Geochemistry of Selenium Mobilization from the Elk River Valley Coal Mines

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Selenium in the Elk River
Selenium Biogeochemistry
Selenium in the Mist Mountain Formation
Geochemical Associations of Selenium
Selenium Mobilization
Conclusions
Mining in the Elk River Valley

• Five open-pit coal mines

• Generate approximately 24 million tonnes of coal annually

• Main product: medium- to low-volatile bituminous coking coals

• Have generated an estimated 2.5 billion tonnes of waste rock since the 1970’s
Selenium in the Elk River

• The provincial freshwater guideline for Se is 1 µg/L

• In the main tributaries of the Elk River Se concentrations of up to 20 µg/L were detected

• Se concentrations as high as 542 µg/L were measured in waste dump seepage
Selenium in the Elk River

• Se concentrations in algae and invertebrates downstream from the mines were 2 to 5 times greater than at references sites.

• Se levels in fish were 2 times greater than the published toxic effects thresholds.

However, no negative effects were observed in biota.
Essentiality and Toxicity of Selenium

• Essential micro-nutrient involved in the destruction of free-radicals
• Narrow range of tolerance
• Can disrupt reproduction of fish and aquatic birds
• Can cause embryo defects in fish at concentrations as low as $2\mu g/L$ in water

Thornton, 1995
Selenium Speciation

Selenium is a sulphur analog

OXIDATION STATES

Poorly soluble
- Selenide (-2)
- Elemental Se (0)

Highly soluble
- Selenite (+4) → Adsorbs to sediment
- Selenate (+6) ← Most bioavailable
Selenium in the Mist Mountain Formation

<table>
<thead>
<tr>
<th>Se Concentration (mg/kg)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>1.9</td>
</tr>
<tr>
<td>Hanging wall</td>
<td>4.2</td>
</tr>
<tr>
<td>Foot wall</td>
<td>4.2</td>
</tr>
<tr>
<td>Partings</td>
<td>3.2</td>
</tr>
<tr>
<td>Coarse refuse</td>
<td>2.8</td>
</tr>
<tr>
<td>Interburden</td>
<td>1.1</td>
</tr>
<tr>
<td>Coal world average</td>
<td>2.2</td>
</tr>
<tr>
<td>Crustal average</td>
<td>0.05-0.1</td>
</tr>
</tbody>
</table>

Ryan and Dittrick, 2000
Possible Associations of Selenium in Coal and Associated Lithologies

- Se in Coal
  - Organic/Maceral Association
    - Covalently Bound
    - Discrete Minerals
  - Inorganic/Mineral Association
    - Ionically Bound
    - Dispersed in Minerals
    - Bound to Clay Minerals or HFMO

Adapted from Dale (1996)
Objectives

• Identify Se-bearing mineralogical components in the Mist Mountain Formation

• Evaluate the rate of Se release from different lithologies

• Suggest possible geochemical mechanisms of Se mobilization

• Provide mine operators with information needed to assess the risk of Se release from waste rock and plant refuse
Sampling

Coal

Interburden

Parting
Sample Selection

• 375 samples were collected and analyzed for Se by INAA

• 16 samples, representing the 5 main lithologies, were selected to study the mineralogical associations of Se

• 5 of these samples were used to study the rate of Se release
Methodology

Samples from Pit Wall < 5 cm

Disc Crusher <3 mesh

Sequential Extractions

Elemental and Oxide Analyses

Pulverizer <200 mesh

Settling Columns <2 µm

Humidity Cells

Heavy Liquid Separation

X-Ray Diffraction

Scanning Electron Microscopy
X-Ray Diffraction

- **Q** = quartz
- **K** = kaolinite
- **I** = illite
- **A** = ankerite
- **C** = calcite
- **S** = siderite

2\(\theta\) (CuK\(\alpha\))

XRD Intensity (cps)
## Mineralogy

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sample Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite</td>
<td>3.90 – 22.5</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.80 – 20.8</td>
</tr>
<tr>
<td>Quartz</td>
<td>1.30 – 22.3</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.20 – 5.85</td>
</tr>
<tr>
<td>Sulphides</td>
<td>0.03 – 0.84</td>
</tr>
</tbody>
</table>
Se versus TOC

Organic S versus TOC

- **refuse**
- **coal**
- **parting**
- **interburden**
- **hanging wall/foot wall**
Se versus Sulphides

