Final Report

Review of Available Technologies for the Removal of Selenium from Water

Prepared for

North American Metals Council

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Executive Summary

This document describes industry-specific approaches to prevention, control and removal of selenium in water, with a focus on water treatment approaches for selenium removal. Industries represented in the North American Metals Council - Selenium Work Group (NAMC-SWG) are faced with managing selenium in water from processes that include the mining, agriculture, power generation, and oil and gas industry sectors. Case studies of pilot-scale and full-scale treatment technologies for selenium removal are presented for each industry sector.

The development of low cost, reliable technologies to remove selenium from water is a priority for the industry sectors as environmental standards and criteria applicable to their surface water discharges are currently very low with a potential for them to be even lower given pending guidance by regulatory agencies in North America.

Water treatment for the removal of selenium will likely be a component of a successful selenium management strategy for industry to achieve selenium discharge requirements on the order of 1-5 µg/L. Potential for selenium treatability should be considered in conjunction with water reuse, prevention and source control measures. Prevention of release and source control strategies for selenium may be more or less desirable or feasible depending upon the nature of the industrial process and associated costs compared to end of pipe water treatment. Generally, complete source control will not be possible or practical for process-affected waters from the various industry sectors.

Source control approaches vary by industry sector. Agricultural strategies generally focus on improved irrigation practices and crop selection. Selenium release reduction strategies for mining operations have generally focused around waste rock and tailings management. Power plants can minimize selenium release through design and selection of fly ash handling and flue gas desulfurization systems. For the oil and gas sector, selenium in produced water is a function of the production technology applied, and the resource deposit it is contained in, thereby posing significant challenges to applying source control approaches. Downstream refining source control strategies are generally limited to sour water management, crude washing and crude desalting operations.

Achieving selenium levels on the order of 1-5 µg/L in surface water discharges from the various industry processes poses a challenge 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 chemicals);
- Treatment generally results in a concentrated by-product or residual; and,
- Re-release from the residuals can occur.

Significant variation in selenium levels and forms exists among the different industry types, within each industry type, and even sometimes within the same facility over time. 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, there is no treatment technology that is a "one-size fits all" solution.

Adequate characterization of wastewater or industrial process residuals that captures its seasonal variation and speciation should be performed to determine the applicable technology for removal. Selection of the correct technology is highly dependent on the speciation of selenium and the competing and interfering water chemistry of industry-specific waters. The flows for some discharges vary greatly over the course of time and selection of the best technology will be limited by the minimum and maximum feasible ranges of design flows for a treatment system to function properly.

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 treatment technology process. Because the performance of each technology is flow based, the system may require flow equalization infrastructure. The end result is a treatment plant that can have significant total installed and operations and maintenance costs.

Costs presented in this document generally were either based on the literature referenced, or 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 only present the capital costs or direct costs for equipment as that is what is typically provided by the equipment supplier. These costs unfortunately are only a fraction of the total installed cost for a water treatment system.

Total installed costs by definition include everything that will be required to install the system. This typically includes the following elements:

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

Total installed cost and operation and maintenance cost estimates and associated parametric cost graphs presented in this document are considered Class 5 cost estimates with an estimated accuracy of +100% and -50%.

Tertiary treatment will generally be required to meet both the selenium and other conventional surface water discharge guidelines or criteria (e.g., dissolved oxygen, total suspended solids, biochemical oxygen demand, etc.). 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., USEPA RCRA Hazardous Waste). By-products may require further treatment to ultimately reduce the selenium to a less hazardous form.

Table ES-1 is a summary table of the treatment technologies (arranged alphabetically) discussed in this review. It includes technology description, removal treatment, key design considerations such as flow or concentration limitations or the extent and significance of any confounding factors, main advantages and disadvantages, and capital and operating costs.

While these physical, chemical and biological treatment technologies have the potential to remove selenium, there are very few technologies that have successfully and/or consistently removed selenium in water to less than 5 µg/L at any scale. There are still fewer technologies that 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. 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.

Information exchange among and within industries is necessary to advance technologies for selenium removal. This includes the need to consider process engineering principles applied to both the science behind the physical, chemical, or biological treatment technology, and an overall system configuration for the core treatment technology.

Table ES-1
Technology Summary

Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
ABMet®	4.4.2.2	The ABMet® system is a bioreactor that is an attached growth (comprised of a biofilm, or a layer of microorganisms that grow on the surface of a solid phase media) downflow granular activated carbon bed filter.	Full Scale	1. Flow equalization/diversion required as part of the treatment train. 2. Pretreatment a. pH adjustment may be required. b. Suspended solids to be removed to prevent clogging of granular activated carbon media. 3. Core Technology a. Competing ions and oxyanions. b. Addition of carbon in proportion to oxyanions to prevent sulfate reduction. c. Temperature in mesophilic range (15ºC to 40ºC). d. Addition of other macronutrients and micronutrients as well. e. Mass transfer driven technology. f. Hydraulic retention time is an important design parameter as selenium removal can be limited by kinetics. 4. Post-Treatment a. Possibly pH adjustment. b. Re-aeration to increase dissolved oxygen and remove biochemical oxygen demand. c. Media filtration for suspended solids and particulate selenium removal. 5. Residuals Treatment a. Treatment of backwash. b. Sludge generated that will require handling and disposal.	• Commercially available technology that has been demonstrated to remove selenium to low levels (e.g., less than 5 µg/L) in pilot-scale and full-scale applications. • Process uses naturally occurring microbes and molasses-based nutrient feed to maintain biomass. • Biologically reduced elemental selenium is in an insoluble form as nanoparticles integral to the biological solids.	• Potential need for pre-treatment to remove suspended solids. • Backwash water required to periodically slough off excess microbial growth, prevent short-circuiting of flow and for de-gassing. • Large footprint required given the low hydraulic loading rate (e.g., 2-4 gpm/ft^2 or 81-162 Lpm/m^2) requirements and high minimum hydraulic residence requirements (4-6 hours). • Presence of an excessive amount of nitrates will require proportional amount of carbon or energy source. This excess carbon source will also generate some additional biomass. • External carbon source is required if soluble influent organic content or COD is insufficient. • Wasted biomass residuals contain elemental selenium that may be hazardous depending upon the TCLP results. • Media replacement may be required over the life of the system. • Biological residuals will need to be thickened and dewatered for landfill disposal.	• Section 4.4.2.2 contains parametric cost curves for capital and operating costs, process flow diagram and assumptions for development of costs. • Total installed cost for 1 million U.S. gallons per day system is estimated as $30 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 U.S. million gallons per day system is estimated as $3 million (2010 USD) (+100%/-50%).
Activated Alumina	4.3.2.4	Activated alumina is a general term for various granular, porous oxides and hydroxides of aluminum that have been exposed to sodium hydroxide at high temperature and have a high surface area that has the	Laboratory	Further research and optimization are needed to determine the feasibility of using activated alumina in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available

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Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
		properties to provide physical adsorption of selenium similar to ferrihydrite.					
Activated Carbon	4.3.2.3	An adsorption process using activated carbon (e.g., granular or powdered) that by design has a high surface area for potential adsorption.	Laboratory	Not effective for selenium removal.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Adsorption to Peanut Shells	4.3.2.6	Peanut shells are treated with strong sulfuric acid to carbonize the shells, oxidizing the cellulose and hemicelluloses and fragmenting the lignin. After treatment, the carbonized peanut shells will physically adsorb selenium.	Laboratory	Further research and optimization are needed to determine the feasibility of using treated peanut shells in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Algal Assimilation	4.4.4.3	Significant amount of selenium is assimilated by algae, particularly in proteins, where selenomethionine is the dominant form (Frankenberger et al., 2004).	Laboratory	Further research and optimization are needed to determine the feasibility in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Algal-Bacterial Selenium Removal	4.4.4.1	Algal-bacterial selenium removal (ABSR) is a process in which bacterial growth is stimulated by the addition of algae as a food source (NSMP, 2007).	Pilot	Core Technology a. Seasonally limited with treatment affected by duration of solar light and ambient temperatures.	• Potentially low cost-treatment approach. • Results in some direct volatilization of selenium out of the water column. • Can be applied as an *in situ* approach to selenium treatment. • Possibilities for future research include harvest of algae and bacteria as a source of protein and selenium to supplement cattle feed and harvest of algae for biofuel.	• Requires excess nutrients that can create eutrophic conditions in receiving streams. • Seasonally limited with treatment affected by duration of solar light and ambient temperatures. • Difficult to separate algae from water, requiring further treatment with coagulants and flocculants. • Effluent contains more bioavailable forms of selenium that have resulted in higher selenium levels in invertebrates compared to those exposed to untreated	Algal treatments have generally low cost (e.g., \$.0008 USD per U.S. gallon) (NSMP, 2007). However, high cost can be associated with the land needed for the ABSR pond (e.g., \$200 USD per acre-foot) (NSMP, 2007), as well as the need for separation of the high-rate and reduction ponds (Lenz and Lens, 2009).

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						water. • Has not been demonstrated to treat to low levels of selenium (less than 5 µg/L). • High residence time required for treatment. • Large footprint required as algae growth limited to the upper surface of the water due to light penetration limits.	
Algal Volatilization	4.4.4.2	Algal volatilization occurs when selenium is methylated and converted to a gaseous form (Frankenberger et al., 2004). Algal volatilization treatment involves the removal of selenium from wastewater by selenium biomethylation and further volatilization (Golder, 2009a,b).	Pilot	<u>Core Technology</u> a. Seasonally limited with treatment affected by duration of solar light and ambient temperatures.	• Potentially a lower cost treatment approach. • Can be applied as an *in situ* approach to selenium treatment. • Possibilities for future research include algal harvesting as a source of protein and selenium to supplement cattle feed and for biofuel.	• Requires excess nutrients that can create eutrophic conditions in receiving streams. • Seasonally limited with treatment affected by duration of solar light and ambient temperatures. • Difficult to separate algae from water, thereby requiring coagulants and flocculants. • Effluent contains more bioavailable forms of selenium that have resulted in higher selenium levels in invertebrates compared to those exposed to untreated water. • Has not been demonstrated to treat to low levels of selenium (less than 5 µg/L). • High residence time required for treatment. • Large footprint required as algae growth limited to the upper surface of the water due to light penetration limits.	Similar to the algal-bacterial treatments, this treatment has low costs (Golder, 2009a). However, treatment cost can increase depending on land requirements (e.g., $104 to $272 USD per acre-foot treated) (USBR, 2002b).
BioSolve®	4.4.2.4	The BioSolve® technology system, developed by Calcon using the Hall reactor, consists of a continuously stirred tank reactor with plastic sponge media used as a surface for biofilm development	Laboratory	Further research and optimization are needed to determine the feasibility in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available

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Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
		(Nurdogan et al., 2009).					
Capacitive Deionization Process (SeClear™)	4.3.2.8	The Capacitive Deionization Process (SeClear™) is a direct current driven ion exchange technology with an electrostatic charging system that operates like a capacitor.	Laboratory	Further research and optimization are needed to determine the feasibility in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Catalyzed Reduction (Cementation)	4.3.3.2	The addition of copper or nickel to a zero valent iron treatment process has been demonstrated to catalyze the reduction of selenium by creating a greater electrochemical potential between the elemental iron and soluble selenium.	Pilot	Design and operational considerations for catalyzed cementation are similar to the zero valent iron technology, including the potential need for pretreatment, and the presence of interfering anions such as nitrate, sulfate, etc.	• Basic technology is demonstrated in laboratory studies to remove selenate and selenite to low concentrations.	• Technology has not been proven in full-scale treatment. • Potential for long residence times. • Spent media must be removed, disposed of and replaced. May require disposal as hazardous waste. • Sludge disposal may be significant cost. • Media replacement may be a significant cost. • Other potential issues with copper and nickel discharges.	Reagent consumption of this technology is estimated to be \$8.11 (USD) per 1,000 U.S. gallons treated. Design, equipment purchase, construction, and startup costs for a 300 U.S. gpm system were estimated as \$1,083,285 (2001 USD) (MSE, 2001); annual O&M costs for a 300 U.S. gpm system were estimated as \$1,165,358 (2001 USD) (MSE, 2001).
Constructed Wetlands	4.4.3.1	Engineered wetlands are designed and constructed to use vegetation, soil, rock and other civil structures to promote the appropriate microbial and plant activity to provide selenium treatment. They can be designed in vertical upflow, subsurface horizontal and surface flow configurations depending upon selenium ecological requirements.	Full Scale	1. <u>Flow equalization/diversion</u> required as part of the treatment train. 2. <u>Pretreatment</u> a. pH adjustment may be required. b. Service water addition may be required if concentrations of other parameters such as chlorides or boron could cause adverse effects in the wetlands plants. c. Suspended solids removal required. 3. <u>Core Technology</u> a. Control of stoichiometry is limited because it is a natural treatment process. b. The rate of flow, strength of influent, and target effluent criteria influence the design size of the wetland. c. Typical retention times for passive treatment systems can be several days or more. d. Due to the large retention time required, the footprint of constructed wetlands is generally large and can be several acres. e. The performance of a wetland can be	• Basic technology is reasonably demonstrated to remove selenium at low concentrations. • Process requires minimal operator supervision. • Process can operate passively without energy or chemicals. • Subsurface flow wetlands can operate in cold climates with installations in Northern Europe and Canada. • Able to treat large volumes of water.	• Potential for long residence time. • Large and flat footprint is required. • Uncertainties relating to consistently meeting very low selenium discharge limits (less than 5 µg/L). • Performance of surface flow wetlands is affected by temperature. Selenium removal is greater in summer months during warmer period. • Monitoring may be required to assess ecological risk from bioaccumulation of selenium, including toxicity to aquatic life and animals (nesting birds); if significant, exclusion measures may be required. • Potential for groundwater	• Section 4.4.3.1 contains parametric cost curves for capital and operating costs, process flow diagram and assumptions for development of costs for subsurface flow wetland. • Total installed cost for 1 million U.S. gallons per day system is estimated as \$17 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as \$150,000 (2010 USD) (+100%/-50%).

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				affected by the density of plant growth. Plant detritus is used as organic substrate for microbial reduction of selenium. If there is insufficient plant cover within a wetland, an additional organic substrate may be used to improve selenium removal.		contamination.	
Electrocoagulation	4.3.2.5	A physical adsorption process where ferrous iron is produced by applying direct electrical current to the water where an iron anode oxidizes to form ferrous iron that can reduce selenate and the resultant ferric iron can co-precipitate selenite.	Laboratory	Further research and optimization are needed to determine the feasibility of using electrocoagulation in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Enhanced Evaporation System	4.2.2.2	An enhanced evaporation system is similar to an evaporation pond but with a mechanical device added to increase the evaporation rate of water through aspirating or spraying the water into the air.	Full scale for salt management, not implemented specifically for selenium management.	1. <u>Core Technology</u> a. Only applicable for areas with favorable climates (where evaporation rate exceeds precipitation rate). b. Mechanical aspiration/spraying of the pond results in increasing the surface area of the water exposed to air thereby resulting in enhanced evaporation. c. Realized enhanced evaporation potential a function of the spray equipment's ability to discharge above the water saturated vapor headspace of the pond. d. Can result in suspended particulate drift. e. The volume of the pond is reduced due to the increased efficiency of evaporation using mechanical sprayer equipment. f. Scaling potential for mechanical equipment as the dissolved solids increase.	• Lower costs because the technology relies on solar radiation for evaporation. • Can potentially be disposed of in place with proper design and permitting. • Increased evaporation efficiency over evaporation ponds due to mechanical spraying. • Requires a slightly smaller footprint than conventional evaporation ponds.	• Large space requirements due to efficiency decline as the total dissolved solids increases. • Generally will not result in a completely dry residual, which limits disposal alternatives. • Ineffective in areas with cold wet climate. A dry climate in which evaporation greatly exceeds precipitation is required. Alternate treatment is needed during cold weather. • Risk of infiltration to groundwater (depending on liner type) could occur. • Evaporation results in a net loss of water that may be a concern to areas with scarce water resources. • May pose risk to wildlife. An ecological risk assessment should be performed prior to implementation. • Higher operation and maintenance costs considering the mechanical aspiration/spraying.	The cost for an enhanced evaporation system in the San Joaquin Valley was $480 (2005 USD) per acre-foot (Salton Sea Ecosystem Restoration Program, 2005).

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						- Potential corrosion and scale issues with the mechanical aspiration/spraying equipment as the salinity increases.	
Enhanced *in situ* microbial reduction	4.4.3.4	Enhanced *in situ* microbial reduction of oxidized forms of selenium is accomplished by addition of organic amendments, nutrients or inoculated micro-organisms. Selenium removal with this technology is based on the presence of microorganisms to remove selenium.	Pilot	Anoxic conditions are required for *in situ* microbial reduction of selenate and selenite to occur. Microcosm testing can be performed to determine the available microbial populations and whether treatment may be effective for selenium reduction prior to implementation.	- Lower cost alternative for remediation of large volumes of water. - Low maintenance.	- Long retention times required. - Anoxic water may require aeration/settling as post-treatment prior to discharge to receiving water.	Less than USD \$1.00/1,000 U.S. gallons, due to low capital costs (Sobolewski, 2005).
Enzymatic Selenium Reduction	4.4.2.5	An enzyme is a protein that can bring about digestion (breakdown) of molecules into smaller units and greatly speed up chemical reactions. Enzyme extracts were tested from microbes that were previously demonstrated to treat selenium.	Laboratory	Further research and optimization are needed to determine the feasibility in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Evaporation Pond	4.2.2.1	Concentrates dissolved salts by natural evaporation of water to various levels of salinity based on the prevailing climate conditions.	Full scale for salt management, not implemented specifically for selenium management.	1. <u>Core Technology</u> a. Efficiency declines as total dissolved solids increases, requiring large footprint. b. Only applicable for areas with favorable climates (where evaporation rate exceeds precipitation rate).	- Lower costs because the technology relies on solar radiation for evaporation. - Simple operation. - Can potentially be disposed of in place with proper design and permitting.	- Large space requirements due to efficiency decline as the total dissolved solids increases. - Generally will not result in a completely dry residual, which limits disposal alternatives. - Ineffective in areas with cold wet climate. A dry climate in which evaporation greatly exceeds precipitation is required. Alternate treatment is needed during cold weather. - Risk of infiltration to	Evaporation pond treatment in the San Joaquin Valley cost \$630 USD per acre-foot of treated water with \$2.8 million/year (USD) for O&M (Salton Sea Ecosystem Restoration Program, 2005).

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Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
						groundwater (depending on liner type) could occur. • Evaporation results in a net loss of water that may be a concern to areas with scarce water resources. • May pose risk to wildlife. An ecological risk assessment should be performed prior to implementation.	
Ferrihydrite Adsorption or Iron Co-Precipitation	4.3.2.2	Ferrihydrite adsorption is a two step physical adsorption process in which a ferric salt is added to the water source at proper conditions such that a ferric hydroxide and ferrihydrite precipitate results in concurrent adsorption of selenium on the surface; also known as iron co-precipitation.	Full Scale	1. Flow equalization/diversion required as part of the treatment train. 2. Pretreatment a. pH adjustment may be required, optimal pH for treatment is between 4 to 6. 3. Core Technology a. Only applicable for selenite, very little selenate removal. b. Staged mixing generally required for coagulation and flocculation of iron precipitation solids. c. Gravity sedimentation required to separate iron solids and adsorbed selenium from water matrix. 4. Tertiary Treatment a. Media filtration and pH adjustment may be required. 5. Residuals Management a. Iron residuals with adsorbed selenium will require thickening and dewatering for disposal as solid waste in a landfill. b. Will require toxicity characteristic leaching procedure (TCLP) testing to determine whether sludge should be disposed as hazardous waste.	• Widely implemented at full-scale throughout the industry • Established by US EPA as best demonstrated available technology for selenium (e.g., selenite) removal. • Relatively simple and low cost chemical adsorption technology.	• Selenium removal not proven to low µg/L (less than 5 µg/L). • Produces relatively large quantities of sludge that may need to be disposed as a hazardous waste depending upon outcome of TCLP testing. • Iron co-precipitation is pH dependent with optimal conditions in the range of pH 4 to 6. • Not able to remove selenate. Requires oxidation of selenocyanate to selenite prior to removal. • Potential release of selenium from ferrihydrite residuals.	• Section 4.3.2.2 contains parametric cost curves for capital and operating costs, process flow diagram and assumptions for development of costs. • Total installed cost for 1 million U.S. gallons per day system is estimated as $11 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as $4 million (2010 USD) (+100%/-50%).
Ferrous Hydroxide	4.3.3.3	A two step reduction oxidation and physical adsorption process where ferrous iron is added resulting in the reduction of selenate to selenite and the subsequent physical adsorption or co-precipitation of selenite by ferrihydrite or ferric	Full Scale	Similar design considerations for ferrihydrite adsorption or iron co-precipitation. Reduction and subsequent adsorption are best accomplished under reducing conditions at a pH of approximately 8-9 (Twidwell et al., 2009).	• Widely implemented at full-scale throughout the industry. • Relatively simple and low cost reduction oxidation and physical adsorption technology.	• Selenium removal not proven to low µg/L (less than 5 µg/L). • Large quantities of sludge may need to be disposed as a hazardous waste. • Reduction and subsequent adsorption is pH dependent with optimal conditions in the range of pH 8 to 9. • Not as effective at the reduction of selenate to	Costs were reported for a 300 U.S. gpm FGD water treatment plant as $15 million (2000 USD); annual O&M cost of $1.5 to $2 million (2000 USD).

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Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages^1	Disadvantages^1	Capital and Operating Costs^2
		hydroxide.				selenite as zero valent iron.	
Fluidized bed reactor	4.4.2.3	In a fluidized bed reactor, water containing selenium is passed through a granular solid media (e.g., sand or granular activated carbon) at high enough velocities to suspend, or fluidize the media creating a completely mixed reactor configuration for attached biological growth or biofilm.	Pilot	1. <u>Flow equalization/diversion</u> required as part of the treatment train. 2. <u>Pretreatment</u> a. pH adjustment may be required. 3. <u>Core Technology</u> a. Competing ions and oxyanions. b. Addition of carbon in proportion to oxyanions to prevent sulfate reduction. c. Temperature in mesophilic range (15ºC to 40ºC). d. Addition of other macronutrients and micronutrients. e. Mass transfer driven technology. f. Hydraulic residence time is an important design parameter as selenium removal can be limited by kinetics. 4. <u>Post-Treatment</u> a. pH adjustment may be needed. b. Re-aeration to increase dissolved oxygen and remove biochemical oxygen demand (BOD). c. Media filtration for suspended solids.	• Process uses naturally occurring microbes and biodegradable carbon sources to maintain biomass. • Biologically reduced elemental selenium is in an insoluble form as nanoparticles integral to the biological solids. • Smaller footprint given completely mixed reactor configuration resulting in lower total installed costs. • Requires little to no pretreatment for suspended solids. • No backwash water required. Biomass separated from centrifugal separator on reactor effluent.	• Presence of an excessive amount of nitrates will require proportional amount of carbon or energy source. This excess carbon source will also generate some additional biomass. • Commercially available technology operating in similar full scale applications (e.g., nitrate and perchlorate removal) but no full scale selenium treatment for fluidized bed reactor is currently utilized. • External carbon source is required if soluble influent organic content or chemical oxygen demand (COD) is insufficient. • Wasted biomass sludge contains elemental selenium that may be hazardous depending upon the TCLP results. • Media replacement required periodically. • Biological residuals will need to be thickened and dewatered for landfill disposal.	• Section 4.4.2.3 contains parametric cost curves for capital and operating costs, process flow diagram and assumptions for development of costs. • Total installed cost for 1 million U.S. gallons per day system is estimated as $11 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as $3 million (2010 USD) (+100%/-50%).
Hydrogen-Based Membrane Biofilm Reactor	4.4.2.6	Hydrogen is used as an alternative electron donor to the carbon-based electron donors used in other reactors cited. The membrane is used within this treatment system to directly supply dissolved gas to a biofilm growing on the membrane surface.	Laboratory	Further research and optimization are needed to determine the feasibility in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Ion Exchange	4.3.2.1	An adsorption process where undesirable ions in the water are exchanged for like charged ions by	Pilot	1. <u>Flow equalization/diversion</u> required as part of the treatment train. 2. <u>Pretreatment</u> • a. Suspended solids removal is required to reduce fouling potential	• Generally greater than 90% recovery rates given resin specificity for target constituent and regenerant and back wash requirements.	• Uncertainty regarding performance for selenium removal to low levels (e.g., less than 5 µg/L) given small amount of test data in literature.	• Section 4.3.2.1 contains parametric cost curves for capital and operating costs, process flow diagram and

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Technology Summary

Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
		electrostatic attraction to sites of opposite charge on the surface of granular chemicals known as ion exchange resins.		of membrane. • b. pH adjustment may be needed. • c. Potential scale removal to prevent resin fouling. 3. Core Technology a. The resin type (e.g., weak or strong base), the volume and type of regenerant, backwash water source, backwash quantities, pre-filtration for solids, pH adjustment before and after ion exchange, column configuration, mode of operation, and cycle length are all considerations for operations of an ion exchange system. b. Configuration of ion exchange columns- requires potentially lead- lag-lag serial column configuration with full caustic regeneration to minimize leakage. 4. Residuals Management a. Concentrated regenerant to be treated with core selenium removal technology and/or concentrated and disposed.	• In the right application, capable of treating to potentially low levels (e.g., 5 µg/L or less) with proper resin selection and system design with consideration to competing water chemistry. This same technology has been applied to perchlorate in similar water matrices. • Concentrates the selenium reducing the volume for treatment.	• Ion exchange capacity for selenium can be greatly reduced by competing anions (e.g., sulfates, nitrates). • Resin may need to be disposed if it cannot be regenerated, meaning high disposal costs. • Concentrated regenerant stream requires treatment and/or disposal.	assumptions for development of costs. • Total installed cost for 1 million U.S. gallons per day system is estimated as $28 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as $4 million (2010 USD) (+100%/-50%).
Katchall Filtration Systems, LLC Media	4.3.2.9	An adsorbent media that is called "Heavy Metals Removal Media" that consists of coarse and fine-granular materials loaded into an enclosed vessel through which water is passed for treatment. Metals are removed by chemical bonding onto organic molecules (media), producing a discharge with low metal concentrations (NSMP, 2007).	Laboratory	Further research and optimization are needed to determine the feasibility in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Mechanical Evaporation/ Crystallization	4.2.2.4	Provides an external heat source, mechanical mixing, and/or pressure or vacuum to enhance the evaporation potential of water resulting in brine concentration and crystallization.	Full Scale for industrial applications, has not been implemented specifically for selenium management.	1. Flow equalization/diversion required as part of treatment train. 2. Pretreatment a. Because of the high cost of treatment, wastewater is usually pre-concentrated with nanofiltration, reverse osmosis, ion exchange, or other concentrating technology to reduce the volume for treatment by mechanical	• Provides a high level of treatment producing a concentrated selenium salt cake and pure water distillate. • Generally would be effective at reducing the volume of pre-concentrated streams of selenium from reverse osmosis and ion	• Disposal of solid waste stream could be hazardous and may be large in quantity, depending on the wastewater volume and characteristics. • Pretreatment can be required depending upon the water quality.	• Section 4.2.2.4 contains parametric cost curves for capital and operating costs, process flow diagram and assumptions for development of costs. • Total installed cost

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Technology Summary

Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
				evaporator/crystallizer. 3. <u>Core Technology</u> a. Scale, corrosion, and high ionic strength must be considered during design and selection of materials of construction. b. Flow limitations- although there are no limitations, it is recommended to treat a reduced volume that has been pretreated due to expense of treatment. 4. <u>Tertiary Treatment</u> a. Distillate may need to be recombined with other streams prior to discharge. 5. <u>Residuals Management</u> a. The crystallizer system concentrates the dissolved solids in the brine from the evaporator further resulting in up to 90% total solids residual that may require further dewatering. The solid requires disposal and may be hazardous: toxicity characteristic leach procedure (TCLP) testing needs to be performed to characterize the residual.	exchange technologies. • Concentrates the selenium reducing the volume for treatment.	• Requires electric, steam and cooling water utilities. • Distillate will require blending to reconstitute with minerals depending upon the discharge requirements. • Redundancy requirements given maintenance outages. • High capital and operation and maintenance cost.	for 1 million U.S. gallons per day system is estimated as $70 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as $8 million (2010 USD) (+100%/-50%).
Nanofiltration	4.2.1.3	Nanofiltration is a pressure driven membrane process similar to reverse osmosis that retains selenium and other dissolved salts between 0.001 and 0.01 microns but is operated at pressures approximately one-third of reverse osmosis.	Pilot	Design considerations are similar to reverse osmosis. However, unlike reverse osmosis, nanofiltration is limited by the pore size being in the molecular weight cutoff range that is similar to the size of the selenite and selenate oxyanions. Therefore, depending upon the exact cutoff, performance may not be as effective as reverse osmosis.	• Operates at one-third of the pressure requirement of reverse osmosis technology. • Small space requirements, modular type construction, and easy expansion. • Can offer improved recoveries by rejecting a smaller portion of the salts including selenium, thereby reducing scale potential. • Concentrates the selenium reducing the volume for ultimate reduction treatment.	• Not tested at full-scale for selenium removal. No actual performance data are available yet for selenium removal. • Requirements for pretreatment and chemical addition (micro filter, mixed media filter) to reduce scaling/fouling. • Frequent membrane monitoring and maintenance. • Pressure, temperature, and pH requirements to meet membrane tolerances. • Requires treatment and disposal of the reject stream. • Temperature operating issues due to viscosity effects at extreme low and high temperatures.	• Total installed cost and operations and maintenance costs are similar to reverse osmosis cost estimates. • Total installed cost for 1 million U.S. gallons per day system is estimated as $40 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as $3 million (2010 USD) (+100%/-50%).
Octolig® system	4.3.2.7	Octolig® system consists of an organic ligand that	Laboratory	Further research and optimization are needed to determine the feasibility of using the Octolig® system in applications	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-	Not available

Table ES-1
Technology Summary

Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
		has been chemically immobilized onto a silica gel substrate. The Octolig® media is used in a flow-through column arrangement similar to an ion exchange system.		to remove selenium from water.		scale only.	
Passive biochemical reactor	4.4.3.2	Passive biochemical reactors consist of an excavated lined area that has been filled with an organic substrate. They are generally operated in a gravity down-flow mode, although up-flow mode is also a possible configuration.	Full Scale	1. <u>Flow equalization/diversion</u> can be part of treatment train. 2. <u>Pretreatment</u> a. Suspended solids removal as pretreatment can increase lifespan of passive biochemical reactor. 3. <u>Core Technology</u> a. Hydraulic retention time is a key design parameter.	• Low capital and operations and maintenance costs, including low cost of organic substrate; local materials can be used for organic substrate. • Process requires minimal operator supervision. • Process can operate passively without energy or chemicals. • Subsurface design means that system can operate in cold climates.	• Uncertainty regarding potential re-mobilization of selenium. • Large footprint required. • Uncertainty in consistently meeting very low selenium discharge limits (less than 5 µg/L). • Organic substrate degrades over time and may require replacement.	The design and construction cost of the first module of the Montana gold mine passive treatment system was approximately $200,000 (2007 USD). A total of three modules are planned to treat a total of 20 US gpm (75 Lpm), with annual operating costs estimated at $0.95 per thousand gallons (Golder, 2009a).
Permeable Reactive Barriers	4.4.3.3	Permeable reactive barriers are a type of passive, *in situ* treatment for shallow groundwater (generally employed at depths less than 50 to 70 feet) (USEPA, 1998) and can be employed for source zone treatment.	Full Scale	Zero valent iron is often used as the reactive media in implementation of permeable reactive barriers. The corrosion of zero valent iron causes an increase in pH values and a decrease in oxidation state. Monitoring of pH and oxidation reduction potential can be used to help evaluate the performance of permeable reactive barriers.	• Lower cost alternative than other technologies. • Low maintenance. • Can be used as a source control measure to mitigate exposure to downgradient receptors.	• Finite life span. • Potential to be clogged due to precipitation of secondary metals. • Has not been fully demonstrated to achieve low µg/L levels in the effluent (less than 5 µg/L).	$24 per 1,000 U.S. gallons (2004 USD) (USDOE, 2004).
Photoreduction	4.3.3.4	Photoreduction is a chemical reduction and adsorption technology. Photoreduction uses irradiation of ultraviolet light at a certain wavelength and in the presence of titanium dioxide to convert selenate and selenite to elemental selenium (Shamas et al., 2009).	Laboratory	Further research and optimization are needed to determine the feasibility in applications to remove selenium from water.	Advantages are not provided for technology demonstrated at laboratory-scale only.	Disadvantages are not provided for technology demonstrated at laboratory-scale only.	Not available
Reverse Osmosis	4.2.1.2	Reverse osmosis is a membrane	Full Scale	1. <u>Flow equalization/ diversion</u> required	• Demonstrated at full scale to remove selenium	• Higher capital cost to purchase, install, and	• Section 4.2.1.2 contains parametric

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Technology Summary

Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
		separation process that uses high pressure to force a solution through a membrane that retains the soluble selenium (e.g., selenite and selenate) and other dissolved salts less than 0.001 microns on the reject side of the membrane and allows the purified water pass to the permeate side.		as part of the treatment train. 2. <u>Pretreatment</u> a. Suspended solids removal to reduce fouling potential of membrane to a silt density index of less than 5. b. May require temperature control at low and high temperatures to minimize viscosity effects. c. pH adjustment may be required. d. Antiscalant addition to prevent membrane fouling may be required. 3. <u>Core Technology</u> a. Can remove high levels of total dissolved solids (TDS), but not practical above 10,000 mg/L TDS. b. Scale-forming ions will irreversibly foul the membranes and create selenium removal issues by allowing leakage. c. A heuristic approach for osmotic pressure requirements is to assume that 10 pounds per square inch gauge of osmotic pressure is exerted for every 1,000 mg/L TDS. 4. <u>Tertiary Treatment</u> a. Effluent blending of the reverse osmosis and the crystallizer distillate. b. Effluent may need to be re-constituted as ions may need to be added to discharge prior to receiving water. 5. <u>Residuals Management</u> a. Brine concentrates require treatment with core selenium removal technology and/ or further concentrated for disposal.	(selenite or selenate) to less than 5 μg/L. • Can remove high levels of TDS, approximately 90 to 98% removal. • Produces a high water quality with relatively high recoveries as a function of scale treatment. • Small space requirements, modular type construction and easy expansion. • Concentrates the selenium reducing the volume for ultimate reduction treatment.	operate than other membrane separation processes. • Requirements for pretreatment and chemical addition (microfilter, mixed media filter) to reduce scaling/fouling. • Pressure, temperature, and pH requirements to meet membrane tolerances. • Frequent membrane monitoring and maintenance. • Requires treatment and disposal of the brine (reverse osmosis reject stream). • Reverse osmosis permeate stream will require treatment (pH and TDS buffering) prior to discharge to receiving waters to meet aquatic toxicity test. • Operating issues will result from viscosity changes at extreme low and high temperatures.	cost curves for capital and operating costs, process flow diagram and assumptions for development of costs. • Total installed cost for 1 million U.S. gallons per day system is estimated as $40 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as $3 million (2010 USD) (+100%/-50%).
Salinity Gradient Solar Pond	4.2.2.3	Salinity gradient solar ponds are deep bodies of saline water that develop a temperature gradient from top to bottom and utilize trapped solar radiation with mechanical circulation to enhance evaporation.	Full scale for salt management, not implemented specifically for selenium management.	1. <u>Core Technology</u> a. Enhances performance of an atmospheric evaporation pond by utilizing stratification due to salinity gradients within the pond to more effectively trap heat from solar radiation or other heat inputs within the pond.	• Takes advantage of solar radiation and climate to provide a less expensive mechanical evaporator. • Relatively simple to construct. • Improved performance compared to evaporation ponds with and without mechanical enhancements.	• Requires relatively large footprint with a relatively deep side depth. • The fate of selenium is unknown within salinity gradient solar ponds as they have not been used for selenium treatment. • Potential corrosion and scale issues with the mechanical equipment.	Costs for solar gradient ponds can range up to $6,100 (USD) per acre-foot (NSMP, 2007). Operation and maintenance costs can be about 10 times greater than an evaporation pond (NSMP, 2007).
Upflow anaerobic sludge blanket (UASB) bioreactor	4.4.2.1	In a UASB bioreactor, the wastewater flows upward through the granular sludge at a high enough velocity	Pilot	1. <u>Flow equalization/diversion</u> required as part of the treatment train. 2. <u>Pretreatment</u> a. pH adjustment may be required.	• Requires no attached growth media and therefore no media replacement. • Process uses naturally occurring microbes and biodegradable nutrient to	• Commercially available technology typically applied to high strength organic wastewater. • Long hydraulic residence (e.g., > 6 hours) and solid	The total cost for a 1 million U.S. gallons per day (4000 cubic meter per day (m^3/day) system is estimated at $0.36 to $0.42/ m^3 of water

Table ES-1
Technology Summary

Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
		to keep the sludge suspended without washout. The upper part of the bioreactor contains a gas/solids separator to allow gases produced to be vented and solids entrained by the gases to be recovered.		3. Core Technology a. Competing ions and oxyanions may exist in water matrix. b. Addition of carbon in proportion to oxyanions is required. c. Temperature required is in the mesophilic range (15 ºC to 40 ºC).	maintain biomass. • Biologically reduced elemental selenium is in insoluble form as nanoparticles integral to the biological solids. • Requires little to no pretreatment for suspended solids.	residence (e.g., > 10 days) time requirements result in larger reactor sizes and footprint. • No full scale proof of concept. • Presence of an excessive amount of nitrates will require proportional amounts of carbon or energy source. This excess carbon source will also generate some additional biomass. • External carbon source is required if soluble influent organic content or chemical oxygen demand is insufficient. • Prone to washout conditions given very low nitrate, nitrite and/or selenium concentrations coupled with poor liquid solids separation, thereby requiring concentration of these through ion exchange or reverse osmosis. • Long periods of time for startup to acclimate the seed given washout and difficulty in controlling the solids residence time. • Requires granulating solids to perform at a high removal rate and minimize solids washout. • Biological residuals will need to be thickened and dewatered for landfill disposal.	treated, with operating costs representing \$0.28 to \$0.34/ m^3 (Frankenberger et al., 2004). The cost for the organic carbon that is added to the water accounts for 5 to 25% of the operating costs if methanol is used (Frankenberger et al., 2004).
Zero Valent Iron (ZVI)	4.3.3.1	ZVI chemically reduces the oxidized forms of selenium: selenate and selenite. ZVI media can be in powder, granular or fibrous forms.	Pilot-Scale	1. Flow equalization/diversion required as part of the treatment train. 2. Pretreatment a. pH adjustment may be required. 3. Core Technology a. Mass transfer driven technology. b. Hydraulic residence time is a key design parameter. c. pH control at pH 4 to 5 is key to green rust formation for reduction..	• Basic technology is demonstrated in laboratory studies to remove selenate and selenite at low concentrations. • Provides two reduction mechanisms for selenium including: green rust for reduction of selenate to selenite and selenite to elemental selenium; and ferrous iron for reduction of	• ZVI technology has not been proven in full-scale treatment and at higher selenium concentrations. • Potential for long residence times. • Spent ZVI must be removed, disposed of and replaced. • Dissolved oxygen and other oxyanions can oxidize the ZVI at certain	• Section 4.3.3.1 contains parametric cost curves for capital and operating costs, process flow diagram and assumptions for development of costs for a column-based (using steel wool) system and a stirred-tank based

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Technology	Section Reference in Text	Technology Description	Development Stage for Selenium Removal	Key Design Considerations	Advantages[1]	Disadvantages[1]	Capital and Operating Costs[2]
				d. Presence of other oxyanions (e.g., carbonate, sulfate, nitrates, phosphates) can interfere with reduction. 4. Tertiary Treatment a. Due to iron content and reducing environment, aeration followed by clarification is recommended to remove iron. 5. Residuals Management a. Media requires periodic replacement and disposal. b. Iron residuals with adsorbed selenium will require thickening and dewatering for disposal as solid waste in a landfill. c. Will require TCLP testing to determine whether sludge should be disposed as hazardous waste.	selenate to selenite. • Provides ferric iron for ferrihydrite adsorption of selenite.	conditions. • Sludge disposal may be significant cost. • ZVI treatment is temperature and pH dependent.	system (using granular ZVI). For Column-Based System (Using Steel Wool) • Total installed cost for 1 million U.S. gallons per day system is estimated as $13 million (2010 USD) (+100%/-50%). • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as $3 million (2010 USD) (+100%/-50%). For Stirred-Tank Based System (Using Granular ZVI) • Total installed cost for 1 million U.S. gallons per day system is estimated as $11 million (2010 USD) (+100%/-50%) • Annual operation and maintenance cost for 1 million U.S. gallons per day system is estimated as $3 million (2010 USD) (+100%/-50%).

Notes:

[1] Advantages and disadvantages are not presented within this table for technologies that have been demonstrated at laboratory-scale only, because further research and optimization are needed to determine the feasibility in applications to remove selenium from water.

[2] Capital and operations and maintenance cost assumptions associated with costs developed as part of this document are provided within the section text for specific technologies. Costs developed for this document are defined by the American Association of Cost Engineers International as Class 5 with an accuracy of +100% and -50%. This estimate is prepared based on limited information, where little more than proposed plant type and the capacity are known. 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, location and site conditions, final project scope, implementation schedule, and other variable factors. As a result, the final total installed cost will vary from the total installed cost and operations and maintenance costs prepared.

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Acronyms and Abbreviations

AA	activated alumina
ABMet®	Advanced Biological Metals Removal
AACEI	American Association of Cost Engineers International
ABSR	algal-bacterial selenium removal
°C	degrees Celsius
°F	degrees Fahrenheit
µg/g	micrograms per gram
µg/L	micrograms per liter
µg Se/L	micrograms selenium per liter
BOD	biochemical oxygen demand
$CaCO_3$	calcium carbonate
COD	chemical oxygen demand
DBA	dibasic acid
DO	dissolved oxygen
DRC	dynamic reaction cell
EC	electrocoagulation
ED	electrodialysis
EDR	electrodialysis reversal
EES	enhanced evaporation system
EP	evaporation pond
EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
FBR	fluidized bed reactor
FGD	flue gas desulphurization
GAC	granular-activated carbon
H_2Se	hydrogen selenide
HRP	high-rate pond

HRT	hydraulic retention time
ICP-MS	inductively coupled plasma mass spectrometry
IFDM	Integrated On-Farm Drainage Management
Lpm	liters per minute
m^3	cubic meters
m^3/day	cubic meters per day
MDL	method detection limit
MF	microfiltration
mgd	million gallons per day
mg/L	milligrams per liter
mg/kg	milligrams per kilogram
mg Se/kg	milligrams selenium per kilogram
mm	millimeter
MSE	MSE Technology Applications, Inc.
MW	molecular weight
NAMC-SWG	North American Metals Council - Selenium Work Group
NF	nanofiltration
NPDES	National Pollutant Discharge Elimination System
NSMP	Nitrogen and Selenium Management Program
NTU	Nephelometric turbidity unit
O&M	operation and maintenance
ODA	overburden disposal area
ORP	oxidation reduction potential
PRB	permeable reactive barrier
psig	pounds per square inch gauge
RCRA	Resource Conservation and Recovery Act
redox	oxidation-reduction
RO	reverse osmosis
SBA	strong base anion
SBR	sequencing batch reactor

SCR	selective catalytic reduction
SDI	silt density index
SeO_2	selenium dioxide
SF	safety factor
SSW	stripped sour water
SWS	sour water stripper
TCLP	Toxicity Characteristic Leaching Procedure
TDS	total dissolved solids
TIC	total installed cost
TiO_2	titanium dioxide
TOC	total organic carbon
TSS	total suspended solids
UASB	upflow anaerobic sludge blanket
UF	ultrafiltration
USBR	United States Department of Interior, Bureau of Reclamation
USD	United States dollar
USDOE	United States Department of Energy
USEPA	United States Environmental Protection Agency
US gpm	United States gallons per minute
UV	ultraviolet
VSEP®	Vibratory Shear Enhanced Processing
WSPA	Western States Petroleum Association
ZLD	zero liquid discharge
ZVI	zero-valent iron

1.0 Introduction

Selenium is widely distributed throughout most soils and natural waters. Increasingly, as regulatory limits are becoming more stringent, selenium is presenting a significant challenge to wastewater treatment. Like any constituent that is present in water at low concentrations, it is difficult to consistently achieve low parts per billion effluent limits with water treatment technologies. Management and treatment of selenium to these low limits is technically challenging and expensive.

This review is centered on industry-specific approaches to selenium management. Industries represented in the North American Metals Council - Selenium Work Group (NAMC-SWG) are faced with managing selenium in water from processes that include the mining and agriculture, power generation, and oil and gas industry sectors. The water and wastewater characteristics discharged from each industry's processes differ from those of other industries, so treatment technologies and source-control management strategies cannot be applied uniformly for each industry.

