

NAMC White Paper Report Addendum

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Executive Summary

This addendum was prepared for the North American Metals Council Selenium Working Group (NAMC-SWG) as an update to an earlier report, *Review of Available Technologies for the Removal of Selenium from Water*, prepared by CH2M HILL in June 2010. This addendum

presents information collected related to the advancement of selenium (Se) removal since the issuance of the 2010 report in recognition that considerable treatment work has been done by industry, equipment suppliers, and engineering firms.

This addendum reviews studies, design, and construction of treatment systems for selenium reduction. The information included in this report has been prepared by NAMC-SWG members or through CH2M HILL contacts and research, including updates and advances to selenium treatment pilot plant studies and full-scale designs. This document also covers treatment of other parameters required as a result of the selenium treatment.

Challenges

Achieving selenium levels less than 5 micrograms per liter ($\mu\text{g/L}$) in surface water discharges from the various industry processes poses many challenges given that selenium:

- Removal is limited by the minimum and maximum feasible ranges of design flows that can vary greatly over time;
- Exists in a variety of chemical forms;
- Is relatively dilute in concentration;
- Removal from water is confounded by the water matrix (e.g., temperature, pH, and other constituent concentrations);
- Treatment generally results in a concentrated by-product or residual;
- Performance for chemical and biochemical reduction processes will be a function of the starting selenium concentration and the efficiency of the secondary and/or tertiary liquid solids separation process; and,
- Re-release from the residuals can occur.

Significant variation in selenium levels, water flows, and forms exists among the different industry types, within each industry type, and even sometimes within the same facility over time. As an example, at some locations the flow of water requiring treatment changes dramatically due to seasonal factors. This increases the complexity of how to determine applicable selenium removal technologies to a wide variety of industries. Because of the various complexities associated with industry-specific waters, no treatment technology is a “one-size fits all” solution.

For core selenium treatment technologies that either chemically or biochemically reduce selenium, as the selenium concentrations increase, the amount of reduced selenium particles increase proportionally, thereby requiring greater efficiencies in the secondary and/or tertiary liquid-solids separation technology. Conventional liquids-solids separation (e.g., gravity clarifiers, lamella clarifiers, ballasted clarifiers, and/or media filters) is needed to meet a 5 $\mu\text{g/L}$ total selenium limit with influent selenium concentrations of less than 50 $\mu\text{g/L}$; however, the treatment method for influent selenium concentrations greater than 50 $\mu\text{g/L}$ should be carefully evaluated. Based on CH2M HILL’s experience, at some point above an influent selenium concentration of 50 $\mu\text{g/L}$, a higher level of treatment using membranes (e.g., ultra filters) will likely be required to meet discharge requirements at 5 $\mu\text{g/L}$, thereby adding considerable cost to treatment.

Tertiary treatment will generally be required to meet both the selenium and other conventional surface water discharge guidelines or criteria (e.g., dissolved oxygen [DO], total suspended solids [TSS], biochemical oxygen demand [BOD], phosphorus, nitrogen, temperature, pH, etc.). In surface waters containing trout or other sensitive aquatic life, the discharge criteria can be very low for some of these parameters, and there may be instream requirements for temperature and DO that will not affect the seasonal reproduction. Iron, aluminum or organic based coagulants, required for enhanced liquid solids separation, can also require tertiary treatment depending upon the discharge limitations for certain water quality parameters. Iron and aluminum based adsorption media will have similar issues. Ion exchange and reverse osmosis technologies which remove bulk ions will require tertiary treatment for reconstitution of the discharge so as not to create ion imbalances that could create aquatic life issues. In some cases, treatment requirements for these parameters can be more challenging and costly than the removal of selenium.

Residuals or by-product treatment will be required for most systems. The residuals will contain concentrated levels of selenium that, if disposed of as a solid or liquid waste, will need to comply with other disposal regulations (e.g., U.S. Environmental Protection Agency [EPA] Resource Conservation and Recovery Act [RCRA] Hazardous Waste). By-products may require further treatment to ultimately reduce the selenium to a less hazardous form.

While these physical, chemical, and biological treatment technologies have the potential to remove selenium, very few technologies have successfully and/or consistently removed selenium in water to less than 5 µg/L at any scale. Still fewer technologies have been demonstrated at full-scale to remove selenium to less than 5 µg/L, or have been in full-scale operation for sufficient time to determine the long-term feasibility of the selenium removal technology. A 2,800 gpm full scale biological based selenium treatment system commissioned in February 2013, treating water from a surface mining operation, has been operating in compliance for over a month with a 4.7 µg/L monthly average discharge selenium limit. No single technology has been demonstrated at full-scale to cost-effectively remove selenium to less than 5 µg/L for waters associated with all industry sectors. Therefore, performance of the technology must be demonstrated on a case-specific basis.

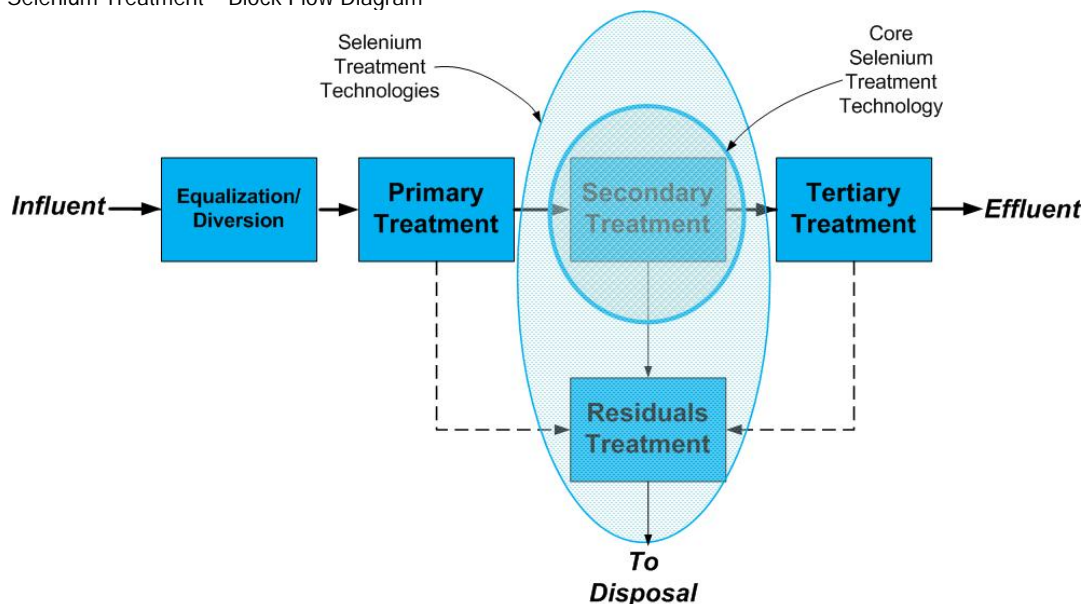
Given these challenges, there is a tendency by some to point to even higher cost technologies such as reverse osmosis (RO). While RO can provide ultrapure water discharge by removing selenium to low levels, it creates even more challenges in treatment with even greater costs because of the pretreatment, tertiary treatment, and brine recovery requirements. A great deal of work needs to be done to better define discharge reconstitution requirements from RO processes, as well as brine disposal to mitigate release of selenium in the environment. With the RO brine, selenium exists in the native form such as soluble selenite, selenate, selenocyanate, etc., instead of in the insoluble elemental selenium.

Systems Approach Required

A variety of physical, chemical and biological treatment technologies have been shown to remove selenium from water. Applying these treatment technologies must consider the aforementioned challenges. This typically means that the treatment technology must be configured as a “system” that includes primary, tertiary, and residual treatment processes in addition to the core selenium reduction treatment technology process. Because the

performance of each technology is flow based, the system may require flow equalization infrastructure, as shown on Figure ES-1. The end result is a treatment plant that can have significant total installed, as well as operation and maintenance (O&M) costs.

FIGURE ES-1
Selenium Treatment – Block Flow Diagram



Water treatment for the removal of selenium will likely be a component of a successful selenium management strategy to achieve selenium discharge requirements. Potential for selenium treatability should be considered in conjunction with water reuse, management, prevention and source control measures. This document focuses on advancements in treatment for the following technologies:

- Physical Treatment
 - Reverse Osmosis (RO)
- Chemical Treatment
 - Ion Exchange (IX)-chemical exchange
 - Zero Valent Iron (ZVI)-chemical oxidation/reduction
 - Adsorption
 - Co-precipitation
- Biological Treatment
 - Active Biological
 - Passive Biological

Overview of Key Findings

A pilot study using low-pressure RO was completed for a phosphate mine complex. The two-month pilot study resulted in consistent permeate (effluent) selenium concentrations below 1.0 µg/L. Concentrate (RO reject) from the system will be treated chemically or biologically for reduction of selenate. Influent pretreatment included filtration and anti-scalant addition.

Ion exchange has been tested in treatment of coal mine runoff water at bench, pilot, and full-scale levels. Effluent concentrations were in the range of 1.0 to 5.0 µg/L with an influent concentration of 7 to 14 µg/L. The influent must be pretreated. Regeneration of the ion exchange media is required and the regenerant solution must be treated for selenium before disposal, since selenium still exists in native concentrated forms such as soluble selenite, selenate, selenocyanate, etc., instead of insoluble elemental selenium. In addition, competing ions will be removed from solution and reduce the capacity of the resin to remove selenium.

ZVI has been tested at the bench, pilot and full-scale level for treatment of coal mine runoff and bench and pilot scale level for Flue Gas Desulfurization (FGD) blowdown. Passivation of the ZVI occurred in previous work, increasing the ZVI dose required; however, this was not observed in the case studies presented. A steel wool-based ZVI system at a coal mine reduced selenium concentrations from about 19 µg/L to less than 4.7 µg/L. A powdered hybrid ZVI pilot system reduced selenium concentrations in FGD blowdown from 2 milligrams per liter (mg/L) to below 10 µg/L. The hybrid ZVI system uses an unnamed reagent to avoid passivation of the ZVI. The ZVI process produces significant quantities of iron, which must be disposed of.

There has been some work with fixed bed adsorption, but limited information has been published. An enhanced activated alumina (EAA) product, Sorbster™, has been tested on coal mining and refinery wastewater. In one of the tests, a significant quantity of adsorbent was required to reduce selenium concentration below 5-10 µg/L. In addition, an activated carbon based media, SeRT™, has been developed for removal of selenocyanate from refinery stripped sour water. A proprietary adsorbent has been tested on uranium mining wastewater, and a demonstration unit has been installed meeting a target effluent selenium concentration of 0.1 mg/L. These systems will produce waste adsorbent, which must be disposed of.

Co-precipitation is used to adsorb selenite onto ferric hydroxide, and is frequently used in conjunction with other technologies that reduce selenate to selenite. Research has been conducted on FGD scrubbers, where an iron solution is injected into the scrubber and selenite adsorbs onto ferric hydroxide before it is oxidized to selenate. Full-scale tests that demonstrated the addition of iron prevents the formation of selenate have been conducted. However, longer duration tests are needed to completely replace the contents of the scrubber and determine the final treated effluent concentrations.

Much of the work since 2010 has centered on active and passive biological treatment. Active biological treatment has been implemented at the full-scale level for treatment of FGD blowdown, tested at the pilot-level for mining runoff water and refinery effluent, and recently implemented full-scale for mining runoff water. Passive systems have been tested at the pilot scale and implemented full scale. Since both active and passive biological treatment are conducted under reducing conditions and require supplemental organic carbon, post-treatment is typically required to remove residual biochemical oxygen demand (BOD) and raise the DO level.

Active biological treatment work has been conducted on the ABMet® reactor and a Fluidized Bed Reactor (FBR). The ABMet® reactor is a down flow, attached growth, granular activated carbon (GAC) filter. As presented in Figure ES-1, selenium removal technologies will likely require some form of flow equalization and primary treatment.

Suspended solids removal requirements vary by selenium treatment technology with most requiring some treatment. The influent must be pretreated for solids removal if it is high to avoid plugging the beds, and the beds must be periodically backwashed to remove entrained gas. For a mine water ABMet® pilot treatability study, with influent nitrates and selenium ranges of 5 to 100 mg/L and 20 to 300 micrograms per liter ($\mu\text{g/L}$), respectively, the effluent filtered selenium concentration ranged from 3 to 10 $\mu\text{g/L}$. In a full-scale system treating FGD blowdown, effluent concentrations of 0.7 to 2.0 $\mu\text{g/L}$ were achieved. However, influent concentrations were not provided. Achievable effluent concentrations depend on influent selenium loadings among other design and operating parameters. There are several other full-scale ABMet® systems in operation treating FGD blowdown, some of which were covered in the 2010 report. Additional data on these systems was not available for this document.

In the FBR system, wastewater is passed through granular solid media at high enough velocities to suspend the media and cause it to behave as though it were a fluid. While it can be sensitive to suspended solids levels in the influent, it is less sensitive than a down flow filter. A liquid/solid separation process is required downstream to remove sloughed off biomass, including particulate Se. For influent nitrates and selenium concentrations ranges of 5 to 100 mg/L and 20 to 300 $\mu\text{g/L}$, respectively, effluent filtered selenium concentrations ranged from 4 to 10 $\mu\text{g/L}$ in the pilot studies treating mining water. In a test on refinery wastewater at influent selenium concentrations of 70 to 130 $\mu\text{g/L}$, the FBR was able to maintain effluent filtered selenium concentrations of ≤ 10 $\mu\text{g/L}$. At higher influent selenium concentrations (150 to 230 $\mu\text{g/L}$), effluent filtered selenium concentrations were ≤ 20 $\mu\text{g/L}$. In a second FBR refinery pilot test, the system was able to reduce selenium concentrations from 29 to 85 $\mu\text{g/L}$ to below 6.6 $\mu\text{g/L}$ (filtered).

Much work has been completed on passive biological treatment, using biochemical reactors (BCR). Substrates comprised of wood chips, saw dust, mushroom compost, horse manure, field hay, yard wastes, and limestone granules have been utilized in varying proportions. Pilot and full-scale testing has been performed on mine water runoff. Inlet concentrations averaging 10 $\mu\text{g/L}$ selenium were reduced below detection levels in pilot and full-scale systems. Inlet concentrations averaging approximately 20 $\mu\text{g/L}$ were reduced to 2 to 3 $\mu\text{g/L}$. Larger earthen-basin demonstrations and full-scale systems exhibited a wider range of removal efficiencies of 63 to 95 percent, possibly reflecting a greater influence of hydraulics or ambient conditions. Higher concentration ranges were treated using passive biochemical reactors in Alberta, with an influent concentration of 180 $\mu\text{g/L}$, and effluent concentrations ranged from 3 to 33 $\mu\text{g/L}$, for an average removal of 90 percent. This system has been operating for 4 years. Most of the passive systems treated flows of about 200 gallons per minute (gpm), with one system treating a flow of 1500 gpm.

Costs

Total installed costs and O&M costs are presented in this document for IX, ZVI, and active and passive biological treatment. Costs presented in this document are a Class 5 cost with an estimated accuracy of +100 percent and -50 percent, and generally were either based on the literature referenced, or were developed as part of completion of this document. Careful consideration of the costs and the basis of the estimates should be given in using any cost information. Many references will present costs for treatment systems without providing clear definitions of the basis for the cost estimate. Most documents will present only the

capital costs or direct costs for equipment that is typically provided by the equipment supplier. The direct equipment costs are only a fraction of the total installed cost for a water treatment system.

Introduction

This technical addendum was prepared for the North American Metals Council Selenium Working Group (NAMC-SWG) as an update to an earlier report, *Review of Available Technologies for the Removal of Selenium from Water*, prepared by CH2M HILL in June 2010. This addendum presents information collected related to the advancement of selenium (Se) removal since the issuance of the 2010 report in recognition that considerable treatment work has been done by industry, equipment suppliers, and engineering firms as well as lessons learned.

This addendum reviews studies, design, and construction of treatment systems for selenium reduction. CH2M HILL and NAMC collected the following types of information related to treatment of selenium removal:

1. Pilot plant studies showing performance for selenium removal as well as any other “secondary” parameters that require treatment based on water quality regulations (e.g., total suspended solids [TSS], BOD, nutrients [e.g., total phosphorus and total nitrogen], total dissolved solids [TDS], pH, and DO). Other information that was collected if available includes operating and installed capital costs for a full scale system, O&M issues, ability to handle varying loads, flows and/or temperature.
2. Design, construction, and performance reports for demonstration or full-scale selenium treatment operation. This included facilities that have been constructed or are in the process of being constructed. This information included cost information and/or performance data for operating systems.

The information included in this addendum has been prepared by NAMC-SWG members and through CH2M HILL contacts and research, including updates and advances to selenium treatment pilot plant studies and full-scale designs. This addendum also covers treatment of other parameters required as a result of the selenium treatment.

Treatment technology advancements are presented for the following core treatment technologies:

- Physical Treatment (RO)
- Chemical Treatment (IX, ZVI, fixed bed adsorption, and co-precipitation)
- Biological Treatment (active [such as ABMet® and fluidized bed reactor] and passive biological [such as biochemical reactor])

Each technology is covered in the Core Treatment Technology Overview section, providing a high level summary of advancements in the technology, and then more details on the projects are covered in the Technology Advancements section. In general, the following topics are covered:

- Overview of the technology and the mechanism for selenium removal including operating conditions such as pH or temperature. Key advancements and updates to design principles and components of the technology since 2010.
- Treatment Effectiveness, including forms of selenium removed, interfering compounds, and performance information (influent and effluent concentrations).
- Design and Operational Considerations, which provides a summary of the technology's operating flows, land requirements, pretreatment requirements, other constituents that may affect treatment, post-treatment requirements and O&M requirements, and where information is available.
- Status of the technology (bench tested, pilot tested, full-scale installation).
- Residuals Management, which summarizes discharge concerns and options for treatment of residuals.
- Capital and Operating Costs.

Core Treatment Technology Overview

This section provides an overview by technology of advancements in selenium treatment since the 2010 report. Details on the projects and advancements are presented in the following section.

Physical Treatment

Reverse Osmosis

With RO, water is forced through a membrane under pressure to create a reject or concentrated stream containing the dissolved constituents in the water. The concentrated stream must be treated for selenium following RO. A pilot study using low-pressure RO was completed for a phosphate mine complex. The two-month pilot study resulted in consistent permeate (effluent) selenium concentrations below 1.0 µg/L. Concentrate from the system will be treated chemically or biologically for reduction of selenate to elemental selenium for ultimate disposal. Influent pretreatment included filtration and anti-scalant addition. The flux was relatively constant throughout the study with an average of 14.7 gallons per square foot per day.

Chemical Treatment

Ion Exchange

Chemical exchange or IX removes ionic-forms of selenium by exchanging selenate for like charged ions on a resin backbone structure. IX resins are typically contacted with the wastewater in fixed beds and operated until the resin is saturated. Key developments since 2010 includes bench and pilot-scale tests, as well as full-scale operation, at a surface coal mine in West Virginia. This technology may also be applied to other industry wastewaters for selenium removal and the performance will depend on the complexity (interfering compounds) of the wastewaters. Pilot testing of IX of surface runoff water reduced influent dissolved selenium (soluble selenate form) from an average of 7.3 micrograms per liter (µg/L) and maximum of 12 µg/L to less than 1 µg/L, continuously for a 4-week period. The

pilot testing showed that IX can be effective for selenium, in the selenate form, with dissolved sulfate concentrations up to 250 mg/L. The treatment stream did not have selenite present; therefore, the technology cannot be assessed for selenite removal. A small full-scale system, with influent selenium of 7 to 14 µg/L and sulfate as high as 690 mg/L, met stream discharge permit limits (4.7 µg/L monthly average) for a system treating about 50 gpm for only for an initial short period, less a 1 month, due to issues with the configuration (parallel instead of series operation).

Pretreatment requirements for IX can include removal of TSS or any scale forming or precipitating materials, such as high calcium and sulfate or iron or manganese, to avoid fouling or plugging of the IX resin media. Additionally, IX can cause notable pH shifts potentially requiring pH control as post-treatment. Sulfate, bicarbonate, and nitrate may also be removed, and exert a demand on the IX resin, depending on the resin utilized. IX systems are easily automated and can be run with little operator attention. Since sulfate, and some bicarbonate and nitrate, are exchanged for chloride, chloride in the effluent will increase in proportion to the other anions removed. The regeneration process will produce a spent regenerant (brine) that will require disposal or subsequent treatment. The IX media is regenerated in situ and would be expected to last as long as 3 to 5 years, depending on site water quality and pretreatment for parameters that over time can foul the resin (e.g., concentration of organics, biological and charged clay suspended solids).

Pilot and full-scale systems run to date have demonstrated that IX is a viable technology for the wastewater tested.

Zero Valent Iron

The chemical oxidation reduction mechanisms with ZVI or elemental iron in steel wool treat the oxidized forms of selenium: selenate or selenite. ZVI media can be in powder, granular or fibrous forms. ZVI acts as a reducing agent in the redox reaction. The iron acts as both a catalyst and electron donor for the reaction. It also provides a source of ferrous and ferric iron that can provide further reduction and adsorption of selenium. ZVI oxidation can result in the formation of a complex ferrous ferrihydroxide co-precipitate known as green rust. Green rust formation is generally a function of pH and equilibrium concentrations of ferrous and ferric iron. It is the form of ZVI required to abiotically reduce selenate to selenite, and selenite to elemental selenium.

When water containing selenate and selenite comes into contact with ZVI, the ferrous and ferric iron products of ZVI will either directly reduce selenate to selenite and then to elemental selenium, or reduce selenate to selenite and adsorb the selenite to the ferrihydrite solids formed during the redox reaction with ZVI.

ZVI will first react with any oxygen present in the water, and can also react with other oxygenated compounds such as nitrate, perchlorate, carbonate, sulfate, and phosphates. Therefore, other oxygenated compounds in the water will also consume ZVI.

Passivation of ZVI or a condition where the ZVI forms an oxide coating on the surface such that it has a very limited reduction capacity has been reported in previous work. An oxide coating is believed to form on the iron, inhibiting the reactivity and increasing the mass of ZVI required in a treatment system to meet treatment goals. However, several case studies presented in this addendum did not observe this. The case studies for surface mining

application indicate that effective ZVI steel-wool systems require that the feed water pH be reduced to a range of 6.0 to 6.5 standard units (s.u.) to maintain an active ZVI media surface. The case study for treatment of desulfurization (FGD) blowdown indicated that an unnamed reagent is added to maintain reactivity.

