ENHANCED SULFATE REDUCTION TREATMENT OF MINING-INFLUENCED WATER USING BIOCHEMICAL REACTORS

IMPACTS ON MERCURY SPECIATION

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National Conference on Mining-Influenced Waters
Approaches for Characterization, Source Control and Treatment
Albuquerque, NM

August 13, 2014
Presentation Objectives

• Mercury in the Environment
  – Prevalence
  – How a Mole Hill Turns into a Mountain

• Biochemical Reactors – Mining Impacted Water
  – Formosa Treatability Study
  – ORD Bench Top Study

• General Conclusions

• Recommendations for Moving Forward
Anthropogenic Point Source Impacts

Minamata Bay

California Gold/Mercury Mines
Non-Point Source Impact

• 367 Stream Sites Sampled Across United States

• Sites with Fish Greater than 0.3 µg/g
  • 25% Exceedances

• Sites with Fish Greater than 0.6 µg/g
  • 10% Exceedances
Bioaccumulation

Wood et al., 2013

\[ BAF = \frac{C_B}{C_{DW}} \]

- BAF = Bioaccumulation Factor (1/kg)
  - (Gobas and McCorquodale, 1992)
- \( C_B \) = Concentration in Biota or Particle (ng/kg)
- \( C_{DW} \) = Concentration Dissolved in Water (ng/L)

Mountains out of a Mole Hills
Working the Problem Backwards (MeHg)

- **USGS: Mean, ng/L**
  - All Sites: 0.19
  - Unmined: 0.2
  - Mined: 0.18

- **Range, ng/L**
  - All Sites: 4.11-ND
  - Unmined: 4.11 – ND
  - Mined: 2.02 – ND

- **California Water Control Board:**
  - 0.06 ng/L – Implementation Goal
Mine Impacted Water

• “Aqueous waste generated by ore extraction and processing, as well as mine drainage and tailings runoff.” ~ITRC, 2013

• AMD: Sulfidic Rock in Contact with Surface Water and Oxygen
  – pH Decreases
  – Metals Dissolve
Biochemical Reactors

• BCRs are engineered systems that use an organic substrate (electron donor) to drive microbial and chemical reactions to reduce concentrations of metals, acidity, and sulfate in MIW.

  – ChitoRem® SC-20
  – Woody Substrate/Manure Including Limestone

  \[
  \text{SO}_4^{2-} + 2 \text{CH}_2\text{O} \rightarrow \text{HS}^- + 2 \text{HCO}_3^- + \text{H}^+
  \]

  \[
  \text{S}^{2-} + \text{Me}^{2+} \rightarrow \text{MeS(s)} \text{ and } \text{HS}^- + \text{Me}^{2+} \rightarrow \text{MeS(s)} + \text{H}^+
  \]

  – See Angela Frandsen’s Talk; Section 10 @ 1:30 Today
Treatability Study Flow Diagram

NOTE:
AUGUST 8, DISCHARGE TUBING LOWERED TO BE 25° ABOVE BOTTOM OF BARREL

FORMOSA MINE SUPERFUND SITE
DOUGLAS COUNTY, OREGON

Figure 1-2
Pilot-Scale Treatability Study
Process Flow Diagram (Record Drawing)
AUGUST 2013
## Composition

<table>
<thead>
<tr>
<th>Substrate Mix</th>
<th>Volume (gallon)</th>
<th>Substrate Mix</th>
<th>Volume (gallon)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pre-Treatment ChitoRem®</strong></td>
<td></td>
<td><strong>Pre-Treatment SAPS</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compost</td>
<td>--</td>
<td>12.50</td>
<td>4.38</td>
</tr>
<tr>
<td>Fresh dairy manure</td>
<td>--</td>
<td>12.50</td>
<td>4.38</td>
</tr>
<tr>
<td>Limestone chips 3/4-inch to 1.5-inch</td>
<td>--</td>
<td>75.00</td>
<td>26.25</td>
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<tr>
<td>3/4-inch inert gravel</td>
<td>--</td>
<td>7.50</td>
<td>7.50</td>
</tr>
<tr>
<td>ChitoRem®</td>
<td>40</td>
<td>14.00</td>
<td>--</td>
</tr>
<tr>
<td>Construction sand</td>
<td>40</td>
<td>21.00</td>
<td>--</td>
</tr>
<tr>
<td>Inert pea gravel</td>
<td>20</td>
<td>7.00</td>
<td>--</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100</td>
<td>49.50</td>
<td>100.00%</td>
</tr>
</tbody>
</table>
## Composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Woody Material Mixture</th>
<th>ChitoRem® and Sand Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Substrate Mix (v/v Percent)</td>
<td>Volume (gallon)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>15.00</td>
<td>5.25</td>
</tr>
<tr>
<td>Wood chips</td>
<td>30.00</td>
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<tr>
<td>Compost</td>
<td>15.00</td>
<td>5.25</td>
</tr>
<tr>
<td>Fresh dairy manure</td>
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<td>7.00</td>
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<tr>
<td>Inert pea gravel</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
<td><strong>42.50</strong></td>
</tr>
</tbody>
</table>

