Anaerobic Biochemical Reactor (BCR) Treatment of Mining-Influenced Water (MIW): Evaluation of Reduction in Concentrations of Metals and Aquatic Toxicity

Presented in Webinar Series:

*FRTR Presents...Heavy Metals-Mining Site Characterization and Treatment Session 2*

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The views expressed in this presentation are those of the author’s and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.
Presentation Outline

- BCR Treatment
- Research Questions
- Study Sites
- Methods
- Metals Removal
- Aquatic Toxicity (Acute)
- Concluding Remarks
BCR Treatment

• Passive / semi-passive treatments
  ▪ May be completely anaerobic, aerobic, or combination of both
  ▪ Natural processes
  ▪ Minimal or no energy requirement
    ◦ Solar power has been used

• Anaerobic biochemical reactor
  ▪ Previously (and sometimes still) called sulfate-reducing bioreactor
    ◦ A primary mechanism is microbial sulfate reduction to sulfide that precipitates metal sulfides
  ▪ Sometimes called anaerobic wetland
    ◦ But, no vegetation
BCR Treatment

- Chemical, biological, and physical processes
  - Reduction, precipitation, adsorption, retention
- Hay, straw, wood chips, sawdust, compost, limestone, manure, ethanol, waste milk...
- Aerobic polishing
  - Increase oxygen
  - Decrease biochemical oxygen demand (BOD)
  - Settle solids
    - Some release of sulfide precipitates, which will oxidize and re-precipitate as metal oxyhydroxides
  - Degas sulfide and ammonia
BCR Treatment

• Overall goal of remediation is to minimize environmental and human health impacts

• Evaluation of BCR treatment generally through metal removal efficiency
  ▪ Percentage of dissolved metals removed by the system
    o 100% * [(influent concentration – effluent concentration) / influent concentration]
Research Questions Asked

• Are the effluents from the different pilot BCRs toxic (i.e., are there adverse effects to either test species that is statistically different from control water)?

• Is the toxicity reduced, relative to the influent?

• If effluents are toxic, is a toxicant identifiable?
Study Sites

• Luttrell Repository, Helena, MT
• Peerless Jenny King, Helena, MT
• Park City Biocell, Park City, UT
• Standard Mine, Crested Butte, CO
Luttrell Repository, MT

- Upper Ten-Mile Creek Superfund site
- 7,644 ft AMSL
- 2002
- 1.5 gpm treated
- Al, As, Cd, Co, Cu, Fe, Mn, Zn
Peerless Jenny King, MT

- Upper Ten-Mile Creek Superfund site
- 7,600 ft AMSL
- 2003
- 20-25 gpm treated
- Cd, Fe, Zn
Peerless Jenny King, MT

- Upper Ten-Mile Creek Superfund site
- 7,600 ft AMSL
- 2003
- 20-25 gpm treated
- Cd, Fe, Zn
Park City Biocell, UT

- Prospector drain in Silver Creek Watershed
- 2002
- 6,900 ft AMSL
- 29 gpm treated
- Cd, Zn
Park City Biocell, UT

- Prospector drain in Silver Creek Watershed
- 2002
- 6,900 ft AMSL
- 29 gpm treated
- Cd, Zn
Crested Butte

2007

11,000 ft AMSL

1.2 gpm treated

Cd, Cu, Fe, Pb, Mn, Zn

Standard Mine, CO
Standard Mine, CO

- Crested Butte
- Aerobic polishing cells added in 2008
Methods
Methods

• Triplicate influent and effluent samples from Luttrell, PJK, and Park City
• Duplicate influent and effluent samples from the Standard Mine BCR and from the APC
Methods

- Filtered metals (0.45 µm) – inductively coupled plasma – optical emission spectroscopy (ICP-OES)
- Sulfate – ion chromatography
- Total sulfide – ion selective electrode
- Total ammonia – gas sensing electrode
Methods

• Whole effluent toxicity tests [WET]
  ▪ Series of dilutions of the influent and effluent water samples
• Acute 48-hr LC50
  ▪ Percentage of water mixed with moderately hard dilution water
• Ceriodaphnia dubia [water flea]
• Pimephales promelas [fathead minnow]
  ▪ Control survival > 90%
Results - Metals
## Influent Metals Concentrations