Key advancements since 2010 includes use of steel wool in both pilot-scale and multiple full-scale systems at surface coal mine site in West Virginia and a pilot-scale phosphate mine in Idaho. The use of a powdered ZVI has been tested at bench and pilot-scale system for a power plant FGD blowdown stream. Bench and pilot testing of powdered ZVI on FGD blowdown indicated that effluent selenium concentrations could be reduced from 2 mg/L to below 10 µg/L.

Full-scale operation (up to 160 gpm) on mine runoff water resulted in a reduction of influent selenium (selenate or selenite form) from about 19 to less than 4.7 µg/L monthly average, to 8.0 µg/L daily maximum, continuously for a 4-month period.

Pretreatment requirements for ZVI processes can include removal of TSS and pH adjustment typically within the range of 6.0 to 6.5 s.u. The ZVI process will release significant quantities of soluble iron in solution. Following ZVI treatment, the soluble iron will usually require removal, typically through oxidation and/or pH adjustment, followed by solids removal via sedimentation and/or filtration. Waste iron rust media from the ZVI reactor and precipitated iron sludge from the precipitation process must be dewatered and disposed.

ZVI, as applied to selenium treatment, is a developing technology. However, it has established a significant foothold at one Appalachian surface coal mine, with multiple full-scale installations that have been shown to be a reliable and cost effective technology.

Fixed Bed Adsorption

Chemical adsorption is potentially capable of removing selenium by providing a media with surface conditions that favor adsorption over the aqueous phase. Adsorption systems have a vessel to hold the adsorbents in either a fixed or loose bed such that wastewater can contact the media or adsorbent at an appropriate bed residence time and hydraulic loading rate to remove the parameter of concern. . All adsorbents discussed in this section are typically contacted in fixed beds. Key developments include vendor testing of an enhanced activated alumina (EAA) on 10 different coal mine pond waters. Additionally, CH2M HILL observed the use of granular ferric hydroxide (GFH) for a groundwater treatment application.

Bench-scale testing by a materials supplier of EAA provided data that showed selenium in the selenate and selenite forms can both be treated to less than 5 µg/L as Se. However, results indicate that the treatment would likely be more expensive than other technologies. No large scale operating facilities using EAA for treating selenium are known. The EAA vendor has operated a small (1 gpm) demonstration system using EAA on wastewater at a refinery with an average of 30 µg/L selenite. After 1,118 bed volumes (BVs) were treated, the effluent average was 9 µg/L; however, at the end of the test, the effluent was less than 5 µg/L and trending downward. In contrast, in another refinery wastewater example with influent selenite of 109 µg/L, the EAA achieved about a 90 percent reduction, but never

below 5 µg/L, in 14.5 BVs. Thus, the ability for EAA to cost effectively treat selenite is uncertain and as with other technologies is dependent on water quality.

Limited information is available about GFH used to remove selenium. Vendor literature does not specify which form of selenium the material removes. Limited CH2M HILL field experience with this media suggests that the service life may be limited.

Philips 66 has developed a selenium removal media/system, called SeRT™, targeted for refinery sour water stripper systems that have selenium primarily in the selenocyanate form. A full-scale system has been operating since 2008, with an additional full-scale system planned for 2014. Pretreatment needs are similar to an IX system. Adjusting pH, pretreatment and post treatment, may be necessary to optimize the adsorbent service life. Other materials may also be removed, exerting an additional demand on the adsorbent. The process will produce a waste adsorbent material that will require disposal or subsequent treatment. Likely, this material will be considered hazardous for disposal because of the classification of biologically untreated stripped sour water.

Bench, pilot and full-scale demonstration testing has been conducted on a proprietary adsorbent. Pilot testing reduced influent Se concentrations from 0.07 to 0.86 mg/L to effluent concentrations of 1 to 11 µg/L. Both selenate and selenite were removed. In the demonstration scale system, the average influent total selenium concentration of 0.5 mg/L was reduced to the target of 0.1 mg/L of total selenium. Cost information was not provided.

Co-precipitation

Co-precipitation is a process under which a parameter of concern can be removed or precipitated through chemical adsorption via ionic attraction and occlusion in the solid matrix ultimately removing the target contaminant. Selenite can be removed by ferric iron co-precipitation.

Pretreatment requirements for co-precipitation would typically include pH adjustment to an acidic range, 5.5 to 6.5 s.u., and may include removal of organic materials if bench testing indicated interference with the co-precipitation mechanism. Additionally, moderate concentrations of TSS (e.g., under 100 mg/L) should be acceptable in most applications since the addition of ferric salts will cause additional solid production. After the ferric salt addition, the stream is flocculated and clarified through typical liquid solids separations systems, usually a clarifier followed by media filtration. Direct filtration by a microfilter is also plausible. Soluble selenium in FGD blowdown can be removed by ferric hydroxide (ferrihydrite) co-precipitation before it is oxidized to the selenate form. While ferric co-precipitation may be suitable to achieve significant selenite reductions in FGD applications, data are not available to determine whether selenite selenium concentrations can be reduced to below 5 µg/L, a common threshold for surface water discharge. Liquid solids separation technologies are key to meet low concentration values in the treated effluent. Two full-scale demonstration tests were conducted in 2009 and 2011 using ferric iron to treat FGD liquor. The full-scale tests demonstrated that effluent soluble selenium was reduced 70 to 83 percent. Data from the 2009 and 2011 full-scale tests demonstrate an iron dose of about 250 lb of ferric (as Fe)/ lb of selenite (as Se) was required. The 2009 and 2011 full-scale demonstration tests showed that the technology was effective and did not indicate ancillary

issues associated with the technology that would affect FGD operation and gypsum thickening, dewatering and residuals management.

Ferric iron treatment of FGD forced oxidation scrubber liquor recirculation loop to minimize the formation of selenate is in the developmental stage. The two full-scale demonstrations, in 2009 and 2011, were successful in reducing effluent soluble selenium and the overall success of those trials suggest that the technology can be more widely adapted at full-scale relatively quickly.

One case study was submitted on co-precipitation of Se in raffinate from a uranium mine. The most recent data for part of 2012 indicated that Se concentrations were reduced from an average of 0.213 mg/L to an average of 0.014 mg/L.

Biological Treatment

Active Biological

Selenium removal by biological treatment has been found to be effective. The process uses certain heterotrophic facultative (e.g., capable of operating in aerobic, anoxic and anaerobic conditions) bacteria, which in addition to reducing nitrate to nitrogen gas, also reduce the selenate and selenite in wastewater to elemental Se, which in turn can be removed as insoluble solids along with bacterial solids. Under anoxic/anaerobic conditions, heterotrophic facultative bacteria use nitrates, chlorates, perchlorates, and sulfates as electron acceptors as means of respiration. Selenate and selenite are also reduced to elemental Se under anoxic/anaerobic conditions with the same mechanism. The bacteria's preference of electron acceptor is for DO first, followed by nitrites and nitrates, selenite and selenate, chlorates and perchlorates, and sulfites and sulfates. At present, two active anoxic/anaerobic biological (attached growth) water treatment technologies are proven and viable for consistent Se removal: advanced biological metals removal (General Electric [GE] ABMet®) system and the Envirogen fluidized bed reactor (FBR) system.

The ABMet® water treatment system is a down flow attached growth granular activated carbon (GAC) filter that uses heterotrophic bacteria. These were typically operated as parallel trains with two reactors in series with the first and second generation of the technology. Microbes are seeded into the bioreactor where they attach to the GAC media to create an attached growth ion-reducing environment for selenate and selenite reduction. The reactors are pulsed periodically to reduce gas entrainment in the GAC bed, and require backwashing to prevent excess influent TSS and biomass including reduced elemental Se buildup that can impede the flow through the filter. Backwash water with solids and elemental Se is discharged to a separate holding tank or basin for liquid solids separation, where the separated solids with elemental Se are subsequently thickened and dewatered. The ABMet® system is designed as either single-stage or two-stage depending on the nitrates and Se loadings, and molasses-based organic carbon with nutrients is used as electron donor for bacterial growth. This system generally operates at empty bed contact time (EBCT) range of 2.0 to 6.0 hours depending on the nitrates loading and the oxidation reduction potential (ORP) range of -250 to -350 millivolts (mV). The required minimum operating temperature is 50°F (10°C), although the system may perform at slightly lower temperature of 46°F (8°C). Given the down flow filter relies on surface loading to create the mass transfer through the bioreactor, the hydraulic loading rate (HLR) is an important

design criteria for the ABMet®. Typically, the HLR range for this technology is from 0.3 to 1.0 gallons per minute per square foot (gpm/ft²), depending on the influent quality.

The third generation ABMet® system came to the market in 2011 and has deeper carbon bed and head space to increase hydraulic loading rate, as well as parallel reactors in a single stage. Pretreatment will be required for influent suspended and colloidal solids removal if more frequent backwashing is warranted, such as once a day since the vendor design normally assumes the frequency of once or twice a month. This pretreatment is also required to prevent limitations on hydraulic throughput capacity. Typically, an aeration tank is required as a post-treatment to increase the ABMet® effluent DO from zero (-250 to -350 mV ORP) to greater than 3 to 5 mg/L, depending on the discharge requirements. For the influent nitrate-nitrogen and dissolved selenium concentrations, ranges of 5 to 100 mg/L and 20 to 300 µg/L, the effluent nitrate-nitrogen concentration of less than 0.1 mg/l and filtered selenium concentration range of 3 to 10 µg/L were observed in the pilot studies treating mining water. The effluent total selenium concentration will depend upon the ABMet® effluent TSS. This technology was pilot tested on mining water and power industry wastewater, and there are full-scale installations for the power industry wastewater treatment for Se removal. Currently, one ABMet® based full-scale treatment plant is planned for installation for Se removal from mining water.

In the Envirogen FBR system, wastewater is passed through a granular solid media at high enough velocities to suspend the media through recirculation such that it maintains a plug flow mixing regime with a suspended bed in the column. Fluidization keeps the media with attached biomass in suspension and expanded in depth to provide good contact of contaminated water with biomass for effective treatment. Microbes cultured in the FBR media beds create an ion-reducing environment (anoxic/anaerobic condition) for selenate and selenite reduction. In order to remove sloughed off biomass including particulate Se from the FBR effluent, a liquid/solids separation unit process (e.g., ballasted sand clarifier, membrane filter, or sand filter) is required. The unused electron donor or residual dissolved BOD from the FBR, depending upon the BOD discharge requirements, can also require oxidation. This can be done a variety of ways but most efficiently in an aerobic environment with another attached growth system (e.g., an aerobic moving bed bioreactor [MBBR]), given the low BOD concentrations. The FBR system is designed as either single-stage or two-stage, depending on the nitrate and Se loadings. Typically, engineered readily degradable organic carbon is used as electron donor for bacterial growth given the short hydraulic retention times (HRT) in which the FBRs are operated. This system generally operates at a HRT range of 0.5 to 1.0 hour (based on expanded bed height) depending on the nitrate loading and the ORP range of -150 to -200 mV. The required minimum operating temperature is 50°F (10°C), although the system may perform at a slightly lower temperature of 46°F (8°C).

This system is more forgiving for some level of influent suspended and colloidal solids than down flow or up flow filter based systems due to fluidization. However, pretreatment is required for excess influent solids, depending on the nature of solids in order to reduce the in-bed cleaning frequency. For the influent nitrate-nitrogen and dissolved selenium concentrations ranges of 5 to 100 mg/L and 20 to 300 µg/L, the effluent nitrate-nitrogen concentration of less than 0.1 mg/l and filtered selenium concentration range of 4 to 10 µg/L were observed in the pilot studies treating mining water. The FBR effluent total

insoluble particulate elemental selenium concentration will be high because of the nature of the technology given by design it will slough off biological solids from the media. Therefore, a liquid-solids separation system is necessary to remove the biomass and insoluble elemental Se from the FBR effluent.

Generally, as selenium concentrations increase the amount of reduced selenium particles increase proportionally, thereby requiring greater efficiencies in the liquid-solids separation technology. Conventional liquids-solids separation (e.g., gravity clarifiers, lamella clarifiers, ballasted clarifiers, media filters) needed to meet a 5 µg/L total selenium limit with the selenium concentrations greater than 50 µg/L should be carefully evaluated. Based on CH2M HILL's experience, at some point above an influent selenium concentration of 50 µg/L, a higher level of treatment by membranes (e.g., micro- and ultra-filters) will be required to meet discharge requirements at 5 µg/L.

The FBR technology was also pilot tested on mining water and refinery wastewater for Se removal, and several full-scale treatment systems for nitrate and perchlorate removal from contaminated groundwater have been installed. Currently, a FBR based full-scale treatment plant for Se removal from mining water was commissioned in early 2013, and a second one is scheduled to be operational in mid-2014. Three full-scale two stage anoxic/anaerobic moving bed bioreactor (MBBR) based Se treatment systems are under construction in West Virginia. These systems are scheduled to be operational in 2014 and have not been previously pilot tested, and are not covered in this document.

Regardless of whether the BOD discharge limitations dictate aerobic polishing, or treatment for other parameters discharged as a result of treatment for ABMet®, FBR, and MBBR effluents, the low ORP or anoxic/anaerobic conditions will dictate aeration to meet the discharge DO requirements. A tertiary media filter (e.g., sand filters or membrane filters) may be required to remove TSS prior to final discharge depending upon the TSS and BOD limits. Nutrients such as nitrogen and phosphorus may need to be removed to lower levels depending upon the discharge requirements, thereby requiring similar or other tertiary treatment.

Passive Biological

Passive biological treatment systems rely on naturally-occurring biological, chemical, and physical processes to achieve treatment. Typically more land-intensive than active treatment systems, passive biological systems can be less expensive to operate and manage because of lower or negligible energy or chemical inputs. In passive treatment systems, oxidized forms of selenium (selenite and selenate) can be reduced to selenite, elemental selenium and selenides through microbial reduction, followed by sequestration in soil and sediments. Labile organic carbon released from the substrate serves as an electron donor. Common electron acceptors that must be removed prior to selenium include dissolved oxygen and nitrate.

Passive treatment systems designed for vertical or horizontal subsurface flow of water through a reducing organic substrate can achieve microbial and chemical reduction of selenium with shorter residence times and smaller areas than constructed wetlands. Termed biochemical reactors (BCRs), these passive systems have been employed previously for treatment of a variety of mine-impacted waters, but their incorporation into passive treatment systems for selenium reduction is new. Substrates comprised of wood chips, saw

dust, mushroom compost, horse manure, field hay, yard wastes, and limestone granules have been utilized in varying proportions. Hydraulic application rates designed to achieve a nominal media residence time of 1 day have been shown in different pilot studies to be sufficient to reduce selenium concentrations.

The geochemistry of BCRs is relied on in a staged approach for trace metal removal. Sulfate-reducing BCRs precipitate trace metals with biogenic sulfide, while selenate-reducing BCRs remove selenium as elemental precipitates. Because selenium compounds are more readily reduced than sulfur compounds and because reduced sulfur compounds can act as a chemical reductant, any sulfides precipitated in the BCR (e.g., acid volatile sulfides) provide additional reducing capacity within the substrate.

Other removal processes occurring in passive treatment systems include volatilization and adsorption. Volatilization of selenium through bacterial, fungal, or algal-mediated methylation of selenium has been shown to be a significant loss of selenium in wetlands through the conversion to organic forms such as dimethyl selenide. Physical adsorption or removal of selenite occurs readily in passive treatment systems. This occurs via the iron, aluminum, or manganese oxy-hydroxides present within soil or sediments and the organic matter present in the passive treatment system.

Because the BCR is comprised of organic media, secondary byproducts (e.g., BOD, color, sulfide, and reduced nitrogen) are generated that require treatment before discharge. Varying across different projects, post-BCR treatment has included aerated and non-aerated ponds, surface flow constructed wetlands, and subsurface flow gravel beds, singly or in combination. Frequently described as aerobic polishing cells, these treatment units trap particulate organic particles and increase the DO content of the BCR effluent which oxidizes the residual chemical oxygen demand (COD) or BOD present. The aerobic polishing cells also polish residual selenium remaining in the biochemical reactor effluent. Consistent with active water treatment systems, passive systems may require tertiary treatment for constituents like nutrients (e.g., total phosphorus, total nitrogen, iron, sulfides, etc.) and other parameters depending up the discharge requirements.

Specific advances since the publication of the 2010 report have come through the implementation of treatability pilot studies, full-scale systems, and additional projects discovered through professional contacts and continued review of the literature. Pilot studies conducted for coal mining companies in southern Appalachia have indicated consistently that total selenium can be reduced to levels below the state regulatory standard of 4.7 µg/L monthly average selenium and daily maximum of 8.2 µg/L. As described in the Selenium Removal Technology Advancements by Technology section, inlet concentrations averaging 10 µg/L selenium were reduced below detection levels in pilot and full-scale systems. Inlet concentrations averaging approximately 20 µg/L were reduced to 2 to 3 µg/L. Concentration reduction efficiencies ranged from 89 to 92 percent in the pilot barrel systems, while larger earthen-basin demonstrations and full-scale systems exhibited a wider range of removal efficiencies of 63 to 95 percent, possibly reflecting a greater influence of hydraulics or ambient conditions.

Higher concentration ranges were treated using passive biochemical reactors in Alberta, with an influent concentration of 180 µg/L, and effluent concentrations ranged from 3 to 33 µg/L, for an average removal of 90 percent. This system has been operating for 4 years. A nominal 12-hour HRT within a bioreactor comprised of a mix of high-strength organic

substrates was shown to meet the regulatory standard of 4.7 µg/L, but full-scale media HRT ranges on the order of 24 to 48 hours allowed greater resilience to dynamic flow and load inputs. The aforementioned Alberta system demonstrated that a longer HRT is required to treat higher concentrations, and that a longer HRT may be required as the system matures and the availability of labile carbon released from substrate changes.

High strength substrate initially generates elevated concentrations of secondary parameters (BOD, COD, low DO, etc.). Concentrations typically decrease within 8 to 12 weeks and can be treated with aerobic polishing cells of reasonable size. Low strength (i.e., peat) substrate results in lower selenium removal rates but also lower secondary parameters.

For coal-mine drainage water systems, full-scale passive treatment systems sizes were determined by estimating the 90th percentile selenium mass load from available flow and inflow concentration data. Obtaining reliable, long-term base flow estimates proved to be a critical requirement to establishing a system sized with enough capacity to absorb a potential doubling of concentration and a five-fold increase in flow. Flow can be dynamic in passive systems treating surface flow inputs, and this had an inverse effect on system treatment performance and secondary treatment systems. For this reason, flow equalization and/or diversion is required to reduce the maximum range of inflow rates.

Flows treated by full-scale systems constructed since 2010 have ranged from 75 gpm to 1500 gpm at valley fill drains in southern Appalachia; but a general range of application of BCRs to-date appears to be on the order of 200 gpm.

Flow to BCRs tested in pilot studies and full-scale systems in southern Appalachia were derived from seepage from valley fills, which have relatively low average suspended solids content (<10 mg/L TSS) and circum-neutral pH (6.0 to 8.5 s.u.). In practice, pretreatment for a BCR will require reduction of TSS to relatively low concentrations (<20 mg/L) to minimize the potential for excessive accumulation of solids within the BCR.

In southern Appalachia, temperature was not shown to have a nominal effect on selenium removal during the winters of 2010 to 2011 and 2011 to 2012. Average selenium concentration reductions ranged from 83 to 92 percent through a water temperature range of 4.2°C to 29.4°C. During December 2011-February 2012, the average minimum and maximum air temperatures were 3°C and -2.1°C, respectively. The average water temperature during this period was 8.2°C. This has been attributed to the warmer temperature of valley fill drain water entering the BCR during the winter relative to the ambient air temperature, and the self-insulating properties of the constructed systems, which are typically excavated and bermed. Similarly, insulating properties of the bed grade and water content insulates and sustains system flow in systems in Canada. System start-up at the onset of winter with seasonal hydraulic loading rates sustained above average design criteria did not adversely affect performance.

Significant production of secondary, or byproduct parameters such as BOD and COD was observed from all BCR substrates with the exception of peat. From the high-strength substrates, BOD was >250 mg/L and turbidity 30 to 250 nephelometric turbidity units (NTUs), while peat BOD was <5 mg/L, with virtually no turbidity. The elevated BOD and turbidity values decreased with time by about 90 percent. DO in the outflow generally averaged 1 to 3 mg/L. Filtration of the outflow demonstrated that high BOD values are associated with particulate matter and that the dissolved fraction is very low (<10 mg/L,

occasionally 40 mg/L). This finding suggests that much of the BOD released from the BCR substrate can be retained in the downstream units as particulate BOD, which can be utilized and even beneficial over the long-term operation of the system. Moreover, the dissolved BOD is within the treatment capabilities of the downstream aerobic polishing wetlands.

The pH of outflows from BCRs comprised of mixed organic wastes tends to be consistently near-neutral, with little variation. Temperature in the BCR outflow tends to track monthly average ambient air temperatures but not below freezing temperatures in cool temperate regions. The outflow conductivity matches the influent conductivity, but reductions in total dissolved solids can be apparent in the beginning of the system startup. In one study, this was consistent with observations of bacterial sulfate reduction of 439 mg/L to 284 mg/L. Bioreactors exhibit evidence of bacterial sulfate reduction by the presence of sulfide in the effluent and the presence of colloidal sulfur in the water pooled atop the substrate. Oxidation reduction potential in the substrate is one of the strongest indicators of selenium reduction potential, since it describes the overall chemical reduction capacity of the substrate. The ORP is generally reducing to -200 to -250 mV in high-strength media. Similar to ORP, DO values measured in biochemical reactor outflow is typically <1.0 mg/L.

First-order, area-based rate constants calibrated from pilot studies are on the order of 1,000 m/yr for a 3-foot deep bed of organic media. This factor can be used in the equations of Kadlec and Wallace for BCR sizing (Kadlec, R.H. and S. Wallace. 2009. *Treatment Wetlands*, 2nd Ed. CRC Press, Boca Raton, FL). Media-based selenium removal rates established by pilot studies have been calculated to be on the order of 0.2 mg/d/ft³ of substrate. Nitrate-nitrogen concentrations in these systems are typically on the order of 3 mg/L or less; higher nitrate concentrations may yield a relatively lower removal rate. The additional volume of substrate required to reduce nitrate to low concentrations (e.g., 1 mg /L) should be factored into overall system size. Substrate profile testing at the conclusion of two pilot studies typically found higher total selenium concentrations at the inflow end of the system, consistent with expectations that selenium removal is a load-dependent, first-order removal process. Selenium speciation of substrate samples indicated that in the early stages of selenium removal, the dominant mechanism is reduction of selenate to reduced forms of selenium that are weakly adsorbed to the substrate, with approximately more than half being attributable to selenite. Highly immobile elemental selenium and/or selenosulfide account for about a quarter of the total selenium retained, while very little metal selenide was found.

