THE REMOVAL OF SELENIUM FROM WATER USING *ZERO VALENT IRON SYSTEMS* ZVI MEDIUM

Steven A. Bouse, June 2013

ABSTRACT

The discharge of selenium to natural water systems is regulated by law. Those with permitted outfalls must treat the waste stream to below the US EPA regulatory limit for selenium of 4.8 ug/L. Dissolved selenium exists primarily as selenate (+6) and selenite (+4) ions. While there are several technologies that can remove selenium from water, the use of zero valent iron (ZVI) has proven to be a low-cost, effective technology for large scale water treatment systems in Appalachia. It is estimated that equipment and operating costs are less than $2.00 per thousand gallons treated*.

INTRODUCTION

Elevated levels of selenium in mining surface waters are a result of precipitation and groundwater percolating through disturbed strata. If selenium contaminated water reaches natural waterways, it can bioaccumulate in aquatic wildlife, causing birth defects and death to certain species[1]. For humans, when selenium contaminates drinking water above the US EPA established Maximum Contaminant Level (MCL) of 50 ug/L, long term health effects may include fingernail loss, numbness in fingers or toes, or problems with circulation[2].

Methods such as reverse osmosis, ion exchange and biological systems have been used to mitigate aqueous selenium at a cost of anywhere from $2.40 to $30.00 per thousand gallons treated[3]. Constraints such as water quality, flow rate, selenium concentration, the availability of large swaths of land and installed cost influence which selenium removal technologies best fit each situation. No one type of system has been identified that will work in all cases[3]. In 2011, an Appalachian coal mining company installed multiple high-flow selenium treatment systems based on cost-effective ZVI technology and achieved consistent compliance below the 4.8 ug/L US EPA selenium regulatory limit for an extended time period. This mining company tested several different selenium removal technologies including reverse osmosis and active biological reactor systems. The mining company chose this particular ZVI technology due to its pilot-proven efficacy and low cost. After demonstrating compliance over an extended period of time, the company received court permission to utilize this particular type of ZVI to treat selenium laden water at several outfalls.

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The company turned to Zero Valent Iron Solutions (ZVIS) to help solve the selenium capture problem. ZVIS supplied reactors containing high surface area ZVI to harness the reactivity of elemental iron to reduce the aqueous species of selenium (selenate and selenite) to sparingly soluble elemental selenium, which remains bound in the matrix of the reactor. The ferric hydroxide formed in the ZVI matrix also adsorbs selenite[4], which enhances removal efficiency. ZVI has been shown to have similar reductive and/or adsorptive properties for removing arsenic[5,6], aluminum[11], antimony[7], copper[8,11], cadmium[6,11], hexavalent chromium (chromate)[9,12], mercury[10,11,12], nickel[11], molybdenum[11], lead[6,11,12], uranium[12], zinc[11] and other dissolved pollutants from water.

Achieving consistent, long term removal of dissolved pollutants using ZVI technology has historically been a challange. In all previous cases, using ZVI technology resulted in rapid surface passivation by iron oxyhydroxides and loss of water contact with the solid medium caused preferential water flow (channeling). In this case study, ZVIS' systems incorporate finely divided, high surface area, porous, uniformly dense ZVI medium. The ZVI medium maintained good contact with the incoming water and removed selenium over a seven month time period from September 2011 to April 2012.

SYSTEM DESCRIPTION

In conjunction with the mining company, ZVIS supplied a ten reactor, parallel flow system (see Figure 1), designed for a water flow of 200 gallons/minute (GPM). Water from a collection pond was pumped through a filter followed by pH adjustment, which improved the selenium reduction kinetics. Water (about 20 GPM per reactor) was introduced at the top of the reactor and flowed down through the ZVI medium. The treated water was collected by a common effluent piping system. The water level in each reactor was controlled by a standpipe such that the ZVI medium in each reactor was constantly submerged. Due to the presence of ferrous iron generated by bed oxidation, effluent water was aerated in conjunction with a pH increase to roughly 8.0 using sodium hydroxide. The resulting ferric oxyhydroxides were removed in a downstream clarifier. Water from the clarification process was discharged into a second pond, where it flowed directly to the NPDES outfall.

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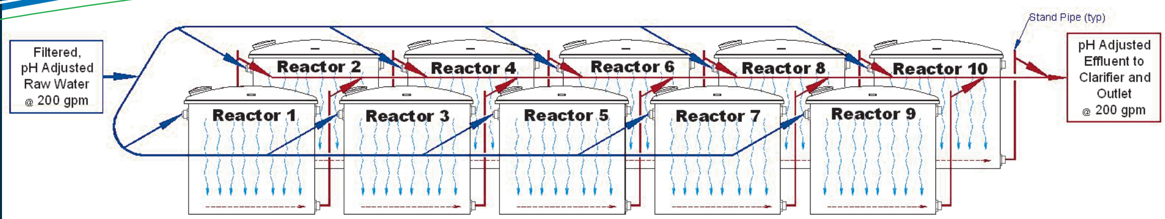

Figure 1 - Ten Reactor Flow Pattern

SYSTEM OPERATION AND PERFORMANCE

After demonstrating the technology could achieve selenium removal compliance over an extended period, the mining company received federal court permission to expand this technology to other seeps and the system was placed into service in September 2011. Influent water pH averaged 7.55 over the seven month period. TDS ranged from 1,500 to 2,150 mg/L[3] and sulfate concentration from 770 to 1,020 mg/L[3].

