At source control of Selenium

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Objectives:
• Identify practical methods for immobilizing Se in source rock
• Identify Se oxidation/leaching kinetics
• Estimate duration of Se production

In-situ Selenium Treatment

Postulated selenium weathering process:
1. Selenide: \( \text{Se}^-_2 \) FeSe
   Rapidly oxidizes to:
2. Selenite: \( \text{Se}^{+4} \) \( \text{SeO}_3^{2-} \) Sorbs to FeOOH
   Slowly oxidizes to:
3. Selenate: \( \text{Se}^{+6} \) \( \text{SeO}_4^{2-} \) Highly Mobile !!

The goal is to catch selenium at step #2

Selenium occurs in two important oxidized forms:
- Selenite
- Selenate

Higher pH favors selenate

Selenium leaching study: Coal Refuse

- Begun in November 2008 at WRI lab
- Objective: to Identify:
  - What proportion of selenium is leachable
  - How rapidly selenium will leach from coal refuse
  - How to immobilize leached selenium
- Method:
  - Samples of coal refuse were placed in humidity cells
  - Treatments: ferrihydrite, steel wool, FGD cake
  - Leachate collected every two weeks
Treatments

- Steel wool or zero valent iron (ZVI)
  - If there was significant selenate in the leachate, ZVI might reduce it to an immobile form
- Ferrihydrite, FeOOH, AMD sludge
  - Donated by Bob Hedin, Hedin Environmental, Inc.
  - Low moisture content
  - If most of the leachate is selenate, ferrihydrite will adsorb it
- FGD cake or scrubber sludge
  - If there was significant selenate then the sulfite in FGD cake might reduce it to selenite or elemental selenium
  - Proved to be a significant net source of selenium

Selenium Content of Test Refuse

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Se] mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.71</td>
</tr>
<tr>
<td>2</td>
<td>1.48</td>
</tr>
<tr>
<td>3</td>
<td>1.28</td>
</tr>
<tr>
<td>Mean</td>
<td>1.55</td>
</tr>
<tr>
<td>Std dev.</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Treatment Application Rates

<table>
<thead>
<tr>
<th>Treatment</th>
<th>grams appl.</th>
<th>rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOOH *</td>
<td>72 dry 555 refuse</td>
<td>13%</td>
</tr>
<tr>
<td>Steel wool</td>
<td>30 dry 555 refuse</td>
<td>5%</td>
</tr>
<tr>
<td>* 63% Fe = 45 g of Fe</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Distribution of Selenium in Kanawha Formation
(from Roy and Vesper sequential extraction study):
Refuse values are averages of shale and coal

<table>
<thead>
<tr>
<th></th>
<th>Org shale</th>
<th>Coal</th>
<th>Tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble/Exchange</td>
<td>12%</td>
<td>10%</td>
<td>11%</td>
</tr>
<tr>
<td>Fe, Mn Oxides</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Sulfides</td>
<td>10%</td>
<td>10%</td>
<td>11%</td>
</tr>
<tr>
<td>Organic</td>
<td>18%</td>
<td>5%</td>
<td>11%</td>
</tr>
<tr>
<td>total extracted</td>
<td>40%</td>
<td>25%</td>
<td>33%</td>
</tr>
<tr>
<td>Residual</td>
<td>60%</td>
<td>75%</td>
<td>68%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Estimated Se in each humidity cell assuming 33% extractable

| Se/humidity cell | 0.86 | 0.280 mg |

Results after 76 weeks of leaching

1. The selenium leaching rate is about 0.06%/day
2. FeOOH kept [Se] near to or below 0.5 µg/L
[Se] remains near 5 μg/L with FeOOH

![Graph showing Se concentration over weeks of leaching with control and FeOOH conditions.]

Does 5 μg/L really mean 5 μg/L?
- The refuse pile in question leaches the conservative anion chloride.
- The liquid to solid ratio for each leach cycle was about 2:1.
- The resulting concentration was adjusted mathematically such that chloride concentration in the leachate matched that for the field site (a several million ton tailings pile).
- Observed [Se] x 7.2 = estimated field [Se].
- Very close to field [Se] observations.
- Nonetheless, it's unlikely that a field site will leach with the efficiency of a humidity cell so let's not get carried away.

27% of mobile Se Leached by week 76

![Graph showing Se leaching rate over weeks of leaching.]

Se Leaching Rate is about 0.06%/day

Assume 33% of Se is leachable: leaching rate ~ 0.06%/day

![Graph showing cumulative Se leached over weeks of leaching.]

Estimated 10 years to leach 90%

![Graph showing cumulative Se leached over weeks of leaching with predicted and observed data.]

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Y=cumulative % Se leached  
X= weeks

Compared to Sulfide Oxidation Rates
- Iron sulfide oxidation rates:
  - 0.0006%/day-Coal iron sulfides to
  - 0.0007%/day-Hydrothermal pyrite
- Iron selenide in coal:
  - 0.06%/day
  - Or, 10 to 100 times faster
- However:
  - Unlike AMD, there is nothing to ‘neutralize’ selenium and,
  - Field leaching will likely be slower

And, there just isn’t that much selenium to start with
- Typical high total sulfur level in coal associated rock:
  - 5.0%
- An exceptionally high selenium concentration in coal associated rock would be:
  - 5.0 mg/kg or:
  - 0.0005%
  - Or, 10,000 times more S than Se

Why Selenite Sticks to Ferrihydrite and Selenate does not
- Ferrihydrite-fresh AMD treatment sludge
- Hydration sheath limits sorption
- Weak bond

What is Ferrihydrite?
- By product of AMD treatment: AMD sludge
  - Starts out at about 98% water
  - Contains Iron, Aluminum, Manganese hydroxides
  - Plus gypsum, silicate, calcite depending on AMD treatment process
  - The useful components are the iron oxyhydroxides:
- Iron oxyhydroxides undergo dehydration:
  1. Ferric hydroxide: \( \text{Fe(OH)}_3 \) minus \( \text{H}_2\text{O} \)
  2. Ferrihydrite/Goethite: \( \text{FeOOH} \)
Ferrihydrite-dried out, turning into goethite

Application: Lining a Pit Floor with Ash

Segregated Pit Cleaning Cell

Special Handling Cell: Ferrihydrite application in unlined cell

Questions?

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