The projects completed since the publication of the 2010 report have demonstrated that passive treatment is a practical, cost effective and technologically appropriate way to manage selenium, particularly in the southern Appalachia because of low influent soluble selenium concentrations (10 to 20 µg/L), and relatively higher ambient and water temperatures than cold weather locations such as northern Canada. Similar cost-effective solutions are expected for selenium removal in other regions where siting and sizing constraints can be met. Pilot testing is recommended for application of passive BCR treatment technology at locations or for wastewaters where prior passive experience is not available.

Selenium Removal Technology Advancements by Technology

This section presents a discussion of selenium treatment case studies that have occurred since 2010. Where available, reference information is presented in the References section.

1.0 Reverse Osmosis

With osmosis, water passes through a semi-permeable membrane into a solution of higher dissolved salts, until the concentrations of salts on either side of the membrane are equal. With RO, external pressure is applied to the concentrated solution to reverse the osmotic process, and induce water flow into a solution of lower salt concentration. This section presents a pilot study on low pressure RO.

Project 1A – Phosphate Mine Reverse Osmosis Pilot Study

Previous studies at a phosphate mine in Idaho focused on biological and chemical reduction methods for removal of selenium. The mine had large flows with low selenium concentrations, and therefore, wanted to evaluate concentration of the selenium into a lower flow using RO, followed by biological or chemical treatment, with the goal of reducing overall capital and operation and maintenance costs. Low pressure RO was selected as the technology for evaluation. RO was selected over nanofiltration because of the smaller pore size in the membranes, and as a result, lower selenium concentrations in the effluent. Table 1 presents a summary of the water quality data for surface water at the mine complex.

A pilot study was operated for approximately two months. The pilot unit included pretreatment through a sock-filter and a cartridge filter, followed by anti-scalant addition. The RO system included a three-stage system in a 3-2-1 array.

TABLE 1
2010 Mine Complex Surface Water Quality

Analyte	Concentration Range
Calcium	53 – 63 mg/L
Magnesium	19 – 25 mg/L
Sodium	3 – 13 mg/L
Potassium	0.5 – 10 mg/L
Alkalinity	172 – 424 mg/L CaCO ₃
Sulfate	12 – 57 mg/L
Total Dissolved Solids	220 – 296 mg/L
Turbidity	0.04 – 2.6 NTU
pH	7 – 9 s.u.
Temperature	9 – 13 °C
Dissolved Oxygen	6 – 14 mg/L

The flux was relatively constant throughout the study with an average flux of 14.7 gallons per square foot per day (gfd). The differential pressure increased by about 14 psi during the study, suggesting that fouling occurred. The feed pressure increased by about 20 psi (from 100 psi to 120 psi), which indicates fouling as well. The membranes were cleaned at the end of the study. Following cleaning, the flux was 14.7 gfd, differential pressure was 0 psi and the feed pressure was 97 psi. Average recovery during the study was 74%.

Table 2 presents a summary of the selenium concentrations for the study. Permeate concentrations were consistently below the surface water standard of 5 µg/L. On average, the RO system removed 99.26% of the selenium.

TABLE 2
Summary of Selenium Concentration (mg/L)

Location	Influent	Concentrate	Permeate	% Removal
Sample Date				
8/16/2010	0.0418	0.146	0.00027 J	99.35
8/20/2010	0.0395	0.15	0.0002 U	99.49
8/23/2010	0.0397	0.14	0.0002 U	99.50
8/30/2010	0.036		0.00057 J	98.42
9/2/2010	0.0383	0.169	0.00023 J	99.40
9/7/2010	0.0396	0.149	0.0002 U	99.49
9/11/2010	0.0395	0.15	0.0002 U	99.49
9/23/2010	0.0401	0.171	0.0002 U	99.50
9/30/2010	0.0412	0.163	0.0002 U	99.51
10/5/2010	0.0391	0.145	0.00044 J	98.87
10/7/2010	0.0366	0.138	0.00046 J	98.74
10/11/2010	0.0405	0.141	0.00022 J	99.46
10/13/2010	0.0388	0.142	0.00034 J	99.12
Maximum	0.0418	0.171	0.00057	99.51
Minimum	0.036	0.138	0.0002	98.42
Average	0.0393	0.150	0.00029	99.26

Notes:

Concentration higher than benchmark level of 0.005 mg/L.

U = Not detected at or above the MDL

J = Estimated

2.0 Ion Exchange

IX removes ionic-form selenium by exchanging selenate for like charged ions on a resin backbone structure. IX resin are typically contacted with the wastewater in fixed beds and operated until the resin is saturated. Ion exchange case studies are described below for bench, pilot, and full scale treatment systems for coal surface mine surface runoff treatment.

Project 2A – Appalachian Surface Coal Mine Bench-Scale Treatability Test for Selenium Removal Using Ion Exchange

A bench-scale study was conducted to evaluate the removal of selenium from a surface coal mine outfall site using IX technology. This bench-scale test effort used water with sulfates in excess of 1,900 mg/L and selenium (primarily in selenate form) up to 30 µg/L. The initial phase of the bench-scale testing consisted of jar tests to develop adsorption isotherms to screen 10 anion exchange resins. The isotherms were used to evaluate their gross chemical exchange adsorption for selenium, predominantly in the form of selenate (SeO_4^{2-}), and sulfate (SO_4^{2-}). Based on these screening tests, the three most optimal ion-selective resin configurations for selenium and sulfate (i.e., major competing ion to selenium) removal were selected for column testing.

The IX column tests results showed that a column configuration featuring a weak base anion (WBA) resin which was highly selective for sulfate (SO_4^{2-}) followed by a strong base anion (SBA) resin which was highly selective for selenate (SeO_4^{2-}), was able to successfully remove selenium to meet the discharge permit limits. However, the sulfate (SO_4^{2-}) did not chromatographically displace selenate (SeO_4^{2-}) as expected in this resin configuration. Therefore, pilot testing was recommended using just SBA resins. A configuration using a lead column with macroporous SBA resin, for organics removal, followed by three lag columns using gel form SBA was recommended.

Project 2B – Appalachian Surface Coal Mine Ion Exchange Pilot Study

As follow-on to the IX bench-scale laboratory study, a larger scale IX pilot study was conducted to validate selenium removal and performance using source water from a surface mine effluent stream in West Virginia. The IX pilot study was successfully operated for 4 weeks (24 hours per day, 7 days per week). Key findings of the IX pilot study are summarized below.

- The IX pilot study demonstrated consistent total recoverable selenium reduction to less than the required West Virginia Department of Environmental Protection (WVDEP) National Pollutant Discharge Elimination System (NDPES) limit of 4.7 µg/L (average monthly) and 8.2 µg/L (daily maximum) for the 4-week duration of the study. The final effluent selenium concentration was below the method reporting limit (less than 1 part per billion [ppb]) for the entire pilot study period.
- IX pilot equipment operated for the pilot study duration without major process or mechanical issues.
- Using Purolite 300A and sodium chloride brine regeneration, sulfate was found to breakthrough first, at high concentrations, before selenium broke through above its average monthly effluent discharge standard, thus, sulfate could be used as a surrogate for selenium breakthrough.

- Results indicated approximately 2.75 pounds of sulfate per cubic foot of resin could be removed before breakthrough in the lead column.
- For runs completed after all virgin resin was regenerated, sulfate and selenium (primarily in the form of selenate) were consistently removed to low levels, and the amount of sulfate removed before breakthrough was consistently 45 to 54 pounds per service period, indicating the resin can be regenerated successfully without immediate or significant loss of capacity.
- IX regeneration brine waste was collected, processed, and successfully reduced to below target WVDEP NPDES permit limits in both a full-scale ZVI system and a pilot-scale anoxic/anaerobic FBR system followed by an aerobic MBBR.
- Because of the fluctuation in the effluent pH observed during the pilot study, a chemical addition system to add caustic and elevate the effluent pH would be required for a full-scale system.

Project 2C – Appalachian Surface Coal Mine, Full-Scale System

An Appalachian surface coal mine company installed a 50 gpm IX system at a remote outfall. At this site, the typical inlet selenium was 7 to 14 µg/L with inlet sulfate measured at 690 mg/L in a single sample. The system used two 48-inch diameter IX vessels, with about 4-foot deep resin beds (about 50 ft³ per vessel).

The system included sand filtration prior to IX, the IX regenerant brine solution (e.g., sodium chloride) and the regeneration system. The site was reusing the sodium chloride brine for multiple regenerations, which is not a recommended practice to achieve consistently high selenium removal. The total salt dosage was about 10 lb NaCl/ ft³ which equates to about a 2.5 times the stoichiometric requirement.

System performance was erratic, operating well when regenerated with fresh brine and poorly when regenerated with used, partially spent brine. Additionally, the evaluation process involved reuse of rinse water which can add selenate into the following service cycle reducing the resin efficiency by preloading it with selenium.

3.0 Zero Valent Iron

Case studies for ZVI treatment include pilot and full scale demonstration testing of a steel-wool column-based ZVI system for coal mine surface runoff treatment. In addition, a powdered ZVI treatment concept has been developed and tested at the bench- and pilot-scale levels for treatment of FGD blowdown at a coal-fired power plant. Lastly, a foam-based ZVI product was used to evaluate selenium treatment from a phosphate mine. Both the powdered ZVI and steel-wool-based ZVI treatment system case studies resulted in significant reduction of selenium. However, the foam-based ZVI product did not result in sufficient selenium concentration reductions.

Project 3A – Appalachian Surface Coal Mine Steel Wool-Based ZVI Pilot Study

A steel wool-based ZVI pilot study was conducted to evaluate selenium removal from mine runoff. The pilot consisted of five parallel treatment trains, each with two tanks in series, configured or operated differently. The inlet selenium varied from about 15 to 29 µg/L and was primarily in selenate form. TDS was typically above 3,000 mg/L and sulfate ranged

from 1,400 to 1,900 mg/L. The pilot plant operated for a period of about 4 months, from December 2010 to March 2011.

Key findings of the steel wool-based ZVI pilot study are summarized below:

- Of the media configurations tested, steel-wool reels, pressed into the tanks, were found to be the preferred media. Bagged steel wool ZVI reels and disc-formed steel wool ZVI layers are not recommended because of the increased mechanical issues observed during the pilot test. Other forms of ZVI media, such as granular iron pellets, were not tested in this pilot because of time limitations.
- pH adjustment was required to achieve selenium removal below the monthly average permit limit of 4.7 µg/L. pH adjustment, using either carbon dioxide or sulfuric acid was effective. The increased buffer capacity offered by the carbon dioxide appears to result in a performance advantage. However, the added buffer capacity may result in increased caustic demand for the subsequent pH adjustment. Adjusted influent pH values in the range of 5.5 to 6.0 s.u. were found to be effective for selenium removal.
- During this pilot test, the lead reactor tanks were observed to typically break through as a result of the chemical degradation of the steel wool media, which results in slumping of the media and eventual short-circuiting. Media life of 4 weeks was observed for the later phase of the study (after some optimization efforts).
- CH2M HILL observed that a majority of the selenium is accumulated within the steel wool reactors. Previous toxicity characteristic leaching procedure (TCLP) tests indicated that the steel wool waste rust matrix did not release selenium under test conditions.
- A post-treatment clarification system will likely be required to remove total iron from the effluent. CH2M HILL observed that steel wool reactors can release up to 100 to 200 mg/L of soluble iron in the effluent, particularly in the carbon dioxide pH adjusted systems. The soluble iron released by the steel wool reactors is in the ferrous form.

Project 3B – Steel Wool-Based ZVI Surface Coal Mine Full-Scale Installation Study

An Appalachian surface coal mine developed the concept for a full-scale ZVI system, termed iron-facilitated selenium reduction (IFSeR). The modular treatment system uses reels of steel wool in vessels to reduce and remove selenium from the surface water runoff. A demonstration system was constructed and put into operation in September 2011. During the data review period, total system flows ranged from 50 to 130 gpm. Inlet selenium averaged 9.8 µg/L with a peak value of 17.6 µg/L. The inlet TDS typically ranged from 1,500 to 2,150 mg/L and sulfate from 770 to 1,020 mg/L.

The influent pH was reduced in the range of 6.0 to 6.5 s.u. using carbon dioxide prior to the ZVI columns. The system consists of vessels containing steel-wool operated in parallel, where each vessel is sized for a flow of approximately 10 to 16 gpm. Effluent from the ZVI reactors is combined, the pH is raised, and the water is aerated to oxidize the iron remaining in solution. Oxidized iron is removed through clarification, and the clarified water is discharged to a pond, and then to an NPDES-permitted outfall.

Selenium concentrations in the effluent were below the method detection limits of 1 µg/L for approximately 35 percent of the samples and varied from 1.1 to 7.8 µg/L for the

remaining samples. Average monthly values ranged from 1.1 to 2.4 µg/L, with a maximum concentration of 7.8 µg/L.

Three additional IFSeR systems have been installed at other outlets. These systems also treat runoff from valley fills, and are showing similar results to the system described above.

Project 3C – Bench and Pilot Demonstration of Hybrid ZVI Process for FGD Blowdown Treatment

A process using powdered ZVI has been developed and evaluated in small-scale pilot and demonstration scale systems. The system consists of four completely mixed reactors operated in series. ZVI was added to one or more of the reactors, and an unnamed surface regeneration solution was added to the first reactor. The surface regeneration solution was added to maintain reactivity on the ZVI surface. Downstream of the ZVI reactors, the solution is aerated to oxidize remaining iron in solution and the iron solids are removed through clarification.

A 5-week bench test was conducted with a flow rate of 30 liters per day (0.0055 gpm), and total HRT of 24 hours in the four reactors combined. Influent wastewater contained about 20 g/L of TDS, with about 3,600 to 5,000 mg/L of chloride and 1,100 mg/L of sulfate. Influent dissolved selenium and nitrate concentrations ranged from approximately 2,000 to 3,000 µg/L and 21 to 26 mg/L, respectively. Table 3 presents the effluent nitrate and selenate concentrations. Over 99 percent of the selenate-Se was removed by the first two stages (see Table 3).

TABLE 3
Removal of Nitrate and Selenate along Prototype Treatment Train

Time	Concentrations (mg/L)						
		Influent	R1	R2	R3	R4	Effluent
23 Oct (Startup)	NO ₃ -N	25.8	9.62	2.46	0.4	0.02	0.42
	Selenate-Se ^a	3.87	1.12	0.2	0.05	0.015	
29 Oct	NO ₃ -N	20.7	5.56	0.4	n/d	n/d	0.1
	Selenate-Se	1.92	0.36	0.02	n/d	n/d	n/d
5 Nov	NO ₃ -N	21.30	11.30	2	0.1	n/d	0.15
	Selenate-Se	2.04	0.40	0.03	n/d	n/d	n/d
12 Nov	NO ₃ -N	22.53	3.34	0.5	0.05	n/d	0.12
	Selenate-Se	2.58	0.62	n/d	n/d	n/d	n/d
19 Nov	NO ₃ -N	22.41	3.24	n/d	n/d	n/d	0.05
	Selenate-Se	2.61	0.72	n/d	n/d	n/d	n/d

^aOnly the selenate form of selenium was reported.

n/d = not detected (detection limit not provided)

mg/L = milligrams per liter

R = Reactor

Based on the results of the bench test, to treat 1 cubic meter of FGD wastewater would consume 150-250 grams (g) of ZVI, 50 g of lime, and an unnamed amount of the unknown reagent. Estimated chemical costs were \$0.3 to 0.6 per m³ of wastewater.

Subsequently, a 5-month pilot-scale field test was conducted with a similar configuration to the bench test. Total volume of the pilot test was approximately 1,000 gallons, with an influent flow rate of 1 to 2 gpm, for an HRT of 8 to 16 hours. Influent selenium and nitrate concentrations ranged from 1,000 to 2,000 µg/L and 10 to 40 mg/L, respectively. TDS ranged from 7,500 to 15,000 mg/L.

The pilot test evaluated different numbers of reactors in series with varying retention times. Test results indicated that a two-stage system could reduce selenium to below 50 µg/L, a three-stage reactor reduced selenium to below 20 µg/L, and a four-stage reactor system reduced selenium below 10 µg/L.

Project 3D – Phosphate Mine Water ZVI Pilot Study

A pilot study was conducted by Simplot using a ZVI-based treatment process developed by Liberty. The study was performed at the Smoky Canyon Mine from October 5, 2009 to September 12, 2011. The influent and effluent dissolved selenium concentrations including flow rates are shown in Figure 1.

Liberty's technology is different from typical ZVI systems in that it utilizes micro-scale ZVI permanently adhered to a sponge-like matrix, which provides a high porosity. The Liberty ZVI treatment media is placed in a closed container and influent water is fed into the treatment unit through gravity flow. As water flows through the media, selenium in the form of selenite chemical adsorbs with ferric iron or the selenate is reduced to elemental selenium thereby resulting in an effluent with a lower concentration than the influent. According to Liberty, the sponge-like matrix eliminates scale and plugging issues typically associated with ZVI systems.

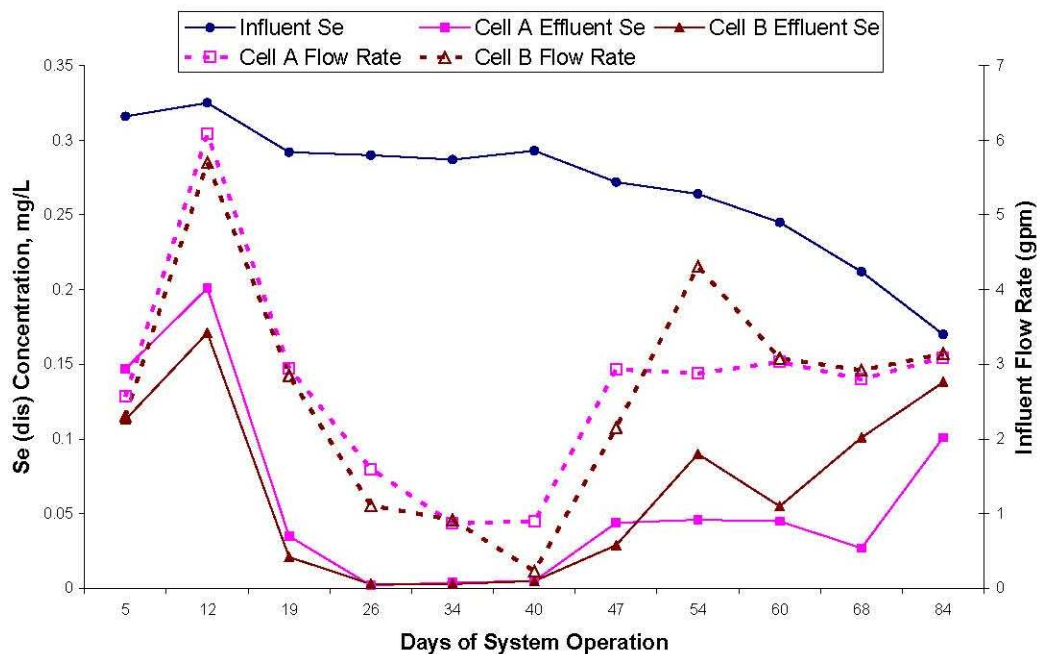
Overall, the pilot study demonstrated that the Liberty process was not effective for removal of selenium at South Fork Sage Creek Springs. The system operated at the design conditions for the duration of the pilot study; however, selenium removal was not sufficient to achieve the Idaho surface water quality criterion for protection of aquatic life (0.005 mg/L = chronic criterion; Idaho Administrative procedure Act [IDAPA] 58.01.02.210) at any time during the test. Furthermore, the treatment effectiveness dropped off sharply after just 5 months of operation, as the ZVI media became exhausted.

Operational difficulties were encountered with plugging of the metering valves and plugging of the flow meters with invertebrates or debris that had been flushed through the system.

In addition, post treatment was required to remove soluble and colloidal iron as well as increase the DO prior to discharge. Passive approaches to add DO were successful; however, the associated iron precipitation quickly overwhelmed the settling pond/sand filter.

FIGURE 1

Total Se in Influent and Effluent of ZVI Reactors A and B with Influent Flow Rate



4.0 Fix Bed Adsorption

This section presents case studies on two vendor-supplied adsorbents: SeRT™, an activated carbon-based adsorbent, and Sorbster™, an activated alumina material, as well as a GFH case study and a study on a proprietary adsorbent.

Project 4A – Sorbster™ Adsorption Treatment for Selenium from Coal Mining Wastewater

Mars Systems, the manufacturer of Sorbster™, a proprietary enhanced activated alumina (EAA) material, tested 10 different coal mine pond wastewater samples for selenium removal. Per Mars Systems literature, Sorbster™ is produced from an activated alumina substrate coated with various proprietary chemistries. As reported by Mars the treatment binds functional groups to the activated alumina media which complex soluble selenium in the selenate and selenite oxyanion forms. Sorbster™ is typically contacted with the wastewater in fixed beds.

Mars tested the coal mine wastewaters using small columns packed with Sorbster™ media. The data indicated selenium removal from 16 percent to greater than 95 percent. Details of how the samples were taken and the site conditions were not provided. Table 4 presents dissolved selenium removal from coal mine water using Sorbster™ media.

Coal mine wastewater Sample H is indicated to contain selenium in the selenate form, with inlet concentration of 54.5 µg/L and sulfate is 315 mg/L, with less than 50 percent removal after treating 13 Bed Volumes (BV) (see Tables 5 and 6). MARS Systems developed a summary of the difference between calcium and magnesium concentrations and compared to selenium removal rates. The results presented in Table 6 suggest that a higher difference in calcium and magnesium concentrations correlated to lower selenium removal rates.

However, Samples E and H both had similar calcium and magnesium values, yet Sample E achieved over 95 percent reduction and Sample H achieved less than 50 percent reduction.

The EAA reported cost is about \$5.50/lb or about \$302/ft³. If this material treated as much as 50 BVs that equates to \$0.81/gal. By comparison, IX resin has comparable costs and routinely achieves 200 to 300 bed volumes before 50 percent breakthrough of selenate and it is regenerable.

Coal mine wastewater Sample K with an extended contact time contained 389 µg/L of selenate and 1,370 mg/L of sulfate, and when treated, resulted in 35 percent reduction of selenate after treating 4 BVs. Both of these applications indicate that Sorbster™ is not a cost effective treatment for selenate.

