Evaluating Effectiveness and Permanence of Selenium Treatment in a Bag House Material Matrix Using an Aqueous-Mediated Zero Valent Iron Reaction

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AGENDA

Background

Development of Methods and Testing

Results

Treatment Model

Conclusions
Solid Waste Management Concerns

Aluminum Industry

- Se added to Mn electro extraction to reduce energy consumption
  - Mn is alloyed with 3xxx series Al
  - Particulates resulting from air pollution control
    - Estimated 2.2 M MT/yr generated
    - Up to ~10 g Se / kg particulates

Power Industry

- ~ 115M tons/yr in 2013 (over 50% disposed / impounded)
- Bottom ash, fly ash, FGD sludge (0.2-600 ppm)
**Background**

**Program Objective:**
Prove efficacy and permanence of treatment using ZVI

**Regulatory Drivers**

**Current disposal and leachate discharge regulations**
- TCLP disposal limit of 1 mg/L
- Aquatic limit 5 µg/L

**Iron filing / Lead Foundry Sands LDR Phase IV Final Rule**
- 40 CFR 268.3
- Zero Valent Iron (ZVI) addition is “Impermissible Dilution”
- A state level agency has tied this to Se in other waste matrices
Relevant Species of Selenium

- **Se$^{+6}$** Selenate
- **Se$^{+4}$** Selenite
- **Se$_0$** Zero Valent Form

Mobile Forms

- Immobile Form
  - Low Solubility $\sim$0.24 µg/L
Redox Reaction and Landfill Conditions

\[ Fe_0 \leftrightarrow Fe^{2+} + 2e^- \]
\[ HSeO_4^- + 3H^+ + 2e^- \leftrightarrow H_2SeO_3 + H_2O \]
\[ H_2SeO_3 + 4H^+ + 4e^- \leftrightarrow Se_0 + 3H_2O \]

\[ E_0 = -0.41 \text{ V} \]
\[ E_0 = +1.15 \text{ V} \]
\[ E_0 = -0.74 \text{ V} \]
Aqueous-Mediated Reaction / Stabilization

Various Ratios of Amendments Tested

Fly ash, portland cement *(deemed infeasible)*

Zero Valent Iron (ZVI)

Water

Identified Optimum Blend

96 parts BHD : 35 parts water : 4 parts ZVI
Testing Approach

**Bench-Scale**

- Mix ratios – trials in 0.5 L jars
- TCLP and other laboratory data

**Proof of Concept for Scale-up**

- Designed, built, operated system
Importance of Water to Mediate Redox Reaction
Importance of Curing

**Graph:**

- **Average % reduction in selenium TCLP after adjusting for dilution from added solids and H₂O**

- **Trial Trials:**
  - No Cure
  - Transit Cure
  - 3 Day Cure
  - 10 Day Cure

- **Percentage Reduction:**
  - No Cure: 60%
  - Transit Cure: 90% (±1%)
  - 3 Day Cure: 95%
  - 10 Day Cure: 99%
Curing – Physical Occlusion vs. Chemisorption?

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Leached Concentration</th>
<th>% Reduction</th>
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</thead>
<tbody>
<tr>
<td>Monolith Cure</td>
<td>&lt;0.06 mg/L</td>
<td>98.7%</td>
</tr>
<tr>
<td>Crushed Sample (Particle size: 1-10 cm³)</td>
<td>0.199 mg/L</td>
<td>95.6%</td>
</tr>
<tr>
<td>Pulverized Sample 24 hour soak</td>
<td>0.178 to 0.310 mg/L</td>
<td>96.1% to 93.2%</td>
</tr>
<tr>
<td>Pulverized Sample 7 day soak</td>
<td>0.390 mg/L</td>
<td>91.4%</td>
</tr>
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*TCLP prior to stabilization = 4.55 mg/L
Assessing Permanence When Iron is Not Present

**SiO₂ powder used as surrogate for BHD matrix**

**Laboratory grade ZVS dust**
- Triple anoxic wash to remove surface oxidation

**Percentage basis**
- 0.125 g ZVS per 100g sample
  - Represented actual total in BHD that exhibited 8 mg/L Se TCLP (design basis)
- 1.1 g ZVS per 100 g sample
  - 10X design basis

<table>
<thead>
<tr>
<th>Dry Mix Formula</th>
<th>TCLP</th>
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<tr>
<td></td>
<td>Selenium (mg/L)</td>
</tr>
<tr>
<td>Silica</td>
<td>Zero Valent Selenium</td>
</tr>
<tr>
<td>99.875 g</td>
<td>0.125 g</td>
</tr>
<tr>
<td>99.625 g</td>
<td>0.375 g</td>
</tr>
<tr>
<td>98.9 g</td>
<td>1.1 g</td>
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Treatment Model

Treatment

\[ A = A_1 + A_2 \]

TCLP Testing

C is physically bound fraction of Se\(^+\)
Mixture Passes TCLP

Disposal

C may become leachable
\[ C << A_1 + A_2 + B \]
Projected Landfill Mass Balance
(Based on lab data)

Total $Se_{\text{in}} = 100.9\ \text{mg/kg}$

- A $\% Se^+$: 63.66 mg/kg
- A$_2$ $\% Se_0$: 29.87 mg/kg
- B $\% Se_0$: 4.07 mg/kg
- TCLP = 0.22 mg/L
- TCLP$^*$ = 0.165 mg/L
- Total $Se_{\text{out}} = 3.3\ \text{mg/kg}$
Conclusions

Aqueous mediated reaction is very effective for conversion
• Consistent results < 1 mg/L threshold

Approach supports permanence of treatment
• Small fraction may be physically bound and mobile over time

Future Development

Long term dynamic testing
• LEAF tests – dynamic testing utilizing Method 1314 or 1315

Additional materials
QUESTIONS
Thank you!
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