# West Virginia Mine Drainage Task Force

## 40th Annual Meeting

Morgantown, WV
March 27, 2019

# Experiences and Challenges with Selenium Treatment

Jim Constant, P.E.
ERP Environmental Fund, Inc.
Madison, WV
(304) 369-8181

# Selenium

- What is Selenium (Se)
  - A semi metallic element
  - On the Periodic Table near Sulfur and Arsenic
    - It mimics the characteristics of each
    - Usually associated with sulfide ores

Uses

- Electronics, photo conductors, optics, glass, ceramics, plastics, paints, anti-dandruff shampoos, and in nutritional supplements for animals and humans.

Why is Selenium regulated?

- Se in small amounts is needed for human and animals diets
  - **FDA Issued Final Rule to Add Selenium to the List of Required Nutrients for Infant Formula**
- Toxic in large doses:
  - Se can be toxic if ingested over periods of time at amounts only 5-10 times higher than those required for normal functioning.
    - Some selenium compounds are carcinogenic.
- Can be harmful to aquatic life and aquatic life's predators
  - Can cause birth defects and reproduction problems
  - Se bio-accumulates

- Selenium is a world wide problem
    - Some areas deficient – must supplement
- Many Industries Affected
    - Mining
    - Coal ash ponds
    - Petroleum refineries
    - Solid waste land fills

- Selenium discharge limits
    - WVDEP adopted the USEPA National Recommended Water Quality Criteria in its water quality standards (WQS) (1992)
        - 5 ppb – chronic criterion
        - 20 ppb – acute criterion
    - Emerged as "parameter of concern" during preparation of programmatic EIS published in 2003 pursuant to a settlement arising from litigation surrounding mountaintop mining
    - WQS translates to "end-of-pipe" NPDES limits
        - 4.7 µg/L monthly average and 8.2 µg/L daily maximum
    - USEPA Drinking Water Standards
        - 50 ppb is protective of human health

# Where is Selenium Found?

- Found in the dark shales (carbonaceous shales)
- Found in the coal
  - Partings and immediate roof and floor
- Sandstones and grey shales are not usual contributors
  - Unless there is embedded coal spars
  - Adjacent to coal seams
- Selenium laden rock is throughout the stratigraphic column in the coal regions
  - Not only a surface mining issue
  - Underground
  - Refuse

# Speciation of Selenium

- Selenide (-2 valance)
- Elemental Selenium (zero valance) Inert
- Selenite (+4 valance) Less toxic for animals, more toxic for aquatics
- Selenate (+6 valance) More toxic for animals, less toxic for aquatics

- In southern West Virginia
  - Selenate: 90-95 %
  - Selenite: 5-6 %
  - Others: Few %

# Selenium Reduction Methods

# Have Tested:

- Reverse Osmosis (RO) (Pilot) (Filtering)
- VSEP (Vibrating RO) (Pilot) (Filtering)
- Fluidized Bed Reactor - FBR (Pilot/full scale) (Biological)
- Ion Exchange (Multiple Resins) (Pilot) (Adsorbent)
- Electrocoagulation (Pilot)
- Gravel Bed Reactor - GBR (Pilot) (Biological)
- In-situ Bioremediation (Pilot)(Biological)
- AB Met - GE Water (Pilot) (Biological)
- Moving Bed Biological Reactor (Pilot) (Biological)
- Adsorbent Material (Chitosan, Zeolites) (Pilot)
- Ferrihydrite (Fe amendment added to Se material) (Pilot)
- Zero Valent Iron (ZVI) steel wool reels (Pilot/full scale) (chemical/adsorption)
- Iron Impregnated Foam (Pilot)
- Sulfur Modified Iron (SMI) (Pilot/full scale)

