Iron and Manganese Removal Processes
Presentation Agenda

• Arsenic Background: chemistry and treatment options
• Treatment selection considerations
• Treatment options
  – Iron removal
• Case studies
• Conclusions
Arsenic Chemistry

- Arsenic has two primary valence states:
  - As (III) \[ As +3 \text{ Arsenite} \]
  - As (V) \[ As +5 \text{ Arsenate} \]

- Arsenic Occurrence by valence state
  - *Surface waters* - predominately As (V)
  - *Ground waters* – usually found as As (III), however, concentrations of As (V) or a combination of As (III) and As (V) can be found
Iron-based Arsenic Removal Processes

- Adsorptive properties of iron mineral toward arsenic are well known
- That knowledge is the basis for many arsenic treatment processes
  - Coagulation with iron coagulant
  - Iron-based adsorption media
  - Iron removal processes
Arsenic Removal by Iron
As(III) vs As(V)

As(III) is removed during iron removal and other iron-based processes, but just not as well as As(V)
As (III) Oxidation

Effective!
- Free Chlorine
- Potassium Permanganate
- Ozone
- Solid Oxidizing Media (MnO₂ solids)

Ineffective
- Chloramine
- Chlorine Dioxide
- UV Radiation + Sulfide
- Oxygen
Arsenic Treatment Issues

• Treatment complexity/cost
• Pre- and Post-treatment needs
• Residuals – Disposal Issues
  – Ion exchange & RO produce liquid wastes
  – Adsorbent media produce wasted solids
  – Coagulation/filtration and iron removal processes produce solids
    • Filter backwash waste
    • Sediment in contactor (pass TCLP test)
Arsenic Treatment
Simplified Process Selection Guide

Iron - mg/L
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

Arsenic - ug/L
0 5 10 15 20 25 30 35 40 45 50

A
Iron Removal Process
(Optimized for Maximum As Removal)

B
Modified Iron Removal Process
Fe - SMCL

C
Media Adsorption
Iron Coag/Filt
Ion Exchange
Iron Removal(M)
RO / NF

20:1 Fe/As ratio

As MCL
0 or above
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- **C** Media Adsorption; IX; RO; Nanofiltration
- **B** Modified Iron Removal
- **A** Iron Removal Process (optimized for maximum arsenic removal)

- **20:1 Fe/As ratio**

Axes:
- **Arsenic (µg/L)**
- **Iron (mg/L)**
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- Media Adsorption (IX)
- RO Nanofiltration
- Modified Iron Removal
- 20:1 Fe/As ratio
- Iron Removal Process (optimized for maximum arsenic removal)

Graph showing arsenic concentration (µg/L) vs. iron concentration (mg/L) with different treatment options and removal processes.
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- **Media Adsorption:** IX; RO; Nanofiltration
- **EPA - Fe secondary MCL**
- **Modified Iron Removal**
- **Iron Removal Process** (optimized for maximum arsenic removal)
- **20:1 Fe/As ratio**

**Areas:****
- **A:** Iron (mg/L)
- **B:** Modified Iron Removal
- **C:** Media Adsorption: IX; RO; Nanofiltration
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- **Media Adsorption**: IX (Ion Exchange), RO (Reverse Osmosis), Nanofiltration
- **EPA - Fe secondary MCL**
- **Modified Iron Removal**
- **Iron Removal Process** (optimized for maximum arsenic removal)
- **20:1 Fe/As ratio**
Q: When should a stand alone AD26 System be considered vs. a two stage treatment system for arsenic?

A: The figure shown provides some guidance on the appropriate configuration for a specific water chemistry. Mainly, it will be selected by iron and arsenic levels in the feed water. High levels of arsenic combined with high iron would favor a two stage treatment train for optimal performance to meet the Arsenic MCL. For low arsenic concentrations, a stand alone AD26 system may achieve the treatment goals. Consult AdEdge for guidance on the best approach.

Q: Is chlorine needed for the system and does the media need replacement?

A: A low Hypochlorite dose is recommended for optimal performance of the AD26 systems. It enhances the removal process, improves longevity, and keeps the surface of the media oxidized to prevent buildup of solids. Media life is typically 5+ years before replacement.