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Luttrell</th>
<th>PJK</th>
<th>Park City</th>
<th>Standard Mine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (mg/l)</td>
<td>28 ± 0.3</td>
<td>BMDL</td>
<td>BMDL</td>
<td>BMDL</td>
</tr>
<tr>
<td>As (mg/l)</td>
<td>2.5 ± 0.03</td>
<td>BMDL</td>
<td>BMDL</td>
<td>BMDL</td>
</tr>
<tr>
<td>Cd (mg/l)</td>
<td>1.6 ± 0.11</td>
<td>BMDL</td>
<td>0.1 ± 0.01</td>
<td>0.18 ± 0.003</td>
</tr>
<tr>
<td>Cu (mg/l)</td>
<td>27 ± 0.1</td>
<td>BMDL</td>
<td>BMDL</td>
<td>0.24 ± 0.006</td>
</tr>
<tr>
<td>Fe (mg/l)</td>
<td>27 ± 0.3</td>
<td>0.27 ± 0.015</td>
<td>BMDL</td>
<td>0.12 ± 0.008</td>
</tr>
<tr>
<td>Ni (mg/l)</td>
<td>0.31 ± 0.003</td>
<td>BMDL</td>
<td>BMDL</td>
<td>BMDL</td>
</tr>
<tr>
<td>Pb (mg/l)</td>
<td>BMDL</td>
<td>BMDL</td>
<td>BMDL</td>
<td>0.21 ± 0.025</td>
</tr>
<tr>
<td>Zn (mg/l)</td>
<td>270 ± 25</td>
<td>1.2 ± 0.03</td>
<td>8.4 ± 0.15</td>
<td>27 ± 0.6</td>
</tr>
<tr>
<td>SO₄ (mg/l)</td>
<td>4.6 ± 1.1 (g/l)</td>
<td>49 ± 15.8</td>
<td>642 ± 39</td>
<td>254 ± 9</td>
</tr>
</tbody>
</table>
## Influent & Effluent pH and DO

<table>
<thead>
<tr>
<th>Parameter (average)</th>
<th>Luttrell</th>
<th>PJK</th>
<th>Park City</th>
<th>SM-BCR</th>
<th>SM-APC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Influent</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>3.6 ± 0.23</td>
<td>6.7 ± 0.08</td>
<td>6.2 ± 0.13</td>
<td>6.1 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>4 ± 0.8</td>
<td>3 ± 0.1</td>
<td>5 ± 0.1</td>
<td>6 ± 0</td>
<td></td>
</tr>
<tr>
<td><strong>Effluent</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.4 ± 0.02</td>
<td>7.8 ± 0.04</td>
<td>7.1 ± 0.03</td>
<td>6.7 ± 0.06</td>
<td>8.6 ± 0.07</td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>0.3 ± 0.24</td>
<td>3 ± 0.3</td>
<td>2 ± 0.1</td>
<td>0.6 ± 0.45</td>
<td>1 ± 0</td>
</tr>
</tbody>
</table>
# Percentage of Metals Removed

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Luttrell</th>
<th>PJK</th>
<th>Park City</th>
<th>SM-BCR</th>
<th>SM-APC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>99 ± 1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>As</td>
<td>98 ± 2</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Cd</td>
<td>99 ± 10</td>
<td>n/a</td>
<td>96 ± 12</td>
<td>100 ± 2</td>
<td>100 ± 2</td>
</tr>
<tr>
<td>Cu</td>
<td>100 ± 0.3</td>
<td>n/a</td>
<td>n/a</td>
<td>94 ± 9</td>
<td>94 ± 9</td>
</tr>
<tr>
<td>Fe</td>
<td>99 ± 2</td>
<td>90 ± 12</td>
<td>n/a</td>
<td>-266 ± -518</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>Ni</td>
<td>94 ± 5</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Pb</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>94 ± 16</td>
<td>91 ± 17</td>
</tr>
<tr>
<td>Zn</td>
<td>100 ± 13</td>
<td>94 ± 11</td>
<td>100 ± 3</td>
<td>100 ± 3</td>
<td>100 ± 3</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>72 ± 29</td>
<td>-78 ± -137</td>
<td>-1 ± -8</td>
<td>39 ± 4</td>
<td>72 ± 5</td>
</tr>
</tbody>
</table>
Results - Acute Aquatic Toxicity
Effluent samples more toxic to fathead minnow

Influent samples more toxic to water flea

Highest dilution volume tested (25%) had 35% mortality

LC50 below lowest volume tested

< 0.1%

Gray – water flea
Black – fathead minnow

Sample ID
Influent samples more toxic to water flea

Not different from control

Gray – water flea
Black – fathead minnow

Sample ID

LC$_{50}$ (% v/v)

Peerless Jenny King
Influent samples more toxic to water flea

Not different from control

Highest dilution volume tested (20%)
35-45% mortality

Gray – water flea
Black – fathead minnow

Sample ID
Gray – water flea
Black – fathead minnow

35% mortality

Influent samples more toxic to water flea

BCR effluent samples more toxic to fathead minnow than to the water flea

Not different from control

Sample ID

INF-A  INF-B  BCR-EFF-A  BCR-EFF-B  APC-EFF-A  APC-EFF-B
Acute Aquatic Toxicity

• What caused acute toxicity in Luttrell and Standard Mine BCR effluent samples?
• Low dissolved oxygen?
  ▪ SM-BCR field average 0.6 mg/l DO; Luttrell field average 0.3 mg/l DO
  ▪ Test units must have > 4 mg/l
    o Generally > 6 mg/l
• Metals, sulfide, ammonia?
# Acute Aquatic Toxicity