Mars Systems technical literature for applications related to refinery wastewater provides information on selenite treatment by Sorbster™ (see Project 4B below).

TABLE 4
Selenium Removal from Coal Mine Pond Waters by Sorbster™ Media

Coal Mining Pond	Speciation Reported by Customer	Se in Pond (ppb)	Se after Sorbster™ Treatment (ppb)	Percent Se Removal	Contact Time (minutes)	Pond water pH	Bed Volumes Treated**
A	Significant Selenate	8.8	ND	>95	23	7.1	12
B	Mostly Selenate	14.1	ND	>95	21	7.0	13
C	Unknown	48.1	ND	>95	21	1.5	15
D	Unknown	48	ND	>95	21	8.0	15
E	Selenate	13	ND	>95	20	7.8	48
G	Mostly Selenate	11.8	6.2	47	21	7.5	12
H	Selenate	54.6	28.2	48	22	7.5	13
I	Mostly Selenate	12	7.5	38	21	7.5	12
J	Selenate	37.6	31.5	16	25	6.8	20
K	Selenate	389	305	20	21	7.7	13
K with extended Contact time		389	253	35	51	7.7	4

*Water evaluated as received in flow-through vessels at ambient temperature, EPA 200.7 and SM3114C Methods used.

**Bed volumes treated limited to available amount of water

ND = not detected

TABLE 5
Additional Coal Mine Pond Water Quality Parameters

Coal Mining Pond	Percent Se Removal	Total Fe (ppm)	Total Ni (ppm)	Chloride (ppm)	Sulfate (ppm)	Nitrate (ppm)	Silica (ppm)	TSS
A	>95	0.103	ND	NA	129	0.44	NA	ND
B	>95	0.043	0.008	NA	1,570	5.06	NA	7
C	>95	0.117	0.003	17	855	674	2.5	7
D	>95	0.24	0.011	14	890	1,740	2.4	16
E	>95	NA	NA	NA	245	NA	NA	NA
G	47	0.065	0.003	NA	1,040	6.07	NA	20
H	48	0.234	ND	NA	315	1.43	NA	17
I	38	0.094	ND	NA	879	3.69	2.1	ND
J	16	ND	0.003	32.5	718	18.6	6.8	NA
K	20	0.022	0.700	6.1	1,370	0.03	NA	NA

NA = not analyzed for

ND = not detected

TABLE 6
Calcium and Magnesium Influence on Sorbster™ Selenium Removal

Waters with >95% Se Removal				Waters with <50% Se removal			
Coal Pond	Calcium (ppm)	Magnesium (ppm)	Δ CA from Mg	Coal Pond	Calcium (ppm)	Magnesium (ppm)	Δ CA from Mg
A	38	11	+27	G	196	184	+12
B	179	210	-31	H	78	29	+49
C	209	246	-37	I	206	106	+100
D	181	281	-100	J	205	187	+18
E	76	27	+47	K	497	95	+402
Average	137	155	-18		236	120	+116.2

Project 4B – Sorbster™ Adsorption Treatment of Selenium in Refinery Wastewaters

Mars Systems, the manufacturer of Sorbster™, a proprietary EAA material, tested five refinery wastewater samples for selenium removal and performed a small-scale pilot test at one refinery. As described in Project 4A above, Sorbster™ is normally used in fixed beds and laboratory scale tests are performed with small columns packed with Sorbster™. Refinery wastewaters bench tested in this study are reported to contain selenium primarily in the selenite form. Refinery E sample, which had high sulfate of approximately 1,300 mg/L and selenium of 109 µg/L, assumed to be selenite, when treated through the

Sorbster™ media achieved a 90 percent reduction after treating 14.5 BVs. Se concentrations at the conclusion of the test were trending up as presented in Figure 2.

Conversely, the 1-gpm pilot test, treating 35,000 gallons of Refinery A wastewater with low sulfate of approximately 221 mg/L and selenium averaging 30 µg/L, assumed to be selenite, treated 1118 BVs to an effluent selenium concentration of approximately 5 µg/L with a downward concentration trend at the conclusion of the test, along with a downward trend in influent concentrations (see Figure 3).

FIGURE 2

Western Refinery E – Sorbster™ Media Selenium to below Target of 20 ppb in effluent Water – 90% Average Removal

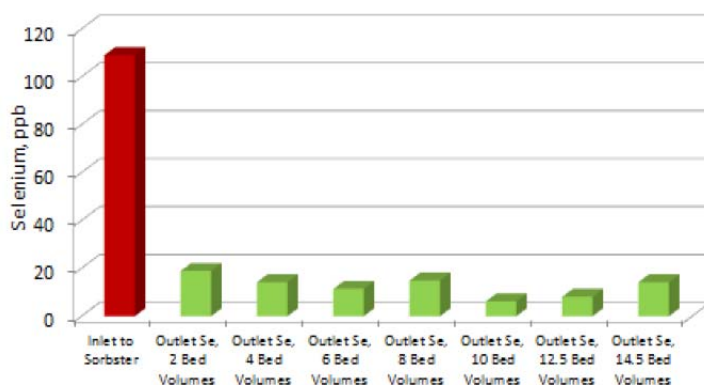
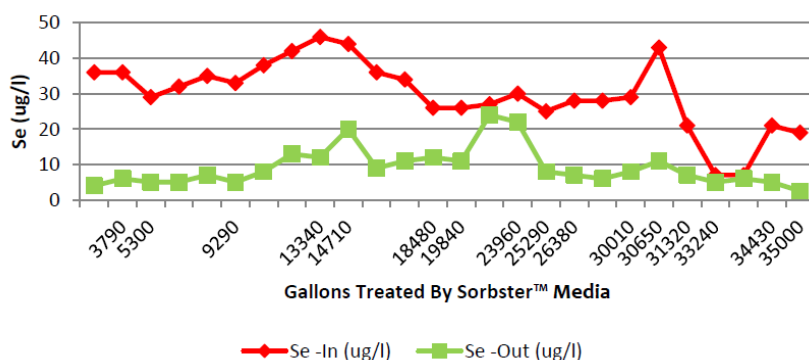


FIGURE 3

Midwestern Refinery A-2 –35-000-gallon Evaluation with Changing Crude Oil Sources, 30 ppb Reduced to 9 ppb Average, Removal as Low as 2.5 ppb



Project 4C – CH2M HILL Project: Small Scale Groundwater Pump and Treat System

GFH was installed at a confidential small-scale groundwater treatment facility monitored by CH2M HILL. The treatment system consisted of a train of liquid phase granular activated carbon (LPGAC) to remove volatile organic compounds (VOCs), followed by chelating cation IX and anion ion exchange beds to remove trace metals. However, selenium was

passing through. On a trial basis, GFH was installed as a fixed bed at the end of the previously described treatment train. The total inlet selenium was $<10 \mu\text{g/L}$. Within the first week of operation (maximum of 3,500 BVs), the fresh bed of GFH had completely broken through. This site did not speciate the selenium; however, the aquifer is aerobic and selenium is most likely in the selenate form. GFH would be expected to perform better on the selenite form; however, data has not been collected in this effort to confirm performance for selenite.

Project 4D – SeRT™ Selenium Adsorption Technology

The Phillips 66 Company Selenium Removal Technology or SeRT™ technology is a fixed bed chemisorption technology that uses a specially formulated, commercially-available sorbent (activated carbon-based), developed primarily for use in oil refineries with selenium discharge challenges in their stripped sour water (SSW). Selenium removed by the SeRT™ process is immobilized on the sorbent and is reported not to desorb under SeRT™ operating conditions as it might for a physical adsorption process.

Basic SeRT™ technology specifically targets the selenocyanate anion (SeCN^-) for removal. Selenocyanate typically makes up 95 to 100 percent of the selenium found in refinery SSW, the balance being selenite. Elemental selenium is also removed by the SeRT™ sorbent. Pretreatment may include pH reduction and heavy organics removal. Finally, additional additives may be required to improve selenite removal efficiency to meet total selenium targets.

Phillips 66 Company literature states that pilot testing on a refinery SSW slip stream has demonstrated the capability of SeRT™ technology to deliver effluent selenium $<10 \mu\text{g/L}$ (detection limit is not specified). An existing full-scale commercial unit has operated successfully to achieve the targeted treatment objective since start-up in 2008. A second full-scale unit at a different West Coast refinery is scheduled for start-up in 2014 and a demonstration unit at non-Phillips 66 refinery began in summer 2012 (results not yet available).

Phillips 66 reports that the kinetics of selenium removal by SeRT™ technology is significantly improved by reducing the pH of the SSW. The SeRT™ technology is adversely affected by the presence of significant concentrations of high molecular weight organics with low water solubility in the SSW. Lowering the pH further can mitigate the effects of these organics. If, however, the treatment objective requires a very low effluent selenium concentration or the influent concentration of high molecular weight organics is high, the influent may require pretreatment prior to contacting the SeRT™ sorbent. If the effluent pH must be near neutral prior to discharge or further treat, the effluent may be neutralized after treatment.

Project 4E – Proprietary Selenium Adsorption Technology

Cameco Corporation has developed a fixed bed adsorption technology using a proprietary media for removal of selenium in the forms of selenite and selenate. Testing was conducted on purge water from uranium mining operations at Cameco Resources Smith-Highland Ranch operations. The wastewater or purge water typically contains 0.53 mg/L of selenite and 0.89 mg/L of selenate. Testing included bench top, pilot, and a demonstration scale system. The systems consisted of two columns of the fixed bed media operated in series. Pilot testing resulted in effluent total selenium concentrations below the method detection

level (1 ppb) up to 9 ppb, with influent concentrations ranging from 0.07 to 0.86 mg/L. Both selenate and selenite were removed. The demonstration scale system treats 0.68 m³/min, and includes pretreatment for radium removal using barium chloride followed by two fixed bed adsorption columns operated in series. Average influent total selenium concentrations to the commercial unit were 0.5 mg/L, and the effluent concentrations met the target of 0.1 mg/L of total selenium. The commercial scale unit treated 75,000 m³ of purge water in one column before breakthrough occurred where the concentration of selenium in the effluent was over 0.1 mg/L.

5.0 Co-precipitation

This section describes the application of co-precipitation using iron hydroxide to remove selenium in FGD forced oxidation scrubber liquor loop as well as in a uranium mine processing wastewater stream.

Project 5A – Iron Addition to a FGD Absorber to Enhance Flue Gas Selenium Removal

Tightening regulation of sulfur dioxide flue gas emissions is leading more electric utilities to install FGD scrubber systems on coal-fired power plants, often in the form of limestone forced-oxidation wet-scrubbers. These FGD scrubbers also remove a portion of the selenium and other volatile metals from the flue gas stream. Selenium is principally adsorbed from the flue gas in the selenite form. Selenite can be oxidized to selenate by the forced oxidation process in the scrubber. Selenite can be removed by adsorption on precipitated iron hydroxide particles at a mildly acidic pH, typically less than 6.5 s.u. High surface area ferric hydroxide (or ferrihydrite) will tend to adsorb the selenite, but not selenate. FGD scrubbers typically operate at a pH of 5.5 to 6.0 s.u. Therefore, the addition of an iron salt to a limestone forced-oxidation scrubber could result in the absorption of selenite on the ferric hydroxide before it can be oxidized to selenate, thereby lowering the soluble selenium in the FGD wastewater, and allowing removal of the particulate selenium in solids-removal processes.

Two full-scale pilot tests were performed in 2009 and 2011 to evaluate the effectiveness of the technology. In each test, a solution of ferric chloride was added to the scrubber at a dose of a minimum of 250 pounds of iron to 1 pound of selenium. In both tests, liquid in the scrubber was not replaced with new water, therefore, each test started with a baseline selenate concentration in the scrubber. Therefore, the amount of new selenate formed was used to evaluate the technology. Selenate concentrations will decrease as water from the scrubber is blown down, and would stabilize after one or more HRTs.

The 2009 test operated for 2 weeks and resulted in a net reduction of soluble selenium of about 83 percent, selenate concentrations decreased from 3,909 to 661 µg/L. The HRT in the system was 36 days. Therefore the test would need to be extended significantly to evaluate potential effluent selenium concentrations once the system reaches steady state. The 2011 test was operated for 6 weeks or one HRT and, after the system was optimized, indicated a net reduction of about 70 percent of the influent soluble selenium concentration which ranged from 300 to 500 µg/L. However, the dose of ferric chloride was based on a lower mass loading of selenium, and sufficient iron may not have been present.

Project 5B – Selenium Control in Wet FGD Systems (Katherine Searcy, Trimeric Corp, et.al.)

Bench- and pilot-scale tests were conducted to determine factors that impact selenium speciation and phase partitioning in wet FGD systems. During 2010 and 2011, 27 bench-scale scrubber tests and associated analyses were completed in synthetic FGD liquors, and six tests were conducted with actual FGD and limestone slurries. Testing in synthetic liquors confirmed the following key conclusions:

- Selenium oxidation increases with increasing ORP conditions and excess oxidation air.
- The phase and oxidation state of manganese tends to correlate with selenite oxidation. Conditions that favor dissolved phase Mn(II) do not favor selenite oxidation; whereas conditions that favor solid phase Mn(IV) do favor selenite oxidation.
- Scrubber additives may decrease selenite oxidation in the scrubber and downstream FGD dewatering or wastewater treating equipment. The additives tested included dibasic acid and two unnamed additives.
- Selenite adsorbs to iron, and the amount of sorbed selenite increases with increasing iron concentration.

Testing in actual liquors showed that the presence of full-scale gypsum and limestone solids, and perhaps the impurities in those solids, may lead to selenium precipitation. The mechanism is uncertain.

Project 5C – Selenium Treatment through Precipitation at a Uranium Mine

A full-scale mine water treatment system was modified to increase selenium (Se) and molybdenum (Mo) removal. Enhancements were completed and the system was fully commissioned after the first quarter of 2009. Changes to the treatment system allowed Se and Mo to be removed from the effluent stream using a high-rate thickener operating at pH 3.8 s.u. The uranium barren waste solution and other contaminated water streams were mixed with slaked lime to raise the pH from 1.5 s.u. to between 3.5 and 4.2 s.u. This process solution was then pumped to a high-rate thickener (Se-Mo removal thickener) where Se and Mo co-precipitated with ferrihydrite. These chemical precipitates were thickened to 30 percent solids and pumped to a pH adjustment tank. The slurry was adjusted to a pH 6 to 7 s.u. with the slaked lime, then blended with other tailings streams and pumped to downstream processes for removal of other metals, and final pH adjustment. The final effluent discharges to monitoring ponds where a composite sample is collected and analyzed. Effluent is released to the downstream environment if all the regulatory criteria are met.

Tables 7 and 8 summarize the yearly average concentration of selenium in the raffinate solution feeding the treatment system and the final effluent, respectively from September 2008 to July 2012. After the modification work was completed in 2009, there was a significant reduction in concentration of selenium in the final effluent. The downward trend of selenium has been sustained through 2011 and to date in 2012, resulting in selenium concentrations below the administration level of 0.028 mg/L.

TABLE 7

Summary of Yearly Average Concentration of Selenium in Raffinate Solution
(Feed stream to bulk neutralization circuit)

Year	Se in Raffinate (mg/L)	Se in Final Effluent (mg/L)
2008	0.175	0.039
2009	0.049	0.022
2010	0.152	0.017
2011	0.241	0.016
2012*	0.213	0.014

Note 2012 average is for the period from January 1 to July 31.

TABLE 8

Summary of yearly average of selenium in final effluent

Year	Se in Final Effluent (mg/L)	Standard Deviation (mg/L)	Internal Administrative Control Limit (mg/L)
2008	0.039	0.003	-
2009	0.022	0.007	-
2010	0.017	0.004	-
2011	0.016	0.001	0.028
2012*	0.014	0.001	0.028

Note 2012 average is for the period from January 1 to July 31.

6.0 Active Biological Treatment

Since 2010, several pilot studies have been conducted for Se removal using FBR technology on mining waters and on biologically treated refinery effluents. Pilot studies were also conducted using ABMet® technology. Information on one full-scale ABMet® system was provided for this document. Other full-scale ABMet® systems are in operation but published information was not available for this report. Results of the pilot studies and full-scale installation provided are presented below, including description and operating conditions.

Project 6A – Coal Mining FBR Pilot

An FBR pilot study was conducted from February to May 2010 for a mining site in West Virginia for Se removal. The FBR pilot unit, supplied by *Envirogen Technologies* (Ewing, NJ), consisted of a 2 feet (diameter) by 13.5 feet (height), 200-gallon, stainless steel (304 SS) column, filled with 400 pounds (lbs) of GAC media. The initial bed height with GAC was approximately 5.8 feet with an expanded bed height of about 7.5 feet with fluidization of GAC without biomass growth. The FBR column was located outdoors. Major equipment associated with the FBR pilot included a fluidization pump, air compressor, chemical feed pumps, instrumentation, piping and an electrical control panel, housed in an 8 × 10-foot equipment container (Conex). The FBR pilot was operated at a flow rate of 8 gpm with a fluidization flow of approximately 40 gpm required for the target bed expansion of approximately 30 percent without biomass growth. Target bed expansion with biomass growth is approximately 60 percent of the unexpanded bed height.

The FBR influent (mine water) was heated using an in-line electric heater to maintain a minimum operating temperature of 50°F (10°C) in the FBR. The FBR influent had an average total Se concentration of 42 µg/L with Se predominantly occurring in a soluble selenate (Se (VI)) form. FBR feed water had an average NO₃-N concentration of 9.8 mg/L, which was found to be sufficient to sustain the required microbial growth for Se removal. Influent average TSS, calcium, magnesium, TDS, and sulfate concentrations were approximately 10 mg/L, 260 mg/L, 320 mg/L, 2,600 mg/L, and 1,430 mg/L, respectively. Influent temperature and pH varied from 50 to 70°F and 7.5 to 8.1 s.u. Influent dissolved oxygen concentrations were typically at the saturation concentration. Influent COD and nutrients (nitrogen and phosphorus) were negligible.

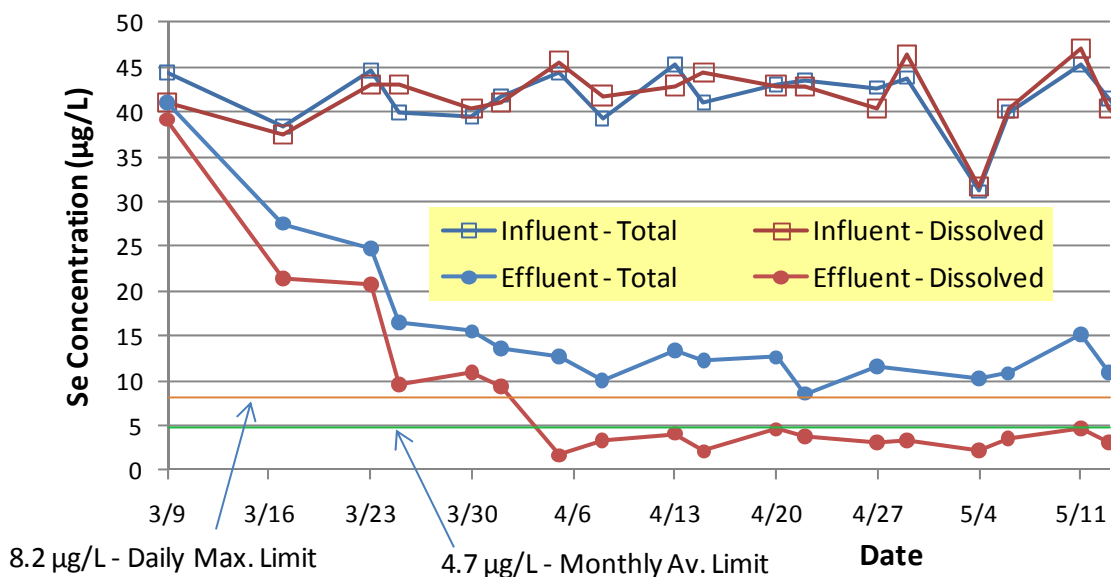
MicroCg, an engineered organic carbon, was fed as the electron donor (carbon substrate/COD source) at a dosage based on satisfying COD requirements for removal/reduction of DO, NO₃-N, selenate/selenite, and some sulfate. At the system flow rate of 8 gpm, average concentration of soluble COD in the FBR influent with MicroCg addition was approximately 160 mg/L. Phosphorus (macronutrient) and micronutrients were added for biological growth.

The average HRT of the FBR at 8 gpm flow rate was approximately 27 minutes based on expanded bed volume. FBR was monitored for ORP, temperature, DO, pH, and expanded bed height. Operating ranges for these parameters were approximately -135 to -280 mV, 56 to 70 °F, 0.2 to 1.2 mg/L, 6.5 to 7.1 s.u., and 8.8 to 9.5 ft, respectively. DO measurements may have been inaccurate since they are high at low operating ORP.

The FBR effluent nitrate-N concentrations were close to zero. Average sulfate reduction of approximately 30 mg/L was reported with an average total sulfide concentration of approximately 1.2 mg/L in the FBR effluent. The average filtered (through 0.45 micron filter) Se concentration was approximately 3.3 µg/L and was consistently below the monthly average total discharge limit of 4.7 µg/L for the duration of the study. However, the average total Se was 11.6 µg/L, which is above the discharge limit. This is due to a combination of some absorbed elemental Se on the FBR effluent TSS, colloidal Se particles in the effluent, and potentially some accumulated Se within the bacterial cells. Hence, in order to be in compliance for total Se, the FBR effluent needs to be clarified or filtered to remove the reduced particulate (elemental) Se and TSS.

Figure 4 shows Se removal by comparing influent and effluent total and filtered Se concentrations. It took about 4 weeks for the microbes to acclimatize and reduce dissolved Se to below 4.7 µg/L from an influent Se concentration of 42 µg/L. Low effluent Se concentrations were maintained for the duration of steady-state operations.

FIGURE 4
Pilot Effluent Selenium



The carbon source (MicroCg) was dosed at a higher rate than that stoichiometrically required for DO removal, nitrate reduction, selenate/selenite reduction, and new bacterial cell synthesis in order to drive/force the bacteria to use selenate/selenite as electron acceptor to the maximum extent possible, and so there was excess degradable COD in the FBR effluent. This condition contributed to some sulfate reduction to sulfides also. The average total COD in the FBR effluent was approximately 100 mg/L, whereas the average soluble COD was approximately 50 mg/L. Total COD includes particulate COD contributed by the effluent TSS (biomass) also. Effluent average total BOD concentration was 52 mg/L including particulate BOD contributed by effluent TSS (primarily biomass), and the average soluble BOD concentration of 34 mg/L.

