Seasonality of Progressive Iron Removal within the Initial Oxidation Cell of a Passive Treatment System

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Importance of Iron Removal

• Accessibility via chemical activity (order of operations)

• Physical and chemical complications with other treatment cells staged later in the series.

• Side benefit of sorption of other trace metals (zeta potential dependent)
Influent water quality and loading rates
  – Metals species and concentrations
  – Flow rates (hydroperiod)

Removal efficiency (rate)
  – Overall and per surface area unit (kg/m²/year)
  – System sizing and transport state (aqueous vs. solid)

Settling and storage
  – Short term performance (seasonal)
  – Long term performance (over design life)
Remediation of AMD impacted waters rely on a two step process for iron removal:

- Iron Oxidation – $\text{Fe}^{2+}$ oxidized to $\text{Fe}^{3+}$
  
  \[
  4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}
  \]

- Iron Hydrolysis: Iron Precipitation
  
  \[
  \text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 3\text{H}^+
  \]
Cell Performance Monitoring

Influent Water Quality/Quantity

Effluent Water Quality/Quantity
Why Profile a Treatment Cell?

• Additional mechanistic information to aid in troubleshooting or design enhancement within the current or future designs.

• Detailed performance comparison to design for proof of concept or validation.
Objective and Purpose

• To investigate the performance of the preliminary oxidation cells of a passive treatment system with respect to season.

• To determine if seasonal variability in total iron removal can be mitigated through system design features (secondary oxidation cells as surface flow wetlands)
The Mayer Ranch Passive Treatment System (MRPTS) was designed to treat AMD that is:

- net-alkaline
- ferruginous
- lead-zinc drainage

Tar Creek Superfund Site, Commerce OK.
AMD and System Characteristics

- Q varies between 400-700 L/min annually
- Influent pH = 5.95 ±0.06
- Net Alkaline (Alkalinity 393 ± 13 mg/L CaCO₃)
- Mean mass loading = 106 kg Fe / Day (1st year)
- Average iron removal rate = 22 g/m²/day (1st year)

<table>
<thead>
<tr>
<th></th>
<th>Iron</th>
<th>Zinc</th>
<th>Lead</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Influent</td>
<td>192±10 mg/L</td>
<td>11.0±0.7 mg/L</td>
<td>60±13 µg/L</td>
<td>17±4 µg/L</td>
</tr>
</tbody>
</table>
MRPTS Layout and Design
## Sample Locations

<table>
<thead>
<tr>
<th>Site #</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2, 3</td>
<td>AMD Influent</td>
</tr>
<tr>
<td>4</td>
<td>Catwalk 1</td>
</tr>
<tr>
<td>5</td>
<td>S2 Bottleneck</td>
</tr>
<tr>
<td>6</td>
<td>S2 U-Bend</td>
</tr>
<tr>
<td>7</td>
<td>Catwalk 2</td>
</tr>
<tr>
<td>8</td>
<td>Catwalk 3</td>
</tr>
<tr>
<td>9</td>
<td>Cell 1 Effluent</td>
</tr>
<tr>
<td>10</td>
<td>C1 Out</td>
</tr>
<tr>
<td>11</td>
<td>C2Nout</td>
</tr>
<tr>
<td>12</td>
<td>C2Sout</td>
</tr>
</tbody>
</table>
• Seasonal sampling was conducted four times a year for three years
  – (Jan, Apr, July, Oct 2009-2012)

• Iron concentrations (total and dissolved) with respect to:
  – Position
  – Depth
  – Time (season)

<table>
<thead>
<tr>
<th>Grab Samples</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Metals</td>
<td>SONDE: pH, DO, SC, ORP, T, R, Sal, etc.</td>
</tr>
<tr>
<td>Dissolved Metals</td>
<td>Turbidity</td>
</tr>
<tr>
<td>Anions</td>
<td>Alkalinity</td>
</tr>
</tbody>
</table>
Spring (April 2010-2012):
Total Iron Removal Profile (n=3 year average)

<table>
<thead>
<tr>
<th>Mass Loading</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>In (kg/day)</td>
<td>123</td>
<td>121</td>
<td>122</td>
</tr>
<tr>
<td>Out (kg/day)</td>
<td>4</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>Removal (gm(^{-2}) day(^{-1}))</td>
<td>21</td>
<td>20</td>
<td>21</td>
</tr>
</tbody>
</table>

Average Seep
Summer (July 2009-2011)
Total Iron Removal Profile (n= 3 year average)

<table>
<thead>
<tr>
<th>Mass Loading</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>In (kg/day)</td>
<td>100</td>
<td>90</td>
<td>91</td>
</tr>
<tr>
<td>Out (kg/day)</td>
<td>15</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Removal (gm⁻² day⁻¹)</td>
<td>12</td>
<td>11</td>
<td>12</td>
</tr>
</tbody>
</table>
Fall (Oct 2009-2011)
Total Iron Removal Profile (n= 3 year average)

<table>
<thead>
<tr>
<th>Mass Loading</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>In (kg/day)</td>
<td>108</td>
<td>113</td>
<td>106</td>
</tr>
<tr>
<td>Out (kg/day)</td>
<td>6</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Removal (gm(^{-2}) day(^{-1}))</td>
<td>15</td>
<td>17</td>
<td>16</td>
</tr>
</tbody>
</table>
Winter (Jan 2010-2012)
Total Iron Removal Profile (n= 3 year average)

Mass Loading

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>In (kg/day)</td>
<td>86</td>
<td>82</td>
<td>83</td>
</tr>
<tr>
<td>Out (kg/day)</td>
<td>49</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Removal (gm^{-2} day^{-1})</td>
<td>4</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>

Bar chart showing total iron concentration and removal per location.
Total Iron Removal Comparison
Cell 1 Removal Profile (n= 3 year average)

% Removal of Total Iron vs Relative Sample Collection Position

- Spring
- Winter
- Summer
- Fall
Objective: To investigate performance with respect to season and design specification

- For most of the year (spring, summer, and fall), approximately 88% of loaded iron is removed in the first section of oxidation pond, and nearly all of it (~90%) is removed before reaching Cells2N&S.

- However, winter conditions reduce the removal of iron in the first section of the oxidation pond to a mere 20% with only 80% total removal within Cell 1.
  - Up to 90% removal observed at C2(N&S) effluent.
Purpose: To determine if seasonal variability can be mitigated through secondary oxidation wetlands

Comparison between the relative standard deviation (%) between area adjusted removal efficiencies (g m⁻²day⁻¹)

<table>
<thead>
<tr>
<th>Removal Conditions</th>
<th>Cell 1 Only (% RSD)</th>
<th>Cells 1 and 2 Together (%RSD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Seasons</td>
<td>40.5%</td>
<td>35.6%</td>
</tr>
<tr>
<td>No Winter</td>
<td>28.3%</td>
<td>28.5%</td>
</tr>
</tbody>
</table>

Small improvement in variability with oxidation cell series, but not as dramatic as expected.

Extracting the winter data from the set yields less variability overall.
Future Work

• Tracer study to determine actual hydraulic retention time of Cell 1.

• Interpretation of iron concentrations from depth samples as an indicator of solids accumulation.
  – core sampling for accumulation profiling and assessment
Acknowledgements

Sampling

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Selected References


- EPA Tar Creek Fact Sheet (Region 6). Updated Spring 2009. EPA ID# OKD980629844 Site ID:0601269