Q: How do I determine the best way to achieve my treatment goals for my particular site?

A: Begin first by obtaining a complete site specific water profile from a qualified lab. This information can then be submitted to AdEdge technical support to discuss your application, equipment sizing, and costs.

**Operating Conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH Range</td>
<td>6.5 – 9</td>
</tr>
<tr>
<td>Treatment Goals</td>
<td>&lt; 0.3 mg/L Fe; &lt; 0.05 mg/L Mn &lt; 0.010 mg/L As</td>
</tr>
<tr>
<td>Service Flow Rate</td>
<td>10-12 gpm / Sq Ft</td>
</tr>
<tr>
<td>Backwash Flow Rate</td>
<td>18-20 gpm / Sq Ft</td>
</tr>
<tr>
<td>Bed Expansion</td>
<td>20-30% typical</td>
</tr>
<tr>
<td>Pressure Drop</td>
<td>&lt; 5 psi typical across system</td>
</tr>
<tr>
<td>Oxidant</td>
<td>Hypochlorite feed for best results</td>
</tr>
<tr>
<td>Oxidant Contact Time</td>
<td>30 seconds</td>
</tr>
<tr>
<td>Typical Oxidant Dosage</td>
<td>0.5 – 2.0 ppm</td>
</tr>
<tr>
<td>Backwash Frequency</td>
<td>Site Specific (1-2X per week typical)</td>
</tr>
<tr>
<td>Media Life Expectancy</td>
<td>Site specific; typically 5+ years</td>
</tr>
</tbody>
</table>

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AdEdge Treatment Selection

Co-occurrence of As and Fe and removal to meet 10 ug/L MCL

Selection Criteria:
- As
- Fe, Mn
- pH
- Silica
- TOC
- Hardness, Alkalinity
- Space
- Operator time
- Chemicals
- Backwash options
- Efficiency

Arsenic Concentration ug/L

Iron Concentration ug/L

AD26 OXIDATION / FILTRATION SYSTEM

+ ADEDGE ADSORPTION POLISHING

AD26 OXIDATION / FILTRATION SYSTEM (Stand Alone)

 Bayeroxide E/AD33
Removal of 1 mg/L of iron achieves removal of 50 ug/L arsenic (Optimized conditions and As[V])
Arsenic Removal During Iron Removal Considerations

Iron in water (>20/1 Fe/As ratio)?
• Form of arsenic, III or V?
  Oxidation:
  – Type of oxidant: oxygen, chlorine, KMnO₄…?
  – Point of application?
• Contact time?
  – Iron and As oxidation
  – Arsenic adsorption
• How can arsenic removal be predicted?
• Ways to improve arsenic removal during iron removal?
Iron (and Mn) Removal Basics

Fe II → Fe III → Fe(OH)₃ (S)
Mn II → Mn IV → MnO₂ (S)

Oxidation, Particle Development
15 – 30 minutes

Filtration particle removal
Iron and **Arsenic** (and Mn) Removal

- Fe II $\rightarrow$ Fe III
- As III $\rightarrow$ As V

**Oxidation**

- Aeration
  - Cl$_2$
  - KMnO$_4$
  - other

**Note:** Aeration will not oxidize As III to As V
Iron and **Arsenic** (and Mn) Removal

Fe(III)/As particles + arsenic

Contact Basin

Oxidation, particle development
Iron and Arsenic (and Mn) Removal

**Filtration**
**Fe III/ As Particle Removal**
Oxidant Selection

• Depends on As, Fe (and Mn)
• Aeration
  – Will not oxidize Mn II and As III (-)
  – May need contact basin (-)
  – Iron particles have less surface area (-)
  – Longer filter run lengths (+)
• Strong oxidants (chlorine, permanganate, etc)
  – Address Mn and As oxidation (+)
  – More particle surface area (+)
  – Probably no contactor needed (+)
  – Difficult to feed (-)
  – Shorter filter run lengths (-)
Assessment Tool