Average TSS concentration in the effluent was 28 mg/L with volatile suspended solids (VSS) concentration of 24 mg/L, indicating that the effluent solids were primarily biomass. Average observed solids yield for the FBR pilot operation was calculated to be approximately 0.2 lb TSS/lb of COD consumed, which is close to typical yields observed for similar anoxic/anaerobic attached growth systems.

Toxicity Characteristic Leaching Procedure (TCLP) analysis was performed on the biosolids to determine if they would be classified as nonhazardous solids. Selenium concentrations in all three solids samples were below the method detection limit of 0.2 mg/L. For the solids to be considered hazardous, the Se concentration would have to exceed the maximum contaminant level (MCL) of 1 mg/L.

Project 6B – Coal Mining FBR – Aerobic MBBR Pilot

A FBR pilot study was conducted from September 2010 to February 2011 at one of the mining sites in West Virginia for Se removal similar to that described in Project 6A. However, this pilot study also included an aerobic MBBR to aerobically polish the FBR effluent prior to liquid-solids separation.

The main objectives of this pilot study were as follows:

1. Determine the level of BOD polishing required following FBR treatment including increasing the DO concentration.
2. Determine the potential to re-oxidize reduced insoluble elemental selenium to soluble selenite and/or selenate forms in an aerated MBBR polishing treatment step in the absence of liquid-solids separation step prior to aerobic MBBR.
3. Determine the need for an intermediate liquid-solids separation step to remove particulate selenium (selenium as part of TSS) between the FBR and MBBR units to prevent potential reoxidation of selenium in the polishing aerobic MBBR.
4. Simulate various influent flows and loading conditions to define full-scale plant turn-up capacities.

The pilot FBR system for this study was the same as the one used for Project 6A. Operating conditions were also similar to Project 5A, except this pilot was operated at different influent flow rates or HRTs to evaluate Se removal performances at these conditions. The FBR influent (mine water) was heated using an in-line electric heater to maintain a minimum operating temperature of 50°F (10°C) in the FBR.

The aerobic MBBR pilot system used in this pilot study was supplied by N.A. Water Systems (a Veolia water company). The MBBR tank was a stainless steel vessel 4 ft in diameter and 6 ft high. It was filled with neutrally buoyant high density polyethylene (HDPE) carrier media for biofilm growth to approximately 60 percent of the total tank volume. The carrier media had a diameter of 10 millimeters (mm) and height of 7 mm. Mixing of the vessel was accomplished through aeration. The MBBR equipment was located outdoors. Major equipment associated with the MBBR pilot included an aeration blower, instrumentation, piping, aeration grid, and an electrical control panel, housed on a 14 ft long by 6 ft wide skid. The MBBR tank is equipped with a horizontally-mounted wedge wire pipe sieve with appropriate wire spacing to retain the media. Aeration is by a medium bubble system, using 4 mm holes on stainless steel laterals of 1 inch to 1.5 inch diameter and diffusers. The media, FBR effluent, and air are completely mixed resulting in very efficient contact between the biofilm and substrates within the reactor. Air flow was maintained at 24 SCFM (standard cubic feet per minute) to maintain a DO of 2 to 5 mg/L in the tank. To provide additional nitrogen (nutrient) for cell synthesis to sustain adequate bacterial growth under aerobic conditions and to prevent any nitrogen-limiting condition in the MBBR, ammonium sulfate was added to the MBBR to maintain a residual ammonia-nitrogen concentration of at least 1.0 mg/L in the MBBR effluent. Sufficient phosphorus was carried over in the FBR effluent for biological growth in the MBBR. FBR – aerobic MBBR pilot unit operating conditions and performances are summarized in Table 9.

TABLE 9
Pilot Unit Operating Conditions and Performance Summary

Parameter	Units	8 gpm Condition 1			10 gpm Condition 2			12 gpm Condition 3		
		Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max
FBR Influent										
Temperature	°F	39	36	45	47	36	63	42	37	47
pH	s.u.	-	7.5	8.1	-	7.3	8.1	-	7.7	8.0
Nitrate – N ¹ (NO ₃ -N)	mg/L	9.0	4.2	13.3	7.7	2.6	12.5	4.8	3.1	5.5
Se (Total)	µg/L	35.4	22.1	44.1	36.9	26.1	50.8	32.3	39.2	25.8
Se (Filtered)	µg/L	35.7	22.4	46.1	35.7	20.1	51.6	32.2	26.1	35.9
Selenite (Se (IV))	µg/L	0.5	0.4	0.5	0.4	0.3	0.7	0.4	0.4	0.4
Selenate (Se (VI))	µg/L	34.6	26.8	41.7	31.6	22.3	47.3	25.5	21.1	27.7
TSS ¹	mg/L	24	20	34	23	4	45	20	7	30
FBR Reactor										
Temperature after Heater	°F	53	49	58	54	48	61	53	49	57
Reactor Temperature	°F	53	50	61	55	50	63	54	48	58
pH	s.u.	-	6.6	7.1	-	6.7	7.3	-	6.8	7.0
DO	mg/L	0.4	0.2	0.9	0.4	0.2	0.9	0.5	0.3	0.7
Oxidation Reduction Potential (ORP)	mV	-207	-249	-150	-191	-313	-61	-222	-276	-176
Hydraulic Retention Tim (HRT)	min	29	26	30	22	19	25	19	18	21
Chemical Oxygen Demand (COD) Loading ^{a, b, 1}	mg/L	189	167	246	180	148	229	181	144	221
	lb/ft ³ /d	0.58	0.50	0.71	0.72	0.57	0.95	0.83	0.67	0.89
Total Sulfide ¹	mg/L	4.4	1.4	9.5	3.5	1.6	6.5	5.6	3.5	9.5
FBR Effluent										
NO ₃ - N ¹	mg/L	ND	-	-	ND	-	-	ND	-	-
Se (Total)	µg/L	10.5	4.4	14.2	11.6	1.9	26.2	12.5	6.8	18.4
Se (Filtered)	µg/L	2.2	1.4	3.7	2.8	0.9	4.6	3.7	1.6	5.5
Selenite (Se (IV))	µg/L	0.2	0.0	0.3	0.2	0.1	0.5	0.2	0.1	0.4
Selenate (Se (VI))	µg/L	0.6	0.2	1.4	0.5	0.2	1.0	0.9	0.5	1.7
TSS ¹	mg/L	44	27	59	42	27	68	40	30	44

TABLE 9
Pilot Unit Operating Conditions and Performance Summary

Parameter	Units	8 gpm Condition 1			10 gpm Condition 2			12 gpm Condition 3		
		Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max
COD (Total) ¹	mg/L	89	68	120	72	36	104	79	60	128
COD (Soluble) ¹	mg/L	48	30	93	39	15	70	38	14	62
BOD (Total)	mg/L	45	35	65	29	15	47	28	21	37
BOD (Soluble)	mg/L	26	15	51	16	9	31	16	7	29
Observed Yield	lb TSS/ lb COD	0.24	-	-	0.22	-	-	0.21	-	-
MBBR Reactor										
Temperature	°F	54	51	59	56	50	64	54	49	59
DO ^c	mg/L	5.1	2.8	7.9	4.7	1.6	7.8	5.2	3.7	5.8
pH	s.u	-	7.1	7.6	-	7.1	7.9	-	7.3	7.5
HRT ^b	Min	50	48	53	40	38	44	34	32	36
Total Sulfide ¹	µg/L	211	169	330	147	47	230	286	219	458
MBBR Effluent										
Se (Total)	µg/L	14.4	10.4	20.7	14.4	4.7	43.5	18.8	12.3	28.8
Se (Filtered)	µg/L	9.4	3.1	15.0	10.1	4.0	21.7	13.6	4.7	19.0
Selenite (Se (IV))	µg/L	5.3	0.9	7.6	8.7	0.3	21.5	8.0	5.5	9.9
Selenate (Se (VI))	µg/L	0.7	0.3	1.1	0.6	0.3	1.0	1.1	0.6	1.6
TSS ¹	mg/L	55	38	64	48	31	66	51	41	61
COD (Total) ¹	mg/L	67	34	102	52	32	95	66	45	94
COD (Soluble) ¹	mg/L	14	10	20	16	4	42	13	3	28
BOD (Total)	mg/L	27	19	35	21	12	38	26	20	31
BOD (Soluble)	mg/L	3.6	2.4	5.3	3.0	1.4	4.7	4.5	2.0	6.9
Observed Yield	lb TSS/ lb COD	0.37	-	-	0.34	-	-	0.45	-	-

¹ Analysis performed onsite

^a COD loading from MicroC addition + COD in the influent

^b Bed volume for determining COD loading and HRT calculated based on measured expanded bed height and reactor diameter

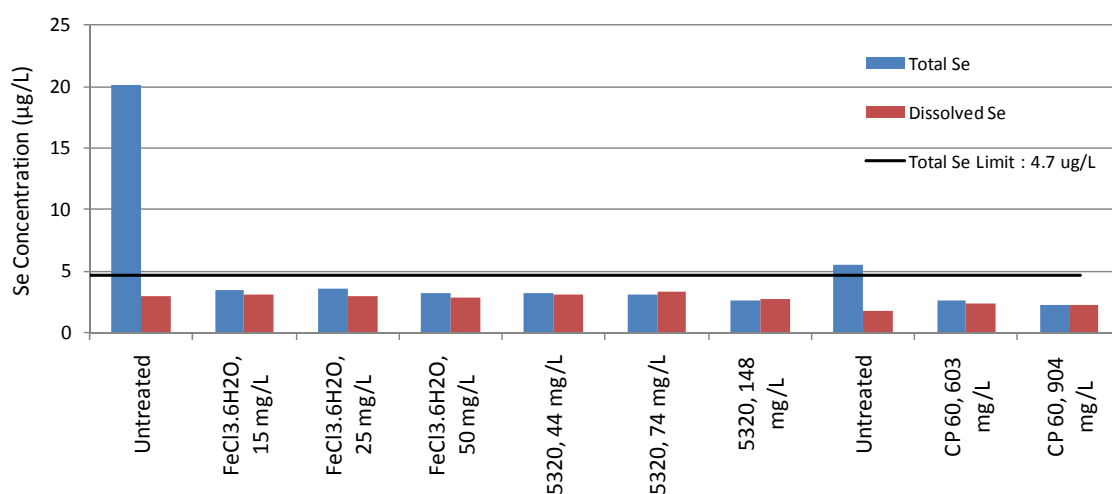
^c DO result adjusted due to change in measurement procedure modified

ND = Non detect

As shown in Table 9, there was some reoxidation of reduced elemental Se to soluble selenite in the aerobic MBBR following FBR. Hence, a liquid-solids separation step was necessary after FBR and before aerobic polishing to remove elemental Se along with biomass (TSS) from the FBR effluent.

To evaluate potential options for liquid-solids separation, bench-scale jar testing was performed on the FBR effluent with organic and inorganic coagulants. The objective was to remove Se-laden biosolids prior to the aerobic polishing step to prevent reoxidation of insoluble elemental Se to soluble oxidized Se forms. Several jar tests were performed to simulate sand filters and ballasted sand clarifier. Based on the TSS production rate with coagulant chemical, ballasted sand clarifier was determined to be a better option as liquid-solids separation process for FBR effluent. Additional coagulation jar tests were performed to simulate the ballasted sand high rate clarification system and to optimize dosages for coagulant and flocculant chemicals. Results of the jar tests on the FBR effluent with the selected coagulants are shown in Figure 5. Note that the total Se concentrations were significantly lower than the concentration of the untreated sample and well below the target total Se value of 4.7 µg/L.

FIGURE 5
Jar Test Results for Se Removal from FBR Effluent



TCLP analysis was performed on the biosolids to determine if they would be classified as nonhazardous solids. Se concentrations in all three solids samples collected at three flow conditions were below the method detection limit of 10.5 µg/L. The Se concentration would have to exceed the MCL of 1 mg/L for the solids to be considered hazardous.

Project 6C – Coaling Mining FBR – Aerobic MBBR Pilot

FBR followed by aerobic MBBR pilot study was conducted at a mining site in British Columbia, Canada for Se removal from March to July 2011. The FBR pilot unit was similar to that described under Project 6A, except the dimensions are slightly different (1.67 ft diameter and 14.75 ft high). The MBBR pilot system was supplied by *World Water Works*. The MBBR consisted of a skid mounted 360-gallon (1.4 cubic meter [m³]) poly tank, 3.4 ft (1.0 m) long by 4.75 ft (1.2 m) wide and 3.7 ft (1.1 m) high. It was filled with HDPE carrier media, with a diameter of 12 mm and height of 12 mm for biofilm growth to approximately 37 percent of the total tank volume. All the pilot units including pumps were located indoors in a heated building for freeze protection.

The FBR influent (mine water) was heated using an in-line electric heater to maintain a minimum operating temperature of 50°F (10°C) in the FBR. Table 10 summarizes FBR pilot

feed water quality based on samples collected during steady-state operation of the pilot plant.

TABLE 10
Pilot Influent Water Quality during Steady-State Operation¹

Parameter	Units	Average	Minimum	Maximum
Temperature ^a	°C	4.3	3.5	5.8
pH ^a	s.u.	—	7.3	8.4
DO ^a	mg/L	11.4	10.1	12.5
Specific conductance ^a	µmhos/cm	1,838	1,061	2,557
ORP ^a	mV	103	23	188
Nitrate, N ^a	mg/L	30.6	12.7	44.4
COD ^a	mg/L	< 3.0	< 3.0	< 3.0
Selenium Total ^b	µg/L	359	155	588
Selenium Filtered ^b	µg/L	357	147	551
Selenium speciation				
Selenite (Se (IV)) ^c	µg/L	0.26	0.05	0.72
Selenate (Se (VI)) ^c	µg/L	381	135	548
Magnesium	mg/L	148	72	212
Calcium	mg/L	245	133	334
Sulfate	mg/L	796	131	1,190
Phosphate, P	mg/L	< 0.01	< 0.01	< 0.01
TDS	mg/L	1,679	788	2,340
TSS	mg/L	7	3	31

¹ Pilot influent sample collection point upstream of the in-line heater

^a Analysis performed onsite

^b Based on 48 samples/data points

^c Based on 22 samples/data points

Since phosphate concentrations were negligible (below method detection limit) in the influent water, all the phosphorous (nutrient) requirements were met by dosing of nutrient solution containing phosphoric acid and by adding micronutrients to the phosphorus solution feed container.

Table 11 lists the various process operating parameters associated with the FBR - MBBR during steady-state operation. The FBR pilot was operated mainly at two different feed flow rates for extended period of time, as indicated below. The electron donor was switched from molasses to MicroCg midway through the study because the FBR was not able to meet the target Se removal performance at the required HRTs with molasses. Although molasses

TABLE 11
Reactor Process Parameters during Steady-State Operation

Parameter	Units	Condition 1			Condition 2a			Condition 2b			Condition 3			Condition 4 ^a		
		11.4 Lpm			5.7 Lpm			5.7 Lpm			11.4 Lpm			11–13 Lpm		
		Molasses			Molasses			MicroCg			MicroCg			MicroCg		
		Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max
FBR																
Influent Temperature	°C	4.0	3.7	4.5	4.4	4.0	5.2	4.1	3.9	4.5	4.4	3.9	5.8	4.7	3.9	5.7
Temperature after Heater	°C	8.9	7.2	14.2	9.0	6.8	11.2	8.6	6.3	9.8	8.6	6.8	11.3	4.2	3.6	6.0
Reactor Temperature	°C	11.5	10.5	16.8	11.7	7.4	14.9	12.2	10.5	15.3	10.6	8.9	13.4	6.6	5.4	7.9
Fluidization Flow	Lpm	80.5	76.6	81.7	84.8	81.7	86.5	83.2	80.1	86.5	81.5	78.4	81.7	74.9	56.6	91.0
Bed Height	m	3.3	3.3	3.4	9.6	8.2	10.7	10.4	8.8	10.8	3.2	2.8	3.4	3.3	3.2	3.5
pH	s.u.	—	6.7	7.2	-	6.7	7.0	-	6.4	7.0	—	6.7	7.1	—	7.0	8.0
DO	mg/L	0.2	0.0	1.8	0.1	0.0	0.2	0.3	0.1	0.8	0.4	0.2	0.7	0.6	0.2	2.3
ORP	mV	-66	-119	-24	-132	-150	-90	-148	-194	-114	-169	-190	-153	-124	-164	-33
HRT	Min	60	58	61	104	89	116	113	96	118	57	50	61	56	49	67
COD Loading ^{b, c}	mg/L	208	187	241	384	368	414	354	223	447	261	261	261	222	133	295
	kg/m ³ /d	5.0	4.4	6.0	5.3	4.8	6.2	4.7	3.3	5.6	6.6	6.1	7.5	5.8	3.2	7.8
MBBR																
Temperature	°C	12.2	11.3	17.0	13.7	11.0	16.5	14.0	12.5	16.8	11.6	9.9	13.9	7.5	5.9	9.1
DO	mg/L	4.1	1.5	6.3	3.7	2.4	5.8	4.2	1.3	6.5	4.2	3.5	5.0	5.9	1.8	8.4
pH	s.u	—	7.4	7.8	-	7.6	7.9	-	7.5	7.8	—	6.9	7.5	—	7.3	8.2
HRT	Min	61	61	61	121	121	121	121	121	121	61	61	61	57	52	65

^a Cold weather data

^b COD loading from molasses or MicroC addition

^c Bed volume for determining COD loading and HRT was based on measured expanded bed height and reactor diameter

primarily contains sugar based compounds, it consists of organic fractions with varying levels of degradability, some of which are slowly degradable and some non-degradable fractions. As a result, molasses is not as readily biodegradable at lower HRTs as MicroCg, which is a proprietary engineered carbon source.

The FBR pilot was operated at four test conditions:

- Condition 1: 3.0 gpm (11.4 liters per minute [Lpm]) flow – Molasses as carbon source
- Condition 2: 1.5 gpm (5.7 Lpm) flow – Carbon source switched from Molasses (Condition 2a) to MicroCg (Condition 2b)
- Condition 3: 3.0 gpm (11.4 Lpm) flow – MicroCg as carbon source
- Condition 4: 3.0–3.5 gpm (11–13 Lpm) flow – MicroCg as carbon source, no heating of influent

Despite colder influent water temperatures, a minimum temperature of 10°C (50°F) was maintained in the reactor using the inline heater at the first three test conditions. During test condition 4, when no heating of the influent was employed, the average reactor temperature was 6.6 °C, which was about 2 °C warmer than the influent during the same period.

Substantial foaming was observed on the top of the FBR column using cane molasses as the carbon feed. The foam prevented operators from easily obtaining bed height readings, as well as verifying that the biomass separator air supply was flowing. Hence, de-foaming agent was dosed on the surface of the water at the top of the FBR column.

Table 12 summarizes effluent water quality based on samples collected during the various operating conditions of the pilot plant. Effluent filtered Se concentration of $\leq 10 \mu\text{g/L}$ was considered acceptable due to influent high Se concentrations. Filtered Se (filtered through a 0.1 micron filter) is considered to be true representation of the FBR Se removal performance since the FBR effluent also contains some reduced elemental Se in colloidal form in addition to attached with biomass because of the nature (fluidized media with attached biomass sloughing off in the effluent) of FBR technology. Reduced elemental Se is typically removed in the downstream liquid-solids separation unit along with biomass, with chemical addition compared to other treatment technologies where the reduced Se is retained within the bioreactors since they act like biological filters.

