Ongoing case study, berry branch selenium pilot treatment system using sulfur modified iron, former hobet surface mine site, Lincoln County, West Virginia

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Abstract

Estate to treat selenium (Se) discharges at the former Hobet Surface Mine site in the Mud River watershed of southern West Virginia using sulfur modified iron (SMI) technology. The Berry Branch Se pilot system became operational in early August 2023 and utilizes sulfur-modified catalytic zero valent iron particles as an adsorptive medium to reduce selenite and selenate to elemental selenium. Over the first 4½ months of system operation, pilot system influent has averaged 25.6 µg/L Se. Dependent upon pilot system flow rates and the state of SMI media depletion, percent reduction in Se concentrations at the immediate discharge from the pilot system has averaged 49.7% to as high as 97.3%. Se not fully removed at the immediate discharge of the pilot system appears to be bound to iron (Fe) being released from the pilot system. As Fe from the SMI media is oxidized and precipitated in post-treatment settling basins, additional reduction in Se concentrations is observed. Post-settling Se effluent concentrations at the NPDES outlet have averaged approximately 1.0 µg/L, well below the state water quality standard for Se of 5 µg/L. Based upon pilot system results to date, SMI's potential to effectively treat for non-compliant concentrations of Se appears feasible and promising, although the life of SMI media will need to be extended, potentially with pre-treatment to lower influent ORP and better influent pH management. Additionally, the cost of SMI media will need to be reduced in order to make SMI treatment technology more cost effective and practicable. The Berry Branch SMI pilot system is planned to be operated for an additional 12 to 18 months using different source waters that exhibit both higher and lower Se concentrations. Future study will focus on: replenishing SMI media to study system effectiveness and media life using different influent water sources; attempting to extend SMI media life by pre-treating to lower influent ORP and better control of influent pH prior to entering the SMI vessels; analytically determining the extent to which Se is bound to Fe discharge from the immediate pilot system and the extent that Se concentrations can be further reduced by post-treatment settling and precipitation; performing economic evaluation of capital and operating costs of the Berry Branch pilot system to date; and estimating capital and operating costs to scale the SMI system to be able to treat larger throughput volumes.

Keywords: Selenium treatment, sulfur modified iron, SMI, hobet, ERP receivership

Background

The former Hobet Surface Mine in Boone and Lincoln Counties was one of the largest mountaintop removal coal mining operations in West Virginia, operating from approximately 1974 to 2015. Hobet has a history of elevated and non-complaint Se discharges, particularly on the western/Mud River watershed side of the mining operation. As a result of the Patriot Coal Company bankruptcy in 2015, the Hobet site and other legacy reclamation sites were passed to Virginia Conservation Legacy Fund, which attempted to reclaim and remediate the sites through its subsidiary ERP Environmental Fund, Inc. (ERP). ERP, however, became insolvent and ceased operations in late 2019. ERP was placed

into receivership in March 2020. The Receivership Estate is presently charged with raising funds and attempting to reclaim abandoned mine sites, obtaining permit and bond releases, improving environmental compliance, and treating water discharges – all as possible and practicable.

Prior Se Treatment Efforts at Hobet

Former owners and operators of the Hobet property attempted over the years to treat and remediate Se discharges using various methods that included water management (pumping and dilution), zero valent iron (ZVI) technology, biochemical reactors (BCRs), underground injection, and so forth – but with mixed and inconsistent results. These treatment systems were subsequently abandoned, fell into disrepair, became inoperable, and are now economically impracticable to refurbish and operate. The Receivership Estate has thus sought out new Se treatment technology for evaluation and potential long-term application at the Hobet property.

Berry Branch Se Pilot Treatment System

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. Two SMI adsorption vessels (96" × 51" × 56") are operated in an upflow configuration, with high velocity "fluffing" of the SMI media scheduled to occur daily. Eight multimedia filtration tanks (40" × 40" × 77") are installed on the influent side of the pilot system. This consists of two sets of four multimedia filters, utilizing macrolite and activated carbon media, respectively. These multimedia filters are scheduled to be backwashed bi-weekly. Because alkaline mine water is being treated, pH adjustment must be made using sulfuric acid to lower influent pH to optimum levels prior to passing through the 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 aeration. The pilot system currently has the capability to be operated between roughly 50 to 150 gpm (189–568 L/min), dependent upon Se reduction needs. Although the pilot system can be gravity fed from the multiple available Se water sources, a variable frequency drive (VFD) pressure pump is utilized on the inlet side of the pilot treatment system to better control and regulate system throughput. The pilot system is PLC controlled with remote monitoring capabilities and was assembled on-site inside two "high cube" shipping containers (≈ 40' × 8' × 9') utilizing local labor. Although the pilot treatment system should ideally be operated on 3-phase electrical power, only single-phase 220-V power was available at the remote Lincoln County, Berry Branch location. As a result, electrical inverters and specially ordered single-phase pumps were required and installed, which increased capital costs.