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**Treatability Study Flow Diagram**

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**FORMOSA MINE SUPERFUND SITE**
**DOUGLAS COUNTY, OREGON**

**Figure 1-2**

**Plot-Scale Treatability Study**
**Process Flow Diagram**

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**CDM Smith**

**August 2013**
Mercury Results

Trace Mercury (EPA 1631) ~ 2 months

Formosa Treatability Study
Mercury Results (Continued)

Methyl Mercury (EPA 1630) ~2 months

SC-20 pH: 3.26 6.36 6.25 6.34

MeHg
Formosa Mercury Evaluation Summary

• All SC-20 BCRs Increased THg and MeHg
  – THg Increased by 10 to 20 ng/L
  – MeHg Increased by 1 to ~3 ng/L

• THg Potentially Sourced from Media
  – Crab Hg Body Burden ~ 0.16 mg/kg

• MeHg From Release Or Generation
  – Potential Resident Source:
    • Aquatic Organisms Typically Enriched in MeHg
  – Potential MeHg Generation from Resident and Influent Hg(II)
    • Evidence of SRB Activity
      – ORP, Sulfide, Volatile Fatty Acids
ORD Bench Top Study

Influent and Column Specifics
24 hr Hydraulic Residence Time

- Column 1: SC-20 (140 g) + sand (420 g) – Pretreated MIW
- Column 2: Wood Chips (253 g) + Hay (17 g) + Manure (4 g) – Pre
- Column 3: SC-20 (140 g) + Sand (420 g) – Raw MIW
- Column 4: Wood Chips (253 g) + Hay (17 g) + Manure (4 g) – Raw
- Column 5: SC-20 (140 g) + Sand (420 g) – Na Azide Raw MIW
- Column 6: Sand (420 g) – Na Azide Raw MIW
Total Filtered Mercury: 31 and 34 Weeks into Test

- Dissolved Fraction (<0.45 um) Comparable to Field Study
  - Fraction Most Available for Methylation
- Raw FMW Columns ~ GLI 1.3 ng/L
- PreTreat Columns < GLI 1.3 ng/L
- Na Azide Columns >> GLI 1.3 (With Elevated Hg Influent)
Methylmercury 31 and 34 Weeks into Test

Evidence of SRB Activity:
- SRB Lab Test: (+) In Raw and Pretreat Columns
- Elevated Volatile Fatty Acid In Raw and Pretreat Columns
- pH Elevated in Raw and Pretreat Columns
- ORP Depressed in Raw and Pretreat Columns

Data Provided by EPA ORD Laboratory
Bench Top Study Observations

- SC-20 Pretreated: THg and MeHg Maintained Below Levels of Concern (1.3 ng/L for THg GLI & 0.06 ng/L for MeHg CWCB)

- SC-20 Effluent (Raw & Na Azide) ~75% MeHg in Dissolved Fraction

- Natural Production of MeHg Typically ~5% of Total

- MeHg as THg
  - Raw FMW: 0.4 to 0.5
  - Pretreat: 0.08
  - Na Azide: 0.5 to 0.6
Key Difference Between Lab and Field Test

• Duration:
  – Field Test Sampled One Time ~2 Months Into Test
  – Lab Test Sampled Twice, at 7 and 8 Months Into Test

• Flow Consistency:
  – Field Test Flow Decreased Over Time
    • Much of Media Left Unreacted
  – Lab Test Flow Remained Consistent

• Variability of Mercury Concentrations in Influent
  – Formosa Adit Stable
    • ~ 2 ng/L
  – ORD Laboratory Influent
    • Range 1.1 to 9.6 ng/L
General Conclusions

• Effect on Total Mercury
  – Field Test: THg Increased in all SC-20 BCRs
  – Lab Test: THg Decreased in all Columns

• MeHg in SC-20 Effluent Elevated relative to Influent
  – Two Possible Explanations
    • SRB Activity Methylate Hg(II) to MeHg, or
    • Resident MeHg Released from Media

• Need for More In Depth Evaluation to Quantify and Understand Mercury Dynamics Associated with the Application of SC-20 in MIW Applications
Recommendations for Further Study

• Fully Quantify Resident Mercury Concentration and Speciation in BCR Media
  – Both SC-20 and Sand

• Evaluate Conditions that Promote Mercury Release from BCR Media

• Evaluate Conditions that Promote Methylation of Hg(II)
  – From Influent Source
  – From Resident Source
Acknowledgements

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Questions?

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