has been less openly-published material on the wet oxidation method, even though this is the method of choice among water treatment researchers doing bench-scale studies. Modern laboratory methods using room-temperature wet oxidation achieve 50-70% yields with a final crystalline product of 99% purity (e.g., Li et al., 2005). Stability and probably yield can be improved with exclusion of trace metals that can catalyze ferrate decomposition.

---

[1] Based on figures from Tom Waite, FTT, and presuming a 2 mg/L dose; personal communication August 2011.
[2] Many from: Lynntech (e.g., US6,946,078), Battelle (e.g, US2009/0205973), FIT (e.g., US2011/0076223)

There is little doubt that proprietary studies have been conducted by firms wishing to commercialize this technology (e.g., Ferrate Treatment Technologies, LLC). The FTT technology uses ferric chloride, caustic and sodium hypochlorite to produce aqueous ferrate in an on-site reactor. FTT claims the wet oxidation method can produce ferrate at less than 10% of the cost of acquiring commercial dry ferrate.

$$Fe(OH)_3 + \tfrac{3}{2}OCl^- + 2OH^- \rightarrow FeO_4^{-2} + \tfrac{3}{2}Cl^- + \tfrac{5}{2}H_2O$$

(1)
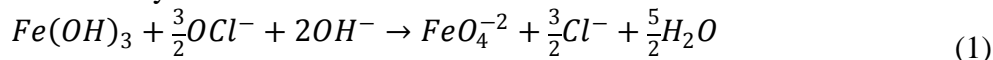
Ferrate chemistry and reactivity are highly pH-dependent. Ferrate exists in various protonated forms in water with pKas of 1.6, 3.5 and 7.3 (Licht et al., 2001). Ferrate will spontaneously decompose in the presence of water at neutral pHs forming oxygen and ferric hydroxide (equation 2). Li and co-workers found ferrate solutions to have a half-life of about 3 minutes at pH 7.1, increasing to a maximum of about 2 hours at pH 9.2 and then gradually decreasing to about 14 minutes at pH 11.9. Ferrate has a higher redox potential at lower pHs and the mono-protonated form (which becomes significant below pH 8.5) is the more reactive. Lee and von Gunten's (2010) found ferrate to be similar to chlorine and chlorine dioxide in its rate of loss in secondary wastewater effluent, except that it didn't show an initial rapid loss (i.e., "immediate demand"). Schink and Waite (1980) presented evidence for autocatalytic decomposition of ferrate, possibly catalyzed by the formation of ferric hydroxide solids.

$$FeO_4^{-2} + \tfrac{5}{2}H_2O \rightarrow Fe(OH)_3 + \tfrac{3}{4}O_2 + 2OH^-$$

(2)
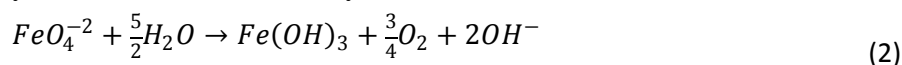
There is a large body of literature extending as far back as the 1970s on the effectiveness of ferrate for oxidation of metals, non-metals, and organic contaminants in water and wastewater treatment. These include ammonia, cyanide, thiocyanate and sulfide (Licht & Yu, 2005; Sharma, 2002), iodide (Sharma, 2010), arsenic (Lee et al., 2003), carbohydrates (BeMiller et al., 1972), alcohols (Delaude & Laszlo, 1996; Ohata et al., 2001; Norcross et al., 1997; Firouzabdi et al., 1988; Audette et al., 1972), toluene and cycloalkanes (Delaude & Laszlo, 1996), ketones and hydroquinones (Firouzabdi et al., 1988), phenols (Huang et al., 2001; Graham et al., 2004; Lee et al., 2005), aminobenzene (Huang et al., 2001), estrogens (Lee et al., 2005; Sharma et al., 2008), Bisphenol A (Sharma et al., 2008; Zhang et al., 2010), pharmaceuticals (Sharma et al., 2008; Lee et al., 2009; Lee & von Gunten, 2010), cyanotoxins (Luca et al.,. 2010), triclosan (Yang et al., 2011a) and benzotriazoles (Yang et al., 2011b). Lee and von Gunten (2010) conducted comparative studies of 5 oxidants commonly used in drinking water treatment. They concluded that ferrate was "more efficient to transform phenol-containing than olefin- and amine-containing compounds." Nevertheless, most organic amines will degrade in the presence of relevant levels of ferrate (e.g., review by Sharma, 2010). Many of the rate constants cited by these authors and others correspond to contaminant half-lives of well below one minute under normal ferrate dose conditions. Unlike ozone, ferrate does not oxidize bromide (Sharma, 2010), and therefore it does not form bromate or brominated organic byproducts, nor does it form chlorinated byproducts. Kinetic evidence supports mono-hydrogen ferrate ($HFeO_4^-$) as the primary reactive species, which can undergo both one electron and two electron transfers as well as oxygen transfer, depending on the reactant (Sharma, 2010). When one and two electron transfers occur, the highly reactive Fe(V) and Fe(IV) may form, giving rise to a much faster reacting, transient, oxidant species. Despite the extensive literature, there is still quite a bit of uncertainty about pH effects, solute effects, and reaction pathways involving ferrate oxidation.

Ferrate is also known to be an effective disinfectant. Coliphage (Kazama, 1995), f2 virus (Schink & Waite, 1980), coliform bacteria (Sharma et al., 2005) and algae (Ma & Liu, 2002) can be effectively removed or inactivated with ferrate. Inactivation seems to occur faster as the pH

drops, a phenomenon that has been attributed to the mono-protonated form of ferrate ($HFeO_4^-$; Sharma, 2007). Even though they have similar redox potentials, ferrate was found to be substantially less effective at inactivating *B. subtilis* spores as compared to ozone (Makky et al., 2011). These authors attribute the difference to decomposition and precipitation of Fe(III) on the spore coat layer, which could protect the spore from further oxidation.

Ferrate treatment will impact subsequent treatment in many ways. Most directly, added ferrate rapidly forms an equivalent amount of ferric hydroxide floc, thereby serving as an in-situ coagulant. Some have reported that the ferric coagulant formed by ferrate is actually more effective on a mole-Fe basis than conventional ferric sulfate for removal of color and UV absorbance (White & Franklin, 1998; Jiang et al., 2001) and THM precursors (Jiang & Wang, 2003). In other studies it has been less effective, at least at higher doses (Jiang & Wang, 2003). Graham and co-workers (2010) explored these effects in greater detail, trying to separate direct effects of NOM oxidation from subsequent removal of NOM by ferric floc. They determined that moderate doses of ferrate resulted in about 3 % loss in TOC at pH 7, increasing up to 30% at pH 5, an effect that is a direct result of oxidation of NOM to CO_2. In addition, there is molecular fragmentation and increases in oxygenated functional groups in partially oxidized NOM molecules, manifesting itself in the form of increased acidity and charge. These authors also observed improved floc formation by ferrate addition as compared to ferric chloride.
In many ways, the addition of ferrate is much like the combined use of pre-ozonation and alum coagulation, the latter having been much more intensively studied. Low doses of a strong pre-oxidant can result in direct oxidation, and possibly better removal by subsequent coagulation via a number of postulated mechanisms (Reckhow et al., 1986). By analogy, one would expect high doses of ferrate to excessively oxidize the NOM rendering it less adsorbable to ferric floc, much as ozone does (e.g., Reckhow et al., 1986).

