Use of ferrate in small drinking water treatment systems

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Background

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.

Ferrate (VI) basics:

- Highly selective oxidant
  - No any known hazardous byproducts (e.g., no brominated or chlorinated DBPs, no bromate or chlorite).
- Disinfectant
- Coagulant: Fe $^{3+}$ and Fe(OH)$_3$
Becoming Cost Competitive

- Comparison from Roy, 2010 [JAWWA 102(3)44-51]
Project Objectives

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.

Working Hypothesis

- Ferrate is more effective and less detrimental than conventional oxidative technologies such as chlorination, chloramination, and permanganate oxidation.

- Ferrate is comparable in performance to alternative oxidants such as ozone or chlorine dioxide, which are more costly, more hazardous or require specialized expertise to operate.
Bench-scale tests

Process Descriptions

- No Ferrate
- Borate Buffer
- Raw Water
- 0.5–1 hr. reaction time
- Ferrate 25 uM (pH 6.2, pH 7.5)
- Ferrate 50 uM (pH 6.2, pH 7.5)
- Ferric Chloride Jar Test (pH = 5.5)

Ferrate Treatment

Coagulation

Filtration (GF/F)

Chlorination

Select Optimal Dose for Chlorination Based on Filtered UV Absorbance

Measurements/Analyses

- pH, TOC, Hardness, Alkalinity, Fe, Mn, ammonia, sulfide
- CT (Ferrate)
- TOC
- Metals (fractionation)
- NH$_3$, S$^{2-}$
- Chlorine Demand
- DBPFP (THMs, HAAs)
- UV254 Absorbance
- DOC
- Metals (fractionation)
- Chlorine Demand
- DBPFP (THMs, HAAs)
Outline

1. Ferrate decomposition and lifetime in natural waters
2. Direct Ferrate impacts on NOM and precursors
3. Direct ferrate impacts on Fe/Mn
4. Conclusions
Ferrate proton speciation

Monoprotonated and unprotonated anions are dominate at most pHs.
Decomposition kinetics

• Ferrate decomposes in water.

\[ FeO_4^{2-} + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + \frac{3}{4}O_2 + 2OH^- \]

• Carr model (2008)
  ❖ Overall mixed order

\[ -\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)] + k_2[Fe(VI)]^2 \]

• First order term

\[ k_1[Fe(VI)] = k_{H_2FeO_4}[H_2FeO_4] + k_{HFeO_4}[HFeO_4^-] + k_{FeO_4}[FeO_4^-] \]

• Includes phosphate catalysis

\[ k_{HFeO_4}[HFeO_4^-] = k_{HFeO_4}[HFeO_4^-] + k_{HFeO_4}[H_2FeO_4^-][HPO_4^-] \]
Decomposition in pure water

- The Carr model does a good job of describing ferrate decomposition in pure waters containing borate.
- Borate buffer may slightly increase the rate of ferrate loss.
Effect of carbonate on ferrate decay

Carbonate concentration increases, ferrate decay rate decreases.

Carbonate slowed ferrate decay. This might be attributed to radical reactions that accelerate ferrate decomposition but are partly quenched by carbonate scavengers.
## Raw Water Quality

<table>
<thead>
<tr>
<th>Location</th>
<th>TOC (mg/L)</th>
<th>DOC (mg/L)</th>
<th>UV$_{254}$ (cm$^{-1}$)</th>
<th>SUVA (L/mg/m)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amherst, MA</td>
<td>2.40</td>
<td>2.39</td>
<td>0.065</td>
<td>2.7</td>
<td>7.1</td>
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<tr>
<td>Houston TX</td>
<td>6.64</td>
<td>6.53</td>
<td>0.221</td>
<td>3.4</td>
<td>7.3</td>
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<tr>
<td>Palmer, MA</td>
<td>2.03</td>
<td>2.01</td>
<td>0.092</td>
<td>4.6</td>
<td>6.5</td>
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<tr>
<td>Readsboro, VT</td>
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<td>2.03</td>
<td>0.119</td>
<td>5.9</td>
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<tr>
<td>Bolton, VT</td>
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<td>5.18</td>
<td>0.215</td>
<td>4.2</td>
<td>6.6</td>
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<td>Holton, KS</td>
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<td>5.79</td>
<td>0.107</td>
<td>1.8</td>
<td>7.0</td>
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<tr>
<td>Stockbridge, MA</td>
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<td>2.87</td>
<td>0.078</td>
<td>2.7</td>
<td>6.6</td>
</tr>
<tr>
<td>Lantern Hill, CT</td>
<td>3.48</td>
<td>3.40</td>
<td>0.153</td>
<td>4.4</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Ferrate Decay, 50 uM

Natural waters have a stabilizing effect on ferrate compared to similarly-buffered lab grade water.