## Have Reviewed:

- “Frontier” Water System (Similar to FBR technology)
- “Bugs in a Bag” (Bags of microbes/nutrients placed in ponds)
- Evaporation (Snow making type machine) (our climate is too humid)
- Phytoremediation (selenium reduction using vegetation)
- Electro Biochemical Reactor (EBR)(Adds electrons electrically to microbes)
- White Rot Fungus (Very new technology) (very little data)

# Treatment System Issues

- From lab studies to full scale implementation
  - Is it scalable
  - Is it cost effective
- Vendor Selenium packages
  - Most are not turn-key packages
  - Most systems require pre-treatment/post treatment
- Would recommend Pilot Studies on site
  - Water variability

# Se Reduction Systems using Zero Valent Iron (ZVI)

- Zero Valent Iron (ZVI) (Pilot)
  - Dr. Ray Lovett (WVU) ShipShaper, LLP
  - Presentation at the 2007 Mining Drainage Task Force Symposium

- Preforms better at lower pH (5-6 pH)
- ZVI generates ferrous iron
- Ferrous iron must be converted to ferric iron and removed

# Apparatus 1 (circa 2007)


Dr. Ray Lovett

# Apparatus 2 (circa 2007)

# ZVI Reels

# ZVI (Iron Media)

- ZVI pilot systems
  - No pH adjustment
  - No iron recovery
  - No electricity

- Steel wool reels (Global Material Technology)
  - Wound steel wool
  - 7' Diameter reels - 21" thick
  - 2 reels per tank
  - 3 tanks in series

- Matric/ Liberty Hydrologic (ZVI impregnated foam)
  - Reticulated foam
  - ZVI particles glued into the foam
  - Rectangular tanks


# Global Materials Technology ZVI (GMT)

7' diameter tank with (2) 21" thick steel wool (ZVI) reels in 1,300 gallon tanks
(no pH adjustment, no iron recovery)
Eventually (2+ gpm/tank (3) tanks in series)

# Matric - Liberty Hydrologic

## Iron impregnated foam

(no pH adjustment, no iron recovery initially)

## Morphed to full scale systems

- Patriot Coal's IFSeR (Iron Facilitated Selenium Reduction System)
  - 200+ gpm systems
  - Adjust pH to 6 or lower
  - Iron recovery after iron conversion
  - 20 gpm/tank (nominal)
  - 2 NPDES outlets in compliance
  - "Special Master" Approved