There are three management approaches for control of selenium in water: prevention of release, control of the source of selenium in the environment, and water treatment (Brienne et al., 2009). Prevention of release and source control strategies are more desirable than water treatment as these strategies are generally more cost-effective than removal of selenium by water treatment while minimizing risk to potential ecological receptors. Treatment may be a component of a successful selenium management strategy, but it is to be considered only if prevention and source control measures cannot be feasibly implemented. Although the focus of this report is on treatment technologies for the removal of selenium from water, prevention and source control strategies are also discussed.

1.1 Objectives

The objectives of the review are to:

- Summarize industry-specific approaches to management of selenium in water by reviewing strategies for prevention, source control, and treatment.
- Provide a clear and detailed summary of the available physical, chemical, and biological selenium removal technologies.
- Describe case studies of selenium treatment applications to aqueous effluents at the pilot or full-scale stage for the following industry sectors:
  - Mining and agriculture
  - Power generation
  - Oil and gas

1.2 Approach

The information included within this review is based on:

- Literature surveys;
- Interviews conducted with industry-specific facility managers;
- Case studies provided by agriculture, mining, power generation, and oil and gas industries; and,
- CH2M HILL's water and wastewater treatment subject matter and industry expertise.

This review includes a discussion of the treatment process, treatment configuration, typical removal levels for selenium, factors that affect selenium removal, advantages and limitations of the technology, and capital and operating costs of the technologies.

1.3 Review Limitations

The data presented in this review came from a variety of sources, including a literature search of published data, case studies from NAMC-SWG members, and CH2M HILL experience. Because data were collected from various sources, the quality of the data could not be verified. Sample methods, sample filtration, sample preservation, and analytical methods differed among the data reviewed.

This review summarizes case studies of full-scale and pilot-scale technologies implemented for selenium removal from water. This is based on technologies currently implemented at facilities and therefore represents a snapshot in time of selenium removal technologies being used by the various industry sectors.

1.4 Organization

This review is organized into the following sections:

- Section 1.0, Introduction—provides a summary of the purpose, objectives, approach, and report organization.
- Section 2.0, Selenium Sources and Important Characteristics—provides a brief review of:
  - Selenium benefits/toxicity and biological reactions involving selenium;
  - Description of different (natural and anthropogenic) sources of selenium in the target industries;
  - Selenium chemical properties and speciation;
  - Selenium-metal (cation/anion) interactions and their effects on selenium toxicity and treatment effectiveness;
  - Potential analytical methods for its detection in biological and non-biological samples; and,
  - Current environmental and regulatory challenge regarding selenium.
- Section 3.0, Source Control and Prevention Strategies presents strategies to mitigate release of selenium in the specific processes in each industrial operation where selenium predominates.

- Section 4.0, Overview of Water Treatment Technologies for Selenium Removal, includes a summary of available physical, chemical, and biological treatment technologies that have been tested at bench, pilot or full-scale for selenium removal.
- Section 5.0, Industry-Specific Approaches to Management of Selenium: Mining and Agriculture, includes characterization, prevention, source control, and treatment approaches for the mining and agriculture sector. Case studies for full-scale and pilot-scale treatment approaches are provided.
- Section 6.0, Industry-Specific Approaches to Management of Selenium: Power Generation, includes characterization, prevention, source control, and treatment approaches for the power generation sector. Case studies for full-scale and pilot-scale treatment approaches at coal-fired power plants are provided.
- Section 7.0, Industry-Specific Approaches to Management of Selenium: Oil and Gas, includes characterization, prevention, source control, and treatment approaches for the oil and gas sector. Case studies for full-scale and pilot-scale treatment approaches for oil refineries are provided.
- Section 8.0, Conclusions, presents the conclusions of this review.
- Section 9.0, References, presents the works cited during compilation of this review.

2.0 Selenium Sources and Important Characteristics

This section provides a brief description of selenium sources and some of the more important characteristics of selenium as background for the evaluation of removal technologies. More extensive background information is available in other reviews (Frankenberger and Engberg, 1998; Eisler, 2000; Ohlendorf, 2003; Hamilton, 2004; Canton et al., 2008; Ralston et al., 2008; Ohlendorf et al., 2008; Chapman et al., 2009a; DeForest, 2009) and in a book resulting from a week-long workshop focusing on ecological assessment of selenium in the aquatic environment (Chapman et al., 2010).

2.1 Natural and Anthropogenic Sources of Selenium

Selenium is a naturally occurring element in the Earth's crust that is redistributed in the environment through multiple natural and anthropogenic processes (Chapman et al., 2010). The major geologic sources of selenium include crustal rock such as black shale, phosphate rocks, and coal, while other formations such as igneous rock and limestone are minor sources. Natural processes that redistribute selenium include volcanic activity, terrestrial weathering of rocks and soils, wildfires, and volatilization from plants and water bodies.

Selenium is redistributed from the various enriched geological sources into aquatic, sedimentary, atmospheric, and terrestrial compartments (Chapman et al., 2010). In addition to transporting selenium, the natural processes mentioned above transform the element into different species (or chemical forms, such as from selenate to selenite) and transfer these forms between phases (e.g., from liquid to solid). The variations in selenium sources, phases, and speciation in different locations create region-specific risk profiles that should be recognized when managing selenium contamination in the environment.

Regionally, human activity is a major factor in the mobilization of selenium (Chapman et al., 2010). Mining, fossil fuel combustion, oil refining, and discharge of seleniferous drainage water from irrigated agriculture are all anthropogenic sources of selenium to aquatic systems that may be regionally or locally important. Other agricultural activities, including field application of biosolids (from wastewater treatment facilities), manure, chemical fertilizers, and selenium supplements for livestock, are relatively minor sources. The major human activities affecting mobilization of selenium are briefly described in Sections 2.1.1 through 2.1.4 and described in more detail in Sections 5, 6, and 7 which discuss specific approaches for the mining and agriculture, power generation and oil and gas sectors, respectively.

2.1.1 Mining

Coal, phosphate, and sulfidic ore mining produces waste rock (e.g., overburden) that is excavated during active mining to reach the coal, phosphate, or ore body. Runoff or other releases from waste rock piles, tailings impoundments, backfilled mining excavations, and reclaimed areas that have been mined can release large amounts of selenium which, in uncontrolled settings, can eventually reach aquatic ecosystems. In addition, mineral concentrate containing selenium from ore mining may be released to the environment through mishandling before smelting. Sources of selenium in the mining industry are discussed further in Section 5.2.2.

2.1.2 Fossil Fuel Combustion

Combustion of fossil fuels (coal and oil) releases significant quantities of selenium into the environment. Historically, coal-fired power plants emitted selenium as selenium dioxide (SeO_2), mostly in the vapor phase, to the atmosphere and as aqueous selenate. The primary route of selenium discharge into the aquatic environment from coal-fired power plants was from sluicing fly ash into settling ponds and subsequently discharging ash pond effluent. Several notable examples of the effects of fly ash disposal include Belews Lake and Hyco Reservoir in North Carolina and Martin Lake in Texas. Recently, however, power plants have been adding wet flue gas desulphurization (FGD) systems to their process, changing the nature of discharges to include scrubber wastewater that must be managed. Sources of selenium in the power generation industry are discussed further in Sections 6.1 and 6.2.

2.1.3 Oil Refining

Crude oil from certain geological formations such as marine shales can be rich in selenium, making refinery effluents a major source of loading to aquatic environments, depending on their source(s) of crude oil (e.g., San Francisco Bay, California). Sources of selenium in the oil and gas industry are discussed further in Section 7.1.

Figure 2-1 shows worldwide petroleum basins and phosphate deposits that likely contain seleniferous deposits.

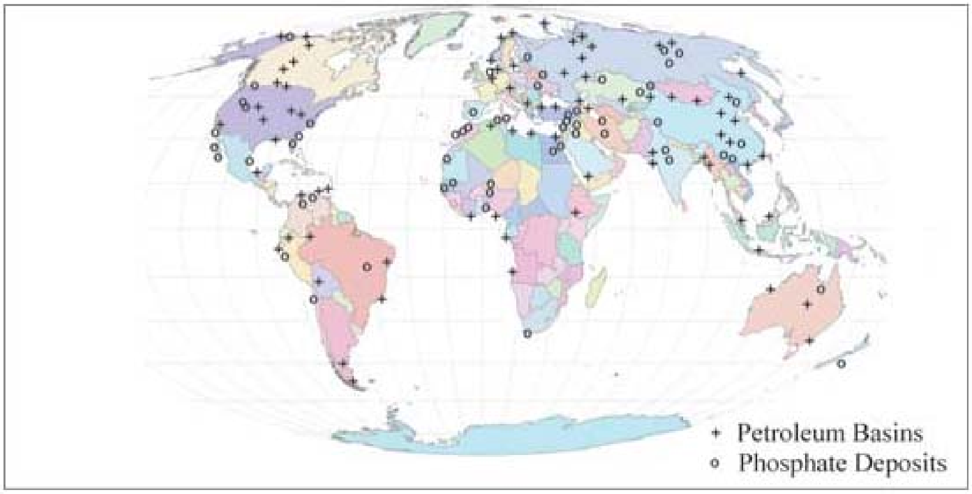


FIGURE 2-1
Global Distribution of Petroleum Basins and Phosphate Deposits
Source: United States Geological Survey, http://wwwrcamnl.wr.usgs.gov/Selenium/intro.htm

2.1.4 Agricultural Irrigation

Irrigation of saline and sometimes seleniferous soils, such as those found in parts of the Central Valley of California and several other areas in the western United States, has led to significant selenium contamination in aquatic ecosystems from impoundment of irrigation drainage (e.g., Kesterson Reservoir in California) (Presser and Ohlendorf, 1987). Sources of selenium in the agriculture industry are discussed further in Section 5.1.1.

2.2 Selenium Chemistry

Selenium exists in a wide variety of chemical and physical forms (or species) that are linked by many biogeochemical transformation reactions (Chapman et al., 2010). These species can be grouped into the four major categories of: (1) inorganic selenium, (2) volatile and methylated selenium, (3) protein and amino acid selenium, and (4) non-protein amino acids and biochemical intermediates. Selenium typically occurs in the environment in one of four oxidation states that include Se(VI), Se(IV), Se(0), and Se(-II). It is usually found as the oxyanions selenate (SO_4^{2-}) and selenite (SO_3^{2-}) in oxidized systems and as elemental selenium (Se[0]) and selenides (HSe^-) in anaerobic zones and unweathered mineral formations. Reduced selenium species [such as Se(0), Se(-II)] and strongly adsorbed selenium species are insoluble and therefore are more likely to be released as fine particulates to the atmosphere or as colloidal suspensions in surface waters than in dissolved forms.

Selenium species in water can exist in dissolved and suspended particulate forms (Chapman et al., 2010). In the pH range of 6 to 8, only Se(0), selenite, biselenite ion ($HSeO_3^{-1}$), and selenate are present in water. Suspended particles containing selenium can be an important part of the selenium load in the water column. For example, selenite partitioning to amorphous iron oxyhydroxides and manganese dioxide on particles have been shown to be important in the sequestration of selenium.

A simplified selenium-water system Pourbaix diagram showing major thermodynamically stable selenium species as a function of pH and oxidation-reduction potential (ORP) is shown in Figure 2-2. However, these conversions may not occur in the environment because ambient systems are not in thermodynamic equilibrium and speciation may not be accurately predicted by only pH and ORP (Ralston et al., 2008).

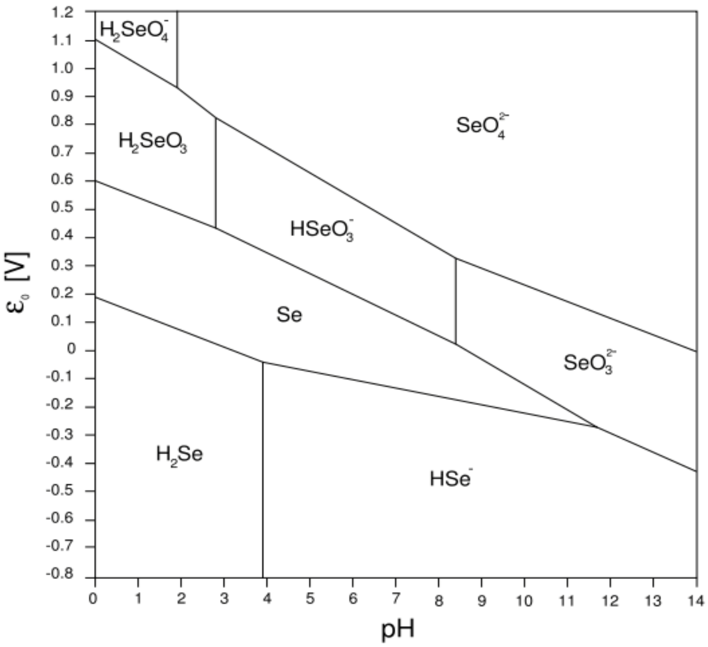


FIGURE 2-2
Selenium Pourbaix Diagram

Selenite oxidation is enhanced by factors that increase the concentrations of strong oxidants in the water column such as ultraviolet (UV) radiation, redox-active transition metals (such as iron) or by the presence of a high abundance of selenite-oxidizing bacteria. Although selenite is thermodynamically unstable in oxic waters, it is frequently encountered due to its slow oxidation kinetics and the presence of reducing bacteria. Selenite and selenate are normally stable in natural waters, but they can be oxidized or reduced on mineral surfaces. Selenate can be quickly removed from the water column to sediment via reduction to Se(0) and through binding to organic matter. Organoselenium compounds undergo photooxidation in water, and their mineralization eventually yields inorganic selenium species. Volatile species of selenium—H_2Se, CH_3SeH, $(CH_3)_2Se$, and $(CH_3)_2Se_2$—are also known to be formed in selenium-containing water bodies.

Aquatic sediments represent a dynamic, complex medium where selenium speciation is controlled by chemical and physical properties of sediments and by various biotic factors (Chapman et al., 2010). In freshwater environments, selenium is adsorbed onto iron-manganese oxyhydroxides at sediment surfaces, released by the reduction of those oxyhydroxides, mineralized with organic matter, and removed from pore water as Se(0) and as selenopyrites. Low ORP conditions favor low selenium solubility as iron selenide or Se(0) phases are formed.

Selenium speciation can vary within a facility as water flows through process units and through water treatment systems. Sampling and analyses of selenium species may be required at multiple locations within a facility to adequately characterize selenium in water through various facility processes. Characterization of the various selenium species present within water throughout a facility is required to determine the appropriate treatment method. Some treatment methods can be applied only to certain selenium species. This is discussed further in Section 4.

2.3 Selenium Toxicity

Selenium is an essential element for animal nutrition, but there is a narrow range of dietary concentrations between those that are adequate for nutrition and those that cause adverse effects. Diet is the primary pathway for exposure/uptake of selenium by animals. Selenium is necessary for the proper functioning of structural proteins and cellular defenses against oxidative damage, and selenium deficiency is a more widespread problem than is excess selenium that causes toxicity (Chapman et al., 2010; Ralston et al., 2008; Raisbeck et al., 2007). Traditional methods for predicting toxicity on the basis of exposure to dissolved concentrations in water do not work for selenium because the behavior and toxicity of selenium in aquatic systems vary greatly based upon site-specific factors such as food web structure and hydrology.

Nutritional requirements for fish, amphibians, and birds (generally the potential receptors of concern in receiving waters) are less than 0.5 milligrams selenium per kilogram (mg Se/kg) in the diet, whereas toxicity may occur in sensitive species when diets contain concentrations as low as approximately 5 mg Se/kg. Toxicity thresholds for fish and birds are summarized by Canton et al. (2008), Ohlendorf et al. (2008), and Ohlendorf and Heinz (2010). Toxicity is primarily expressed as reproductive impairment due to maternal transfer, resulting in embryo mortality and deformities as well as poor survival of exposed hatchlings.

When present in appropriate ratios, selenium provides protective action against the toxicity induced by mercury, cadmium, arsenic, thallium, copper, zinc, silver, and various pesticides in some animals (Eisler, 2000). For example, selenium reduced the toxicity of mercury when both selenium and mercury were fed to adult mallards at equal dietary concentrations (10 milligrams per kilogram [mg/kg]) (Heinz and Hoffman, 1998). However, when both selenium and mercury were fed to adult mallards at those concentrations (10 mg/kg), the negative effects on embryos (expressed as mortality and deformities) were greater than when either selenium or mercury alone were added to the diet. Thus, there is not a universal protective action, and the ratios of exposure concentrations are important.

2.4 Analytical Methods

Assessment of selenium in effluents and in the aquatic environment depends heavily upon adequate analytical methodologies for reliable measurement of selenium concentrations in environmental materials (ores, soils, sediment, and water) and in biological tissues (Ralston et al., 2008). The relationship between environmental selenium concentrations and the amounts of selenium bioaccumulated from the environment are essential components in assessing potential risks related to selenium exposure. Risk assessment, management, and remediation decisions must be based on accurate and precise analytical data. The determination of selenium and its various chemical forms (species) at ambient concentrations is complicated, and inappropriate analytical procedures have frequently been used. Analytical instrumentation and methods vary in their capability for measuring selenium in various media, so it is important to recognize the relative strengths and weaknesses of different analytical methods. Ralston et al. (2008) provide a review of current state-of-the-science methods, with recommended methods for various media. Selecting the best analytical approach makes it possible to obtain the most reliable data regarding selenium's concentration-dependent effects in supporting normal physiology or potentially inducing toxicity. Analyses of total selenium and selenium speciation should be used in a complementary and comparative manner for risk assessment and management/ remediation strategies.

Assessment and treatment of selenium in liquid streams depends heavily upon adequate analytical methodologies for reliable measurement of total and dissolved selenium concentrations as well as various selenium species concentrations. Chemical analysis is often difficult due to matrix interferences which can be problematic when performing analytical methods such as United States Environmental Protection Agency (USEPA) Methods 200.7 and 200.8. Inductively coupled plasma is used for both Methods 200.7 and 200.8. The basis of Method 200.7 is the determination of concentration via optical emission spectrometry. Concentration determination by Method 200.8 involves inductively coupled plasma in conjunction with mass spectrometry (ICP-MS).

A low-level analytical method that has been applied in aqueous samples for total and dissolved selenium determination is USEPA Method 1638, which uses ICP-MS. Method 1638 is not approved for National Pollutant Discharge Elimination System (NPDES) permit compliance monitoring, although it has been allowed in some cases. A modification of Method 200.8 that includes the clean procedures and performance specifications of Method 1638 also has been allowable in some cases (Electric Power Research Institute [EPRI], 2009a). A collision/reaction cell or dynamic reaction cell (DRC) is sometimes used to reduce matrix interferences using Methods 200.8 or 1638. Samples are typically diluted to minimize these interferences which additionally decreases the amount of dissolved solids introduced into the plasma. This, as a result, increases the detection limits. The DRC technology removes these interferences while maintaining low detection limits. However, no draft method has been published by the USEPA for ICP-MS analyses with collision/reaction cells or DRCs. Measuring low levels of selenium (e.g., 5 micrograms per liter [µg/L]) may require "clean" sampling methods and using techniques such as DRC to minimize matrix interferences.

Although there is no method currently promulgated by regulatory agencies, there are various methods available for selenium speciation analysis:

- Ion chromatography inductively coupled plasma mass spectrometry;
- Hydride generation atomic absorption spectrometry;
- Gas chromatography inductively coupled plasma mass spectrometry;
- Capillary electrophoresis inductively coupled plasma mass spectrometry;
- Liquid chromatography electrospray ionization mass spectrometry; and,
- High-performance liquid chromatography inductively coupled plasma mass spectrometry.

Speciation methods that rely on chemical conversion do not adequately characterize the composition of a complex matrix. The most commonly used technique for measuring selenite and selenate is hydride generation atomic absorption spectrometry. In this approach, selenite is determined directly, while selenate is determined by subtraction after conversion to selenite. However, other selenium species may be present in wastewater such as selenocyanate, methylseleninic acid, selenosulfate, selenomethionine, and other unknown selenium compounds. These other selenium species can be quantified using ion chromatography inductively coupled plasma mass spectrometry. This method uses a chromatographic column to separate the various species before directly measuring the quantity of each selenium-containing species by ICP-MS. The ICP-MS may be equipped with DRC to overcome interferences from other substances in the complex wastewater matrix. A study was performed for the Orange County, California Nitrogen and Selenium Management Program (NSMP) to evaluate hydride generation atomic absorption spectrometry, ICP-MS, and high-performance liquid chromatography system to an inductively coupled plasma mass spectrometry using DRC. The high-performance liquid chromatography system to an inductively coupled plasma mass spectrometry using DRC method provided the lowest method detection limit (MDL) (NSMP, 2006).

Sample handling and preparation methods may also affect analytical results for selenium. For selenium speciation, the method of preservation (e.g., cryopreservation versus acid preservation versus no preservation) may also impact the results of samples collected (Shamas et al., 2009). For total selenium, the method of digestion may impact results. USEPA Methods 200.7 and 200.8 do not call for a closed vessel digestion. However, using a closed vessel can prevent volatilization loss of selenium during digestion (EPRI, 2009a). Ralston et al. (2008) recommend that total selenium and selenium speciation analysis should be used in a complementary and comparative manner for developing the best informed risk assessment, management, and remediation strategies.

2.5 Regulatory Issues

For the United States, information on the current and proposed USEPA National Recommended Water Quality Criteria for selenium can be found at www.epa.gov/waterscience/criteria (Chapman et al., 2010). The federal Clean Water Act requires the USEPA to develop criteria for “priority pollutants,” among which selenium is included. States and tribes must either adopt the national recommended criteria or develop their own. After criteria are adopted, point source dischargers with reasonable potential to cause exceedance of criteria are given appropriate effluent limits in their NPDES permits. Beyond that, waters listed as “impaired” (not attaining goals) are subject to total maximum daily load restrictions on both point and nonpoint sources.

The existing National Recommended Water Quality Criteria are based on total recoverable selenium concentration in water, with a chronic value of 5 micrograms selenium per liter (µg Se/L) (USEPA, 1987). In 2004, USEPA published draft criteria that included chronic exposure limits based on selenium concentrations in whole-body fish (USEPA, 2004). Since 2004, new information has become available (Chapman et al., 2010), including USEPA’s (USEPA, 2008) repeat of the study by Lemly (1993) using the same simulated winter exposure scenario. Results of the USEPA study indicate that Lemly’s results were conservative, but regulations for selenium by USEPA are currently in flux.

USEPA is leaning toward the use of a two-part criterion including selenium concentration in fish egg-ovary coupled with a water screening value (Delos and McIntyre, 2009). If the latter is exceeded, the former must be either measured or may be estimated using whole-body concentrations. It is expected that the water screening value will be conservative and will thus be lower than the current 5 µg/L USEPA water criterion. The least defined values for uptake from water are the water-to-algae numbers, which vary by orders of magnitude between sites and which are empirical (they cannot presently be modeled). There is less variability among the transfer factors from one trophic level to another than in the initial uptake factors from water. It is expected there will be no implementation guidance provided with the draft criterion document. The Office of Management and Budget does not carefully review criterion documents but does rigorously review implementation guidance, which includes policy not just science. USEPA may not provide implementation guidance with the draft criterion.

In Canada, aquatic ecosystems are protected in part by the Fisheries Act, which prohibits the deposit of substances that are deleterious to fish into waters frequented by fish (Fisheries Act 1985) (Chapman et al., 2010). While this is a federal regulation, it is delegated to some provinces that can authorize the deposits of deleterious substances through various effluent permitting processes. Permits are negotiated by the stakeholder and the government and may contain specific limits on chemical concentrations and toxicity of the effluent and directions on monitoring and/or compliance requirements. With respect to selenium, permits may require stakeholders to monitor levels in water or the biota or possibly comply with the Canadian Water Quality Guideline of 1 µg/L total selenium in surface waters (Canadian Council of Ministers of the Environment, 2007).

In contrast, British Columbia developed a Water Quality Guideline of 2 µg/L for both freshwater and marine aquatic life (Nagpal and Howell, 2001). The 2 µg/L guideline for the water column is intended to protect aquatic life from direct toxic effects as well as from accumulating undesirable levels of selenium via the food chain. The guideline to protect from direct toxicity of selenium was based on the lowest observed effect level of 10 µg/L and a safety factor (SF) of 5, which is lower than 10 recommended in the Canadian Council of Ministers of the Environment protocol. This choice for the lower SF was in recognition of the facts that (a) selenium is an essential element for animal health, and (b) food (and not water) is the major source of selenium in the food chain. Another basis for this guideline is a fish tissue threshold of 1 micrograms per gram (µg/g) wet weight. Assuming average moisture content for bony fish of 75% (USEPA, 1993), the dry-weight equivalent of this threshold is 4 µg/g.

3.0 Prevention and Source Control Strategies for Selenium Management

A successful strategy for managing selenium in water involves identifying target goals and potential ecological receptors, characterization to understand sources and the nature and concentrations of selenium in water discharges, understanding pathways to receptors, identifying mitigation and source control strategies to prevent receptors from coming into contact with selenium, and developing treatment strategies if mitigation and source control strategies are not applicable (Chapman et al., 2009b).

As evident in Canadian and United States environmental legislation, waste minimization is a major goal of environmental pollution prevention programs. There are three management approaches for control of selenium in water: prevention of release, control of the source of selenium in the environment, and water treatment (Brienne et al., 2009). Prevention of release and source control strategies are more desirable than water treatment as these strategies are generally more cost-effective than removal of selenium by water treatment while minimizing risk to potential ecological receptors. As discussed in Section 4, one of the inherent challenges of selenium treatment is the dilute nature that selenium typically is found in waters from mining and agriculture, power generation, and refining processes. Prevention and source control strategies can reduce or in some cases eliminate the volume of water that requires treatment. Prevention eliminates or mitigates selenium at the source by modifying processes, increasing efficiency in the use of raw materials or water, implementing conservation techniques, and re-using materials (Higgins, 1995).

Where water minimization, recycling or re-routing are not possible, selenium may be removed by various treatment strategies. Treatment technologies for the removal of selenium from water may be implemented at the source or at the “end-of-pipe”, or a combination of both locations. Treatment systems may be required to treat selenium at upstream and/or downstream locations based on the treatment target level or as speciation of selenium varies at different locations within a facility.

A combination of prevention, source control, and treatment may be required for a successful selenium management strategy. Reducing the volume of water to be processed through prevention and source control strategies may reduce capital and operating costs for treatment systems. A reduction in volume of water to be treated also means a smaller footprint is required for the treatment system. Segregating and treating upstream sources may be sufficient to meet required target levels and avoid the costs of a centralized treatment system that ties in multiple sources at the facility. Sections 5, 6, and 7 discuss in detail and provide examples of prevention and source control methods with discussion of site factors that influence management for each of the three industry sectors: mining and agriculture, power generation, and oil and gas. General prevention and source control strategies are discussed in this section by industry.

3.1 Agriculture

Since selenium can be widely distributed in the alluvial deposits and thereby indigenous to soil used for agriculture in certain geographies (e.g., San Joaquin Valley, California) agricultural drainage from these areas contains elevated levels of selenium. However, there are a variety of source control and mitigation strategies for agricultural drainage from these areas to minimize selenium exposure to ecological receptors. Mitigation strategies for the agricultural sector center on modifying irrigation practices to control selenium release to the environment. Source control includes limiting deep percolation losses from supply canals and other structures that convey irrigation water. These practices are discussed further in Section 5.1.2.

3.2 Mining

Hard rock and mineral mining (e.g., gold, copper, phosphate, uranium et al.) can result in selenium release to the environment either through waste rock or tailings produced from surface or pit mining, and/or through mineral extraction processes for concentration and recovery of the metal of concern. Soft rock mining (e.g., coal, bitumen) can also result in the release of selenium to the environment, primarily through waste rock and tailings produced from surface or pit mining operations. Selenium tends to concentrate with the sulfur-containing minerals in both of these mining operations. In soft rock mining there is selenium organically bound in the coal or bitumen that will not leach.

Waste rock from both hard and soft rock mining operations generally is the primary source of selenium from these operations. Typically the selenium in the tailings or waste rock or metal bearing rock will oxidize over time when exposed to air through materials handling activities, and/or other through processing techniques to extract the metal. Once oxidized, the selenium will generally exist as selenite or selenate, depending upon the level of oxidation. In these forms selenium will leach when exposed to water, or migrate from the rock.

Source control in mining is focused on management of waste rock to first minimize oxidation of selenium and secondly minimize release of selenium through prevention of water contact with the waste rock or materials containing leachable forms of selenium. The large area of the mining operation, large volume of waste rock, overburden, or tailings, and the dispersion of selenium through the rock all complicate the source control of selenium. Careful consideration in the design of water diversions, rock dumps, valley fills, rock drains, landforms, final reclamation cover, pit lakes, and tailings ponds can reduce selenium release to the environment.

Various mitigation and source control practices have been implemented in the mining industry, as described in Section 5.2.3. Chapman et al. (2009b) present an assessment tool that can be adapted for other coal mining facilities and potentially for other types of mining facilities or even other industry sectors. The components of the assessment tool include management actions at selenium sources, geochemical interventions to reduce organic selenium formation, institutional controls, environmental enhancement (i.e., mitigation actions), and treatment. The assessment tool provides guidance on the development of data quality objectives to define the problem to be investigated through different studies, developing a conceptual model to provide linkage among those studies, as well as actions that might be taken to minimize selenium discharges and identifying where management actions could be taken. This assessment tool is described further in Section 5.2.3.

3.3 Power Generation

Pulverized coal combustion to produce steam for either single cycle electrical power, or for thermal energy will result in the release of selenium to the environment. Selenium contained in the combusted coal will volatilize to the flue gas and in part condense to particulates (e.g., fly ash and bottom ash) in the combustion process (e.g., boiler). Air pollution control of particulate matter by bag houses and electrostatic precipitators, and volatile emissions (e.g., sulfur oxides) by FGD scrubbing will capture the majority of selenium from the combusted coal. Solid waste in the form of bottom ash from the boiler and fly ash from the flue gas particulate control contain selenium primarily in the form of selenite. Water, or lime from wet or dry scrubbing flue gas desulfurization processes will also contain selenium in either selenite and/or selenate forms depending upon the scrubber type.

Mitigation and source control strategies for selenium in the power generation sector are generally for coal-fired power plants to reduce selenium loading to water sources. Wet sluicing of fly ash to ash ponds is a significant source of selenium to ash pond water. Conversion from wet fly ash handling to dry fly ash handling reduces the load of selenium in process waters at coal-fired power plants. This is described further in Section 6.3.

Wet flue gas desulfurization processes that do not use forced oxidation will result in wastewater that contains selenium primarily in the selenite form. Wastewater from forced oxidation FGD scrubbers is predominantly comprised of the selenate form of selenium. Source control of selenium in the scrubber is complicated, thereby limiting practical control and minimization techniques. Section 6 discusses options for treatment and source control of selenium from the power industry.

3.4 Oil and Gas

Trace levels of selenium can be found with produced water from oil and gas upstream activities. It varies by location, formation and well type (e.g., gas, oil, coal bed methane) but is primarily associated with gas production. Produced water from gas production generally is from either flow back water (e.g., water added for enhancing gas recovery/well fracturing) or water produced with the gas. Produced water associated with enhanced oil recovery (e.g., water and steam flooding) is generally treated and reused for flooding. Selenium associated with crude oil and bitumen (e.g., heavy oil) production is primarily organically bound. Where present it will be associated with the sulfur contained in the crude.

Processing of oil into gasoline and petrochemicals through downstream refining or upgrading (i.e., heavy oil) processes will result in selenium release to the environment. The primary point of selenium release from the oil to water in downstream processing is in sour water from crude oil fractionation processes and to a much lesser degree crude oil desalting/washing/dewatering operations. Selenium in refinery wastewater generally is found as hydrogen selenide, selenocyanate, selenite and selenate. The levels of selenium in crude oil are a function of the source of oil. The levels typically are proportional to the sulfur levels.

Prevention and source control options for the oil and gas sector are limited since there is no control over the composition of crude oils that are extracted. Wastewater recycling and reuse options for refineries are discussed in Section 7.1. The speciation of selenium changes through various processes and treatment steps within a refinery. Treatment at the source consists of implementation of treatment systems to treat selenocyanate at the sour water stripper (SWS) within a refinery. Treating the stripped sour water (SSW) may be a more cost-effective solution than a centralized treatment system since it represents the majority of the selenium produced in a refinery, however it requires a different approach to treatment since selenium will primarily exist as selenocyanate. Treatment of the SWS is discussed further in Section 7.3.

4.0 Overview of Treatment Technologies for Selenium Removal

Treatment of relatively dilute (e.g., less than 25 milligrams per liter [mg/L]) contaminants, or chemical constituents in water to very low concentrations (e.g., less than 5 µg/L) poses many technical challenges. Selenium treatment is no different. In fact, selenium removal from water is considerably more challenging than most contaminants considering the following:

- Treatment of relatively dilute streams at high flow rates;
- Stringent regulatory water quality limits (e.g., 5 µg/L and less);
- Complex chemistry of the element (i.e., it exists in many soluble and particulate forms) as certain treatment approaches may be ineffective based on the species of selenium present in the wastewater and speciation may vary through various processes within a treatment system;
- Competing and interfering water chemistry of industry-specific waters containing selenium;
- Perturbations in concentration of selenium and variability of water flows for treatment; and,
- Residuals and by-products from treatment technologies with concentrated selenium that, without proper handling and end disposal, can be released back into the environment.

Where prevention and source reduction strategies cannot be used, treatment technologies are implemented to remove selenium from water.

The treatment technologies described within this section are organized into physical, chemical, and biological treatment technologies. The discussion for each technology contains the following categories:

- General Technology Description, which highlights key guiding design principles and components of the technology.
- Treatment Effectiveness, which provides an overview of previous studies that have achieved selenium removal.
- Design and Operational Considerations, which provides a summary of the technology's operating flows, land requirements, pretreatment requirements, other constituents that may affect treatment, and operation and maintenance requirements, where information is available.

- Residuals Management, which summarizes discharge concerns and options for treatment of residuals.
- Capital and Operating Costs.
- Advantages and Disadvantages, which summarizes advantages and disadvantages of the technology.

Descriptions are also included of emerging technologies that have not been fully demonstrated.

4.1 Treatment System Design Considerations

There are numerous issues that must be considered with process design and selection of each core selenium treatment technology. While the scope of this document precludes covering every one, or any single issue in great detail, the key issues can be generally grouped into the following areas:

- Water Matrix Influences
- Systems Design
- Costs

4.1.1 Matrix Influences

There are various factors that affect the water matrix associated with process waters from the mining and agriculture, power generation and oil and gas sectors. Matrix interferences specific to each of the industry sectors are discussed further in Chapters 5, 6, and 7. The physical, chemical and biological treatment technologies for selenium removal are all affected by the water matrix. Water flow quantity, flow variability, pH, pressure, and temperature will affect each technology by influencing the water chemistry. Flow quantity and variability change the concentration and mass loading of selenium. The pH, pressure, and temperature will affect the solubility and activity of the chemistry of the water matrix. These variables affect the chemical, physical and biological treatment technologies by influencing the reaction kinetics, the mass transfer of the water and constituents through the water treatment process. The water matrix also impacts analytical methods, with a complex matrix influencing the reporting limit by increasing the dilution required to analyze the sample.

4.1.1.1 Ionic Strength

The ionic strength, or the relative concentration of all cations and anions in the water, will affect the solubility and activity of the chemistry, osmotic pressure, and biological treatment. Total dissolved solids (TDS) and electrical conductivity are good relative indicators of the ionic strength of the water. Generally the higher the TDS the more competing matrix chemistry impacts there will be on a water treatment technology for selenium.

4.1.1.2 Alkalinity

Alkalinity is a measure of the carbonate chemistry in water. All water will reach some equilibrium concentration of alkalinity given that carbon dioxide will dissolve in water to different forms of carbonate at different temperatures and pH. Understanding alkalinity concentrations and forms is important in understanding the potential for carbonate scale formation which can impact the various treatment technologies. Calcium carbonate ($CaCO_3$) is a common scale formed in waters with high alkalinities and moderate to high hardness. The theoretical relationship of the three (carbonate, bicarbonate, and carbonic acid) carbonate species (assuming that the total alkalinity is 100 mg/L as $CaCO_3$) at standard conditions assuming that the solution is ideal where activity equals ionic strength is shown as Figure 4-1. Above pH 10.3, carbonate is the principal form of the three species. Carbonate and bicarbonate are equal at pH 10.3. At pH 8.3, the predominant species is bicarbonate and little carbonate or carbonic acid is present. Bicarbonate and carbonic acid are equal at pH 6.3. Below this pH carbonic acid predominates.

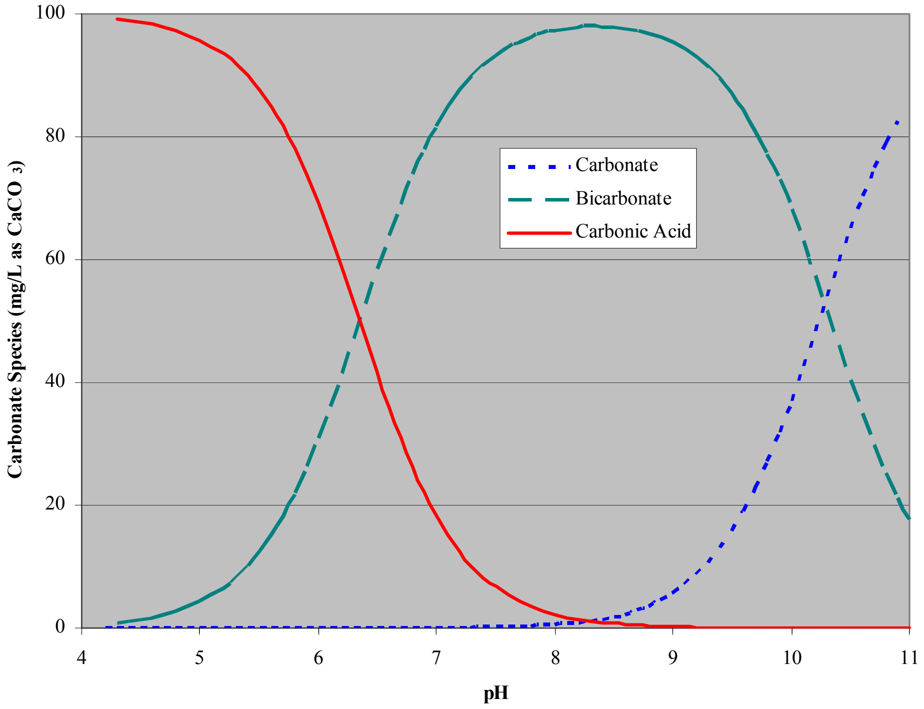


FIGURE 4-1
Theoretical Carbonate Concentration as a Function of pH (Total Alkalinity = 100 mg/L as $CaCO_3$)

4.1.1.3 Scale Formation

Various cations and anions will combine to form insoluble precipitates or scale. Solubility is a function of the ion concentration, the solution ionic strength, ion activity, pH, temperature, and pressure. Sparingly soluble salts such as calcium carbonate, sulfate salts of calcium, barium and strontium, reactive silica or silica dioxide, and metal oxides are typical scales that can be problematic with scale-sensitive treatment technologies. Table 4-1 provides a list of common cation and anion combinations and their relative solubilities. Selenium in the most common soluble forms of selenate and selenite are very soluble in water regardless of the cations present. Alkaline earth metals calcium and magnesium salts are ubiquitous in most ground and surface waters. They are notable scale-forming ions that are quantified by hardness measurements. Additionally, strontium and barium can be found in groundwater and surface waters. They too will form scale with certain anions. Sulfate, which is present in various process waters associated with the various industry sectors (mining, power generation, oil and gas), is also a significant scale-forming ion that combines with calcium, strontium and barium to form scale over a wide pH range. Reactive silica in water will create scale fouling issues with membranes. Each water source is subtly different and therefore will have a different scale potential. Scale typically can be controlled by softening, controlling the pH and temperature, and/or through the addition of antiscalants or complexing agents. Scale formation will affect many of the physical, chemical and biological treatment processes.

TABLE 4-1
Relative Solubilities of Cations and Anions
Source: Adapted from Kemmer, 1988

Cation/Anion	F^-	Cl^-	Br^-	I^-	HCO_3^-	OH^-	NO_3^-	CO_3^{2-}	SO_4^{2-}	S^{2-}	CrO_4^{2-}	PO_4^{3-}
Na^+	S	S	S	S	S	S	S	S	S	S	S	S
K^+	S	S	S	S	S	S	S	S	S	S	S	S
NH_4^+	S	S	S	S	S	S	S	S	S	S	S	S
H^+	S	S	S	S	CO_2	H_2O	S	CO_2	S	H_2S	S	S
Ca^{2+}	I	S	S	S	SS	VSS	S	I	VSS	X	S	I
Mg^{2+}	VSS	S	S	S	S	I	S	VSS	S	X	S	I
Ba^{2+}	VSS	S	S	S	VSS	S	S	VSS	I	X	I	I
Sr^{2+}	VSS	S	S	S	VSS	SS	S	I	VSS	X	VSS	I
Zn^{2+}	S	S	S	S	VSS	I	S	I	S	I	VSS	I
Fe^{2+}	SS	S	S	S	SS	VSS	S	VSS	S	I	X	I
Fe^{3+}	SS	S	S	S	I	I	S	I	S	X	X	I
Al^{3+}	S	S	S	S	X	I	S	X	S	X	X	I
Ag^+	I	I	I	I	I	I	S	VSS	S	I	I	I
Pb^{2+}	VSS	S	SS	VSS	I	VSS	S	I	I	I	I	I
Hg^+	I	I	I	I	I	I	S	S	VSS	I	VSS	I
Hg^{2+}	SS	S	S	I	I	I	S	I	VSS	I	SS	I
Cu^{2+}	SS	S	S	VSS	I	I	S	I	S	I	I	I

Notes:
S- Soluble, over 5,000 mg/L
SS- Slightly soluble, between 2,000 to 5,000 mg/L
VSS- Very slightly soluble, between 20 to 2,000 mg/L
I- Insoluble, less than 20 mg/L
X- Not a compound

4.1.1.4 Solids

Particulate or colloidal material will influence the physical, chemical and biological treatment of selenium. Particulates (usually measured as total suspended solids [TSS] or total solids) will plug or foul many treatment unit processes, thereby requiring removal. Particulates are present in most waters from the various industry sectors. Particulates may occur in water as a result of chemical scale, silt, sediment, biological solids and organic emulsions. Colloidal materials may require coagulation and flocculation to increase the particle size to aid in sedimentation or media filtration. Silt density index (SDI) is a measure of the fouling potential for membranes and must typically be below 5 and ideally between 2 to 3 for high pressure membrane separation processes.

4.1.1.5 Other Matrix Influences

There are numerous other influences on the water matrix that will affect selenium removal. These include but are not limited to the following:

- Soluble and insoluble organics;
- Complexing or chelating agents;
- Microbiological activity;
- Oxidizing and reducing agents, and,
- Competing oxyanions.

4.1.2 Systems Design

Each core selenium treatment technology is generally part of several other treatment technologies or unit processes that form an overall treatment system, especially when target discharge requirements are less than 5 µg/L. Water treatment technologies are designed for a specific flow and loading. Variations in the flow and mass loading from the design will affect the performance. Each technology has a finite minimum and maximum range of feasible design flow rates for which a treatment technology can operate within. Careful consideration of this during system design is important for the performance of the treatment system. A heat and material balance for the system is very important to show how both influent flows and recycle flows can influence not only the core selenium treatment process but the other processes that make up the treatment system.

4.1.2.1 Primary Treatment

Generally, treatment systems require flow and/or load equalization in order to ensure that the influent or feed to the system will not exceed the capacity of the treatment process. The more variable the flow and loadings the greater need for equalization. Water discharges requiring selenium treatment that are influenced by storm water (e.g., rain, snow melt), or highly variable process water discharges from batch or block operated processes require careful attention to the design of equalization and diversion systems. The design of equalization and diversion systems is not covered in this document but is a very important primary treatment element.

Other primary treatment may be required to pre-treat the water for other constituents that will affect selenium removal. These primary treatment technologies for selenium treatment systems typically consist of the following:

- Media filtration for low concentration (e.g., less than 75 mg/L TSS) particulate or colloidal solids removal;
- Gravity sedimentation for high concentration (e.g., greater than 100 mg/L TSS) solids removal;
- pH adjustment to enhance physical, chemical and biological treatment;

- Temperature adjustment to enhance physical, chemical and biological treatment;
- Scale removal; and,
- Dilution to avoid matrix-related problems (e.g., phytotoxicity of boron to wetland vegetation).

4.1.2.2 Tertiary Treatment

After the core technology for removal of selenium has been applied there generally will be a need for post treatment of the water to comply with other discharge permit parameters (e.g, dissolved oxygen, TSS, biochemical oxygen demand (BOD), etc). Tertiary treatment for selenium treatment systems will typically consist of the following:

- Media filtration for particulate, or colloidal material that could contain reduced selenium and/or exceed the discharge TSS requirement;
- Re-aeration to maintain an adequate level of dissolved oxygen and/or to treat trace levels of BOD;
- pH and/or temperature adjustment; and,
- Blending to reconstitute de-ionized water from treatment processes to maintain an isotonic solution that will not impair aquatic life.

