Integrated Treatment Options for Meeting Stringent Selenium Regulatory Limits Using Anaerobic Bioreactors

Thomas Rutkowski, P.E., Rachel Hanson, E.I.T., Kevin Conroy, P.E.
Overview

1) Background

2) Selenium Block Flow Diagram

3) 4 case studies

4) Conclusions
Background – Selenium (Se)

- Naturally occurring non-metal
- Essential for health of humans, other animals, some plants
- In excess and in critical chemical species in diet can cause reproductive failures / abnormalities in egg-laying vertebrates (fish, birds, amphibians, reptiles)
- Concentrations increasing globally due to mining, power generation, agriculture and animal husbandry
4 oxidation states

- +6  selenate ($\text{SeO}_4^{2-}$)
- +4  selenite ($\text{HSeO}_3^-$ and $\text{SeO}_3^-$)
- 0   elemental selenium $\text{Se}_0$
- -2  selenide $\text{Se}^{-2}$
Background: Mine Water Challenges

**Problem:** How to achieve ~5 µg/L end-of-pipe

**Challenges**
- Variable water quality
- Competing electron acceptors
- High flow, low concentrations

**Few full-scale, proven treatment alternatives to achieve < 5 µg/L**
- RO
- Biological Treatment

**A single technology is not always sufficient to achieve < 5 µg/L**
Biological treatment relies on oxidation-reduction reactions.

- **Electron Donor**: Organic Carbon
- **Electron Acceptor**: $\text{O}_2$
- **Electron Transfer**
- **Bacterial Cell**
  - $\text{CO}_2$
  - $\text{H}_2\text{O}$
Treatment Technologies: Biological

Electron Donor

Organic Carbon

CO₂ + Biomass

Electron Transfer

Bacterial Cell

Electron Acceptor

O₂

NO₃

SeO₄²⁻

Fe³⁺

SO₄

CO₂

H₂O

N₂

Se

Fe²⁺

H₂S

CH₄

Decreasing Energy Yield
Treatment Technologies: Biological

- Biological selenium reduction:
  \[ SeO_4^{2−} + 2CH_2O → Se^0 + 2CO_2 + 2H_2O \]

- Elemental selenium retained in bioreactor
- Anaerobic reaction (ORP range from -180 to -350 mv)
- HRTs: minutes to hours to days
- Facultative heterotrophic bacteria (denitrifiers, selenium reducers)
- Includes packed bed reactors, fluidized beds and passive reactors
- Biological treatment capable of 80 to >95% removal
  - When influent > 50 µg/L, additional unit processes may be necessary to reach 5 µg/L.
Residual selenium in bio-effluent –
1) particulate
2) reduced species

**Se pathways** -
1) Dissimilatory reduction
2) Assimilatory reduction
3) Alkylation
4) Dealkylation
5) Oxidation
6) Bio-induced precipitation

Adapted From Lenz 2008.

Se removal pathways are shown in red.
Treatment Technologies: Block Flow

- **Influent**
  - Pre-treatment (e.g., reverse osmosis, filtration)
  - Bulk Selenium Removal (e.g., Anaerobic Biological Treatment)
  - Selenium Post-Treatment (e.g., coagulation/flocculation, clarification, filtration)
  - Polishing treatment for residual nutrients and TSS (e.g., aerobic biological, filtration)

- **Treated Effluent**

- **Treatment residuals management** (e.g., biosolids, chemical treatment sludge)

April 1, 2014
Case Studies
Case Study 1

- Waste rock seepage
- 250 - 700 gpm capacity
- Molasses used as carbon source
- Reverse osmosis system used during high flow – 700 gpm
- Selenium treatment goal of 4.6 µg/L
## Case Study 1: Influent Concentrations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low Flow Raw Seepage</th>
<th>High Flow RO Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium, µg/l</td>
<td>~30 µg/l</td>
<td>~70 µg/l</td>
</tr>
<tr>
<td>Sulfate, mg/l</td>
<td>~6,000 mg/L</td>
<td>~13,500 mg/L</td>
</tr>
</tbody>
</table>

*Plant has been in compliance for 6 years.*

**Conclusion:** RO + Bio able to achieve 5 µg/L
Case Study 2: Project details

- Coal mine water
- Process Evaluation– RO, Bio, Se post-treatment (Coagulation/flocculation/filtration)
Case Study 2: Total and Dissolved Se

- Complete nitrate removal achieved (165 mg/L as N)

- Influent Se= 175 - 250  
  Effluent Se = 25

- Switch to brine did not raise effluent concentrations

- RO removal was >99%
Selenium speciation after each ICB cell –

- Se (VI) and Se (IV) are less than 5 µg/L after 1<sup>st</sup> ICB.