Jar Test
### Oxidation - Point of Application

**Case Study - Michigan**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic – ug/L</td>
<td>19 - 24</td>
</tr>
<tr>
<td>As III</td>
<td>95 %</td>
</tr>
<tr>
<td>As V</td>
<td>5 %</td>
</tr>
<tr>
<td>Calcium – mg/L</td>
<td>74 - 84</td>
</tr>
<tr>
<td>Magnesium – mg/L</td>
<td>30 - 33</td>
</tr>
<tr>
<td>Iron – mg/L</td>
<td>0.5 - 0.6</td>
</tr>
<tr>
<td>Manganese –mg/L</td>
<td>0.02</td>
</tr>
<tr>
<td>Sulfate – mg/L</td>
<td>50 - 60</td>
</tr>
<tr>
<td>Silica – mg/L</td>
<td>12 - 13</td>
</tr>
<tr>
<td>pH - units</td>
<td>7.1 - 7.3</td>
</tr>
</tbody>
</table>
Oxidation - Point of Application
Case Study - Michigan

As = 19-24 ug/L
Fe = 0.5 -0.6 mg/L

Cl₂
Pressure filters
50 % removal

Wells
Aeration tower
20 min CT
Oxidation - Point of Application

Case Study - Michigan

Wells

Aeration tower

Cl₂

Pressure filters

20 min CT

As = 19-24 ug/L
Fe = 0.5 - 0.6 mg/L

50% removal
Oxidation - Point of Application
Case Study - Michigan

Wells

Cl₂

Aeration tower

Pressure filters

20 min CT

As = 19-24 ug/L
Fe = 0.5 - 0.6 mg/L

75 % removal
Oxidant Selection

- Depends on As, Fe (and Mn)
- Aeration
  - Will not oxidize Mn II and As III (-)
  - May need contact basin (-)
  - Iron particles have less surface area (-)
  - Longer filter run lengths (+)
- Strong oxidants (chlorine, permanganate, etc)
  - Address Mn and As oxidation (+)
  - More particle surface area (+)
  - Probably no contactor needed (+)
  - Difficult to feed (-)
  - Shorter filter run lengths (-)
The Effect of Oxidant on Visual Properties of Iron Particles

The effect of oxidant type on the color of iron particles collected from filter backwash.
Utility with iron removal in place or will be in place but cannot meet MCL:

- Change point of oxidant addition
- Increase iron concentration
- Adjust pH
- Replace media w/ As adsorption media
Climax, MN  Iron Removal System
Climax, MN Iron Removal Process

- **Date**: 2004/2005
- **Arsenic concentration - ug/L**: 0 to 55
- **Iron concentration - mg/L**: 0.0 to 2.0

**Graph Details**
- **Raw Water Arsenic**
- **Treated Water Arsenic**
- **Raw Water Iron**

**MCL**: 0.8 mg/L Fe added

**Legend**
- **Raw Water Arsenic**
- **Treated Water Arsenic**
- **Raw Water Iron**

**Dates**
- Aug 2004
- Sep 2004
- Oct 2004
- Nov 2004
- Dec 2004
- Jan 2005
- Feb 2005
- Mar 2005
The Effect of Initial Arsenic(V) Concentration on the Capacity of Iron to Remove Arsenic

(Fe(II)_{init}=1 \text{ mg/L}, \text{DIC}=10 \text{ mg C/L}, \text{pH}=8, 24^\circ\text{C})

1 mg Fe/L reduces 150 μg As/L by 115 μg As/L to 35 μg As/L

1 mg Fe/L reduces 35 μg As/L by 23 μg As/L to 12 μg As/L
The Effect of pH, Iron and Free Chlorine on Arsenic Removal

1 mg Fe/L, 100 mg As(V)/L, 5 mg C/L DIC, PO2= 0.122 atm, 24 °C

![Graph showing the effect of pH on arsenic removal with different conditions.](image-url)
Effect of Water Quality

1 mg Fe/L, 100 ug As(V)/L, 5 mg C/L DIC, pH=8, 24 °C

![Graph showing the effect of phosphate concentration on arsenic removal with and without 1 mg/L chlorine.]
Lidgerwood, ND

Two Wells:
• 100 feet deep
• As Raw 135 – 150 ug/L (mostly As III)
• As Finished 35 ug/L
• Fe Raw 1.3 – 1.6 mg/L (9/11:1)
• Superfund site – arsenic for grasshopper control
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- **A**: Iron Removal Process (optimized for maximum arsenic removal)
- **B**: Modified Iron Removal
- **C**: Media Adsorption; IX; RO; Nanofiltration