The analogy between ozone and ferrate is not perfect, however. Differences include the unavoidable coupling of oxidant dose with coagulant dose when both are a result of the same chemical addition (i.e., ferrate). Also, the higher reactivity of ferrate at low pH is in contrast to ozone, which undergoes more rapid decomposition forming hydroxyl radicals at high pH. Also, it's quite likely that the initial ferric hydroxide precipitate is different between the ferrate and ferric system. In the former case, Fe(III) is generated in-situ at lower rates as pH increases. This is probably not the case with ozonation-coagulation as the coagulant is added in the same fashion regardless of whether it is preceded by ozone.

Addition of ferrate also results in elevated levels of biodegradable organic compounds. Ramseier and colleagues (2011) found nearly identical formation of assimilable organic carbon (AOC) when equimolar doses of ozone and ferrate were applied to Lake Zurich water. These authors also measured oxalate formation (a component of AOC) and found a linear relationship with dose that differed between ferrate and ozone (~1% molar yield vs ~4%). For reasons that are not well understood, ozone produced AOC that is richer in oxalate than does ferrate. This means that much like ozone, ferrate treatment should be followed by biological treatment, generally biologically-active filtration. This is very much in accord with the need to remove residual ferric solids by filtration.

Objectives

Many small drinking water systems are at a comparative disadvantage due to their size (e.g., limited financial and human resources), and sometimes due to their remote location. The challenge in meeting emerging regulations can be a formidable one. The objective of this project

is to test the ability of ferrate oxidation to solve a wide range of water quality and treatment problems faced by small systems. The general working hypothesis is that ferrate is: (1) more effective and less detrimental than existing conventional oxidative technologies such as chlorination, chloramination, and permanganate oxidation, and that it is (2) comparable in performance to advanced technologies such as ozonation or chlorine dioxide oxidation that are more costly, more hazardous or require specialized expertise to operate.

The fundamental hypothesis of this proposal is that use of ferrate in small drinking water systems
1. can be done without great expense. In most systems, it will simply require the addition of some mixing equipment, possibly a change in coagulant, and may even make use of existing feed pumps, and
2. will bring substantial improvements in finished water quality, especially as regards to trace organic contaminants and DBPs.

For systems treating surface water, conversion to ferrate treatment is viewed as a relatively minor process change that can have a major impact on water quality and treatment performance. Most surface water plants, regardless of size, use a coagulant along with a chemical disinfectant and corrosion control chemicals. Quite frequently the disinfectant is some form of chlorine, caustic is used for pH control and in a substantial number of plants, the coagulant is an iron salt. From the standpoint of operations and chemical needs, ferrate is little more than a pre-mix of the three treatment chemicals. Of course, the mixing conditions are quite important, but the "footprint" for the mixing units can be quite small. Once prepared, ferrate can be added to an existing treatment train at any one of a number of locations depending on the objectives, raw water quality and treatment process layout. In general ferrate would be added at the head of treatment in plants were pre-oxidation is needed or desirable (e.g., for Fe/Mn control, control of microbial growth, for stimulation of biodegradation in slow sand filters, for general oxidation/disinfection if adequate contact time isn't provided in subsequent processes). Since ferrate addition results in the precipitation of ferric hydroxide, it will generally be desirable to apply ferrate prior to particle removal (e.g., rapid media filtration, pressure filtration, low pressure membrane treatment).

For systems treating groundwater, the use of coagulants and disinfectants is not nearly as universal as it is for surface water plants. For some of these with existing treatment for iron and manganese, the use of ferrate may be as simple as it is for the surface water plants. However, groundwater systems without treatment or those only adding disinfectants or corrosion control chemicals, it may be necessary to add a particle removal step (e.g., filtration) if ferrate treatment is to be incorporated.

Approach:
In this section we describe:
1. How the proposed innovative treatment (ferrate oxidation) will be **demonstrated** for use in small water systems such that we can determine performance, sustainability and economic viability
2. How this available treatment technology (ferrate oxidation) can be further developed and demonstrated to **remove or mitigate groups of chemical contaminants and precursors** from drinking water systems. As part of this we will describe how specific drinking water quality improvements will be measured.

3. How we will show that the proposed treatment (ferrate oxidation) represents an **improvement** over existing technology regarding capital, operation and maintenance costs.
4. How the results of this project can be **communicated and transferred** to small water systems so they can deliver safe water at reduced costs with energy efficient technologies.

This work will be conducted at bench-scale, laboratory pilot-scale, on-site pilot-scale and full-scale. We will be using raw waters from 17 small drinking water systems representing a wide range of quality characteristics and treatment needs. These will be treated in the laboratory using lab-scale versions of existing treatment processes, both with and without ferrate as a pre/intermediate or post oxidant, depending on the nature of the treatment train. In many cases we will add trace contaminants so as to challenge the system. Conditions (e.g., ferrate dose, pH, etc.) will be established to achieve a range of treatment goals. In 6 of these cases, we will establish small-scale continuous flow pilot plants using that same water and properly scaled versions of the full-scale treatment processes. In each of the lab studies, we will add challenge compounds, including a suite of PPCPs, EDCs and pesticides. These will be measured at various points across treatment to determine effectiveness of removal. This will allow us to collect more data on chemical performance while getting other data on aspects that cannot be readily investigated at the bench scale (e.g., biological removal, sludge production, buildup of filter headloss. This work will culminate with an on-site 3-season pilot program with the intention of getting approval in MA for use of ferrate. Finally, tests will be run on the only existing full-scale ferrate system to examine effects on finished water in the distribution system.

One important step in use of ferrate is to decide on the most appropriate point of addition. In general ferrate should be added prior to a filtration or particle removal step such as:
- Conventional rapid media filtration
- High rate systems (e.g., trident, actiflow)
- Pressure filters
- Slow sand filtration
- Low pressure membranes

In some cases, modifications might need to be made to accommodate the expected ferric floc. For example, sand of larger-than-normal grain size might be needed to allow for less frequent cleaning of slow sand filters. This is the approach that has been used at locations such as Portsmouth NH which treats a water with very high natural levels of iron (Collins, 2011 [personal communication]).

Task 1: Finalization of Participant Systems and Selection of Challenge Compounds

There are numerous small systems representing a wide range of types (e.g., differing raw water sources, raw water quality, sizes, and existing treatment technologies) within easy driving distance from both UMass and Haskell Indian Nations University. We will make use of this fortunate geographical situation to cast a wide net, while minimizing travel/transport costs. Near Haskell, we have already identified two systems to work with, one serving the Kickapoo tribe and one serving the Potawatomi Tribe. In addition to these two, we will select 15 more for

bench-scale study (Tier 1). Of these 7 will be chosen for the lab-scale pilot studies (Tier 2), and one will be selected for a full on-site 3-season pilot study.

