# Selenium Treatment Technologies

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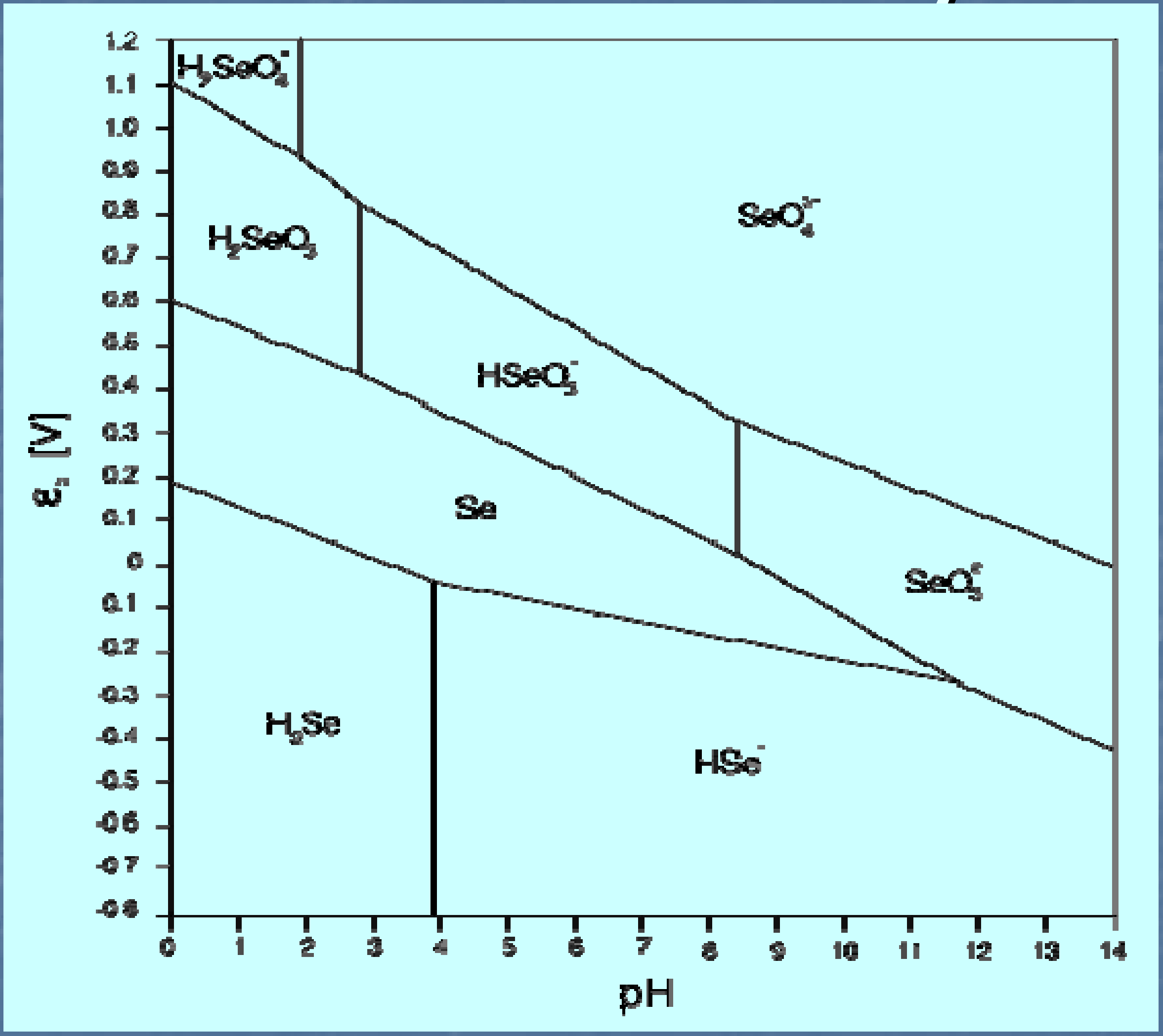
# Overview