# IFSeR System (Patriot Coal)(circa 2011)

# IFSeR

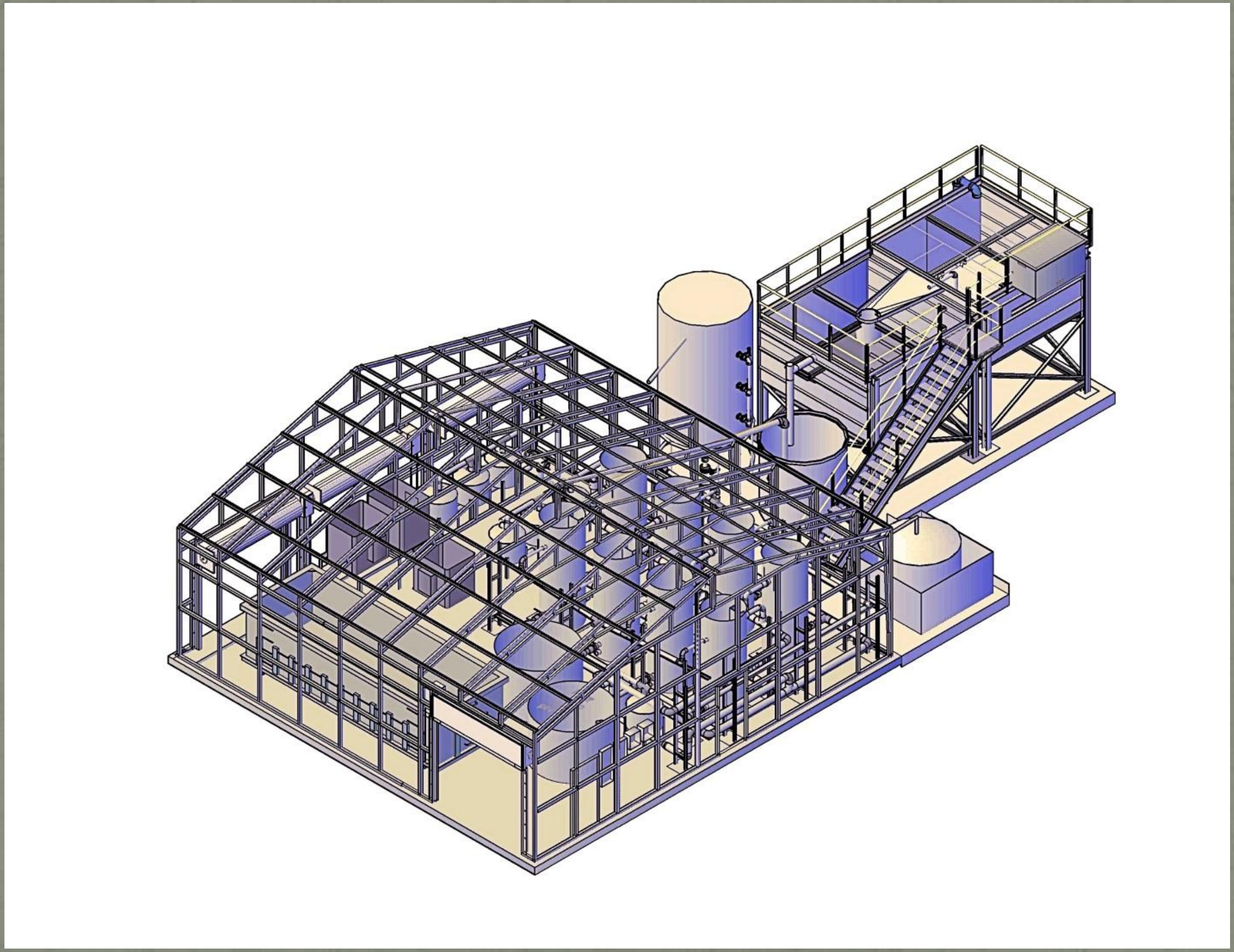
- Pros:
  - Removes selenite and selenate
  - Small foot print (locate near Se source)
  - Relatively low capital cost
  - Non-biological system
  - Spent media will pass TCLP
  - Iron sludge will pass TCLP
  - Full system can be placed in a building
  - Install parallel systems for higher flows or add additional tanks
  - Single phase power for plant
- Cons:
  - Fe sludge generation
    - Sludge moisture (must pass paint filter test prior to disposal)
  - Requires chemicals (pH adjustment)
    - Safety (remote locations)
    - Site access for chemical deliveries
  - High O/M
    - Multiple pumps (water, sludge, metering)
    - Labor intensive
      - Fe media - change out frequency
      - Due to water short circuiting through steel wool
  - Possible iron passivation

- **Sulfur Modified Iron** – SMI (chemically bonded sulfur to iron)
  - Patriot installed a full scale system - 8 tank system with pH adjustment and iron recovery
- Pros:
  - Removes selenite and selenate
  - Longer iron media longevity
    - Not as labor intensive or as frequent media change outs
    - Minimal water bypass through media
      - Due to backwashing
  - Open top Vessels
    - Scalable for larger flows/tank or add additional tanks for higher system flows
  - Small foot print (locate near Se source)
  - Relatively low capital cost
  - Non-biological system
  - Spent media will pass TCLP
    - Can be recycled for scrap iron
  - Iron sludge will pass TCLP
  - Full system can be placed in a building
    - Many different arrangements
  - Treated 30+ ppb Se to compliant levels
  - Fe generation less than IFSeR
  - Currently being piloted in oil refineries and full scale project at coal ash pond closeout

