
R.C. Thomas, M.A. Girts, J.J. Tudini, J.S. Bays, K.B. Jenkins, L.C. Roop, and T. Cook

June 3 2013
Overview of Presentation

Outline

- Selenium Issues
- Mechanisms of Selenium Removal
- Historical Systems
- New Full Scale Systems
- Non-mining Examples
- By-Product Treatment
- Conclusions

NAMC Selenium Report 2010

http://www.namc.org/docs/00062756.PDF
Key Points about Selenium Control

- Se control can be critical to agriculture runoff, power generation, and mining industries
- Includes active and passive control technologies
- Passive treatment:
  - Uses natural processes to reduce and capture Se
  - Requires less operational effort and management
  - Demonstrated as a viable option for Se treatment
Selenium Chemistry and Toxicity

- Trace concentrations are essential for diet
- Large concentrations can be toxic
  - Bioaccumulates; aquatic bird egg hatchability, fish larval deformities
- Oxidation state determines bioavailability, toxicity
  - Elemental (Se\(^0\)) Not toxic, unavailable
  - Inorganic selenide (Se\(^2-\)) Less bioavailable
  - Selenate (SeO\(_4\)^{2-}, Se\(^6+\)) Soluble, bioavailable, less toxic
  - Selenite (SeO\(_3\)^{2-}, Se\(^4+\)) Soluble, bioavailable, more toxic
  - Organic selenide (org-Se) Most bioavailable, most toxic

- State NPDES effluent limits
  - 4.7 µg/L average month; 8.2 µg/L daily max
Wetland Processing and Storage of Selenium

**Dissimilatory Reduction**
- $\text{SeO}_4^{2-} \rightarrow \text{SeO}_3^{2-} \rightarrow \text{Se}^0 \rightarrow \text{Se}^{2-}$
- Anaerobic process (Eh -200 mV, DO<2)
- Distribution in wetland sediments:
  - 0:13:41:46
- *Wetlands*: 90% reduction 10 - 16 days
- *Bioreactors*: 90% reduction <1 - 2 days

**Volatilization**
- Organic + $\text{SeO}_3^{2-} \rightarrow (\text{CH}_3)_2\text{Se}$
- Volatilized from plant tissues
- 5-30% cumulative loss from sediments and plants

**Sorption**
- Selenite sorbs to sediments and soil constituents: Fe-, Mn- or Al-oxyhydroxides and organic matter

**Plant Uptake**
- Rapid uptake
- Tissue concentrations increase but not detrimental
- No long term storage in plants; Se transferred to sediments
Biological Selenium Treatment

- Organics + Selenite/Selenate + N + P $\rightarrow$ New Cells + CO$_2$ + H$_2$O + Se$^0$

- Order of reduction:

$$DO \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow SeO_3^{2-} \rightarrow SeO_4^{2-} \rightarrow ClO_4^{2-} \rightarrow SO_4^{2-}$$
Selenium Passive Treatment Systems: Free Water Surface Wetlands Provide Starting Point

- Area: 36 ha
- Flow: ~6,540 m³/d
- Date: since 1991
- HRT: 7-10 days
- Se reduction: 89%
- Se in: 20-30 µg/L
- Se out: <5 µg/L
- Volatilization: 10-30%

Chevron’s Water Enhancement Wetland, Richmond CA

Hansen et al, 1998
### Early Passive Treatment Data

<table>
<thead>
<tr>
<th>Site/ Date</th>
<th>GPM</th>
<th>pH</th>
<th>Influent Se ug/L</th>
<th>Effluent Se ug/L</th>
<th>Percent Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>NV Gold Tailing (Aerobic) 1994</td>
<td>10</td>
<td>7.5</td>
<td>40</td>
<td>16</td>
<td>60%</td>
</tr>
<tr>
<td>NV Waste Rock (BCR) 1994</td>
<td>6</td>
<td>2.7</td>
<td>22</td>
<td>&lt;5</td>
<td>&gt;78%</td>
</tr>
<tr>
<td>Brewer Mine (BCR) 1995</td>
<td>1</td>
<td>2</td>
<td>1,500</td>
<td>50</td>
<td>97%</td>
</tr>
</tbody>
</table>

Source: Gusek (2013)  
CLU-IN Bioreactor Overview
Great Recent Progress in Bioreactor Design

Denitrifying Bioreactors for Agricultural Wastewater Treatment

Full-Scale Sequential Systems

Pilot Projects

Bioreactors for Minewater Treatment
Case History
Anaerobic “Bioreactor” Wetland Demonstration
Showed High Efficiency in Minimal Area

- Source: gravel pit seep
- Volume: 4,380 ft³
- Flow: 2-24 gpm
- Date: 9/08-10/09
- HRT: 2.4 d
- Se in flow: 1-34 µg/L
- Se reduction: 98% (90% winter)
- Se removal rate: 16 mg/d/m³
- Se out: 0.5 µg/L
- TCLP <1 µg/L Se