4.1.2.3 Residuals/By-Product Management

Each treatment system will produce a residual, or by-product as part of selenium removal from water. The by-product form will vary by treatment system and will be in liquid, semisolid or solid form. Residuals from primary, core selenium removal and tertiary treatment processes are likely dependent upon the system configuration and the core selenium removal technology selected. By-product or residual wastes will have elevated concentrations of selenium. They will therefore require proper handling and compliance with local, state, and federal waste disposal regulations.

The Resource Conservation and Recovery Act (RCRA) governs the management of hazardous wastes. Toxicity is defined through a laboratory procedure called the Toxicity Characteristic Leaching Procedure (TCLP). Residuals containing selenium (USEPA Hazardous Waste Number D010) are considered hazardous above 1.0 mg/L.

4.1.3 Capital and Operating Costs

Costs presented in this document generally were either based on the literature referenced, or 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 what the basis for the cost estimate is. Most documents will only present the capital costs or direct costs for equipment as that is what is typically provided by the equipment supplier. These costs, unfortunately are only a fraction of the total installed cost for a water treatment system.

Total installed costs by definition include everything that will be required to install the system. 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 4-2 shows the class of total installed cost estimates, the relative accuracy and the project definition percent complete for each estimate.

TABLE 4-2
Cost Estimating Guideline
Source: Adapted from American Association of Cost Engineers International Recommended Practice 18R-97 (AACEI, 2005)

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%	50-100%

Total installed cost (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 as an order of magnitude estimate and are generally prepared based on limited information containing a wide estimated accuracy range of +100% and -50% (American Association of Cost Engineers, 2005). 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 the other costs provided in this document there generally is very little information available to provide the basis for the estimate, or the classification of the estimate. 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.

4.2 Physical Treatment

This section discusses physical treatment processes to remove selenium from water. These technologies include membrane filtration and evaporation.

4.2.1 Membrane Filtration

Pressure-driven membrane filtration technology employs a process-specific membrane to provide a physical barrier to the passage of particulate, colloidal, and soluble constituents into the filtered stream or permeate. There are four subcategories of membrane filtration technology, classified by particle size removal: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Figure 4-2 shows a process schematic of a pressure-driven membrane process.

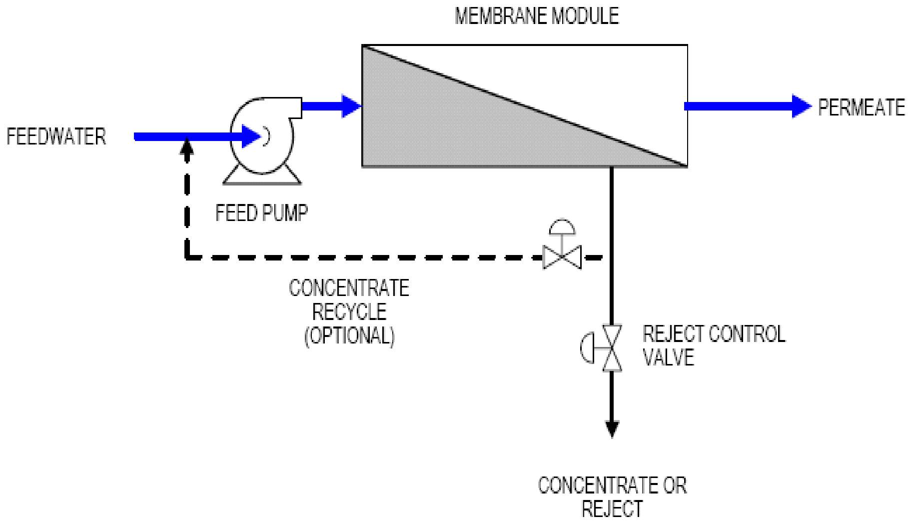


FIGURE 4-2
Simplified Flow Schematic for Pressure-Driven Membrane Process
Source: CH2M HILL, 2005

The feed pressure or operating pressure for a membrane consists of the sum of the net driving, differential, permeate and osmotic pressures, or dynamic head losses. Feed pressure provided by a pump discharge, or suction is required in membrane filtration to transfer the water across the membrane as permeate, leaving the constituents that cannot pass through the membrane in higher concentrations in the reject stream. It should be noted that membrane filtration always has a permeate stream and a reject stream.

The wastewater stream physical/chemical characteristics (e.g., particulate solids, scale solids, TDS, and temperature) as well as the membrane pore size will determine the net driving pressure for a specific membrane. The smaller the membrane pores, the larger resistance to liquid passing through and the higher the net driving pressure. The differential and permeate pressure are generally a function of the membrane system hydraulics and configuration or array. Typical feed pressure ranges required to force water through the membranes are shown in Table 4-3.

TABLE 4-3
Membrane Filtration Pressures
Source: CH2M HILL, 2005

Process	Typical Feed Pressure (psig)
Microfiltration	2 to 40; (-3 to –12 vacuum)
Ultrafiltration	7 to 150
Nanofiltration	70 to 300
Reverse Osmosis	
Seawater	800 to 1,200
Brackish Water	
Low Pressure	150 to 350
Standard Pressure	350 to 600

psig = pounds per square inch gauge.

Osmotic pressure is determined by the pressure differential due to the dissolved salt concentration gradient across a membrane. This term will only apply to membranes (e.g., RO and NF membranes) as their pore size is small enough to separate dissolved or soluble salts. By definition UF and MF membranes will not have an osmotic pressure differential. A heuristic approach for osmotic pressure requirements is to assume that 10 pounds per square inch gauge (psig) of osmotic pressure is exerted for every 1,000 mg/L TDS. Figure 4-3 illustrates the osmotic pressure within an RO system.

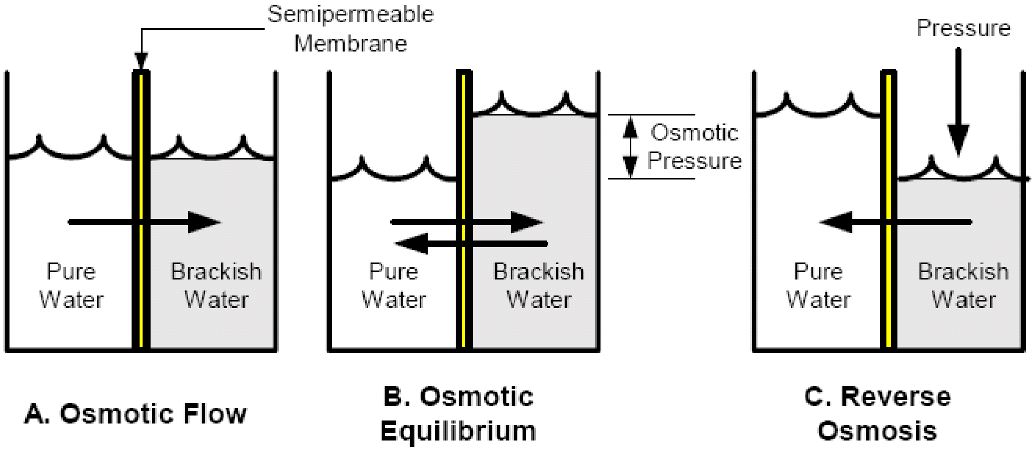


FIGURE 4-3
Osmotic Pressure within a Reverse Osmosis System
Source: CH2M HILL, 2005

As the water temperature increases, the viscosity decreases, resulting in a lower driving force or pump operating pressure required to force the water through the membrane. The reverse is true as water temperature decreases. As the water viscosity increases with decreasing temperature additional net driving pressure is required to maintain the same flux. Therefore, the minimum operating temperature should always be used to determine the maximum anticipated feed pressure at the design flux rate. Additionally, the rate of water and solute flow through the membrane is directly proportional to the temperature of the water. Heuristically there is approximately 3 percent change in solute flow per 1°C temperature change. All polymeric membranes typically have a maximum operating temperature of between 35 and 45°C, the actual upper limit depends on type and polymer.

Particulate solids or colloidal material can foul or plug the membrane pores resulting in very high operating pressures. The smaller the pore size of the membrane, the more sensitive it is to particulate solids. Both RO and NF are particularly susceptible to fouling by natural colloidal material or from particulate formed by scale or metals precipitation. Turbidity and SDI are typically used as indicators of fouling. Turbidities of 0.3 nephelometric turbidity units (NTUs) and SDIs of 3 are typically recommended for application of RO and NF.

Membrane technology is capable of producing very high-quality permeate. Membrane filtration is most often used for water reuse, boiler feed water, and drinking water applications. However, the coarser membrane types are amenable to tertiary wastewater treatment applications requiring high-quality discharge.

Selenium is typically present in water in the soluble forms of selenite and selenate. Selenite and selenate have an approximate molecular weight (MW) and size of 127 and 143 g/mole, respectively, and a size of approximately 2.4 angström. Because of this RO and very small pore size NF membranes are the only membranes that will be effective at removing these from water.

Most membrane materials consist of synthetic organic polymers. Care must be taken to select and test membrane material chemical compatibility with wastewater constituents. Membrane selection is particularly difficult and critical for a complex organic wastewater such as refinery effluent. MF and UF membranes can be prepared from inorganic materials such as ceramics or metals.

There are four general types of membrane configurations: plate-and-frame, tubular, spiral-wound, and hollow-fiber. Spiral-wound and hollow-fiber membrane modules are typically used for NF and RO applications and require an influent that is essentially solids-free. Most wastewater streams require media filtration and/or coarser membrane filtration (MF or UF) prior to NF or RO filtration. Tubular and plate-and-frame membranes are more tolerant of solids and typically are used for MF and UF applications.

One important consideration of membrane system design is that as the reject streams are concentrated to minimize volume for the reject flow, the concentrations of the chemicals in the reject stream can approach and then exceed their solubilities. As a result, the precipitates foul/plug the pores of the membrane.

Electrically-driven membrane processes, which include electrodialysis (ED) and the variant electrodialysis reversal (EDR), use a difference in electrical potential to induce dissolved ions to pass through a water-impermeable membrane to remove the ions from the feed water. With ED, the direction of current flow is always the same. With EDR, the direction of current flow is reversed several times an hour by reversing the voltage polarity applied to the electrodes. Polarity reversal produces a change in the direction of ion movement through the alternating pairs of membranes and causes an electrical flushing of scale-forming ions from the membrane surfaces. ED is generally more expensive than RO, especially when TDS exceeds 2,000 to 3,000 mg/L (Frankenberger et al., 2004). Frankenberger et al. (2004) reports that in previous studies with agricultural drainage, RO was favored over ED. Energy consumption of both processes is directly related to the feed water salt content.

4.2.1.1 Microfiltration and Ultrafiltration

MF has the largest pore size of the membrane technologies, separating molecules with a MW of 100,000 (0.05 to 20 microns) or greater. MF membranes typically are selected to reject large particles and various microorganisms. UF is the next-largest in pore size, as it separates molecules above a MW of 1,000 (0.0015 to 0.20 microns). UF membranes can reject bacteria and soluble macromolecules in addition to the large particles and various microorganisms separated by MF. The MF and larger pore size UF operate at the lowest pressures, ranging from 2 psig to 150 psig.

MF and UF systems can either be pressure-driven or vacuum-driven systems. MF and UF systems may be operated in a cross-flow or dead-end arrangement. With a dead-end flow pattern, all of the feed water passes through the membrane, trapping particles on the membrane surface until backwashing or chemical cleaning removes them. In a cross-flow mode, the feed water flows tangential to the membrane surface to limit the extent of particle deposition and cake layer formation on the membrane surface. In order to achieve a significant scour velocity at an acceptable product water recovery, it is necessary to recirculate the concentrate from the membrane process, which requires additional pumping and, thus, can substantially increase operating costs. Figure 4-4 represents the differences in the two flow patterns.

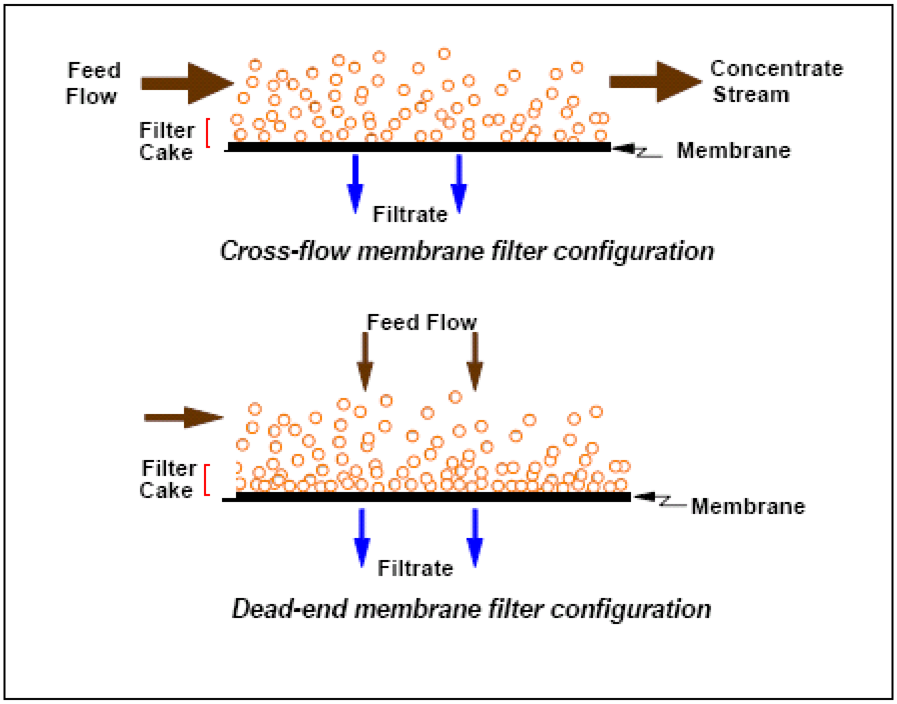


FIGURE 4-4
Cross-Flow and Dead-End Membrane Flow Configurations
Source: CH2M HILL, 2005

MF and UF membranes can have either flat-sheet or hollow-fiber configurations. Hollow-fiber membranes are operated in either an inside-out or outside-in mode. During inside-out operation, the feed enters and passes through the fiber wall to generate filtrate. During outside-in operation, the filtrate is collected in the membrane after the feed is passed through the membrane. Figure 4-5 presents a schematic of these two hollow-fiber membrane flow modes.

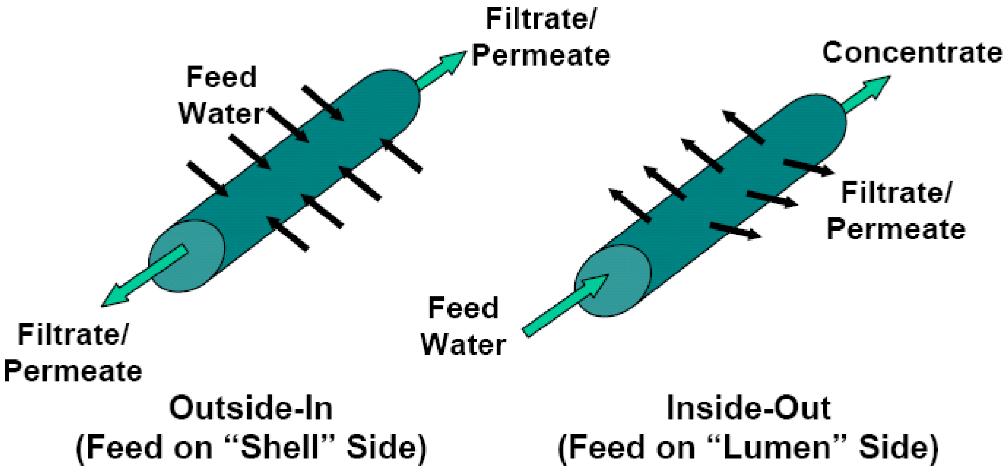


FIGURE 4-5
Schematic of Hollow-Fiber Membrane Flow Configurations
Source: CH2M HILL 2005

Treatment Effectiveness. Given the pore sizes of MF and UF filter media, they would typically be used only in treatment of selenium from water in either a primary application as a pretreatment step in the treatment process or as a tertiary application as post-treatment filtration for selenium removal. Because of the pore size, MF and UF membranes will not be effective at removal of soluble selenium in the selenite and selenate forms. Both MF and UF systems would remove particulate selenium provided the particle size is above the pore size for the membrane. As primary treatment, MF and UF could be applied to remove colloidal and particulate solids that could affect the performance of the core selenium treatment process. As tertiary treatment they could be applied to separate particulate solids or suspended solids from the discharge of the selenium reduction process that could contain trace amounts of selenium. MF and UF would be applicable in selenite precipitation systems, or in zero valent iron (ZVI) systems for liquid solids separation of the iron solids. A short-term pilot study on FGD water was performed using a combination of iron co-precipitation and MF with solids recycle and was shown to remove 50% of the influent selenium to a level of 2,800 µg/L (EPRI, 2009b). This removal was attributed to precipitation of selenite using iron and creation of a large enough floc for removal using a microfilter.

MF and UF systems may be used as pretreatment to remove suspended solids prior to use of RO and NF systems to treat to low µg/L levels of selenium (less than 5 µg/L). MF and UF membrane flux and fouling rates are also impacted by the presence of suspended solids and other contaminants in surface water (e.g., organic material and iron). Suspended solids (e.g., SDIs greater than 5) and other contaminants can result in more rapid fouling of the membrane, decreases in flux, and increases in transmembrane pressure. As a result, most

MF/UF systems may require some level of pretreatment to remove suspended solids and other contaminants from the feed water.

4.2.1.2 Reverse Osmosis

Technology Description. RO is a widely used and tested technology for water treatment applications. Reverse osmosis differs from other membrane technologies in that it involves a semi-permeable membrane so that separation efficiency is dependent on influent solute concentration, pressure, and flux. Flux is the rate of water flow through a membrane, expressed in units of gallons per square foot of membrane area per day. RO is a membrane separation process that uses high pressure to force a solution through a membrane that retains the soluble selenium (e.g., selenite and selenate) and other dissolved salts on the reject side of the membrane and allows the purified water pass to the permeate side (Figure 4-3). The efficiency by which water is separated from the concentrated salts is typically referred to as recovery rate which is normally expressed in percentages. An RO treating 100 United States gallons per minute (US gpm) (378 liters per minute [Lpm]) with a 90% recovery rate will produce 90 US gpm (340 Lpm) of permeate and 10 US gpm (38 Lpm) of reject or concentrate. RO membranes are capable of removing very small molecules, color, sulfates, nitrates, sodium, and other dissolved ions, as well as selenium. These systems can be designed in multiple stages and arrays to provide the required performance and efficiency.

RO has the smallest pore size of the membrane filtration technologies with an ability to separate nearly all molecules that are greater than 0.0015 microns in size. RO membranes are effectively non-porous and therefore can exclude particles and even low molar mass species such as salt ions and organics.

With RO and NF systems, the flat-sheet polymer membranes are most commonly assembled into a spiral-wound module or element in which membrane “leaves” composed of two membrane sheets and an interfacing permeate carrier are wound around a central permeate core tube and a flow spacer material is placed between each leaf.

Another configuration of an RO, NF or UF membrane is a circular flat sheet stack as utilized in the VSEP® (for Vibratory Shear Enhanced Processing) process. In a VSEP® system, the feed water flows between parallel membrane leaf elements while shear cleaning action is created by vigorously vibrating the leaf elements in a direction tangential to the faces of the membranes. The shear waves produced by the membrane's vibration cause solids and foulants to be lifted off the membrane surface and remixed with the bulk material flowing through the membrane stack.

This high shear processing as claimed by the VSEP® manufacturer, exposes the membrane pores to improve flux and reduce scale formation potential and subsequent membrane fouling. This can reduce the level of required primary or pretreatment. Figure 4-6 provides a schematic depicting this comparison of conventional membranes versus the VSEP® application. The concentrate is extruded between the vibrating disc elements and exits the machine once it reaches the desired concentration level.

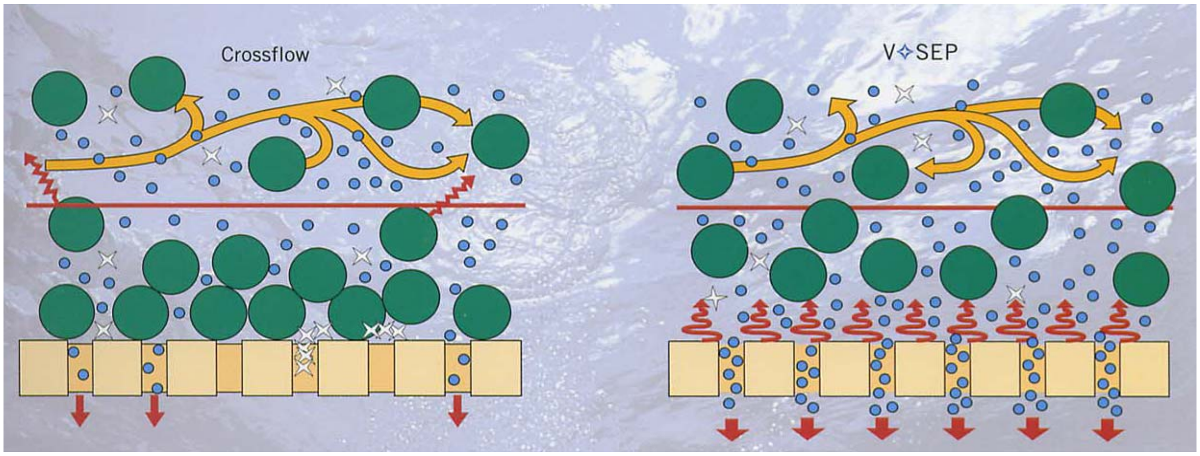


FIGURE 4-6
Schematic Comparing VSEP® Operation with a Conventional Membrane Process
Source: http://www.vsep.com/pdf/VSEP_Brochure.pdf

There are many vendors who provide membrane treatment systems in a variety of configurations, arrays and sequences with primary and tertiary treatment processes each with their own nuances, advantages, and disadvantages. Presentation of each of these is beyond the scope of this document.

Nearly all RO/NF membrane systems require some form of pretreatment equipment to condition the treated water source prior to membrane processing. At a minimum, as is typical for groundwater, this may be a cartridge filter. In cases in which the quality of the feed water is poor (e.g., high levels of suspended solids, sparingly soluble salts, dissolved organic carbon, and biological matter), some sort of solids clarification process (conventional treatment, direct filtration, or MF/UF) or lime softening may be necessary. The degree and complexity of the pretreatment equipment are determined by the feed water requirements of the membrane, the quality of the raw water, and other design factors. If the feed water contains significant microbial activity, pretreatment may include chlorination or disinfection/oxidation by other methods (e.g., ultraviolet, ozone).

Treatment Effectiveness. RO has been demonstrated at pilot-scale and full-scale to remove selenium to less than 5 µg/L in mining-influenced water and agricultural drainage. At the Barrick Richmond Hill Mine, RO was selected to treat mine water that is pretreated by iron reduction and precipitation. The 200 US gpm (750 Lpm) RO system treats an influent of 12 to 22 µg/L to about 2 µg/L (Sobolewski, 2005). The RO unit is operated at 250 psig (17 bar) and higher, which contributes substantially to the operating cost. The brine is cycled back to the iron treatment circuit. Given that selenium originates from 52 acres (21 hectares) of leach pads, water treatment is expected to be required for at least 50 years (Sobolewski, 2005).

At a former historic gold mine site in California, RO was used to treat impounded water for reduction of selenium from about 60 µg/L to less than 5 µg/L (Golder, 2009a). The RO treatment system was implemented on an emergency basis to prevent the impounded water from overtopping into a drinking water reservoir located below the mine. Trailer-mounted RO systems were leased along with pre-filtration and manganese removal columns. The flow to the system was greater than 100 US gpm (378 Lpm) and was operated for about 4 months. The system was operated at about 40% recovery rate due to the high TDS of the influent water. The system was operated until the surface water levels in the impoundment were reduced to acceptable levels.

Gusek et al. (2008) reported that a full-scale treatment system, including RO and biological treatment, was designed for selenium and TDS removal for a Western United States metal mine waste rock leachate that was discharged to surface water. The selenium concentration in the influent at this site is about 30 μg/L. The treatment system has an effluent goal of 10 μg/L. The influent has a TDS level from about 5,000 mg/L to 8,000 mg/L. The flow rate for this system ranges from 70 to 700 gpm with surge events in excess of 2,000 gpm. The RO system concentrates the selenium in the reject stream, and the reject is treated using an anoxic/anaerobic bioreactor for selenium removal. The bioreactor influent selenium level is 70 μg/L with an influent TDS of 16,000 mg/L. The treated reject water is recombined with the permeate stream prior to discharge.

RO has also been pilot-tested for refinery wastewater for selenium removal at a Shell Refinery. This is presented as a case study for the oil and gas sector in Section 7.3.1. RO has also been pilot-tested for agricultural drainage water at Red Rock Ranch and Panoche Drainage District in California. The feed for the Red Rock Ranch pilot study was 760 μg/L, and the effluent was 1 μg/L (United States Department of the Interior Bureau of Reclamation, 2008a).

RO membranes may be fouled due to the presence of calcium, magnesium, alkalinity, sulfate, silica, chloride, iron, total organic carbon (TOC) and TSS. Adsorption of organic substances on the membrane surface causes a reduction in flux and can be irreversible. The use of filter aids, such as inorganic coagulants or organic polymers, should be carefully examined before implementation. The major difficulty with filter aids is that if the dosage is too great or if carryover occurs after pretreatment filtration, the filter aids will foul most RO/NF membranes.

Design and Operational Considerations. RO systems are modular and therefore can be sized up or down to the design flow rate by adding units or using larger RO units. Operating flow depends upon the chemical composition of water to be treated and if pretreatment has been employed.

The life spans of RO systems vary significantly based on the influent water being treated. Life span can be increased if pretreatment is used. An RO membrane, in a system that uses pretreatment and is cleaned and well maintained, will last about 3 to 5 years in a large system, or 1 to 2 years in a portable or modular system (NSMP, 2007).

Land requirements for RO treatment are not significant since RO treatment, especially when accomplished with portable units, does not require large amounts of space. System sizing and the amount of land required depends on the desired flow rate to be treated. A general industry-wide estimate of land required is about 2,000 square feet (185 square meters) of base area for the electrical and control room and about 1,500 square feet per million U.S. gallons per day of production permeate (NSMP, 2007). Additional land may be required for pretreatment needed in association with RO treatment, depending on the pretreatment selected.

Operation and maintenance of RO systems includes regular monitoring of membrane performance to determine fouling, scaling, or other forms of membrane degradation. Acidic or caustic solutions are regularly flushed through the system at high volume/low pressure with a cleaning agent to remove fouling and scaling. The frequency of membrane replacement depends on the influent, pretreatment, and maintenance.

Residuals Management. In RO filtration, selenium is retained primarily in the reject (e.g., concentrate), with the filtered permeate discharge having a very low selenium concentration (e.g., less than 5 µg/L). However, the selenate and other compounds are only concentrated in the reject; therefore, the reject requires further treatment (either chemical or biological) to reduce the soluble selenium to a particulate form. The reject can also be treated with evaporation technology to further concentrate it to salt or dry solids form. The RO recoveries and reject quantities will vary by water source. An appropriate application of the technology that is well designed will typically have recoveries between 70% and 90%. The Barrick Richmond Hill RO system produced a waste stream of 100 U.S. gpm (50%) of the influent (NSMP, 2007).

Examples of technologies that could be applied to the RO reject stream include evaporation and crystallization, ZVI, and biological treatment. A common treatment for the concentrated stream is an evaporator crystallizer system. The residuals in solid, or semisolid form would have to meet end disposal requirements for a landfill. This could include paint filter testing, bearing capacity estimate, as well as hazardous characteristic (TCLP) testing.

The residual dry solids (e.g., >90% for a crystallizer, >15% for biological solids and >25% for zero valent iron [ZVI] solids) will contain compounds such as nitrates, selenate, selenite, and sulfates. The reject quantity typically varies by water source and is a function of ionic strength or inorganic constituent concentrations. Generally, the reject quantities increase in proportion to the constituent concentration of the water because the pressure required to overcome the osmotic pressure to pump the water through the membrane increases with increasing constituent concentrations. At low water temperature, the recovery will drop due to the higher density of water.

Capital and Operating Costs. Figures 4-7 and 4-8 present the TIC and O&M costs for a RO treatment system for selenium reduction to below 5 µg/L. These costs are Class 5 costs as defined by the AACEI with an accuracy of +100% and -50% as shown by the variance bands based on 2009-2010 market conditions. These are parametric cost estimates based on the RO system shown in Figure 4-9. This system is a grass roots or green field selenium treatment system with costs for stand alone utilities (e.g., power, potable water, heating, etc.) and an equipment/control room building included in the estimate. The TIC estimate does not include flow equalization and diversion infrastructure. Given the unknown variation in flows and concentration it would misrepresent the costs for that infrastructure. As discussed in Section 4.1.2 equalization and diversion of flows and/or loadings are generally required for most treatment systems. Operational costs include maintenance, labor, energy, cleaning, chemical and residual disposal costs. Residuals were assumed to be non-hazardous and disposed in a non-hazardous waste landfill. They do not include wholesale periodic replacement costs for all the membranes. Membranes typically require replacement every 5 to 10 years. This can vary by application and is a function of scale and fouling.

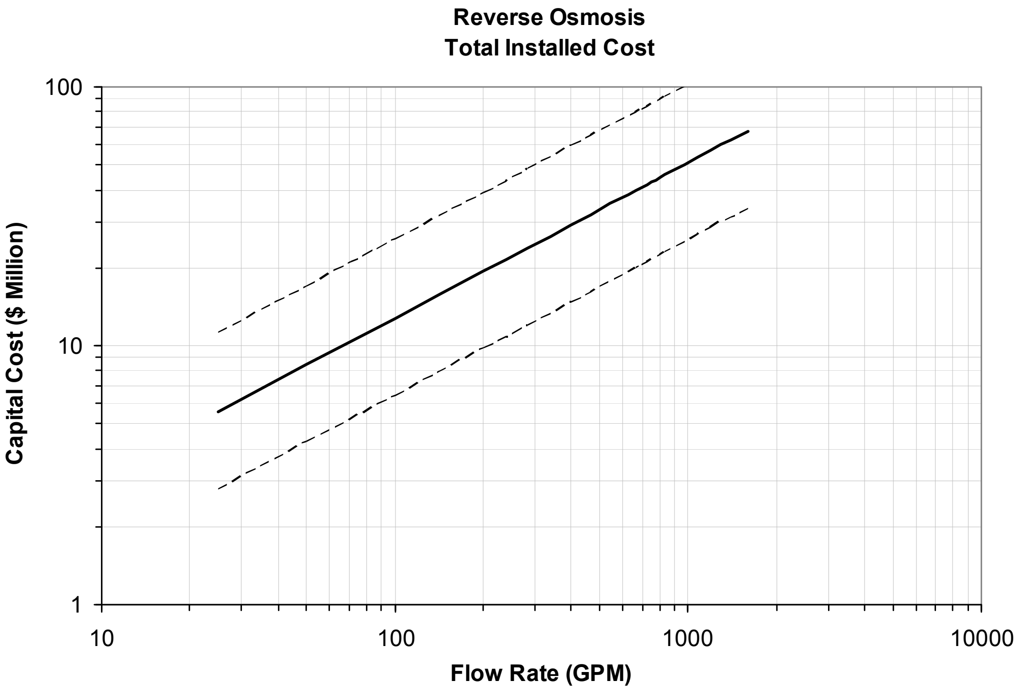


FIGURE 4-7
Total Installed Capital Cost Curve for Conventional Reverse Osmosis (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

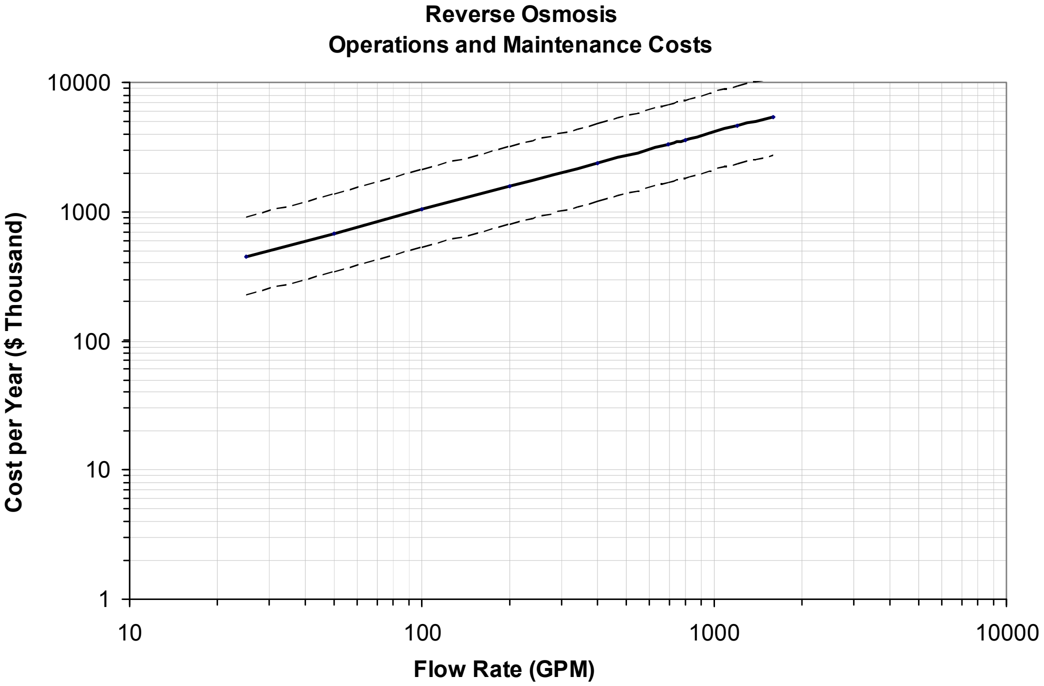


FIGURE 4-8
Operating Cost Curve for Conventional Reverse Osmosis (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

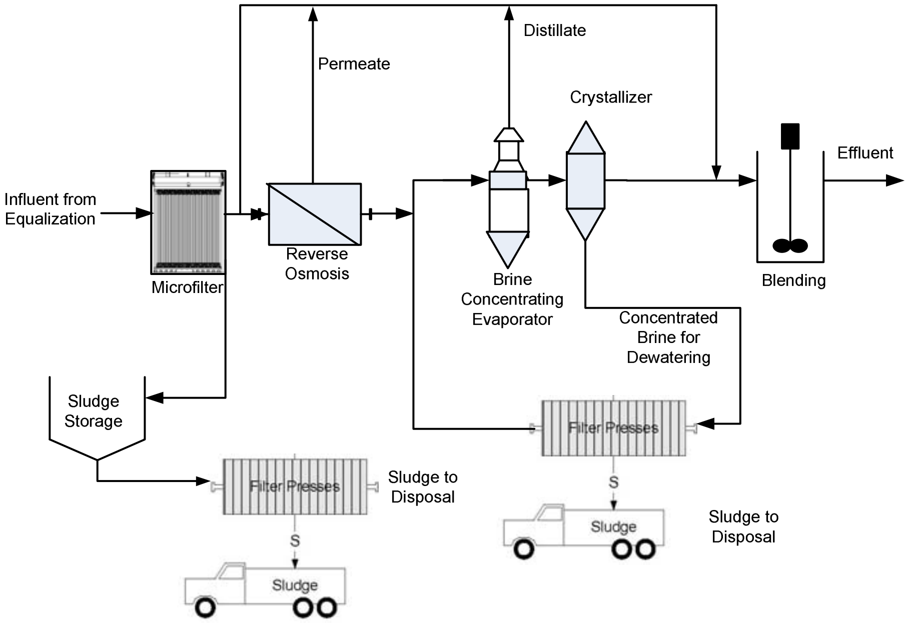


FIGURE 4-9
Conventional Reverse Osmosis System Process Flow Diagram for Cost Estimate

Advantages and Disadvantages. The advantages and disadvantages of the RO technology are presented in Table 4-4.

TABLE 4-4
Advantages and Disadvantages of Reverse Osmosis Technology

Advantages	Disadvantages
• Demonstrated at full scale to remove selenium (selenite or selenate) to less than 5 µg/L. • Can remove high levels of TDS, approximately 90 to 98% removal. • Produces a high water quality with relatively high recoveries as a function of scale treatment. • Small space requirements, modular type construction and easy expansion. • Concentrates the selenium reducing the volume for ultimate reduction treatment.	• Higher capital cost to purchase, install, and operate than other membrane separation processes. • Requirements for pretreatment and chemical addition (microfilter, mixed media filter) to reduce scaling/fouling. • Pressure, temperature, and pH requirements to meet membrane tolerances. • Frequent membrane monitoring and maintenance. • Requires treatment and disposal of the brine (reverse osmosis reject stream). • Reverse osmosis permeate stream will require treatment (pH and TDS buffering) prior to discharge to receiving waters to meet aquatic toxicity test. • Operating issues will result from viscosity changes at extreme low and high temperatures.

4.2.1.3 Nanofiltration

Technology Description. Nanofiltration utilizes a smaller pore size than UF but larger than RO; therefore, it will not have as high a removal efficiency for certain constituents particularly those that are small enough to pass through the pores of the membrane. NF membranes are sometimes called “loose” RO membranes, exhibiting performance between the RO and UF membranes. NF is similar to RO but is operated at pressures approximately one-third that of RO. NF will let some salts pass through and in some cases reduce the scale potential for the membrane. Selenate and selenite are at or near the MW cut-off and therefore could potentially pass through the membrane in certain conditions. Nanofiltration membranes like all membranes will build up a salt or even a colloidal layer at the surface of the membrane that can effectively reduce the pore size. This improves the performance removal of selenium that is at cutoff for this membrane nominal filtration range.

Treatment Effectiveness. Kharaka et al. (1996) reported using a laboratory scale NF system to remove selenium from agricultural drainage water. More than 95% selenium was removed from inflows containing selenium concentrations up to 1,000 µg/L. Based on the results of this laboratory study, a pilot study was conducted in the Imperial Valley in California to remove selenium in drainage water from three selected agricultural drains in the valley. The influent concentrations from the three drains ranged from 42 to 63 µg/L and effluent concentrations ranged from 1.0 to 3.2 µg/L (United States Department of Interior Bureau of Reclamation [USBR], 2002a). A 6 US gpm (22 Lpm) pilot study was also conducted at Red Rock Ranch to remove selenium from agricultural drainage. The pilot study had an NF feed concentration of 1,080 µg/L and an effluent concentration of 47 µg/L (USBR, 2008b).

In an additional laboratory-scale study using iron coagulation treatment prior to NF, selenium removal from water containing uranium mill waste was greater than 95% at pH 10 (Chellam and Clifford, 2002).

Design and Operational Considerations. Pretreatment requirements for NF systems are very similar to RO systems and require filtration for removal of TSS or other constituents that could cause membrane fouling and reduce membrane life. The life span of the NF membranes also depends on proper operation and maintenance. Regular monitoring of membrane performance and regular cleaning are required to maintain membrane life. The life span of an NF membrane is generally 2 to 3 years, depending on proper maintenance and care of the system (NSMP, 2007; Golder, 2009a).

The range of operating flows for NF depends on the membranes used. NF membranes are available for a large variety of flow rates. Energy requirements are less than those of RO due to reduced pressure needed for the NF process.

Residuals Management. Discharge concerns are similar to RO, although the reject flow is expected to be less than that of an RO system. Pretreatment waste streams and spent membranes all require approved disposal (NSMP, 2007).

Capital and Operating Costs. For a Class 5 cost estimate at this level of engineering, the TIC and O&M costs of the NF based selenium treatment system will be very similar to the RO based selenium treatment system presented in Figures 4-7, 4-8, and 4-9. Costs will be slightly less given the lower operating pressures and higher flux rates; however, given the relative uncertainty of these cost estimates it is difficult to discern a notable difference.

Advantages and Disadvantages. The advantages and disadvantages of the NF technology are presented in Table 4-5.

TABLE 4-5
Advantages and Disadvantages of Nanofiltration Technology

Advantages	Disadvantages
• Operates at one-third of the pressure requirement of reverse osmosis technology. • Small space requirements, modular type construction, and easy expansion. • Can offer improved recoveries by rejecting a smaller portion of the salts including selenium, thereby reducing scale potential. • Concentrates the selenium reducing the volume for ultimate reduction treatment.	• Not tested at full-scale for selenium removal. No actual performance data are available yet for selenium removal. • Requirements for pretreatment and chemical addition (micro filter, mixed media filter) to reduce scaling/fouling. • Frequent membrane monitoring and maintenance. • Pressure, temperature, and pH requirements to meet membrane tolerances. • Requires treatment and disposal of the reject stream. • Temperature operating issues due to viscosity effects at extreme low and high temperatures.

4.2.2 Evaporation

Various evaporation technologies are available, including evaporation ponds, enhanced evaporation systems, salinity-gradient solar ponds, and evaporator/crystallizer technologies.

4.2.2.1 Evaporation Ponds

Technology Description. Evaporation ponds (EP) are used in zero-discharge wastewater systems, where the EP performance is wholly dependent on ambient climatic parameters. Therefore EPs are only a viable option in arid regions where available land is abundant. Climates where annual evaporation exceeds annual rainfall are generally suitable for EPs. In this application water containing selenium is fed to lined ponds for evaporation by solar radiation. Initially the evaporation will follow a lake effect evaporation approximation, where a salinity correction factor is applied to a pan evaporation rate corresponding to ambient conditions. As the salt concentration increases the pond becomes hyper-saline, resulting in a greater decrease of the vapor pressure of water and the subsequent evaporation rate. This decline generally dictates a large footprint for the pond and a high solids salt residual. It generally is necessary to periodically remove accumulated sludge and salts for disposal, but most commonly, the ponds are designed to accommodate solids disposal. It has been reported that selenium is reduced within EPs from selenate to selenite, and selenite is adsorbed onto minerals and sediments (NSMP, 2007). Figure 4-10 shows evaporation ponds at the Tulare Lake Drainage District in California.

FIGURE 4-10
Photo of Evaporation Ponds at Tulare Lake Drainage District, San Joaquin Valley, CA
Source: http://ucce.ucdavis.edu/files/repository/calag/img5402p47.jpg

Treatment Effectiveness. The selenium concentrations in subsurface drains discharged to EPs in the San Joaquin Valley in California vary widely, ranging from less than 2 µg/L to more than 200 µg/L. Selenium removal is approximately 25% within EPs compared to the influent to the ponds within the San Joaquin Valley, with influent selenium concentrations of 20 µg/L lowered to 15 µg/L (NSMP, 2007). Influent typically had about 91% selenate, 7% selenite, and 2% organic selenium. The water within the EP contained about 21% selenate, 62% selenite, and 17% organic selenium (NSMP, 2007). Gao et al. (2007) measured selenium concentrations within the EPs at the Tulare Lake Drainage District in California. Selenium concentrations in pond water were in general significantly lower than the influent drainage water. Selenium accumulated preferentially in sediments of the initial pond cell receiving drainage water (Gao et al., 2007).

Design and Operational Considerations. EPs consist of an earthen pond lined with clay overlain by a synthetic liner. EPs are constructed in multiple cells to enable evaporation to occur in one cell while another cell is filled with fresh brine.

Efficient evaporation requires shallow water depths of 1 to 2 feet, and a 1-acre pond can treat between 1 and 2 acre-feet of water (1,200 to 2,500 cubic meters) (NSMP, 2007). Selenium in EPs can create a significant hazard to aquatic birds from potential exposure and bioaccumulation in the food chain. An ecological risk assessment can be performed to review risks to wildlife prior to implementation.

In colder regions, evaporation might be ineffective for the majority of the year. In addition, this technology can be ineffective in areas where rainfall approaches or exceeds the rate of evaporation.

Residuals Management. Effluent from EPs often does not meet waste discharge requirements and ponds have been shut down for that reason (NSMP, 2007). There is also the potential for infiltration of constituents into groundwater. Accumulation of wastes within an EP will create waste that will need to be disposed once the EP shuts down. This waste may be considered hazardous and require hazardous waste disposal (NSMP, 2007).

Capital and Operating Costs. Evaporation pond treatment costs range from $630 USD per acre-foot of treated water to an estimated $2,050 per acre-foot with $2.8 million/year (USD) for O&M costs (USBR, 2002a; Salton Sea Ecosystem Restoration Program, 2005).

Advantages and Disadvantages. The advantages and disadvantages of the EP technology are presented in Table 4-6.

TABLE 4-6
Advantages and Disadvantages of Evaporation Pond Technology

Advantages	Disadvantages
• Lower costs because the technology relies on solar radiation for evaporation. • Simple operation. • Can potentially be disposed of in place with proper design and permitting.	• Large space requirements due to efficiency decline as the total dissolved solids increases. • Generally will not result in a completely dry residual, which limits disposal alternatives. • Ineffective in areas with cold wet climate. A dry climate in which evaporation greatly exceeds precipitation is required. Alternate treatment is needed during cold weather. • Risk of infiltration to groundwater (depending on liner type) could occur. • Evaporation results in a net loss of water that may be a concern to areas with scarce water resources. • May pose risk to wildlife. An ecological risk assessment should be performed prior to implementation.

