Challenges in Municipal Water Treatment and the MIOX Solution

Part 2 of 3: Groundwater Treatment

Tuesday, January 22th at 11AM EST
Agenda for Part 2

- Brief Introduction of MIOX
- General system and chemistry information
- Iron and Manganese
- Hydrogen Sulfide
- Ammonia
- Arsenic
What is On-Site Chemical Generation?

SALTS + ON-SITE WATER + POWER = CUSTOM CHEMICAL

- Specialty chemistry generated on site, on demand
- Replaces multiple delivered chemicals
- Ability to create unique product characteristics
MIOX® Process
Two System Configurations Include:

- **Basic Bleach Generators**
  - Nominally 0.6 – 0.8% concentration
  - Very efficient salt and energy conversion efficiencies
  - Good “general purpose” biocide

- **Mixed Oxidant Generators**
  - Uses slightly more power to make stronger oxidant
  - Great biopenetrant for better biofilm and organism control
  - Also has stronger oxidation power for certain applications
MIOX On-Site Generators

- Revolutionary self-cleaning generator in the industry
- Patented self-adjusting flow control to accommodate wide pressure variations
- Direct link to DCS, ORP, SCADA
- Air-cooled power supply - Allows hotter feed water to cell
- Reduces chiller requirements and associated need for pressure boost
Why On-Demand Chemistry?

Safe...Less Hazardous

- Sodium Hypochlorite
- Chlorine Dioxide
- Mixed Oxidant (0.4% chlorine)
- Sodium Hypochlorite (0.8% chlorine)

NFPA Rating
- Health = 1
- Flammability = 0
- Instability = 0

Reduced Carbon Footprint

- Delivering bulk bleach
- Salt - chlorine equivalent

MIOX Proprietary & Confidential – Do Not Distribute
Groundwater Treatment
General and Advanced Treatment
Typical Issues in Groundwater Treatment

- Iron (Fe) removal
  - SMCL: 0.3 mg/l

- Manganese (Mn) removal
  - SMCL: 0.05 mg/l

- Hydrogen Sulfide reduction
  - Odor control

- Ammonia removal

- Arsenic removal
Mixed Oxidants Tend to Speed or Extend Oxidation Reactions

- **Iron and Manganese Removal**
  - Can be used to oxidize iron and manganese
  - Effective for manganese when used with Greensand Plus filter
  - Eliminates use of potassium permanganate
    - Saves cost
    - Safer

- **Hydrogen Sulfide Removal**
  - Drives reaction to soluble form
    - $\text{H}_2\text{S}$ to elemental sulfur
    - Sulfur to $\text{H}_2\text{SO}_4$
  - Eliminate odor easily with little or no additional equipment
    - No detention tank
    - No filters
    - Maintain head from wells to distribution
Iron Oxidation Converts Soluble Iron to Something that Can be Filtered

- Iron typically exists in Ferrous form \((\text{Fe}^{2+})\) which is soluble
- Can be converted to the insoluble form \((\text{Fe}^{3+})\), which can then be removed
- Requires an electron acceptor…

\[
2\text{Fe}^{2+} + 6\text{H}_2\text{O} + \text{Cl}_2 = 2\text{Fe(OH)}_3(s) + 2\text{Cl}^- + 6\text{H}^+ 
\]
Iron Oxidation Converts Soluble Iron to Something that Can be Filtered

\[2\text{Fe}^{2+} + 6\text{H}_2\text{O} + \text{Cl}_2 = 2\text{Fe(OH)}_3(s) + 2\text{Cl}^- + 6\text{H}^+\]

- Can use this to calculate “ideal” dosage
  - Ratio molecular weights of the iron and chlorine:
    - \(\text{Fe: } 2 \times 55.845 \text{ g/mol} = 111.69\)
    - \(\text{Cl: } 2 \times 35.453 \text{ g/mol} = 70.91\)
    - Ratio \(\text{Cl}_2/2\text{Fe} = 70.91/111.69 = 0.635\)
- Keep in mind “ideal” rarely happens…so you might want to be conservative
Iron Oxidation and Removal

- Hypochlorite and Mixed Oxidants will oxidize iron
- Must be filtered afterward to remove formed solids
Manganese Oxidation is Similar, but the Reaction is More Complicated

- Manganese has 8 oxidation states
- Manganese most commonly exists in Mn(II) form (Mn$^{2+}$) in groundwater, which is soluble
- Can be converted to the insoluble form (Mn$^{4+}$), which can then be removed
- Requires an electron acceptor...

\[ \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{Cl}_2 = \text{MnO}_4(s) + 2\text{Cl}^- + 4\text{H}^+ \]
Manganese Oxidation is Similar, but the Reaction is More Complicated

\[ \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{Cl}_2 = \text{MnO}_4^{(s)} + 2\text{Cl}^- + 4\text{H}^+ \]