*Influent Selenium ~ 200 µg/L selenate*
Case Study 2: Coagulation Testing

Fe:Se ratio (mg/µg) >= 1 was effective

Effluent Selenium (µg/L)

Fe:Se Ratio (mg/µg)

T-Se (10 um)  D-Se (0.45 um)  Removal
Case Study 2: Conclusion

With elevated selenium (175 - 224 µg/L) and nitrate (165 mg/L as N):

- Bio achieved 23 µg/L
- RO + Bio + Se Post-Treatment achieved 5 µg/L
Case Study 3: Project Details

- Location - Sand and gravel pit in Grand Junction, Colorado
- Bench and pilot testing funded by the US Bureau of Reclamation
Case Study 3: Passive Biological Treatment

- Downward flow vertical biochemical reactor (BCR)
- Solid phase media: 30% sawdust, 30% wood chips, 20% limestone, 10% hay, 10% cow manure
- Design flow rate of between 3 and 15 gpm
- Pilot operated for one year
Case Study 3: Results

Test Condition 1

Test Condition 2

Total Selenium (mg/L)

Date


Influent  Effluent
## Case Study 3: Results

### Test Condition 1

<table>
<thead>
<tr>
<th>Description</th>
<th>Influent Selenium, Total (ug/L)</th>
<th>Biological Effluent Selenium, Total (µg/L)</th>
<th>Biological Treatment, Percent Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>22.3</td>
<td>1.0</td>
<td>94%</td>
</tr>
<tr>
<td>Minimum</td>
<td>5.3</td>
<td>0.5</td>
<td>75%</td>
</tr>
<tr>
<td>Maximum</td>
<td>41.6</td>
<td>1.5</td>
<td>98%</td>
</tr>
</tbody>
</table>

### Test Condition 2

<table>
<thead>
<tr>
<th>Description</th>
<th>Influent Selenium, Total (ug/L)</th>
<th>Biological Effluent Selenium, Total (µg/L)</th>
<th>Biological Treatment, Percent Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>68.5</td>
<td>8.5</td>
<td>87%</td>
</tr>
<tr>
<td>Minimum</td>
<td>61.5</td>
<td>1.1</td>
<td>69%</td>
</tr>
<tr>
<td>Maximum</td>
<td>79.5</td>
<td>18.9</td>
<td>98%</td>
</tr>
</tbody>
</table>
Case Study 4

- Mine pit dewatering
- Design Build - 400 gpm demonstration plant
- Influent selenium – 30 µg/L
- Treatment goal of 4.6 µg/L
- Side by side biological pilot testing
Overall Conclusions

- When Se < 50 µg/L, biological and other technologies can achieve 5 µg/L.

- When Se > 50 µg/L, achieving 5 is a challenge.
  - Bio alone may be insufficient
  - Additional unit processes may be necessary
    - Pre-treatment with RO
    - Selenium post-treatment

- New bio technologies are providing a more competitive market
Questions?
## Potential Benefit of RO

### Bio Only

<table>
<thead>
<tr>
<th>Influent</th>
<th>Bio Effluent (90% Removal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µg/L</td>
<td>10 µg/L</td>
</tr>
</tbody>
</table>

### RO + Bio

<table>
<thead>
<tr>
<th>Influent</th>
<th>RO Brine (99% Se rejection rate, 75% recovery rate)</th>
<th>Bio Effluent (95% removal)</th>
<th>Recombined flow (permeate + bio-treated brine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µg/L</td>
<td>400 µg/L</td>
<td>20 µg/L</td>
<td>5 µg/L</td>
</tr>
</tbody>
</table>