To save on transportation costs, we will first look to utilities within a 100 mile radius of UMass. This gives us a very large and diverse group to work from. In the western region of MA alone, there are 164 small community water systems. In this region are 12 slow sand filtration plants, which offer us an easy opportunity to work with this technology. We have a longstanding collaboration with Robin Collins of UNH[3], and we would engage him as an advisor for any SSF studies. In contrast the Central Region of MA has many small groundwater systems with high arsenic levels.

For example, likely locations in the Western Region of Massachusetts for this work include:
- Package Plants: North Adams, South Deerfield, Stockbridge, Palmer
- Slow Sand Filtration Plants: Dalton, Hinsdale, Hatfield, Russell
- Ozone/SSF: Blandford

The PIs (Reckhow & Tobiason) have extensive experience in working with local utilities. We will consult with the state primacy agency (MA DEP) and representatives of the candidate utilities to determine a final list.

The selection of challenge compounds will depend on factors such as cost, availability, health and future regulatory relevance, co-occurrence, and local occurrence/interest. One of the PIs is mid-way through a WRF study (#4260) on developing guidance for utilities interested in monitoring for PPCPs and EDCs. One of the objectives of that work is to develop a set of indicator PPCPs that represents the larger universe of compounds. The proposed work will benefit from this effort. As a point of departure, we would first select the list of compounds that we have been monitoring in related water treatment studies (Table 1.). Once the final selection is made, we will prepare one or more aqueous spiking solutions for use in the Task 2 and 3 treatment studies.

Table 1. Current List of PPCPs, EDCs and Pesticides Monitored in the UMass Lab

Atenolol	Caffeine	Acetaminophen
Atorvastatin	Cimetidine	4-androstene-2,17-dione
Ciprofloxacin	Cotinine	Diclofenac
DEET	Diltiazem	Diethylstilbesterol
Naproxen	Diphenhydramine	Doxorubicin
Propanolol	Metformin	Estradiol
Ranitidine	Miconazole	Estrone
Ranitidine d6	Salbutamol	5-fluorouracil
Sulfamethoxazole	Thiabendazole	Ibuprofen
TCEP	Warfarin	Nonyphenol
Trimethoprim	Xanthine	4-(tert)-octyl)phenol
Atrazine	Triclosan	Primidone

---

[3] We did not seek a formal letter from Dr. Collins as he is also responding to this same RFA.

Task 2. Bench-Scale Demonstration of Feasibility

Bulk samples will be collected from each of the tier 1 utilities and treated both with and without ferrate under a variety of conditions to test for treatment performance. Chemical usage can be assessed by comparing the necessary usage rate of chemicals under the ferrate scenario (i.e., ferric salts and chlorine) vs the usage rate from the existing plant.

A volume of 40 liters will be collected from each raw or partially-treated waters (collected just prior to planned point of addition of ferrate) and transported to the UMass or Haskell laboratories for testing. Once at UMass/Haskell the water will be subject to a series of bench-scale treatments. An experimental control will be run that follows the full-scale treatment plant in terms of chemical doses, order of addition, process sequence and reaction times. Non-ferrate experimentals will follow the control sequence but incorporate alternative coagulant dosing so that a range of doses is examined. If the plant under investigation doesn't use ferric salts, a set of experimental runs will be added where ferric chloride is used instead and a range of ferric doses will be used. The ferrate experiments will, of course, include application of ferrate (in pure form, prepared in accordance with Thompson et al. (1951)). Dose will be a variable to be explored as will pH. Tests will be run to determine natural organic matter concentrations and character (e.g., DOC, UV abs), particles (e.g., turbidity), inorganic contaminants (e.g., Fe, Mn), trace organic contaminants (e.g., pesticides, PPCPs, EDCs) and residual ferrate. Following final disinfection, chlorination byproducts will be determined (e.g., THMs, HAAs). One of the PIs (Reckhow) recently completed a laboratory study of 15 utilities aimed at determining PPCP and EDC removal using their existing treatment systems. Samples of the full-scale filtration media were extracted and used in the lab to best simulate chemical and biological removal mechanisms. The proposed study would benefit from our recent experience of running lab-scale treatment units for assessment of emerging contaminant control.

Task 3. Small Pilot Scale Demonstration

For these tests, we will study the seven tier 2 utilities. Large volume (325 gal) samples will be collected in a truck-mounted polyethylene tank and transported to the UMass laboratory on a daily basis or as needed. These will be spiked with the challenge compounds and the water will be pumped through a continuous flow pilot with two parallel trains. We will use the pilot area of the UMass environmental engineering laboratory and select unit sizes depending on the particular treatment sequence in the full-scale plant. For example, rapid media filters may be simulated in 2, 3 or 4 inch columns (Table 2), packed with actual media from the plant, acquired with a cylindrical coring device driven into the fluidized bed during backwash. The filters will be fitted with manometers so that headloss can be monitored at various depths.

Table 2. Example Run Lengths for Single batch dual train operation at 2-8 gpm/ft^2 for three column sizes

Filter Column Diameter	Flow Rate	Run Lengths
2 in	0.09-0.35 gpm	15-62 hr
3 in	0.2-0.8 gpm	7-27 hr
4 in	0.35-1.4 gpm	4-15 hr

Parameters to be measured will include those listed for the Task 2 studies. In addition, we will be monitoring headloss buildup during each filter run. The laboratory-scale pilot studies will be

run repeatedly until sufficient data is acquired to assess performance regarding water quality, likely filtration run time, biodegradation in the filters and sludge production.

Task 4. On-site Large Pilot Scale Demonstration

Following task 3 we would identify on utility for installation of an on site pilot plant. The purpose would be to demonstrate the process for approval by the State primacy agency. One of the commercial Ferrate suppliers will provide the ferrate production equipment, free of charge. Currently only FTT has reached the stage where they can provide full-scale equipment (letter attached), but others may be available by the time Task 4 is initiated. We would conduct the study in accordance with MA DEP Guideline #90-04 (http://www.mass.gov/dep/water/laws/9004.doc), which opens the door for full acceptance for new and innovative treatments in the Commonwealth of Massachusetts. Acceptance of ferrate in MA will substantially reduce the burden for interested utilities and consultants to do likewise in other states. The exact operating and monitoring requirements for this pilot will have to be established in consultation with MA DEP. This will likely involve submission of data from Tasks 2 and 3. Preliminary discussions with the new technologies team at DEP have shown them to be quite receptive to testing and possible acceptance of ferrate.

Task 5. Full Scale Demonstration

Long term impacts of ferrate, especially on impacts on distribution systems, can really only be assessed in full-scale. Fortunately, there is a system in Florida that is just starting to use ferrate on the water distributed to their customers. While this is a rater unusual case (high sulfide groundwater), we will take advantage of this unique opportunity and do some detailed assessments. We will collect data on costs, water quality, operations and consumer complaints, both before and after the switch. We also expect to collect some finished water from various locations in the distribution system to look at emerging contaminants, especially emerging DBPs. One of the PIs (Reckhow) is currently leading a WRF study (#4242) on unregulated DBPs in distribution systems. The proposed study will take advantage of the analytical methodologies developed for a wide range of compounds of human health concern (e.g., halonitromethanes, haloketones, haloaldehydes, haloacetamides, halobenzoquinones, iodo-THMs, TOCl, TOBr and TOI).

