Ongoing Case Study Berry Branch Selenium (Se) Pilot Treatment System Using Sulfur Modified Iron (SMI)

Former Hobet Surface Mine Site, Lincoln County, WV

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Background

- The Berry Branch Se Pilot Treatment System is located at the former Hobet Surface Mine
- Hobet was one of largest mountaintop removal coal mining operations in Appalachia
 - Operated from approximately 1974 to 2015
 - Boone and Lincoln Counties, WV
- The Hobet property has a history of elevated and noncomplaint Se discharges, particularly on the western / Mud River watershed side of the mining operation

Background

- As a result of Patriot Coal Company's 2015 bankruptcy, Hobet and other Patriot legacy sites in six states were passed to Virginia Conservation Legacy Fund (VCLF)
- VCLF attempted to reclaim and remediate these legacy sites through its subsidiary ERP Environmental Fund Inc (ERP)
- After limited success, however, ERP became insolvent and ceased operations in late 2019

Background

- ERP was placed into receivership at the request of WVDEP by the Circuit Court of Kanawha County, West Virginia in March 2020
- The ERP Receivership Estate is presently charged with, among other things, raising funds and attempting to reclaim abandoned mine sites, obtaining permit and bond releases, improving environmental compliance, and treating noncompliant water discharges

Prior Se Treatment Efforts at Hobet

- Former operators of the Hobet / Patriot properties attempted to treat and remediate Se discharges using various methods that included:
 - Water management
 - Pumping and dilution
 - Underground injection
 - Zero valent iron technology (ZVI)
 - Biochemical reactors (BCRs)
 - Fluidized Bed (biological) Reactor (FBR)
 - ETC

All with mixed and inconsistent results, and at great cost

Prior Se Treatment Efforts at Hobet

- Under ERP, these prior Se treatment systems:
 - Fell into disrepair
 - Became inoperable
 - Were subsequently abandoned
 - Are now economically impracticable to refurbish and operate
- The ERP Receivership Estate has thus sought out new Se treatment technology for evaluation and potential long-term application at the Hobet property

- The Berry Branch Se pilot system utilizes sulfur-modified catalytic zero valent iron particles (SMI®) as an adsorptive medium to reduce selenite and selenate to elemental selenium
 - SMI is a patented blend of chemically modified iron particles that are more reactive than ZVI and ZVI blends
 - To date, SMI has reportedly been successfully tested to remove and reduce arsenic, nitrate, hexavalent chromium (Cr VI), vinyl chloride, selenium, trichloroethelene (TCE), chlorinated solvents, halogenated pesticides, technetium and a variety of petroleum hydrocarbons

- Major components are two (2) SMI adsorption vessels (96" x 51" x 56") operated in an upflow configuration
 - High velocity "fluffing" of SMI media is scheduled to occur daily
 - Eight (8) multimedia filtration tanks (40" x 40" x 77") are installed on the influent side of the pilot system
 - Consists of two (2) sets of four (4) multimedia filters, utilizing macrolite and activated carbon media, backwashed bi-weekly
- Because alkaline mine water is treated, pH adjustment must
 be made using sulfuric acid to lower influent pH to optimum
 levels prior to passing through SMI vessels

- Effluent from the pilot system is discharged into abandoned former BCR cells for settling of Fe residual from the SMI media and to allow for mechanical aeration
- The Se / SMI Pilot system has the capability to be operated between roughly 50 to 150 gpm, dependent upon Se reduction needs
- Variable frequency drive pressure pump is utilized on the inlet side of the pilot treatment system to control and regulate system throughput

- The pilot system is PLC controlled with remote monitoring capabilities
- System was assembled on-site inside two "high cube" shipping containers (~40' x 8' x 9') utilizing local labor
- Subsequent to initial deployment, the pilot system was retrofitted with:
 - Ventilating fans, dehumidifiers, heaters, climate sensors, additional insulation, security and observations cameras, satellite internet, and back-up electric generator

- Although the pilot treatment system should ideally be operated on 3-phase electrical power, only single-phase 220volt power was available at the remote Berry Branch site
- As a result, electrical inverters and specially ordered singlephase pumps were required and installed, which increased pilot and operating costs