4.2.2.2 Enhanced Evaporation System

An alternative to solar evaporation is the use of an enhanced evaporation system (EES) to produce concentrated brine followed by crystallization, drying, and solid waste disposal. An EES increases the rate at which water evaporates by mechanically spraying water in the air using a blower. Mechanically spraying, or aspirating, the EP contents will improve the contact of the water containing selenium with the air, thereby improving the evaporation rate. This improves the rate of water transfer to the air which is directly dependent on the surface area, and the relative difference between the equilibrium vapor pressure of the water to the existing partial pressure of water in air. However at some point as the TDS concentration increases it will begin to reduce vapor pressure and limit the mechanical sprayer’s relative efficiency. Additionally, in order to realize any gain in evaporation through use of EES systems the discharge or spray will need to be above, or out of the saturated water vapor headspace that can exist over the evaporation pond. Otherwise, an EES functions similarly as an EP. An EES requires less land area than an EP. Mechanical evaporators can result in drift as well as air emissions in the form of total suspended particulate from the dissolved salts or TDS. Figure 4-11 shows mechanical sprayers being used within an EES system.

FIGURE 4-11
Spray Evaporators used in an Enhanced Evaporation System
Source: United States Department of Interior Bureau of Reclamation, 2008

A study on EES has shown average evaporator efficiency of 67%, assuming that the evaporator was running 70% of the time (Salton Sea Ecosystem Restoration Program, 2005). This efficiency means that the volume of water is reduced to approximately one-third of the starting volume. In a study of EPs in El Paso, Texas, an EES would require a pond area of 294 acres (119 hectares) to get the same evaporation rate as a 772-acre (312-hectare) EP (NSMP, 2007). Because an EES mechanically sprays water, a scale may form on mechanical parts.

Capital and Operating Costs. The cost for an EES system in the San Joaquin Valley was $480 per acre-foot (Salton Sea Ecosystem Restoration Program, 2005). This process has higher operational costs than EPs because of the O&M of mechanical blowers (e.g., energy to operate the evaporation systems).

Advantages and Disadvantages. The advantages and disadvantages of the EES technology are similar to the EP technology with the advantage of increased efficiency of evaporation due to mechanical spraying. However, the mechanical equipment may require maintenance adding to expense whereas the EP technology does not require mechanical equipment.

4.2.2.3 Salinity Gradient Solar Pond

Salinity gradient solar ponds are deep bodies of saline water that develop a temperature gradient from top to bottom. They combine solar energy collection with long-term storage. They are relatively simple in design and low in cost. If properly designed and operated solar gradient ponds can be a reliable source of heat. This difference in temperature from top to bottom can be used to generate electricity. Solar ponds consist of three zones: a surface layer, a gradient zone where there are gradients in salinity and temperature, and a lower storage zone. The pond thus allows visible solar radiation to penetrate and heat the bottom zone while retaining the heat because of the low thermal conductivity of the non-convective stable gradient zone (Frankenberger et al., 2004). The salinity gradient is sufficient to maintain a stabilizing density gradient.

Treatment Effectiveness. Successful installations exist in Texas that have not been designed specifically for selenium removal, and research ponds are planned for the Central Valley (NSMP, 2007). At its Demonstration Desalting Facility in Los Banos, California, the California Department of Water Resources tested a salinity-gradient solar pond to treat agricultural drainage water from 1985 through 1989 (Frankenberger et al., 2004).

Capital and Operating Costs. Costs for solar gradient ponds can range up to $6,100 (USD) per acre-foot (NSMP, 2007). Operation and maintenance costs can be about 10 times greater than an EP (NSMP, 2007).

Advantages and Disadvantages. The advantages and disadvantages of salinity gradient solar pond technology are similar to the EP technology. The fate of selenium is unknown within salinity gradient solar ponds as they have not been used for selenium treatment (NSMP, 2007).

4.2.2.4 Mechanical Evaporator/Crystallizer

Technology Description. The first step involved in mechanical evaporation/crystallization may require pretreatment of the wastewater, possibly with physical/chemical treatment, including clarification; chemical treatment, such as with iron; and softening with reverse osmosis to reduce scale formation or suspended solids from the high concentration of dissolved salts in water exceeding their solubility. Pretreatment is not always needed and is dependent upon the water chemistry of the water.

The second step involves the use of a mechanical evaporator. There are numerous types and configurations of mechanical evaporators. However, the two principal types of evaporators discussed here are multiple-effect evaporators and vapor compression evaporators. Mechanical evaporators overcome the limitations of EP and EES by providing an external heat source and mixing to improve the vapor equilibrium and increase the vapor pressure even as the water becomes hypersaline or the TDS concentrations approach 20%.

Typically the mode of evaporation in mechanical evaporators can be film-type (e.g., falling or rising) referring to the liquid film that is formed on the heat exchanger to evaporate the water, or forced circulation where the liquid is circulated at a high rate through the heat exchanger, such that boiling is prevented within the unit by static water head above the heat exchanger tubes or plates. Evaporation in mechanical evaporators is typically accomplished by heating to near the boiling point of the liquid (i.e., it varies by liquid).

In multiple-effect evaporators low pressure steam is used as a primary heat source to evaporate water. The resulting water vapor from the evaporation in the first stage is used to evaporate water at a lower temperature and pressure in a subsequent effect or stage. Typically on a once through multiple-effect evaporator a heat exchanger preheats the feed water containing the selenium with the product water or distillate from the system. The optimal number of effects is determined by balancing the increased capital cost of additional effects with the increased energy savings. Typically four to six effects are used in multiple-effect evaporation.

In a vapor compression evaporator the vapor produced from evaporating the water with selenium is compressed to elevate its temperature and then used as the heat source in the same evaporator. The amount of energy required to compress the vapor is much smaller than that required to evaporate water; therefore, less energy is consumed than if external steam were used as a heat source. Vapor can be compressed mechanically or thermally with steam in a jet ejector. The use of mechanical compressors is most common. Vapor compression systems have a higher capital cost than a multiple-effect evaporator but a lower energy cost.

Mechanical evaporators operate by transferring latent heat from condensing steam across a tube surface to evaporate the wastewater. Depending upon the salts in water, corrosion can be substantial, thereby requiring expensive metallurgy to minimize the effects on the system.

Brine concentrators are specific types of falling-film evaporators used to treat wastewaters saturated or supersaturated with calcium sulfate or silica (USEPA, 2009). The majority of the evaporation is performed in a falling-film evaporator. Operation features a vertical shell and tube heater situated directly above the vapor body. The brine concentrator or falling-film evaporator employs calcium sulfate seed crystal in the circulating brine in the evaporator. This process produces a concentrated wastewater stream and salts. The brine concentrator can typically concentrate the wastewater 5 to 10 times, which reduces the inlet wastewater volume by 80% or 90%. Air pollution control equipment may be required on the vent line of a mechanical evaporator prior to discharge to the atmosphere. Typically, three options are available for eliminating the brine concentrate: (1) final evaporation in a brine crystallizer, (2) evaporation in a spray dryer, or (3) using the brine to condition solids and disposal of the mixture in a landfill.

Brine crystallizers are thermal devices similar in function to evaporators except they produce a moist solids stream instead of a concentrated brine stream as well as a high quality distillate. Most crystallizers feature a forced circulation evaporator with tube or plate heat exchangers, pump circulation systems, and mechanisms to wipe the film from the heat exchange surface. The process consists of evaporating a sufficient quantity of the liquid phase of a wastewater to increase the solids concentration of the remaining brine to the point where salts contained in the wastewater crystallize out. Depending upon the volume and concentration, crystallization can be used to produce a moist solid from reverse osmosis reject, ion exchange regenerant, and from concentrated brines from evaporator blowdown streams. The moist cake from the crystallizer may be placed in a suitable impoundment or may be further dried in sludge dewatering/drying equipment. Depending upon the type of brine it may be deliquescent, meaning that when exposed to humidity the brine uptakes moisture, resulting in a gelatinous residual.

While forced circulation evaporators are efficient and effective, because of the cost given the vessel size, heat exchanger size and materials of construction, they typically are only used in low flow applications (e.g., crystallizer applications with low volumes and high salt concentrations). Typically a forced circulation evaporator will only be feasible to implement when the flow rates are 100 US gpm (378 Lpm) or less. Pretreatment may be required for direct crystallizer applications to minimize scale and corrosion issues.

The crystallizer system concentrates the dissolved solids in the brine from the evaporator further and produces a 10 to 20% moisture content salt solid (containing no free-draining liquid). This is done by evaporation and concentration to the point where the salts are crystallized from solution. The evaporated water is condensed to form a distillate that can be combined with RO permeate and evaporator distillate. The crystallized salts are dewatered by a centrifuge (or pressure filter), and the solids are typically disposed of in a landfill.

Design and Operational Considerations. Evaporators and crystallizers are mechanically and thermodynamically complex systems. They will require annual to semi-annual maintenance such that the units will be required to be taken off line several days at a time for cleaning and removal of scale. Equipment redundancy and water storage capacity should be considered in the design of any evaporation/crystallization system. Scale and corrosion considerations are important considerations to designing a system that will perform well and minimize maintenance. These systems will require both steam and cooling water utilities in addition to electricity.

Capital and Operating Costs. Figures 4-12 and 4-13 present the TIC and O&M costs for an evaporator/crystallizer system for selenium reduction to below 5 µg/L. These costs are Class 5 costs as defined by the AACEI with an accuracy of +100% and -50% as shown by the variance bands based on 2009-2010 market conditions. These are parametric cost estimates based on the evaporator/crystallizer system shown in Figure 4-14. This system is a grass roots or green field selenium treatment system with costs for stand alone utilities (e.g., power, potable water, heating, etc.) and an equipment/control room building included in the estimate. 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. As discussed in Section 4.1.2, equalization and diversion of flows and/or loadings are generally required for most treatment systems. Operational costs include maintenance, labor, energy, cleaning, chemical, and residual disposal costs. Residuals were assumed to be non-hazardous and disposed in a non-hazardous waste landfill.

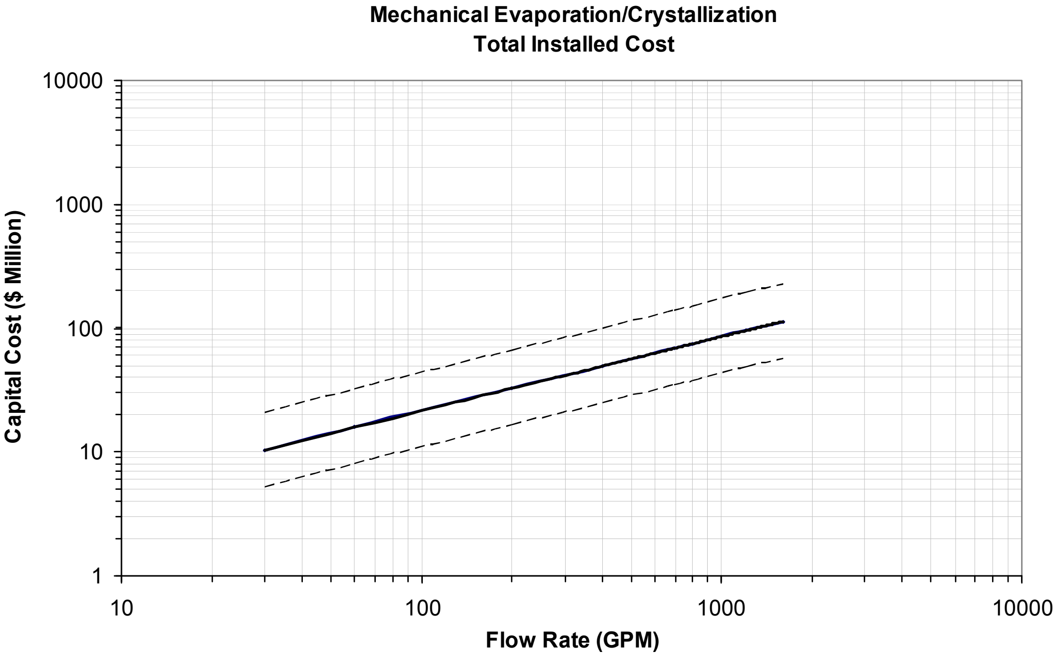


FIGURE 4-12
Total Installed Capital Cost Curve for Mechanical Evaporation/Crystallization (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

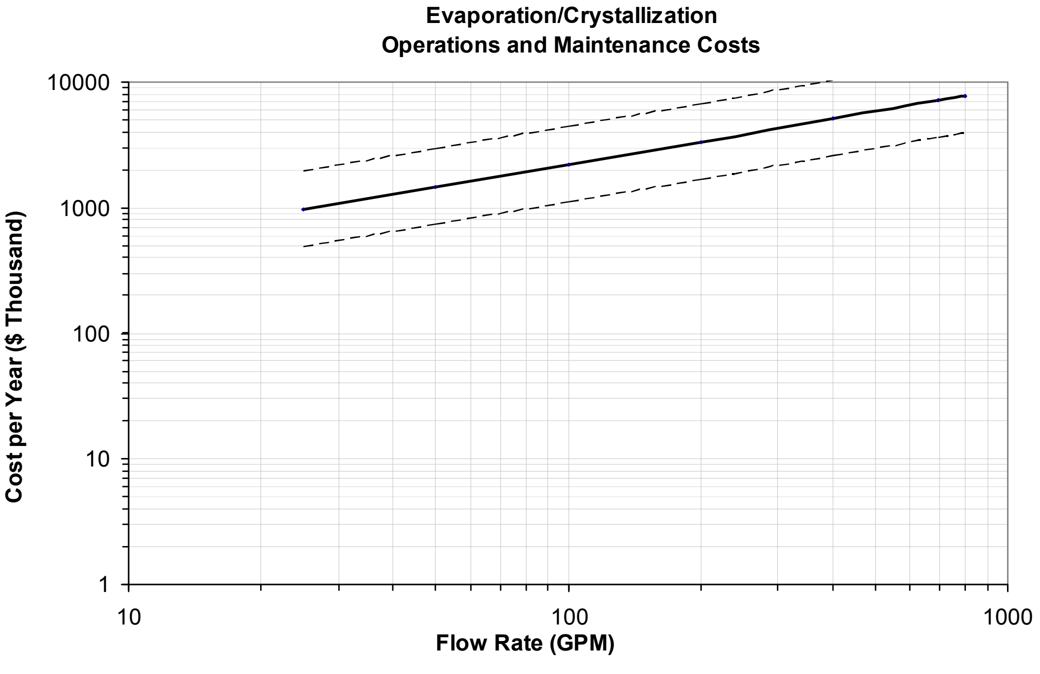


FIGURE 4-13
Operating Cost Curve for Mechanical Evaporation/Crystallization (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

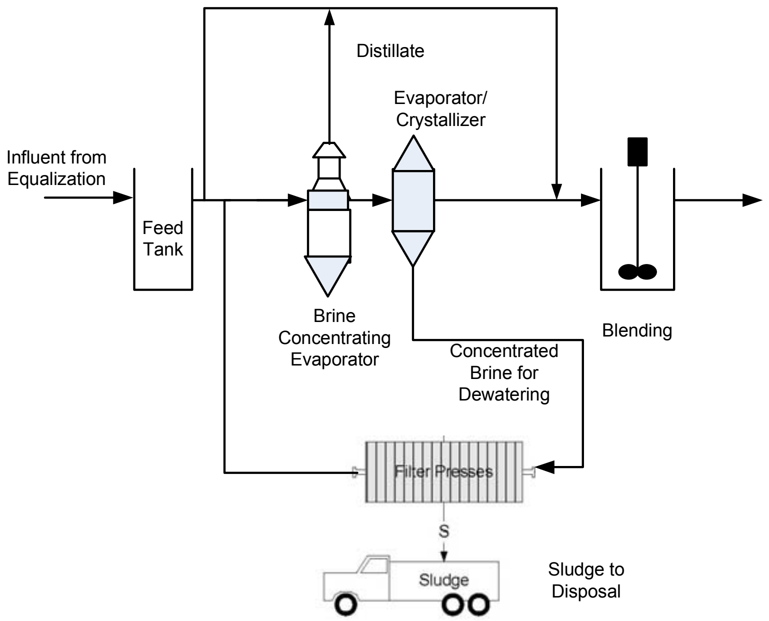


FIGURE 4-14
Mechanical Evaporator/Crystallizer Process Flow Diagram for Cost Estimate

Advantages and Disadvantages. The advantages and disadvantages of the evaporator/crystallizer technology are presented in Table 4-7.

TABLE 4-7
Advantages and Disadvantages of Mechanical Evaporator/Crystallizer Technology

Advantages	Disadvantages
• Provides a high level of treatment producing a concentrated selenium salt cake and pure water distillate. • Generally would be effective at reducing the volume of pre-concentrated streams of selenium from reverse osmosis and ion exchange technologies. • Concentrates the selenium reducing the volume for treatment.	• Disposal of solid waste stream could be hazardous and may be large in quantity, depending on the wastewater volume and characteristics. • Pretreatment can be required depending upon the water quality. • Requires electric, steam and cooling water utilities. • Distillate will require blending to reconstitute with minerals depending upon the discharge requirements. • Redundancy requirements given maintenance outages. • High capital and operation and maintenance cost.

4.3 Chemical Treatment

There are three predominant chemical treatment mechanisms by which soluble selenium (e.g., selenite, selenate and selenocyanate) in water can be removed from water. They are as follows:

- Precipitation
- Adsorption
- Oxidation/Reduction

In addition to these, it has been reported that selenocyanate forms a chemical complex with a proprietary organic soluble chelating compound (USEPA, undated).

Precipitation. Generally, selenium in the soluble forms of selenite and selenate will not react chemically with a reagent, or soluble chemical added to the water solution to yield a product of limited solubility under commonly encountered waste stream temperature, pH and ionic strength. Selenocyanate, a soluble form of selenium that exists primarily in refining wastewater (i.e., sour water stripper [SWS] bottoms) has been reported to be precipitated from aqueous solutions upon reaction with silver, cadmium, mercury, thallium, lead and copper (Manceau and Gallup, 1997). Similar to selenite and selenate, selenocyanate may form a variety of complexes with several transition metals.

Adsorption. When soluble forms of selenium (e.g., selenate, selenite and selenocyanate) present in water tend to condense and concentrate on the surface of another phase (e.g., coagulated suspended or colloidal solids, ion exchange resin, or activated alumina) this is called adsorption. Alternatively, absorption involves the partitioning of a contaminant from one phase into another (e.g., from water directly to air). There are three types of adsorption:

- Chemical
- Physical
- Exchange

Chemical. Chemical adsorption does not, or has not been reported in literature to occur with selenium. Physical and exchange adsorption are discussed below.

Physical. Selenium adsorption mechanisms are primarily physical and exchange based. Physical adsorption is relatively non-specific. It is a result of weak forces of attraction (e.g., van der Waals) between molecules such that the adsorbed molecule (e.g., selenite) is not affixed to a particular site on the surface of a solid particle made up of many coagulated particles (e.g., ferric hydroxides), or a solid amorphous phase (e.g., ferrihydrite {FeOOH}, aluminum hydroxide {$Al(OH)_3$}/activated alumina{Al_2O_3}). These coagulated particles are also referred to as particulate, scale, precipitate or colloidal solids. Furthermore, the selenite and to a far lesser degree selenate may further concentrate to form several superimposed layers on the surface of the adsorbent or solid amorphous phase precipitate. This phenomenon is referred to as co-precipitation. The net effect of physical surface adsorption is the removal of an otherwise soluble compound (e.g., selenite and very little selenate) as a surface contaminant on the amorphous phase solid.

Physical adsorption is reversible; with a decrease in concentration the selenite is desorbed to the same extent that it was originally adsorbed. Additionally, peptization, or dispersion of the coagulated colloidal particles will result in dissolution of the selenium. Selenite and to a much lesser degree selenate have been reported to co-precipitate in, or on, the surface with coagulated chemicals that have limited solubility.

Under certain conditions the amorphous coagulated solids will crystallize to a more thermodynamically stable solid phase (e.g., ferrihydrite to goethite) or directly form crystalline solids. Unlike coagulated solids the specific surface area of a crystalline precipitate is relatively small. Thus co-precipitation by direct adsorption is negligible in crystalline lattices. However, there are two other forms of co-precipitation which involve incorporation of the selenium within the interior of crystals. They are:

- Inclusion
- Occlusion

Inclusion involves the random distribution of selenium throughout the crystal. Occlusion is the non-homogeneous distribution of selenium ions within the imperfections of the crystal lattice of the solid phase. Occlusion tends to trap the selenium in pools between the crystal lattice more effectively than inclusion. Understanding the fate of selenium in crystalline and amorphous solid matrices is important in determining the effectiveness of the treatment for removal of the selenium from water and the leachate potential for selenium from the residual waste from the treatment process.

Exchange. Ion exchange resin is a solid phase media, either synthetic (e.g., organic polymer), or naturally occurring (e.g., clinoptolite), which promotes an electrical attraction between the soluble ions and the surface of the media. This is also referred to as exchange adsorption as the anions (e.g., selenite and selenate) are concentrated at the cationic charged sites of a weak or strong base synthetic anion exchange media by electrostatic attraction.

Adsorption on ion-exchange resin is a surface phenomenon. Thus the rate and extent of adsorption are generally a function of not only the charge (e.g., van der Waals, electrostatic), but the surface area of the absorbent (e.g., ion exchange resin, amorphous precipitate, etc) and the size of the ion.

Oxidation/Reduction. Oxidation-reduction (redox) chemical reactions are important chemical reactions in determining the reduction or precipitation of selenium and the solubilization of the oxidized metal. As with solubility product and complex formation, redox reactions are a function of chemical equilibria in the water and generally influenced by pH, temperature and ionic strength.

Oxidation is the removal of electrons from a chemical. The chemical being oxidized is often referred to as an electron donor, because it gives electrons to another chemical. Reduction is the addition of electrons to a chemical. The term reduction is used because the chemical valence is lowered by accepting the negatively charged electron. The reduced chemical is also referred to as an electron acceptor. In a reaction, oxidation and reduction must be balanced.

In the reduction of selenium with ZVI (Fe^0), oxyanions such as bicarbonate, carbonate, phosphate, sulfate, nitrate, selenate, and selenite act as electron acceptors (e.g., oxygen removed), and reduced iron (e.g., ZVI) acts as an electron donor (e.g., accepts oxygen). Redox reactions occur in an order, or hierarchy, as a function of the unique electron activity for each reaction or the ORP.

In this electromotive series, oxygen will be reduced preferentially first followed by nitrates, nitrites, selenite, selenate and sulfates. Therefore, if there is significant oxygen present, and not enough ZVI, the ZVI will be oxidized to the point that it will not have enough reductive capacity to reduce the selenate in the water. In the absence of oxygen, nitrate is reduced to nitrogen gas first, followed by selenate and selenite being reduced to elemental selenium under anoxic (e.g., no dissolved oxygen) or anaerobic conditions. The iron is chemically oxidized to ferrous and/or ferric forms.

This elemental iron and selenate/selenite redox reaction in water essentially is an electrochemical cell which is referred to as a galvanic cell. Galvanic protection is a method of corrosion protection where a sacrificial metal (e.g., ZVI) promotes a reducing environment for the metal of concern (e.g., selenium) such that it does not dissolve or oxidize in solution. It can be catalyzed by other metals such that the net electrode potential remains positive or proceeds in the desired net redox reaction.

4.3.1 Precipitation

4.3.1.1 Selenocyanate Precipitation

Treatment of selenocyanate containing wastewater from a refinery was tested to determine whether selenium was precipitated as elemental selenium or immobilized in the form of cyanate complexes. Copper salts were used to precipitate selenocyanate from petroleum refinery process water containing approximately 6 mg/L selenocyanate as part of a laboratory study (Manceau and Gallup, 1997). The results of the laboratory study indicated that incorporation of selenium in the copper thiocyanate lattice was proven by X-ray diffraction (Manceau and Gallup, 1997).

4.3.2 Adsorption

4.3.2.1 Ion Exchange

Technology Description. In ion exchange, undesirable ions in the water are exchanged for desirable ions as the water passes through granular chemicals known as ion exchange resins. Ion exchange has several applications in water treatment processes such as hardness removal, desalination, alkalinity removal, radioactive waste removal, ammonia removal, and metal removal. Similar ion exchange resin can remove selenite and selenate ions from water. Both weak base and strong base anionic resins have been reported as providing treatment for selenium (Patterson, 1985; Twidwell et al., 1999). Typically, divalent anions (e.g. SeO_4^{2-}) will have a higher affinity towards strong base anion resins, but it should be noted that some resins have mixed weak and strong base resin and are called intermediate base anion exchange resins.

Pretreatment of the water prior to ion exchange is generally required. Exchange sites generally vary functionally at varying pH thereby sometimes requiring pH adjustment to optimize the performance of the resin. Similarly temperature can affect the performance of the resin. Suspended solids will plug the resin bed and increase headloss. If this is significant enough to reduce the capacity in the resin, then pre-filtration will be used. Organics can foul the resin as most resins are organic polymers. Strong oxidants and high temperatures can degrade the resin. Additionally, there are many competing oxyanions with selenite and selenate that can consume resin capacity.

There typically will be competing anions for the resin capacity that must be considered in design. In most ion exchange resins the major anions to be removed have different degrees of affinity or selectivity for the resin being used and tend to band on the resin accordingly.

Because of this ion exchange columns are typically configured in a serial lead-lag or lead-lag-lag configuration. This configuration allows for monitoring of breakthrough for selenium between the lead and lag or lag and lag column prior to discharge. The lag column at this point becomes the lead and the lead column is regenerated.

Once the ion exchange sites on the resin are completely full the resin must be regenerated for further use. In practice a resin is considered to be exhausted when the concentration of the selenium in the effluent is at the allowable maximum. Ion exchange resins are normally placed pressure vessels similar to pressure media filters with the wastewater pumped through the bed in a down-flow pattern. When the resin is exhausted it must be regenerated. In regeneration a sodium hydroxide solution is used to regenerate weak and strong base anion exchange resins. In order to minimize leakage of the targeted anions and maximize capacity ion exchange resins for selenium applications must be fully regenerated.

There are typically four operations carried out in a complete ion exchange process cycle: service, backwash, regeneration, and rinse. Service water and backwash quantities can be significant, thereby requiring storage tanks, especially if a potable water supply is not available for service water and the treated effluent must be utilized. If the backwash water is moderate to very hard, the calcium and magnesium present can precipitate with the hydroxides in a completely exhausted bed. Additionally calcium can react with concentrate levels of sulfate if present in the resin column.

There are various types of ion exchange resins available. The higher the concentration of TDS in the water, the greater the concentration of competing anions and therefore the more frequently the resins will need to be regenerated. Generally nitrates, sulfates, and chlorides will have preference over selenite and selenate for a weak base anion exchange. Carbonates and silicates will be loosely held in a weak base anion exchange resin. In a strong base resin sulfates and carbonate will have a greater affinity than selenite and selenate as well as silicates. It is important to always work with the ion exchange resin manufacturer (e.g., Dow, Rohm & Haas, and Purolite to name a few) and conduct tests to select an appropriate resin for the source water in which selenium is being treated. Some organics in the water may also foul resins, thus reducing the exchange capacity; therefore, ion exchange can be a polishing technology for selenium removal if segregation of selenium from chlorides occurs. The regenerating solution will contain the concentrated selenium and will require treatment either onsite or offsite.

Treatment Effectiveness. A laboratory-scale investigation was performed by the Western States Petroleum Association (WSPA) to remove selenium from stripped sour water (SSW) and biotreater effluent. The following ion exchange resins were tested as part of this study: (1) strong base anion (SBA), (2) tailored zeolite/solid phase extraction, (3) ligand exchange using chelated resins in the copper form, (4) ligand exchange using weak acid cation resins in the ferric form, and (5) other proprietary ion exchange resins. Of the various resins tested, the most effective was the SBA resin for the SSW effluent with or without oxidative pretreatment (Aware Engineering, 1995). Over 700 bed volumes were treated prior to breakthrough (0.25 mg/L). Both selenite and selenocyanate were treatable using SBA resins. Selenium concentrations within the influent were up to 4,870 μg/L and were inconsistently treated to below 50 μg/L (Montgomery Watson, 1995a).

The WSPA study indicated that treatment with ion exchange was not cost-effective for biotreater effluent due to interference with sulfate (Aware Engineering, 1995). The only medium that was effective for selenite treatment of biotreater effluent was not effectively regenerated so the resin would need to be disposed without regeneration (Montgomery Watson, 1995a). Sulfate competes with selenium for active sites on the ion exchange resin, which can saturate the resin with sulfate ions and prevent removal of selenium.

Ion exchange has also been tested for wastewater from mining applications. Ion exchange was pilot-tested for treatment of gold heap leach solution effluents (Sobolewski, 2005). A laboratory test was conducted using process solutions from Kennecott Mining Company on a silica polyamine resin made from polyethyleneimine impregnated with zirconium. The Kennecott process solution contained 0.93 mg/L selenium and 80 mg/L sulfate at pH 4. The resin removed selenium to less than 1 µg/L (Golder, 2009a).

Laboratory studies conducted on a polyamine-type weakly basic ion exchange resin showed that sulfate affects the removal performance (Nishimura and Hashimoto, 2007). Barium chloride was used to reduce aqueous concentrations of sulfate and selenate. Ion exchange was then used as a polishing step to further reduce selenate concentrations (Golder, 2009a). This resulted in selenium reduction from 1 mg/L to below 0.1 mg/L for the combination of barium chloride and ion exchange treatment (Golder, 2009a).

Design and Operational Considerations. Ion exchange systems depend on the resin type; therefore, design will be performed in conjunction with the resin manufacturer and testing of the resin. In addition to the resin type, the volume and type of regenerant, backwash water source, backwash quantities, pre-filtration for solids, pH adjustment before and after ion exchange, column configuration, mode of operation, and cycle length are considerations for design. Monitoring breakthrough between the lead-lag or lag-lag column will be required. This is typically done with conductivity and/or pH provided the TDS levels are not too high. High sulfate levels are a concern for ion exchange systems as sulfate competition can result in exhaustion of the resin. Land requirements are similar to RO systems.

Ion exchange is generally used as a polishing step to remove low-concentration contaminants; therefore, pretreatment would likely be required. Pretreatment requirements include removal of oil and grease, pH effects on resin selected, and damage of resin, depending on oxidants in groundwater.

A conceptual design of a full-scale ion exchange system was created as part of the WSPA study for treatment of the SSW effluent at a flow rate of 700 gpm (Aware Engineering, 1995). To reduce costs, it was assumed that treatment of spent regenerant by ferric co-precipitation would reduce the quantity of liquid waste for disposal. This method of residuals management was not fully demonstrated during the study. A portion of the spent regenerant would be wasted to limit buildup of sulfate or other dissolved constituents that could interfere with resin regeneration.

Residuals Management. The resin is considered exhausted when a maximum allowable effluent concentration is reached. The higher the concentration of TDS in the water, the more frequently the resin will need to be regenerated with caustic soda and rinsed with backwash water. In regeneration, a concentrated solution of ions that is originally in contact with the active sites on the resin is contacted with the spent resin to regenerate the resin. The solution must then be treated prior to ultimate disposal. Treatment of the regenerant would include evaporation and crystallization, biological treatment, or ZVI treatment. The residuals in solid or semisolid form would have to meet end disposal requirements for a landfill. This could include paint filter testing, bearing capacity estimate, as well as hazardous characteristic (TCLP) testing. It too would be disposed of as a solid waste.

Capital and Operating Costs. Figures 4-15 and 4-16 present the TIC and O&M costs for an ion exchange system for selenium reduction to below 5 µg/L. These costs are Class 5 costs as defined by the AACEI with an accuracy of +100% and -50% as shown by the variance bands based on 2009-2010 market conditions. These are parametric cost estimates based on the ion exchange system shown in Figure 4-17. This system is a grass roots or green field selenium treatment system with costs for stand alone utilities (e.g., power) and an equipment/control room building included in the estimate. 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. As discussed in Section 4.1.2 equalization and diversion of flows and/or loadings are generally required for most treatment systems. Operational costs include maintenance, labor, energy, cleaning, chemical, and residual disposal costs. Residuals were assumed to be non-hazardous and disposed in a non-hazardous waste landfill. They do not include wholesale periodic replacement costs for all the ion exchange resin. Ion exchange resin typically requires replacement every 3 to 5 years. This can vary by application and is a function of scale and fouling.

A cost estimate was developed for the WSPA studies to treat a SSW effluent of 700 US gpm (average dry-weather flow) with similar influent characteristics as the pilot study. The SSW treatment system was a 700 US gpm system for $13.3 million installed cost (1995) (Montgomery Watson, 1995a). The annual O&M cost was estimated to be $8.8 million, with over half of the cost ($4.8 million) based on spent regenerant disposal. This included costs of treatment of regenerant with iron prior to disposal ($1,580/lb selenium removed) (Montgomery Watson, 1995a). The primary O&M cost is associated with regenerating or replacing the resins, which must be done periodically.

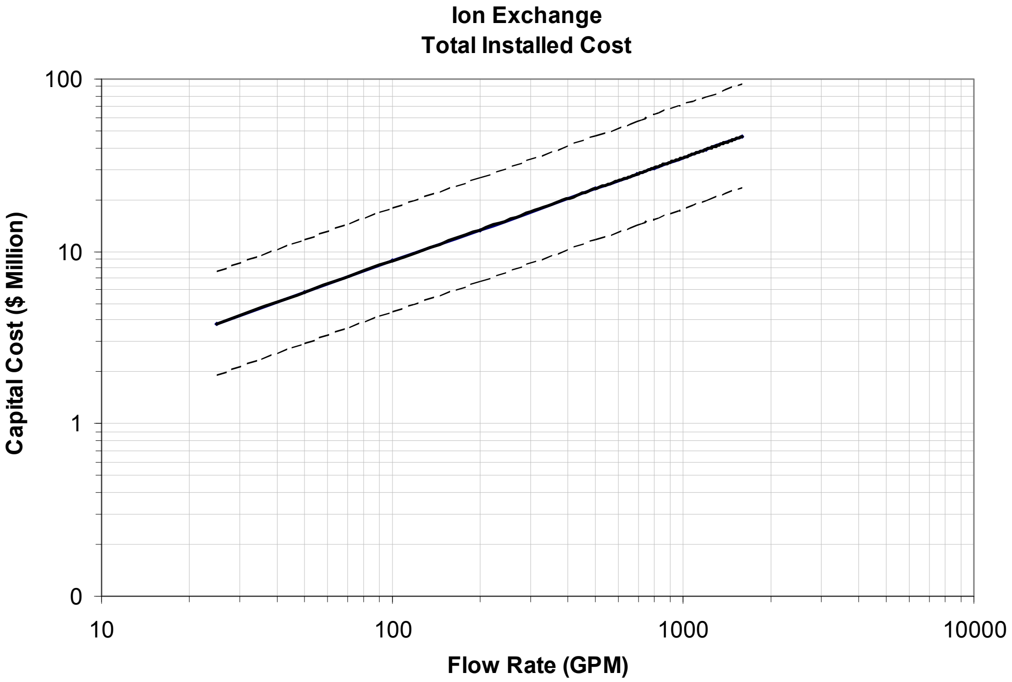


FIGURE 4-15
Total Installed Capital Cost Curve for Ion Exchange (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

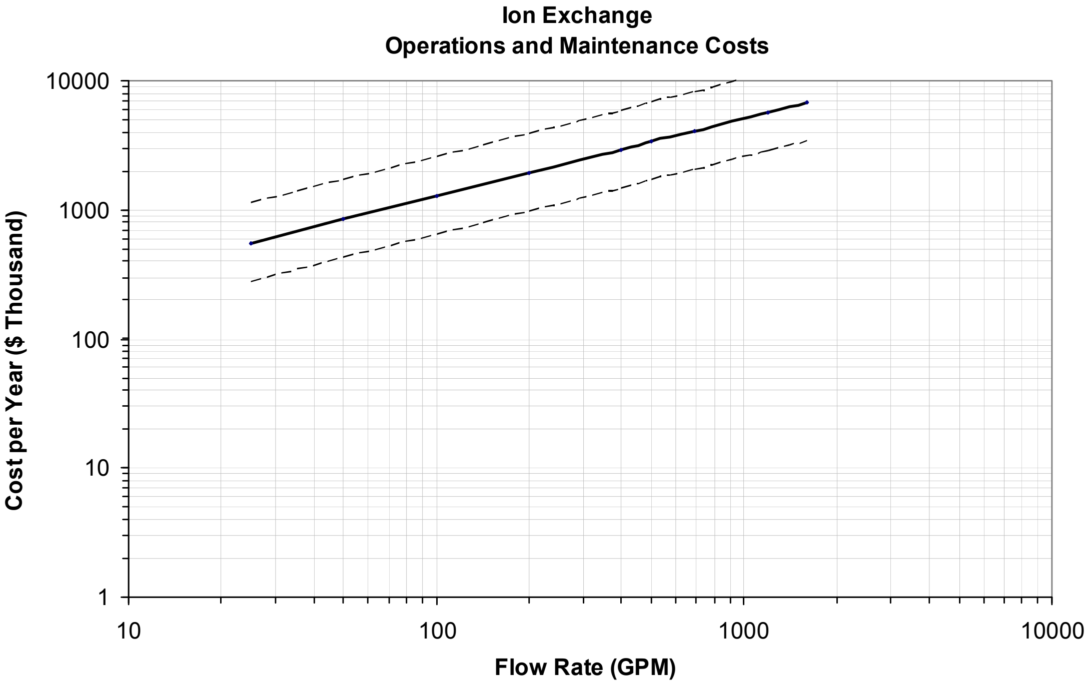


FIGURE 4-16
Operating Cost Curve for Ion Exchange (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

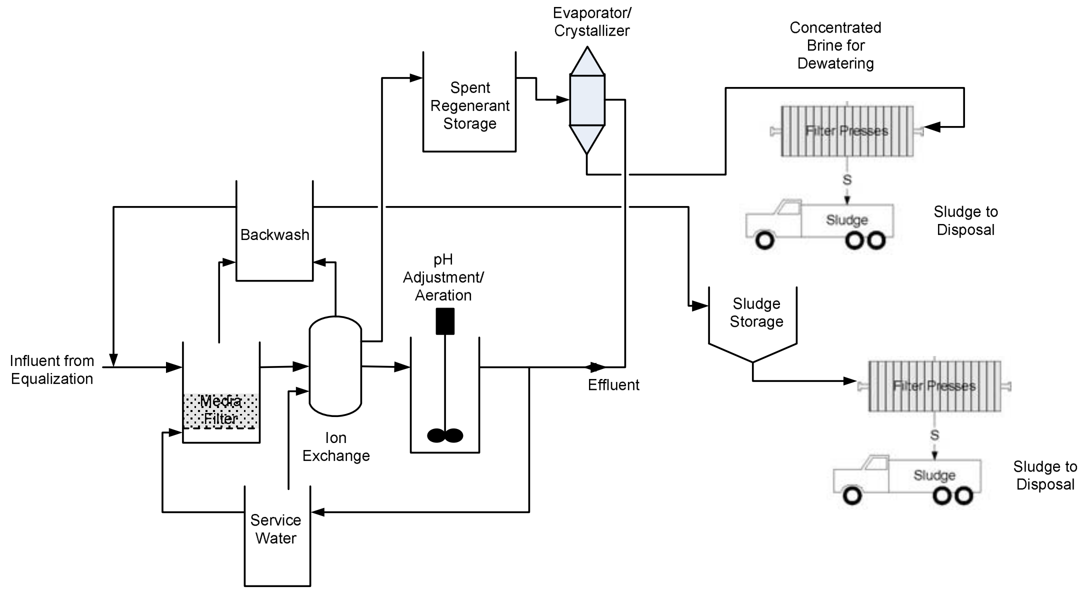


FIGURE 4-17
Ion Exchange Process Flow Diagram for Cost Estimate

Advantages and Disadvantages. The advantages and disadvantages of the ion exchange technology are presented in Table 4-8.

TABLE 4-8
Advantages and Disadvantages of Ion Exchange Technology

Advantages	Disadvantages
• Generally greater than 90% recovery rates given resin specificity for target constituent and regenerant and back wash requirements. • In the right application, capable of treating to potentially low levels (e.g., 5 µg/L or less) with proper resin selection and system design with consideration to competing water chemistry. This same technology has been applied to perchlorate in similar water matrices. • Concentrates the selenium reducing the volume for treatment.	• Uncertainty regarding performance for selenium removal to low levels (e.g., less than 5 µg/L) given small amount of test data in literature. • Ion exchange capacity for selenium can be greatly reduced by competing anions (e.g., sulfates, nitrates). • Resin may need to be disposed if it cannot be regenerated, meaning high disposal costs. • Concentrated regenerant stream requires treatment and/or disposal.

4.3.2.2 Ferrihydrite Adsorption

Ferrihydrite adsorption is a two step chemical treatment process in which a ferric salt (e.g., ferric chloride ($FeCl_3$) or ferric sulfate ($Fe_2(SO_4)_3$) is added to the water source with pH adjustment, rapid mixing, polymer or coagulant addition, and flocculant addition to form a ferrihydrite ($Fe_2O_3 \cdot 0.5 H_2O$) solid, which is a poorly soluble crystalline form of ferric hydroxide ($Fe(OH)_3$). This is sometimes referred to as ferric hydroxide ($Fe(OH)_3$). The chemical formula for ferrihydrite is fundamentally indeterminant because ferrihydrite is not in a single phase with variable levels of water of hydration. Ferrihydrite will mature to more crystalline ferrioxyhydrites (FeO(OH)) (e.g., goethite, lipidocrocite) and ferrioxides (e.g., Fe_2O_3 {hematite}) (Twidwell et al., 1999). The following is the simplified chemical equation to represent this reaction.

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(solid)} + 3H^{+} \text{ (Equation 4-1)}$$

Ferrihydrite precipitation with concurrent adsorption of selenium onto the ferrihydrite surface or iron co-precipitation is commonly used for selenium (as selenite) removal as it can also be effective for removal of metals at neutral to alkaline pH.

Selenium may adsorb onto the resulting ferrihydrite floc or solids matrix, however, sorption is dependent on the oxidation state of the selenium and the solution pH. While selenite is strongly adsorbed on the ferrihydrite floc, selenate is more loosely bound (Merrill et al., 1986). It is not an effective approach for removal of selenate (Twidwell et al., 1999).

Balistrieri and Chao (1987) determined the order of adsorption of anions onto the ferrihydrite matrix at a pH of 7 to be: phosphate > silicate > selenite = arsenite, bicarbonate, carbonate and citrate = selenite, molybdate, oxalate> fluoride, selenate and sulfate. Sulfate can reduce the effectiveness of co-precipitation of selenate by ferrihydrite. Selenite can still be removed via iron co-precipitation; removal strongly depends on conditions during the reaction. Moderately acidic pH levels have been found to be most effective for selenite removal. Hayes et al. (1987) concluded that selenite co-precipitation to ferrihydrite matrix is through absorption into the inner-sphere matrix. However, selenate adsorbs as an outer-sphere hydrated complex at the surface of the ferrihydrite matrix which is more easily replaced by other solution anions such as sulfate.

Merrill et al. (1986) described the mechanism of iron adsorption/co-precipitation for removing selenium from the ash pond effluent of a coal-fired power plant. The iron co-precipitation process has been tested and employed at full-scale in various industries. The technology has been shown to be fairly effective for removal of selenium if present as selenite when formed at pH 4 to 6, with decreasing removal with increasing pH.

Precipitation of sulfate via barium chloride addition has been explored as a pretreatment step for ion exchange treatment for agricultural and mining wastewaters (Lalvani, 2004; Nishimura and Hashimoto, 2007). If selenium is present in the form of selenate, minor removal could occur concurrently with barium sulfate precipitation.

Treatment Effectiveness. Sections 6 and 7 present various studies for removal of selenium using iron co-precipitation. A pilot study at the Kennecott Utah Copper Corporation's Garfield Wetlands-Kessler Springs site was conducted by USEPA and reported a mean effluent selenium concentration of 90 µg/L (with a reported minimum selenium concentration of 35 µg/L) from influents containing 1,950 µg /L (1,870 µg/L selenate and 49 µg/L selenite) and using an iron concentration of 4,800 mg/L (MSE Technology Applications, Inc. [MSE], 2001). The iron co-precipitation technology has not been demonstrated to achieve low levels of selenium removal (less than 5 µg/L).

Design and Operational Considerations. Design and operational considerations are discussed as part of the presentation of case studies within Sections 6 and 7.