Task 6. Summary and Assessment of Treatment Costs

Assessment of treatment costs will incorporate data from all three experimental scales: bench, pilot and full. The cost assessment will include changes due to ferrate addition in:
- Chemical costs
- Capital costs
- Electrical costs
- Personnel costs
- Sludge disposal costs

Each of these must consider:
- Incorporation of ferrate addition to the treatment train

- Changes in other processes that result from the use of ferrate (e.g., reduced chlorine addition, elevated acid addition)
- Changes in sludge volume and treatability

Of special interest will be the chemical and electrical costs observed in the on-site pilot plant and the full-scale plant.

Analytical Methods

This study involves a wide array of analytical methods ranging from the conventional water quality parameters to the most recent emerging contaminants. For the conventional parameters (e.g., turbidity, pH, alkalinity, residual chlorine, chloramines, TOC, DOC, UV absorbance) we will follow Standard Methods (APHA et al., 2006). Analysis of regulated DBPs will be done in accordance with EPA methods 551.1 and 552.2 for the THMs and HAAs, respectively.

Measurement of Residual Ferrate. Concentrations of ferrate in pure stock solutions can be determined by direct spectrophotometry at 510 nm (pH 9.1 absorptivity of 1150 $M^{-1}cm^{-1}$; Bielski & Thomas 1987), but care must be taken as this requires baseline correction at 385 nm for colloidal iron (Li et al., 2005) and careful attention to pH. Residual concentrations in treated water samples have often been determined by oxidation of Cr(III) to Cr(IV) and back titration with a standardized ferrous ammonium sulfate solution (Vicenteperez et al., 1985; Jiang & Wang, 2003). However a simpler and more sensitive method makes use of the rapid oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) or ABTS, and subsequent detection of the oxidized form by absorbance at 415 nm (ε=34,000 $M^{-1}cm^{-1}$; Lee et al., 2005).

Emerging, Non-Regulated DBPs. For this group of compounds we will use the methods that have been developed in the UMass lab for WRF project #4242. For example, a Bond Elut SPE/GC/ECD method has been modified and used for about 40 chlorinated and brominated semi-volatile compounds (Chinn et al., 2007). For the halobenzoquinones we use an HLB/LC/MS/MS method developed as part of another WRF project (Zhao et al., 2010). Hua and Reckhow (2006) serves as the basis for our TOCl, TOBr and TOI methods.

Endocrine Disrupting Compounds (EDCs), Pharmaceutical and Personal Care Products (PPCPs) and Pesticides. We have focused most of our analytical efforts in this area using liquid chromatography with triple quadrupole mass spectrometry (LC/MSMS). In the PIs lab (Reckhow), we have two such instruments that will be available for this project, in addition to an LC/MS ion trap, a GC/MS ion trap and a time-of-flight GC/MS. Our early work has employed methods based on USEPA 1694 with isotope dilution (Vanderford & Snyder, 2006). More recently, we've been moving toward the method that will ultimately be recommended by the Round Robin Study group (WRF #4167), also know as the San Jose Creek WQL method.

Haskell Indian Nations University Partnership

Haskell, located in Lawrence KS, is a full member of the White House Initiative on Tribal Colleges and Universities. Through their research-active faculty and their BS Program in Environmental Science, they have a long history of working with local Indian tribes on environmental research. The primary contact at Haskell for this project will be Professor Carole Tomlinson, Chair of the Natural Sciences Faculty. The Natural Science faculty supports a Bachelor of Science degree in Environmental Science

Before the beginning of year 1, four Haskell students will be selected to work with the UMass researchers on this project. These students will work primarily under the direction of Dr. Tomlinson. They will work part-time on this during the semester, earning independent study credits. One of the UMass PIs (Reckhow) will travel to Haskell for the purpose of initial training. During the summer the Haskell students will transition to paid full-time positions and two of them will travel to UMass for a period of 3 weeks for additional training with UMass graduate students and researchers.

The work conducted at Haskell will focus on application of ferrate to two local tribal water supplies, those used by the Kikapoo and Potawatamee communities. The Kansas Kikapoo Tribe has been in its current location, 60 miles northwest of Lawrence KS since 1832. The tribe operates a surface water plant using water from the nearby Delaware River, and has been plagued by poor water quality and high disinfection byproduct levels. The kikapoo filtration plant was recently modified to incorporate chloramines as a residual disinfectant. It is currently in the monitoring phase for the Stage 2 D/DBP Rule.

The Prairie Band Potawatomi Nation has existed on its current reservation near Holton and Mayetta KS northeast of Lawrence since the 1860s. Most of the Potawatomi community is served by the Jackson County Rural Water District #3. This supply draws its water from the Banner Creek Reservoir and serves a total population of 4,060. The remaining population is served by Jackson RWD #1, which is a separate surface water supply (total pop served: 2500). The Haskell students will collect samples from both supplies and treat them with ferrate and subsequent treatment processes (e.g., filtration) in the laboratory of Dr. Tomlinson. They will monitor the samples for the same set of process parameters as followed at UMass (e.g., residual ferrate, Fe, Mn, UV abs, turbidity, pH). Final treated samples will be shipped to UMass for analysis of DBP Precursors and NOM. The Haskell students will develop relationships between ferrate dose, coagulant dose, pH and chlorine dose and finished water quality. They will also perform a comparison of full treatment costs with the existing system and several alternative systems employing ferrate.

Haskell faculty and students who participate in this project will benefit in a number of ways. Biology faculty will learn up-to-the-minute technological applications in water analysis and treatment and gain new capabilities, using research supplies provided by the grant, to teach such skills and concepts to students. Students will gain real world knowledge of tribal community needs and build skills that will be in demand in their post-baccalaureate experience as they meet and solve environmental challenges. Both faculty and students will add to a network of environmental scientists as they meet staff in tribal environmental offices. Finally, the project will meet strategic goals of the university: to maintain high quality baccalaureate degrees in environmental science, to improve student advancement, to provide specific opportunities for faculty and experiences for students, to enhance communication in meeting educational needs, to encourage and support academic research and creative activities that advance knowledge, and to serve Native communities.

NIWR Water Center Partnership

WRRC Role – Dialogue, Dissemination, Translation. Housed in the country's top land-grant universities in each of the 50 states, the District of Columbia, the Virgin Islands, Puerto Rico and Guam, the 54 National Institutes for Water Resources (NIWR) provide a national platform for research, training and collaboration. Collectively, the water institute program is an established network with capabilities both broad and deep, addressing the cutting

edge of virtually every facet of water resources and providing linkages across multiple sectors (academic – regulatory - private – non-profit) and scales (local – state – regional - federal). The institutes are well versed at providing hands-on educational opportunities, helping to train the workforce necessary to meet the Nation's water resources challenges, and through technology transfer efforts provide scientifically credible communication of research results and needs. NIWR institutes focus on science. As such, they are not limited by policy-driven or regulatory missions, can serve as objective brokers of information among constituencies, are not limited by policy-driven or regulatory missions, are equipped to examine long-term consequences of policies and practices, and can be flexible and adaptive to local cultures, institutions of governance, and regional socio-economic and physical conditions.