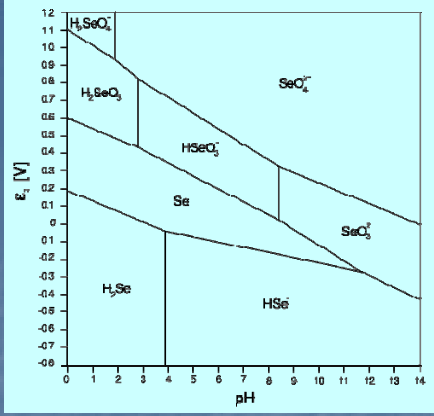
- Geochemistry
- Treatment technologies
  - Chemical
  - Physical
  - Biological
- Things to think about

# Geochemistry




http://commons.wikimedia.org/wiki/File:Pourbaix_diagram_for_Selenium.svg

# Geochemistry




- Selenate (+6)
  - Soluble
  - Weakly sorbed (outer-sphere)

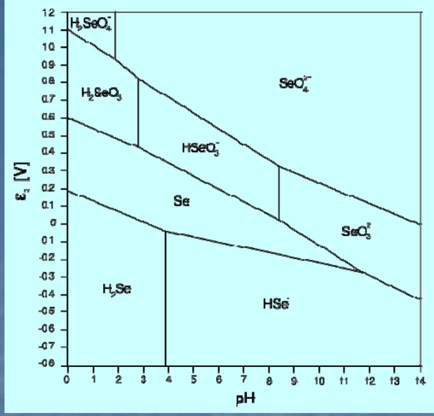
# Geochemistry

- Sorption
  - Surface hydroxyl group
  - Oxyhydroxide surface charge
    - Net positive at lower pH
      - Anions sorption
    - Net negative at higher pH
      - Cation sorption

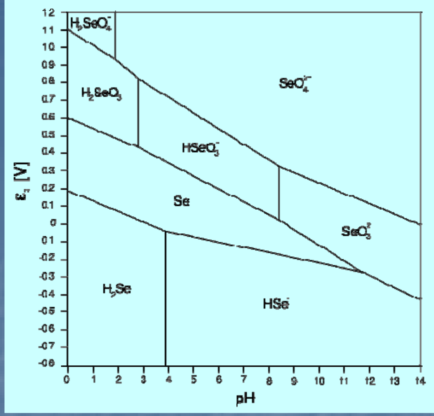
# Geochemistry

- Sorption
  - Two main types
    - Outer-sphere
      - Weak ionic charge attraction
        - Ionic strength, pH
    - Inner-sphere
      - Strong covalent bonds
        - pH

# Geochemistry



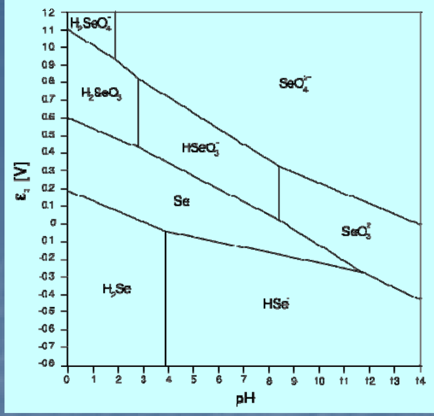

- Selenate (+6)
  - Slow reduction kinetics
  - Microbial reduction to selenite and elemental selenium




# Geochemistry

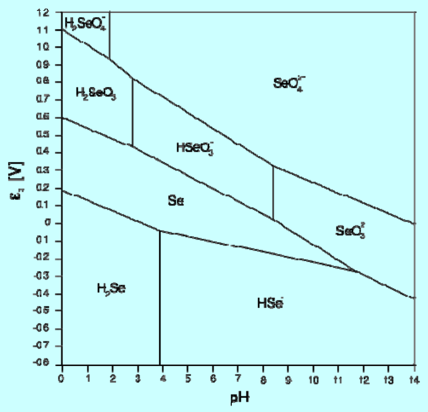
- Selenite (+4)
  - Soluble
  - More strongly sorbed (inner-sphere)
  - Reduction kinetics faster than selenate