Bench-scale jar testing was performed on the FBR pilot effluent to simulate liquid-solids separation. The primary objective was to remove colloidal Se-laden biosolids prior to the MBBR aerobic polishing to prevent reoxidation of some insoluble elemental Se to soluble oxidized Se forms. Jar tests were performed to simulate high rate clarification (ballasted sand clarification) of the FBR effluent using ferric chloride as the coagulant and an emulsion polymer, *Drewfloc 2205*, as the flocculant. Treatment of FBR effluent with coagulant chemical and flocculant chemical in the presence of microsand resulted in rapid formation and settling of heavy solids floc, and produced a clear supernatant with low turbidity and TSS. Figure 6 shows the results from the three sets of jar tests performed to demonstrate removal of particulate Se-containing biosolids. Most of the Se reduction is due to removal of particulate and colloidal Se; however, some of the reduction in filtered Se may also as a result of the removal of selenite as a result of iron co-precipitation. Based on the jar test results on FBR

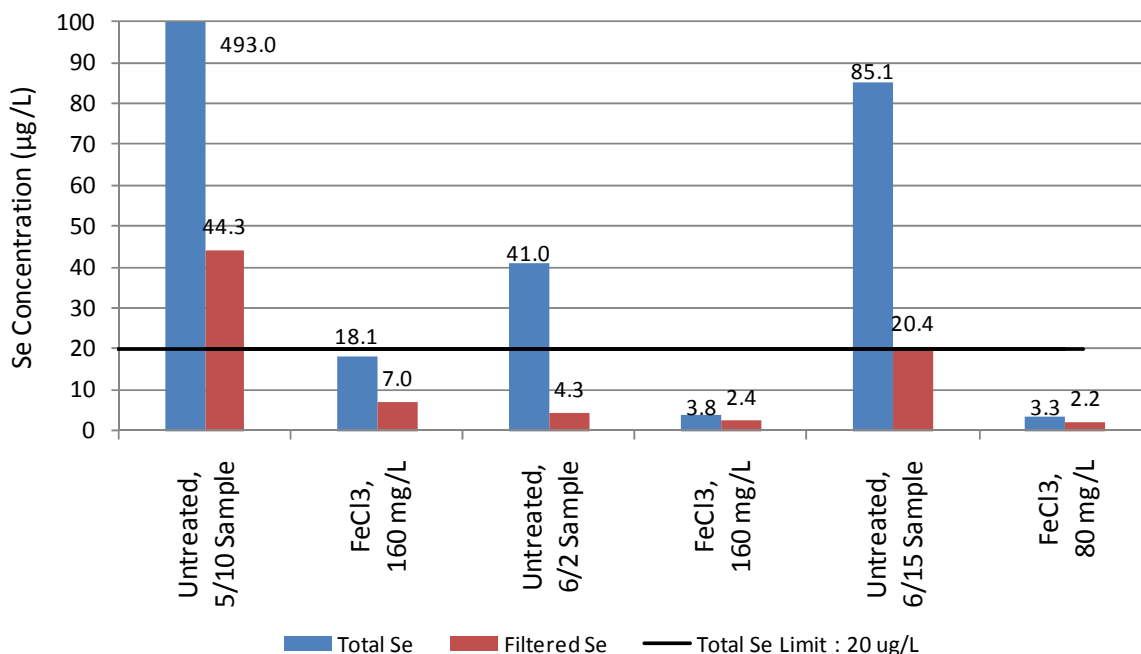
TABLE 12
Pilot Effluent Water Quality during Steady-State Operation

Parameter	Units	Condition 1 11.4 Lpm, Molasses			Condition 2a 5.7 Lpm, Molasses			Condition 2b 5.7 Lpm, MicroCg			Condition 3 11.4 Lpm, MicroCg			Condition 4 ^b 11-13 Lpm, MicroCg,		
		Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max
FBR																
NO ₃ -N ^a	mg/L	1.3	0.2	8.6	0.5	0.2	0.7	0.3	0.0	0.7	0.4	0.0	0.9	0.1	0.1	0.1
Se (Total)	µg/L	251	115	435	247	138	493	169	60	545	70	23	195	65	23	211
Se (Filtered-0.45 µm)	µg/L	132	44	313	26.4	9.8	44	12.8	2.3	27.0	10.7	2.3	20.4	18.0	6.8	51.6
Se (Filtered-0.1 µm)	µg/L	-	-	-	10.8	6.1	15.5	4.6	1.7	9.7	5.1	1.6	7.8	7.4	3.6	16.4
Selenite (Se (IV))	µg/L	101	3	268	14.5	1.5	36.4	5.7	1.2	10.3	4.3	2.5	7.8	2.4	0.6	4.8
Selenate (Se (VI))	µg/L	10.4	4.1	47.2	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.3
TSS ^a	mg/L	32	21	50	47	36	68	32	14	80	34	12	67	19	2	38
COD (Total) ^a	mg/L	229	112	300	273	134	400	240	136	424	218	126	384	189	84	388
COD (Soluble) ^a	mg/L	174	88	300	164	60	232	157	72	272	148	82	308	133	36	312
BOD (Total)	mg/L	84	25	256	106	82	140	113	43	194	104	58	158	73	36	182
BOD (Soluble)	mg/L	58	12	191	79	71	87	89	27	167	84	54	131	55	22	143
Observed Yield	lb TSS/ lb COD _R	0.32	0.11	0.56	0.20	0.12	0.37	0.28	0.20	0.37	0.25	0.11	0.46	0.21	0.20	0.21
MBBR																
Se (Total)	µg/L	294	138	685	270	156	524	168	62	375	84	4	246	81	29	219
Se (Filtered-0.45 µm)	µg/L	153	60.3	312	77	24.9	224	36.6	6.2	62.4	12.0	3.5	27.5	21.5	9.4	51.7
Se (Filtered-0.1 µm)	µg/L	-	-	-	21.4	17.5	25.2	16.1	4.4	26.5	8.2	2.8	20.2	11.6	4.6	30.6
Selenite (Se (IV))	µg/L	103	4.5	264	11.4	5.2	21.0	5.7	3.2	9.4	1.7	1.1	2.6	5.0	0.9	11.1
Selenate (Se (VI))	µg/L	16.8	0.1	58.3	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.1	0.3
TSS ^a	mg/L	29	11	80	73	24	105	38	15	78	57	23	94	40	9	87
COD (Total) ^a	mg/L	141	68	182	170	94	266	95	44	168	116	48	248	127	46	300
COD (Soluble) ^a	mg/L	105	64	140	89	46	140	42	14	112	60	9	168	76	6	234
BOD (Total)	mg/L	46	12	81	86	40	220	47	7	108	44	24	72	25	15	36
BOD (Soluble)	mg/L	20	4	68	13	7	21	9	2	30	13	2	46	12	9	19
NH ₃ -N ^a	mg/L	1.5	0.0	2.8	0.6	0.0	2.4	1.6	0.0	4.5	0.7	0.1	2.0	2.3	0.2	16.4
Observed Yield	lb TSS/ lb COD _R	0.38	0.38	0.38	0.52	0.13	0.76	0.28	0.24	0.35	0.31	0.16	0.55	0.33	0.15	0.67

^a Analysis performed onsite ; ^b Cold weather data

effluent with MicroCg as the carbon source, the average sludge production from chemical addition was 104 mg/L, which is approximately two times the average FBR effluent TSS of 58 mg/L during the jar tests.

FIGURE 6
FBR Effluent Colloidal Se Removal Jar Test Results



TCLP analysis was performed on both the FBR biosolids and on the solids generated during jar testing of the FBR effluent to determine if they would be classified as nonhazardous solids. Se concentrations in two FBR biosolids samples were 0.54 and 0.49 mg/L, which are below the MCL (maximum contaminant level) of 1 mg/L for the solids to be considered hazardous. TCLP on biosolids generated during jar testing of the FBR effluent, which would be representative of the full-scale solids production, had a Se concentration of less than the method detection limit of 20 µg/L, thereby rendering non-hazardous solids for disposal.

Project 6D – Coal Mining ABMet® Pilot

ABMet® pilot study was conducted from March to July 2011 at a mining site in British Columbia, Canada, for Se removal. The ABMet® pilot system was supplied by GE. It included one bioreactor train of two ABMet® bioreactor cells that operated in series. The bioreactor cells were 2.3-m³ (600-gallon) polyethylene tanks, which contained a mixture of microbes and GAC that supports the microbial growth. The bioreactor tanks were housed in a 12.2-meter (40-foot) long by 2.4-meter (8-foot) wide container with temperature control.

The ABMet® influent (mine water) was heated using an in-line electric heater to maintain a minimum operating temperature of 50°F (10°C) in the reactors. The ABMet® pilot feed water quality was the same as the influent water quality presented in Table 10 under Project 6C.

A proprietary nutrient solution was fed as the electron donor to satisfy COD requirements for removal/reduction of DO, NO₃-N, selenate/selenite, and some sulfate. The average

concentration of soluble COD in the reactor influent with nutrient addition ranged between 160 and 340 mg/L. Nutrient solution feed rates were adjusted remotely by GE based on the process performance. The ABMet® pilot was operated at the following three test conditions:

- Condition 1: 1.5 gpm (5.7 Lpm) flow
- Condition 2: 2.0 gpm (7.6 Lpm) flow
- Condition 3: 1.8 gpm (6.8 Lpm) flow – No heating of influent

During the operation of the ABMet® system, degas events were used to release pockets of gases (mainly nitrogen and carbon dioxide) that build up in the GAC bed during normal operation due to bacterial activity, especially in the stage 1 reactor. This maintains the downward flow without significant head loss through the GAC filters. Degas events were initially performed as required but were optimized throughout the pilot to a final frequency of once per day. Table 13 compares the ABMet® steady state operational parameters at the three test conditions listed above.

TABLE 13
ABMet® Pilot Process Parameters during Steady-State Operation

Parameter	Units	Condition 1 5.7 Lpm			Condition 2 7.6 Lpm			Condition 3 6.8 Lpm, cold water data		
		Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max
Influent Temperature	°C	4.0	3.7	4.5	4.2	3.5	5.8	4.7	3.9	5.7
Temperature after Heater	°C	9.3	7.2	14.2	8.8	6.3	11.5	4.2	3.6	6.0
Effluent Temperature	°C	11.3	8.1	12.9	10.7	8.1	13.1	6.8	5.2	9.4
Effluent pH	s.u.	–	7.1	7.4	–	6.9	8.0	–	7.7	8.5
Effluent DO	mg/L	3.5	1.7	4.7	1.0	0.1	4.6	0.7	0.3	2.2
Effluent ORP	mV	-130	-165	-84	-198	-304	-96	-242	-350	-204
EBCT ^a										
Reactor 1	Min	247	240	258	187	179	209	200	191	205
Reactor 2	Min	326	317	341	247	236	275	264	252	271
COD Loading ^{a, b}	mg/L	341	267	414	232	101	385	164	154	189
	kg/m ³ /d	0.9	0.7	1.1	0.8	0.3	1.3	0.5	0.5	0.6

^a Bed volume for determining COD loading and EBCT was calculated based on bed height and reactor tank diameter information provided by GE

^b COD loading based on nutrient solution addition to both reactors 1 and 2 and calculated from dosing rate information provided by GE

Table 14 summarizes effluent water quality based on samples collected during steady-state operation of the pilot plant at the three test conditions.

TABLE 14
ABMet® Effluent Water Quality during Steady-State Operation

Parameter	Units	Condition 1 5.7 Lpm			Condition 2 7.6 Lpm			Condition 3 6.8 Lpm, cold water data		
		Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max
NO ₃ -N ^a	mg/L	0.4	0.1	0.6	0.6	0.0	6.8	0.3	0.2	0.6
Se (Total)	µg/L	9.6	7.5	12.1	10.2	4.1	24.5	4.7	3.2	6.1
Se (Filtered-0.45 µm)	µg/L	5.7	4.6	7.4	7.3	3.2	17.7	4.0	1.9	5.8
Se (Filtered-0.1 µm)	µg/L	—	—	—	5.1	3.1	11.5	3.4	1.9	5.2
Selenite (Se (IV))	µg/L	1.2	0.5	2.6	2.5	0.8	4.6	1.2	0.3	2.0
Selenate (Se (VI))	µg/L	0.4	0.1	2.0	0.1	0.1	0.3	0.2	0.1	0.3
TSS ^a	mg/L	8	2	23	8	0	25	2	0	7
COD (Total) ^a	mg/L	42	16	61	55	10	118	26	13	43
COD (Soluble) ^a	mg/L	44	26	67	50	6	144	22	5	34
BOD (Total)	mg/L	12	4	29	24	3	85	4	2	8
BOD (Soluble)	mg/L	7	3	18	21	2	76	3	2	5
ABMet® Degas/ Backwash										
TSS	mg/L	—	—	—	58	29	147	17	17	17
Se (Total)	µg/L	—	—	—	147	10	321	104	68	128
Se (Filtered-0.45 µm)	µg/L	—	—	—	102	5	291	49	25	84

^a Analysis performed onsite
—Not Measured

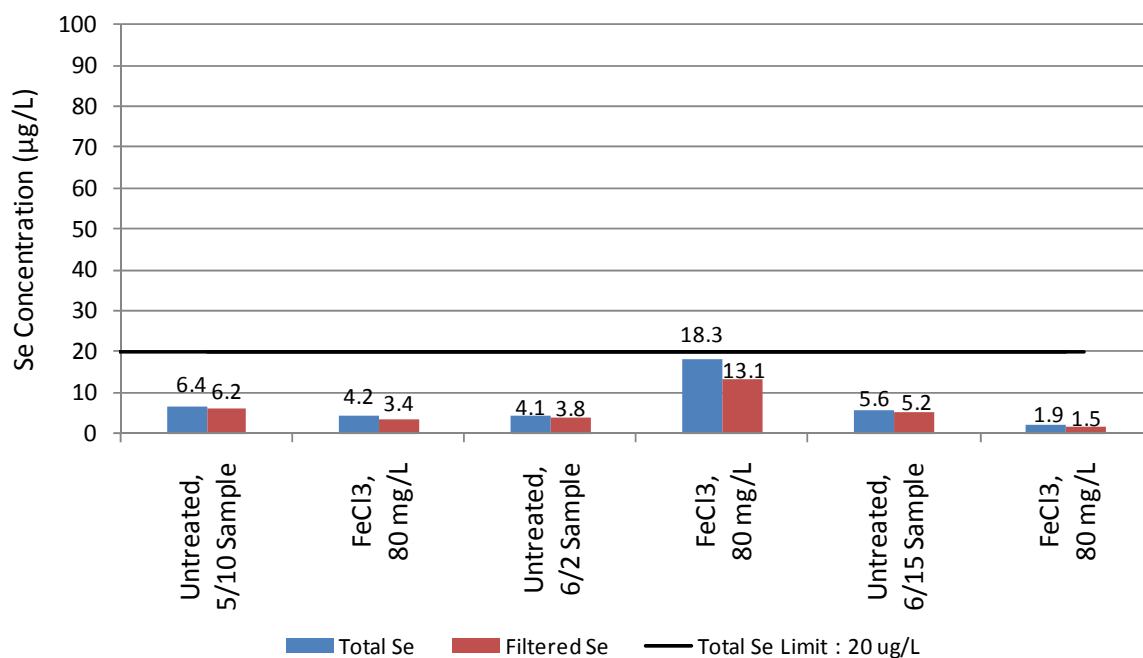
Flow through the bioreactors is estimated to have been lower than 7.6 Lpm due to the periodic bypass of influent water from the reactor caused by high head loss. Periodic high head loss is attributable to hydraulic design limitations of the pilot unit and the un-optimized degas event frequency existing throughout most of the pilot study. It is estimated that the actual flow through the bioreactor 1 could be 4.7 Lpm, which would equate to roughly 4.0 hours EBCT. The system was able to maintain Se removal performance during Condition 3 with an average influent water temperature 4.2°C and an average reactor temperature of 6.8°C.

Also, the pilot data indicates the soluble Se concentration in the backwash waste stream (102 and 49 µg/L for test conditions 2 and 3, respectively) was significantly higher than the effluent selenium concentration measured while the unit was in production. The higher filtered (soluble) Se concentrations in the backwash waste stream was probably due to untreated influent water accumulated on the top of the carbon bed in the head space prior to requiring backwash that is flushed out in the backwash waste stream. The backwash waste stream will have a higher Se concentration than the treated effluent used for the backwash.

Since the ABMet® is a biological filter; the effluent TSS was low, with the average concentration less than 10 mg/L at all three test conditions. This indicates that most of the biosolids and reduced elemental Se was captured inside the reactor media. Average TSS concentration of approximately 60 and 20 mg/L were measured in the backwash waste stream for test Conditions 2 and 3, respectively (Table 14). Due to the packed bed biofilter nature of the ABMet® system, the biological yield of the system was not determined.

Bench-scale jar testing was performed on the ABMet® pilot effluent to remove colloidal Se particles to simulate liquid-solids separation, although this may not be necessary since the GAC bed acts as filters, unlike FBR. Jar tests were performed to simulate high rate clarification (ballasted sand clarification) using ferric chloride as the coagulant and an emulsion polymer, *Drewfloc 2205*, as the flocculant. Figure 7 shows the results from the three sets of jar tests performed to demonstrate removal of particulate Se-containing biosolids.

FIGURE 7
ABMet® Effluent Colloidal Se Removal Jar Test Results



Project 6E – Confidential Refinery FBR Pilot

An FBR pilot study was conducted in 2011 on a biologically treated refinery wastewater effluent at a site in the USA for selenium removal. The FBR pilot unit consisted of a 3-foot (diameter) by 17-ft (height), stainless steel (304 SS) column filled with 1,200 lb of GAC media. The initial bed height with GAC was approximately 7.5 feet with an expanded bed height of about 9.75 feet, with fluidization of GAC without biomass growth. The FBR column was located outdoors. Major equipment associated with the FBR pilot included a fluidization pump, air compressor, chemical feed pumps, instrumentation, piping and an electrical control panel, housed in an 8× 40-foot equipment container. The FBR pilot was operated at influent (biologically treated effluent) flow rates of 10 gpm, 15 gpm, and 19 gpm, with a fluidization flow of approximately 100 gpm required for the target bed expansion of approximately

30 percent without biomass growth. Target bed expansion with biomass growth is approximately 60 percent of the unexpanded bed height.

FBR influent total Se concentration varied from 70 to 230 $\mu\text{g/L}$ with Se predominantly occurring in a soluble oxidized selenite (Se (IV)) form. Influent average TSS, TDS, and sulfate concentrations were approximately 50 mg/L, 2,000 mg/L, and 300 mg/L, respectively. Influent temperature, pH, and DO varied from 70 to 80°F, 7.0 to 7.5 s.u., and 3.0 to 5.0 mg/L, respectively. Influent soluble COD, nitrate-N, and ortho-phosphate varied from 100 to 200 mg/L, 3 to 10 mg/L, and 0.2 to 1.5 mg/L, respectively.

MicroCg, an engineered organic carbon, was fed as the electron donor (carbon substrate/COD source) at a dosage based on satisfying COD requirements for removal/reduction of DO, $\text{NO}_3\text{-N}$, selenate/selenite, and some sulfate. Phosphorus (macronutrient) and micronutrients were added for biological growth.

Average HRTs of the FBR at 10 gpm, 15 gpm, and 19 gpm flow rates were approximately 60 minutes, 42 minutes, and 35 minutes, respectively, based on expanded bed volume. FBR was monitored for ORP, temperature, DO, pH, and expanded bed height. General operating ranges for these parameters were approximately -150 to -300 mV, 70 to 80°F, 0.2 to 1.2 mg/L, 6.6 to 7.8 s.u., and 11.5 to 12.8 ft, respectively. DO measurements may have been inaccurate since they are high at low operating ORP.

Results of the pilot study are summarized below.

- The pilot study showed the FBR was able to consistently convert > 87 percent of the influent dissolved selenium species to particulate elemental selenium at the three HRT conditions that were tested.
- At the 15 gpm test condition (HRT= 42 minutes), lower influent selenium concentrations were experienced (70 to 130 $\mu\text{g/L}$) and the FBR was able to maintain dissolved selenium concentrations of $\leq 10 \mu\text{g/L}$. At 19 gpm (HRT= 35 minutes) and 10 gpm (HRT = 60 minutes) test conditions, higher influent selenium concentrations (150 to 230 $\mu\text{g/L}$) were experienced and the FBR was able to maintain dissolved selenium concentrations of $\leq 20 \mu\text{g/L}$.
- Solids in the WWTP Clarifier effluent, which was the pilot influent, had to be regularly removed from the influent/feed tank by either skimming from the top or draining and cleaning the bottom. Removal of these solids prevented their entry and accumulation in the FBR and avoided potential adverse effect on the performance. A full scale system should provide removal of this material upstream of the FBR by pretreatment such as a dissolved air flotation (DAF) process or sand filters.
- Toxicity characteristic leaching procedure test results showed that the solids generated in the FBR pilot unit treatment process would be classified as non-hazardous for selenium. However, for industrial wastewaters other than surface coal mining water, this test needs to be conducted for other parameters of concern also.

Project 6F – Confidential Refinery FBR Pilot

A second FBR pilot study was conducted in 2011 on a biologically treated refinery wastewater effluent at a site in the USA for Se removal. The FBR pilot unit consisted of a 2-foot (diameter) by 13.5-foot (height), stainless steel (304 SS) column filled with 400 lb of GAC media. Initial bed height with GAC was approximately 6 feet with an expanded bed height of about 7.5 feet with fluidization of GAC without biomass growth. The FBR column was located outdoors. Major equipment associated with the FBR pilot included a fluidization pump, air compressor, chemical feed pumps, instrumentation, piping and an electrical control panel, housed in an 8×10-foot equipment container (Conex). The FBR pilot was operated at the influent (biologically treated effluent) flow rates of 5.0 gpm, and 4.0 gpm with a fluidization flow of approximately 35 gpm required for the target bed expansion of approximately 25 percent without biomass growth. Target bed expansion with biomass growth is approximately 60 percent of the unexpanded bed height.

A Siemens Membrane Bioreactor (MBR) was used for liquid-solids separation of the FBR effluent following the FBR pilot unit. The MBR pilot consisted of an anoxic tank, aeration tank, and a membrane tank with ultrafiltration (UF) membrane module. The membrane filter unit capacity was 2.0 gpm. Nitrogen was used instead of air to prevent exposing the elemental particulate selenium to oxygen, which could result in potential re-oxidation back to soluble forms. The membrane tank system incorporated a nitrogen scour to minimize the accumulation of suspended solids on the membrane surface and to prevent reoxidation of elemental Se to soluble oxidized forms.

FBR influent total Se concentration varied from 29 to 85 µg/L, with Se predominantly occurring in a soluble oxidized selenite (Se (IV)) form. Influent TSS, soluble COD, nitrate-nitrogen, and ortho-phosphate varied from 20 to 540 mg/L, 20 to 420 mg/L, 0.5 to 5.0 mg/L, and 2.0 to 19.5 mg/L, respectively. Influent average TDS, and sulfate concentrations were approximately 1,400 mg/L, and 290 mg/L, respectively. Influent temperature, pH, and DO varied from 68 to 98°F, 6.0 to 8. s.u., and 0.5 to 5.0 mg/L, respectively.

MicroCg, an engineered organic carbon, was fed as the electron donor (carbon substrate/COD source) at a dosage based on satisfying COD requirements for removal/reduction of DO, NO₃-N, selenate/selenite, and some sulfate. Adequate phosphorus (macronutrient) was present in the influent wastewater and hence only micronutrients were supplemented for biological growth.

Average HRTs of the FBR of 5.0 gpm and 4.0 gpm flow rates were approximately 45 minutes, and 60 minutes, respectively, based on expanded bed volume. FBR was monitored for ORP, temperature, DO, pH, and expanded bed height. General operating ranges for these parameters were approximately -100 to -370 mV, 69 to 96°F, 0.05 to 0.8 mg/L, 6.8 to 7.7 s.u., and 8.5 to 10 feet, respectively. DO measurements might have been inaccurate since they are high at low operating ORP.

Results of the pilot study are summarized below:

- The average pilot system effluent filtered selenium concentration in the FBR effluent was 6.6 µg/L at the 60-minute HRT which was above the target value of 4.6 µg/L. This may be due to complexed organic selenium in the biologically treated effluent that may not have been broken down by bacteria and removed with biological reduction. Another

potential issue may have been the impact of the influent solids on the FBR's performance. Accumulation of influent solids within the FBR could reduce the FBR's performance by causing short circuiting and reduced contact with the active biomass attached to GAC that reduce selenite and selenate to elemental selenium.

- Significant variation in influent COD and TSS impacted operations and performance of the pilot system. Swings in influent COD concentration made achieving the optimal dose of electron donor (MicroCg) very difficult. Elevated concentrations in TSS required daily in-bed cleanings.
- The membrane module was successfully cleaned, backwashing with hypochlorite followed by a caustic soak. Citric acid cleaning might also be required during long-term operation.
- TCLP test results on the sludge generated in the FBR pilot unit treatment process were non-detect for selenium, and as such, would be classified as non-hazardous for selenium.