We propose to collaborate with the national network of NIWR institutes to open a dialogue on the applicability of ferrate oxidation to solve water quality and treatment problems across the Nation, broadly disseminate the results of this research, and foster translational adoption of the technology by small drinking water systems through education and training. We will coordinate these efforts through the Massachusetts Water Resources Research Center (MaWRRC) at UMA, created in 1965 as one of the 54 NIWR institutes.

To foster dialogue, disseminate information and research results, and promote translation of ferrate oxidation technology, we propose the following:

1. **Survey of Small Drinking Water Utility Needs** – We will develop a brief electronic informational survey for distribution to small drinking water utilities across the U.S. to gain a better understanding of the breadth of challenges across the Nation., The survey will seek information on three basic topics: treatment technologies and process flow, plant challenges/issues where help is needed, and the nature of raw water sources. The survey will be much shorter than, but complementary to the EPA WTP eSurvey conducted in 2007 for WTPs serving 10,000 or more people.

    We propose distributing the survey to medium-size drinking water systems, those serving populations between 3,301 and 10,000, for which we can readily obtain email contact information. We estimate that there are approximately 8,000 systems within this category. Because we are not aware of a current national email contact list for these systems, we will develop as comprehensive a list as possible by contacting the following organizations to obtain any email contact information they have: 1) the eight EPA Small Drinking Water System Technical Assistance Centers (MT, PA, NJ, MS, WV, AK, CA, New England), 2) the 10 regional EPA offices, 3) the department of environmental protection in each state, and 4) the 54 NIWR institutes. We will also advertise the survey through Newsletters (#3 below) and our website (#2 below).

    The MaWRRC will work with our NIWR institute peers to distribute this survey in each state –, the request to participate in the survey will come from the local NIWR institute staff. Through endorsement by the NIWR institutes, a trusted and known entity, greater participation in the survey is anticipated. The MaWRRC will cover all dissemination costs and be responsible for collating all responses. While the project PIs and MaWRRC staff will create the initial distribution lists for each state, local NIWR institute staff will help develop the final distribution list.

    Besides providing information on the potential for ferrate oxidation technologies to address small drinking WTP needs, data from the survey will help us identify the most strategic locations for our technology transfer workshops (described below).

2. **Massachusetts Small Drinking Water System Clearinghouse (MaSDWS)** – The MaWRRC will develop a web site to *demonstrate* effective translation of information on treatment technologies, including emerging innovative technologies, of relevance for small drinking water systems. To our

knowledge, such information is currently not available in one-place, online, and in a user-friendly format, even through the eight EPA Small Drinking Water System Technical Assistance Centers. EPA's Tech Brief on the topic (*Treatment Technologies for Small Drinking Water Systems*), the best source in one place, is available only as a poster pdf. The MaSDWS demonstration website will include the following:

a.   With EPA's permission, information from the Tech Brief will be posted in a user-friendly format and updated to include available information for up to five emerging innovative technologies.

b.   We will provide documents and links to other relevant sources for information on novel and innovative treatment technologies and approaches for small public drinking water systems.

c.   We will develop and post an individual Technical Brief for up to five emerging innovative technologies, including ferrate oxidation, and utilizing a standard format. Pending availability of information, each technical brief will include the following sections: 1. *Technical Overview* (treatment chemistry, typical location within process stream, capital investment needs, maintenance needs, footprint requirements, operator skill level requirements); 2. *Applications and Limitations* (type of compliance technology, compatibility with other processes, public acceptance, aesthetics, potential/known issues, raw water quality range and considerations); 3. *Regulatory Status* (acceptance status, effectiveness, applicability for anticipated future regulatory needs); 4. *Sustainability Statement;* 5. *Associated Costs;* 6. *Contacts & Further Information* (supplier list, operators who have utilized the technology, researchers familiar with technology, pertinent references).

d.   We will start to develop a database of treatment technologies for small drinking water systems. Ultimately (e.g., *beyond this project*) we aim to expand the scope of MaSDWS by seeking external funding to make this a searchable database of innovative technologies and to support review of technology specification and performance data submitted through a data entry tool as well as from the scientific literature.

The web site will also be used as an outreach tool, advertising project workshops, presenting research results for ferrate oxidation, and providing survey results. The MaWRRC has a history of successfully serving as a clearinghouse for such information (see www.mastep.net).

3.   **NIWR Institute Newsletters** – Most of the NIWR institutes distribute a newsletter for their constituents at least once a year. The MaWRRC will work with our NIWR institute peers to include a brief article about our research project in their Newsletter, providing direct contact information as well as the links to the informational survey and the MaSDWS clearinghouse, and advertising the workshop described in #4 below**.** We will also request that the eight EPA Small Drinking Water System Technical Assistance Centers publish a similar notification. This task will help support grass-root level information and technology transfer.

4.   **Technical Transfer Workshops –** Most of the NIWR institutes hold conferences and workshops each year. These are unique venues where agencies, operators, academics, and consultants can readily be brought together. We propose to work with four regionally distributed NIWR institutes to hold a 2-day workshop at each of the 4 locations directed towards small drinking water system operators (providing TCHs and CEUs), regional regulators, and other interested parties. The workshops will be based on a subset of the material typically offered through the 3-day UMass Drinking Water Treatment Institute with a 21-year history of presenting the fundamentals of drinking water treatment processes, discussing new developments in drinking water treatment, applying processes discussed to existing and proposed drinking water requirements, and illustrating applications of principles and practice using case studies. Workshop content will be re-developed to focus on small drinking water system needs and to include ferrate oxidation as one of the treatment processes overviewed. The NIWR workshops will be offered free of charge, excluding travel and food, to participants by working with our NIWR partners to provide local facilities to host the workshop at no charge. Travel

and remuneration for the course instructors (PIs: Reckhow & Tobiason), course material costs, and workshop organization and management will be provided through the EPA grant.

We will work with the NIWR host to ensure that the workshop invitation distribution list includes interested parties (e.g., small drinking water treatment operators and regulators) from nearby states as well as those within state. As for the survey, invitations and advertising for the workshop will come from local NIWR institute staff. Through endorsement by the NIWR institutes, a trusted and known entity, greater participation in the workshops is anticipated.

The four-pronged approach described above for dissemination of the project results will facilitate a national two-way dialogue at the grass-roots level as well as expedite potential adoption of the technology by small drinking water systems.

Innovation:

This project is innovative because it creates an opportunity to bring a highly-promising treatment technology (ferrate) out of the rarefied research laboratory and into practice. Until this point only a few research teams have been studying ferrate and mostly for its kinetic rates with trace organic contaminants. The focus has been on the very narrow question of whether ferrate oxidation can remove certain anthropogenic constituents, with little regard as to how it impacts general treatment performance, control of NOM, reduction of DBPs, cost of treatment, etc. With only one very recent exception, ferrate has not been used for potable water treatment in North America. This research will build on the fine fundamental work that has already been done and in just 2-3 years it will supplement it with the key information necessary to bring ferrate into practice in the US.