# Geochemistry

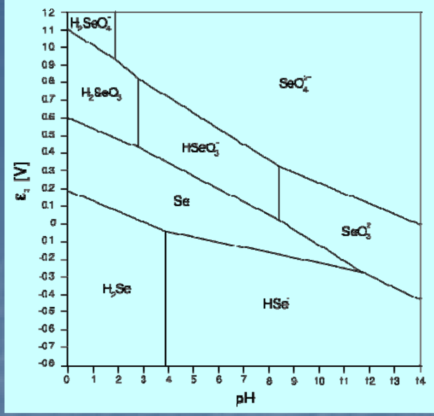



- Selenite (+4)
  - Microbial reduction to elemental selenium and selenide
  - Reduced by organic acids (e.g., ascorbic)
  - More toxic than selenate

# Geochemistry




- Elemental selenium (0)
  - Mildly reducing
  - Insoluble
  - Colloidal
    - 1 nm to 1 µm
  - Red-color
  - Natural organic matter




# Geochemistry

- Selenide (-2)
  - Strongly reducing
  - Soluble unless metals present
    - Precipitation
  - May sorb weakly
  - $H_2Se$ toxicity

# Geochemistry

- Organic selenium
  - Formed from biological activity
    - Plants, microorganisms
    - Some are volatile
      - E.g., dimethyl selenide – smells like garlic

# Overview

- Geochemistry
- **Treatment technologies**
  - Chemical
  - Physical
  - Biological
- Things to think about

# Treatment Technologies

- Active
  - Relatively constant supervision
  - Generally chemical & physical
  - May be energy intensive

# Treatment Technologies

- Passive
  - Little to no energy input
  - Minimal monitoring and maintenance
  - Natural processes and materials

# Treatment Technologies

- Passive
  - Best for low flows
  - Generally require more land
  - Remote locations

# Treatment Technologies

- Chemical
  - Co-precipitation and sorption
  - Zero valent iron (ZVI)
- Physical
  - Membrane
    - Nano-filtration
    - Reverse osmosis (RO)

# Treatment Technologies

- Biological
  - Active
    - Microbial
  - Passive
    - Aerobic wetland
    - Biochemical reactor (BCR)

# Co-precipitation & Sorption

- $FeCl_2$ or $FeSO_4$

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

$$\equiv Fe(OH)_2 - SeO_4^{\ 2-} \qquad \equiv Fe(OH)_3 - SeO_4^{\ 2-}$$

$$\equiv Fe(OH)_2 - SeO_3^{\ 2-} \qquad \equiv Fe(OH)_3 - SeO_3^{\ 2-}$$

# Co-precipitation & Sorption

- $FeCl_2$ or $FeSO_4$
  - Low pH
    - Net positive surface charge
  - Se(IV)
    - Pre-reduction of Se(VI)

# Co-precipitation & Sorption

- Advantages
  - Simple
  - Demonstrated attainment of DW MCL (50 μg/l)

# Co-precipitation & Sorption

- Disadvantages
  - Sludge volume
  - Reagent consumption
  - Inconsistent attainment of < 5 µg/l

# Zero Valent Iron (ZVI)

- $Fe^0$ filings, fiber, sponge, etc

$$Fe^{0} \rightarrow Fe^{2+} and\ Fe^{3+}$$

$$Se^{+6} \rightarrow Se^{+4} + 2e^{-} \rightarrow Se^{0} + 4e^{-}$$

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^{+}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+}$$

# Zero Valent Iron (ZVI)

- $Fe^0$ filings, fiber, sponge, etc
  - Sorption/co-precipitation of Se(IV)
  - Entrapment of $Se^0$

# ZVI

- Advantages
  - Simple
  - Combined processes
  - Can be passive

# ZVI

- Disadvantages
  - Sludge volume
  - Exhaustion
  - Passivation
  - Inconsistent attainment of < 5 µg/l

# ZVI

- Case Study - Catenary Coal, WV
  - Fibrous – steel wool
  - 5-14 µg/l influent
  - Maybe best at T > 65 ˚F, but not consistent

Lovett, R. 2008. "Selenium Removal from Mine Waters." Presented at the Annual Meeting of the West Virginia Surface Mine Drainage Task Force, Morgantown, WV on 23 April.

# ZVI

- Case Study - Catenary Coal, WV
  - Consistently ≤ 5 µg/l at ≥ 5 day retention time (RT)
    - Inconsistent < 5 days
  - Consistently ≤ 5 µg/l at ≤ 5 gpm
    - Inconsistent > 5 gpm

Lovett, R. 2008. "Selenium Removal from Mine Waters." Presented at the Annual Meeting of the West Virginia Surface Mine Drainage Task Force, Morgantown, WV on 23 April.

