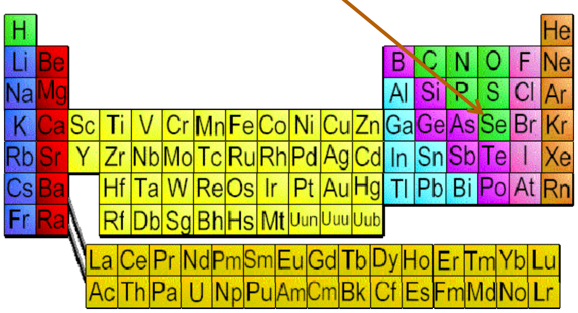
At source control of Selenium

Paul Ziemkiewicz, PhD
Director, West Virginia Water Research Institute
6 Sept 2010

Objectives:

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

Selenium



In-situ Selenium Treatment

- Postulated selenium weathering process:

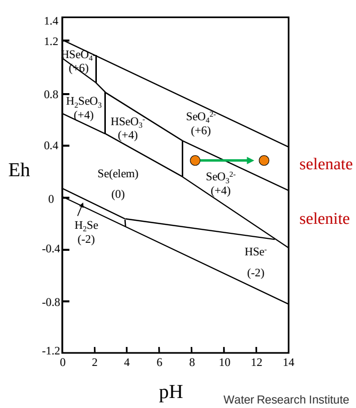
1. Selenide: Se^{-2} FeSe
   Rapidly oxidizes to:
2. Selenite: Se^{+4} SeO_3^{2-} Sorbs to FeOOH
   Slowly oxidizes to:
3. Selenate: Se^{+6} SeO_4^{2-} Highly Mobile !!

- 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 selenite, 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

7 West Virginia University Water Research Institute

Selenium Content of Test Refuse

Sample	[Se] mg/kg
1	1.71
2	1.48
2	1.73
3	1.28
Mean	1.55
Std dev.	0.21

8 West Virginia University Water Research Institute

Treatment Application Rates

	grams		appl.
Treatment	dry	refuse	rate
FeOOH *	72	555	13%
Steel wool	30	555	5%

* 63% Fe = 45 g of Fe

9 West Virginia University Water Research Institute

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

	Org shale	Coal	Tailings
Soluble/Exchange	12%	10%	11%
Fe, Mn Oxides	0%	0%	0%
Sulfides	10%	10%	11%
Organic	18%	5%	11%
total extracted	40%	25%	33%
Residual	60%	75%	68%
Total	100%	100%	100%

10 West Virginia University Water Research Institute

Estimated Se in each humidity cell assuming 33% extractable

	Total	Extractable	
[Se]	1.55	0.505	mg/kg
Se/humidity cell	0.86	0.280	mg

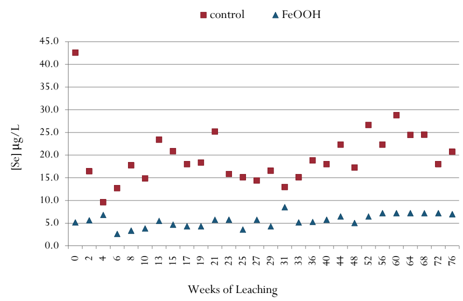
11 West Virginia University Water Research Institute

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

12 West Virginia University Water Research Institute

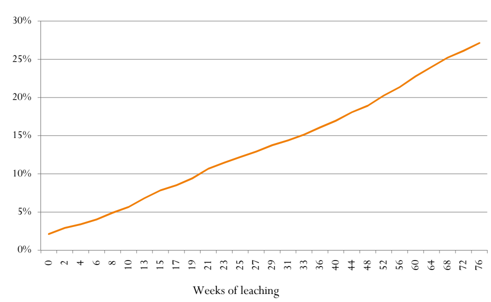
[Se] remains near 5 µg/L with FeOOH



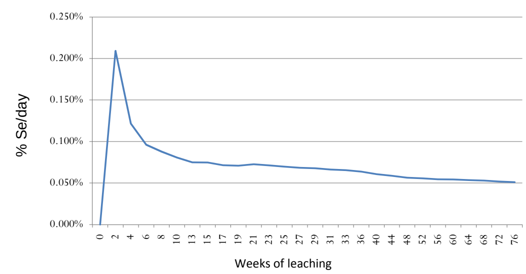
Does 5 µg/L really mean 5 µg/L?

- 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

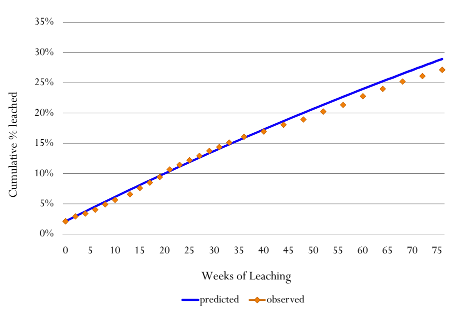
27% of mobile Se Leached by week 76



Se Leaching Rate is about 0.06%/day

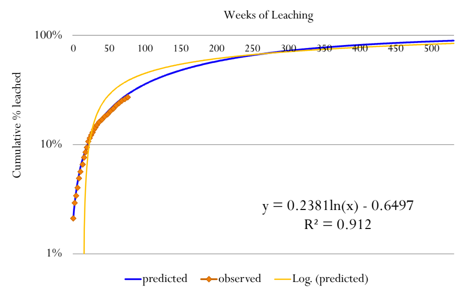


Assume 33% of Se is leachable: leaching rate ~ 0.06%/day



Estimated 10 years to leach 90%

Y=cumulative % Se leached
X= weeks



19 West Virginia University Water Research Institute

Compared to Sulfide Oxidation Rates

- Iron sulfide oxidation rates:
  - 0.006% /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

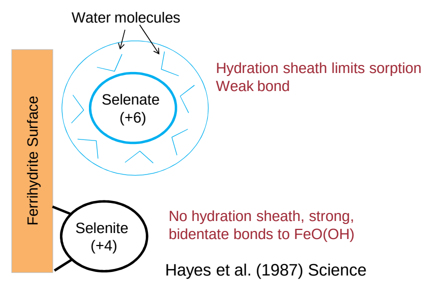
20 West Virginia University Water Research Institute

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

21 West Virginia University Water Research Institute

Why Selenite Sticks to Ferrihydrite and Selenate does not



Hayes et al. (1987) Science

22 West Virginia University Water Research Institute

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: $Fe(OH)_3$ minus H_2O=
  2. Ferrihydrite/Goethite: FeOOH

23 West Virginia University Water Research Institute

Ferrihydrite-fresh AMD treatment sludge

24 West Virginia University Water Research Institute

Ferrihydrite-dried out, turning into goethite

25 West Virginia University Water Research Institute

Application: Lining a Pit Floor with Ash

26 West Virginia University Water Research Institute

Segregated Pit Cleaning Cell

27 West Virginia University Water Research Institute

Special Handling Cell:

Ferrihydrite application in unlined cell

Soil/spoil

Pit cleanings

Ferrihydrite/pit cleanings blend

Pit cleanings

Ferrihydrite/pit cleanings blend

28 West Virginia University Water Research Institute

Questions?

At Source Control of Selenium

Paul Ziemkiewicz, PhD, Director
West Virginia Water Research Institute
West Virginia University
pziemkie@wvu.edu

29 West Virginia University Water Research Institute