# SMI

- Cons:
- Same need for pH adjustment as IFSeR
- Three phase power for plant
- Influent water must be very low turbidity
- Finite Se retaining capacity on media
- Media cannot be regenerated

# SMI Design



# SMI System (Patriot Coal) (circa 2012)

# Current Treatment Methods in the WV Coal Fields

- Biological Chemical Reactor (BCR)
- Fluidize Bed Reactor (FBR)
- MBBR (Moving Bed Bioreactor)
- Underground Injection
- Fish Studies - WV Regulatory Changes (Fish Uptake Studies)
- Water Management

# Fluidized Bed Reactor (FBR)
## Design Flow: 2800 gpm
### Capital Cost: $+50 Million

# Fluidized Bed Reactor (FBR)

- First full scale selenium reduction FBR in the USA
  - Court ordered
  - Two years for design/build
    - Pump water 2 miles to plant
    - 800' vertical lift
- Pros:
  - Controllable biology
    - Actively feed the microbes food and nutrients
  - Mets regulatory limits (4.7 ppb monthly)
- Cons:
  - Capital: cost prohibitive (+$50 million)
  - O&M: cost prohibitive ($+3 million per year)
    - Labor: manned 24/7/365 (10 technical personnel)
    - Chemical Usage: Intensive
    - Volume of sludge generated: Large

# Fluidized Bed Reactor (FBR) Biological

- Microbes grow on burnt coconut shells
  - Granular activated carbon (GAC)
- GAC is levitated by water flow
  - Allows more contact area for the biomass growth
- About a 30 min. contact time (water in contact w/ microbes)
- "Bugs" are feed food and nutrients - 24/7
- Water is heated if below 50 degrees F
- Three vessels do the selenium reduction
  - Remaining structures are pre and post treatment

# Bio-Chemical Reactor (BCR)

Design Flow: 950 gpm

~6,200 Round bales of Hay

Footprint: 6 acres

# Biochemical Reactor (BCR)

- Pros:
  - Most used type of selenium reduction in WV coalfields
  - Less Capital Intensive than FBR/MBBR (still very expensive….)
  - Can met regulatory limits (4.7 ppb monthly)
  - Reduce selenite and selenate to elemental selenium
- Cons:
  - Passive type system but actively managed
    - Pumping
  - Potential biologic upsets must stay anaerobic
  - Microbe's food is in-situ
  - Sluggish response to change of flow and Se concentration
  - Large footprint
  - Public nuisance (smell – hydrogen sulfide)
  - Creates many by-products
    - COD, BOD, sulfides, low DO
  - Very complex biology –always changing
  - Initial startup water is problematic
  - Media permeability
  - Closure unknowns

# BCR - During Construction

# Final BCR Configuration

# Aeration

# BCR Biology

- How does a BCR work:
  - Naturally occurring microbes
  - Food is from the media (hay is the easiest to break down, wood is a longer term carbon source)
  - Respires the O2 molecule from the contaminate
    - Order of reduction: Dissolved Oxygen → Nitrates → Selenates → Sulfates
      - BUT microbes have to be in contact with the contaminates i.e. can have nitrates in effluent but are reducing selenium
- Many different types of microbes (Dependent on the water's ORP and contaminates)
  - Nitrate reducers
  - Selenium reducers (SeRB's)
  - Sulfate reducers (SRB's)
  - Methane producers
- Some microbes will respire individual contaminates some respire multiple
- "Welfare bugs" eating your food but not helping with selenium reduction
  - Fermenters breaking done the wood components
- Food is present at all times in the BCR
- Low Temperature
  - Makes microbes lethargic
    - But .. Bugs still working at 0.2 degree C water temperature (northern British Columbia)
      - Air temperature (-40 degrees C)