S versus Sulphides

Sulphides ≈ 71 % of total S

refuse coal parting
interburden hanging wall/foot wall

Se (mg/kg)

S (mg/kg)

Sulphides (%)

Sulphides (%)

yellow: refuse  blue: coal  green: interburden  red: hanging wall/foot wall
1. The amount of Se substituting for S in sulphides is highly variable

or

2. Other mineralogical associations are of greater importance in determining total Se concentrations
Se versus Sulphides Normalized for TOC

- **Se (mg/kg)**
  - Y-axis from 0 to 10

- **Sulfides/TOC**
  - X-axis from 0.00 to 0.05

Legend:
- **refuse**
- **coal**
- **parting**
- **interburden**
- **hanging wall/foot wall**
Sequential Extractions

2.0 g sample

Distilled Water

1.0 M NH$_2$OH·HCl

KClO$_3$/HCl

HCl-HNO$_3$

FILTER

FILTER

FILTER

SOLUTION

SOLUTION

SOLUTION

Water Soluble/Exchangeable

HFMO

Sulphides and Organics

Residual (silicates)
Geochemical Associations of Selenium

- Residual Organic matter and sulphides
- HFMO
- Water soluble

Percent of Total Se in Sample

Sample

Average contribution to total Se (%)  
15  Residual  
73  Organic matter and sulphides  
4  HFMO  
8  Water soluble
Heavy Liquid Separation

20 g sample

Perchloroethylene
d = 1.6 g/cm³

LIGHy

Methylene iodide
d = 3.3 g/cm³

MEDIUM

HEAVY
Heavy Liquid Separation

Se Concentration (mg/kg)

Light (<1.6 g/cm³)
Medium (1.6-2.9 g/cm³)
Heavy (>2.9 g/cm³)
Humidity Cells

- 5 different materials selected
- 1 kg of material placed in each cell
- 7 day moist-air/dry-air/leach cycle
- Leached once a week with 500 ml of distilled water
- Run for 20 weeks
# Humidity Cells Samples

<table>
<thead>
<tr>
<th>Designation in Tables</th>
<th>Se Content (mg/kg)</th>
<th>Sulphides (%)</th>
<th>TOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interburden</td>
<td>3.2</td>
<td>0.05</td>
<td>4.7</td>
</tr>
<tr>
<td>Refuse</td>
<td>3.4</td>
<td>0.13</td>
<td>12.5</td>
</tr>
<tr>
<td>Parting</td>
<td>5.9</td>
<td>0.07</td>
<td>5.8</td>
</tr>
<tr>
<td>Foot wall</td>
<td>8.4</td>
<td>0.43</td>
<td>4.0</td>
</tr>
<tr>
<td>Coal</td>
<td>8.8</td>
<td>0.12</td>
<td>70.3</td>
</tr>
</tbody>
</table>
Se Concentration in Humidity Cell Leachate

Week

<table>
<thead>
<tr>
<th>Week</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se (µg/L)</td>
<td>400</td>
<td>300</td>
<td>200</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **refuse**
- **coal**
- **parting**
- **interburden**
- **hanging wall/foot wall**
Percent of Total Se Extracted from the Humidity Cells in 20-Weeks
Weekly Se Release

Not correlated with: Sulphides
Weekly Se Release

Not correlated with: Total Se
Weekly Se Release

Not correlated with: NP/AP ratio
Se and Sulphate in Humidity Cell Leachate

![Graph showing the relationship between Se (µg/L) and Sulphate (µg/L) in different materials.](image)

- **refuse**
- **coal**
- **parting**
- **interburden**
- **hanging wall/foot wall**
In which mineralogical associations is Se found?

- 4% HFMO
- 15% RESIDUAL
- 8% WATER SOLUBLE
- 73% SULPHIDES AND ORGANICS
From which lithologies is Se being mobilized?

Se is released from all lithologies parting > coal > refuse > foot wall > interburden
Conclusions

What controls the rate of Se release?

Sample mineralogy plays an important role in controlling the rate of release.

The rate of Se release is not correlated with total Se or sulphide content or with AP/NP.
Conclusions

From what minerals is Se being released?

Humidity cell test results suggest that sulphide oxidation is the main source of Se.
Recommendations

• Conduct longer term humidity cell or field plot tests

• Study the effect of sulphide form and mineralogy on Se release rates

• Perform a mass balance to determine the effect of waste dump hydrology on Se release

• Study abatement methods and their applicability
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