Walker and Golder. 2010. US Bureau of Reclamation
Case Histories: Pilot and Full-Scale Passive Treatment in WV

Overview

- Two outlets assigned stringent selenium discharge standard:
  - 4.7 ug/L monthly mean
  - 8.2 ug/L daily max
- Conducted barrel studies to formulate substrate, calibrate model
- Designed two distinct systems based on landscape, space, treatment
- First system July 2011
- Second system November 2011

Location

Valley fill drainage from reclaimed mines
Case History (2010)
Pilot Study of BCR for Coal Mine Drainage

- 20% woodchips
- 35% sawdust
- 10% peat moss
- 5% limestone sand
- 25% hay,
- 5% composted manure

24 hr HRT
~ 17 mg/d/m³ media

Source: CH2M HILL (2010)
Barrel Study Confirmed Significant Post-Startup “Byproduct” Discharges
Barrel Study Conclusions

- High strength substrate can remove Se at 12-hour HRT (24- to 48-hour HRT for typical design)

- High strength substrate initially generates elevated concentration of secondary parameters (BOD, COD, low DO, etc.)

- Low strength substrate = lower Se removal rates but also lower secondary parameters

- Initial Se removal is largely as weakly adsorbed selenite with minor amounts removed as elemental Se

- Recommend additional long-term investigation
System A: Design Flow Set to Capture Load and Account for Inter-annual Variation

Sample Date

Flow (gpm)

Total Selenium (mcg/l)


Inflow Total Se

Se discharge limit - 4.7 mcg/l

Flow (gpm)
Case History (2011-present)
Two Full-Scale BCR Systems for Coal Mine Drainage Treatment

- Replace existing sediment pond
- Four cells-in-series:
  1. 0.13 ac Downflow BCR Barrel “B” mix
  2. 0.14 ac Anaerobic upflow bed Barrel “A” peat
  3. 0.16 ac Fill-and-drain wetland Gravel; siphon level control
  4. 0.11 ac Surface flow marsh

- 60 gpm base flow
- 100 gpm max
- 12 µg/L mean Se to <4.7

Source: CH2MILL (2912)
Cell 1: Downflow Biochemical Reactor (BCR)

Plan

**Cell 1**

<table>
<thead>
<tr>
<th>m²</th>
<th>Type</th>
<th>Media</th>
<th>Plants</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>526</td>
<td>Downflow biochemical reactor</td>
<td>Mixed organic</td>
<td>None</td>
<td>Selenium reduction</td>
</tr>
</tbody>
</table>
Cell 2: Upflow Anaerobic Wetland

**Plan**

- **CELL 2**
- **TOP OF SUBSTRATE** (1119.00’)
- **SURFACE OVERFLOW STRUCTURE**
- **LIMITS OF HDPE LINER**
- **DWSE (1120.00’)**
- **BYPASS DITCH**

**Profile**

- **CELL 2**
- **SURFACE OVERFLOW STRUCTURE**
- **TOP MEDIA**
- **ROCK**
- **FINISHED GRADE**
- **POND BOTTOM (1115.00’)**
- **DWSE (1120.00’)**

**m² | Type | Media | Plants | Function**
--- | --- | --- | --- | ---
567 | Upflow anaerobic | Peat | Sedges, rush | Selenium reduction, Byproduct polishing
Cell 3: Fill-and-Drain Polishing Wetland

Plan

Profile

<table>
<thead>
<tr>
<th>m²</th>
<th>Type</th>
<th>Media</th>
<th>Plants</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>648</td>
<td>Subsurface fill and drain</td>
<td>Limestone gravel</td>
<td>Cattails</td>
<td>Byproduct polishing</td>
</tr>
</tbody>
</table>
Cell 4: Free Water Surface Polishing Wetland

Plan

Profile

<table>
<thead>
<tr>
<th>m²</th>
<th>Type</th>
<th>Media</th>
<th>Plants</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>445</td>
<td>Free water surface</td>
<td>Topsoil and ponded water</td>
<td>Cattails</td>
<td>Byproduct polishing</td>
</tr>
</tbody>
</table>
PTS A: Completed Passive Se Treatment System

Cell 1 Downflow
Cell 2 Upflow
Cell 3 Fill & Drain Marsh
Cell 4 Surface flow

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>Cell 1 Effluent</th>
<th>Cell 2 Effluent</th>
<th>Final Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>13</td>
<td>30</td>
<td>26</td>
<td>11</td>
</tr>
<tr>
<td>COD</td>
<td>11</td>
<td>43</td>
<td>84</td>
<td>24</td>
</tr>
<tr>
<td>NO₂⁺NO₃⁻N</td>
<td>3.6</td>
<td>1.5</td>
<td>2.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>0.28</td>
<td>0.09</td>
<td>0.13</td>
<td>0.1</td>
</tr>
</tbody>
</table>