# Design of BCR System

- Sizing calculations derived from pilot testing
  - Sizing based on selenium concentration and flow (loading: mg/day)
  - How much selenium is held in the media (retained: mg/day/cft) ????????
  - Calculate the required media needed
- Location of BCR:
  - near selenium source
  - on mine site
- System layout: Variable due to available foot print (topography)
- What media mix is used and what percentages????
  - Hay bales and mushroom compost
  - Hay, wood products, limestone chips, compost, manure, peat

# BCR System Layout

- Two BCR cells (preferred)
  - Allows redundancy
  - Can design more cells depending on available footprint
  - Parallel flow regime
- Two polishing ponds in series (minimum)
  - First: Settling pond removes "Dead Bug Bodies"
    - Will re-oxidize the selenium if aerated
  - Second: Aeration pond (Eliminates COD/BOD, adds Oxygen)
    - Aerator Hp: based on COD calculations
- Water delivery to system
  - Gravity
    - Do not place in storm flow regime – need regulated flow
    - Head pond (multiple concentrations and flows stabilized)
  - Pumped directly from pond to BCR
- Water Removal
  - Where does substandard (coffee) water report during startup
  - Effluent can be selenium reduced but still other wise impaired
    - Narrative water quality standard
    - Sulfides

# BCR System Components

- Limestone gravel base
  - Maintains alkalinity in BCR
  - “French Drain” for system hydraulics
- Carbon source “Bug Food” also “Bug Apartments”
  - Round or square hay bales
  - Mixed media or mushroom compost on top of bales
  - Mixed media (hay, wood chips, sawdust, limestone chips, mushroom compost, peat)

# BCR Issues

- Initial BCR startup
  - Generates tannins, high COD, high BOD
    - Termed "Coffee Water"
      - i.e. "like leaves decaying in a mud puddle"
    - Must be managed (cannot discharge to the environment)
    - Extremely high COD/BOD, initial dark color changing to yellow hues
      - May last weeks, months or longer……
        - "Coffee water" pumped to back stacks until water is clear
- May generate large amount of sulfides
  - Since food is in-situ (bugs have a buffet), no control of microbes
  - Only system variable is "amount of time through the system"
    - Hydraulic Residence Time (HRT)
    - Plug flow "concept"
      - Due to fixed size of cell
        - Need more water per period of time
          - Only variable is THROUGHPUT (GPM)
- Permeability of Media
  - Media slimes over
  - Leaves, algae blockage

# Health of the System

- ORP: -325 to -175 (mV)
  - Creates anaerobic environment
- Dissolved Oxygen (DO): Approach 0.0 mg/l
- Temperature rises through BCR cell
- Reduction in Nitrates
- Reduction in Sulfates
  - Generates hydrogen sulfide
    - Dependent on pH
- Very slow to react to changes (flow/ concentrations)
  - "Bugs" have to grow to meet demand
- Biology works
  - Chemistry/Engineering is the challenge

