The Past, Present and Future for Selenium Treatment

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Where is it found?

- Paint, pigments, dye formulating
- Electronics
- Glass manufacturing
- Insecticide production
- Pulp and paper
- Ash piles, FGD blowdown,
- Coal/oil combustion
- Agricultural water
- Petroleum processing
- **Mining operations**

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Why is it a problem?

- Aquatic life hazard
  - 1983 – Kesterson National Wildlife Refuge - California
  - Birth defects/death of birds, small animals, fish
- Selenium cycle not well understood
  - Uncertainty on bioavailability
  - Even if bioavailable – what is toxic?
- Often times low concentration, high volume - makes treatment expensive

How is it regulated?

- 5 µg/L   Freshwater aquatic life
- 50 µg/L Primary DWS MCL
- U.S. Fish and Wildlife Service has recommended 2 µg/L to protect fish, waterfowl and endangered aquatic species

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Chemistry

- 3 primary oxidation states
  - -2 selenide
  - +4 selenite ($HSeO_3^-$ and SeO_3^-)
  - +6 selenate (SeO_4^{-2})
- Chemical equilibrium principals don’t really apply
- Driven by
  - Redox conditions
  - Biological activity
  - Sorption processes

Past and Present - EPA BAT

- Ferric coagulation/filtration
  - Typically pH <7
  - Coprecipitation effect
  - Effective removal requires reduction of selenate to selenite
  - Problem if arsenic present
- Lime softening
- Reverse osmosis
  - Non-preferential process
  - Pretreatment due to other typical mine water issues may be required

Past and Present - EPA BAT

- Electrodialysis
- Alumina
  - Selenite adsorbed at pH range of 3 – 8
  - Silica can interfere at pH >4
  - Selenate adsorption is poor
- Ion exchange
  - Need oxidized divalent selenate
  - Competing ion effects can hinder effectiveness
  - Some specialty resins tested

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Past and Present - EPA BDAT

- Ferrihydrite precipitation with concurrent adsorption of selenium on the ferrihydrite surface
- For adsorption – need ferric ion (Fe^{+3}) present
- Most effective removal at pH 4-6
- Somewhat effective up to pH 8
- Phosphate, silicate, arsenic, carbonate can interfere

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Past and Present – EPA/DOE MWTP

- *Selenium Treatment/Removal Alternatives Demonstration*
- Report issued in 2001
- Three technologies tested in field
  - Ferrihydrite Adsorption (baseline)
  - Catalyzed Cementation
  - Biological Reduction
- One technology tested on bench scale
  - Enzymatic Reduction

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Past and Present – EPA/DOE MWTP

- Objective – treat to <50 µg/L
- Work done in 1999-2001
- Basis – KUCC Garfield Wetlands-Kessler Springs site
- <50 to >10,000 µg/L Se
- 95%+ selenate
- TDS 1,000 - 5,000 mg/L

Past and Present – EPA/DOE MWTP

- Ferrihydrite
  - Did not work on a consistent basis
  - Various iron types, concentrations and ratios used
  - Could achieve objective but at prohibitive reagent consumption
  - Questions on TCLP stability

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Past and Present – EPA/DOE MWTP

- Catalyzed cementation
  - Developed for arsenic, selenium, thallium removal
  - Removes metals by cementation on the surface of iron particles
  - Believed to work on both selenite and selenate
  - Proprietary catalysts used
  - Bench test work had shown favorable results
  - Did not work on a consistent basis

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Past and Present – EPA/DOE MWTP

- Biological Reduction (BSeR™)
  - Used anaerobic solids bed reactors
  - Selenium reduced to elemental selenium by biofilms and proprietary microorganisms
  - Molasses used as carbon source
  - Was able to consistently meet objective
  - Over 70% of samples less than detection (2 µg/L)

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Past and Present – EPA/DOE MWTP

- Economics

	BDAT	Cementation	BSeR™
Capital	$1.0M	$1.1M	$0.6M
O&M	$2.1M	$1.2M	$0.14M
NPV	$17M	$9.5M	$1.1M
$/1,000 gal	$13.90	$8.17	$1.32

Based on 300 gpm plant, 2 mg/L selenium

2001 dollars

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Past and Present - Nanofiltration