- Can use this to calculate “ideal” dosage
  - Ratio molecular weights of the iron and chlorine:
    - Mn: 54.938 g/mol = 54.938
    - Cl: 2 x 35.453 g/mol = 70.91
    - Ratio Cl\textsubscript{2}/Mn = 70.91/54.938 = 1.29
  - Keep in mind “ideal” rarely happens…so you might want to be conservative
Extensive Experience Indicates Manganese also Catalyzes

- Proper selection of filter media is key
- Manganese Greensand, or coated conventional medias often used
Iron and Manganese Oxidation and Removal

- Mixed Oxidants will oxidize manganese faster than hypo
- “Greensand” media helps catalyze for improved removal
Hydrogen Sulfide Presents Some Unique Issues

- Primarily caused by sulfur-reducing bacteria in well converting elemental sulfur
- Creates “rotten egg” smell at very low dosages
- pH has a major effect on treatment methods
- Hydrogen sulfide is noticeable at very low concentrations
- Annoying at low concentrations, can cause a laxative effect at high concentrations
Hydrogen Sulfide Exists in Gaseous and Soluble Forms Depending on pH

Percent Hydrogen Sulfide as Gas vs. pH
The Reaction is a 2-Step Process

\[ \text{Cl}_2 + \text{H}_2\text{S} = 2\text{HCl} + \text{S}^0 \]
(reacton may stop here)
\[ \text{S}^0 + 3\text{Cl}_2 + 4\text{H}_2\text{O} = 6\text{HCl} + \text{H}_2\text{SO}_4 \]

The combined reaction is as follows:

\[ \text{H}_2\text{S} + 4\text{Cl}_2 + 4\text{H}_2\text{O} = 8\text{HCl} + \text{H}_2\text{SO}_4 \]

- If you use the mass ratios of the 4Cl\(_2\) vs. \(\text{H}_2\text{S}\), you get a ratio of 8.35.
- We then typically assume a little extra to make sure the reaction drives through.
Traditional hydrogen sulfide removal can be onerous and require significant capital upgrades

- **Option 1**: Lower pH, degassify, raise pH

- **Option 2**: Use Ozone to drive reaction to sulfuric acid (soluble, non-odorous)

- **Option 3**: Degas (optional), add bleach, wait 1-2 hours, filter sulfur that is formed

- **Option 4**: Dose Mixed Oxidants – drive reaction to sulfuric acid
Traditional hydrogen sulfide removal can be onerous and require significant capital upgrades.

Remove as much as you can “for free”

Detention Tank (1 – 2 hours)

Portion forms elemental sulfur

Degassifier

Hypochlorite System

Filters remove elemental sulfur

Media Filters (Pressure or Gravity)

To Storage Tanks/Dist.
Mixed Oxidants simplify process and reduces required plant changes

- Mixed Oxidants drive reaction to sulfuric acid, which is soluble

![Diagram showing the process of using mixed oxidants to drive a reaction towards sulfuric acid, which is soluble. The diagram includes a well pump, a mixed oxidant dosing system for H2S and chlorine residual, and a storage tank/distributor.]
Ammonia removal can be accomplished in a few ways

► Removal using Biologically Active Filters
  - Effective but can require the addition of food source
  - Can be a public relations challenge

► Nanofiltration/Reverse Osmosis
  - Operating cost can be high
  - Disposal of concentrate stream can be a challenge

► Breakpoint chlorination to convert to nitrogen
  - Can require high volume of chlorine
  - Can be challenge to control
Breakpoint Reaction Chemistry is Complicated, and Not Entirely Defined

\[
\begin{align*}
\text{NH}_4^+ + \text{Cl}_2 & \rightarrow \text{NH}_2\text{Cl} + \text{Cl}^- + 2 \text{H}^+ \\
\text{NH}_3 + \text{Cl}_2 & \rightarrow \text{NH}_2\text{Cl} + \text{Cl}^- + \text{H}^+ \\
\text{NH}_2\text{Cl} + \text{Cl}_2 & \rightarrow \text{NHCl}_2 + \text{Cl}^- + \text{H}^+ \\
\text{NHCl}_2 + \text{Cl}_2 & \rightarrow \text{NCl}_3 + \text{Cl}^- + \text{H}^+ \\
2 \text{NCl}_3 & \rightarrow \text{N}_2\uparrow + 3 \text{Cl}_2 \\
\text{NH}_3 + \text{HOCl} & \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \\
\text{NH}_2\text{Cl} + \text{HOCl} & \rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \\
\text{NHCl}_2 + \text{HOCl} & \rightarrow \text{NCl}_3 + \text{H}_2\text{O} \\
2 \text{NCl}_3 & \rightarrow \text{N}_2\uparrow + 3 \text{Cl}_2
\end{align*}
\]
The reaction pathways are very complex