Project 6G – Power Plant ABMet® Full-Scale Plant

During 2010 to 2011, a power company in West Virginia installed a GE ABMet® biological reduction system for the purpose of reducing internal waste stream selenium concentrations. The plant was required to achieve a monthly average final effluent limitation of 33 µg/L. The ABMet® system became operational in the 1st quarter of 2012. The basic design was consistent with that described in the 2010 NAMC report (Section 4.4.2.2). The average flow rate of the waste streams entering the bioreactor is approximately 0.5 million gallons per day (MGD). The installed capital cost was approximately \$30 million.

The system is achieving removal efficiencies of total selenium (final bioreactor outlet concentrations range from 0.7 to 2.0 µg/L). Influent concentrations of selenium and bioreactor effluent soluble COD and BOD were not available. Also, other information such as back wash rate and frequency and back wash water, TSS and Se forms and their concentrations were not available.

7.0 Passive Biological Treatment

Five pilot studies and two full-scale passive biological treatment projects undertaken since 2010 have demonstrated reduction of selenium in coal mine drainage, gravel mine seepage, reverse osmosis (RO) membrane concentrate, and contaminated groundwater. This section summarizes key findings of these studies and full-scale installations.

Project 7A – Pilot Study of BCR for Coal Mine

Two BCR pilot systems comprised of four 55-gallon barrels each were constructed and sampled at two reclaimed coal mine outlets in southern Appalachia. One system received inflow by gravity in an upflow configuration for 171 days, and the other received pumped inflow in a downflow configuration for 333 days. Key findings of the study are:

- Average selenium concentration reductions ranged from 83 to 92 percent through a water temperature range of 4.2°C to 29.4°C. During December 2011-February 2012, the average minimum and maximum air temperatures were 3°C and -2.1°C, respectively. The average water temperature during this period was 8.2°C.

- For barrels with average inflow selenium of 12.2 µg/L, average outflow selenium concentrations ranged from 1.3 to 2.4 µg/L. For barrels with average inflow selenium of 8.4 µg/L, average outflow selenium concentrations ranged from 0.74 to 1.0 µg/L.
- Selenium removal was effective at all HRTs tested (12 to 24 hours).
- Cold temperatures (below freezing) did not significantly impact selenium removal rates and selenium outflow concentrations never exceeded the monthly average discharge limit of 4.7 µg/L.
- Substrate profile testing at the conclusion of the study typically found higher total selenium concentrations at the inflow end of the barrel, consistent with expectations that selenium removal is a load-dependent, first-order removal process.
- Selenium speciation of substrate samples indicates that in the early stages of selenium removal, the dominant mechanism is reduction of selenate to reduced forms of selenium that are weakly adsorbed to the substrate, with approximately more than half being attributable to selenite. Highly immobile elemental selenium and/or selenosulfide account for about a quarter of the total selenium retained, while very little metal selenide was found.
- A media mix of 20 percent wood chips, 35 percent sawdust, 25 percent field hay, 5 percent sphagnum peat moss, 10 percent mushroom compost, and 5 percent limestone chips appeared to balance high treatment performance with moderate production of byproducts.

Project 7B – Pilot Study of BCR for Coal Mine

One BCR pilot system comprised of four 55-gallon barrels was constructed and sampled at an outlet from a reclaimed coal mine valley fill drain in southern Appalachia. The system was gravity-fed in an upflow configuration and operated for 90 days in the summer of 2010.

- Four media recipes were tested (Table 15). A media mix of 20 percent wood chips, 20 percent sawdust, 15 percent field hay, 20 percent peat moss, 20 percent organic peat, and 15 percent limestone chips appeared to balance high treatment performance with moderate production of byproducts.
- Average selenium concentration reductions ranged from 85 to 88 percent in three barrels with a mixture of organic media, and 46 percent in a barrel of only peat moss, through a water temperature range of 12°C to 39°C (Table 16).
- For an average inflow selenium of 23.8 µg/L, average outflow selenium concentrations ranged from 2.8 to 3.7 µg/L for the mixed organic media barrels, and 12.8 µg/L for the peat barrel.
- Selenium removal was effective at all HRTs tested (12 to 24 hours), see Figure 8.
- Substrate profile testing at the conclusion of the study typically found higher total selenium concentrations at the inflow end of the barrel.
- Selenium speciation of substrate samples indicates that in the early stages of selenium removal, the dominant mechanism is reduction of selenate to reduced forms of selenium that are weakly adsorbed to the substrate, with approximately more than half being attributable to selenite. Highly immobile elemental selenium and/or selenosulfide account for about a quarter of the total selenium retained, while very little metal selenide was found.

TABLE 15
Barrel Study Media Composition

Tank	Peat Moss	Organic Peat	Composted Manure	Sawdust	Wood Chips	Hay	Limestone Chips
A	100%	--	--	--	--	--	--
B	20%	20%	--	20%	20%	15%	5%
C	--	--	15%	47%	16%	16%	6%
D	--	--	23%	30%	20%	20%	7%

FIGURE 8
Total Selenium by Media Type

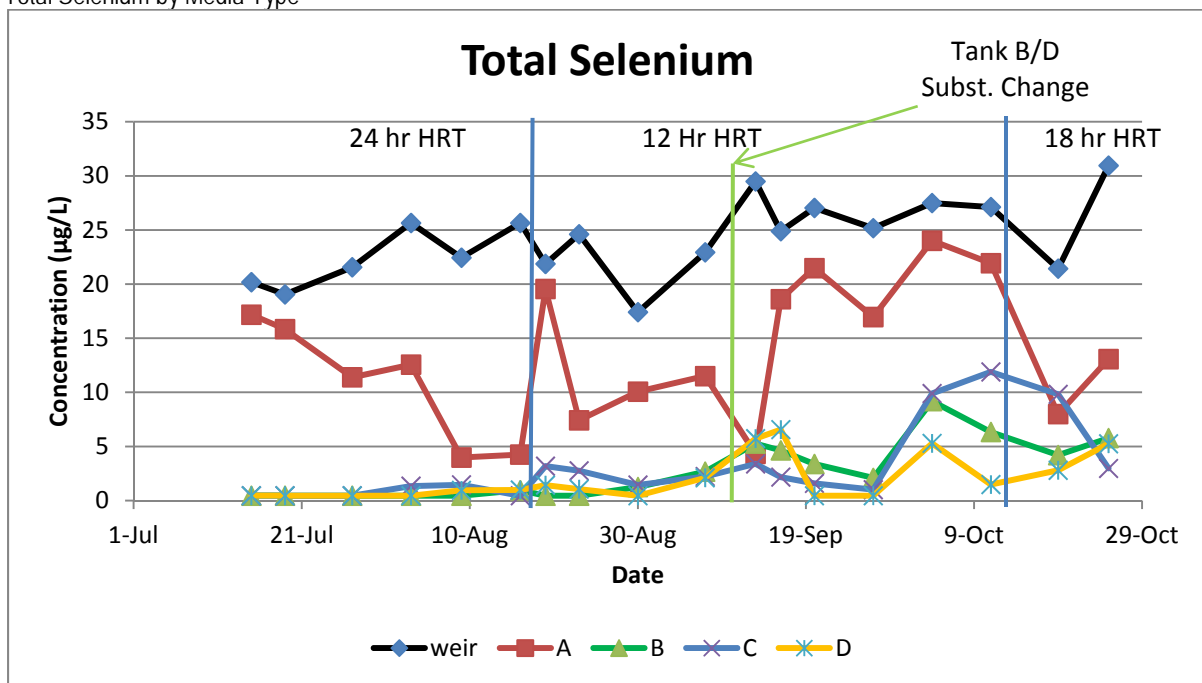


TABLE 16
Project 2-B Pilot Study Results

Barrel	Statistics	pH (s.u.)	Temp (°C)	Conductivity (µmhos)	TSS (mg/L)	Selenium (µg/L)	Dissolved Selenium (µg/L)	Sulfates (mg/L)	TDS (mg/L)	Dissolved Oxygen (mg/L)	Turbidity (NTU)	BOD (mg/L)	COD (mg/L)
Influent	Minimum	6.7	13.0	937	2.0	17.41	16.95	30	676	3.35	0.2	ND	5.4
	Average	7.0	14.7	1341	3.0	23.83	23.26	439	1000	7.04	1.2	ND	19.9
	Maximum	7.5	22.0	1665	5.0	30.95	30.66	760	1270	13.10	7.2	ND	40.2
Barrel A	Minimum	5.1	12.0	910	3.0	1.13	0.38	25	140	0.58	0.1	2.0	10.7
	Average	6.7	22.9	1328	6.6	12.80	121.38	406	932	1.92	2.6	3.0	32.7
	Maximum	7.2	39.0	1547	15.0	42.01	22.38	660	1200	5.28	19.2	4.0	72.3
Barrel B	Minimum	6.4	12.0	973	2.0	0.83	0.37	7	188	0.45	0.3	2.0	18.8
	Average	6.8	22.9	1276	10.7	3.88	3.65	284	900	1.12	103.6	33.8	192.1
	Maximum	7.0	39.0	2679	30.0	9.19	8.98	700	1360	2.70	344.1	179.0	1152.0
Barrel C	Minimum	6.5	12.0	970	2.0	1.01	0.33	15	198	0.29	2.5	3.0	5.4
	Average	6.9	21.9	1388	10.0	4.47	3.43	328	690	0.88	131.7	80.3	125.9
	Maximum	7.2	35.0	1574	30.0	11.89	11.26	640	1325	2.28	613.7	274.0	584.0
Barrel D	Minimum	6.6	12.0	964	2.0	0.95	0.60	7	197	0.43	2.1	2.0	13.4
	Average	6.9	21.6	1453	9.3	2.89	2.76	298	946	1.06	92.8	28.5	71.7
	Maximum	7.2	37.0	2538	30.0	6.56	6.24	620	1425	2.80	334.3	148.0	348.3

Project 7C – Two Coal Mine Full-scale Selenium Passive Treatment Systems

Using the design parameters developed during the barrel studies, two full scale passive treatment systems were constructed in southern Appalachia to treat effluent from two separate coal mining outfalls for selenium removal. The first passive treatment system (PTS-A) consists of four cells in sequence: a downflow biochemical reactor using the substrate mix identified in Project 6B, an upflow biochemical reactor using peat substrate, a fill-and-drain subsurface flow wetland, and a surface flow wetland. Average selenium concentration at the PTS-A site (influent) was 12 µg/L with an average flow rate of 60 gpm, but the system was designed to process up to 100 gpm during storm events. The initial BCR cell is 0.13 acre and the total footprint of the passive treatment system is 0.54 acre. Startup of PTS-A was initiated in July 2011 during a period of below average flow rates. The average flow rate between July 2011 and January 2012 was 10 gpm, not including three storm events where the flow was measured at 50, 70, and 70 gpm. Influent selenium concentration averaged 11 µg/L, while the selenium in the discharge has been consistently below the detection limit (1.08 µg/L). The cost for the design and construction of this system was approximately \$762,000.

The second passive treatment system (PTS-B) consists of three cells: an initial “head tank” cell designed to equalize stormwater inflow by detaining water during storm events and then slowly releasing the water over time; a large, 0.51-acre layered upflow BCR cell with Project B substrate mixture overlain by peat substrate; followed by a single 0.27-acre surface flow wetland for polishing. Water flows into an existing 0.38-acre sedimentation pond before discharging. Selenium concentration at the PTS-B site (influent) averaged 24 µg/L, with an average flow rate of 190 gpm. Startup of PTS-B was in November 2011 during the onset of cooler temperatures and wetter conditions at the site. With the exception of the first week of startup, the system has consistently been receiving flow at rates above the design average of 263 gpm between November 2011 and February 2012, with an average flow rate of 309 gpm. Influent selenium concentration was initially 23 µg/L, but steadily decreased to 9 µg/L through early 2012. Selenium concentration in the system outflow has been consistently below discharge limits, averaging 3.33 µg/L (4.79 µg/L maximum) since startup. The construction cost for this full-scale system was approximately \$700,000.

Project 7D – Pilot Study for Coal Mine Gravel Drainage Treatment

Selenium was successfully removed on a consistent year-round basis from September 2008 until October 2009 during a 13-month pilot BCR study test at a gravel pit in Grand Junction, Colorado. In the pilot study, a single 4,380-cubic-foot pilot BCR was constructed to treat flows ranging from 2 to 24 gpm. The reactor contained media composed of cow manure, hay, sawdust, wood chips, and limestone. Influent was drawn from a gravel pit dewatering trench next to the Colorado River. The pilot achieved maximum selenium removal rates of 98 percent with a hydraulic retention time of 2.4 days and a minimum effluent concentration of 0.5 µg/L. The highest mass removal rate achieved by the biochemical reactor was 73 mg/day/m³ of substrate and the cumulative mass of total selenium removal was 600 grams during the 13-month period. The biochemical reactor treatment process was effective throughout the cold winter months, during which time total selenium removal rates remained greater than 90 percent.

Project 7E – Pilot Study for Passive BCR Treatment for Coal Mining Influenced Water

A pilot BCR treating wastewater from a coal mine in Alberta began operations in November 2008 and has operated continuously to present (September 2012). The pilot continues to operate effectively with removal rates greater than 90 percent for selenium. In 2012, year 4 of pilot operations, the pilot achieved complete nitrate removal, and average and minimum effluent selenium concentrations of 33 and 3 µg/L, respectively. In year 4, the average pilot influent was 180 µg/L. Loading and removal rates vary with time as organic media ages. Longer HRTs are necessary with time to achieve consistently high selenium removal rates. The pilot reactor has operated year-round without electricity or chemical inputs for 4 years. A demonstration scale system is currently underway.

Project 7F – Pilot Study for Passive BCR Treatment of RO Membrane Concentrate

The feasibility of wetlands treatment of RO concentrate is being evaluated to reduce contaminants, followed by blending with treated reclaimed water to create a source of water to restore riparian habitat. A pilot facility consists of seven treatment cells arranged as four separate series, or trains. Each tank is 8 feet wide, 24 feet long, and 4 feet deep, and contains various media, plant types, and hydraulic configurations. The pilot system supports testing to determine the relative importance of hydraulic and mass loading rate, type of media bed, and plant species to performance, and to establish preliminary engineering criteria for a full-scale system. Six of the treatment cells implement vertical flow wetlands type operation for biologically-mediated anaerobic reduction, precipitation of metals, and denitrification of oxidized nitrogen. Inflows range from 0.1 to 0.2 gpm, and cell HRTs range from 5 to 9 days. A final cell is operated and planted as a surface flow marsh for final polishing, excess maintenance period treatment capacity, and wetland habitat. All cells were planted with a variety of wetland plant species native to central Arizona and southwest United States.

First-year results indicate that organic media-based subsurface flow wetlands can reduce concentrations of arsenic, selenium, and chromium from >30, >20 and >45 µg/L to <10, <1, and <5 µg/L, respectively. Nitrate-nitrogen concentrations were reduced from approximately 55 to <1 mg/L. Seasonal water volume reduction through evapotranspiration was found to be significant, leading to a typical increase from 8 g/L in total dissolved solids during the summer to 11 g/L.

Project 7G – Demonstration Scale Passive Treatment System for Coal Mine Drainage

Three demonstration-scale passive biochemical reactors were operated in southern Appalachia for 290, 203, and 203 days from 2011 to 2012, treating drainage water from coal mine valley fills. Average selenium concentration reductions ranged from 64 to 77 percent through a water temperature range of 4.4°C to 21.8°C. For a system with average influent selenium concentration of 8.1 µg/L, outflow selenium concentrations averaged 1.9 µg/L. For systems with an average inflow selenium of 8.5 µg/L, average outflow selenium concentrations ranged from 2.9 to 3.1 µg/L.

Cost Curve Updates

Costs presented in this section generally were based on the estimates presented in the 2010 report, but updated based on recent available cost data as part of completion of this addendum. Careful consideration of costs and basis of the estimates should be given in using any cost information. This addendum includes total installed cost (TIC), which

includes equipment costs, installation (which make up the construction cost), plus engineering, permitting, and other non-construction cost and owner-related costs. This typically includes the following elements:

- Direct costs - equipment, delivery, taxes, and installation costs; and,
- Indirect costs - engineering, construction, contingency for undefined, escalation permitting, startup and commissioning costs.

The American Association of Cost Engineers International (AACEI) Recommended Practice 18R-97 provides guidelines classifying cost estimates and their relative accuracy. The accuracy of the cost estimate is generally a function of the amount of engineering completed at the time of the estimate. Table 17 shows the class of total installed cost estimates, the relative accuracy and the project definition percent complete for each estimate.

TABLE 17
Cost Estimating Guideline

Estimate Class	Level of Accuracy	Project Definition
5	+100%/-50%	0-2%
4	+50%/-30%	1-15%
3	+30%/-20%	10-40%
2	+20%/-15%	30-70%
1	+20%/-10%	65-100%

Source: Adapted from American Association of Cost Engineers International Recommended Practice 18R-97 (AACEI, 2005)

TIC and operation and maintenance (O&M) cost estimates and associated parametric cost graphs presented in this section are considered Class 5 cost estimates. Class 5 cost estimates are defined by the American Association of Cost Engineers as an order of magnitude estimate and are generally prepared based on limited information containing a wide estimated accuracy range of +100 percent and -50 percent. These estimates were prepared to provide guidance in evaluation of each of the technologies. They are based solely on the information available at the time of the estimate. Actual final costs will depend on the actual labor and material costs, competitive market conditions, site conditions, final project scope, implementation schedule, and other variable factors.

For costs provided in the case study summaries, little information was generally available to provide the basis for the estimate or the classification of the estimate. The basis for the cost estimate must be provided in order to compare costs. The basis should describe whether it included only the core treatment technology or complete treatment system with both liquid and solids management including disposal. Frequently, only capital costs or direct costs for equipment will be provided. These costs unfortunately are only a fraction of the total installed cost for a water treatment system. Additionally, many of these estimates are not current and will therefore require consideration of the time value of money through use of construction cost indices such as the Engineering News Record Construction Cost Index published monthly by McGraw Hill.

Cost curves for the following technologies have been updated and are presented below:

- RO
- IX
- ZVI
- Active biological (ABMet® and FBR)
- Passive biological

The following assumptions apply to the cost curves presented in this section:

- These are parametric cost estimates based on a complete treatment system within the treatment plant boundary not including intake structures and conveyance pipes since this will vary significantly from site to site.
- The TIC estimate does not include flow equalization and diversion infrastructure. Given the unknown variation in flows and selenium concentration, the costs specified for that infrastructure may be imprecise. Equalization and diversion of flows and/or loadings are generally required for most treatment systems.
- O&M costs include maintenance, labor, energy, media replacement, cleaning, chemical and residual disposal costs. Residuals were assumed to be non-hazardous and disposed in a non-hazardous waste landfill.
- TIC may be significantly affected depending on the location of the Se treatment plant. For example, plants in cold weather locations like Canada, all the equipment may need to be installed inside the building for operational purposes or the need for extensive heat tracing of all equipment and pipes if installed outside, which will increase the TIC significantly. High labor cost may also affect the TIC. Costs presented in this section do not account for location specific costs such as labor or cold weather.
- Discharge requirements for parameters such as total phosphorus, temperature, sulfates, and TDS will also affect the TIC and were not considered in the TIC.
- Depending on the equipment installation and discharge requirements, the TIC range provided in this TM may increase from 30 to 150 percent, especially the higher range for sulfate and TDS removal. Similar to TIC cost, the O&M cost range will increase significantly if sulfate and TDS removals are required (energy cost for membrane and reject treatment).
- Cost estimates presented assume a water quality with characteristics presented in Table 18. This water quality was selected based on the historical cost and performance information available at the time.
- Costs were estimated for a base case of 800 gpm and then adjusted for other flow rates based on the ratio of the two flow rates raised to the $6/10^{\text{th}}$ power. The $6/10^{\text{th}}$ exponent is generally accepted for water/wastewater equipment and this method of adjusting costs is accepted by the American Association of Cost Engineers.

TABLE 18
Assumed Water Quality Basis for Cost Estimates

Parameter	Units	Influent Approximate Range	Effluent Approximate Range
pH	s.u.	7.0 - 8.5	6.5 - 8.5
Temp	°F	35 – 65	45 - 75
Nitrate-N	mg/L	5 – 50	<0.10
Sulfate	mg/L	600 - 1,700	NA
Selenium (Total)- Active Biological	µg/L	20 – 300	5 – 20
Selenium (Total)- Passive biological, ZVI, IX	µg/L	20 – 50	5 - 10
Magnesium	mg/L	240 – 370	NA
Calcium	mg/L	200 – 300	NA
BOD	mg/L	NA	20 - 30
TSS	mg/L	NA	20 - 30
DO	mg/L	NA	Minimum of 5.0
Total Phosphorus (active/passive biological only)	mg/L	NA	0.5 – 1.0

NA = parameter not applicable to influent or effluent criteria

1.0 Ion Exchange

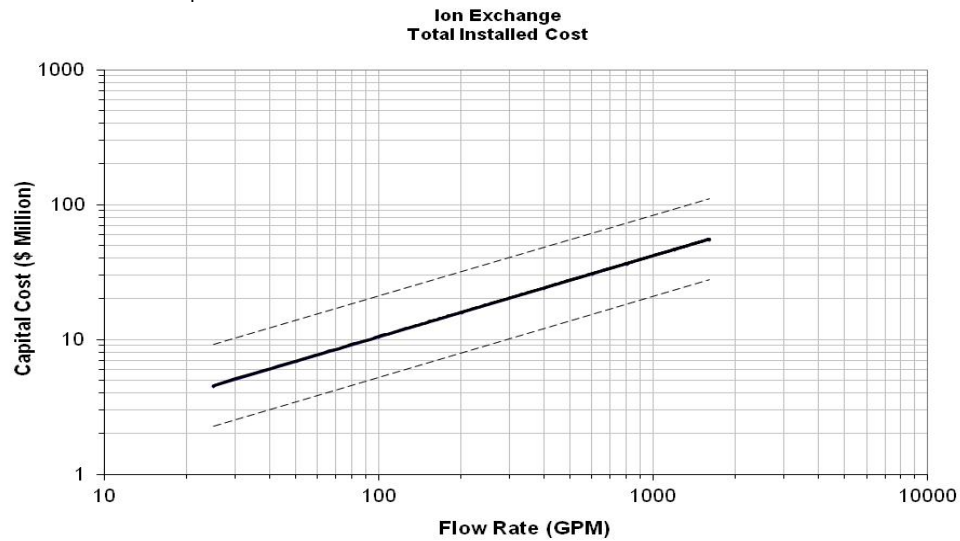
Figures 9 and 10 present TIC and O&M costs for selenium reduction through IX. In addition to the global cost assumptions outlined above, the following assumptions apply to the IX cost estimates:

- This application is limited strictly to removal of selenium as selenate.
- Sulfate does not exceed 500 mg/L. IX is assumed impracticable with sulfate above 500 mg/L.
- Inlet water is strained for large debris and pretreated by coagulation, flocculation, gravity clarification, and media filtration.
- The clarified influent is treated two IX beds, operated in series. Spare pair of IX columns is included.
- Effluent pH adjustment is provided to address pH swings from IX process.
- Waste inlet solids are thickened to a liquid sludge for offsite disposal.
- Operating costs include replacement of ion exchange resin on a 5-year basis. Resin life can vary by application and is a function of scale and fouling.
- The waste regeneration brine is treated by evaporation and crystallization, with disposal of the resulting salt cake in a landfill.