Residuals Management. Management of ferrihydrite sludge is required. This process can generate large volumes of sludge that need to be dewatered and disposed of offsite based on the influent mass load of selenium and the target selenium level for treatment. Typical sludge management options include centrifuge, belt press, or plate and frame press (Higgins et al., 2009). Twidwell et al., (1999) question whether the ferrihydrite selenium co-precipitated residuals will continue to adsorb selenium as the amorphous ferrihydrite solids crystallize to a more thermodynamically stable phase of goethite (FeOOH) or anhydrous ferrihydrite, or hematite (Fe_2O_3) which can result in large decreases of surface area, thereby potentially releasing selenium. Leachate characteristic testing will be required to determine if the residuals will be hazardous. TCLP analyses were performed on samples of filter cake from the pilot study at the Kennecott Utah Copper Corporation's Garfield Wetlands-Kessler Springs site. Results showed that the filter cake selenium concentration was greater than the allowable limit of 1 mg/L with concentrations of 1.1 mg/L to 1.6 mg/L (MSE, 2001).

Capital and Operating Costs.

Figures 4-18 and 4-19 present the TIC and O&M costs for an iron co-precipitation system for selenium reduction to below 5 µg/L. These costs are Class 5 costs as defined by the AACEI with an accuracy of +100% and -50% as shown by the variance bands based on 2009-2010 market conditions. These are parametric cost estimates based on the iron co-precipitation system shown in Figure 4-20. This system is a grass roots or green field selenium treatment system with costs for stand alone utilities (e.g., power, potable water, heating, etc.) and an equipment/control room building included in the estimate. 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. As discussed in Section 4.1.2 equalization and diversion of flows and/or loadings are generally required for most treatment systems. Operational costs include maintenance, labor, energy, cleaning, chemical and residual disposal costs. Residuals were assumed to be non-hazardous and disposed in a non-hazardous waste landfill. Costs reported in literature indicate ferrihydrite precipitation treatments is greater than $1,000,000 (2001 USD) for a 300 US gpm system, plus O&M costs of greater than $2,000,000 (MSE, 2001).

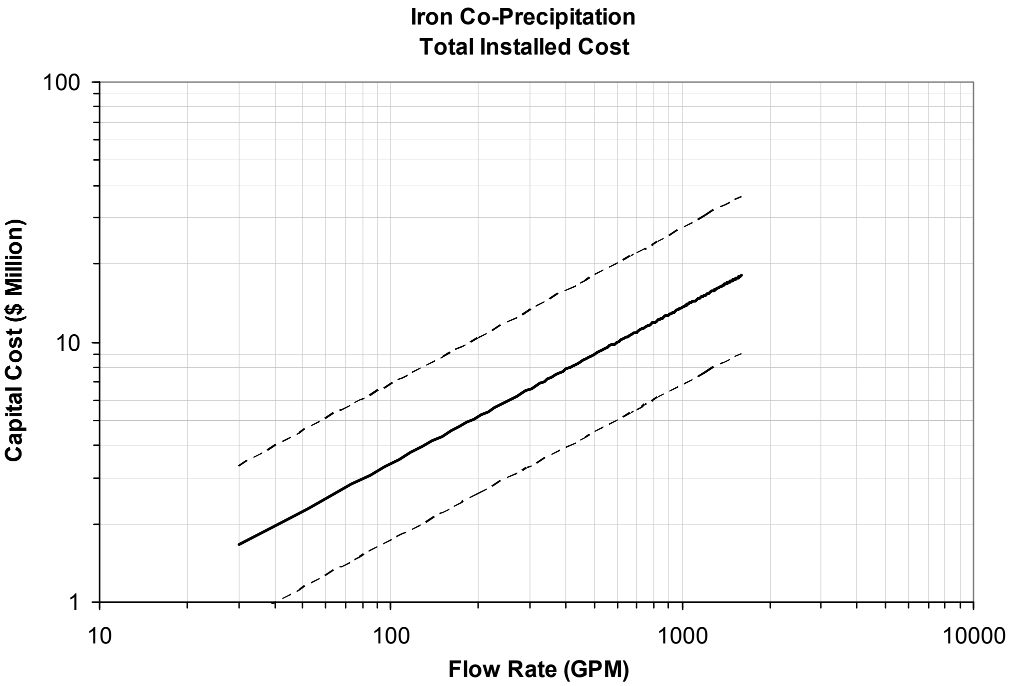


FIGURE 4-18
Total Installed Costs for Iron Co-Precipitation (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

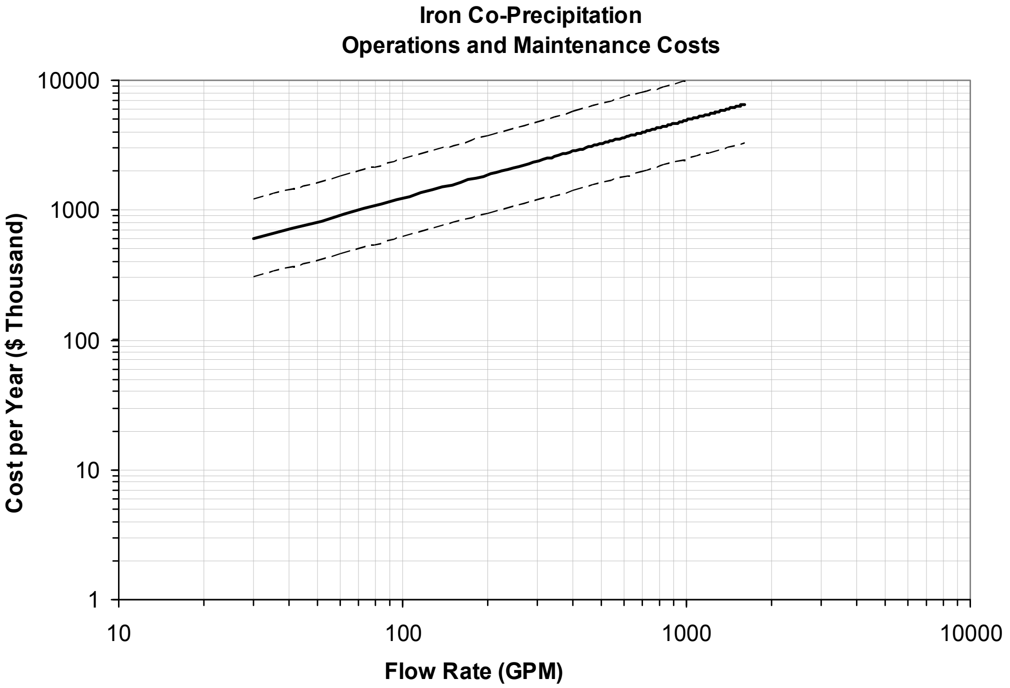


FIGURE 4-19
Operating Cost Curve for Iron Co-Precipitation (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

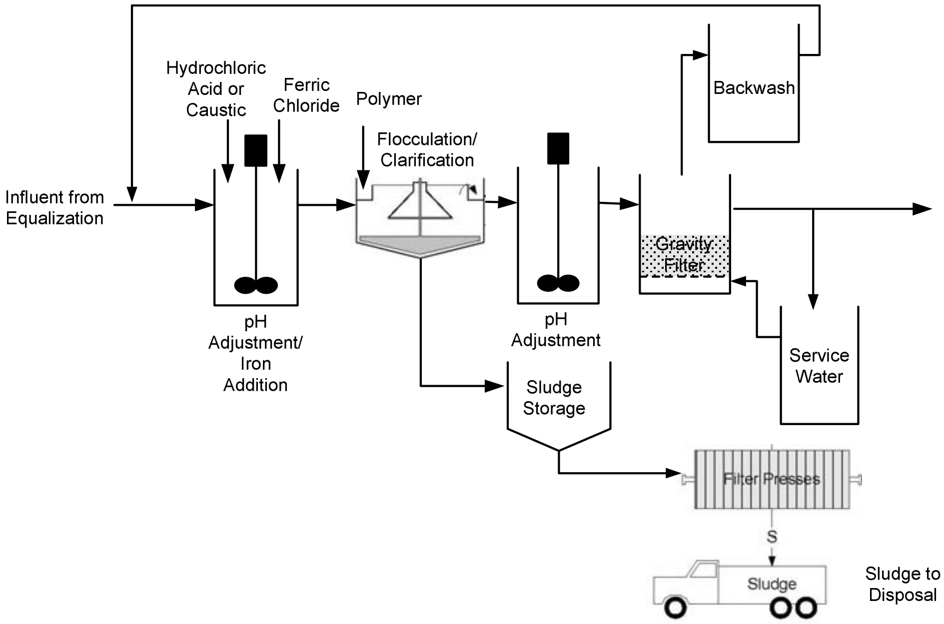


FIGURE 4-20
Iron Co-Precipitation Process Flow Diagram for Cost Estimate

Advantages and Disadvantages. The advantages and disadvantages of the ferrihydrite selenium co-precipitation technology are shown in Table 4-9.

TABLE 4-9
Advantages and Disadvantages of Ferrihydrite Selenium Co-Precipitation Technology

Advantages	Disadvantages
• Widely implemented at full-scale throughout the industry • Established by US EPA as best demonstrated available technology for selenium (e.g., selenite) removal. • Relatively simple and low cost chemical adsorption technology.	• Selenium removal not proven to low µg/L (less than 5 µg/L). • Produces relatively large quantities of sludge that may need to be disposed as a hazardous waste depending upon outcome of TCLP testing. • Iron co-precipitation is pH dependent with optimal conditions in the range of pH 4 to 6. • Not able to remove selenate. Requires oxidation of selenocyanate to selenite prior to removal. • Potential release of selenium from ferrihydrite residuals.

4.3.2.3 Activated Carbon

Technology Description. Because adsorption is a surface phenomenon, the rate and extent of adsorption for activated carbon is a function of the surface area and the solids used. Activated carbon is used extensively for adsorptive purposes because of its tremendous surface area in relation to its mass. Activated carbon, either granular or powdered, has been used extensively for organics, particularly those that are nonpolar, high MW, low solubility and have a low degree of ionization. Granular activated carbon is typically configured in columns much like ion exchange and pressure media filters. Powdered activated carbon is generally added to a completely stirred tank reactor. Activated carbon adsorption of selenium is ineffective (Twidwell et al., 1999) and is therefore not discussed further.

4.3.2.4 Aluminum Hydroxide/Activated Alumina

Technology Description. Activated alumina (AA) is a general term for various granular, porous oxides and hydroxides of aluminum that have been exposed to sodium hydroxide at high temperature. AA is similar to activated carbon in its adsorptive capacity given the surface area that is presented by the porous aluminum oxide. It can be configured much the same way as powdered activated carbon in a mixed reactor where after adsorption it can be separated from water by gravity sedimentation and/or filtration. Testing has determined that it has a high adsorptive capacity for oxyanions such as sulfate, arsenate, selenite, and to a lesser degree selenate. Aluminum oxide (Al_2O_3) is typically activated or calcined under alkaline conditions with magnesium hydroxide and/or dolimitic lime to produce a calcined hydrotalcite or magnesium aluminum oxide (Twidwell et al., 1999). However, there are many different forms of AA. AA has a relatively low specific adsorption for anions and a weak exchange adsorption attraction. Adding lanthanum oxide to the AA was found to adsorb onto the alumina by formation of an insoluble lanthanum complex and thereby improve the selectivity (e.g., less sensitive to sulfate adsorption) and capacity for selenium adsorption (Twidwell et al., 1999).

Aluminum salts (e.g., aluminum sulfate [$Al_2(SO_4)_3$], aluminum chloride [$AlCl_3$] and polyaluminum chloride [polyhydroxide chlorides of aluminum]), like ferric salts, are cationic coagulants. Adding these to water at or near neutral to alkaline pH will form hydroxide $Al(OH)_3$ which has been reported to remove selenium (e.g., primarily selenite) through adsorption via co-precipitation. The application of aluminum salts in a selenium water treatment process would be nearly identical to that of ferrihydrite systems.

Treatment Effectiveness. When AA was tested in a mining-influenced water matrix at a gold mine, selenium removal was demonstrated to be ineffective (Twidwell et al., 1999). Activated alumina is not effective for selenate removal. Activated alumina adsorption is typically applied in the fixed bed adsorption. The adsorption of selenite is pH dependent, with an approximate three-fold decrease experienced when increasing the pH from 5 to 7.

AA was tested at laboratory-scale for treatment of selenium in agricultural drainage and found to be effective for selenite removal (94% to 99% removal efficiency) but ineffective for selenate removal.

Capital and Operating Costs. Capital and operating costs information for use of AA in removal of selenium from water is not provided in the literature.

Advantages and Disadvantages. Further research and optimization are needed to determine the feasibility of using AA in applications to remove selenium from water.

4.3.2.5 Electrocoagulation

Technology Description. An electrocoagulation (EC) process utilizes reduction oxidation (redox) reaction chemistry to produce ferrous iron by applying direct electrical current to an electrochemical cell where the iron anode oxidizes to release ferrous iron in the water matrix. The term EC is used because the iron (Fe^{2+}) produced will act as a coagulant. However, true EC treatment will apply an appropriate amount of direct electrical current to not only oxidize the iron or aluminum electrode to provide a coagulant but will also destabilize the charge on colloids that are suspended or emulsified thereby causing agglomeration or coagulation of the solids. Secondarily EC may result in reduction of metals, ionization, electrolysis, hydrolysis and free radical formation depending upon the applied current.

A typical EC unit consists of a chamber with a series of iron, or aluminum, metal plates. As wastewater flows through the chamber, a direct current is applied to the chamber by attaching positive and negative leads to the first and last terminals. The wastewater within the chamber is a conductor, allowing the DC current to pass through the chamber. The metal blades are electrified, act as an induced electrode, and release metal ions into solution. Precipitates formed by the process can be separated by gravity sedimentation, or membrane filtration (e.g., UF or MF) at higher concentrations. A media filter could be required for tertiary treatment of the gravity sedimentation effluent. Thickening and dewatering of the residuals will be required to reduce the sludge volume and for disposal into a landfill.

Treatment Effectiveness. A laboratory study using EC treatment reduced the selenium concentrations present in industrial wastewater at a copper production facility from 2,320 to 30 µg/L (approximately 98.7%) by combining iron co-precipitation with MF using a flat sheet ceramic membrane (Mavrov et al., 2006). The wastewater was pre-treated with lime addition and settling.

Design and Operational Considerations. This treatment technology has not been applied at full-scale for design of selenium removal. For some wastewater sources, EC can provide adequate removal of trace metals and some organic removal or destruction. Limitations of EC units include frequent acid cleaning of plates, bubble formation due to hydrogen gas formation, which can cause difficulty in settling floc during subsequent treatment steps and foaming problems. A solids separation step is required after EC in order to remove precipitated metals from the waste stream.

Residuals Management. This treatment technology will have very similar residual management issues as the ferrihydrite adsorption chemical treatment described in Section 4.3.2.2. Generally thickening, dewatering and leachate testing will need to be considered depending upon the end disposal. Selenium adsorption may decrease over time as the residuals dry and crystallize. Leachate characteristic testing will be required to determine if the residuals will be hazardous and disposed of appropriately based on these test characteristics.

Capital and Operating Costs. Cost information is not reported for full-scale applications of this technology for selenium removal.

Advantages and Disadvantages. The advantages and disadvantages of the EC technology are presented in Table 4-10. Further research and optimization are needed to determine the feasibility of using EC in applications to remove selenium from water.

TABLE 4-10
Advantages and Disadvantages of Electrocoagulation Technology

Advantages	Disadvantages
• Generates ferrous ion without chemical addition. • May coagulate other colloids further enhancing the co-precipitation of selenium.	• Uncertainty regarding selenium removal can be achieved to low µg/L (less than 5 µg/L). Electrocoagulation treatments have not been tested in full-scale studies. • Large quantities of sludge that may need to be disposed as a hazardous waste. • Requires an electrical current. • Variability in wastewater ionic strength will vary the oxidation of the iron anode to ferrous iron resulting in potential perturbations in the resultant ferrous iron concentration. • Electrocoagulation may require frequent acid cleaning of cathode plates.

4.3.2.6 Selenium Adsorption to Peanut Shells

Technology Description. Selenium removal by adsorption to peanut shells has been studied on a laboratory scale (El-Shafey, 2007). Peanut shells were treated with strong sulfuric acid to carbonize the shells, oxidizing the cellulose and hemicelluloses and fragmenting the lignin. After treatment, the carbonized peanut shells absorb and reduce selenium. Selenium removal as high as 63% was reported for 25 mg/L selenide solutions.

Treatment Effectiveness. This process has only recently been developed on a laboratory scale and has not been demonstrated in the field.

Residuals Management. Disposal of the peanut shell media will be required. TCLP testing will need to be performed to determine whether the media should be disposed of as a hazardous waste.

Capital and Operating Costs. Peanut shells are low cost based on regional availability.

Advantages and Disadvantages. Further research and optimization are needed to determine the feasibility of using treated peanut shells in applications to remove selenium from water. The advantages and disadvantages of the peanut shell technology are presented in Table 4-11.

TABLE 4-11
Advantages and Disadvantages of Peanut Shell Technology

Advantages	Disadvantages
• Potential low-cost option for selenium removal due to inexpensive media.	• Not a proven technology. • Treatment is temperature and pH dependent.

4.3.2.7 Octolig® system

Technology Description. The Octolig® system consists of an organic ligand (substance that binds to another) that has been chemically immobilized onto a silica gel substrate. The Octolig® media is used in a flow-through column arrangement similar to an ion exchange system. The media does not remove dissolved solids which decreases replacement frequency for the media. In 1995, a lab-scale setup tested the Octolig® technology (Davis et al., 2009). However, selenium removal results were inconclusive and the Octolig® technology therefore is not discussed further.

4.3.2.8 Capacitive Deionization Process (SeClear™)

Technology Description. The Capacitive Deionization Process (SeClear™) is a direct current driven ion exchange technology with an electrostatic charging system that operates like a capacitor. The capacitor is comprised of a positive and negative electrode that is energized using a direct current, creating positive and negatively charged surfaces by which ionized cations and anions in the water are attracted to the anode and cathode, respectively. Regeneration of the system is completed by reversing the polarity of the cell causing the capacitor to release the ions into the cell where a small aliquot of deionized water flushes the cell. The operating potential is relatively low such that no electrolysis reactions occur precluding the breakdown of the electrodes (Davis et al., 2009).

Treatment Effectiveness. Historically, this technology has been explored in similar bench to pilot scale systems in removing similar oxyanions and other unwanted constituents from water. The performance of this technology drops off significantly as the TDS levels exceed 1,000 mg/L. Given the surface area of electrodes per unit volume of water, even if it were a proven technology, the footprint required for the system would be extremely large.

Wastewater flows between pairs of high surface area carbon electrodes that are held at a potential difference of 1.3 volts. Selenium species are attracted to and held on the electrode of opposite charge. On a bench-scale unit at the supplier's research facility, the process successfully removed selenium from SSW in July 2008. More than 98% of selenium was removed from SSW, with an average effluent selenium concentration of less than 6 µg/L. Inlet selenium concentrations averaged greater than 300 µg/L, and the unit maintained viable operation during at least one upset scenario (involving amine and low-level oil contamination of the feed). The finished water generated from capacitive deionization was essentially deionized water, with potential for use as boiler feed water or other clean water needs within the refinery. A "reject" stream would be generated, requiring disposal.

Advantages and Disadvantages. This technology has not been demonstrated beyond the laboratory for selenium removal.

4.3.2.9 Katchall Filtration Systems, LLC Media

Technology Description. Katchall Filtration Systems, LLC has developed an adsorbent media that is called "Heavy Metals Removal Media" that consists of coarse- and fine-granular materials loaded into an enclosed vessel through which water is passed for treatment. Metals are removed by chemical bonding onto organic molecules (media), producing a discharge with low metal concentrations (NSMP, 2007).

Treatment Effectiveness. A laboratory test using approximately 0.5 US gpm (total 5 gallons of water) showed a reduction in total selenium concentrations from 71 μg/L to less than 1 μg/L (NSMP, 2007). Pretreatment is required for TSS removal, and pH adjustment is required for waste disposal (NSMP, 2007).

Capital and Operating Costs. The estimated cost for scale-up of a 20,000 gallon per day system is reported as $60,000 (NSMP, 2007).

4.3.3 Chemical Oxidation/Reduction

4.3.3.1 Zero Valent Iron

Technology Description. The zero valent iron (ZVI) technology utilizes ZVI media or elemental iron to reduce the oxidized forms of selenium: selenate and selenite. ZVI media can be in powder, granular, or fibrous forms (NSMP, 2007). The form is important given this is in part a chemical redox and adsorption treatment mechanism and the available surface area is important to improving the efficiency of the reactions.

In the ZVI process, ZVI acts as a reducing agent in the redox reaction. The iron acts as both a catalyst and an electron donor for the reaction (Frankenberger et al., 2004). It also provides a source of both ferrous and ferric iron that can provide further reduction and adsorption of the selenium. If there is oxygen present in the water or oxic conditions exist, the ZVI will first be oxidized in the following reactions (Equations 4-2 through 4-5):

$$2Fe_{(solid)} + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \text{ (Equation 4-2)}$$

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \text{ (Equation 4-3)}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_{2(solid)} \text{ (Equation 4-4)}$$

$$Fe^{3+} + 2OH^- \rightarrow Fe(OH)_{3(solid)} \text{ (Equation 4-5)}$$

The formation of green rust, which is represented as a complex ferrous ferrihydroxide co-precipitate (e.g., $Fe^{+2a}Fe^{+3b}(OH)_{12}X\ 3H_2O$ where X is the interlayer anion [i.e., CO_3^{2-}, Cl^-]), results as the ZVI is oxidized. The formation of green rust is a function of pH and equilibrium concentrations of ferrous and ferric iron. Formation of green rust begins at a pH greater than 4 and begins to diminish at a pH greater than 5. Green rust is the form of ZVI required to abiotically reduce selenate to selenite and selenite to elemental selenium.

When the water containing selenate and selenite comes into contact with ZVI, it will produce a variety of ferrous and ferric iron products that will either directly reduce the selenate to selenite then to elemental selenium, or reduce the selenate to selenite and adsorb the selenite to the ferrihydrite or ferri-oxyhydroxide amorphous solids formed during the redox reaction with the ZVI.

The elemental form of selenium is insoluble and will exist as nanoparticles embedded in the iron solids matrix. Any soluble iron from the ZVI will require removal. This generally could require oxidation and/or pH adjustment followed by solids removal via sedimentation and/or filtration. Equations 4-6 and 4-7 summarize the overall reactions of ZVI with selenate and selenite.

$$3Fe^0(solid) + SeO_4^{2-} + 8H^+ \rightarrow 3Fe^{2+} + Se^0 + 4H_2O \quad \text{(Equation 4-6)}$$

$$2Fe^0(solid) + SeO_3^{2-} + 6H^+ \rightarrow 2Fe^{2+} + Se^0 + 3H_2O \quad \text{(Equation 4-7)}$$

As discussed previously, other oxyanions (e.g., carbonate, sulfate, nitrates, phosphates) can contribute to the oxidation of the ZVI. They may also help form green rust which is an essential component for reduction of selenium. Numerous side reactions can occur using this type of treatment system. One of the side reactions is the reduction of acid to hydrogen gas in the presence of elemental iron. In systems where sulfite is present, iron will undergo a redox reaction with sulfite to form ferrous iron and hydrogen sulfide (EPRI, 2009c).

ZVI treatment systems have typically applied the media in tanks or filter vessels that hold elemental iron. Figures 4-21 and 4-22 show simplified block flow diagrams for two different configurations of ZVI. The elemental iron (shown in Figure 4-21) can come in several forms including filings, steel wool, or iron impregnated foam. The tanks are generally covered to promote anoxic conditions for selenate removal. Tanks may be in series, creating several trains of selenium treatment. If possible, the tanks can be positioned at varying elevations so that hydraulic pressure will move the water by gravity through the ZVI system, eliminating the need for intermediate pumps. The effluent from these reactor tanks can be aerated to oxidize the iron in an aeration tank prior to discharging to the outfall. ZVI has also been applied using permeable reactive barriers. This is discussed further in the Passive Treatment Section 4.4.3 of this report.

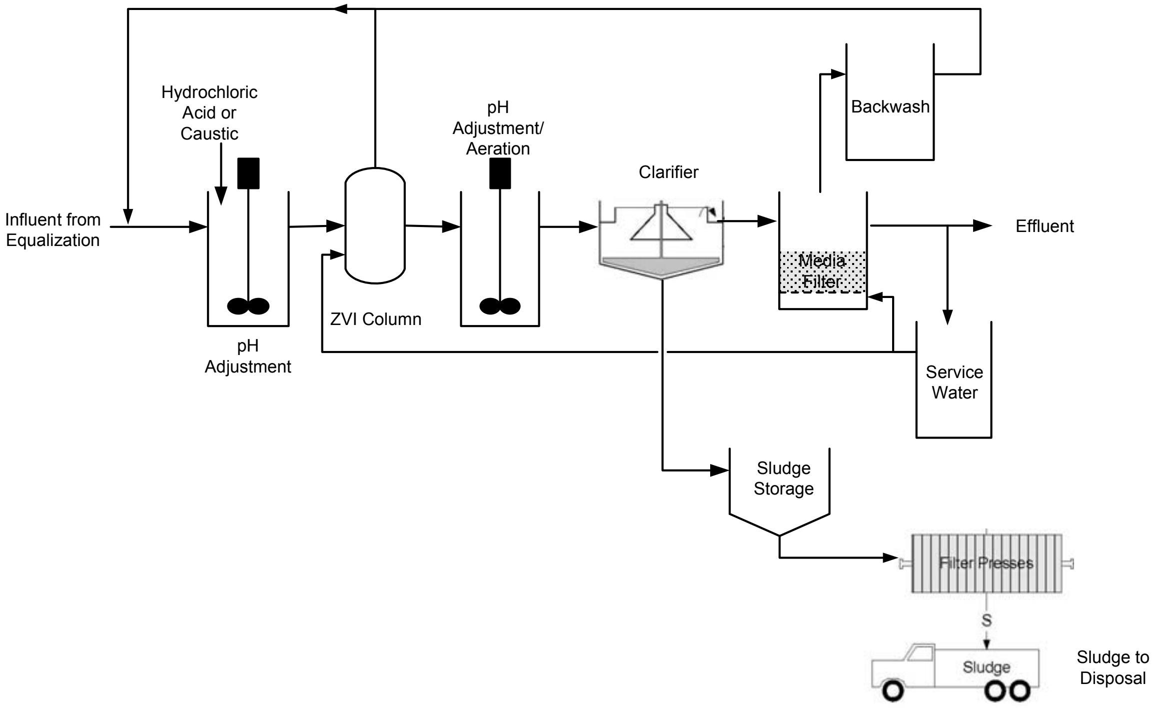


FIGURE 4-21
Zero Valent Iron Process Flow Diagram Using Column Setup with Steel Wool as ZVI Media

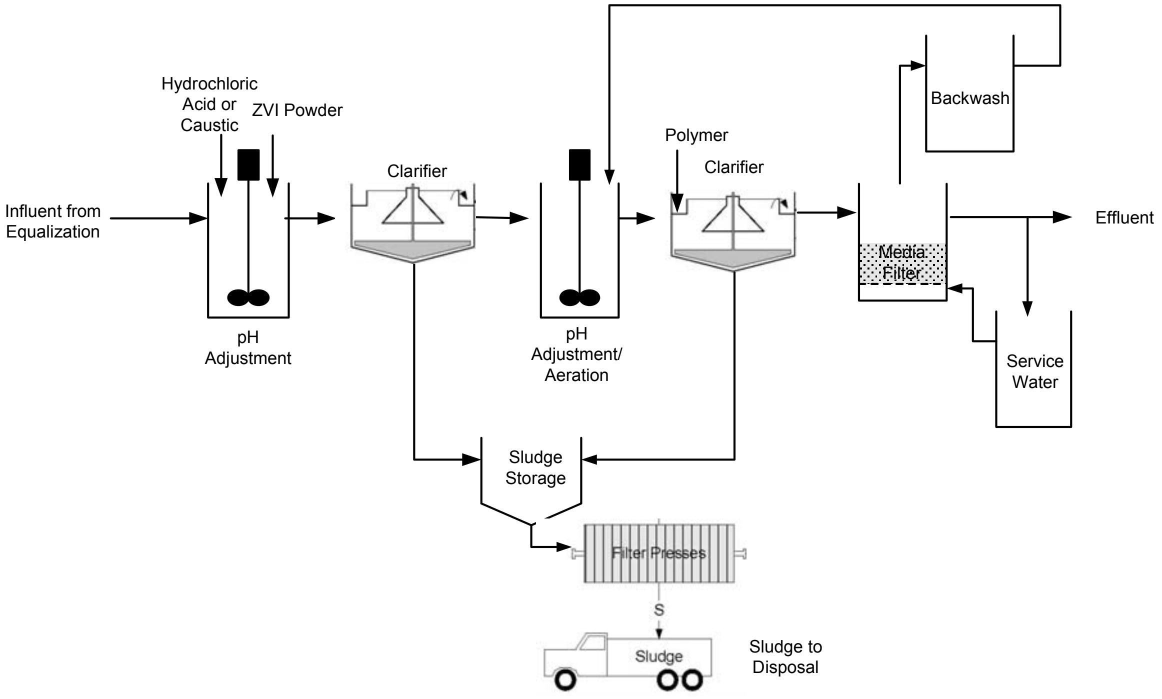


FIGURE 4-22
Zero Valent Iron (Granular) Process Flow Diagram Using Reactor Setup

Treatment Effectiveness. At Barrick's Richmond Hill Mine, ZVI is used to reduce selenate to selenite. Iron co-precipitation technology is used to precipitate selenite at pH 4.5 (Golder, 2009a). The process treats an influent of approximately 100 µg/L to an average effluent concentration of 12-22 µg/L (Sobolewski, 2005). RO is used as a polishing step to reduce selenium for discharge. The same technology of ZVI/followed by ferrous sulfate addition is applied at another mine (Golder, 2009a).

Different agents can be used to reduce selenate to selenite. For example, Meridian Dry Valley Mine used zinc powder while other mine operations used ferrous sulfate at pH 4. The application of ZVI followed by a biological reduction step showed promising results with reduction of both inorganic and organic selenium forms (Zhang et al., 2005).

Treatment of low levels of selenium was tested at pilot-scale using steel wool ZVI for mining-influenced water (Golder, 2009a). Over a 250-day test, influent concentrations of selenium varied from 5 µg/L to 14 µg/L. Effluent concentrations of selenium were not consistently below the regulatory limit of 5 µg/L from this pilot system. The system required a 5 hour residence time.

A brief pilot study was conducted in 2008 for treatment of FGD wastewater at an electric power generating facility that burns Powder River Basin coal. Metallic iron powder was used as a reactive media in a mixed reactor. The pH was raised adding sodium hydroxide so that the ferrous iron would be precipitated as ferrous hydroxide, which was removed in a second solids separation process. Nitrate, present in FGD wastewater, competes with the selenium for the elemental iron and is chemically reduced to ammonia. Nitrates therefore can greatly increase the requirement for treatment chemicals, as well as producing an undesirable byproduct for facilities that may have discharge limitations on ammonia (EPRI, 2009c). The 0.2 US gpm (0.8 Lpm) pilot study treated an influent total selenium concentration of 7,270 µg/L to 159 µg/L. The influent contained 2,240 µg/L selenate and 4,070 µg/L selenite (EPRI, 2009c).

A bench-scale study was conducted from 2002 through 2004 to investigate the viability of reacting stripped sour water (SSW) at an oil refinery through columns of ZVI (iron filings). The results of bench-scale testing showed that influent concentrations of 250 to 500 µg/L (primarily selenocyanate) could be reduced by 79% (Shamas et al., 2009). Although ZVI was proven to facilitate selenium removal, there were drawbacks to the technology, including extended reaction time (more than five hours) and pH sensitivities (Davis et al., 2009).

Design and Operational Considerations. In order to chemically reduce selenate and selenite with ZVI it is important to control the environment (e.g., wastewater and reactor characteristics). The wastewater characteristics (i.e., pH, dissolved oxygen, ionic strength, temperature, and other competing oxyanions such as nitrates, sulfate, carbonate, phosphate, and suspended solids) can greatly affect the removal of selenium by ZVI. The optimum pH range for complete chemical reduction of selenium is between 4 and 7. At a pH between 7 and 9, both chemical reduction and adsorption occur. The presence of oxygen will compete with reduction of selenium, as will nitrates and nitrites. The temperature will affect the reaction kinetics, or rate at which selenium reduction occurs. Low temperature will reduce the reaction kinetics and hence the system should be designed conservatively. It is difficult to consistently remove selenium at low concentration due to very slow reaction kinetics. The reaction kinetics slow as a function of increasing pH and ionic strength, and decreasing temperature. Typically long hydraulic residence times are required (e.g. 4 hours or greater). Mass transfer of the water through the ZVI is also important to improve the level of selenium treatment. Passivation of the iron may also occur depending upon the presence of other metal redox reactions, chemical scale and/or suspended solids that will accumulate on the surface of the iron reducing the reduction capacity.

Tanks and piping may require insulation for outdoor applications in cold weather or placement within a heated building. Suspended solids may become entrapped within the media and clog the system so pre-filtration or settling may be required to remove suspended solids as a pretreatment step.

As shown in Equations 4-6 and 4-7, ferrous iron is produced when ZVI is consumed in the process. The ferrous iron requires treatment, usually with aeration. The precipitated iron from aeration will then be removed in a clarifier.

Residuals Management. The life of the ZVI media is finite and will require removal, disposal and replacement. The frequency is highly dependent on site-specific conditions and may last a few months to a few years before requiring replacement. In addition to unoxidized media there will be selenium and iron residuals that will need to be disposed. Oxidation of ZVI and reduction of selenium will create a large quantity of iron residuals that will need to be separated from water, thickened and dewatered for disposal. For the selenium that was not completely reduced but only adsorbed, selenium adsorption may decrease over time as the residuals dry and crystallize. Leachate characteristic testing will be required to determine if the residuals will be hazardous and disposed of appropriately based on the results of these tests.

Capital and Operating Costs. Figures 4-23 and 4-24 present the TIC and O&M costs for a ZVI system for selenium reduction to below 5 µg/L using a column setup with steel wool as ZVI media. Figures 4-25 and 4-26 present the TIC and O&M costs for a ZVI system for selenium reduction to below 5 µg/L using granular ZVI. These costs are Class 5 costs as defined by the AACEI with an accuracy of +100% and -50% as shown by the variance bands based on 2009-2010 market conditions. These are parametric cost estimates based on the ZVI system shown in Figures 4-21 and 4-22. This system is a grass roots or green field selenium treatment system with costs for stand alone utilities (e.g., power) and an equipment/control room building included in the estimate. 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. As discussed in Section 4.1.2 equalization and diversion of flows and/or loadings are generally required for most treatment systems. Operational costs include maintenance, labor, energy, cleaning, chemical and residual disposal costs. Residuals were assumed to be non-hazardous and disposed in a non-hazardous waste landfill. The ZVI steel wool includes annual replacement costs for the ZVI. Granular ZVI O&M costs include the addition of the granular ZVI.

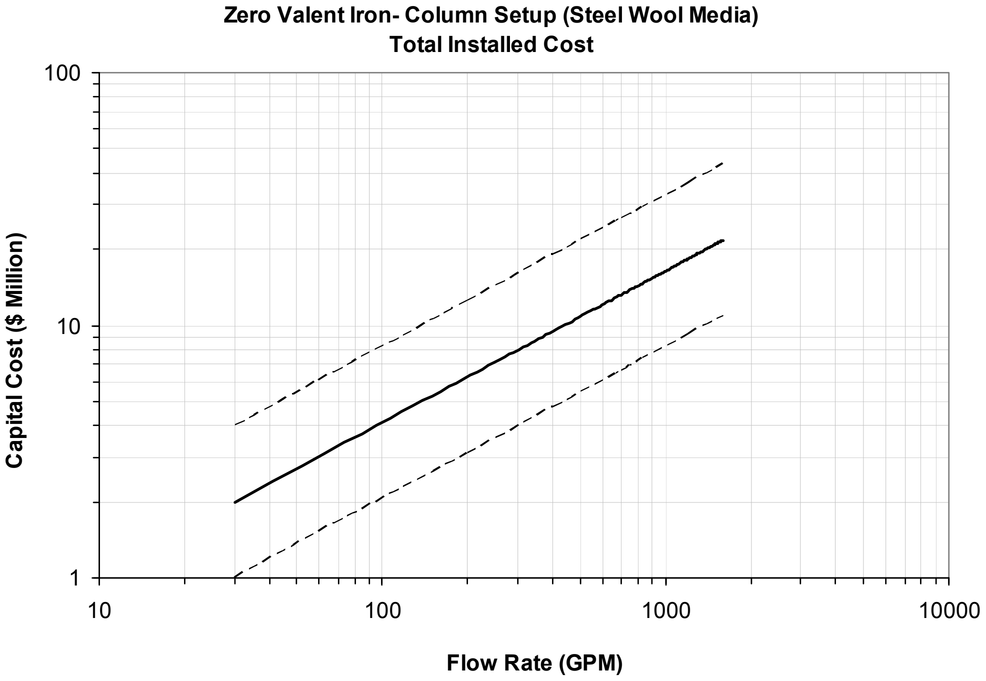


FIGURE 4-23
Total Installed Costs for ZVI Using Column Setup with Steel Wool Media (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

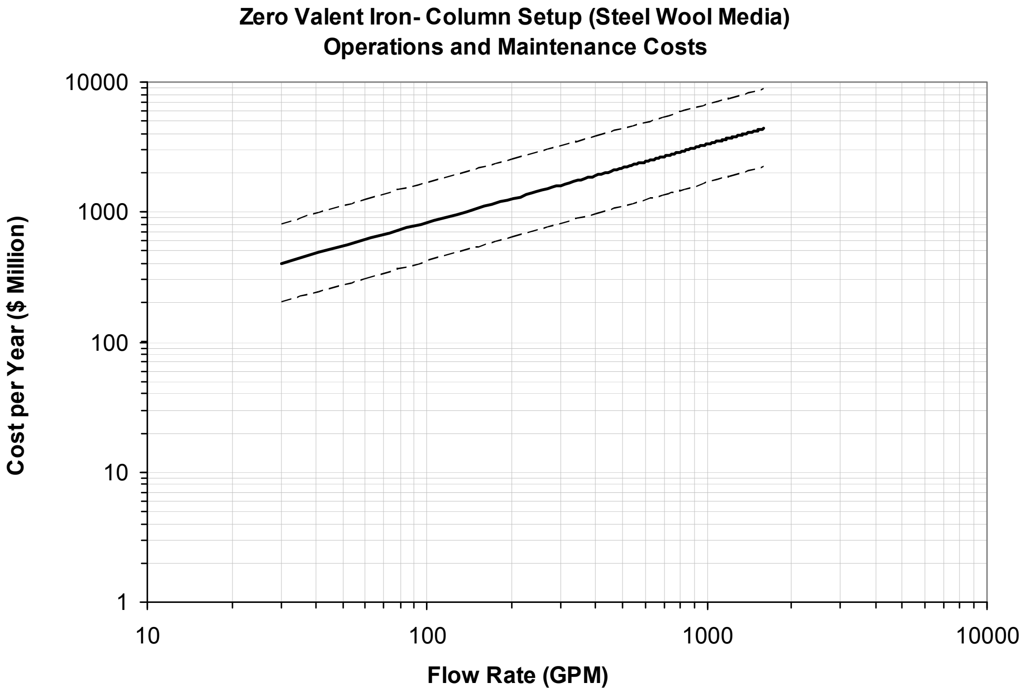


FIGURE 4-24
Operating Cost Curve for ZVI Using Column Setup with Steel Wool Media (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

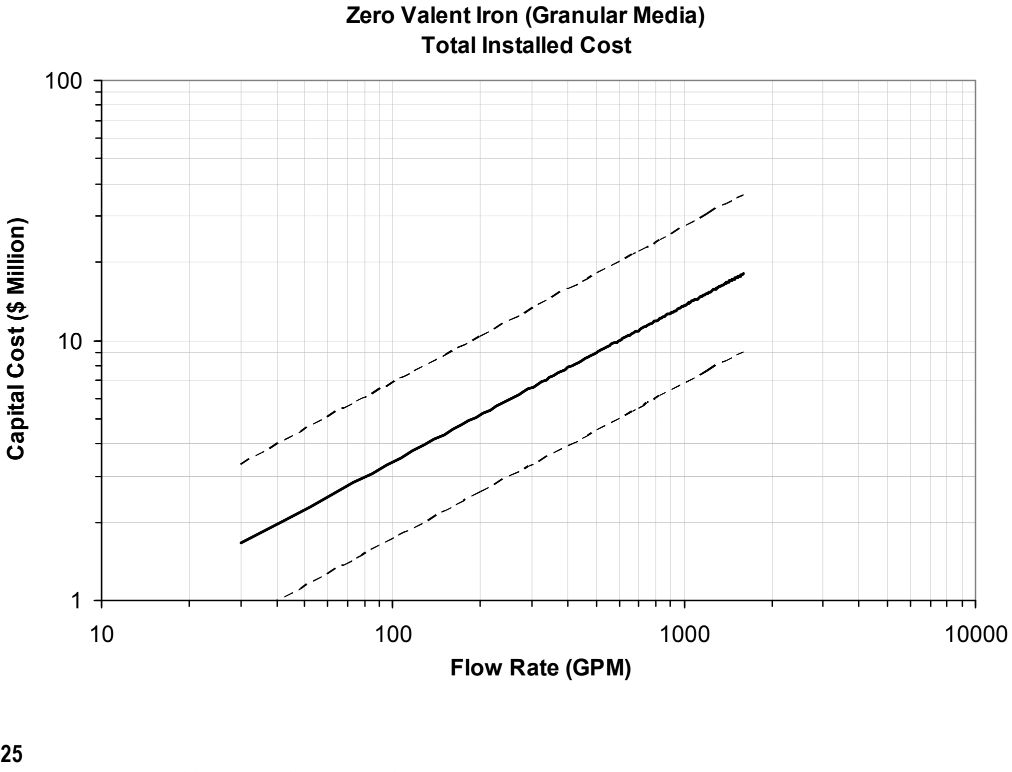


FIGURE 4-25
Total Installed Costs for ZVI (Granular) (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

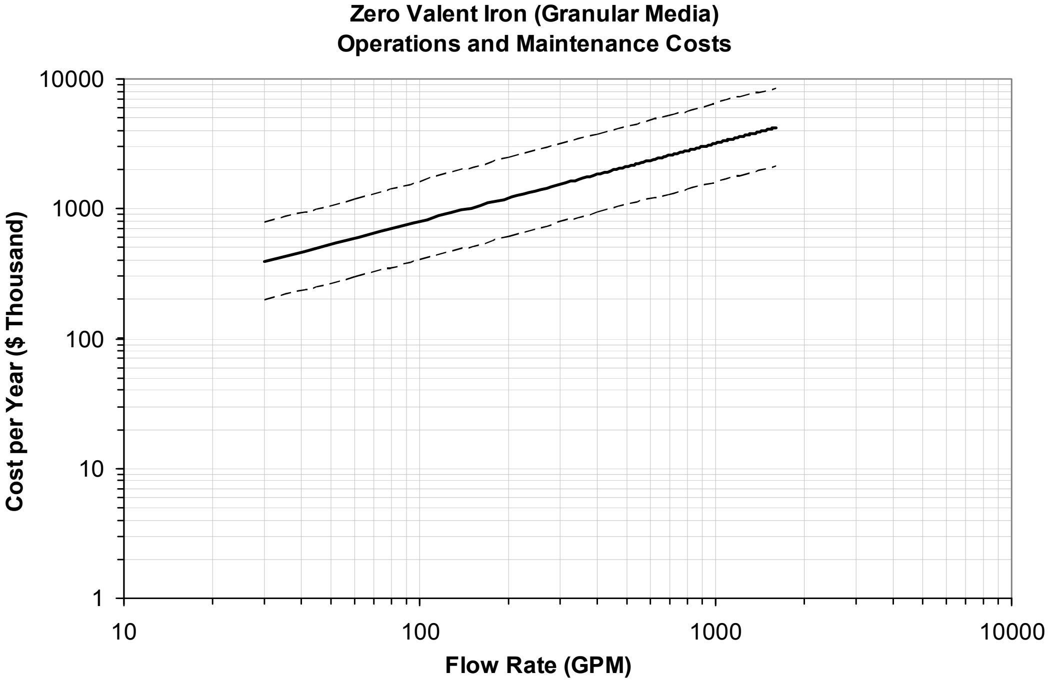


FIGURE 4-26
Operating Cost Curve for ZVI (Granular) (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

Advantages and Disadvantages. The advantages and disadvantages of the ZVI technology are presented in Table 4-12.

TABLE 4-12
Advantages and Disadvantages of Zero Valent Iron Technology

Advantages	Disadvantages
• Basic technology is demonstrated in laboratory studies to remove selenate and selenite at low concentrations. • Provides two reduction mechanisms for selenium including: green rust for reduction of selenate to selenite and selenite to elemental selenium and ferrous iron for reduction of selenate to selenite. • Provides ferric iron for ferrihydrite adsorption of selenite.	• ZVI technology has not been proven in full-scale treatment and at higher selenium concentrations. • Potential for long residence times. • Spent ZVI must be removed, disposed of and replaced. • Dissolved oxygen and other oxyanions can oxidize the ZVI at certain conditions. • Sludge disposal may be significant cost. • ZVI treatment is temperature and pH dependent.