- Some test work by USGS in 1996
  - Agricultural drainage
- Selenate removal better than selenite
  - Not surprising – designed for divalent not monovalent ions
- 95+ % removal at Se<1,000 µg/L
- Membrane scaling is an issue in high SO_4^{-2} water

Problems With the Past and Present

- Non-selective processes
- Large amounts of secondary waste
- Multiple reagents
- Okay for bulk selenium removal with other metals
- Can’t consistently get to <10 µg/L

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Biological Reduction – General

- Studied for decades
- Microbes degrade/transform contaminant because
  - Energy source
  - Detoxification mechanism
  - Resembles another ion
  - Combination of the above
- Anaerobic reactors
  - Reduction to elemental selenium
  - Nitrate/sulfate interference?
- 90%+ removal reported

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Biological Reduction – Ponds/Wetlands

- Panoche Drainage District – San Joaquin Valley
  - 74-1,400 µg/L due to Se rich soil
  - Primarily selenate form
  - Numerous bioremediation studies
  - Algal-Bacterial Selenium Removal (ASBR)
  - Anoxic ponds – reduce selenate to selenite to elemental and settle
  - Generally about 80% maximum removal

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Biological Reduction – Ponds/Wetlands

- Additional California work - 2005
  - Constructed wetlands
  - 9 plant species tested
  - 63% - 71% removal
  - ~20 µg/L influent, 3 – 6 µg/L effluent
- Problem with ponds/wetlands
  - HRT's in days

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Biological Reduction – Advances

- More selective microbes isolated
- Advances in fixed film/biofilm media
- Better understanding of operating conditions
- Result – retention times have been reduced from days to hours for active systems
- Advances also made in passive technology

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Biological Reduction – Advances

ABMet®

- Offered by GE Water and Process Technologies
- Same as BSeR™ process
- Several FGD projects at commercial scale
- 3,000 – 5,000 µg/L selenium
- Up to 20,000 mg/L chloride
- 98% – 99% removal projected
- Effluent as low as 10 µg/L

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Biological Reduction – Advances

Passive Selenium Reducing Bioreactor

- Tested on Colorado Western Slope
- Bureau of Reclamation Science and Technology Program
- Influent typically ~20 µg/L
- Spike to 70 µg/L
- 1,000-2,000 mg/L SO_4^{-2} background

Biological Reduction – Advances

<u>Passive Selenium Reducing Bioreactor</u>

- Four reactors with different substrate compositions
- Organic substrate composed of wood chips, hay, manure
- ZVI incorporated; no advantage
- 12 hour detention time adequate, optimization possible
- Operated for 20 weeks
- Effluent typically <2 µg/L
- Up to 98% removal

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Biological Reduction – Advances

Active Anaerobic Bioreactor System

- Waste rock seepage
- 250 gpm capacity
- Fixed film bioreactor with high surface area media
- Molasses used as carbon source
- Phosphate/urea added
- Reverse osmosis system used during high flow – 700 gpm
- Bioreactor feed switched to RO brine

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Biological Reduction – Advances

Active Anaerobic Bioreactor System

- 18 hour retention time
- Low flow (raw seepage)
  - Se ~30 µg/L
  - SO_4^{-2} ~6,000 mg/L
- High flow (RO brine)
  - Se ~70 µg/L
  - SO_4^{-2} ~13,500 mg/L