Sustainability

Altering existing treatment systems to include ferrate is viewed as a highly sustainable, low impact change. In its most applicable form, it simply involves redirecting currently-used treatment chemicals so that they are mixed prior to addition. Under this most direct scenario, there are no additional chemical or energy costs, nor are there any additional residuals over what is currently used/generated. There will be some cost in purchasing the mixing equipment, but the associated energy & carbon footprint of producing this equipment will be relatively minor compared to the overall treatment and distribution infrastructure.
The oxidative energy (potential) of the aqueous chlorine is passed on to chemical and microbial contaminants in the water via the intermediary, iron. In this way, all of this transferred chemical energy goes to oxidation (electron transfer) and none of it goes to the production of unwanted carbon-halogen bonds (e.g., no halogenated DBPs). Furthermore, the oxidized iron (ferrate) has electron transfer pathways available to it that chorine does not, so it is kinetically advantageous.

Expected Results, Benefits, Outputs and Outcomes

The principal output of this work will be project reports, publications, newsletters, a website, and presentations (at small-system workshops as described above and at professional meetings). The outcome of this work is expected to be a rapid acceptance of ferrate and readily dissemination to small utilities as to where and how ferrate might help. In conducting this research and with the

NIWR outreach plan, we will be fostering a stronger relationship between the NIWR centers and small water utilities in their states. While some NIWR centers have been playing an important role in the potable water arena (e.g., NC's Urban Water Consortium), most have not. Better partnership between the NIWR centers and EPA's Small Drinking Water System Technical Assistance Centers would be a longer term goal.

General Project Information

Each of the project PIs and Co-PIs will meet weekly with students and staff on the project. In addition, all UMass members of the project team will have bi-weekly meetings to discuss progress, problems and the need for changes, if any. The PI, Co-PIs and Subcontractor for this project include:

David A. Reckhow. Dr. Reckhow will be responsible for overall management of the project. He will oversee on of the UMass graduate students, the research associate and coordinate work with Haskell and the MA WRRC. His primary area within the technical work plan will be bench-scale studies, general chemistry, kinetic modeling, and analysis of trace contaminants. Both Drs. Reckhow and Tobiason will work with the local Northeast US water utilities and they will also co-run the four small systems workshops.

John E. Tobiason. Dr. Tobiason will work closely with Dr. Reckhow most aspects of this project. His primary area within the technical work plan will be pilot-scale studies, filtrations, general water treatment, and manganese control. As mentioned previously, Dr. Tobiason will also co-run the four small systems workshops.

Paula S. Rees. As WRRC Director, Dr. Rees will oversee all of the activities undertaken by the Massachusetts center. She will also serve as liaison with the other NIWR Centers

Haskell Indian Nations University. Haskell is the sole subcontractor on this project. Dr. Carole Tomlinson will be the principal contact at Haskell. Dr. Tomlinson will oversee the four Haskell students and direct their work in her Lawrence, KS lab. She will serve as primary liaison with the two tribal communities.

The project schedule is shown below:

Task	2012				2013				2014			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1. utility selection	blue											
2. bench-scale studies	blue	blue	blue	blue	blue	blue						
3. lab pilot studies			blue	blue	blue	blue	blue	blue				
4. field pilot studies								blue	blue	blue		
5. full-scale studies	green	green	green	green								
6. cost analysis									green	green	green	green
Workshops									blue	blue	blue	blue
Reporting				red				red				red

Quality Assurance Statement

The lead PI (Reckhow) is primarily responsible for maintenance of QA/QC. He will work through the Research Associate, Graduate Research Assistants and the Haskell Undergraduate Assistants to make sure criteria are met.

Sampling Methods

Water samples will be collected and analyzed for conventional parameters according to *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 2006) wherever applicable. All samples collected in the laboratory and field will be labeled clearly and legibly with the following information:

> ➢ Parameter
> ➢ Preservative agent
> ➢ Laboratory analyzing sample
> ➢ Date / time of sample collection
> ➢ Facility where sample collected
> ➢ Sample location within facility
> ➢ Sample number
> ➢ Replicate

Sample handling will utilize chain-of-custody forms to track sample handling. This will ensure that acceptable holding times are not exceeded, and allow reporting of sample conditions upon reception. The chain-of-custody forms will be filled out during sample collection, a copy of the chain-of-custody form will be filed for records on site, and the original chain-of-custody form will accompany the samples during transportation. Upon sample reception at the designated laboratory, the integrity of the sample containers will be assessed, the chain-of-custody forms will be completed, and the samples will be stored at 4 ℃ in darkness or processed immediately. No chain-of-custody forms will be required for analyses conducted onsite.

QA/QC Procedure

For each batch of samples processed, the following steps are generally undertaken as part of Quality Assurance/Quality Control procedures and to assure defensibility of analytical results:

(a) Recovery of known additions and Isotope Dilution:

The recovery of known additions and use of isotope dilution (ID) protocols will be part of regular analytical methods. The relative importance of these two approaches will depend on the analyte and the availability of isotopically-labelled forms. When possible, isotope dilution is preferred. Both are used to assess and adjust for matrix effects or the amount of interference. When ID isn't used, the sum of duplicates and known additions will be greater than 20% of the samples. The known addition will be between 1 and 10 times the ambient level. The procedure would not be used above the demonstrated linear range of the method. As part of this method, concentrated solutions will be used so that volume change in sample is negligible.

(b) Analysis of duplicates:

Duplicate samples will be processed on a routine basis. A duplicate sample is a sample that will be processed exactly as the original sample, including preparation and analysis.

The duplicate samples will be used to determine precision. The sum of duplicates and known additions will be greater than 20% of the number of samples.

(c) Analysis of reagent blanks:

Reagent blanks will be analyzed whenever new reagents will be used or 5% of the sample load, whichever is greater. This will monitor purity of reagents and the overall procedural blank. A reagent blank will be run after any sample with a concentration greater than that of the highest standard or that might result in carryover from one sample to the next.

(d) Analysis of externally supplied standards:

As a minimum, externally supplied standards will be analyzed whenever analysis of known additions will not result in acceptable recovery, or once each analysis-day, whichever is greater. All attempts will be made to analyze laboratory control standards near sample ambient levels.

(e) Calibration with standards:

As a minimum, three different dilutions of the standard would be measured when an analysis is initiated. The standard curve would be verified each analysis-day by analyzing one or more standards within the linear range. Reportable analytical results would be those within the range of the standard dilutions used. Values above the highest standard would not be reported unless an initial demonstration of greater linear range has been made and the value is less than 1.5 times the highest standard. If a blank is subtracted, the result will be reported even if it turns out to be negative.

General sample collection and handling will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 2006). Reagent grade chemicals or higher quality when needed will be used throughout the research. Milli-Q treatment of building RO water (purified by reverse osmosis, deionization, and carbon adsorption) will be used for preparation of reagents, sample blanks, and dilution water. Glassware used in the experiments and in analytical analyses will be thoroughly cleaned with a chromium-free sequence of detergent, oxidant and acid to prevent interferences from trace organics.