4.3.3.2 Catalyzed Reduction

Technology Description. The addition of copper or nickel to a ZVI treatment process has been demonstrated to catalyze the reduction of selenium by creating a greater electrochemical potential between the elemental iron and soluble selenium (MSE, 2001). This is also referred to as “galvanic cementation” or simply “cementation” because it will result in a net positive electrode potential that controls redox reaction chemistry, resulting in conditions amenable for selenium reduction. Metals have been removed from mine-influenced water by reduction to an elemental form on the surface of a metal as cementation (Golder, 2009a). For example, aqueous solution species of copper, arsenic, and selenium were reduced to the solid elemental state on an iron surface by adding catalysts that enhance the cementation process to the iron surface at a lowered pH (NSMP, 2007).

The addition of copper to ZVI treatment has been reported to nearly double the selenate reduction rate at a pH of 7 compared to ZVI alone. For ZVI supplemented with reduced nickel the selenate reduction rate increased by a factor of nearly 25 times the rate of ZVI alone in the same configuration (NSMP, 2007).

Treatment Effectiveness. Catalyzed ZVI reduction was laboratory tested at Kennecott's Garfield Wetlands-Kessler Springs as part of the USEPA demonstration project for selenium removal. The lowest effluent concentration achieved in the field was 26 µg/L from influent water containing 1,950 µg Se/L (primarily as selenate) (MSE, 2001). Selenium concentrations were reduced to 3 µg/L after laboratory optimization (Golder, 2009a).

Design and Operational Considerations. Design and operational considerations for catalyzed cementation are similar to the ZVI technology, including the potential need for pretreatment, and the presence of interfering anions such as nitrate, sulfate, etc.

Residuals Management. The life of the media is finite and will require removal, disposal and replacement. The frequency is highly dependent on site-specific conditions and may last a few months to a few years before requiring replacement. The media may need to be disposed of as hazardous waste and TCLP tests should be performed to determine whether this is required.

Capital and Operating Costs. Reagent consumption of this technology is estimated to be $8.11 per 1,000 gallons treated. Design, equipment purchase, construction, and startup costs were estimated as $1,083,285 (2001). Annual O&M costs have been quoted at $1,165,358 (2001) (MSE, 2001).

Advantages and Disadvantages. The advantages and disadvantages of the catalyzed cementation technology are presented in Table 4-13.

TABLE 4-13
Advantages and Disadvantages of Catalyzed Reduction Technology

Advantages	Disadvantages
• Basic technology is demonstrated in laboratory studies to remove selenate and selenite to low concentrations.	• Technology has not been proven in full-scale treatment. • Potential for long residence times. • Spent media must be removed, disposed of and replaced. May require disposal as hazardous waste. • Sludge disposal may be significant cost. • Media replacement may be a significant cost. • Other potential issues with copper and nickel discharges.

4.3.3.3 Ferrous Hydroxide

Technology Description. The U.S. Bureau of Reclamation developed a process using ferrous hydroxide to reduce selenate to selenite, followed by adsorption of the selenite to the ferrihydrite monohydrate amorphous solids which might otherwise be described as ferric hydroxide $Fe(OH)_3$ as well to a lesser degree the ferrous hydroxide solids. Ferrous hydroxide can be precipitated in a near neutral medium by the addition of sodium hydroxide to ferrous sulfate (Lalvani, 2004). Reduction and subsequent adsorption is best accomplished under reducing conditions at a pH of approximately 8-9 (Twidwell et al., 2009). However at this pH and above ferrous hydroxide is only slightly soluble. The general redox and subsequent adsorption reactions (Equations 4-8 and 4-9) are provided below:

$$\text{Dissolution: } Fe^{2+} + H_2O \rightarrow Fe(OH)_2 \quad \text{(Equation 4-8)}$$

$$\text{Redox/Adsorption: } 2SeO_4^{2-} + 4Fe(OH)_2 + H_2O \rightarrow 2SeO_3^{2-} + 4Fe(OH)_{3(solid)} \quad \text{(Equation 4-9)}$$

Interferences in the process are nitrate, dissolved oxygen (DO), and bicarbonate. Residuals management would involve large quantities of iron bearing sludge that are handled and treated for disposal (Lalvani, 2004).

Treatment Effectiveness. Section 6 describes a case study for ferrous hydroxide treatment of FGD water using ferrous chloride as a salt (Site PG1, Section 6.5.1).

Capital and Operating Costs. The total installed cost for Site PG1 300 US gpm FGD water treatment plant built in 2000 was $15 million. Annual O&M costs range from $1.5 to $2 million per year (2000 USD), which includes labor, chemicals, maintenance, disposal, and energy. The majority of the costs are associated with chemicals and residuals management.

Advantages and Disadvantages. The advantages and disadvantages of this technology are similar to the ferrihydrite adsorption technology. The main disadvantages involve residuals handling and disposal of sludge that may be hazardous. TCLP testing may need to be performed to determine whether sludge requires disposal as a hazardous waste. The solids generated from the Site PG1 FGD water treatment system are non-hazardous.

4.3.3.4 Photoreduction

Technology Description. Photoreduction is a chemical reduction and adsorption technology. Photoreduction uses irradiation of ultraviolet (UV) light within a defined waveband and in the presence of titanium dioxide (TiO_2) to convert selenate and selenite to elemental selenium (Shamas et al., 2009). Contaminants that adsorb to the surface of the photocatalyst undergo chemical redox and adsorption reactions induced by the electrons and holes created by UV light exposure. The elemental forms of the treated species are then desorbed, and the surface of the photocatalyst is regenerated (Golder, 2009a).

Treatment Effectiveness. Selenate and selenite can be effectively reduced by TiO_2, which has been found to be an effective photocatalyst for the reduction of selenium forms. Mixed solutions containing 20 to 40 µg/L selenate and selenite were tested with UV light with wavelengths of less than 380 nanometers and a pH of 3.5 in the presence of TiO_2. Final effluent total selenium concentrations were between 31 and 1 µg/L (Nguyen et al., 2005).

Capital and Operating Costs. Cost information is not available for this technology.

Advantages and Disadvantages. The primary disadvantage is the formation of toxic hydrogen selenide gas. Further research and optimization of this technology are needed to determine the feasibility of use for full-scale applications.

4.3.3.5 Carbohydrazide

Technology Description. Carbohydrazide and hydrazine are both strong reducing agents that will remove oxygen from oxyanions such as selenate and selenite thereby reducing them to elemental selenium. They function best as a reducing agent in basic or alkaline conditions and less so at acidic conditions. Anhydrous forms of these chemicals are volatile, toxic, corrosive and form explosive mixtures with air. Even in aqueous solutions they are toxic and must be handled properly. Hydrazine has historically been used as an oxygen scavenger in boiler feed water, but because of its toxicity has been replaced by other chemicals. Carbohydrazide treatment for selenium is done at high temperatures and lower pH (e.g., 2 to 4) to minimize consumption by sulfates. This treatment, while effective, would probably only be applicable on concentrated low volumes solutions of selenium. It may be an effective means by which to further reduce adsorbed selenium in adsorption processes.

Treatment Effectiveness. Experimental setup reported removal of selenium greater than 99%; however, the resulting selenium concentrations did not meet regulatory standards. Selenium was reduced from 1,200 to 1,800 mg/L to 0.015 mg/L in treated water (NSMP, 2007).

Capital and Operating Costs. Cost information is not available for this technology.

Advantages and Disadvantages. Further research and optimization of this technology are needed to determine the feasibility of use for full-scale applications.

4.4 Biological Treatment

4.4.1 Principles of Microbial Reduction Overview

Biological treatment relies on the growth of microorganisms. Microorganisms receive their energy through the transfer of electrons from an electron donor to an electron acceptor. By controlling the environment in which the microorganisms grow, the resulting chemicals and byproducts of their growth can subsequently be controlled. Therefore, in order to use biological treatment to remove selenium from the wastewater, it is paramount to control the environment (i.e., through water pretreatment and reactor design) such that the organisms which reduce selenium flourish.

Biological treatment can be best understood in terms of biological oxidation and reduction (e.g., redox). In essence the same redox chemical reactions for selenium described in Section 4.3.3 on chemical treatment, also apply to biological treatment. The primary difference is that these occur by and are mediated by microorganisms through their biochemical metabolic pathways. They are not a function of chemical redox potentials or chemical catalysts.

The electron donor is the organic carbon source (e.g., food) for the microorganism, and the electron acceptor is the microorganism's means of respiration. The substrate, or food source is generally expressed as chemical oxygen demand (COD), carbonaceous biochemical oxygen demand (BOD) or total organic carbon (TOC) (e.g., measurements for organic strength of water). The products of the oxidation of the electron donor are carbon dioxide and biomass.

There are several electron acceptors available to oxidize the electron donor. Figure 4-27 shows bioreaction kinetics favor the following electron acceptors (in descending order): oxygen, nitrates, selenates, and sulfates, based on ORP established through a bioreactor (EPRI, pending(a)).

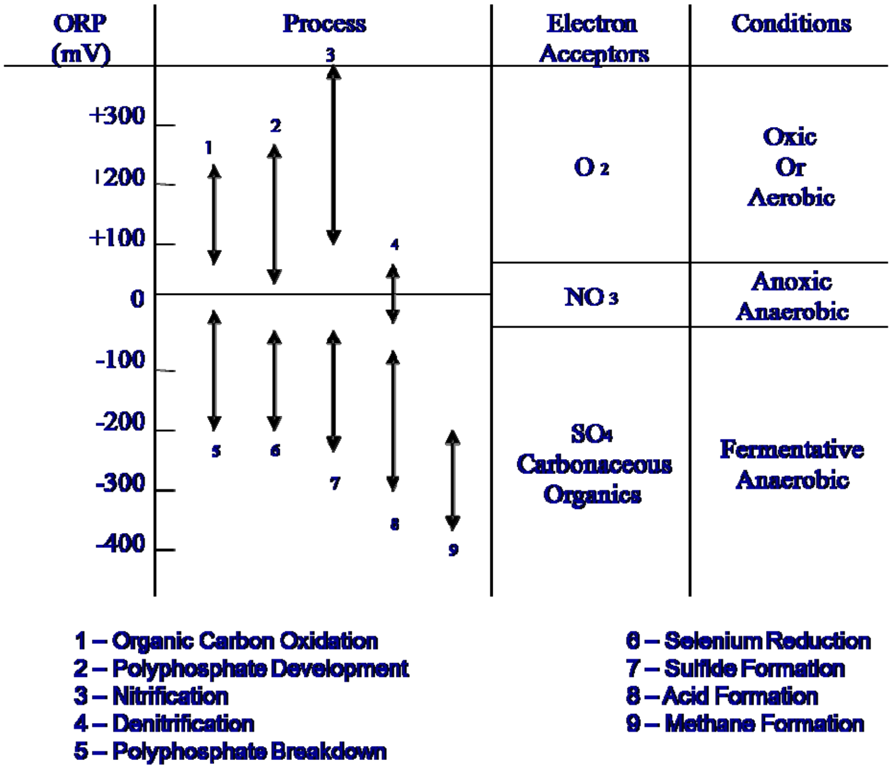


FIGURE 4-27
Redox Profile of Biological Reduction
Source: Electric Power Research Institute, pending (a).

Oxygen is the most favorable electron acceptor for microorganisms. When dissolved oxygen is present, microbial aerobic oxidation of organics for energy production results in the energy source and electron acceptor being converted to carbon dioxide and water. An anaerobic environment exists where oxygen and oxidized nitrogen are not present.

In an environment with insufficient oxygen, oxidized inorganic compounds or oxyanions can serve as the electron acceptor. Many bacteria will use nitrate as an electron acceptor when oxygen is absent (an anoxic environment). These bacteria are called denitrifying bacteria or denitrifiers. These bacteria prefer to use nitrate in the absence of oxygen and the product of the reduction of nitrate is inert nitrogen gas.

Microorganisms that obtain energy from the oxidation of organic compounds are heterotrophs. Those that obtain energy from the oxidation of inorganic compounds are autotrophs. Selenium and nitrate-reducing bacteria are heterotrophic bacteria utilizing organic carbon as their electron donor and selenate and/or selenite as their electron acceptor. They obtain both their energy and cellular growth and synthesis from the organic oxidation reaction with selenite and selenate.

Some denitrifiers can use selenate or selenite as an electron acceptor but only in the absence of oxygen and nitrate. If either of these acceptors is available, selenium will not be reduced biologically. To reduce selenium in wastewater, all oxygen and nitrate must first be reduced. If a significant amount of nitrate is present in the water, then a sufficient amount of organic carbon needs to be added to reduce the nitrates first, as well as any selenium. Therefore, the ratio, or stoichiometry, of the carbon (e.g., electron donor) to nitrates and selenium (e.g., electron acceptor) is extremely important to successful reduction of selenium. This means that the environment must be controlled to exclude oxygen, and there must be enough electron donor (e.g., food) available to reduce the nitrate and the selenium in order to treat the wastewater for selenium. Examples of carbon sources utilized in microbially mediated reduction include methanol, acetate from acetic acid, citric acid, and molasses. The quantity of electron donor provided must be in excess of the quantity required to reduce the nitrate that is present within the system to nitrogen gas in order to achieve extensive selenate reduction in an environment containing nitrate. Therefore, an aerobic process may need to be included downstream of the selenate-reducing bioreactor to remove BOD before discharge.

A wide range of bacteria are able to reduce selenite to selenium (Doran, 1982; Oremland, 1993) and such organisms are ubiquitous (Stolz and Oremland, 1999). Steinberg and Oremland (1990) examined 11 aquatic environments and found selenate reducers in all but those with extreme salinity. This does not imply, however, that all bacteria can reduce selenate all the way to elemental selenium. For example, in one bioreactor system, one type of bacteria reduced selenate to selenite and another type reduced selenite to elemental selenium (Macy et al., 1989). Thus, sometimes consortia are involved. The fact that many types of bacteria are capable of reducing selenate and selenite suggests that it should be relatively easy to obtain and maintain competent bacteria in bioreactors. It also suggests that a wide range of organic compounds should be able to be used as an electron donor for reduction; this has been found to be the case, with different bacteria often using different organic compounds (Stolz and Oremland, 1999).

A challenge for biological treatment is presented when nitrate and/or selenium (e.g., electron donor) concentrations are very low or absent. These conditions will result in little to no growth of heterotrophic bacteria, which can lead to washout or potential loss of the microorganisms to reduce the selenium. If an electron donor (e.g., organic carbon source) is added in the absence of these electron acceptors (e.g., nitrate and selenate), the system could promote sulfate reduction or hydrogen production or even result in methane being produced. Sulfate can also be used as an electron acceptor. It is used only when oxygen is absent and primarily when both nitrate and selenate are absent. Sulfate-reducing bacteria do not use nitrate, selenate, or selenite. Sulfate can also be reduced in environments where selenium is reduced, but sulfate reduction is carried out by an entirely different group of bacteria (Stolz and Oremland, 1999). Both selenate and sulfate compete for the electron donor, but it appears that selenate reduction is faster and can occur at higher ORP. Thus, while some sulfate reduction may occur, it should be possible to operate a selenate-reducing bioreactor on a high sulfate feed (such as FGD wastewater) without significant impacts on selenate reduction, provided sufficient electron donor is provided. Sulfate-reducing bacteria are typically considered nuisance organisms. Although the sulfate reducers are not expected to offer significant competition in the anoxic or anaerobic environment needed for selenium treatment, they can compete for electron donors and also produce sulfide, which is a toxicant to other heterotrophic bacteria; but this condition can typically be controlled.

Ike et al. (1999) studied selenate reduction in lab reactors seeded with samples from aquatic environments. Selenite reduction was observed to be more rapid than selenate reduction in mixed cultures. When they studied pure cultures, however, cases were found in which this was not true and selenite accumulated transiently. The authors suggested that microbial interactions in mixed cultures provided distinct advantages for selenate reduction to elemental form. This suggests that care should be used when using constructed cultures to be sure that selenate reduction proceeds rapidly to elemental selenium.

The growth of bacteria is influenced strongly by the pH and temperature of the environment in which the bacteria are growing. Lortie et al. (1992) found that no reduction of selenate occurred at a pH below 6.5 or above 9.5, whereas the lower and upper bounds for selenite reduction were 5.5 and 9.5, respectively. Thus, as long as neutral pH is maintained in the bioreactor, it is unlikely to be a factor influencing performance.

Temperature will also affect biological reaction kinetics. Most biological wastewater treatment systems operate with mesophilic bacteria, or bacteria that operate at a range of 15 °C to 40 °C. Generally, temperatures of less than 15 °C result in substantial reduction of biological reaction kinetics. Both Wan et al. (2001) and Fujita et al. (1997) observed that the optimal temperature for selenium reduction was 30 °C, with a decrease in rate at temperatures both above and below that value. This suggests that care must be applied in the choice of temperature for biological removal of selenium.

Another factor affecting microbial reduction is the salinity of the wastewater. Zhang et al. (2003) investigated the effects of salinity on selenate reduction in laboratory cultures of *Enterobacter taylorae*, a selenate-reducing bacterium isolated from rice straw. They found that the rate of selenate reduction decreased as the salinity increased. Modest changes will not disrupt the operations of a bioreactor, but significant changes in salinity, pH, or temperature—especially rapid variations—will disrupt the system.

4.4.2 Treatment Systems that Use Microbial Reduction for Removal of Selenium

Anaerobic bacterial removal of selenium can be accomplished using bioreactors, constructed wetlands and/or *in-situ* biobarriers. Although various types of systems can be used for anaerobic biological treatment, only examples of those systems that have been previously tested at laboratory-, pilot-, or full-scale for selenium removal are presented within this section.

As with chemical treatment, the low selenium concentrations in the water as well as competing oxyanions create challenges for biological treatment. A sustainable population of heterotrophs is a key requirement for biological systems to treat selenium to low levels. This requires careful addition of an electron donor in exact proportions to the available electron donor supply as well as an appropriate configuration to provide the microorganisms with ready access to these. Because of these issues, careful design and configuration of the biological treatment system must be considered.

Biological reactor or bioreactor designs can include aboveground tanks or in ground basins containing suspended growth or attached growth systems. Bioreactors can be either active or passive systems. Passive systems do not require chemical and mechanical inputs. In essence an ideal environment is created to promote the necessary biological treatment naturally without outside influences. Active systems are designed to control, enhance, and optimize the environment for biological treatment of the constituents of concern. Reactors typically are either suspended-growth or attached-growth systems. A third type of system is a hybrid system that contains both suspended and attached growth.

Attached growth systems are comprised of a biofilm, or a layer of microorganisms that grow on the surface of a solid phase media (e.g., rock, granular activated carbon, sand, etc) that are wetted by the water. Attached growth systems are ideal for removal of dilute concentrations of constituents because the microorganisms stay attached to the media for relatively long periods of time improving the chance for contact with the constituents before they die, slough off and are washed out of the system. Attached growth microorganisms produce extracellular polymers that allow them to attach to the media. Over time as the film builds to certain levels it will slough off with the water that passes over the film. Suspended growth systems contain microbial solids that are suspended in the bioreactor through mixing. These are typically referred to as activated sludge systems. The microorganisms produce extracellular polymers such that the bacterial cells will agglomerate or coagulate into larger colonies or visible suspended solids. Suspended growth systems rely on liquid solids separation (e.g., plate separator, gravity clarification, membrane separation) to keep the microorganisms in the system by returning a portion of these microorganisms to the bioreactor. Hybrid systems have both attached and suspended growth. They are commonly referred to as integrated fixed film activated sludge.

Key Design Considerations. The key design considerations for biological treatment systems for selenium reduction are as follows:

- Electron acceptor to donor stoichiometry
- Water temperature, pH and ionic strength
- Hydraulic residence time
- Solids residence time
- Macro and micronutrients
- Residuals management

In the design of attached or suspended growth active or passive systems for biological selenium removal the water characteristics must be well understood. The amount of and types of oxyanions or electron acceptors must be known in order to prescribe the correct addition of electron donor in proportion to the electron acceptor.

The water temperature ideally must be above 15 °C and below 35 °C. Biological reduction of selenium will create heat through conversion of the energy source for biological growth and synthesis. Therefore a heat and material balance must be developed for the system to operate within the optimal temperature band. Cooling may be required for refinery or power plant water treatment. The pH of the water should be between 6 and 8. A pH of 7 is ideal in that it will minimize the carbonate concentration that can result in scale.

Hydraulic residence time for water treated for selenium in suspended growth and fixed media attached growth systems typically must be at least 4 to 6 hours for the bioreactor. Longer times may be required depending upon the reactor configuration, concentration of the selenium in the water and the desired discharge concentration. In addition to hydraulic residence time, hydraulic loading rates are important in the design of attached growth systems. For fixed media attached growth systems, hydraulic loading rates typically will need to be between 2 and 6 gpm/ft^2.

Growth histories of the microorganisms in the water environment are important for selenium removal. In essence, the microbiology will adapt and evolve as a function of time to the environment to take advantage of the environmental conditions provided by the water matrix. Long solids residence times for the biomass, or the total time the microorganism are in the reactor of the selenium reduction system are important to having a population that can degrade selenium given the water or wastewater characteristics. Solid residence times of in excess of 5 to 10 days will be required at minimum based on similar denitrification systems. The actual solids residence time requirements can be shorter or longer depending upon the complexity of the wastewater matrix and the availability and/or concentration of the selenium and/or other electron acceptors.

Macronutrients (e.g., nitrogen, and phosphorus) and micronutrients (e.g., potassium, calcium, magnesium, sulfur, sodium, chloride, iron, zinc, manganese, copper, molybdenum and cobalt) are essential for microbial growth and synthesis. If these nutrients are not in the water at levels required for proper growth and synthesis, supplemental addition will be required otherwise the system's performance can be impacted.

The observed yields for biological solids from anaerobic nitrate and/or selenium reduction biological systems will vary by water source and energy source. Since the same or similar heterotrophs that reduce nitrate reduce selenate and selenite, biomass yields will be 0.2 to 0.4 lbs TSS/lbs COD removed, where the COD closely approximates the theoretical oxygen demand of the organic carbon or energy source. More specifically on a selenium or selenate/selenite basis, the biological yields would be between 0.4 and 0.8 lbs TSS/lbs of selenium removed.

4.4.2.1 Suspended Growth Bioreactors: Upflow Anaerobic Sludge Blanket Bioreactor

Technology Description. The biomass in suspended growth systems is in a flocculent state suspended in the liquid phase in the bioreactor. An example of a suspended growth bioreactor is an upflow anaerobic sludge blanket (UASB) bioreactor. In a UASB bioreactor, the wastewater flows upward through the granular sludge at a high enough velocity to keep the sludge suspended without washout. The upper part of the bioreactor contains a gas/solids separator to allow gases produced to be vented and solids entrained by the gases to be recovered. The UASB bioreactor may be the first stage of treatment in a multistage process to reduce selenium. UASB treatment is typically performed for high concentrations of constituents in wastewater, not the dilute (less than 25 mg/L) levels of selenium present in most process waters from the various industry sectors.

Treatment Effectiveness. An UASB pilot test was performed for selenium removal at the Adams Avenue Agricultural Drainage Research Center in the San Joaquin Valley, California. The study reported 58% to more than 90% selenium removal from an influent containing a total selenium concentration of 500 μg/L (State of California Department of Water Resources Division of Planning and Local Assistance San Joaquin District, 2004).

Design and Operational Considerations. Short circuiting was an issue for the Adams Avenue Agricultural Drainage Research Center test. Short circuiting was caused by the accumulation of gas within the pilot reactor that became trapped in the sludge. Reactor design and configuration play a significant role in the treatment efficiency of the process. A full-scale UASB system operated over a 2-year period during which a number of problems were identified. The development of stable biomass took approximately 6 months. This biomass remained stable thereafter, despite variability in sludge volumes retained in the bioreactor. Approximately 90% of selenium was removed during the project, with influent selenium concentrations of 500 μg/L being reduced to an average 50 μg/L in the discharge. However, this level of treatment was not consistently attained, as effluent selenium concentrations occasionally were over 200 μg/L. This was due to the temperature sensitivity of the process, as removal rates reached 88% at 59 °F (15 °C) but declined to 35% at 45 °F (7 °C). A partial solution identified during testing was to insulate reactor tanks for the full-scale treatment system.

Capital and Operating Costs. The total cost for a 1 million US gallons per day (4000 cubic meter per day [m^3/day]) system is estimated at \$0.36 to \$0.42/ m^3 of water treated, with operating costs representing \$0.28 to \$0.34/ m^3 (Frankenberger et al., 2004). The cost for the organic carbon that is added to the water accounts for 5 to 25% of the operating costs if methanol is used (Frankenberger et al., 2004).

Advantages and Disadvantages. The advantages and disadvantages of the UASB technology are presented in Table 4-14.

TABLE 4-14
Advantages and Disadvantages of UASB Technology

Advantages	Disadvantages
• Requires no attached growth media and therefore no media replacement. • Process uses naturally occurring microbes and biodegradable nutrient to maintain biomass. • Biologically reduced elemental selenium is in insoluble form as nanoparticles integral to the biological solids. • Requires little to no pretreatment for suspended solids.	• Commercially available technology typically applied to high strength organic wastewater. • Long hydraulic residence (e.g., > 6 hours) and solid residence (e.g., > 10 days) time requirements result in larger reactor sizes and footprint. • No full scale proof of concept. • Presence of an excessive amount of nitrates will require proportional amounts of carbon or energy source. This excess carbon source will also generate some additional biomass. • External carbon source is required if soluble influent organic content or chemical oxygen demand is insufficient. • Prone to washout conditions given very low nitrate, nitrite and/or selenium concentrations coupled with poor liquid solids separation, thereby requiring concentration of these through ion exchange or reverse osmosis. • Long periods of time for startup to acclimate the seed

TABLE 4-14
Advantages and Disadvantages of UASB Technology

Advantages	Disadvantages
	given washout and difficulty in controlling the solids residence time. • Requires granulating solids to perform at a high removal rate and minimize solids washout. • Biological residuals will need to be thickened and dewatered for landfill disposal.

4.4.2.2 Attached Growth Downflow Filter: ABMet® System

Technology Description. The ABMet® system is an attached growth downflow filter. The ABMet® system was developed by Applied Biosciences and is now marketed by GE Water & Process Technology. The ABMet® system uses microbes cultured in bioreactor granular activated carbon (GAC) beds that create anoxic/anaerobic conditions for selenate and selenite reduction. The GAC material acts as a medium for biofilm development.

The ABMet® process uses certain heterotrophic facultative bacteria which, in addition to reducing nitrate to nitrogen gas, also reduce selenate and selenite in water to elemental selenium. Elemental selenium is then precipitated as insoluble solids along with bacterial solids. The microbes are selected as a site-specific inoculum for the bioreactors. These bacteria are mesophilic bacteria requiring the wastewater temperature typically be between 55 and 100 °F (13 and 38 °C). These microbes use the oxygen in the nitrate/selenate/selenite as an electron acceptor for their respiration and an organic carbon (electron donor) source to meet their food/energy requirements. The carbon source can be either organic matter present in the wastewater, typically expressed as COD, or could be from an external source such as methanol, ethanol, molasses, corn syrup, etc. The ABMet® system uses a molasses-based nutrient supplement, which also is a source of phosphate for the bacteria. Molasses is typically iron-rich. An increase in iron has been observed through treatment (EPRI, pending(a)). Nutrient addition occurs in two stages. The second stage of nutrient addition is generally a small fraction of the first stage dosage (EPRI, pending(a)).

The ABMet® treatment system typically consists of two bioreactors in series in multiple trains and typically sized to provide 4 to 8 hours of detention time depending on specific treatment requirements. The bioreactors are tanks filled with GAC, which provides a support and growth mechanism for the biomass (Pickett et al., 2008). If the COD in the wastewater is not sufficient, the growth of the microbes is supported by feeding them a biodegradable nutrient blend, which contains organic carbon. Because of its high porosity, GAC offers a very large surface area for biological activity to occur. With time, the biomass grows and a biofilm develops on the GAC surface, and selenium reduction occurs on this biofilm.

Biological reduction converts the selenate or selenite ions into elemental selenium, which precipitates as a solid and is enmeshed and attached to the biofilm within the reactor. The reactors are flushed periodically to prevent excess biomass buildup, and the waste stream is then treated by dewatering the solids and disposing of the high-concentration selenium sludge. The effluent water from the ABMet® unit is aerated in a small polishing aeration tank to increase the dissolved oxygen and to aerobically treat any excess soluble organics.

Treatment Effectiveness. Pilot- or full-scale ABMet® systems have been used for selenium removal in mining and agricultural, power generation and oil and gas industry sectors. Results obtained from these industry sectors are detailed individually below.

Mining and Agriculture Sector. A pilot demonstration of the ABMet® technology was performed at the USEPA Kennecott demonstration program (MSE, 2001). The objective of this project was to test and evaluate technologies capable of removing selenium from Kennecott Utah Copper Corporation's Garfield Wetlands-Kessler Springs water. The process was able to lower the concentration of selenium from 1,950 µg/L to below 2 µg/L over a 6-month period (MSE, 2001).

A full-scale ABMet® system was installed at a gold mine in South Dakota. System design can accommodate average flows of 100 US gpm (378 Lpm) and a maximum flow of 300 US gpm (1,135 Lpm) (Maniatis and Adams, 2003). Four cells were designed to remove nitrate from approximately 30 mg/L to below 10 mg/L, and two cells were designed to remove selenium from 100 µg/L and higher to below 5 µg/L (Maniatis and Adams, 2003). The system is operated year-round, and ambient temperatures fall as low as 10 °F (-12 °C) in the winter and treat groundwater at temperatures ranging between 46 ºF to 60 ºF (8 ºC to 16 ºC). The system has consistently been in compliance for nitrate and selenium since startup (Maniatis and Adams, 2003).

The ABMet® system was pilot tested for a 3-month period at a coal mine in West Virginia using flow rates of 1, 2, and 3 US gpm, and selenium concentrations were consistently reduced from average influent concentration of 43 µg/L to less than 5 µg/L in the effluent. The main conclusions of the pilot study were that the ABMet® system was able to meet the selenium treatment requirements and no major process or operational limitations were observed.

Pilot-scale testing was conducted at the Panoche Drainage District, Firebaugh, California for agricultural drainage water, which showed that ABMet® technology can successfully remove selenium and nitrate to below 5 µg/L and 5 mg/L, respectively (USBR, 2008a).

Power Generation Sector. ABMet® treatment systems have been installed at FGD water treatment plants only recently, with a total of four GE ABMet® systems currently implemented at full-scale (two plants installed in 2008 and two plants installed in 2009). Another system will be implemented in 2010 (Blankinship, 2009). Section 6 discusses in further detail case studies of ABMet® systems employed at full scale for treatment of FGD water at coal-fired power plants.

Oil and Gas Sector. There are no full-scale installations using the ABMet® technology to treat refinery wastewater. A 5- to 10- US gpm (19 to 38 Lpm) pilot-scale study was performed that reduced selenium from 50 µg/L to less than 10 µg/L (Nurdogan et al., 2009). A second ABMet® pilot study at a refinery treated 0.2 to 0.5 US gpm (0.8 to 1.8 Lpm) from 700 to 900 µg/L to less than 20 µg/L total selenium (Nurdogan et al., 2009).

A pilot test was conducted in 2002 at a refinery that focused on treatment of SSW. After onsite testing, which used trailer-mounted equipment, the process succumbed to transient toxicity in the feed water (Davis et al., 2009). In addition, a 6-month pilot test was conducted at the biotreater effluent. The ABMet® system reduced selenium concentrations by 95% without upsets during the 6-month run. However, the technology was not able to treat to the 4.6 µg/L goal and had high capital cost for end-of-pipe treatment where the design flow rate was 1 million US gallons per day (4,000 m^3/day) (Davis et al., 2009).

Design and Operational Considerations. The footprint of the ABMet® system is dependent upon the flow to be treated, but the overall treatment footprint can be larger if pretreatment or post-treatment is required. Colder temperatures require longer residence times.

Monitoring of pH and ORP is performed to control the stoichiometry and ensure selenate reduction (EPRI, pending(a)). In the absence of selenite, selenate, nitrate, and nitrite electron acceptors, sulfate will be used as an electron acceptor by a different population of microbes resulting in the formation of hydrogen sulfide which can inhibit selenate and selenite reduction.

Primary treatment consists of temperature control so that operating temperatures can be within the optimal range for biological treatment, pH control so that neutral pH is achieved for biological treatment and TSS removal to prevent clogging of the activated carbon media.

Carbon dioxide and nitrogen gases accumulate within the bioreactor cells over time from biological reduction. The trapped gases reduce the flow path and increase head losses through the system. Therefore, the bioreactor cells are backwashed for degassing. Additional backwashes are performed on a less frequent basis to remove precipitated solids and excess biomass (EPRI, pending(a)).

Residuals Management. Sludge is produced and requires disposal. The solids are typically classified as nonhazardous waste. Solids can be processed using solids dewatering equipment such as a plate and frame press.

Capital and Operating Cost. Figures 4-28 and 4-29 present the TIC and O&M costs for an ABMet® treatment system for selenium reduction to below 5 µg/L. These costs are Class 5 costs as defined by the AACEI with an accuracy of +100% and -50% as shown by the variance bands based on 2009-2010 market conditions. These are parametric cost estimates based on the ABMet® treatment system shown in Figure 4-30. This system is a grass roots or green field selenium treatment system with costs for stand alone utilities (e.g., power) and an equipment/control room building included in the estimate. 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. As discussed in Section 4.1.2 equalization and diversion of flows and/or loadings are generally required for most treatment systems. Operational 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. 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.

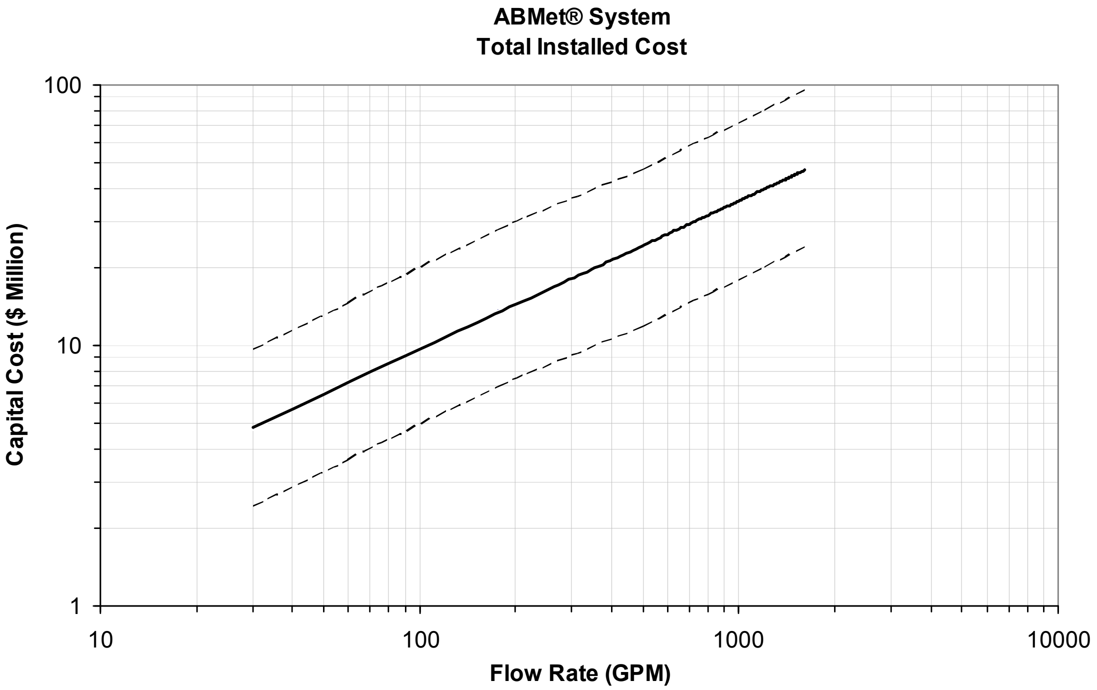


FIGURE 4-28
Total Installed Costs for ABMet® System (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

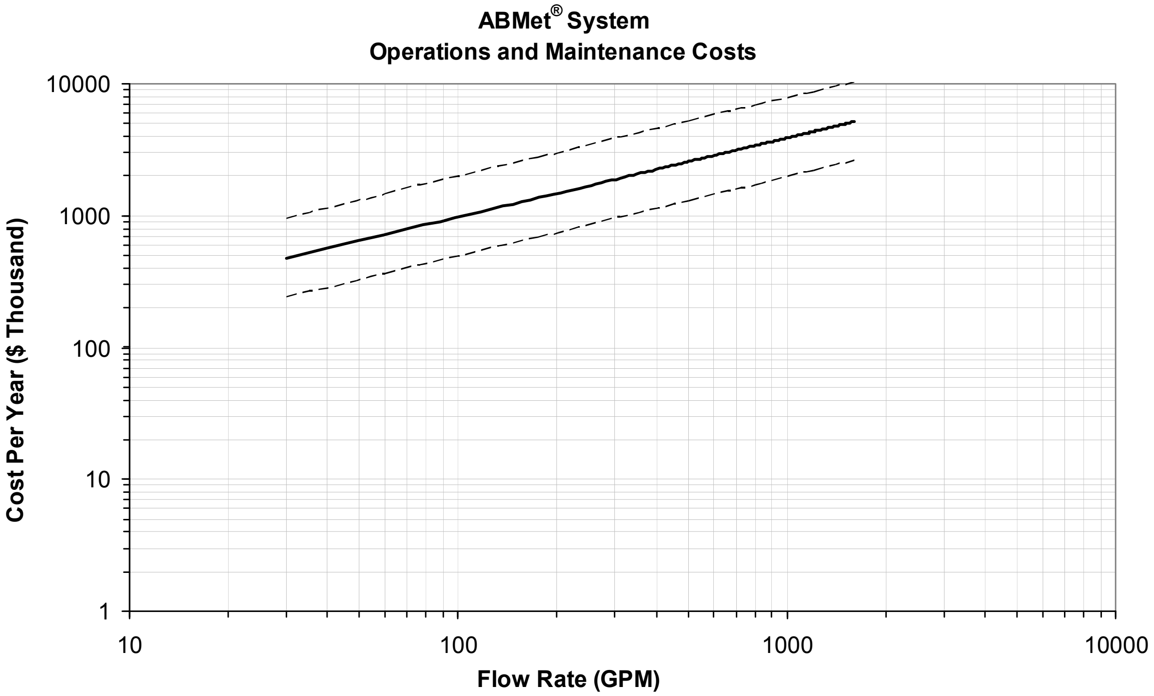


FIGURE 4-29
Operating Cost Curve for ABMet® System (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

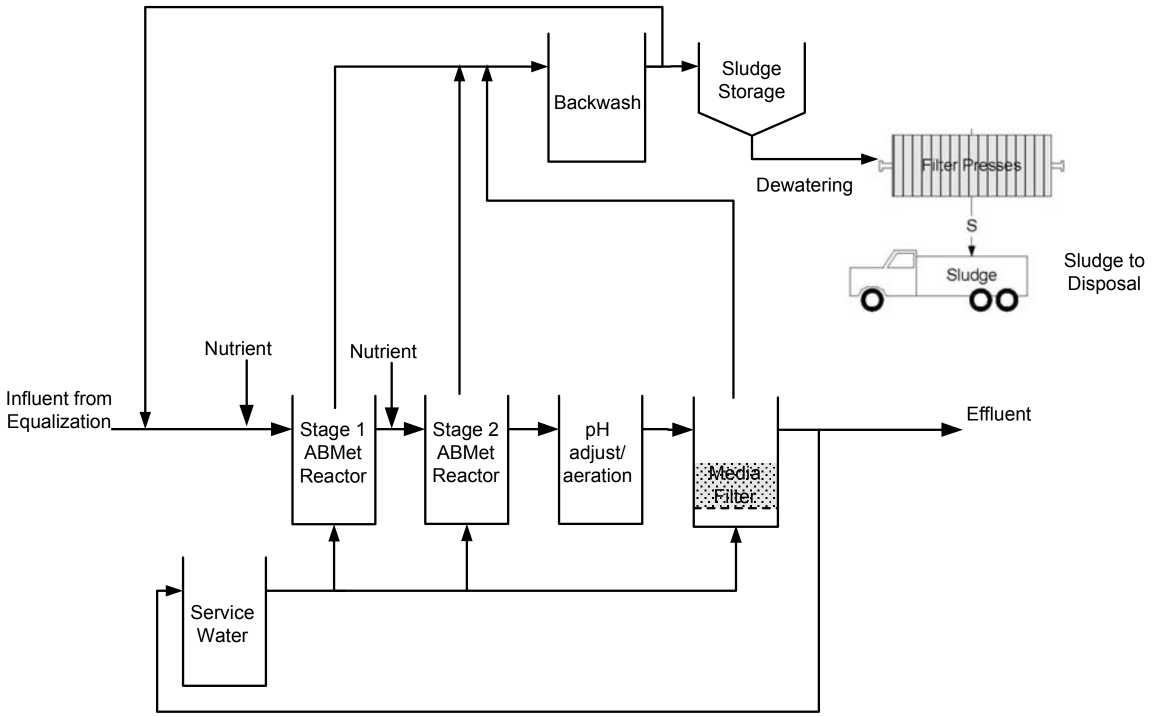


FIGURE 4-30
ABMet® System Process Flow Diagram for Cost Estimate

Advantages and Disadvantages. The advantages and disadvantages of the ABMet® technology are presented below in Table 4-15.

TABLE 4-15
Advantages and Disadvantages of ABMet® Technology

Advantages	Disadvantages
• Commercially available technology that has been demonstrated to remove selenium to low levels (e.g., less than 5 µg/L) in pilot-scale and full-scale applications. • Process uses naturally occurring microbes and molasses-based nutrient feed to maintain biomass. • Biologically reduced elemental selenium is in an insoluble form as nanoparticles integral to the biological solids.	• Potential need for pre-treatment to remove suspended solids. May require post-treatment to remove BOD. • Backwash water required to periodically slough off excess microbial growth, prevent short-circuiting of flow, and for de-gassing. • Large footprint required given the low hydraulic loading rate (e.g., 2-4 gpm/ft^2 or 81-162 Lpm/m^2) requirements and high minimum hydraulic residence requirements (4-6 hours). • Presence of an excessive amount of nitrates will require proportional amount of carbon or energy source. This excess carbon source will also generate some additional biomass. • External carbon source is required if soluble influent

TABLE 4-15
Advantages and Disadvantages of ABMet® Technology

Advantages	Disadvantages
	organic content or COD is insufficient. • Wasted biomass residuals contain elemental selenium that may be hazardous depending upon the TCLP results. • Media replacement may be required over the life of the system. • Biological residuals will need to be thickened and de-watered for landfill disposal.

4.4.2.3 Fluidized Bed Reactor

Technology Description. A fluidized bed reactor (FBR) is another configuration of an attached growth or fixed film biological treatment system. In an FBR, water containing selenium is passed through a granular solid media (e.g., sand or granular activated carbon) at high enough velocities to suspend, or fluidize the media creating a reactor configuration for attached growth. The biological treatment mechanism for selenium removal is reduction of selenate and selenite to elemental selenium under anaerobic conditions.

The FBR is seeded with heterotrophic facultative bacteria that are suited for nitrate and selenium removal. Carbon substrate and nutrients as required are pumped into the FBR to serve as the electron donor and to promote microbial growth and synthesis in anaerobic conditions.

The wastewater is pumped from the feed tank to a covered FBR for nitrate and selenium removal, as shown in Figure 4-31. The FBR vessel contains an integral fluidization and effluent collection system designed to enhance uniform flow distribution for anoxic microbial growth. The water is pumped into the bottom of the FBR in an upflow direction to suspend the sand or GAC media. As the microbes grow on the sand or GAC, the fluidized bed height will expand. Some excess biomass will be removed by shear of the normal flow through the FBR. Both media and excess solids that leave the reactor are discharged to a separator where the biological solids and media are separated such that both can be returned to the FBR, or the media returned to the FBR and the solids wasted from the system are dewatered.