(Products include N2, H2O, Cl-, H+, NO3- and unidentified)

Reaction Path is Often Summarized as Follows

\[
\begin{align*}
3 \text{NH}_2\text{Cl} & \rightarrow \text{N}_2\uparrow + 3 \text{Cl}^- + \text{NH}_3 + 3 \text{H}^+ \\
2 \text{NH}_2\text{Cl} + \text{Cl}_2 & \rightarrow \text{N}_2\uparrow + 4 \text{Cl}^- + 4 \text{H}^+ \\
2 \text{NH}_2\text{Cl} + \text{HOCl} & \rightarrow \text{N}_2\uparrow + 3 \text{Cl}^- + 3 \text{H}^+ + \text{H}_2\text{O} \\
2 \text{NHCl}_2 & \rightarrow \text{N}_2\uparrow + \text{Cl}_2 + 2 \text{Cl}^- + 2 \text{H}^+ \\
2 \text{NCl}_3 & \rightarrow \text{N}_2\uparrow + 3 \text{Cl}_2 \\
\end{align*}
\]

The net Breakpoint Reaction stoichiometry is represented by the form
\[
2 \text{NH}_3 + 3 \text{Cl}_2 \rightarrow \text{N}_2\uparrow + 6 \text{Cl}^- + 6 \text{H}^+
\]

from which the conventional stoichiometric mass dose ratio is derived
\[
\text{FAC/NH}_3\text{-N} = 7.6
\]
This Complexity Creates Challenges in Actual Application

- Often see reports of high dosages of chlorine required
  - As much as 15 – 20 ppm chlorine recommended in some literature
- Control of system can be challenging
  - Need to know where you should be operating
Adapted from Gordon, et al. (1992, pp. 17-18)
Mixed Oxidant Solution Offers Superior Ammonia Removal

- Mixed Oxidants can be dosed closer to stoichiometric ratio
  - 8 – 10 ppm FAC per ppm of ammonia
  - Regular bleach is typically dosed at 15 ppm FAC per ppm ammonia
- Reduces chemical consumption by nearly 50%
- Reduces chemical cost by nearly 50%

ROI less than 2 years

ROI Bulk Hypo vs. MOS For Ammonia Removal (2 MGD Well Source with 0.9 ppm Ammonia)

Cumulative Savings (USD)

0 5 10 15 20

Years

$(500,000)  $1,000,000  $1,500,000

MIOX
Summary of MIOX Experience with the Breakpoint Reaction

- The reaction tends to proceed at near or even below the stoichiometric requirement of FAC/N = 7.6 – sharp contrast with FAC as bleach
- The reaction tends to be very fast – completed in ~20 minutes – reactions with bleach tend to be slower – very important in actual treatment plant operations
- Chlorinous odors – suggested by the data of Gordon et al. (1992) – do NOT develop during the reaction
Arsenic Removal is Relatively Simple

- MIOX is simple, cost effective first step in removal
- Arsenic is naturally a naturally occurring element
- Arsenic is typically found in 2 forms in groundwater
  - As(III) and As(V)
- As(V) is “easier” to remove
- Oxidation is often first step in removal
- Co-precipitation or adsorption with iron is most common method of removal
Oxidation of As(III) to As(V) is Common First Step in Removal

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Very Fast – effective</th>
<th>Very Slow – ineffective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂/HOCl/OCl⁻</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>KMnO₄</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>ClO₂</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Monochloramine (NH₂Cl)</td>
<td></td>
<td>*</td>
</tr>
</tbody>
</table>
Iron is Then Used to Remove

- Naturally occurring iron can be effective
  - Already in groundwater
- Can also add iron salt such as ferric chloride or ferric sulfate
- Adsorption-based media, such as Granular Ferric Hydroxide can be used in place of filter media
- Binds tightly, can be disposed of to landfill in most jurisdictions
# Dosage “Cheat Sheet” for Groundwater Treatment

<table>
<thead>
<tr>
<th>ITEM</th>
<th>CHLORINE DEMAND (Dose Required mg to mg)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stochiometric</td>
<td>Conservative for Estimating</td>
</tr>
<tr>
<td>Iron</td>
<td>0.635</td>
<td>0.7</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.29</td>
<td>1.5</td>
</tr>
<tr>
<td>H$_2$S as Sulfide to (S)</td>
<td>2.22</td>
<td>2.5</td>
</tr>
<tr>
<td>H$_2$S as Sulfide to (SO$_4$)</td>
<td>8.85</td>
<td>9</td>
</tr>
<tr>
<td>Ammonia as NH$_3$</td>
<td>6.3</td>
<td>10</td>
</tr>
<tr>
<td>Ammonia as NH$_3$–N</td>
<td>7.6</td>
<td>10</td>
</tr>
</tbody>
</table>

Don’t forget to add the desired residual to distribution system when sizing the overall system!