Subsequent to initial deployment, the pilot system was retrofitted with ventilating fans, dehumidifiers, heaters, climate sensors, security and observations cameras, and a back-up electric generator.

Case Study Objectives

The pilot system became operational in early August 2023 and is planned to be operated for approximately 12 to 18 months thereafter. Primary pilot system/case study objectives are to:

1. Determine optimum empty bed SMI contact times for various influent Se concentrations;
2. Evaluate SMI media life;
3. Determine pre- and post-treatment requirements (if any);
4. Estimate operating costs; and
5. Estimate capital cost(s) to upscale system to accommodate higher throughput capacity.

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. Nearby and available sources include a deep mine discharge (≈ 24–31 µg/L Se), a valley fill discharge (≈ 9–13 µg/L Se), and surface mine pond water (≈ 40–64 µg/L Se). Preliminary case study results are being collected and will be presented to the West Virginia Mine Drainage Task Force

Symposium & 15th International Mine Water Association Congress in April 2024 covering the initial 8-month study period, running between approximately August 2023 and March 2024. Final case study data will be assembled and made available in 2025.

Pilot System Performance and Operation to Date

Over the first 4½ months of system operation, influent source water has been from a deep mine discharge with Se concentrations varying between roughly 22 and 32 µg/L, averaging 25.6 µg/L. SMI empty bed contact times have been varied on an experimental basis with system throughput rates varying from approximately 60 to 133 gpm (227–503 L/min).

Overall, immediate discharge from the pilot system has averaged 12.9 µg/L Se, with observations as low as 0.64 µg/L. Post-settling Se concentrations at the NPDES outlet have averaged approximately 1.0 µg/L. This is well below the applicable numeric State water quality standard for Se of 5 µg/L. Dependent upon pilot system flow rates and the state of SMI media depletion, percent reduction in Se concentration at the immediate discharge from the pilot system has averaged 49.7% to as high as 97.3%.

Over the study period to date, post-settling percent reduction in Se concentration at the NPDES outlet has averaged 96.2% to as high as 99.1%. One-hundred percent of the post-settling Se observations at the NPDES outlet have been in compliance with (i.e. below) the applicable monthly average NPDES Se discharge limit of 4.7 µg/L. Optimum performance of the pilot system to date was achieved at approximately 64 gpm (242 L/min), with between 89% and 97.3% Se reduction observed.

Concerning other discharge parameters, and dependent upon system throughput rate, the pilot system:

- Increased Fe concentrations in the immediate discharge from the pilot system 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 (NH_3-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 Se pilot system tests to date, all discharge parameters at the Berry Branch NPDES outlet (including Fe and TSS) have met applicable NPDES effluent limits.

Preliminary Conclusions

- Based on pilot system results to date, SMI's potential to effectively treat for non-compliant concentrations of Se appears feasible and promising;
- SMI treatment costs to date are not yet fully developed, however;
- 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 is being released from the SMI treatment system;
- As this Fe discharge from the pilot system is oxidized and precipitated in post-treatment settling basins, additional and observable reductions in Se concentrations continue to occur;
- SMI's ability to reduce Se concentration in the initially studied deep mine discharge water began to deplete quickly after approximately three months;
- Preliminary study evaluation indicates that elevated oxygen reduction potential (ORP) levels in the initial deep mine discharge water accelerated the depletion of SMI media, although more study and data are needed;
    - o ORP of the influent deep mine discharge water was elevated and ranged between 254 and 420 mV, averaging approximately 358 mV;
    - o Future 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;

- The life of SMI media will need to be extended in order to make the SMI treatment technology cost effective and practicable;
  - This may be accomplished by:
- Pre-treatment to lower influent ORP values, and
- Better optimization and control of influent pH prior to entering the SMI vessels to attempt to reduce excessive oxidation of the SMI media;
- The cost of SMI media will need to be reduced in order to make the SMI treatment technology cost effective and practicable; and
  - 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.

Future Study

The Berry Branch SMI pilot system is planned to be operated for an additional 12 to 18 months using different source waters that exhibit both higher and lower Se concentrations. This may include blending of Se source waters. Additionally:

- New / replacement SMI media has been ordered for mid-January 2024 delivery and will be installed at the Berry Branch pilot system in order to study pilot system and 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;
- Additional 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; and
- Economic evaluation will be conducted to determine capital and operating costs of the Berry Branch pilot system to date and estimating capital and operating costs to scale up the Berry Branch system to be able to treat larger throughput volumes.

Acknowledgements

The author thanks and acknowledges the valuable assistance and support of: Peter Santina, founder and owner of SMI-PS, Inc.; John Titus, PE and General Manger, Water & Wastewater Equipment Co. and Robert Loken, VP Sales – Service and Products, Environ Technologies.