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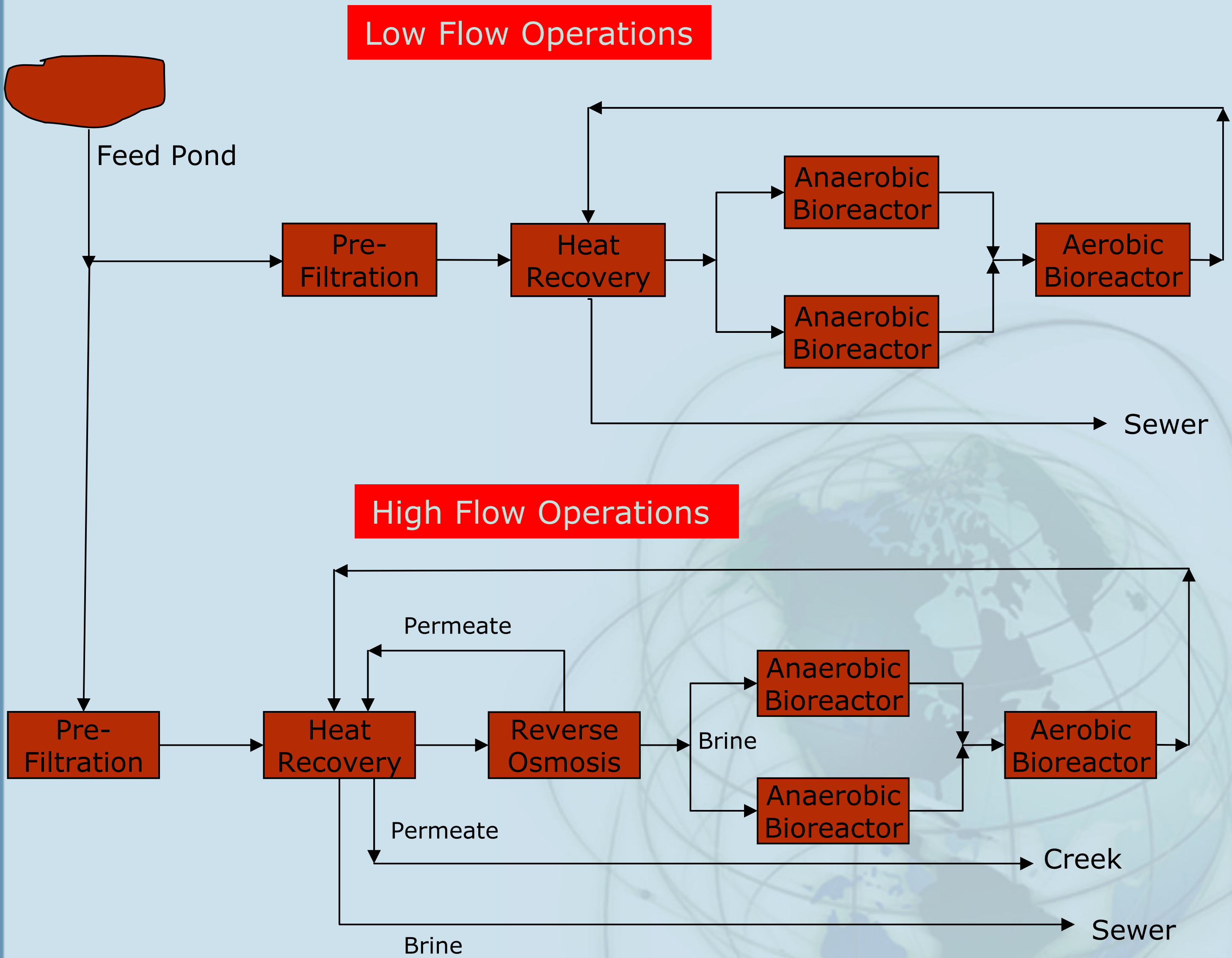
Biological Reduction – Advances



Biological Reduction – Advances

Biological Reduction – Advances

Active Anaerobic Bioreactor System

- Effluent goal is 10 µg/L
- Pilot plant operated for 7 months
- High sulfide was an issue
  - Discharge quality
  - Solids fouling
- Full scale system designed and constructed
- Operating for about 18 months
- Compliant water being produced

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Future?

- Selenium with other metals
  - Conventional lime-iron based processes for bulk removal
  - Biological polishing process
- Low concentration selenium
  - Biological reduction
  - Both active and passive options
- Combinations with other processes – i.e. membranes
- Reduce costs to <$5.00/1,000 gal? Maybe down to $1.00/1,000 gal?

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Biological Reduction – Application Keys

- Nutrients are vital in establishing microbial population
- Understanding of site chemistry and environmental interactions
- Analytical methods
  - Can get discrepancies in total and dissolved
  - Possibly related to digestion
  - Volatile selenide
- Need for aerobic post-treatment
  - High COD, P, N

Conclusions

- There is no silver bullet for selenium removal to low levels
- All sites must be evaluated individually
- Paper designs risky – development work always recommended
- Selenium can be removed to <10 µg/L
- Cost of selenium reduction to low levels is decreasing

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Questions?

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