Analytical Procedures

Standard method protocols will be used to measure pH, conductivity, turbidity, alkalinity, residual chlorine, chloramines, iron, manganese, TOC and DOC (APHA et al. 2006). pH will be measured using a bench top Thermo-Orion pH/ORP meter. Turbidity will be measured using a bench top Hach Ratio turbidimeter. Conductivity will be measured using Thermo Orion Model 105 conductivity meter. TOC and DOC will be measured using a Shimadzu TOCV analyzer. The precision, accuracy and method detection limits will be evaluated, and where there are existing methods, held within the control limits set forth in the accepted references (e.g. APHA et al., 2006). Residual chlorine and chloramines is done via the DPD ferrous titrimetric method. Soluble, colloidal, and total manganese are determined by use of paper filtration and ultrafiltration for prior separation. THM and HAA analysis is done using the accepted LLE/GC/ECD methods published by the USEPA (551.1 and 552.2).

Non-standard or advance analytical methods are done by means of published methods that may be considered the defacto accepted methods. Methods for non-regulated DBPs, PPCPs, and EDCs have already been discussed in the Research Plan, so they won't be repeated here. To verify and maintain a high level of data quality we follow the generic QA/QC approach described above.

Data Reduction, Validation and Reporting

To ensure the accuracy and permanency of collected data, all research data will be recorded with permanent ink in a bound notebook and all QC data (precision, accuracy) will be recorded in instrument log notebooks. Summary QC graphs and tables will be reviewed at least quarterly Concerns and conclusions will be reported to the Project Officer via the project reports. All data will be subject to review by the principal investigators before release. The analysts involved will sign reports as well as all who review them. All signers attest that the data and associated information contained in the report are believed to be correct and that all quality assurance requirements have been fulfilled, unless exceptions are approved and noted. Careful and detailed laboratory records by each analyst will be maintained, including source of reagents, detailed procedures, instrument and conditions of analysis, failed experiments, etc. Data output will be archived.

The documentation required for the project will include the following:
- ❖ project log books
- ❖ raw data log sheets for pilot-scale and bench-scale equipment operating data
- ❖ raw data log sheets for onsite laboratory results
- ❖ raw data log sheets for onsite analytical instrument calibration
- ❖ raw data log sheets for onsite equipment calibration and verification
- ❖ laboratory chain-of-custody forms
- ❖ laboratory reports
- ❖ initialed and dated printouts of verified electronic data.

Data Plan

All process and analytical data are recorded in notebooks and transmitted among the team via MS excel spreadsheets. These are prepared in a standard format so that they can be readily interpreted and understood by all team members. Ultimately they will be made available to any interested parties in the scientific community. The PIs have a great deal of experience in data formatting and storage. All three have been involved in the hydrologic observatory effort by NSF and CUAHSI (e.g., CLEANER, WATERS NETWORK) at various times, and have participated in the discussion on data storage, formatting and documentation for the purpose of metadata analysis.

Survey data collected on small utilities by MA WRRC will be stored in an MS Access database. It is our intent to build this database beyond the currently proposed project. At the same time we would make it fully available to EPA and other researchers. When fully developed (by us or by others), it would be a valuable resource for small utility managers, treatment plant operators, regulators, as well as researchers.

References

Alsheyab, M., Jiang, J.Q. and Stanford, C. Engineering Aspects of Electrochemical Generation of Ferrate: A Step Towards Its Full Scale Application for Water and Wastewater Treatment. Water Air and Soil Pollution 210(1-4), 203-210.

Alsheyab, M., Jiang, J.Q. and Stanford, C. Electrochemical generation of ferrate (VI): Determination of optimum conditions. Desalination 254(1-3), 175-178.

Alsheyab, M., Jiang, J.Q. and Stanford, C. (2009) On-line production of ferrate with an electrochemical method and its potential application for wastewater treatment - A review. Journal of Environmental Management 90(3), 1350-1356.

Anquandah, G.A.K. and Sharma, V.K. (2009) Oxidation of octylphenol by ferrate(VI). Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering 44(1), 62-66.

APHA, AWWA and WEF (eds) (2006) Standard Methods for the Examination of Water And Wastewater, American Public Health Association, Washington, D.C.

Bielski, B.H.J. and Thomas, M.J. (1987) STUDIES OF HYPERVALENT IRON IN AQUEOUS-SOLUTIONS .1. RADIATION-INDUCED REDUCTION OF IRON(VI) TO IRON(V) BY CO2. Journal of the American Chemical Society 109(25), 7761-7764.

Canizares, P., Arcis, M., Saez, C. and Rodrigo, M.A. (2007) Electrochemical synthesis of ferrate using boron doped diamond anodes. Electrochemistry Communications 9(9), 2286-2290.

Chinn, R., Lee, T., Krasner, S.W., Dale, M., Richardson, S.D., Pressman, J., Speth, T., Miltner, R.J. and Simmons, J.E. (2007) Solid-Phase Extraction of 35 DBPs with Analysis by GC/ECD adn GC/MS, pp. Wed 9-5, American Water Works Association, Charlotte, NC.

Cho, M., Lee, Y., Choi, W., Chung, H.M. and Yoon, J. (2006) Study on Fe(VI) species as a disinfectant: Quantitative evaluation and modeling for inactivating Escherichia coli. Water Research 40(19), 3580-3586.

Eng, Y.Y., Sharma, V.K. and Ray, A.K. (2006) Ferrate(VI): Green chemistry oxidant for degradation of cationic surfactant. Chemosphere 63(10), 1785-1790.

Ghernaout, D., Ghernaout, B. and Naceur, M.W. Embodying the chemical water treatment in the green chemistry-A review. Desalination 271(1-3), 1-10.

Graham, N., Jiang, C.C., Li, X.Z., Jiang, J.Q. and Ma, J. (2004) The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate. Chemosphere 56(10), 949-956.

Graham, N.J.D., Khoi, T.T. and Jiang, J.Q. Oxidation and coagulation of humic substances by potassium ferrate. Water Science and Technology 62(4), 929-936.

He, W.C., Wang, J.M., Zhou, L., Chen, Q.Q., Shen, B.C. and Zhang, J.Q. (2007) Study on the synthesis and physicochemistry properties of tripotassium sodium Ferrate(VI). Acta Chimica Sinica 65(20), 2261-2265.

Hives, J., Benova, M., Bouzek, K. and Sharma, V.K. (2006) Electrochemical formation of ferrate(VI) in a molten NaOH-KOH system. Electrochemistry Communications 8(11), 1737-1740.

Hu, L., Martin, H.M., Arcs-Bulted, O., Sugihara, M.N., Keatlng, K.A. and Strathmann, T.J. (2009) Oxidation of Carbamazepine by Mn(VII) and Fe(VI): Reaction Kinetics and Mechanism. Environmental Science & Technology 43(2), 509-515.

Hua, G.H. and Reckhow, D.A. (2006) Determination of TOCl, TOBr and TOI in Drinking Water by Pyrolysis and Off-Line Ion Chromatography. Analytical and Bioanalytical Chemistry 384(2), 495-504.

Jiang, J.Q. (2007) Research progress in the use of ferrate(VI) for the environmental remediation. Journal of Hazardous Materials 146(3), 617-623.

Jiang, J.Q. and Lloyd, B. (2002) Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. Water Research 36(6), 1397-1408.

Jiang, J.Q. and Lloyd, B. (2002) Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. Water Research 36(6), 1397-1408.

Jiang, J.Q., Lloyd, B. and Grigore, L. (2001) Preparation and evaluation of potassium ferrate as an oxidant and coagulant for potable water treatment. Environmental Engineering Science 18(5), 323-328.