- **20:1 Fe/As ratio**
- **Lidgerwood, ND**

Axes:
- Y-axis: Arsenic (µg/L)
- X-axis: Iron (mg/L)
Lidgerwood, ND

Existing Treatment:
• Pre-chlorination
• Aeration
• Oxidation – KMnO₄
• Filtration Aid – polymer
• Filtration – Antrasand (2 gpm/ft²)
• Post chlorination and fluoridation
EPA Demonstration Project:

• Turbidimeters
• Additional polymer feed
• FeCl₃ Coagulation (~1 mg/L)
• As Finished 7-8 ug/L
• Cost - $55,740
Lidgerwood, ND

- Well 1
- Well 2
- Mixing Tank
- Detention Tank
- Aeration Tower
- Filters
- Backwash tank
- Clearwell
- Sludge Tank
- KMnO₄
- Chlorine
- Ferric chloride
- Filter Aid (2)
Sabin, MN

Two Wells:
• As Raw 45 µg/L
• As Finished 40 µg/L
  (20-25 µg/L)

Plant is falling apart!!
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- **C** Media Adsorption: IX; RO; Nanofiltration
- **B** Modified Iron Removal
  - **A** Iron Removal (optimized for maximum arsenic removal)
    - **Sabin, MN**
    - 20:1 Fe/As ratio
Sabin, MN

Existing Treatment:
- Chlorination
- Aeration
- Sand filtration
- Fluoridation
Sabin, MN

Major Capital Improvement:
- Population 400
- $1,200,000 Total cost
  - $800,000 low interest loan
  - $160,000 grant
  - EPA Demonstration Project
Conclusions

• Iron removal = arsenic removal
• Arsenic speciation is important
• Oxidant type is important
• Point of oxidant application is important
  – Arsenic removal impacted
  – Plant operation impacted
Thank-you

QUESTIONS TO DARREN LYTLE EPA/ORD
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

Media Adsorption; IX; RO; Nanofiltration

C

Modified Iron Removal

B

Lidgerwood, ND

EPA - Fe secondary MCL

20:1 Fe/As ratio

Iron Removal Process (optimized for maximum arsenic removal)

Iron (mg/L)

Arsenic (µg/L)
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- **C**: Media Adsorption; IX; RO; Nanofiltration
- **B**: Modified Iron Removal
- **A**: Iron Removal Process (optimized for maximum arsenic removal)

- 20:1 Fe/As ratio
- EPA - Fe secondary MCL

Axial scales:
- Arsenic (µg/L): 0 to 160
- Iron (mg/L): 0 to 1.6
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- Arsenic (μg/L)
  - C: Media Adsorption; IX: RO; Nanofiltration
  - B: Modified Iron Removal
  - A: Iron Removal Process (optimized for maximum arsenic removal)

- Iron (mg/L)
  - 20:1 Fe/As ratio

- Lidgerwood, ND
Arsenic Treatment Selection Guide as a Function of Raw Arsenic and Iron

- **C**: Media Adsorption; IX; RO; Nanofiltration
- **B**: Modified Iron Removal
- **A**: Iron Removal (optimized for maximum arsenic removal)

- 20:1 Fe/As ratio
- Sabin, MN

- Arsenic (µg/L)
  - 0
  - 20
  - 40
  - 60
  - 80
  - 100
  - 120
  - 140
  - 160

- Iron (mg/L)
  - 0
  - 0.2
  - 0.4
  - 0.6
  - 0.8
  - 1
  - 1.2
  - 1.4
  - 1.6
Arсеник: Выбор метода очистки в зависимости от концентрации арсеника в воде

- Медиа-фильтрация
- Адсорбция
- Футеровка: IX, RO
- Фильтрация нанофильтрации

- Увеличенная очистка железа (B)
- Процесс удаления железа (A) (оптимизирован для максимального удаления арсеника)

- EEC: вторичная MCL

- Отношение Fe/As 20:1

- Водопровод Лиджервуд, ND