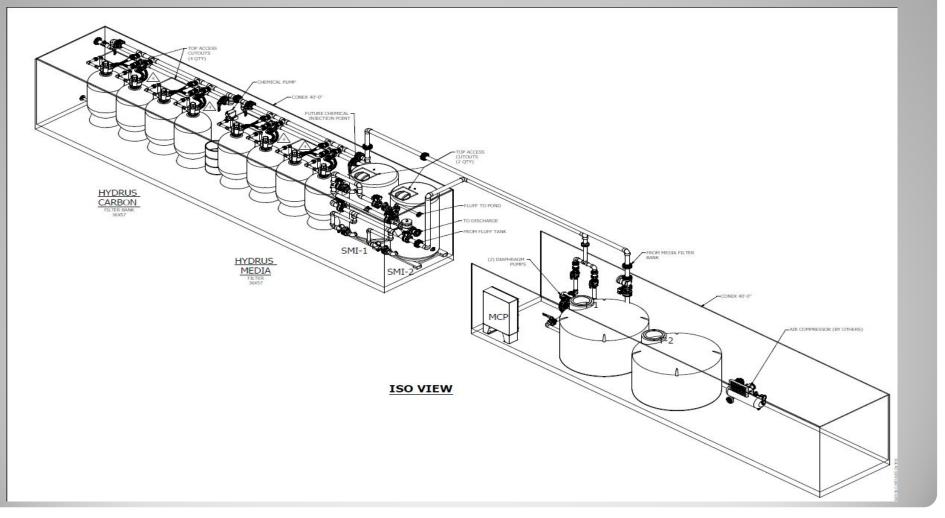
Case Study Objectives

- The Berry Branch Se / SMI pilot system became operational in early August 2023 and is planned to be operated for an additional 12 to 18 months
 - Primary pilot system / case study objectives:
 - Determine optimum empty bed SMI contact times for various influent Se concentrations
 - Evaluate SMI media life
 - Determine pre- and post-treatment requirements (if any)
 - Estimate operating costs,
 - Estimate capital cost(s) to upscale system to accommodate higher throughput capacity

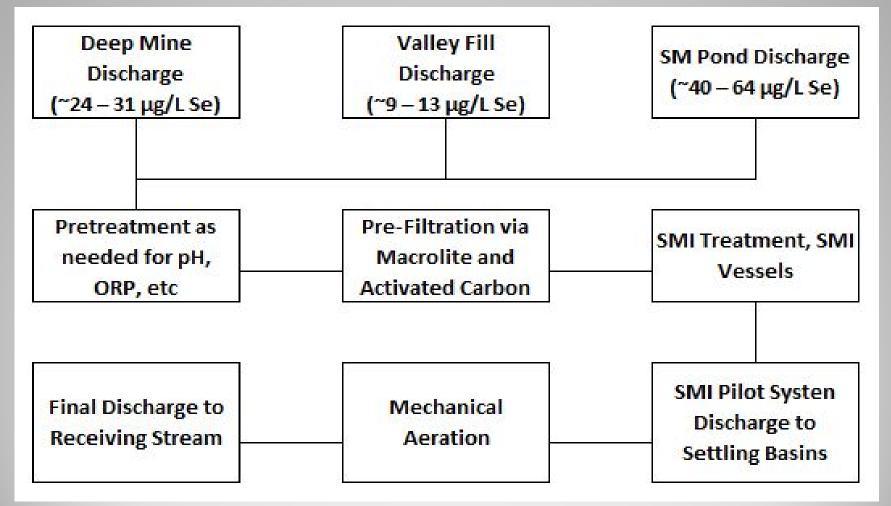
Case Study Objectives

- The study intends to utilize and / or blend influent water sources with various levels of Se concentrations in order to evaluate and optimize Se reduction
- The Berry Branch pilot system can be gravity or pump fed from multiple nearby and available Se water sources:
 - A deep mine discharge (~24 31 μg/L Se)
 - A valley fill discharge (~9 to 13 µg/L Se), and
 - Surface mine pond water (~40 64 μg/L Se)

Treatment System Configuration



Treatment System Configuration



- Over first 4½ months of system operation:
 - Influent source water from deep mine discharge with Se concentrations varying between roughly 22 and 32 μg/L, averaging 25.6 μg/L
 - SMI empty bed contact times varied on an experimental basis with average system throughput rates from ~ 60 to 133 gpm
 - Roughly 4 to 11 minutes of Empty Bed Contact Time
 - Immediate discharge from the SMI vessels averaged effluent of 12.9 $\mu g/L$ Se, with observations as low as 0.64 $\mu g/L$

- Post-settling Se concentrations at the NPDES outlet averaged approximately 1.0 μg/L
 - This is well below the applicable numeric State water quality standard for Se of 5 $\mu g/L$
 - Dependent upon pilot system flow rates and state of SMI media depletion, % reduction in Se concentration at the immediate discharge from the pilot system averaged between 49.7% to as high as 97.3%
 - Post-settling percent reduction in Se concentration at the NPDES outlet averaged 96.2% to as high as 99.1%

- 100% of the post-settling Se observations at the NPDES outlet were in compliance with (i.e., below) the applicable monthly average NPDES Se discharge limit of 4.7 µg/L
- Optimum performance of this SMI pilot system at the immediate discharge was achieved at approximately 64 gpm, with between 89% and 97.3% Se reduction observed