# ZVI

- Case Study - Catenary Coal, WV
  - Costs
    - None for specific study
    - Estimated by Lovett
      - 250 gpm (gravity)
      - Capital $478K
      - O&M $150-$300K

Lovett, R. 2008. “Selenium Removal from Mine Waters.” Presented at the Annual Meeting of the West Virginia Surface Mine Drainage Task Force, Morgantown, WV on 23 April.

# ZVI

- Case Study – Barrick's Richmond Hill Mine, SD
  - > 100 µg/l influent
  - 12-22 µg/l effluent
  - RO polishing step

Microbial Technologies. 2005. Literature review: Evaluation of treatment options to reduce waterborne selenium at coal mines in West-Central Alberta. Report prepared by Microbial Technologies, Inc. for Alberta Environment, Water Research Users Group, Edmonton, AB.

# Nano-Filtration

- Size exclusion
  - Rejects multivalent ions
  - Applied pressure

# Nano-Filtration

- Advantages
  - Effective for all divalent ions
  - Lower pressure (~1/3 of traditional RO)
    - Lowers costs

# Nano-Filtration

- Disadvantages
  - Pretreatment of solids and colloids
  - Fouling (scale)
  - Disposal of concentrate

# Nano-Filtration

- Case Studies
  - No field case studies found
  - Shows promise in the laboratory

# Nano-Filtration

- Estimated Costs
  - Single-stage unit - $2K / gpm
  - Pre-treatment - $300 - $1,000 / gpm
  - Operating - $0.50 – $0.60 / 1K gal
  - Pre-treatment – $0.10 – $0.15 / 1K gal
  - No existing units to verify

Microbial Technologies. 2005. Literature review: Evaluation of treatment options to reduce waterborne selenium at coal mines in West-Central Alberta. Report prepared by Microbial Technologies, Inc. for Alberta Environment, Water Research Users Group, Edmonton, AB.

# RO

- Osmotic pressure and applied pressure
- Semi-permeable membrane
- Applied pressure > osmotic pressure

# RO

- Permeate
  - Ion-free water
- Brine
  - Ion-laden waste

# RO

- Advantages
  - Proven to be effective
  - Removes all ions

# RO

- Disadvantages
  - Pretreatment of solids and colloids
  - Fouling (scale)
  - Requires heated water
  - Considered expensive

# RO

- VSEP (vibratory shear enhanced process) – New Logic Research
  - Resists fouling through torsional vibration to “scour” membrane
  - 50 g to > 1 million g
  - Can achieve < 2 ug/l Se
  - $200K to $20 million

# RO

- VSEP (vibratory shear enhanced process) – New Logic Research
  - Developed in 1987
    - Separation of blood plasma

# RO

- Case Study – Barrick's Richmond Hill Mine, SD
  - 200 gpm
  - 12-22 µg/l influent
  - ~ 2 µg/l effluent
  - Brine to ZVI

Microbial Technologies. 2005. Literature review: Evaluation of treatment options to reduce waterborne selenium at coal mines in West-Central Alberta. Report prepared by Microbial Technologies, Inc. for Alberta Environment, Water Research Users Group, Edmonton, AB.

# RO

- Case Study – Barrick's Richmond Hill Mine, SD
  - Capital costs
    - Used unit - $750K (new are ~ $1.2 M)
    - Pre-filtration - $200K
    - Membrane - $30K
      - Life at site 1-2 yr

Microbial Technologies. 2005. Literature review: Evaluation of treatment options to reduce waterborne selenium at coal mines in West-Central Alberta. Report prepared by Microbial Technologies, Inc. for Alberta Environment, Water Research Users Group, Edmonton, AB.

# RO

- Case Study – Barrick's Richmond Hill Mine, SD
  - Operating $10 - $18 / 1K gal
    - Heating $5.5K / wk
    - Algal growth
    - $CaSO_4$ scale
      - 450 ppm Ca

Microbial Technologies. 2005. Literature review: Evaluation of treatment options to reduce waterborne selenium at coal mines in West-Central Alberta. Report prepared by Microbial Technologies, Inc. for Alberta Environment, Water Research Users Group, Edmonton, AB.