Water was pumped from a seep collection pond into an automated backwash sand filtration system to remove large suspended solids. The influent water pH was lowered from an average of 7.6 s.u. to 6.0 – 6.5 s.u.[3] using an automated carbon dioxide infusion system. Water was distributed to the reactors via manifold and flowed through each reactor in a down-flow pattern. Dissolved oxygen in the influent water averaged 8.2 mg/L, with average effluent DO at or near zero mg/L. Typical effluent pH was about 7.3 s.u.

Over the demonstration period, water from this seep had an average selenium concentration of 9.2 ug/L and a maximum of 17.6 ug/L. After treatment, effluent selenium concentration averaged 1.8 ug/L over the same time period (see Figure 2).

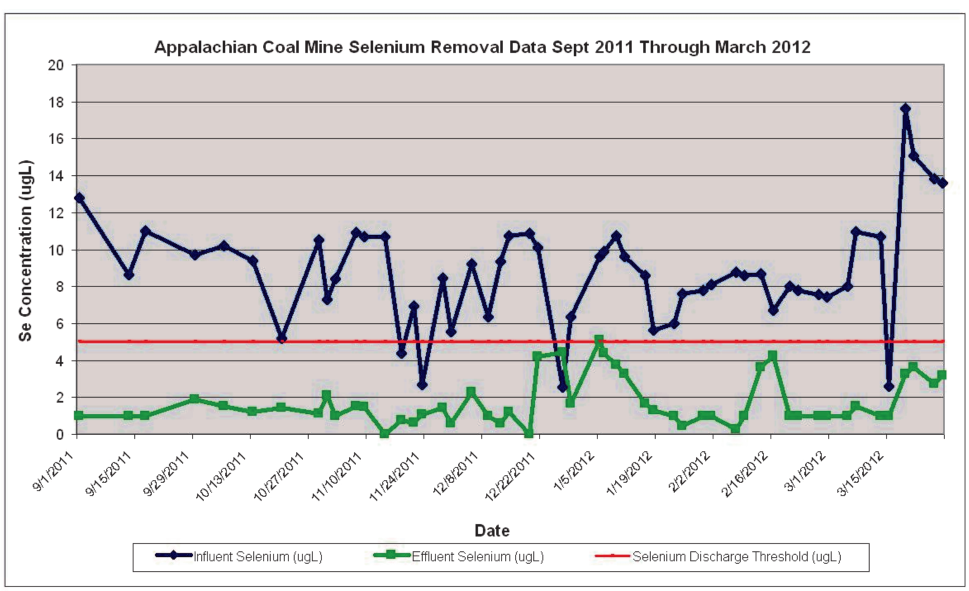

Figure 2

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The highest effluent selenium concentration 5.1 ug/l was the only sampling that exceeded the 4.8 ug/L US EPA regulatory limit for selenium discharge. Effluent selenium concentration was at or below 1 ug/L for approximately 35 percent of the samples taken[3].

With an average flow rate of 161.0 GPM during the demonstration period, each reactor's individual flow rate averaged 16.1 GPM, thus each reactor treated nearly 5,400 bed depths with no ZVI media replacement. It should be noted that spent ZVI medium for selenium removal passed the US EPAs Toxicity Characteristic Leaching Procedure (TCLP), and can safely be disposed of as nonhazardous waste.

SELENIUM REMOVAL SUCCESS MECHANICS

The key components for this successful ZVI application were understanding the conditions that promote optimal selenium removal:

- Lowering TSS
- Adjusting the water's pH
- Water distribution through the medium

Utilizing a form of ZVI that resists surface passivation, ZVIS' systems have the characteristics of being porous, uniformly dense, with high surface area, maintaining viable reaction sites over an extended period of time. The uniform density of ZVI medium promotes the efficient use of available iron thus minimizing the potential for and occurrence of preferential water flow that have historically been the downfall of using ZVI for long term water treatment.

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SUMMARY

At the low end of the cost spectrum per gallon treated, ZVIS' water pollution control medium treated nearly 50 million gallons of selenium laden water. It continuously reduced the average selenium concentration to below the US EPA's natural water regulatory limit of 4.8 ug/L throughout the seven month demonstration period. Additionally, based on pilot program success, the Appalachian coal mining company was able to expand this water treatment process to other outlets[3].

ZVI water treatment systems from ZVIS (www.zerovalent.com) were successfully piloted for the removal of uranium and highly concentrated selenium in a North American refinery over a four month period in 2012. The success of the four month pilot resulted in the procurement of a full scale ZVI water treatment system that is scheduled to start up in the Summer of 2013.

It should be noted that ZVI based water treatment systems from ZVIS have been used to remove dissolved silver from photographic solution for over 25 years. In 2012 ZVIS systems were successfully piloted for the removal of aluminum from water over a six month period in West Virginia.

In conclusion, the general use of ZVI for above-ground water treatment for selenium removal historically has had good, albeit short term success. The lack of long term success has been due to rapid iron surface passivation and the subsequent propensity for preferential water flow. ZVIS' long term success at consistently removing selenium from coal mine seep water to below the 4.8 ug/L US EPA regulatory limit and at a relatively high water flow rate came about by striking the right balance between ZVI surface area, surface characteristics and uniformity of the ZVI medium. The successful use of ZVI in this selenium removal case study combined with the knowledge gained in other installations indicate that ZVI may have a wider range of low-cost, above-ground water treatment applications beyond selenium than are currently being commercially employed.

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FOOTNOTE

* Based on a 200 GPM system with 10 year amortization.

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