- Slower decomposition of ferrate (e.g., carbonate effect), or
- Formation of other secondary oxidants also capable of oxidizing ABTS.
CT values at pH 6.2 are much lower than those at pH 7.5, pH had a great effect on CT values.
Outline

1. Ferrate decomposition and lifetime in natural waters
2. Direct Ferrate impacts on NOM and DBP precursors
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Precursor Testing

- Treat samples with ferrate
- Allow ferrate to dissipate (<60 min)
- Chlorinate in the lab
  - pH 7.0
  - Dose required for 3–5 mg/L residual after 72 hrs
  - 20°C
- Measure DBPs
  - Neutral Extractables (including THMs)
  - Haloacetic Acids (9 total)
Trihalomethanes (THM)

Substantial decrease; little pH effect
Dihaloacetic Acids (DHAA)

Less degradation than THMs
Trihaloacetic Acids (THAA)

More loss than THMs
Dihaloacetonitrile (DHAN)

Substantial decrease
Comparison with ozone

Data from: Reckhow et al., 1986  
Data from: current study
Lessons from Precursor Data

- Ferrate will directly destroy THM precursors by 25-40% at doses of 1.4 mg-Fe/mg-C.
  - THAA precursors are slightly better oxidized (25–55%);
  - DHAA precursors are less well oxidized (-10–30%);
  - DHAN precursors are similarly reduced by 21–36%.
- Precursor oxidation by ferrate is similar to that observed for ozone at equivalent doses.
- Precursor destruction does not seem to diminish at lower pH where exposure (CT) is much lower.
  - Precursor destruction is either faster when the reactants are more protonated, or ferrate decomposition products play an important role.
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# Metals Oxidation – Lantern Hill, CT

<table>
<thead>
<tr>
<th></th>
<th>Total Mn (mg/L)</th>
<th>Dissolved Mn (mg/L)</th>
<th>Total Fe (mg/L)</th>
<th>Dissolved Fe (mg/L)</th>
<th>pH</th>
<th>UV$_{254}$ (cm$^{-1}$)</th>
<th>TOC (mg/L)</th>
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<tbody>
<tr>
<td><strong>Average</strong></td>
<td>0.17</td>
<td>0.17</td>
<td>1.85</td>
<td>1.69</td>
<td>6.51</td>
<td>0.153</td>
<td>3.48</td>
</tr>
<tr>
<td><strong>Range</strong></td>
<td>0.14-0.22</td>
<td>0.12-0.22</td>
<td>1.16-2.39</td>
<td>1.03-2.34</td>
<td>6.35-6.67</td>
<td>0.128-0.165</td>
<td>3.03-4.30</td>
</tr>
</tbody>
</table>

**Mn$^{2+}$ and Fe$^{2+}$ Oxidation with Ferrate:**

\[
3\text{Mn}^{+2} + 2\text{FeO}_4^{-2} + 8\text{H}_2\text{O} \rightarrow 3\text{MnO}_2(s) + 2\text{Fe(OH)}_3(s) + 2\text{H}^+
\]

\[
3\text{Fe}^{+2} + \text{FeO}_4^{-2} + 8\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3(s) + 4\text{H}^+
\]
• Reaction kinetics favor Fe oxidation over manganese.
• The incomplete oxidation of Mn was also likely caused by competition by other oxidant demands, like NOM.
• Both Mn and Fe indicated the overwhelming majority of the oxidized metals exist in the colloidal phase.
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Conclusions so far

- Ferrate is capable of oxidizing regulated DBP precursors, as well as Fe & Mn with an effectiveness similar to ozone.
  - Cost may be similar as well.
  - No apparent issues with DBP formation.
- Depending on EPA action regarding CT credit, ferrate may be an attractive option for meeting DBP regulations.
  - Perhaps especially well suited for small utilities
Future work

• Bench-scale work will continue to test waters with different properties and chemical contaminants (e.g., pesticides, sulfide, arsenic, PPCPs).

• Pilot-scale work will allow us to collect data on aspects that cannot be readily investigated at the bench scale such as biological removal, sludge production, and build-up of filter headloss.
Acknowledgements

- US EPA STAR program
- Dave Reckhow, John Tobiason, Joe Goodwill.
- UMass water research group
  - Sherrie Webb-Yagodzinski, Yun Yu, Arianne Bazilio, John Martin
- Participating Utility Personnel
  - Amherst, Houston, Palmer, Readsboro, Bolton
- Shankar Chellam (U of Houston)
- Carole Tomlinson (Haskell Indian Nations Univ).
THANK YOU!