# Active Biological

- Several types
  - Pond
  - Fixed film bioreactors
  - Sludge blanket bioreactors
  - GE ABMet®
    - formerly BSeRTM from Applied BioSciences

# Active Biological

- Dissimilatory selenate-reducing bacteria (SeRB)
  - Synonymous to sulfate-reducing bacteria (SRB)
    - 'Accidental'
      - Selenate/sulfate ratio > $1.92 \times 10^{-3}$ (mole basis) [1]

[1] Lenz, Markus, Van Hullebusch, Eric D., Hommes, Gregor, Corvini, Philippe F.X., and Lens, Piet N.L. (2008). Selenate removal in methanogenic and sulfate-reducing upflow anaerobic sludge bed reactors. Water Research. 42:2184-2194.

# Active Biological

- Addition of carbon source
  - Molasses or ethanol
- Granular activated carbon (GAC)
- Granular sludge
- Elemental selenium produced
  - Entrapped in media

# Active Biological

- Advantages
  - Treatment of high flows and concentrations to < 5 µg/l
  - Smaller footprint than passive

# Active Biological

- Disadvantages
  - Pretreatment of solids
  - Temperature dependent
  - Plugging & short circuiting

# Active Biological

- Disadvantages
  - Regeneration and disposal
  - Potential to become too reducing
    - In absence of metals, $H_2Se$ would be mobile

# Active Biological

- Case Study – Undisclosed Gold Mine, SD
  - High TDS (5,000-15,000 mg/l)
  - Max flow 700 gpm
  - 70 µg/l influent (average)
  - < 10 µg/l effluent
    - Blended with an RO permeate to meet limits

Golder Associates, Inc. 2009. Literature review of treatment technologies to remove selenium from mining influenced water. Report to Teck Coal Limited, Calgary, AB.

# Active Biological

- Case Study – Kennecott Copper Demonstration, UT (ABMet®)
  - 1,950 µg/l influent
  - 2 µg/l effluent
  - RT 5.5 hours
  - 1 gpm

MSE, 2001, Final Report: Selenium treatment/removal alternatives demonstration project. MWTP, prepared by MSE Technology Applications, Inc. for U.S Environmental Protection Agency, National Energy Technology Laboratory, Office of Research and Development, Cincinnati, OH and U.S. Department of Energy, Federal Energy Technology Center, Pittsburgh, PA.

# Active Biological

- Case Study – Kennecott Copper Demonstration, UT (ABMet®)
  - Capital - $640K
  - O&M - $135K / yr
  - Net $1.32 / 1K gal

MSE, 2001, Final Report: Selenium treatment/removal alternatives demonstration project. MWTP, prepared by MSE Technology Applicatons, Inc. for U.S Environmental Protection Agency, National Energy Technology Laboratory, Office of Research and Development, Cincinnati, OH and U.S. Department ofEnergy, Federal Energy Technology Center, Pittsburgh, PA.

# Active Biological

- Other active biological
  - Capital - $100K to $3 Million
  - O&M - $0.30 – $2.38 / 1K gal

Microbial Technologies. 2005. Literature review: Evaluation of treatment options to reduce waterborne selenium at coal mines in West-Central Alberta. Report prepared by Microbial Technologies, Inc. for Alberta Environment, Water Research Users Group, Edmonton, AB.

# Aerobic Wetland

- Created wetland
  - Phytoremediation
  - Volatilization
  - Reduction and sorption in sediments

# Aerobic Wetland

- Advantages
  - Passive
  - Habitat creation
  - Considered inexpensive

# Aerobic Wetland

- Disadvantages
  - Large area
  - Risk to wildlife
    - Bioaccumulation

# Aerobic Wetland

- Case Study – Chevron Oil Refinery, CA
  - 36 acres
  - 20-30 µg/l influent
  - 2 µg/l effluent

Reported in Hansen, D., Duda, P., Zayed, A., and Terry, N. 1998. Selenium removal by constructed wetlands: role of biological volatilization. ES&T. 32:591-597, but data is in an inaccessible report "Duda, P. J. *Chevron's Richmond Refinery Water Enhancement Wetland*; Report to the Regional Water Quality Control Board; Oakland, CA, 1992."