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ceriodaphnia dubia</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd (ug/l)</td>
<td>Cu (ug/l)</td>
<td>Zn (ug/l)</td>
<td>H₂S (mg/l)</td>
<td>NH₃ (ug/l)</td>
<td></td>
</tr>
<tr>
<td>LR-EFF-A</td>
<td>NA</td>
<td>NA</td>
<td>61</td>
<td>26</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>LR-EFF-B</td>
<td>NA</td>
<td>NA</td>
<td>27</td>
<td>9.3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>LR-EFF-C</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>3.2</td>
<td>0.5</td>
<td></td>
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<tr>
<td>SM-BCR-A</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.29</td>
<td>0.06</td>
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<tr>
<td>SM-BCR-B</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.74</td>
<td>0.1</td>
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<tr>
<td>Comparison Value</td>
<td></td>
<td>31.4</td>
<td>6</td>
<td>425</td>
<td>0.002</td>
<td>500 - 5000</td>
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</table>

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Pimephales promelas</th>
<th></th>
<th></th>
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<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd (ug/l)</td>
<td>Cu (ug/l)</td>
<td>Zn (ug/l)</td>
<td>H₂S (mg/l)</td>
<td>NH₃ (ug/l)</td>
<td></td>
</tr>
<tr>
<td>LR-EFF-A</td>
<td>NA</td>
<td>NA</td>
<td>0.13</td>
<td>0.58</td>
<td>0.1</td>
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<tr>
<td>LR-EFF-B</td>
<td>NA</td>
<td>NA</td>
<td>0.53</td>
<td>1.83</td>
<td>0.4</td>
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<tr>
<td>LR-EFF-C</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.28</td>
<td>0.2</td>
<td></td>
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<tr>
<td>SM-BCR-A</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.298</td>
<td>0.01</td>
<td></td>
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<tr>
<td>SM-BCR-B</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.087</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Comparison Value</td>
<td></td>
<td>29.2</td>
<td>69.6</td>
<td>725</td>
<td>0.002</td>
<td>200 - 3400</td>
</tr>
</tbody>
</table>

NA = none detected in undiluted sample
Dissolved H₂S and NH₃ calculated from total values, temp, and pH
Effect of Aeration

Test species: fathead minnow

Sample ID

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Percent Survival (100% sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR-A</td>
<td>~2%</td>
</tr>
<tr>
<td>LR-B</td>
<td>~2%</td>
</tr>
<tr>
<td>LR-C</td>
<td>~66%</td>
</tr>
<tr>
<td>LR-A aerated</td>
<td>~66%</td>
</tr>
<tr>
<td>LR-B aerated</td>
<td>~66%</td>
</tr>
<tr>
<td>LR-C aerated</td>
<td>&lt;20%</td>
</tr>
<tr>
<td>SM-A</td>
<td>&lt;20%</td>
</tr>
<tr>
<td>SM-B</td>
<td>&lt;20%</td>
</tr>
<tr>
<td>SM-A aerated</td>
<td>100%</td>
</tr>
<tr>
<td>SM-B aerated</td>
<td>100%</td>
</tr>
</tbody>
</table>
Dissolved Gaseous Species
Luttrell Repository

Reference Toxicity Levels
2 ug/l H₂S
.2 to 5 mg/l NH₃

- H₂S (aq)
- NH₃ (aq) (10 °C)
- NH₃ (aq) (20 °C)
Dissolved Gaseous Species
Standard Mine

Reference Toxicity Levels
2 μg/l H₂S
0.2 to 5 mg/l NH₃

Sulfide (mg/l)
Ammonia (mg/l)

pH

H₂S (aq)
NH₃ (aq) (10 °C)
NH₃ (aq) (20 °C)
Concluding Remarks

• Results suggest toxicity from dissolved hydrogen sulfide gas
  ▪ Effluents more toxic to fathead minnow than to the *C. dubia*
  ▪ Fathead minnow known to be more sensitive to dissolved gases than *C. dubia*
  ▪ Dissolved $H_2S$ concentrations above species mean acute values
  ▪ Toxicity from 100% sample removed with aeration at Standard Mine and reduced at Luttrell

• Other BCRs may have different toxicants, depending on:
  ▪ Contaminants present and efficiency of removal
  ▪ Concentrations of dissolved gases and pH of the effluent
Concluding Remarks

- BCR treatment is effective at removing significant proportions of metals from MIW, but aquatic toxicity may still be present.

- Sufficient in-field aeration following BCR treatment is an important step to remove potential toxicants resulting from the processes occurring within the BCR cells.

- Combining chemical and biological monitoring can lead to better treatment system designs.
  - To meet the goal of minimizing environmental and human health impacts.
Acknowledgements

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  ▪ Mark Smith – McConnell Group [deceased, prior contractor to U.S. EPA ORD]

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  ▪ Pegasus and McConnell Group – contractors to EPA
  ▪ Regional RPM’s
  ▪ City of Park City, UT