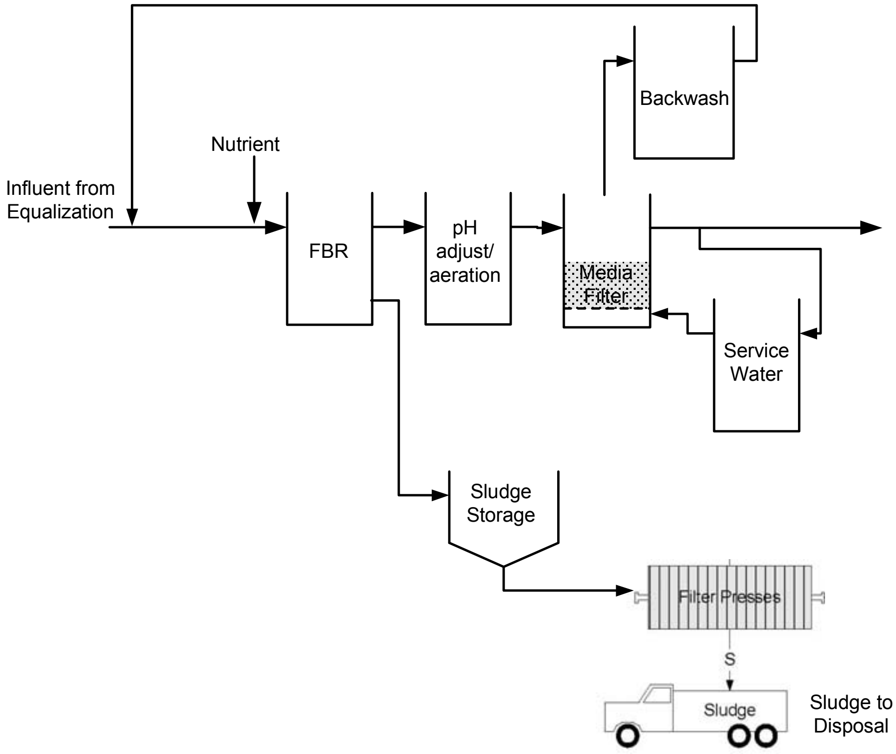


FIGURE 4-31
Fluidized Bed Reactor Process Flow Diagram

If necessary, the pH may be adjusted upstream of the FBR to meet optimal growth conditions. The effluent from the FBR may be aerated in a small polishing aeration tank to increase the dissolved oxygen and remove any excess soluble organics.

Solids from the FBR may be handled similarly, either using a clarifier or settling pond. The TSS will be primarily biomass. If a pond cannot be used, multimedia filters can be installed to remove these solids.

FBR is a proven technology used to remove both nitrates and perchlorate from groundwater. Based on similar biological reduction mechanisms selenate and selenite will be reduced in an FBR system after nitrate but before sulfates, although this has not been commercially demonstrated. The biological mechanisms are identical to those of the ABMet® system, only the configuration is a fluidized bed versus downflow filter configuration.

Treatment Effectiveness. The FBR technology was pilot-tested at the Adams Avenue Agricultural Drainage Research Center for the removal of selenium in the San Joaquin Valley, California and operated between 1993 and 1995 at a flow rate of 1 US gpm (3.8 Lpm). The system was maintained at 50% bed expansion. Total selenium decreased from an average 520 µg/L to an average effluent of 380 µg/L (State of California Department of Water Resources, 2004).

A laboratory-based active biological water treatment system successfully demonstrated selenium removal under a variety of conditions for up to 239 days of continuous operation (Brienne et al., 2009). Six bench-scale active bioreactors were operated using a variety of parameters for eight months, achieving up to 98% selenium removal (Brienne et al., 2009) for treatment of a mining-influenced water. A series of column studies were performed testing various HRTs, flow configurations, and nutrient enrichments. Selenium removal from Bodie Creek water was microbially mediated and occurred on a variety of support materials. The best selenium removal occurred with the reactor operating in an up-flow configuration using ethanol as the nutrient in these investigations (Brienne et al., 2009). The ORP was an important control parameter for the selenium removal system.

Design and Operational Considerations. Operation of the FBR pilot system required daily cleaning of the influent strainer. Other maintenance included cleaning of the tank walls, recycle tank, and piping due to biological growth (State of California Department of Water Resources, 2004).

Capital and Operating Costs. Figures 4-32 and 4-33 present the TIC and O&M costs for an FBR system for selenium reduction to below 5 µg/L. These costs are Class 5 costs as defined by the AACEI with an accuracy of +100% and -50% as shown by the variance bands based on 2009-2010 market conditions. These are parametric cost estimates based on the FBR treatment system shown in Figure 4-31. This system is a grass roots or green field selenium treatment system with costs for stand alone utilities (e.g., power) and an equipment/control room building included in the estimate. 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. As discussed in Section 4.1.2 equalization and diversion of flows and/or loadings are generally required for most treatment systems. O&M costs include labor, chemicals, maintenance and energy. Operational 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. 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 degradation during fluidization.

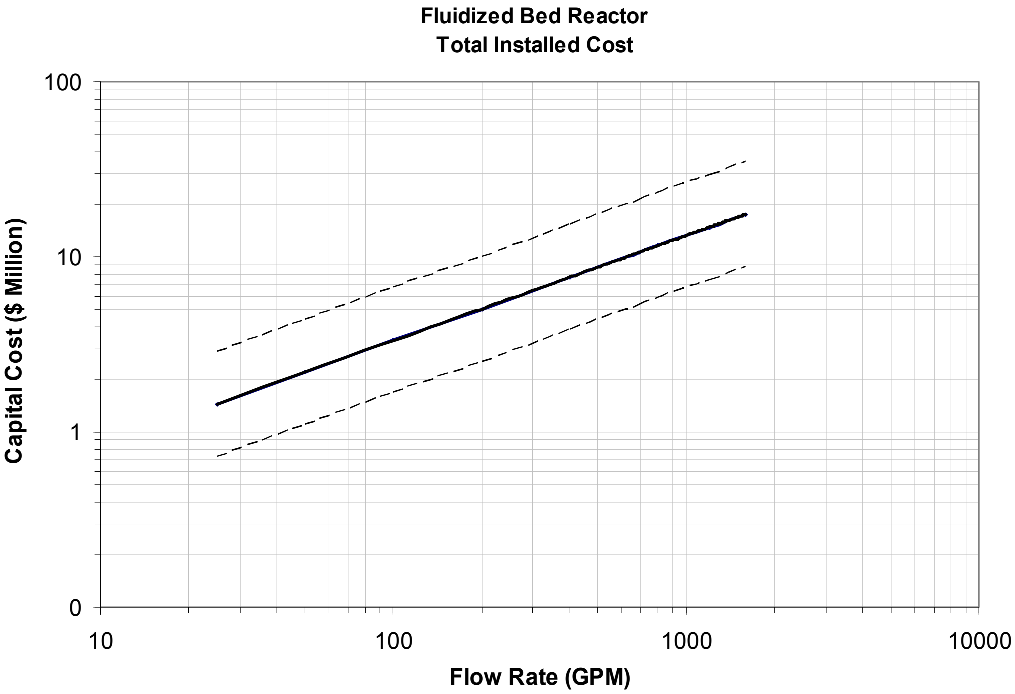


FIGURE 4-32
Total Installed Costs for FBR System (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

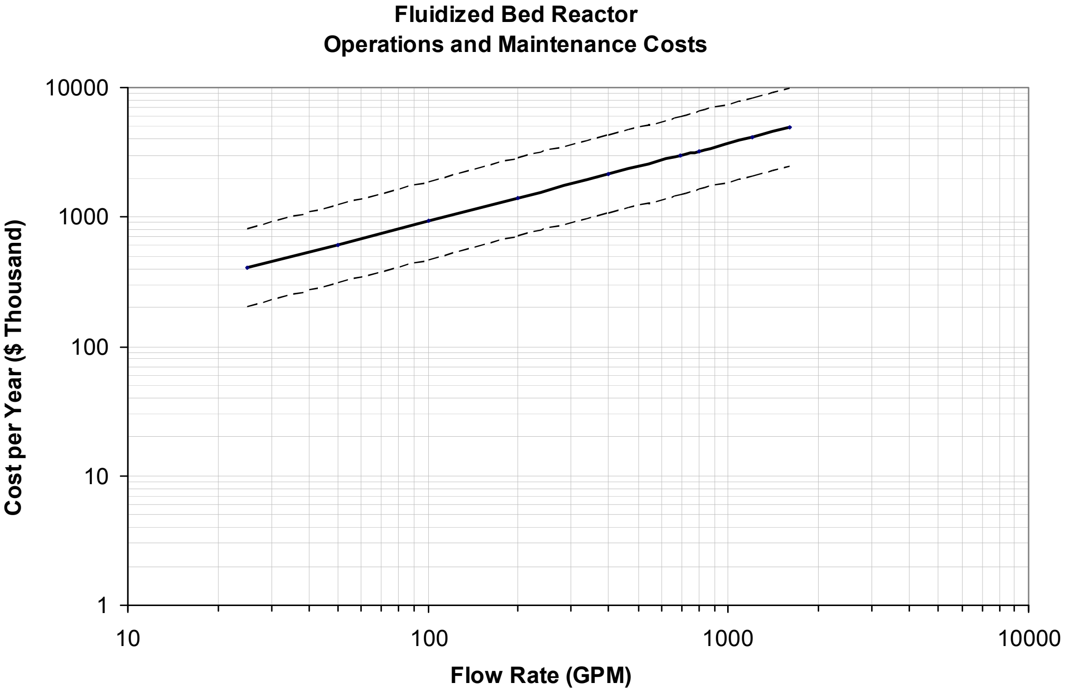


FIGURE 4-33
Operating Cost Curve for FBR System (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

Advantages and Disadvantages. The advantages and disadvantages of the FBR technology are presented in Table 4-16.

TABLE 4-16
Advantages and Disadvantages of FBR Technology

Advantages	Disadvantages
• Process uses naturally occurring microbes and biodegradable carbon sources to maintain biomass. • Biologically reduced elemental selenium is in insoluble form as nanoparticles integral to the biological solids. • Smaller footprint given completely mixed reactor configuration resulting in lower total installed costs. • Requires little to no pretreatment for suspended solids. • No backwash water required. Biomass separated from centrifugal separator on reactor effluent.	• Presence of an excessive amount of nitrates will require proportional amount of carbon or energy source. This excess carbon source will also generate some additional biomass. • Commercially available technology operating in similar full scale applications (e.g., nitrate and perchlorate removal) but no full scale selenium treatment for fluidized bed reactor is currently utilized. • External carbon source is required if soluble influent organic content or chemical oxygen demand (COD) is insufficient. • Wasted biomass sludge contains elemental selenium that may be hazardous depending upon the TCLP results. • Media replacement required periodically. • Biological residuals will need to be thickened and dewatered for landfill disposal.

4.4.2.4 Dynamic Suspended Bed Bioreactor: BioSolve® Process

The BioSolve® technology system, developed by Calcon using the Hall reactor, consists of a continuously stirred tank reactor with plastic sponge media used as a surface for biofilm development (Nurdogan et al., 2009). The process has been used to treat groundwater contaminated with perchlorate, hexavalent chromium, nitrate, and selenium. The sponge media are porous and provide a large surface area. Methanol is used for substrate addition. A 140-US gpm (530 Lpm) pilot-scale-scale system was installed in 2009 and is being piloted in Hollister, California. Operational data are not available for the system.

4.4.2.5 Enzymatic Selenium Reduction

A biological treatment process was tested at laboratory-scale using enzymatic reduction of selenium (MSE, 2001). An enzyme is a protein that can bring about digestion (breakdown) of molecules into smaller units and greatly speed up chemical reactions. Enzyme extracts were tested from microbes that were previously demonstrated to treat selenium. An advantage of using enzymatic extracts is that nutrient addition is not required for selenium reduction. A bench-scale test using mining-influenced water resulted in a selenium concentration reduction from 23,100 µg/L to less than 100 µg/L at a 9-hour HRT (NSMP, 2007).The study concluded that testing was not sufficiently reproducible and the technology was not economical; therefore, testing did not continue (MSE, 2001).

4.4.2.6 Hydrogen-Based Membrane Biofilm Reactor

Bench-scale testing for selenium removal has been performed on a hydrogen-based membrane biofilm reactor (Chung et al., 2006). Hydrogen is used as an alternative electron donor to the carbon-based electron donors used in other reactors cited. The membrane is used within this treatment system to directly supply dissolved gas to a biofilm growing on the membrane surface. Selenium removal increased over the first three weeks. Lowering influent selenate concentration from 1,000 µg/L to 260 µg/L resulted in an average of less than 12 µg/L total selenium. Both selenate and selenite were reduced to elemental selenium (Chung et al., 2006). Both nitrate and sulfate were also reduced within the reactor, although sulfate reduction was affected by hydrogen gas pressure and selenate concentration. Selenate reduction occurred between pH 7 and 9 during the experiment (Chung et al., 2006).

4.4.3 Passive Treatment

Passive systems require less operational support and little to no added resources (e.g. no chemical or energy input) and semi-passive systems refer to systems with activities such as regular substrate/nutrient addition to sustain desired conditions and processes. Examples of passive or semi-passive treatment systems for the removal of selenium from water include constructed wetlands, passive bioreactors, permeable reactive barriers (PRBs), and enhanced *in situ* microbial reduction. Passive treatment systems remove selenium through the following mechanisms (Kadlec and Wallace, 2009; Martin et al., 2009):

1. Microbial reduction of selenate and selenite in anoxic conditions to elemental selenium and selenides and subsequent precipitation to soil or sediments;

2. Bacterial, fungal or algal volatilization (methylation) of selenium and release to the atmosphere;

3. Adsorption of selenite to iron, aluminum or manganese oxy-hydroxides present within soil or sediments;

4. Bacterial, fungal or algal uptake into cells of microorganisms; and

5. Assimilation of selenium through plant uptake in constructed wetlands.

4.4.3.1 Constructed Wetlands

Technology Description. Constructed wetlands have been shown to offer an alternative method of contaminant removal from wastewater. Constructed wetlands differ from other passive treatment systems discussed in this section in that they contain vegetation. Engineered wetlands are designed and constructed to use vegetation, soils, and associated microbial activity to provide treatment of wastewater. Within an ecosystem comprised of dense stands of emergent vegetation in a shallow body of water, wetlands create a layer of biological detritus that, through decomposition, creates an anoxic/anaerobic substrate rich in organic carbon. In the case of selenium, this aquatic environment supports the growth of natural bacteria specialized in utilizing oxidized forms of selenium as an energy source. Selenium is reduced to elemental selenium as well as organic forms of selenium such as dimethyl selenide and dimethyl diselenide (Kadlec and Wallace, 2009). Elemental selenium produced then is sequestered in the wetland sediment (Oremland, 1993).

Constructed wetlands take the form of surface flow wetlands (shallow constructed marshes), subsurface flow wetlands (planted beds of gravel or soil media with water flowing through the root zone), and variations on subsurface flow systems such as vertical down flow wetlands. Vertical flow wetlands can use overlying water to block oxygen and create anoxic conditions within the substrate bed (Kadlec and Wallace, 2009). Figure 4-34 shows a comparison of surface flow and subsurface wetlands. Some constructed treatment wetlands contain monocultures of cattails (*Typha* spp.) or bulrushes (*Schoenoplectus* spp.), while others are planted with diverse plant communities that are adapted to the local seasonal and water quality conditions. Unlike a natural wetland in which depth and duration of inundation vary in response to precipitation, infiltration and evaporation, a constructed treatment wetland is designed to allow inflow rates and water depth to be regulated. These factors influence the hydraulic and mass loading of the system and the hydraulic residence time, all important factors in wetland water quality improvement.

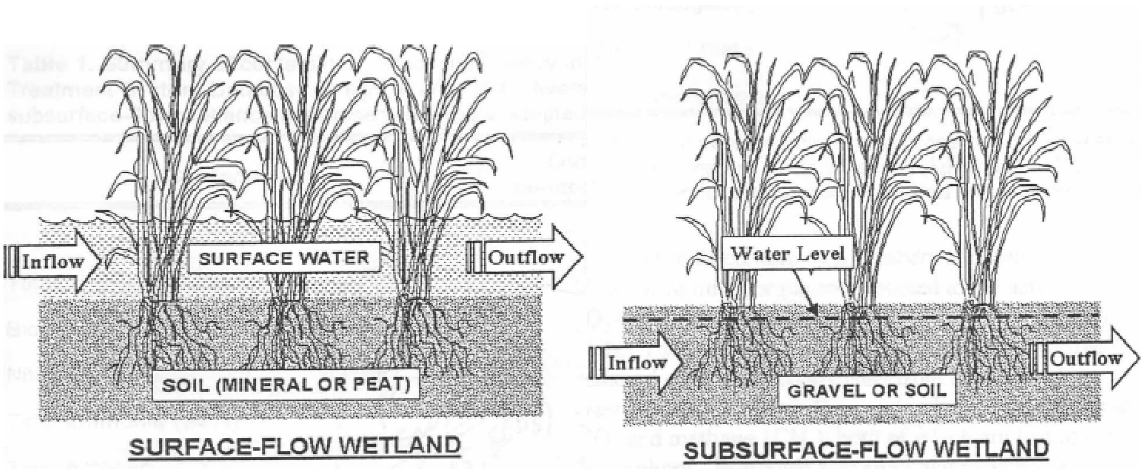


FIGURE 4-34
View of Surface Flow Wetland and Subsurface Flow Wetland
Source: USEPA, 2001

While the plants in constructed treatment wetlands are the recognizable components of the system, much of the actual contaminant removal and storage are accomplished by the microbial flora (bacteria and fungi) attached to the plants and found in organic sediments. Bacteria, fungi, and algae have the natural assimilative capacity to remove biodegradable organic carbon, nitrogen, metals and non-metals such as selenium. Volatilization of selenium in the form of dimethyl selenide has been observed as a result of microbial processes (Hansen et al., 1998; Frankenberger et al., 2004). Much of the treatment that occurs in wetlands is the result of sediment trapping, chemical transformation and precipitation, and microbial action rather than plant uptake. Selenite has a strong affinity for metal oxyhydroxides such as iron, aluminum or manganese that may exist in sediments or soil, trapping selenite within wetland sediments (Kadlec and Wallace, 2009). Organic carbon and microbial transformations influence the availability of selenium for plant uptake (Zhang and Moore, 1997). While metals and phosphorus are sequestered in plant materials and wetland sediments, plant harvesting or sediment removal is performed only rarely at best. These systems continue to function during winter and are aided by the temperature-buffering effect of sediments and ice cover.

Subsurface flow treatment wetlands are similar to constructed surface flow wetlands in many respects and often use some of the same emergent plant species. However, subsurface flow systems are designed to achieve effluent flow through the porous substrate such as gravel or sand supporting the emergent vegetation, rather than above the substrate (see Figure 4-35). Various design approaches may direct flow vertically or horizontally through the media. The large surface area resulting from the porous medium and the plant roots provide ample sites for microbial activity.

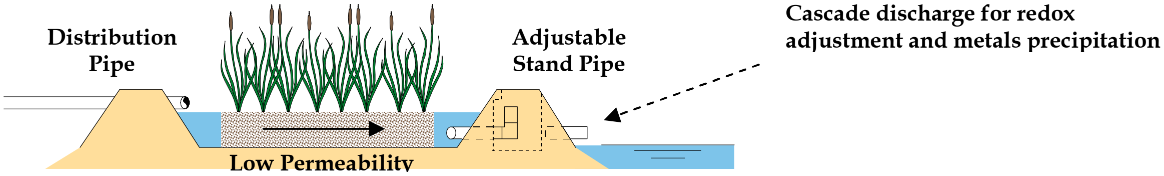


FIGURE 4-35
Diagram of a Subsurface Flow Wetland
Source: CH2M HILL

Subsurface flow treatment wetlands have an advantage in cooler climates because so much of the treatment occurs below the ground surface. Thus, these systems are less affected by cold air temperatures. Also, subsurface flow wetlands may need relatively little maintenance, and they are less likely than lagoons to have odor and/or mosquito problems.

Passive subsurface treatment wetlands are effective at removing biodegradable organic matter and nitrate-nitrogen from wastewaters. Adding aeration through cascades, vertical flow pulsing, pumping air directly into the media or into an aerobic wetland after selenium is removed in an anoxic wetland cell allows contaminants requiring oxygen to be removed and dissolved oxygen levels to be raised prior to discharge.

Treatment Effectiveness. Treatment effectiveness varies widely for selenium removal for surface flow wetlands. Table 4-17 is a summary of selenium removal efficiency at various full-scale installations across the United States that have implemented surface flow wetlands for the mining and agriculture, power generation and oil and gas sectors Table 4-17 shows that selenium removal varies between 0% and 96% among surface flow wetlands. Case studies of the wetlands at Site PG4 and Site PG5 are included within Section 6.

TABLE 4-17
Selenium Removal in Full-Scale Surface Flow Wetlands
Source: Adapted from Kadlec and Wallace, 2009

Site	Description	Influent Total Selenium (µg/L)	Effluent Total Selenium (µg/L)	Percent Removal
Albright, Pennsylvania	coal ash leachate	4	2	50%
Springdale, Pennsylvania	coal ash leachate	2	2	0%
Richmond, California	refinery wastewater	25	5	89%
Imperial, California	agricultural drainage	7.1	5.9	17%
Brawley, California	agricultural drainage	10.1	9.9	2%
Corcoran, California	agricultural drainage	16	9	44%
PG4- Confidential	FGD wastewater	170	150	20%
PG5- Confidential	FGD wastewater	380	345	10%
Great Falls, Montana	Drainage	26	1	96%
Irvine, California	Urban drainage	9.5	8.5	10%

Gao et al (2003) and Chow et al. (2004) have also conducted research to develop a mass balance on selenium in a surface flow wetland. Most of the selenium was contained within the sediments. The results indicated 56% of the selenium was adsorbed and held by the sediment, less than 3% was assimilated by plants and found in the litter, 2% volatilized, 4% seeped into the groundwater, and 35% exited with the outflow (Gao et al., 2003). The data also show average selenium removal ranging from 63-71%, depending on the plant species. Selenium was reduced from an influent concentration of 20 µg/L to 3-6 µg/L in a wetland with a 7-day residence time. Water temperature was a rate-limiting step, with temperatures less than 50 to 59 °F (10 to 15 °C) substantially slowing the selenium reduction process.

An example of a full-scale constructed wetland is the San Joaquin Marsh operated by the Irvine Ranch Water District near the mouth of the San Diego Creek Watershed (Frank et al., 2008). The wetland consists of five treatment cells with 45 acres (18 hectares) of open water and 11 acres (4.4 hectares) of marshland vegetation. Water is pumped from the adjacent San Diego Creek into the wetlands at an average rate of about 3,100-US gpm (11,900 Lpm) and has a HRT of about two weeks (Strecker et al., 2005). Although this system was constructed for nitrate removal and to provide habitat, preliminary data (Site Irvine, California in Table 4-17) show that the wetland is reducing water concentrations of selenium.

Ye et al. (2003) performed a microcosm study to test the potential for surface flow wetlands to remove selenocyanate from wastewater from a sour water stripper at a coal gasification plant. Traditional selenocyanate requires oxidation to selenite followed by precipitation using iron. The wetland microcosm reduced influent selenium (average 1,440 µg/L) by 64% (average effluent 510 µg/L). Of the various plant species tested during the microcosm study, *Thalia*, cattails and rabbitsfoot grass species were the most successful at removal of selenocyanate present in the wastewater. Of the selenium that was removed by the microcosm wetland, 63% was distributed in the wetland sediment, 18% in the effluent water, 11% in the surface water, 4% assimilated in the plants, 3% volatilized, and 1% was unaccounted for (Ye et al., 2003).

Installations of subsurface flow wetlands have not been applied at full-scale for selenium removal. A laboratory-scale subsurface flow wetland treatment of selenium has demonstrated removal to below 0.2 µg/L (Azaizeh et al. 2006). A pilot-scale subsurface wetland has been installed at the City of Oxnard to treat selenium.

The City of Oxnard California conducted a series of mesocosm 35 cubic feet (1 cubic meter) tests to assess the performance of wetlands for treatment of membrane concentrate from reverse osmosis treatment of groundwater (CH2M HILL, 2007). Tanks containing representative communities of vertical upflow, horizontal subsurface flow, surface flow and submersed aquatic vegetation exhibited varying proportions of selenium removal, with vertical upflow beds showing the greatest removal of 22 µg/L to 7 µg/L, or 67% (Figure 4-36). A system consisting of vertical upflow, subsurface flow, and subsurface aquatic vegetation in series (Train 1) reduced selenium by 67% from 12 µg/L to <4 µg/L. A system of vertical upflow, shallow surface flow and deep surface flow wetlands in series (Train 2) reduced selenium by 92% from 12 µg/L to <1 µg/L. A single subsurface flow system reduced selenium from 19 µg/L to <1 µg/L (Table 4-18).

FIGURE 4-36
Wetlands Mesocosm Test, City of Oxnard, California
Source: CH2M HILL, 2007

TABLE 4-18
Selenium Removal in Oxnard Membrane Concentrate Pilot Wetlands
Source: Adapted from CH2M HILL, 2007

Site	Description	Influent Total Selenium (μg/L)	Effluent Total Selenium (μg/L)	Percent Removal
Vertical Upflow, Phase A, Oxnard, California	RO membrane concentrate from groundwater	22	7	67%
Treatment Train 1, Phase A, Oxnard, California	RO membrane concentrate from groundwater	12	<4	67%
Treatment Train 2, Phase B, Oxnard, California	RO membrane concentrate from groundwater	12	<1	92%
Subsurface Flow, Phase B, Oxnard, California	RO membrane concentrate from groundwater	19	<1	95%

Design and Operational Considerations. Often, constructed treatment wetlands are designed to include parallel flow paths of multiple cells arrayed in series operable at different depths. In this way, discharge points to the system can be rotated, depths can be adjusted depending upon plant species tolerance and performance, and hydraulic short-circuiting can be limited. An equalization basin or settling pond is often constructed prior to the wetland for suspended solids removal. Figure 4-37 shows a configuration where vertical flow, subsurface flow and surface flow wetlands are used in series. A wetland with an anoxic zone may be followed by an aerobic zone in order to raise dissolved oxygen levels prior to discharge.

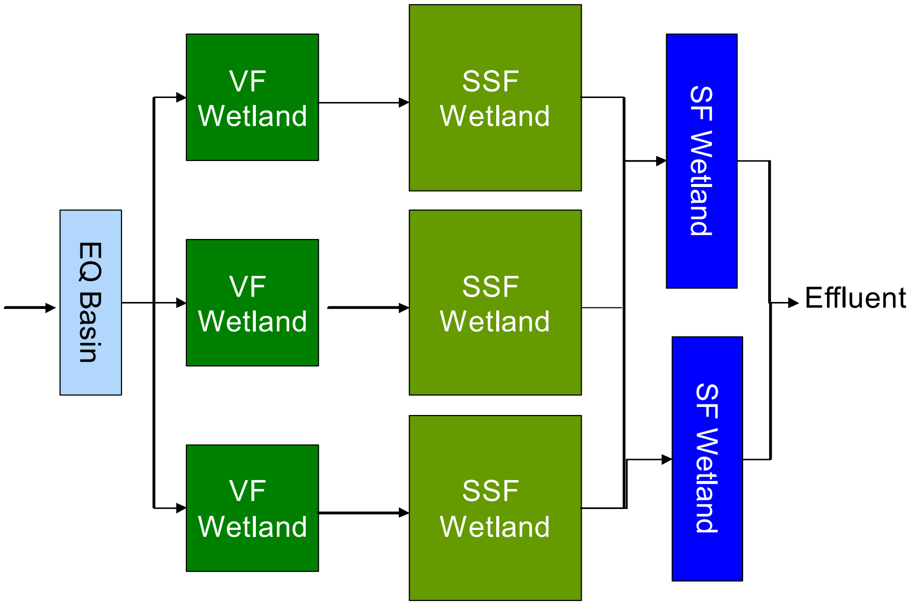


FIGURE 4-37
Example of Multi-Stage Constructed Wetland Configuration
Source: CH2M HILL

Passive subsurface treatment wetlands are most effective at removing biodegradable organic matter and nitrate-nitrogen from wastewaters. Adding aeration through cascades, vertical flow pulsing, or by pumping air into the system allows the wetland to remove contaminants requiring oxygen in the concentration reduction process.

The footprint of a subsurface wetland is relatively similar to the surface flow wetland (Kadlec and Wallace, 2009), but the lack of surface water habitat in a subsurface flow wetland indicates a lesser exposure potential to ecological receptors, which may be desirable for wetlands constructed to treat selenium. However, there is an increased operation and maintenance associated with the subsurface flow wetland.

Retention time is a critical design factor in each type of wetland and is usually based on performance during pilot testing. Typical HRTs for passive treatment systems like constructed wetlands are much longer than for tank-based biological treatment systems, and can be several days or more. Due to the large HRTs required, the footprint of constructed wetlands is generally large. For surface flow wetlands designed to treat wastewater from municipal and industrial processes, wetlands have ranged from about 10 to over 1,000 acres (4 to 400 hectares) in area. For treatment of large flows of agricultural runoff, wetland areas have exceeded greater than 10,000 acres (4,000 hectares). The rate of flow, influent concentrations, and target effluent criteria influence the design size of the wetland.

Various species of plants have been tested for selenium removal. Gao et al. (2003) planted sturdy bulrush (*Schoenoplectus robustus*), Baltic rush (*Juncus balticus*), smooth cordgrass (*Spartina alterniflora*), rabbitsfoot grass (*Polypogon monspeliensis*), saltgrass (*Distichlis spicata*), cattail (*Typha latifolia*), tule (*Schoenoplectus acutus*), and widgeon grass (*Ruppia maritima*). Grasses that have extensive root systems, such as rabbitfoot grass and cordgrass, do a better job of providing surface area for microbes to thrive (Salton Sea Restoration Program, 2005).

A separate study was also conducted that tested among other species the water hyacinth (*Eichhornia crassipes*), a floating wetland plant. Water hyacinth growth development was observed at low concentrations and decreased when the concentration of selenium exceeded 1,000 μg/L (EPRI, 2001).

The performance of a wetland can be affected by the density of plant growth. Plant detritus is used as organic substrate for microbial reduction of selenium. If there is insufficient plant cover within a wetland, an additional organic substrate may be required to improve selenium removal. Filling in the wetland area with plants may require a long period for the plants to mature and optimize selenium removal. Plant re-establishment may be required if areas are allowed to dry out. The hydraulic conductivity of the media may become affected over time due to clogging of the wetland. Excavation and re-construction of the wetland may be needed to re-construct areas that become clogged.

Climate conditions such as amount of precipitation and temperature affects the design of constructed wetlands. Wetlands need to be sized appropriately to achieve desired removal, where removal increases with increasing temperature. Subsurface flow wetlands are not as susceptible to temperature effects as surface flow wetlands. Volatilization within a surface flow wetland has been observed to vary from approximately 9% in the winter to over 50% in the summer months for a wetland in California (Johnson et al., 2009; Terry, 2009).

Operations and monitoring activities may require control of wildlife and management of vegetation. Barriers and noise can be used as wildlife deterrents. Alternative habitat may also be constructed to encourage wildlife away from wetlands areas. Management of vegetation may involve occasional harvesting. An indicator of performance is measurement of ORP and hydrosoil conditions to determine whether reducing conditions are present within a wetland that are favorable for selenium removal. Periodic variation between reducing and oxidizing conditions in the shallow surface flow wetland environments results in alternating sequestration and remobilization of selenium (EPRI, pending(b)).

Wetland owners are responsible for both the operational performance of treatment wetlands and the health of animals that use them. Wetlands owners can be prosecuted under a variety of federal and state laws such as the Migratory Bird Treaty Act and the Endangered Species Act if wildlife poisoning occurs due to operations of the wetland (Ohlendorf and Gala, 2000; Lemly and Ohlendorf, 2002).

Residuals Management. The long-term management requirements of treatment wetland substrate may include the need for periodic removal or replacement. Clogging of subsurface flow wetlands by biological growth has been a management issue in the past, but guidelines are available for minimizing this potential. Similarly, the substrate within a vertical flow wetland may degrade over time, potentially reducing selenium removal effectiveness. Excavation and disposal of the material and replacement with new substrate may be required. The lifespan of a selenium treatment wetland is unknown.

Capital and Operating Costs. Constructed treatment wetlands have relatively low construction, operation, and maintenance costs compared with conventional advanced treatment technologies. Factors that affect the cost of constructed wetlands include: wetland area, need for a liner, pretreatment requirements, system for conveying flow to the wetland, site slope and soil type, adjacent land use and site complexity, flow conveyance system and public use features, if any. Subsurface flow wetlands are more expensive to construct than surface flow wetlands, given the engineered media and placement required and the likely requirement for a liner. Figures 4-38 and 4-39 present the TIC and O&M costs for subsurface flow wetlands for selenium reduction to below 5 µg/L. These costs are Class 5 costs as defined by the AACEI with an accuracy of +100% and -50% as shown by the variance bands based on 2009-2010 market conditions. This system is a grass roots or green field selenium treatment system with costs for stand alone utilities (e.g., power) included in the estimate. 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. As discussed in Section 4.1.2 equalization and diversion of flows and/or loadings are generally required for most treatment systems. Operational costs include maintenance, labor, and energy disposal costs. Periodic replanting and cleanout is not provided in the estimate. Depending upon the system periodic replanting may occur every 5 to 10 years.

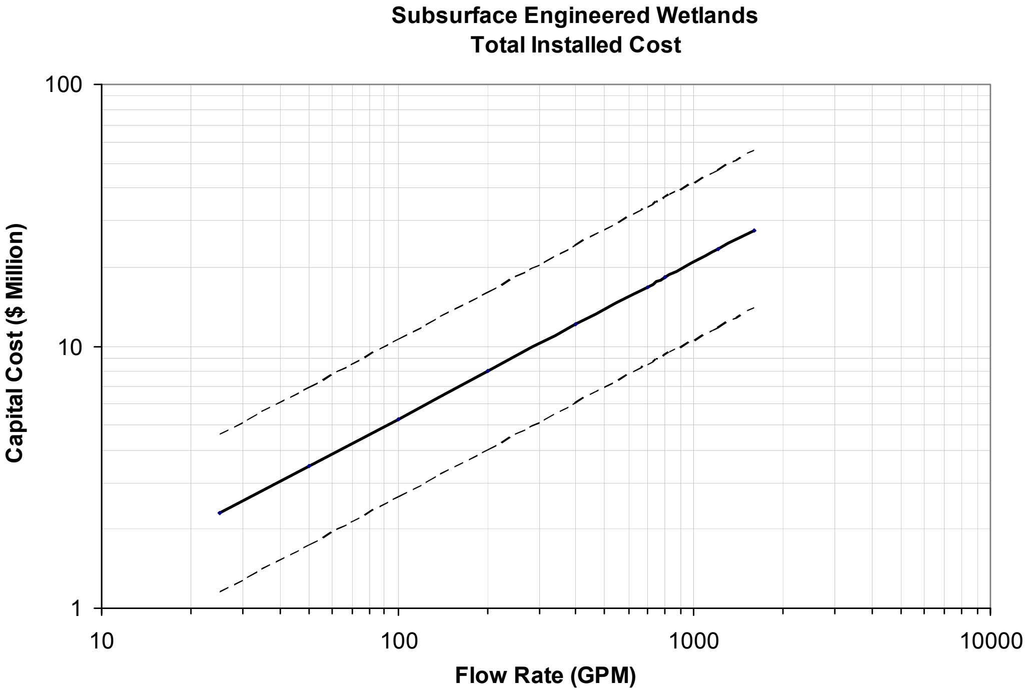


FIGURE 4-38
Total Installed Costs for Subsurface Flow Wetlands (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

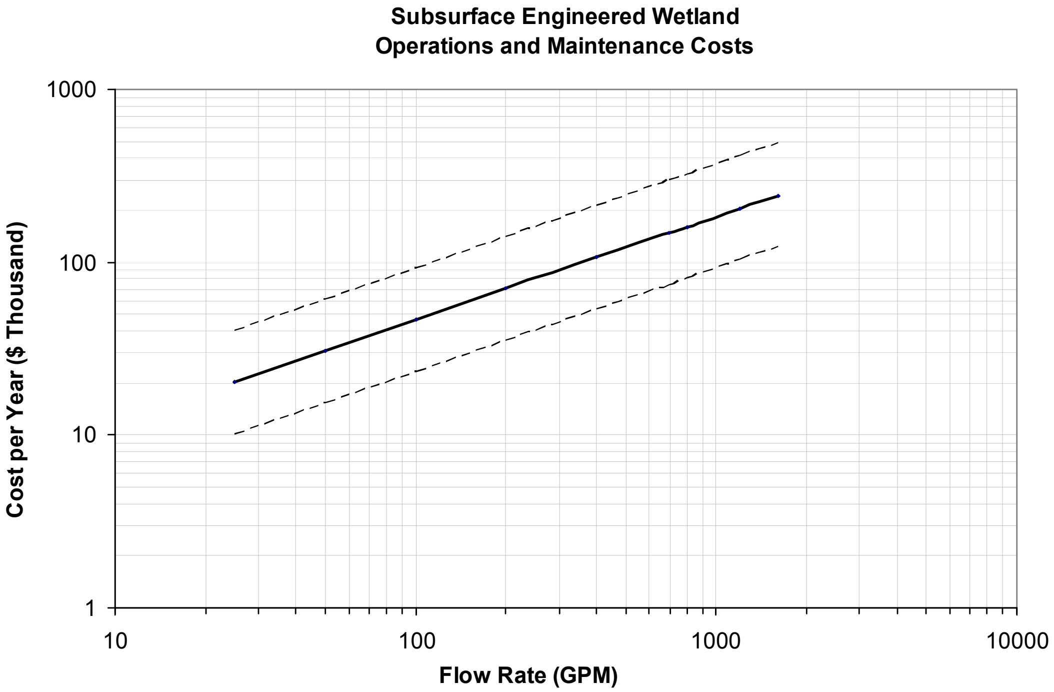


FIGURE 4-39
Operating Cost Curve for Subsurface Flow Wetlands (Year 2010)
Note: Dashed lines represent +100%/-50% Variance

Using a single unit cost estimate is cautioned against, however, since Kadlec and Wallace (2009) presented cost summaries for surface flow and subsurface flow systems indicating an economy of scale with increasing size.

Advantages and Disadvantages. The advantages and disadvantages of constructed wetlands are summarized below in Table 4-19. An important consideration in the use of wetland systems for treatment of selenium is the potential ecological risk associated with systems that create an exposure to wildlife (Ohlendorf and Gala, 2000; Lemly and Ohlendorf, 2002). Ecological monitoring of effects may be a regulatory requirement, particularly for inflow cells. It is important to document the selenium content of the wastewater, understand how it cycles and accumulates in the environment, and evaluate the threat it may pose to fish and wildlife before deciding whether or not to proceed with construction (Ohlendorf and Gala, 2000). An advantage of subsurface flow wetlands over surface flow wetlands is that exposure to ecological receptors is minimized since water flow occurs in the subsurface only.

TABLE 4-19
Advantages and Disadvantages of the Constructed Wetlands Technology

Advantages	Disadvantages
• Basic technology is reasonably demonstrated to remove selenium at low concentrations. • Process requires minimal operator supervision. • Process can operate passively without energy or chemicals. • Subsurface flow wetlands can operate in cold climates with installations in Northern Europe and Canada. • Able to treat large volumes of water.	• Potential for long residence time. • Large and flat footprint is required. • Uncertainties relating to consistently meeting very low selenium discharge limits (less than 5 µg/L). • Performance of surface flow wetlands is affected by temperature. Selenium removal is greater in summer months during warmer period. • Monitoring may be required to assess ecological risk from bioaccumulation of selenium, including toxicity to aquatic life and animals (nesting birds); if significant, exclusion measures may be required. • Potential for groundwater contamination.

4.4.3.2 Passive Biochemical Reactor Treatment

Technology Description. Passive biochemical reactors have been used for treatment of mining-influenced water. Another term for biochemical reactor is sulfate-reducing bioreactor (Gusek et al., 2008). Passive biochemical reactors consist of an excavated lined area that has been filled with an organic substrate. They are generally operated in a gravity down-flow mode, although up-flow mode is also a possible configuration. An underdrain is located at the bottom of the system which is overlain by gravel. Wastewater flows from the top of the biochemical reactor through the media to the underdrain. A water level control can be installed to regulate water levels. Figure 4-40 shows a typical configuration.

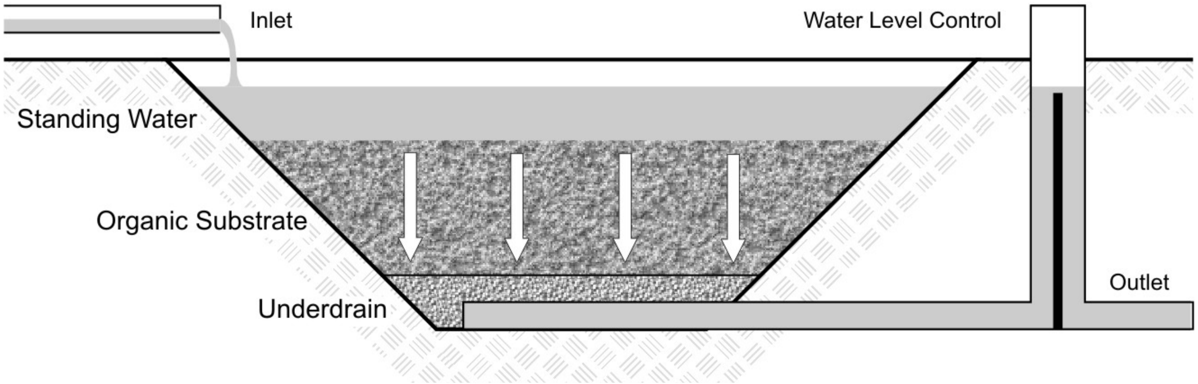


FIGURE 4-40
Passive Treatment System: Biochemical Reactor
Source: EPRI, pending(b)

Anoxic/anaerobic conditions exist within a biochemical reactor. The organic substrate provides a continuing source of carbon for use in microbial reduction which slowly degrades over time. The systems may also be inoculated with selenium-reducing bacteria. Organic substrates may be wood chips, alfalfa, manure, mushroom compost, sawdust, straw, peat, or other organic material. The substrate is sometimes mixed with sand or gravel prior to implementation to increase the hydraulic conductivity of the medium. ZVI may also be mixed with the organic medium to improve selenium removal. These systems do not require continuous chemical or energy inputs. However, microbes may require several months to fully colonize a system. Effluent can contain elevated levels of BOD and may require further treatment with aeration to reduce BOD and increase dissolved oxygen in treated water prior to discharge.

An example of such a system is the Biopass system installed at the Homestake Mining Company's Santa Fe Mine, in Mineral County, Nevada (Sobolewski, 2005). This system treated acidic mining-influenced water containing a variety of constituents including selenium. The Biopass system was constructed in an excavated area lined with a geomembrane. The substrate layer was composed of spent ore gravel and composted cow manure mixture. The system had a vegetative soil cover over a geomembrane liner. Treated solution flowed to a leach field where it was aerobically treated (Sobolewski, 2005).

Treatment Effectiveness. A full-scale biochemical reactor in operation since 2007 at a confidential gold mine in Montana treats 10-US gpm (38 Lpm) of waste rock seepage. The system reduces influent concentrations from 20 µg/L selenium to less than 1 µg/L (Golder, 2009a).

Several pilot studies of selenium removal in biochemical reactors have been conducted. Pahler et al. (2007) compared various types of media for use in passive treatment of gravel pit seepage that resulted in up to 98% removal of selenium. Study results did not indicate additional improvement when ZVI was added to the biochemical reactor (Pahler et al., 2007). This system is presented as a case study in Section 5.2.4.2.

A 6-US gpm (23 Lpm) pilot-scale system tested with mining-influenced water at a pH of 2.7 at an undisclosed mine in Nevada achieved less than 5 µg/L selenium from an influent average of 22 µg/L (Gusek et al., 2008). The system consisted of a down-flow biochemical reactor and aerobic polishing wetland (in series).

An 18-month pilot study was conducted at the Brewer Mine, a closed gold mine in South Carolina, with heap leach pad runoff and mining-influenced water derived from an acidic pit lake. The 0.3-US gpm (4 Lpm) study achieved 97% removal by treating an average influent of approximately 1,500 µg/L selenium to 50 µg/L (Golder, 2009a).

EPRI conducted a pilot study using spent mushroom compost as an organic substrate for treatment of FGD wastewater, resulting in >85% removal of selenium (EPRI, pending(b)). This pilot study is described further in Section 6 of this report.

Based on NAMC-SWG questionnaire responses from Teck Coal Limited regarding selenium treatment systems, a one-year pilot study was conducted at Teck Coal's Cardinal River Operations using a biochemical reactor to treat selenium (as >90% selenate) from seepage captured from the toe of mined rock spoil. The upflow pilot system reduced an average influent of 190 µg/L selenium by 66% to an average effluent concentration of 70 µg/L. Removal efficiencies for selenium ranged from 13 to 92%. Section 5.2.4.3 includes the details of this case study.

Design and Operational Considerations. Biochemical reactors are designed based on targeting a hydraulic retention time (HRT) of sufficient duration to allow selenium removal processes to achieve the water quality objective. Although widely applicable, this technology requires bench-scale and pilot-scale testing to estimate site- and effluent-specific design parameters and removal effectiveness.

Residuals Management. The organic substrate media degrade over time and require replacement. It is uncertain how long the organic substrate will last prior to requiring replacement. Periodic monitoring of substrate quality provides a way to determine the lifespan of the organic substrate and whether it may require disposal as a hazardous waste.