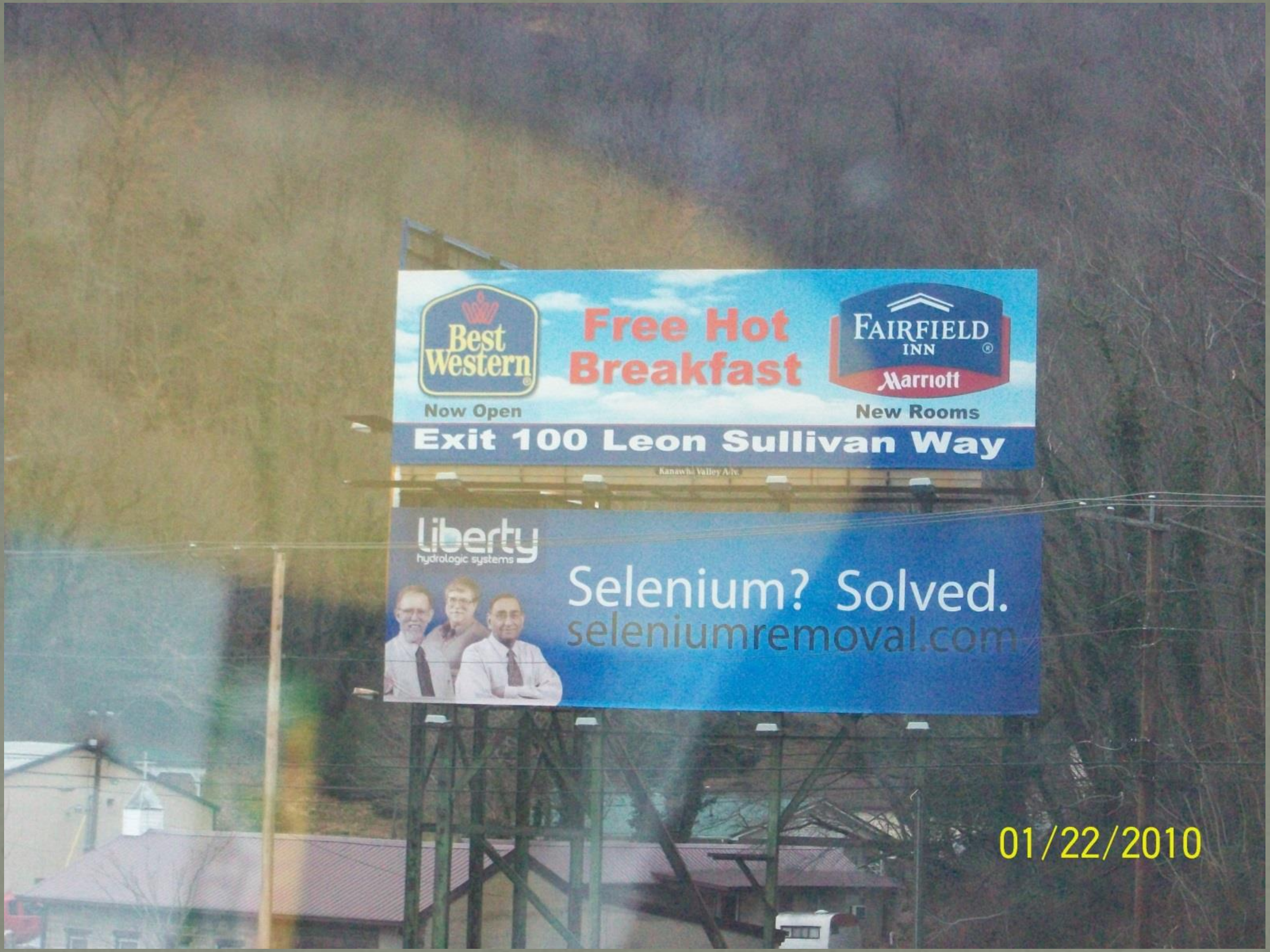
# BCR's
# DO NOT LIKE CHANGE

# Underground Injection (UIC)

- Injection of Selenium water into an underground mine
  - Must be permitted
  - Must be < 50 ppb Se
- Dilution
  - If and when it returns to the surface – hopefully compliant
- Can also be used as conduit for transport to treatment system

# Water Management

- Dilution of the selenium by mixing in ponds and then discharge through an approved NPDES outlet
- Mixing Zones
  - Transfer substandard water to a larger river via pipelines


Best Western
Free Hot Breakfast
Fairfield Inn
Marriott
Now Open
New Rooms
Exit 100 Leon Sullivan Way
liberty
hydrologic systems
Selenium? Solved.
seleniumremoval.com
01/22/2010

# Good Reference Information

- "Review of Available Technologies for the Removal of Selenium From Water"
    - Prepared for : North American Metals Council (June 2010)
        - By CH2MHill (T. Sandy and C. DiSante)
  - Update: 2013

- https://quicksilver.epa.gov/work/HQ/171055.pdf

# Questions????

Jim Constant, P.E.
ERP Environmental Fund, Inc.
Madison, WV
(304) 369-8181