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Overview of Presentation

NAMC Selenium Report 2010

Outline

- Barrel-Study Overview
- Aqueous Results
- Volumetric/Aerial Loading Rates
- Substrate Se Removal
- Volatilization
- Substrate Se Speciation
- Modeling Calibration/Removal Rate Development
- Secondary Parameters
- Conclusions

http://www.namc.org/docs/00062756.PDF
Case History (2011-2012)
Two Concurrent BCR Pilot Studies for Coal Mine Drainage

Outlet A: 389 days
Pumped Inflow

Outlet B: 180 days
Gravity Inflow

TDS 1 g/L
Se in 6–17 µg/L
NO3-N 0.47 mg/L
TP 0.071 mg/L

Source: R. Thomas (2011)
Outlet 022: Variable Flow and Limited Flow Control Resulting in Variable Se Reduction

Outlet 022 Pilot: 180 Days

Selenium Concentration (ppb)


Barrel A  Barrel B  Barrel C  Barrel D  Monthly Avg Limit  Max Daily Limit  Influent
Outlet 033: Consistent Se Reduction Through Winter

Outlet 033 Pilot: 389 days

8.2°C mean
4°C min
<0°C air

Source:
CH2M HILL (2012)
Focus on Winter
Water Minimum Temperature 4°C

Avg Water Temp 8.2°C
Avg Min Air Temp 4.2°C
Average Se Mass Removed Per Day – 022

Outlet 022 - Barrel A,
Avg. Se Mass (µg/day)

- Influent: 3,564 µg/day
- Effluent: 542 µg/day
- Se Removed: 4,106 µg/day
- Se Removed: 87%

Outlet 022 - Barrel B
Avg. Se Mass (µg/day)

- Influent: 3,489 µg/day
- Effluent: 338 µg/day
- Se Removed: 3,827 µg/day
- Se Removed: 92%

Outlet 022 - Barrel C
Avg. Se Mass (µg/L)

- Influent: 2,844 µg/L
- Effluent: 678 µg/L
- Se Removed: 3,523 µg/L
- Se Removed: 83%

Outlet 022 - Barrel D
Avg. Se Mass (µg/L)

- Influent: 2,739 µg/L
- Effluent: 288 µg/L
- Se Removed: 3,027 µg/L
- Se Removed: 90%
**Outlet 033 - Barrel A, Avg. Se Mass (µg/day)**

- **Influent**: 1,587 µg/day
- **Effluent**: 1726 µg/day
- **Se Removed**: 139 µg/day
- **Removal**: 91%

**Outlet 033 - Barrel B, Avg. Se Mass (µg/day)**

- **Influent**: 2,169 µg/day
- **Effluent**: 2,348 µg/day
- **Se Removed**: 179 µg/day
- **Removal**: 92%

**Outlet 033 - Barrel C, Avg. Se Mass (µg/L)**

- **Influent**: 1,563 µg/L
- **Effluent**: 1,761 µg/L
- **Se Removed**: 198 µg/L
- **Removal**: 89%

**Outlet 033 - Barrel D, Avg. Se Mass (µg/L)**

- **Influent**: 1,601 µg/L
- **Effluent**: 1,752 µg/L
- **Se Removed**: 151 µg/L
- **Removal**: 90%
Reaction Fronts in BCR Substrates Over Time
Barrel Selenium Profile

Outlet 022 Substrate Total Se Concentration (180 days)

Sampled 11/22/11 (180 days)

Top

Middle

Bottom

Se Concentration (mg/kg)

Flow Initiated 5/26/11

022A

022B

022C

022D

upflow
Barrel Selenium Profile

Outlet 033 Substrate Total Se Concentration (180 & 389 days)

Sampled 6/18/12 (389 days)
Sampled 11/22/11 (180 days)

Flow Initiated 5/26/11
Selenium Mass Balance vs Sediment Core: Gap Suggests Volatilization Loss
Vertical Distribution and Speciation of Selenium: Reduction, Sorption, Volatilization

Substrate Selenium Speciation after 180 days

Percent Recovery of Sequential Extractions versus the total digests

<table>
<thead>
<tr>
<th>Source: CH2M HILL (2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
</tr>
<tr>
<td>0.3D-Top</td>
</tr>
<tr>
<td>mg/kg Se</td>
</tr>
</tbody>
</table>

In → Out → In → Out
Vertical Distribution and Speciation of Selenium: Reduction, Sorption, Volatilization

Percent Recovery of Sequential Extractions versus the total digests
84% 94% 167% 121% 99% 95% 67% 80% 189%

Substrate Selenium Speciation after 389 days

Source: CH2MILL (2012)
Model Rate Constant Calibration

- Empirical data from barrel studies used to calibrate treatment rates in the development of a sizing model for a full-scale treatment system.
- General terms of mass conservation for a plug flow system are used while maintaining the first order model as the basis.
- Empirical data was modeled using first order area-based treatment wetland model of Kadlec & Knight (1996) & Kadlec & Wallace (2009).
- Model estimates the potential BCR effluent concentration for a given flow rate and concentration for a given BCR area, as adjusted for temperature.

\[ J = k(C_i - C_e) \]

where:
- \( J \) = zero-order contaminant removal rate [g/m^2/yr]
- \( k \) = first-order, area-based rate constant (m/yr)
- \( C_i \) = influent concentration (g/m^3)
- \( C_e \) = effluent concentration (g/m^3)
First-order area-based treatment model was expanded to the P-k-C* model, which is solved by relating: 1) hydraulic loading, 2) removal rate, 3) concentration terms, and 4) hydraulic mixing.
Rate Constant vs Hydraulic Loading Rate

![Graph showing the relationship between rate constant and hydraulic loading rate.]