# Aerobic Wetland

- Case Study – Chevron Oil Refinery, CA
  - ~ 1,000 gpm
  - Required modification due to ecotoxicological issues

Reported in Hansen, D., Duda, P., Zayed, A., and Terry, N. 1998. Selenium removal by constructed wetlands: role of biological volatilization. ES&T. 32:591-597, but data is in an inaccessible report "Duda, P. J. *Chevron's Richmond Refinery Water Enhancement Wetland*; Report to the Regional Water Quality Control Board; Oakland, CA, 1992."

# Aerobic Wetland

- Case Study – Chevron Oil Refinery, CA
  - No specific costs found
  - Expected[1]
    - ~ $1-3M design & construction
    - ~ $100K / yr

[1] Microbial Technologies. 2005. Literature review: Evaluation of treatment options to reduce waterborne selenium at coal mines in West-Central Alberta. Report prepared by Microbial Technologies, Inc. for Alberta Environment, Water Research Users Group, Edmonton, AB.

# Biochemical Reactor (BCR)

- Microbial reduction
  - Selenate to selenite and elemental selenium
- Hay, wood, sawdust, microorganism source

# Biochemical Reactor (BCR)

- Entrapment of elemental Se in pore spaces
- Sorption of Se(IV)

# BCR

- Advantages
  - Passive
  - Expected lifetimes > 10 yr
  - Considered inexpensive

# BCR

- Disadvantages
  - Large area
  - Long RT (2 or more days)
  - Post treatment needed
    - Dissolved oxygen (DO)
    - Biochemical oxygen demand (BOD)
    - Sulfide and ammonia

# BCR

- Disadvantages
  - Low flow requirements
  - Unknown disposal requirements

# BCR

- Case Study – Gravel Pit, CO
  - 13 months
  - 1.7 – 24 gpm
    - Lower flows better removal
  - RT 10 hr – 6.1 days
    - 2.5 days optimal
  - 5-80 ug/l influent
  - 1-31 ug/l effluent

Walker, Russ and Golder Associates, Inc. 2010. Final report: Passive selenium-bioreactor pilot scale testing. Bureau of Reclamation Science and Technology Program (PN 4414).

# BCR

- Case Study – Gravel Pit, CO
  - Capital - $39, 200
  - Operating estimate
    - $4,400 per Kg Se removed

Rutkowski, T., Walker, R., Gusek, J., and Baker, M. 2010. Pilot-scale treatment of selenium in gravel pit seepage water using biochemical reactor technology. Presented at the Annual Meeting of the American Society of Mining and Reclamation, Pittsburgh, PA., June 5-11.

# BCR

- Case Study – Unnamed historic gold mine, MT
  - 13 μg/l avg influent
  - 1 μg/l avg effluent
  - Temps 41-61F
  - < 20 gpm best

Blumenstein, E.P. and J.J. Gusek. 2009. Overcoming the obstacles of operating a biochemical reactor and aerobic polishing cell year round in Central Montana, presented at the 2009 Annual Meeting of the American Society of Mining and Reclamation, Billings, MT.

# BCR

- Case Study – Unnamed historic gold mine, MT
  - 7-10 day RT for thallium
    - 5-7

Blumenstein, E.P. and J.J. Gusek. 2009. Overcoming the obstacles of operating a biochemical reactor and aerobic polishing cell year round in Central Montana, presented at the 2009 Annual Meeting of the American Society of Mining and Reclamation, Billings, MT.

# BCR

- Other BCRs
  - Capital - $80 - $225K
  - Operating - $0.30 / 1K gal

Golder Associates, Inc. 2009. Literature review of treatment technologies to remove selenium from mining influenced water. Report to Teck Coal Limited, Calgary, AB.

# Overview

- Geochemistry
- Treatment technologies
  - Chemical
  - Physical
  - Biological
- **Things to think about**

# Things to think about

- Site-specific overall water chemistry is important
  - Hg
    - SRB methylation
  - As
    - Dissolution of FeOx in anaerobic treatment

# Things to think about

- Site-specific conditions
  - Access, available land, power
    - What is best for one site might not be best for another
- Mix and match
  - Treatment trains

# Things to think about

- Recovery/Reuse
  - Concentration methods
  - Reduction methods
    - Melt and sell elemental selenium