All units = mg/L

a. Monitoring data from February through July 2012

Source:
Thomas, R. (2011)
On Balance, Natural Systems Favored (Coal Mine Drainage Example)

Natural Systems
- BCR+wetland footprint fits (just)
- Construction $762K
- Natural processes
- O&M $15K/yr

Conventional Systems
- Can be made to fit
- Construction $18MM
- Engineered processes
- O&M $500K
PTS B: Higher Flow, Higher Concentration

- Five cells-in-series:
  1. 0.12 ac Head tank
  2. 0.48 ac Upflow BCR
  3. 0.30 ac Upflow BCR
  4. 0.23 ac Surface flow marsh
  5. 0.38 ac Sedimentation pond

- 230 gpm base flow
- 24 µg/L mean Se to <4.7

Source: CH2MILL (2011)
Selenium Treatment Performance Achieved
WQ Targets

Source: CH2MILL (2012)
Case History (2011-2012): Field-Scale Demonstrations for Coal Mine Drainage in WV

- Three reactors: 35 ft x 50 ft
- Duration: 290, 203, 203 days
- Se in: 2-25 µg/L
- Se out: 1-4 µg/L
- Se RR: 0.22 mg/d/ft³
  - 7.7 mg/d/m³
  - 5-10°C
- Substrate: Haybales, MC

Results used for full-scale plan:
- 250,000 ft³ substrate
- 800 gpm
- Se in: 14.88 µg/L
- Se out: 2.35 µg/L
- 10 hr HRT

Source: J Bays (2011)
Source: Meek (2012)
Case History (2008-present)
Cold Climate Coal Mine, Alberta CA

- Date: 2008-present
- Type: Downflow VF
- Volume: 253 m³
- Temp in: 3.2°C avg
- Se in: 195 µg/L
- Se out: 33 µg/L (3 min)
- Se CR: >90%
- NO3N in: 36 mg/L
- NO3N RR: 5 g/d/m³
- Se RR: 17 mg/d/m³
- HRT: 4-8 days
- Year-round operation, passive

Source: Schipper & Rutkowski. 2012.
www.asmr.org
Case History (2010-present)
Continuous Se Removal in Mixed Organic Media for Saline RO Membrane Concentrate


www.usbr.gov
Case History (2012):
Treatment of Saline FGD Wastewaters Shows Selenium Removal

Pilot Study
Downflow Bioreactor

TDS 2-10 g/L
Se in 129 – 290 ug/L

Source:
CH2M HILL (2013)

Vertical Flow Cells for Se, Hg Reduction\(^1\)

- **Se in**: ~70 µg/L
- **Area**: 2 ac
- **TDS**: ~2 g/L

>80% Se Reduction\(^2\)

100% Hg Reduction\(^2\)

Sources:

Passive Treatment of Selenium: BCR Byproducts

- BOD, COD, Low DO, Color, Nitrogen (NH$_4^+$, NO$_3^-$/NO$_2^-$, TKN, etc), Phosphate, and Sulfide
- Recognition of the issue in early studies
- Why byproducts are an issue in Se treatment
- Expectations
  - Initial flush
  - Long-term generation of by products
Functional Role of Aerobic Wetlands in Anaerobic + Aerobic Combination

**Surface Flow Wetlands**

**Functions**

- Treat BCR by-products
  - Oxidize BOD, COD
  - Trap particulates
  - Assimilate excess nutrients
  - Odor reduction
  - Reduce color
- Se polishing to trace levels
  - Biological vegetation uptake, transformation and burial
  - Hydrologic attenuation to equalize possible variation in flows and concentrations
Aerobic Polishing Cells (APCs): How Well Do They Work?

### Conventional Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Removal Efficiency</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>50 – 90%</td>
<td>2 – 10 mg/L</td>
</tr>
<tr>
<td>TSS</td>
<td>50 – 90%</td>
<td>2 – 10 mg/L</td>
</tr>
<tr>
<td>TN</td>
<td>50 – 90%</td>
<td>1 – 3 mg/L</td>
</tr>
<tr>
<td>TP</td>
<td>40 – 90%</td>
<td>&lt; 1 mg/L</td>
</tr>
</tbody>
</table>

Note: Removal efficiencies and effluent concentrations depend on influent concentration and hydraulic loading rate.
Conclusions

- Se control can be critical to agriculture runoff, power generation, and mining industries

- Se control includes active and passive technologies

- Passive treatment:
  - Uses natural processes to reduce and capture Se
  - Requires less operational effort and management
  - Demonstrated as a viable option for Se treatment

- Site-specific applications based on Se concentration, flow rate, topography, and general influent geochemistry

- Early success achieved; optimization ongoing as systems age and performance is evaluated through changing climatic and flow conditions
Acknowledgements

- Thanks to all of our collaborating partners in the West Virginia Coal Mining Industry
- Thanks to supporting engineering and science staff at CH2M HILL
Questions