Jiang, J.Q., Lloyd, B. and Grigore, L. (2001) Preparation and evaluation of potassium ferrate as an oxidant and coagulant for potable water treatment. Environmental Engineering Science 18(5), 323-328.

Jiang, J.Q., Stanford, C. and Alsheyab, M. (2009) The online generation and application of ferrate(VI) for sewage treatment-A pilot scale trial. Separation and Purification Technology 68(2), 227-231.

Jiang, J.Q. and Wang, S. (2003) Enhanced coagulation with potassium ferrate(VI) for removing humic substances. Environmental Engineering Science 20(6), 627-633.

Jiang, J.Q., Wang, S. and Panagoulopoulos, A. (2005) Proceedings of the 9th International Conference on Environmental Science and Technology, Vol A - Oral Presentations, Pts A and B. Lekkas, T.D. (ed), pp. A620-A625.

Jiang, J.Q., Wang, S. and Panagoulopoulos, A. (2006) The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment. Chemosphere 63(2), 212-219.

Lee, Y., Cho, M., Kim, J.Y. and Yoon, J. (2004) Chemistry of ferrate (Fe(VI)) in aqueous solution and its applications as a green chemical. Journal of Industrial and Engineering Chemistry 10(1), 161-171.

Lee, Y., Cho, M., Kim, J.Y. and Yoon, J. (2004) Chemistry of ferrate (Fe(VI)) in aqueous solution and its applications as a green chemical. Journal of Industrial and Engineering Chemistry 10(1), 161-171.

Lee, Y., Yoon, J. and von Gunten, U. (2005) Spectrophotometric determination of ferrate (Fe(Vl)) in water by ABTS. Water Research 39(10), 1946-1953.

Li, C., Li, X.Z. and Graham, N. (2005) A study of the preparation and reactivity of potassium ferrate. Chemosphere 61(4), 537-543.

Li, C., Li, X.Z., Graham, N. and Gao, N.Y. (2008) The aqueous degradation of bisphenol A and steroid estrogens by ferrate. Water Research 42(1-2), 109-120.

Licht, S., Naschitz, V., Halperin, L., Halperin, N., Lin, L., Chen, J.J., Ghosh, S. and Liu, B. (2001) Analysis of ferrate(VI) compounds and super-iron Fe(VI) battery cathodes: FTIR, ICP, titrimetric, XRD, UV/VIS, and electrochemical characterization. Journal of Power Sources 101(2), 167-176.

Licht, S., Wang, B.H. and Ghosh, S. (1999) Energetic iron(VI) chemistry: The super-iron battery. Science 285(5430), 1039-1042.

Lim, M. and Kim, M.J. (2009) Removal of Natural Organic Matter from River Water Using Potassium Ferrate(VI). Water Air and Soil Pollution 200(1-4), 181-189.

Liu, Z.H., Kanjo, Y. and Mizutani, S. (2009) Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment - physical means, biodegradation, and chemical advanced oxidation: A review. Science of the Total Environment 407(2), 731-748.

Luo, Z.Y., Strouse, M., Jiang, J.Q. and Sharma, V.K. Methodologies for the analytical determination of ferrate(VI): A Review. Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering 46(5), 453-460.

Park, G., Yu, M., Go, J., Kim, E. and Kim, H. (2007) Comparison between ozone and ferrate in oxidising geosmin and 2-MIB in water. Water Science and Technology 55(5), 117-125.

Sanchez-Carretero, A., Saez, C., Canizares, P., Cotillas, S. and Rodrigo, M.A. Improvements in the Electrochemical Production of Ferrates with Conductive Diamond Anodes Using Goethite as Raw Material and Ultrasound. Industrial & Engineering Chemistry Research 50(11), 7073-7076.

Schink, T. and Waite, T.D. (1980) INACTIVATION OF F2 VIRUS WITH FERRATE(VI). Water Research 14(12), 1705-1717.

Sharma, V.K. Oxidation of inorganic contaminants by ferrates (VI, V, and IV)-kinetics and mechanisms: A review. Journal of Environmental Management 92(4), 1051-1073.

Sharma, V.K. Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: A review. Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering 45(6), 645-667.

Sharma, V.K. Oxidation of Inorganic Compounds by Ferrate(VI) and Ferrate(V): One-Electron and Two-Electron Transfer Steps. Environmental Science & Technology 44(13), 5148-5152.

Sharma, V.K. (2007) Disinfection performance of Fe(VI) in water and wastewater: a review. Water Science and Technology 55(1-2), 225-232.

Sharma, V.K. (2008) Oxidative transformations of environmental pharmaceuticals by Cl(2), ClO(2), O(3), and Fe(VI): Kinetics assessment. Chemosphere 73(9), 1379-1386.

Sharma, V.K., Li, X.Z., Graham, N. and Doong, R.A. (2008) Ferrate(VI) oxidation of endocrine disruptors and antimicrobials in water. Journal of Water Supply Research and Technology-Aqua 57(6), 419-426.

Sharma, V.K., Mishra, S.K. and Nesnas, N. (2006) Oxidation of sulfonamide antimicrobials by ferrate(VI) [(FeO42-)-O-VI]. Environmental Science & Technology 40(23), 7222-7227.

Sharma, V.K., Mishra, S.K. and Ray, A.K. (2006) Kinetic assessment of the potassium ferrate(VI) oxidation of antibacterial drug sulfamethoxazole. Chemosphere 62(1), 128-134.

Stanford, C., Jiang, J.Q. and Alsheyab, M. Electrochemical Production of Ferrate (Iron VI): Application to the Wastewater Treatment on a Laboratory Scale and Comparison with Iron (III) Coagulant. Water Air and Soil Pollution 209(1-4), 483-488.

Vanderford, B.J. and Snyder, S.A. (2006) Analysis of pharmaceuticals in water by isotope dilution liquid chromatography/tandem mass spectrometry. Environmental Science & Technology 40(23), 7312-7320.

Vicenteperez, S., Losada, J. and Hernandez, P. (1985) FERRATE(VI) - OXIDIMETRY STANDARDIZATION OF REAGENT WITH STANDARD IRON(II) - TITRATION OF ANILINE. Anales De Quimica Serie B-Quimica Inorganica Y Quimica Analytica 81(1), 93-99.

Yang, B., Ying, G.G., Zhang, L.J., Zhou, L.J., Liu, S. and Fang, Y.X. Kinetics modeling and reaction mechanism of ferrate(VI) oxidation of benzotriazoles. Water Research 45(6), 2261-2269.

Yang, B., Ying, G.G., Zhao, J.L., Zhang, L.J., Fang, Y.X. and Nghiem, L.D. Oxidation of triclosan by ferrate: Reaction kinetics, products identification and toxicity evaluation. Journal of Hazardous Materials 186(1), 227-235.

Zhou, W. J., Boyd, J. M., Qin, F., Hrudey, S. E., and Li, X. F. (2009). "Formation of N-Nitrosodiphenylamine and Two New N-Containing Disinfection Byproducts from Chloramination of Water Containing Diphenylamine." *Environmental Science & Technology*, 43(21), 8443-8448.