Prediction of Selenium Leaching

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- Elk Valley Coal Corp.
- Western Canadian Coal: Dillon Mine and Brule Project Assessment.
- NEMI: Trend Mine.
Topics

- Why selenium?
- Overview of selenium chemistry.
- Observations from the Elkview Coal Mine.
  - Mineralogical occurrence.
  - Aqueous chemistry.
- Considerations for predicting selenium leaching.
Why Selenium?

- Routine low level (below ppb) analysis in waters.
- Routine low level (low ppm) analysis in rock.
- Low receiving water standards (low ppb).
- Typically, only heavy element of concern leaching from coal wastes at neutral pH.
Overview of Selenium Geochemistry
Overview of Selenium Geochemistry

Crustal Abundance of Selenium Relative to Other Elements
Mineralogy of Selenium

- Selenium and Sulphur Minerals (~100, compared to ~1000)
  - Native selenium
  - Sulphide ($S^{2-}$) analogues
    - Ferroselite – FeSe$_2$
    - Clausthalite – PbSe
  - Sulphate ($SO_4$) analogues
    - Rare lead selenates ($SeO_4$)
  - Sulphite ($SO_3$) analogues (~6 natural sulphites)
    - 20 lead, copper selenites ($SeO_3$)
- Organic sulphur and selenium association
Overview of Selenium Geochemistry

- $\text{SO}_4^{2-}$
- $\text{HSO}_4^-$
- $\text{H}_2\text{S}(\text{aq})$
- $\text{S}^-$
- $\text{HS}^-$
- $\text{H}_2\text{Se}$
- $\text{H}_2\text{SeO}_3$
- $\text{HSe}^-$
- $\text{HSeO}_3^-$
- $\text{HSeO}_4^-$
- $\text{Se}^{(\text{black})}$
- $\text{SeO}_3^{2-}$
- $\text{SeO}_4^{2-}$

$25^\circ\text{C}$
Overview of Selenium Geochemistry

- $\text{FeSO}_4^+$
- $\text{HSO}_4^-$
- $\text{Sulfur-Rhmb}$
- $\text{H}_2\text{S(aq)}$
- $\text{FeS}_2$
- $\text{SO}_4^{2-}$
- $\text{H}_2\text{SeO}_3$
- $\text{HSeO}_3^-$
- $\text{HSeO}_4^-$
- $\text{FeSe}_2$
- $\text{Se}^{(lack)}$
- $\text{SeO}_3^{2-}$
- $\text{SeO}_4^{2-}$
- $\text{FeSe}_2$
- $\text{FeSe}$
Overview of Selenium Geochemistry

- **Adsorption**
  - SeO$_3^-$ more adsorbable than SeO$_4^-$.
  - Oxyanions – expect sorbed fraction to decrease as pH increases.
Summary of Selenium Geochemistry

- Analogous to sulphur
- Crustal abundance is very low compared to other important heavy elements.
- Pure selenium minerals are rare.
- Similar Eh-pH fields as sulphur but...
  - ...Se more readily reduced under natural conditions.
- Difference between Se(VI) and Se(IV) sorption effects.
Elkview Coal Se Assessment Project

- Elkview Coal
  - Open pits.
  - Waste rock.
  - Coarse Coal
  - Reject.
  - Tailings.
Elkview Coal Se Assessment Project
Elkview Coal Se Assessment Project
Se Content of Rock
Mineralogical Findings

- Sulphur minerals
  - Pyrite (FeS$_2$)
  - Gypsum (CaSO$_4$.2H$_2$O)
  - Barite (BaSO$_4$)

- Carbonaceous matter

- No pure Se minerals observed.
Elkview Coal Se Assessment Project

Se in Waters

- **Waters**
  - Non-acidic.
  - Ca-SO$_4$ dominated.
  - Se as SeO$_4$
  - Lowest Se (<0.0002 mg/L) in reduced waters.
  - SeO$_3$ detected in tailings pond water.

- **Theoretical mineralogical controls**
  - Calcite, dolomite, barite (over)saturated.
  - Gypsum and selenates well undersaturated
Elkview Coal Se Assessment Project

Se in Waters

Dissolved Sulphate (mg/L) vs. Total Se (mg/L) Graph

- Plant area
- Creeks and Rivers
- Waste
- Underground Mine

Graph shows the relationship between dissolved sulphate concentration and total selenium concentration in various water samples.
Elkview Coal Se Assessment Project

Se in Seep Precipitates and Salts

- Calcite, dolomite, gypsum and anhydrite were primary components.
- Se content variable
  - 1 to 61 ppm selenium.
- Carbonate type precipitates had higher Se/S compared to gypsum precipitates.
Elkview Coal Se Assessment Project
Conclusions

- Se content is typical of coal-bearing sequences.
- Se contained mainly in several sulphate and sulphide minerals.
- Se/S ratio in waters suggest common site source.
- Se/S in waters lower than rocks.
- Possible upper limit on Se concentrations.
- Se reduction occurs in reduced waters.
Prediction Thoughts

- **Release of Se analogous to S:**
  - Oxidation of iron sulphide releases sulphate.
  - Oxidation of selenide associated with sulphide releases selenate.
  - Dissolution of calcium or barium sulphate releases sulphate and selenate.

- Since $\text{SO}_4$ and $\text{SeO}_4$ are both highly mobile under oxidizing conditions:
  - $\text{Se}/\text{S}$ should be comparable in rocks and waters....

........but not – why?
Prediction Thoughts

- An attenuation mechanism is implied for oxidized waters.
  - Co-precipitation?
  - Sorption?
  - Ion exchange?
Prediction Thoughts

- Co-precipitation candidates
  - Gypsum – but probably only precipitates from surface waters due to local evaporation.
  - Barite – Chemistry implies barite does precipitate
    - Barium from dissolution of carbonates and weathering of silicates.
    - Barite has low solubility.
    - Good potential Se sink.
Prediction Thoughts

- **Sorption Mechanism**
  - Requires Se as SeO$_3$.
  - Could occur near pyrite grains if Se goes through intermediate step as pyrite oxidizes.
  - Sorption with precipitated ferric hydroxide.

- **Ion exchange**
  - ??
Prediction Thoughts

- Reduced waters
  - Low Se concentrations most likely due to:
    - Sorption of $\text{SeO}_3$ by ferric oxides.
    - Precipitation of elemental Se.
    - Precipitation of selenides.
    - Sulphide co-precipitation.
Conclusions

- Se at Elkview Coal occurs in association with several sulphur minerals.
- Se is highly mobile but occurs at aqueous concentrations too low to form its own minerals.
- Attenuation of Se appears to be occurring perhaps by sulphate co-precipitation or sorption with ferric hydroxide.
- Reduction of selenium effective removal mechanism under reducing conditions.
Questions