FIGURE 9

Total Installed Cost Curve for IX System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance

**FIGURE 10**

Operating Cost Curve for IX System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance



2.0 Zero Valent Iron

Figures 11 and 12 present TIC and O&M costs for selenium reduction through ZVI treatment. In addition to the global cost assumptions outlined above, the following assumptions apply to the ZVI cost estimates:

- This technology can be applied for selenium in both selenite and selenate forms.
- Inlet water is strained for large debris and pretreated by coagulation, flocculation, gravity clarification, and multimedia filtration.
- The clarified influent is pH adjusted to pH of 6.0 using carbon dioxide.
- A series of tanks operated in parallel containing steel wool is assumed for the reaction vessels, and each bed holds 1,100 lbs of steel wool.
- Post treatment includes aeration, caustic addition, and clarification.

FIGURE 11

Total Installed Cost Curve for ZVI System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance

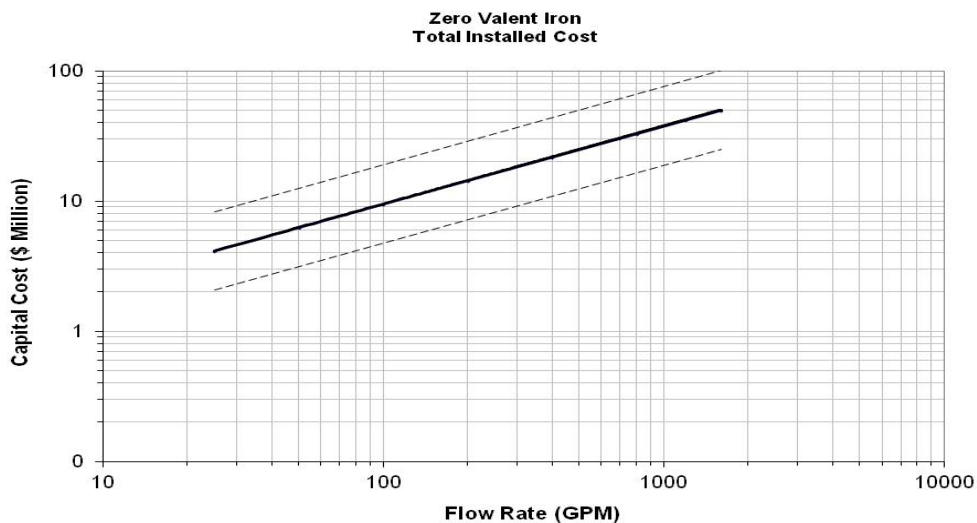


FIGURE 12

Operating Cost Curve for ZVI System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance



3.0 Active Biological

ABMet®

Figures 13 and 14 present the TIC and O&M costs for an ABMet® treatment system for selenium reduction to below 5 to 20 $\mu\text{g/L}$, depending on the influent total Se concentrations. The estimates assume the treatment system include the following:

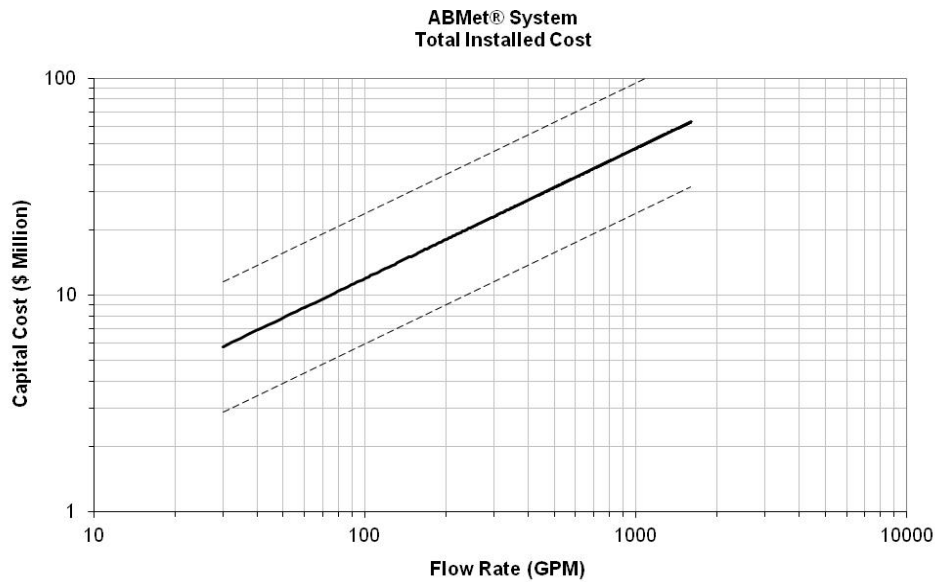
- Influent heating
- Third generation ABMet® unit as a core Se reduction technology
- Aerobic polishing unit to increase the DO from a low negative ORP for discharge requirements
- Backwash water storage and handling, and backwash water TSS thickening and dewatering units to provide a total Se removal and handling system rather than an ABMet® unit for Se removal from the forward flow only.
- Grass roots or green field selenium treatment system with costs for standalone utilities (e.g., power) and an equipment (dewatering system)/control room building included in the estimate.

Most of the unit processes, including ABMet® units, are assumed to be located outside with heat tracing of only interconnecting pipes. They do not include wholesale periodic replacement costs for all the media. Depending upon the application, media replacement will be required and the timing is a function of scale, fouling and media loss during backwashing.

FIGURE 13

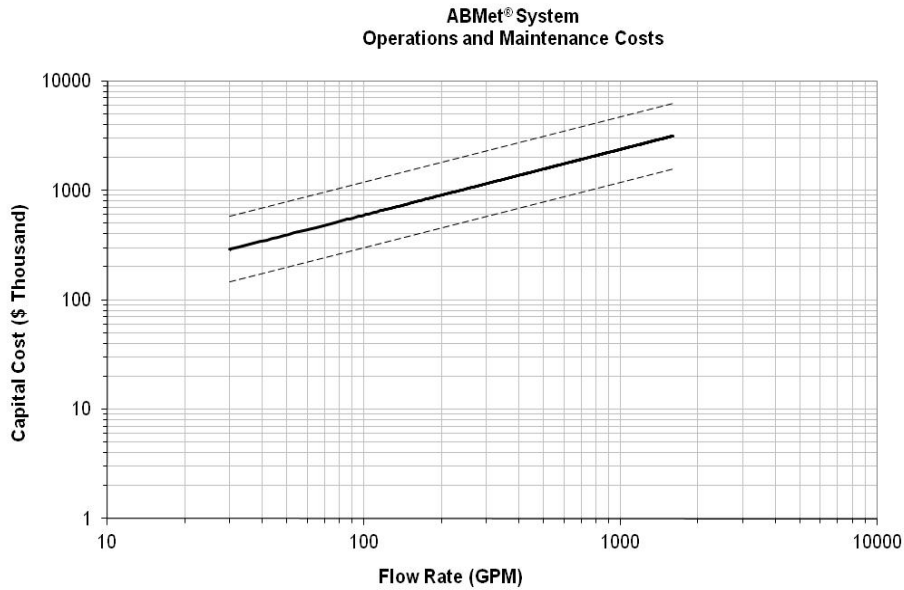
Total Installed Cost Curve for ABMet® System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance

**FIGURE 14**

Operating Cost Curve for ABMet® System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance



FBR

Figures 15 and 16 present the TIC and O&M costs for an FBR system for selenium reduction in the range of 5 to 20 $\mu\text{g/L}$, depending on the influent total Se concentrations. The estimates assume the treatment system include the following:

- Influent heating
- FBR unit as a core Se reduction technology
- Liquid-solids separation unit
- Aerobic polishing unit to increase the DO from a low negative ORP and some BOD polishing for discharge requirements
- Solids stream TSS gravity thickening and dewatering units to provide a total Se removal and handling system rather than just an FBR and liquid-solids separation units for Se removal from the forward flow only.

This system is a grass roots or green field selenium treatment system with costs for standalone utilities (e.g., power) and an equipment (dewatering system)/control room building included in the estimate. Most of the unit processes including FBR units are assumed to be located outside with heat tracing of only interconnecting pipes.

These costs do not include wholesale periodic replacement costs for all the media. Depending upon the application, media replacement will be required and the timing is a function of scale, fouling, and media degradation during fluidization.

FIGURE 15

Total Installed Cost Curve for FBR System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance

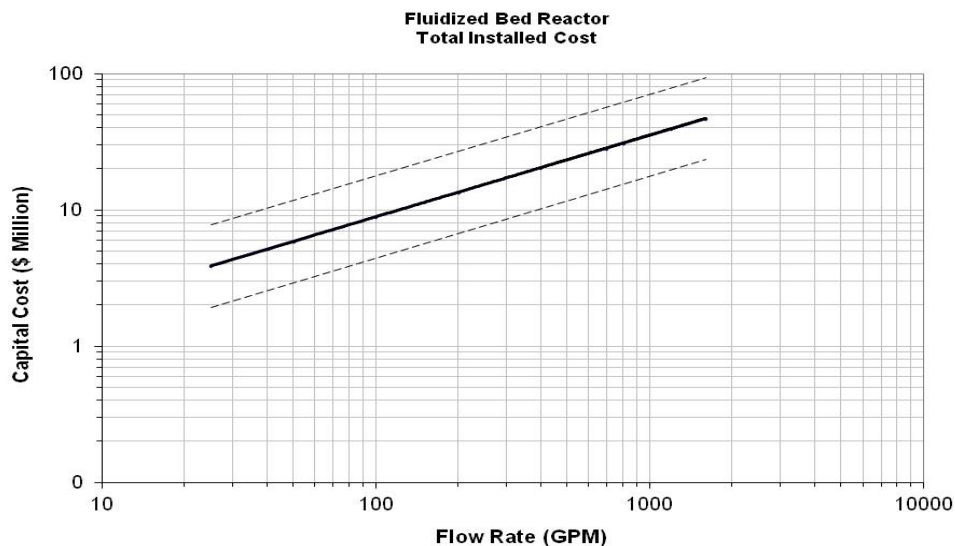
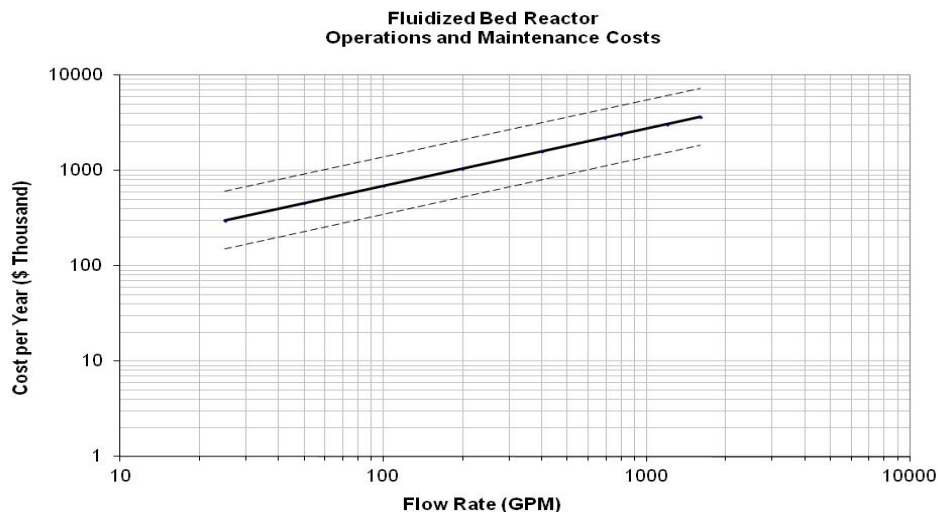


FIGURE 16

Operating Cost Curve for FBR System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance



4.0 Passive Biological

Passive biological systems such as BCRs may be configured to receive a pumped flow of water, or through a gravity feed, if the local topographic gradient allows. The energy and cost requirements to pump and convey water to a BCR will be greater than for a simple gravity feed. In contrast to the other treatment technologies considered in this update, there is limited “turn-up” capacity in passive treatment system. The performance of a BCR is related to the area, volume and flow rate of a treatment system. A system receiving an inflow concentration of 50 µg/L selenium will require a larger and more costly system to achieve a target of 5 µg/L than a system receiving an inflow concentration of 20 µg/L. The cost of a passive biological system will be directly proportional to the flow to be treated.

The conceptual passive biological system used as a basis for cost development for a 200 gpm flow assumed the treatment system includes the following:

- A two-cell BCR system followed by a two-cell aerobic polishing system
- The BCR system is comprised of an initial 0.24-acre vertical downflow bioreactor cell comprised of mixed organic media, followed by a 0.38-acre upflow anaerobic wetland cell for additional selenium reduction and polishing
- The upflow cell is comprised of a bottom layer of gravel media, an intermediate layer of organic peat, and a top layer of sand
- The flow through the BCR system would be through gravity
- The aerobic polishing unit is conceptualized as a 0.61-acre system of sequential vertical flow fill-and-drain subsurface flow wetlands, followed by a 0.11-acre final

filtration bed comprised of an inorganic media engineered for phosphorus adsorption.

- For the passive version, flow is driven from cell to cell through passive dosing siphons. For the version with supplemental power, the aerobic system is a 0.77-acre vertical subsurface flow system receiving air forced through buried tubing at the bottom of the media. The phosphorus removal bed would receive gravity flow

Figure 17 shows the TIC for a biological treatment system with completely passive flow and secondary treatment system, assuming an inflow concentration of 50 $\mu\text{g/L}$. Figure 18 shows the TIC for a biological system with pumped inflow and power available to operate an aerated polishing system for a 50 $\mu\text{g/L}$ inflow concentration. A system with a 20 $\mu\text{g/L}$ influent would require a smaller BCR, however, the reduction in cost is not shown here due to the accuracy of the estimate.

FIGURE 17

Total Installed Cost Curve for Passive Biochemical Reactor System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance

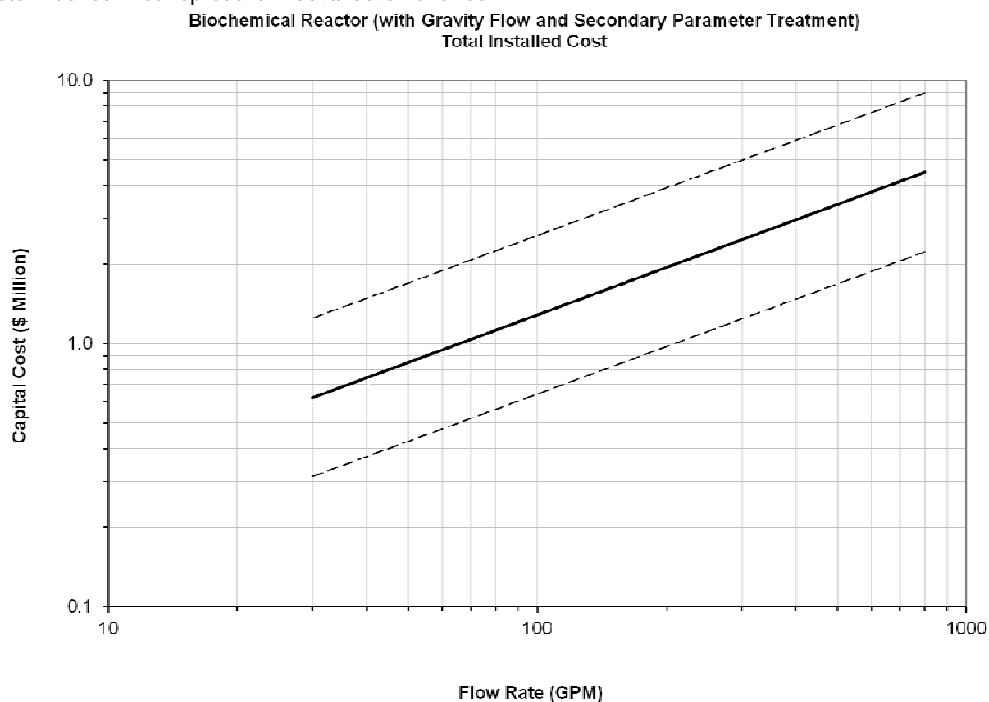


FIGURE 18

Total Installed Cost Curve for Passive Biochemical Reactor System with Power (Year 2012)

Note: Dashed lines represent +100%/-50% Variance

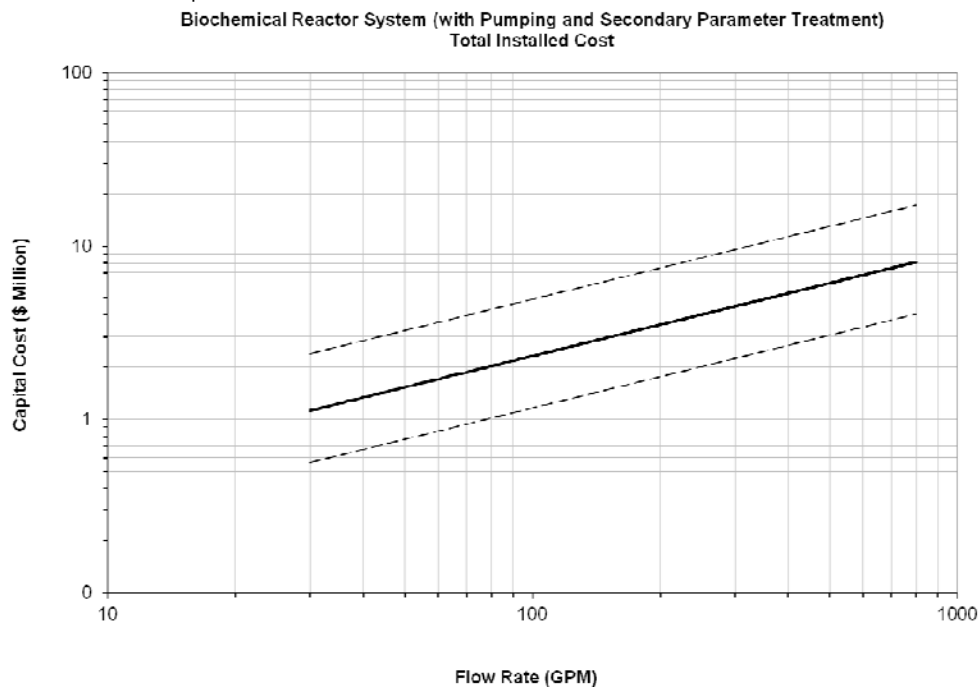


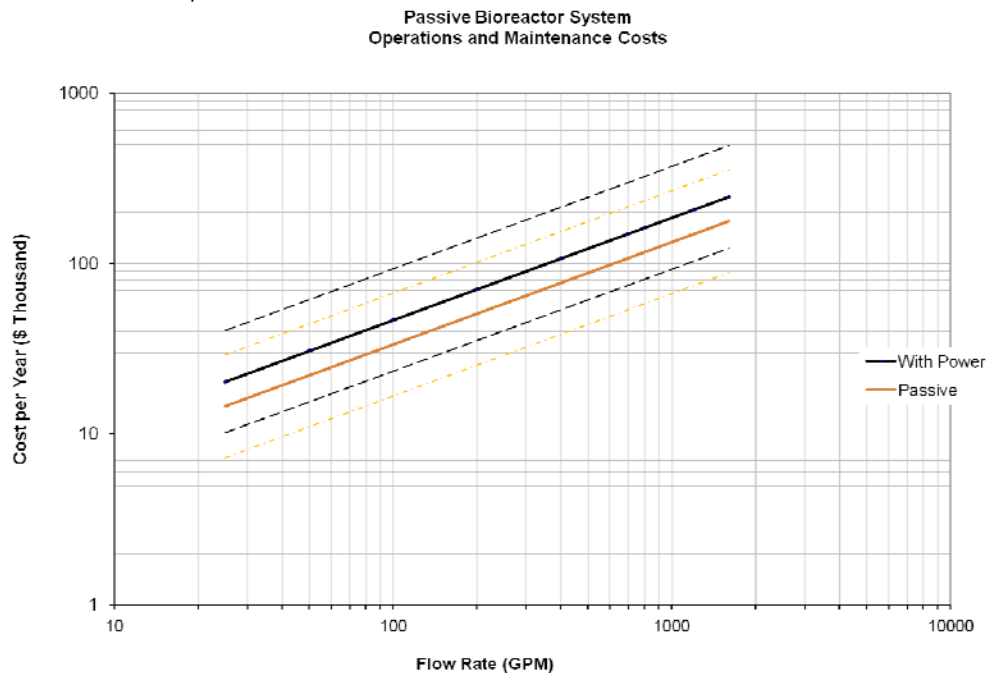
Figure 19 shows the O&M costs for both a completely passive bioreactor wetland treatment system, including passive secondary parameter treatment, and for a passive treatment system receiving pumped inflow and power for an aeration polishing unit. The completely passive system has a lower O&M cost, but there is an overlap between the upper bound of the passive system and the lower bound of the pumped, aerated system.

Operational costs include labor-related maintenance for a passive installation. For systems where water is pumped to the bioreactor system, operational costs will be greater, including pump maintenance, parts replacement, and power costs. Residuals were assumed to be non-hazardous and disposed in a non-hazardous waste landfill. Periodic supplements of media are assumed to be on the order of 10 percent every 5 years. Depending upon the application, media replacement will be required after 20 years, and the timing is a function of carbon content of the media. Annualized costs for removal and landfilling of media after a 20-year period are included. The phosphorus adsorption media in the final polishing cell is assumed to be completely removed and replaced every 5 years.

FIGURE 19

Operating Cost Curve for Passive Biochemical Reactor System (Year 2012)

Note: Dashed lines represent +100%/-50% Variance



References

Following are references, where available, for each case study presented in the TM. References are presented in order of the case studies, and identified using the same numbering/lettering convention. If the information is not publicly available or if the authors did not provide permission, the owner and location are not presented.

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-and-

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