<table>
<thead>
<tr>
<th>Barrel</th>
<th>Trendline Equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlet 022A</td>
<td>$y = 281.32e^{0.0118x}$</td>
<td>0.9888</td>
</tr>
<tr>
<td>Outlet 022B</td>
<td>$y = 413.88e^{0.0108x}$</td>
<td>0.9045</td>
</tr>
<tr>
<td>Outlet 022C</td>
<td>$y = 293.37e^{0.012x}$</td>
<td>1.0000</td>
</tr>
<tr>
<td>Outlet 022D</td>
<td>$y = 311.43e^{0.0134x}$</td>
<td>0.8944</td>
</tr>
<tr>
<td>Outlet 033A</td>
<td>$y = 122.74e^{0.0283x}$</td>
<td>0.9122</td>
</tr>
<tr>
<td>Outlet 033B</td>
<td>$y = 155.06e^{0.0272x}$</td>
<td>0.9892</td>
</tr>
<tr>
<td>Outlet 033C</td>
<td>$y = 201.14e^{0.019x}$</td>
<td>0.9872</td>
</tr>
<tr>
<td>Outlet 033D</td>
<td>$y = 64.395e^{0.035x}$</td>
<td>0.9215</td>
</tr>
</tbody>
</table>

![Table showing the material composition of different barrels.]

<table>
<thead>
<tr>
<th>Material</th>
<th>Barrel A</th>
<th>Barrel B</th>
<th>Barrel C</th>
<th>Barrel D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woodchips</td>
<td>20%</td>
<td>20%</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>Sawdust</td>
<td>35%</td>
<td>35%</td>
<td>35%</td>
<td>35%</td>
</tr>
<tr>
<td>Hay</td>
<td>25%</td>
<td>25%</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>Sphagnum Moss</td>
<td>10%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Bagged Composted Manure</td>
<td>5%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Spent Mushroom Compost</td>
<td>--</td>
<td>10%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Dried Horse Manure</td>
<td>--</td>
<td>--</td>
<td>10%</td>
<td>--</td>
</tr>
<tr>
<td>ChitosREM</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>10%</td>
</tr>
<tr>
<td>Limestone Chips</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Total (by volume)</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
Passive Treatment Systems rarely operate as plug-flow reactors
- Heterogeneous substrate, preferential flow

Passive Treatment Systems are better characterized hydraulically as a series of well-mixed tanks (3 – 6 in series for VFW)

Barrel-study data was configured in a three tank series using the P-k-C* model to assess the variable hydraulic characteristics on overall performance

<table>
<thead>
<tr>
<th>Barrel</th>
<th>Outlet 022(^a)</th>
<th>Outlet 033(^a)</th>
<th>Outlet 033(^b)</th>
<th>Outlet 033(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1,379</td>
<td>1,498</td>
<td>675</td>
<td>675</td>
</tr>
<tr>
<td>B</td>
<td>1,744</td>
<td>1,671</td>
<td>1,177</td>
<td>1,177</td>
</tr>
<tr>
<td>C</td>
<td>1,246</td>
<td>1,180</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>D</td>
<td>1,547</td>
<td>1,115</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Note: Target effluent concentration was set at 4 µg/L.
\(^a\) Influent temperatures monitored during the summer and fall operations used in model (θ set at 1).
\(^b\) Influent temperatures monitored during the winter operations used in model (10.5°C) (θ determined to be 0.95).
\(^c\) Influent temperature set at 9°C in model (θ determined to be 0.96).
Secondary Parameters (Salts & Labile C): Conductivity, TDS, Alkalinity, BOD
Secondary Parameters: Nutrients and Color

Outlet 033

Nitrate+Nitrite (mg/L)

Outlet 033

Phosphorus (mg/L)

Outlet 033

TKN (mg/L)

Outlet 033

Color (η g/L PtCc)
Secondary Parameters: Metals

Outlet 033

Iron (mg/L)

Mn (mg/L)
Conclusions

- Selenium was effectively reduced by ~90% on average in all barrels.
- Selenium removal was effective at all HRTs tested (12 to 24 hours).
- Cold temperatures (below freezing) did not affect selenium removal rates significantly, and effluent selenium concentrations remained below discharge limits following startup.
- The organic substrates tested could generate secondary byproducts:
  - short-term increase in conductivity from the flushing of excess salts from the substrate during startup
  - elevated oxygen demand from excess labile carbon in the effluent
  - suspended solids (mainly fine particulate organic matter)
  - excess nutrients in the substrate mixture
  - release of regulated metals such as iron and manganese, which might also occur in small amounts in the substrate mixture.
Conclusions

- Se removal occurs at the influent water-substrate interface
  - consistent with first-order processes
  - extent of selenium distribution within the substrate is dependent on the selenium load.
- Substrate Se speciation indicates:
  - dominant mechanism is reduction of selenate to reduced forms of selenium that are weakly adsorbed to the substrate during early stages of selenium removal
  - approximately >50% weakly adsorbed Se attributable to selenite
  - Highly immobile elemental selenium or selenosulfide account for about a quarter of the total selenium retained
  - very little metal selenide was found.
- Both substrate coring and water-balance mass-balance evaluation methods show selenium retention
  - higher water balance method suggests a higher overall selenium retention than that observed in the substrate cores, suggesting loss to volatilization.
- Barrel media type B appeared to balance high treatment performance with moderate production of byproducts.
- Selenium treatment BCRs have been shown to treat mine site discharges effectively in order to achieve selenium compliance limits.
Acknowledgements

- Thanks to Alpha Natural Resources
- Thanks to supporting engineering and science staff at CH2M HILL
Questions