- Concerning other discharge parameters, and dependent upon system throughput rate, the pilot system at its immediate discharge:
 - Increased Fe concentrations in the immediate discharge by an average of ~42 mg/L to as high as an observed ~111 mg/L
 - Increased total suspended solids (TSS, primarily in the form of iron) by an average of 58 mg/L
 - Increased ammonia nitrogen (NH3-N) by approximately 1 mg/L
 - Had little apparent effect on Al, Mn, Ca, Mg, hardness, SO4, or conductivity
 - Decreased dissolved oxygen (DO) by approximately 1 mg/L, and
 - Decreased total organic carbon (TOC) and dissolved organic carbon (DOC) by approximately 56% and 50%, respectively

- Overall during the SMI / Se pilot system test to date
- <u>All post-settling discharge effluent parameters</u> at the Berry Branch NPDES outlet (including Fe and TSS) have met applicable NPDES effluent limits

- Based on pilot system results to date, SMI's potential to effectively treat for non-compliant concentrations of Se appears both feasible and promising
- SMI treatment costs to date are not yet fully developed
- Se that was not fully removed at the immediate discharge of the Se pilot system appears to have bound to an undetermined extent to Fe that was released from the SMI treatment system

 That is, as Fe discharge from the pilot system was oxidized and precipitated in post-treatment settling basins, additional and observable reductions in Se concentrations continued to occur

- SMI's ability to reduce Se concentration in the initially studied deep mine discharge water began to deplete quickly after approximately three (3) months
 - Effective depletion from the immediate discharge of the pilot system occurred at ~ 4.5 months
 - Although discharge at the NPDES outlet continued to meet applicable limits for six (6) plus months

- Preliminary evaluation indicates that elevated oxygen reduction potential (ORP) levels in the initial deep mine discharge water accelerated the depletion of SMI media in the initial study
 - ORP of the influent deep mine discharge water was elevated and ranged between 254 and 420 mV, averaging approximately 358 mV
 - Future Se test water sources are known to have materially lower ORP values (~20 mV), although chemical pre-treatment of influent waters may still be necessary in certain circumstances

- Cost of SMI media will need to be reduced in order to make the SMI treatment technology cost effective and practicable
 - SMI media is not currently mass produced, nor are inventories maintained by the producer / patent holder as demand for SMI media is not currently widespread, all of which are limiting factors

- Berry Branch pilot system is planned to be operated for an additional 12 to 18 months using different source waters (or blended sources) that exhibit both higher and lower Se concentrations
- New / replacement SMI media has been ordered and will be installed in order to study SMI effectiveness on influent water from a separate surface mine water source having a materially lower ORP value

- Pre-treatment will be evaluated and utilized if necessary to further reduce influent ORP and potentially extend SMI media life
- Further experimentation will be conducted with influent pH prior to entering the SMI vessels
- Additional pH probes may be installed and linked to the PLC control system to aid in this effort

- Further analytical study will be conducted to quantify the extent to which Se may be bound to Fe discharges from the SMI vessels and the extent to which Se concentrations can be further reduced by post-treatment settling and precipitation
 - Future analytics will include redesign of internal diagnostic sampling locations and parameters

- Economic evaluation will be conducted to determine capital and operating costs of the Berry Branch pilot system
- And to estimate capital and operating costs required to scale up the Berry Branch system in order to be able to treat larger throughput volumes

Challenges and Obstacles

 Experienced significant cost over-runs in initial construction and commissioning of pilot system

Some due to mis-design, some due to construction mistakes

- Replenishment of SMI media delivery has been delayed by manufacturer since December 2023
 - One-off product, not mass produced
 - Delivery of replacement media now expected late April 2024
- Experienced unexpected clumping and solidification of SMI in vessels after removal of spent SMI
 - Proved to be time consuming and difficult to remove





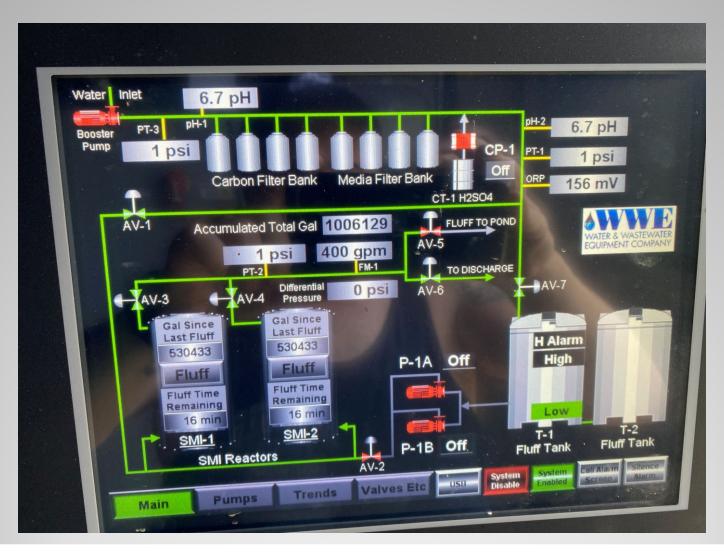


















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Thank You