Another potential issue is re-solubilization of selenium. A study was performed to determine the influence of microbial communities in overburden mining waste. Testing showed that long-term selenium treatment may require an additional stabilizing agent such as iron to prevent re-solubilization (Knotek-Smith, 2003; Knotek-Smith et al., 2006).

Capital and Operating Costs. The design and construction cost of the first module of the Montana gold mine passive treatment system described above was approximately $200,000 (year 2007). A total of three modules are planned to treat a total of 20 US gpm (75 Lpm), with annual operating costs estimated at $0.95 per thousand gallons (Golder, 2009a).

Advantages and Disadvantages. The advantages of passive biochemical reactors are summarized below in Table 4-20.

TABLE 4-20
Advantages and Disadvantages of Passive Biochemical Reactors

Advantages	Disadvantages
• Low capital and operations and maintenance costs, including low cost of organic substrate; local materials can be used for organic substrate. • Process requires minimal operator supervision. • Process can operate passively without energy or chemicals. • Subsurface design means that system can operate in cold climates.	• Uncertainty regarding potential re-mobilization of selenium. • Large footprint required. • Uncertainty in consistently meeting very low selenium discharge limits (less than 5 µg/L). • Organic substrate degrades over time and may require replacement.

4.4.3.3 Permeable Reactive Barriers

Technology Description. Permeable Reactive Barriers (PRBs) are a type of passive, *in situ* treatment for shallow groundwater (generally employed at depths less than 50 to 70 feet) (USEPA, 1998) and can be employed for source zone treatment. PRBs are generally a lower cost alternative to traditional pump-and-treat methods (Martin et al., 2009). Figure 4-41 shows a diagram of a PRB. There are two basic configurations for PRBs: funnel-and-gate design and continuous PRB. The funnel-and-gate design PRB uses impermeable walls (sheet pilings, slurry walls, etc.) as a “funnel” to direct the contaminant plume to a “gate(s)” containing the reactive media. The continuous PRB is a trench design that completely transects the plume flow path with reactive media. ZVI is generally used as a reactive media for converting contaminants to nontoxic or immobile species. Reactive media may include

ZVI, chelators, sorbents, microbes and nutrients (bio-barriers). PRBs with ZVI and bio-barriers have been used to convert selenate to elemental selenium and Fe-selenides (Martin et al., 2009). There are approximately a hundred PRBs operating in the United States for the remediation of various contaminants.

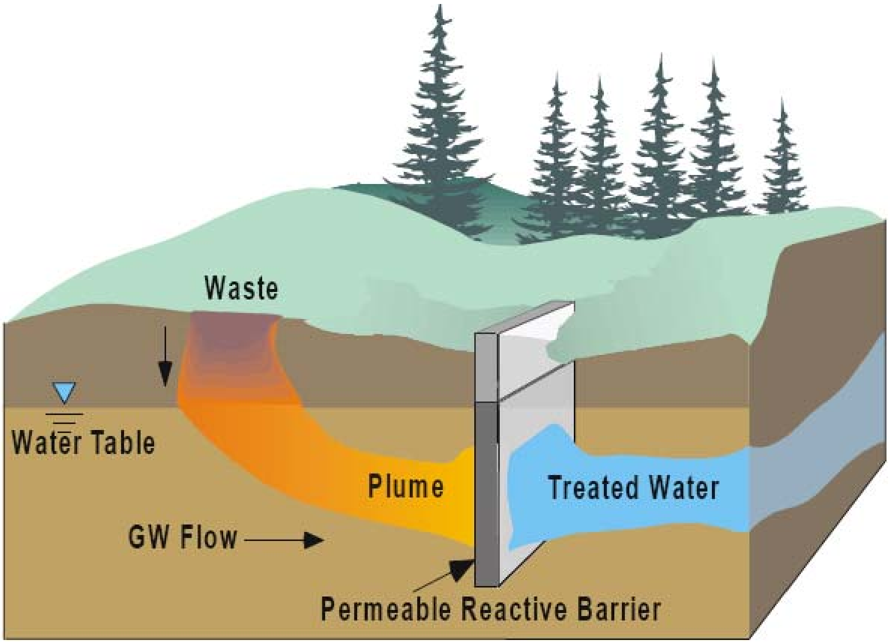


FIGURE 4-41
Conceptual Diagram of a Permeable Reactive Barrier
Source: USEPA, 1998

Treatment Effectiveness. Installation of a PRB hydraulically downgradient of the Monticello, Utah, millsite (former uranium and vanadium ore-processing mill) was completed June 30, 1999 (United States Department of Energy [USDOE], 2004). The remediation system includes a funnel and gate design PRB with ZVI as the reactive media. The funnel barrier was built by driving steel sheet piling into the bedrock forming a rectangular box approximately 100 feet long by 8 feet wide (Martin et al., 2009). The PRB consists of ZVI and gravel packs upgradient and downgradient of the ZVI. The funnel walls are composed of a bentonite and soil slurry mix. Results of groundwater monitoring show that the PRB is able to treat an average influent concentration of 40 µg/L to levels below detection limits (Martin et al., 2009).

A PRB was installed in October 1995 to treat water from a contaminated seep at a uranium mill tailings disposal site at Durango, Colorado (USDOE, 2004). The seep water was collected in a gravel drain and piped to a lined retention pond where it was treated with lime and discharged to a drainage system. Four PRBs were later constructed to treat the contaminated water before it entered the retention pond. Sampling conducted in 2004 indicated that the influent to the PRB received 359 µg/L total selenium. The PRB treated the groundwater contaminated with selenium to an effluent concentration of 8 µg/L (USDOE, 2004).

A field demonstration of an organic substrate amendment was performed at the Smoky Canyon (Idaho) mine. A trench was installed just above the toe of the overburden disposal area (ODA) at the mine and 10,000 US gallons per day (37,854 liters per day) of cheese whey was added for approximately one week. Concentrations of selenium in Pole Canyon Creek water exiting the ODA were reduced to approximately 50 µg/L and quickly rebounded after the test was completed (NewFields, 2006).

Design and Operational Considerations. PRBs can be installed via excavation and trenching, deep soil mixing, pneumatic fracturing and injection, hydraulic fracturing, and injection such as with direct push drilling methods. PRBs can be either permanent or semi-permanent remedial measures and can have a life span of several decades. The corrosion of ZVI causes an increase in pH values and a decrease in oxidation state. Monitoring of pH and ORP can be used to help evaluate the performance of PRBs.

Minimal maintenance is generally required for PRBs. However, losses in PRB performance may occur due to a decrease in hydraulic conductivity associated with the precipitation of other metals such as carbonate and oxide minerals within and adjacent to the barrier. Repair using additional injection of material may be needed to account for losses from clogging. An indicator of clogging would be groundwater mounding observed upgradient of the PRB.

Residuals Management. Reactive material within a PRB may require change out throughout the life of a PRB. Excavation and disposal of the reactive media may be required. In addition, dissolved iron concentrations can be high within the effluent of PRBs and may require additional treatment.

Capital and Operating Costs. PRBs are also more cost effective for well-constrained groundwater flows with relatively-small cross-sectional flow paths. For the Durango PRB, treatment costs were about $24 per 1,000 U.S. gallons (2004 USD) (USDOE, 2004). The major cost of installation of a trench is the excavation and disposal of contaminated soils.

Advantages and Disadvantages. The advantages and disadvantages of the PRB technology are presented below in Table 4-21.

TABLE 4-21
Advantages and Disadvantages of PRB Technology

Advantages	Disadvantages
• Lower cost alternative than other technologies. • Low maintenance. • Can be used as a source control measure to mitigate exposure to downgradient receptors.	• Finite life span. • Potential to be clogged due to precipitation of secondary metals. • Has not been fully demonstrated to achieve low µg/L levels in the effluent (less than 5 µg/L).

4.4.3.4 Enhanced *In Situ* Microbial Reduction

Technology Description. Enhanced *in situ* microbial reduction of oxidized forms of selenium is accomplished by addition of organic amendments, nutrients or inoculated micro-organisms. Selenium removal with this technology is based on the presence of micro-organisms to remove selenium. *In situ* microbial reduction can take place naturally or be enhanced with amendments to increase the rate of removal. The technology has been applied for selenium removal in some mining applications such as:

- Groundwater influenced from mining
- Treatment of pit lakes
- Treatment of mine workings

Martin et al. (2009) described the use of enhancements for treatment of mining-influenced water, which are summarized in this section. Pit lakes often contain mining-influenced water from former mining activities. Pit lakes can be deep, stratified, saline lakes that contain an anoxic layer. Pit lakes are also often sheltered from wind by pit walls (Martin et al., 2009). Amendment addition has been observed to promote oxygen depletion and maintain stratification in pit lakes (Martin et al., 2009).

In situ treatment has also been used for treatment of water in abandoned mine workings. Waters in flooded underground mine workings typically have a long residence time in which microbial reduction can occur. Organic carbon and nutrients have been added to mine workings for contaminant removal (Martin et al., 2009).

Treatment Effectiveness. Enhanced in situ microbial reduction has been demonstrated at full-scale or field demonstration for several mining applications, including:

- Homestake Mining Company reclamation project (New Mexico)
- Sweetwater Pit Lake (Wyoming)
- Gilt Edge Mine Superfund site (South Dakota)
- Beal Mountain mine (Montana).

Enhanced *in situ* microbial reduction has been implemented at full-scale at the Homestake Mining Company's Grants New Mexico Reclamation Project. Selenium in groundwater was reduced from 50 to 100 µg/L to less than 5 µg/L by adding nutrient solutions (Sobolewski, 2005).

The Sweetwater Pit Lake located in the former Sweetwater open pit uranium mine in Wyoming was treated by Kennecott Uranium Company with approximately 550 tons of sugars, fats, proteins, alcohols, phosphates and nitrates over a two-month period in 1999 (Martin et al., 2009). Dissolved selenium was treated from an initial concentration of 460 µg/L to values less than 10 µg/L. The addition of phosphate resulted in algal blooms which provided an organic carbon source for bacterial reduction (Martin et al., 2009).

Enhanced *in situ* microbial reduction has also been able to treat lower levels of selenium within pit lakes. Selenium levels were successfully treated within the Anchor Hill Pit Lake (20 µg/L) at the Gilt Edge Mine near Lead, South Dakota (Martin et al., 2009). Various amendments were tested to reduce selenium including methanol, molasses and wood chips, and nutrients using fertilizer (phosphoric acid). Once reducing conditions were established selenium was treated to below 1 µg/L (Martin et al., 2009).

Another example of pit lake treatment was performed at Beal Mountain Mine, located near Butte, Montana. When the mine was closed, the open pit was backfilled with waste rock. Runoff and seepage eventually filled the voids of the backfilled pit (Martin et al., 2009). Organic carbon was added during the filling period so that it could be distributed through the pore spaces of the waste rock. Organic carbon was added at a rate sufficient to reduce selenium levels from approximately 45 µg/L to between 2 and 3 µg/L (Martin et al., 2009).

Design and Operational Considerations. In situ microbial reduction of pit lakes is a patented process by Alexco Resources, Inc. (Golder, 2009a). Microcosm and pilot testing is recommended prior to implementation of this technology as it is applicable on a site-specific basis. Anoxic conditions are required for *in situ* microbial reduction of selenate and selenite to occur. Microcosm testing can be performed to determine the available microbial populations and whether treatment may be effective for selenium reduction prior to implementation. Nutrient addition may be performed using injection equipment or directly into wells for groundwater applications.

Water treated by enhanced *in situ* microbial reduction may require post-treatment to raise dissolved oxygen levels, to filter particulate metals, and to remove hydrogen sulfide prior to discharge (Martin et al., 2009).

Because substrate addition creates anoxic conditions within a pit lake, this can create lethal conditions for aquatic life that live within a pit lake so this technology is not applicable to lakes that contain aquatic life (Golder, 2009a).

Residuals Management. There is a potential for remobilization of elemental selenium retained in the subsurface that should be evaluated on a site-specific basis for this technology.

Capital and Operating Costs. This process is very cost-effective, at less than USD $1.00/1,000 U.S. gallons, due to low capital costs (Sobolewski, 2005). Depending on the type of application, capital costs for *in situ* microbial reduction include the equipment used to feed amendments to the water being treated. Operating costs would include labor, maintenance of equipment, and costs of amendments. The costs of bacterial inoculation, substrate addition, and nutrient additions are expected to be the largest portion of the total operating costs for this technology. Treatment process of the pit lake at the Sweetwater Uranium Mine required minimal equipment (a hydroseeder) at an estimated cost of less than $0.16/m^3 (Martin et al., 2009).

Advantages and Disadvantages. The advantages and disadvantages of enhanced *in situ* microbial reduction of selenium are presented below in Table 4-22.

TABLE 4-22
Advantages and Disadvantages of Enhanced *In Situ* Microbial Reduction Technology

Advantages	Disadvantages
• Lower cost alternative for remediation of large volumes of water. • Low maintenance.	• Long retention times required. • Anoxic water may require aeration/settling as post-treatment prior to discharge to receiving water.

4.4.4 Selenium Removal by Algae

Selenium may be removed by the algal-bacterial selenium removal process, algal volatilization, and algal assimilation.

4.4.4.1 Algal-bacterial Selenium Removal

Technology Description. Algal-bacterial selenium removal (ABSR) is a process in which bacterial growth is stimulated by the addition of algae as a food source (NSMP, 2007). The process has been tested for selenium removal in agricultural drainage in the Panoche Drainage District, California. The process consists of two ponds in series: a high-rate pond (HRP) to grow algae by nutrient addition and a reduction pond, which provides an anaerobic environment where bacteria use decomposing algae as a food source promoting the reduction of selenium to its elemental form (NSMP, 2007). Carbon dioxide may be added to stimulate growth of algae within HRPs. Algae in the HRP are pumped to the reduction pond, where the algae are used as a carbon source for bacterial reduction of selenium (Quinn et al., 2000). Molasses may be used as an additional substrate to improve reduction of selenium. Elemental selenium is then precipitated to the bottom of the pond where it can be effectively removed (NSMP 2007). While HRPs are shallow, reduction ponds can be approximately 20 feet deep. Conditions at the bottom of the reduction pond are anoxic so that selenium remains in precipitated form within sediments (Quinn et al., 2000). Quinn et al. (2000) also tested an alternate configuration to the ABSR process, which resulted in an increase in selenium removal.

Treatment Effectiveness. The cumulative 2-year mass removal of selenium during the test performed by Quinn et al. (2000) was 45% for the initial configuration and 80% for the high-efficiency system. Colder winter temperatures slowed activity to 68% removal, whereas from April to December 1998, removal was 92%, indicating the microbial activity was sensitive to water temperature. Quinn et al. (2000) reported 82 to 92% selenate removal from wastewater presenting inflow selenium concentrations from 402 to 422 μg/L. Influent selenium consisted of mainly selenate. The selenium concentration in the final effluent ranged from 32 to 77 μg/L. The algal component of the treatment process was discontinued after experiments showed that it did not contribute significant additional selenium removal (Golder, 2009a).

Frankenberger et al. (2004) reported reductions of selenate from 400 to 10 μg/L using a prototype system in Mendota, California. The microalgal treatment removed selenium from 300 to 500 μg/L to 80 to 100 μg/L and was also treated with iron to achieve 10 μg/L.

Algal treatment has also been shown to be effective for selenium removal in conjunction with *in situ* carbon treatment of pit lakes (Golder, 2009b). The Sweetwater Uranium Mine in Wyoming employs *in situ* pit lake biological treatment with phosphate addition to maintain the growth of algae, which provides a continuous source of organic carbon as a substrate for bacterial reduction of selenium. Microbial reduction is responsible for the removal of dissolved selenium from an initial concentration of 460 μg/L to values less than 10 μg/L (Martin et al., 2009).

Consistent with previous discussion on microbial reduction, Quinn et al. (2000) reported that constituents that interfere with selenium in the ABSR process include dissolved oxygen, nitrate, and nitrite. Martin et al. (2009) also noted that anoxic conditions were required for successful biological reduction of selenium. Takata (2003) studied the effect of salinity within the ABSR process and found that selenium removal remained the same regardless of the salinity concentration of the tested samples.

Selenium speciation results indicate that while the influent mainly consisted of selenate the effluent contained selenite and organoselenium compounds which resulted in two to four times greater selenium concentration in test invertebrates compared to those exposed to untreated water (Higashi et al., 2005). The bioavailability of selenium increased by two to ten times between the influent and effluent, creating an increased toxicological risk to ecological receptors (Amweg et al., 2003).

Design and Operational Considerations. The ABSR systems received between 2.5 and 19 US gpm (7 to 72 Lpm) (Golder, 2009a). The HRT for the first configuration was 25 days and 20 days for the high-efficiency configuration (Quinn et al., 2000). Construction of the pilot-scale system at the Panoche Drainage District included excavation and placement of a liner (NSMP, 2007). The reduction ponds used in the study were 10 feet deep, but full-scale systems may be 20 feet (6 meters) deep (Quinn et al., 2000). The pilot-scale ABSR system was 0.2 acre (0.08 hectare) (NSMP, 2007).

Residuals Management. The initial configuration accumulated much more sludge than the high-efficiency configuration (Quinn et al., 2000). Periodic disposal of sludge would be required either in a landfill or dried and added to soil as a nutrient amendment (Quinn et al., 2000).

Capital and Operating Costs. Algal treatments have generally low cost (e.g., $.0008 per gallon) (NSMP, 2007). However, high cost can be associated with the land needed for the ABSR pond (e.g., $200 per acre-foot) (NSMP, 2007), as well as the need for separation of the high-rate and reduction ponds (Lenz and Lens, 2009). The treatment process at the Sweetwater Uranium Mine pit lake in Wyoming required minimal equipment (a hydroseeder) at an estimated cost of less than $0.16/m^3 (Martin et al., 2009).

Advantages and Disadvantages. The advantages and disadvantages of the ABSR technology are presented in Table 4-23.

TABLE 4-23
Advantages and Disadvantages of ABSR Technology

Advantages	Disadvantages
• Potentially low cost-treatment approach. • Results in some direct volatilization of selenium out of the water column. • Can be applied as an *in situ* approach to selenium treatment. • Possibilities for future research include harvest of algae and bacteria as a source of protein and selenium to supplement cattle feed and harvest of algae for biofuel.	• Requires excess nutrients that can create eutrophic conditions in receiving streams. • Seasonally limited with treatment affected by duration of solar light and ambient temperatures. • Difficult to separate algae from water, requiring further treatment with coagulants and flocculants. • Effluent contains more bioavailable forms of selenium that have resulted in higher selenium levels in invertebrates compared to those exposed to untreated water. • Has not been demonstrated to treat to low levels of selenium (less than 5 µg/L).

TABLE 4-23
Advantages and Disadvantages of ABSR Technology

Advantages	Disadvantages
	• High residence time required for treatment. • Large footprint required as algae growth limited to the upper surface of the water due to light penetration limits.

4.4.4.2 Algal Volatilization

Technology Description. Algal volatilization occurs when selenium is methylated and converted to a gaseous form (Frankenberger et al., 2004). Algal volatilization treatment involves the removal of selenium from wastewater by selenium biomethylation and further volatilization (Golder, 2009a; Golder, 2009b). Microalgae are responsible for transformation of selenate into volatile alkylselenides, selenium ions, and proteinaceous selenomethionine species. The main product of selenium volatilization by fungi, algae, and bacteria is dimethylselenide, which volatilizes to gaseous selenium in the atmosphere (Frankenberger et al., 2004).

Treatment Effectiveness. A laboratory study has shown that approximately 70% of selenium was removed from the Tulare Lake Drainage District in California containing 20 to 1,000 µg/L selenium by algae, the majority of which was due to volatilization (Frankenberger et al., 2004).

Artemia (brine shrimp) and microalgae strains have adapted to agricultural drainage water with high salinity and high selenium at the Red Rock Ranch at Five Points, California (Terry, 2009). Selenium has been consistently removed through one year of evaporation/drainage water addition cycles. Iron has been identified as a limiting factor in volatilization of selenium. Selenium volatilization rates are influenced by nitrate concentration. Elevated nitrite concentrations may inhibit volatilization (Frankenburger et al., 2004).

Cyanobacteria and green algae *Chlorella* mats have been shown to actively volatilize over 60% of selenite from an aquatic medium with initial selenium concentrations ranging from 10 to 10,000 µg/L (Fan et al., 1998). A pilot study at the Cardinal River Operations coal mines in Hinton, Alberta, reported reductions in selenium concentrations from 194 to 142 µg/L (Golder, 2009b).

Design and Operational Considerations. Pond-based systems are most effective in warm climates near the equator where the sun is as close to 90 degrees to the surface of the pond as possible. Algal growth takes places at the surface of the ponds because dense algal mats block sunlight needed for growth at greater depths.

Residuals Management. The algal ponds would generate minimal sludge that would periodically require disposal.

Capital and Operating Costs. Similar to the algal-bacterial treatments, this treatment has low costs (Golder, 2009a). However, treatment cost can increase depending on land requirements (e.g., $104 to $272 per acre-foot treated) (USBR, 2008b).

Advantages and Disadvantages. The advantages and disadvantages of the algal volatilization technology are presented in Table 4-24.

TABLE 4-24
Advantages and Disadvantages of Algal Volatilization Technology

Advantages	Disadvantages
• Potentially a lower cost treatment approach. • Can be applied as an *in situ* approach to selenium treatment. • Possibilities for future research include algal harvesting as a source of protein and selenium to supplement cattle feed and for biofuel..	• Requires excess nutrients that can create eutrophic conditions in receiving streams. • Seasonally limited with treatment affected by duration of solar light and ambient temperatures. • Difficult to separate algae from water, thereby requiring coagulants and flocculants. • Effluent contains more bioavailable forms of selenium that have resulted in higher selenium levels in invertebrates compared to those exposed to untreated water. • Has not been demonstrated to treat to low levels of selenium (less than 5 μg/L). • High residence time required for treatment. • Large footprint required as algae growth limited to the upper surface of the water due to light penetration limits.

4.4.4.3 Algal Assimilation

Technology Description. Although selenium volatilization accounts for a major loss of total selenium from wastewater, a significant amount of selenium is assimilated by algae, particularly in proteins, where selenomethionine is the dominant form (Frankenberger et al., 2004). Selenium is a micronutrient and is required for growth of some, but not all, species of algae. Algae have the ability to take up selenium in various forms and by many species of algae to varying degrees. Research indicates that selenium is assimilated as selenoproteins via a sulfate reduction pathway in the cyanobacteria *Synechocystis* (Gouget et al., 2005).

A conceptual process has been developed by Bionavitas to remove selenium from wastewater byproduction and harvesting of algae. The algae can then be used as a biofuel or as a nutrient supplement. Algae are grown using a proprietary Light Immersion Technology™. As wastewater containing selenium enters the pond, carbon dioxide, ammonia, and phosphates are added as nutrients to enhance algal growth. The light source is immersed in the wastewater so that light can reach the total depth of the pond.

Based on feedback submitted by a NAMC-SWG member, Bionavitas conducted laboratory experiments to test four algal species (*Anabaena cylindrica*, *Anabaena flos-aquae, Chlamydomanas reinhardtii, Scenedesmus obliquus)* grown in artificial media at room temperature with water spiked with sodium selenate at 25, 250, and 2,000 μg/L. The length of the experiments ranged from 5 to 12 days. Significant algal growth rates were observed with concentrations up to 250 μg/L. Based on questionnaire responses by a NAMC-SWG member, a pilot plant for this technology is being designed for mining-influenced water that will be approximately 2 to 3 acres. Expected algal uptake rates of selenium are between 0.9 mg Se/kg algae to 4.4 mg Se/kg.

Capital and Operating Costs. Cost information is not available for the Light Immersion Technology™.

Advantages and Disadvantages. Further research and optimization are needed to determine the feasibility of this technology in applications to remove selenium from water. The advantages and disadvantages of the algal assimilation technology are presented in Table 4-25.

TABLE 4-25
Advantages and Disadvantages of Algal Assimilation Technology

Advantages	Disadvantages
• Harvest of algae for biofuel or nutritional supplement. • Results in volatilization of some of the selenium out of the water column. • Reduces light and temperature issues associated with seasonal weather and sun.	• Unproven beyond conceptual and laboratory scale evaluations. • Light Immersion Technology™ method for algal assimilation of selenium has not been demonstrated to treat selenium to low levels (less than 5 µg/L). • Requires excess nutrients that can create eutrophic conditions in receiving streams from process discharges. • Difficult to separate algae from water and thereby requiring coagulants and flocculants. • Requires solids dewatering systems. • Has not been demonstrated to treat to low levels of selenium (less than 5 µg/L). • High residence time required for treatment. • Large footprint required.

5.0 Industry-Specific Approaches to Selenium Management: Mining and Agriculture

5.1 Agricultural Approaches to Managing Selenium

The information presented within this section is based on the state of the practice for the agriculture industry's response to managing selenium in agricultural drainage. The focus of this section is on the assessment and application of strategies to mitigate exposure and release of selenium to the environment.

5.1.1 Overview of Sources and Fate of Selenium in Agricultural Waters

As described in Section 2, irrigation of saline and seleniferous soils has led to selenium contamination in water associated with agricultural drainage. Agricultural drainage water can either be surface drainage water from runoff that does not infiltrate the ground or subsurface drainage water, which is collected in subsurface drains and pumped to an impoundment. Subsurface drainage is collected because certain agricultural areas in the Western United States contain shallow clay layers which impede percolation of water through the subsurface (Lemly, 2004). Subsurface drainage is collected to prevent water logging of the crop root zone and a build-up of excess salts as water evaporates. Several factors can contribute to elevated selenium in agricultural drainage including oxidized, alkaline soils promoting selenate formation; an arid climate with a higher evaporation rate than precipitation rate that concentrates salts; and, saline groundwater aquifers located in alluvial clay layers that prevent percolation of irrigation water (Lemly, 2004; Seiler et al., 1999). The predominant species of selenium in agricultural drainage is selenate due to the oxidation of selenium in seleniferous soils with highly oxygenated irrigation water (Seiler et al., 2003). Deeply weathered shales in the Western United States have been observed to contain 95% of selenium as soluble selenate (Presser, 1994; Presser and Ohlendorf, 1987). In the United States, 2.6 million acres of irrigated land has been identified as potentially susceptible to leaching of selenium (Seiler et al., 1999).

Selenium concentrations vary throughout the year in seleniferous soils due to rainfall. These soils, high in salts and trace elements, are similar to those that occur in a marine environment. At some sites seleniferous soils may result in selenium fluctuations of more than an order of magnitude throughout the year or from year to year. Selenium levels may be low during normal or wet conditions in some areas and rise during a drought period due to evaporative concentration (Seiler et al, 2003).

The sites shown in Figure 5-1 encompass areas where historically agricultural drainage or open-range forage plants have contained elevated levels of selenium. Irrigation of seleniferous soils can result in drainage water that contains hundreds to thousands of micrograms per liter of selenium, as has been found in shallow wells near irrigated areas (Seiler et al, 2003). A study was performed by the United States Department of the Interior National Irrigation Water Quality Program where samples were collected from areas across the western United States believed to have elevated selenium as shown in Figure 5-1.

Selenium ranged from 1 to 8,300 µg/L with a median value of 7 µg/L in sites associated with marine sedimentary rocks compared with 1 to 390 µg/L with a median value of 4 µg/L in other sites (Seiler et al, 2003).

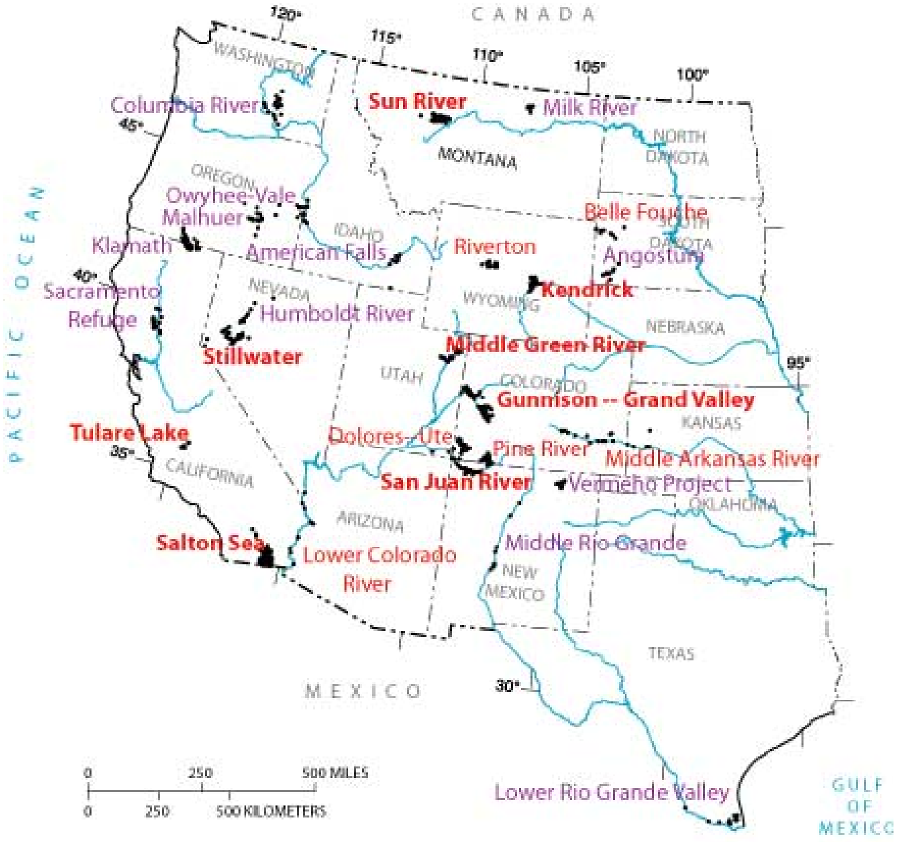


FIGURE 5-1
Agricultural Areas Susceptible to Elevated Selenium Levels in Drainage in the Western United States
Source: United States Geological Survey, http://wwwrcamnl.wr.usgs.gov/Selenium/irrigation.htm

Table 5-1 contains ranges of water chemistry parameters measured for agricultural drainage associated with the San Luis drain in the San Joaquin Valley, California (Presser and Ohlendorf, 1987).

TABLE 5-1
Water Chemistry Parameters for Irrigation Waters from San Luis Drain
Source: Adapted from Presser and Ohlendorf, 1987

Parameter	Concentration (mg/L)
Selenium	<0.002 to 1.4
Sodium	30 to 10,500
Sulfate	48 to 22,500
Potassium	3.6 to 19
Calcium	29 to 765
Magnesium	9.4 to 705
Bicarbonate	59 to 397
pH	7.5 to 8.7

5.1.2 Mitigation and Source Control Strategies

There are various source control and mitigation strategies for agricultural drainage to control selenium exposure to ecological receptors. Source control includes limiting deep percolation losses from supply canals and other structures that convey irrigation water. Mitigation and source control practices include improving irrigation efficiency, lining irrigation canals, conducting soil moisture monitoring to determine appropriate flows for irrigation, retiring areas with highly saline soils, re-using irrigation water, and planting selenium-resistant crops (USBR, 2006; State of California Department of Water Resource, 2004; Salton Sea Restoration Program, 2005; NSMP, 2007). The amount of irrigation can be carefully controlled to limit the depth of application so that soil water is not completely replaced and to allow for some available soil water storage for rainfall. Adopting this practice may require a change in early season water management to ensure germination and crop stand development (Westside Resource Conservation District, 2004a).

5.1.2.1 Integrated On-Farm Drainage Management

Mitigation strategies for the agricultural sector center on modifying irrigation practices to control selenium release to the environment. An example of this is using the Integrated On-Farm Drainage Management (IFDM) system, which was developed to reduce drainage volume, mitigate exposure of selenium and salts to ecological receptors and minimize effects on water quality from agricultural drainage by improving irrigation efficiency and providing solutions for water disposal (Westside Resource Conservation District, 2004a). IFDM is based on the agroforestry concept of interactive benefits from combining growing trees and shrubs with crops. IFDM employs sequential reuse of irrigation water on increasingly more salt-tolerant crops. Reuse of irrigation water can be successfully managed such that root zone soil salinity is controlled and adequate soil permeability to water and air can be maintained (Oster and Grattan, 2002).

In the IFDM approach, high quality irrigation water is used in the first stage of the process to irrigate salt-sensitive crops planted in the first of a sequence of fields. The irrigation water is then collected in subsurface drains and re-used to irrigate salt-tolerant crops. The used irrigation water from the second stage may be collected for 3rd and 4th stage irrigation of increasingly more salt-resistant crops, trees, and salt-tolerant grasses such as cordgrass (Westside Resource Conservation District, 2004a). Figure 5-2 shows a diagram of an IFDM system employing three-stage sequential water reuse. After the final stage of irrigation, the drainage water flows to a solar evaporator (Westside Resource Conservation District, 2004b). Sprinklers discharge water to solar evaporators at a low discharge rate to avoid standing water from collecting within the evaporator to reduce risks to wildlife. If a water catchment basin is used in conjunction with a solar evaporator, the entire area is to be covered with netting or otherwise designed to prevent access to avian wildlife. Evaporation ponds are being used in some locations, but the requirements to mitigate exposure to ecological receptors and to perform environmental monitoring limit the viability of ponds to those areas with very low levels of selenium. Active management including developing and implementing irrigation schedules is necessary for the success of this irrigation management system (Westside Resource Conservation District, 2004a).

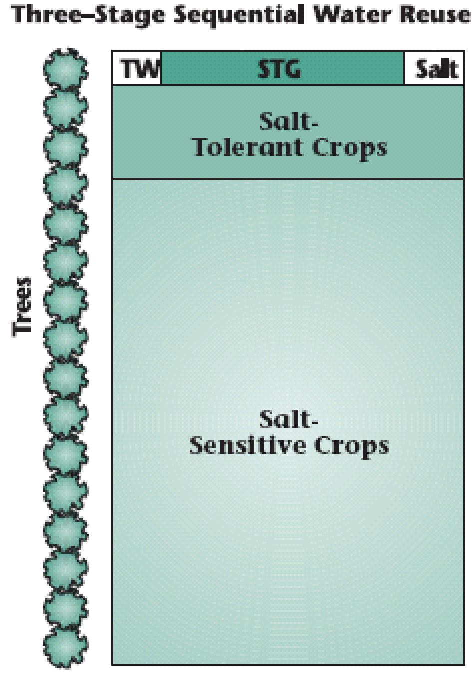


FIGURE 5-2
Integrated On-Farm Drainage Management Example
Source: Westside Resource Conservation District, 2004b
Note: STG- salt-tolerant grass; TW- tail water pond

Buffer strips of salt-tolerant trees such as eucalyptus serve as a windbreak, use large amounts of shallow groundwater, and lower the water table in the area (Westside Resource Conservation District, 2004b).

IFDM has been implemented at Red Rock Ranch in Five Points, California since 1995. Concentrations of selenium up to 1,500 µg/L were historically observed at the Red Rock Ranch (Seiler et al., 1999). The IFDM system employs four stages, including salt-sensitive crops, salt-tolerant crops, salt-tolerant trees, and halophytes before discharge to a solar evaporator (Westside Resource Conservation District, 2004b). Andrews Agricultural

Research Center in Bakersfield, California has employed a three-stage IFDM system since 1999.

5.1.2.2 Selenium-Resistant and Selenium-Accumulating Crops and Plants

Research is being performed on selenium-resistant and salt-tolerant crops and plants that can be planted in areas with seleniferous soils. The plants have an added effect of remediating selenium-impacted water (phytoremediation) (Banuelos et al., 2003; Banuelos, 2007; Stapleton and Banuelos, 2009). Selenium can be accumulated by plants and volatilized. Because selenium and sulfur chemistry are similar, plant uptake of selenate occurs via sulfur transporters and enzymes (Pilon-Smits et al., 2009). This process occurs in both selenium-accumulator and non-selenium-accumulator plant species and wetlands plant species (NSMP, 2007).

Different plants accumulate selenium at different rates. Pickleweed (*Salicornia bigelovii*) was determined to hyperaccumulate selenium within roots and plant tissues by converting selenate to organic forms of selenium and accumulating 65% to 70% of total selenium (Lee et al., 2001). Research is being conducted on selenium that accumulates in plants as fortified foods (Pilon-Smits et al., 2009). Based on research conducted at Red Rock Ranch between 2002 and 2007, various crops can be utilized for removal of selenium from agricultural drainage waters, including members of the *Brassica* family (e.g., broccoli, canola, mustard) (Banuelos, 2009). Potential uses identified in the research are selenium-enriched animal feed, vegetables, or biodiesel products (Banuelos, 2009; Banuelos and Lin, 2009). Results of a study on selenium uptake indicate that the rate of plant uptake was two to three times as great with selenite than with selenate in Indian mustard (*Brassica juncea*) (de Souza et al., 1998).

5.1.3 Treatment Approaches

Programs to conduct research in selenium treatment of agricultural drainage were first formed in response to the bioaccumulation of selenium at Kesterson Reservoir from the San Luis Drain containing subsurface agricultural drainage water flow. For examples, the San Joaquin Valley Drainage Program was established in 1983 and has been responsible for various laboratory and pilot studies for physical, chemical and biological treatment (USBR, 2008a).

Due to a decrease in irrigated water supply, modification of irrigation practices, avoiding growing crops in areas of high seleniferous soils where “hot spots” occur, and growing salt-resistant crops or hyperaccumulators of selenium, full-scale water treatment facilities are not typically required to treat agricultural drainage (G. Banuelos, personal communication, January 21, 2010). In some areas groundwater remains impacted from previous contamination associated with subsurface drainage from irrigation of seleniferous soils.

Examples of previous studies conducted for treatment of selenium in agricultural drainage include: laboratory studies conducted on adsorption technologies using commercially available adsorbents (Lalvani, 2004); reduction using metallic particles and immobilization via precipitation of selenium from contaminated agricultural drainage water (Lalvani, 2004); a pilot facility for reverse osmosis constructed at the Buena Vista Storage District northwest of Bakersfield, CA that operated from 2000 to 2002 during irrigation seasons (Boyle Engineering, 2003); demonstration testing for ion exchange, reverse osmosis, and a solar salinity-gradient pond at the Los Banos Demonstration Desalting Facility from 1984 to 1986 (Kovac, 2004); and pilot testing of various biological treatment systems including UASB, FBR, and fixed-film system for removing selenium from agricultural subsurface drainage water at the Adams Avenue Agricultural Drainage Research Center in Western, Fresno County, California (State of California Department of Water Resources Division of Planning and Local Assistance San Joaquin District, 2004). The results of the various tests are discussed in Section 4 under technology-specific sections. They are not discussed further in this section as the focus of the state of the practice selenium management solutions implemented at full-scale for the agricultural industry are generally prevention and source control measures.

5.2 Mining Industry Approaches to Managing Selenium

This section is an overview of the sources and fate of selenium, mitigation and source control activities to minimize the release of selenium to ecological receptors, and case studies of technologies that have been piloted or implemented at full-scale to treat selenium in the mining industry.

5.2.1 Overview of Sources and Fate of Selenium in Mining

The mining of metals and minerals (e.g., gold, copper, phosphate, uranium, zinc, etc.) can result in selenium release to the environment either through waste rock or tailings produced from surface or pit mining, and/or through mineral extraction processes for concentration and recovery of the metal of concern.

Soft rock surface mining (e.g., coal, bitumen) can also result in the release of selenium to the environment, primarily through waste rock and tailings produced from surface or pit mining operations. Selenium tends to concentrate with the sulfur containing minerals in both of these mining operations.

Waste rock from mining operations generally is the primary source of selenium from these operations. Typically the selenium in the tailings or waste rock or metal bearing rock will oxidize over time when exposed to air through materials handling activities, and/or through processing techniques to extract the metal or mineral. Once oxidized, the selenium will generally exist as selenite, or selenate depending upon the level of oxidation. In these forms selenium when exposed to water will then leach, or migrate from the rock. Therefore, source control in mining is focused on management of waste rock to first minimize oxidation of selenium and secondly minimize release of selenium through prevention of water contact with the waste rock or materials containing leachable forms of selenium. The large area of the mining operation, large volume of waste rock, overburden, or tailings, and the dispersion of selenium through the rock all complicate the source control of selenium. Section 5.2.3 provides a more detailed discussion of source control and release techniques for the mining industry.

5.2.2 Sources and Fate of Selenium in the Mining Industry

5.2.2.1 Phosphate Mining

Certain mineral formations sought for mining phosphate contain more selenium than others, and among those with higher concentrations is the Phosphoria Formation. The Phosphoria Formation is centered in Idaho, but extends regionally into northern Utah, through western Wyoming, and into southwestern Montana. Phosphate ore is found within the upper and lower parts of the Meade Peak member of the Phosphoria Formation (Ryser, 2005). Samples of waste rock from the area contain an average of 125 mg/kg selenium with a maximum of 1,500 mg/kg (Knotek-Smith, 2003). Interbedded shale and mudstone approximately 170 feet thick are present throughout the region (Buck and Jones, 2002).

Open pit phosphate surface mining involves removal of the topsoil (which is used later for reclamation purposes) followed by removal of overburden (known as waste rock) to reach the phosphate ore. Waste rock is often placed either back in the pit or in areas known as overburden disposal areas (ODAs). Certain layers of the waste rock (middle waste shales) contain elevated concentrations of selenium. When the middle waste shale comes into contact with air and moisture, oxidative weathering of the rock occurs, leaching selenium generally in the selenate form as precipitation enters the overburden (Knotek-Smith, 2003). Often, seeps form near the bottom of overburden disposal areas. These seeps often go back into the ground or form small pools at the base of the overburden disposal areas. Seeps leaving overburden piles have contained selenium levels up to 2,000 µg/L (Knotek-Smith, 2003). Figures 5-3 and 5-4 show an example of seeps that have developed from waste rock piles.

FIGURE 5-3
Seep Observed Near Toe of Waste Rock Impoundment
Source: Möller, 2002

FIGURE 5-4
Seep Flowing into Pond
Source: Möller, 2002

Using micro-X-ray absorption spectroscopy, Ryser (2005) identified three primary selenium-bearing minerals in phosphate mining waste rock from Southeastern Idaho (Phosphoria Formation). The three minerals identified in the waste rock included a ferroselite ($FeSe_2$) compound called dzharkenite, a di-selenide carbon compound, and a selenium-substituted pyrite. The middle waste shale contained high levels of selenium and is located between two phosphate ore zones. The ores contained very low concentrations of selenium in comparison with the middle waste shale (Ryser, 2005). Ryser (2005) also determined that there were four oxidations states for selenium present in the reclaimed mine soil: Se(-II), Se(0), Se(IV), and Se(VI), and that the selenium in the reclaimed mine soil was predominantly in the reduced form.

5.2.2.2 Surface Coal Mining

In the United States and Canada, coal surface mining deposits from overburden shales containing selenium are located in such areas as the Coalburg coal seam in the Appalachia region (West Virginia, Kentucky, Virginia, Tennessee), Powder River Basin (Wyoming, Montana), and Elk Valley (Elk Valley watershed British Columbia). Surface mining approaches vary by geography. Surface mining typically done for coal production in the Elk Valley is by pit mining with truck and shovel equipment. Strip surface mining is practiced primarily in the Powder River Basin. Mountain top surface mining is the primary technique used for surface mining coal in the Coalburg seam in the southeastern Appalachian Mountains.

Selenium in coal-bearing strata that can release to the environment is primarily associated with sulfur-bearing minerals. Potential selenium sources associated with mining activities include waste rock, tailings, the coarse-rejects stockpiles, coal storage, breaker rejects, ash from coal-fired dryers, and coal spillage (e.g., from conveyor and tipple operations) (Chapman et al., 2009b). Pit lakes are formed from mines in areas with high water tables, where groundwater infiltrates into the vacant mining pit and/or surface runoff accumulates after dewatering operations have ceased (Martin et al., 2009). Overburden, or waste rock from surface coal mining operations, is typically placed in waste piles, valleys, or as backfill to the coal seam removal area for the various mining operations. Generally the topography and landform engineering requirements for the waste rock limit the degrees of freedom for management approaches for overburden from coal mining operations.

Selenium can be in the range of 1 to 1,000 µg/L in mining-influenced water associated with coal mining activities. Selenium is generally present in the selenate form (Vesper et al., 2004) as a result of the relatively rapid oxidation or weathering of selenium on the surface of the waste rock. Oxidation will vary by handling or management methods during mining. There can be proportionally larger quantities of selenium that are organically bound in the coal that are relatively stable and will not leach. This will vary by coal type. Once the selenium has oxidized to either selenite or selenate if exposed to water at the surface interface, it is readily soluble in water and will leach or transfer to the water matrix.

Sources of mining-influenced water are generally precipitation, groundwater intrusion, surface runoff, surface water discharges and snow melt. Flows are heavily affected by precipitation and seasonal changes (e.g., snow melt). In addition to precipitation, mine-water discharges are influenced by groundwater and surface water flowing through mining areas. Waste-rock storage areas are influenced by groundwater and precipitation percolating through the storage areas. Mine and road construction also involve soil movement, which can be affected by precipitation inputs.

Example of Characterization Efforts at an Appalachian Coal Mining Facility. At a confidential coal mining facility, characterization efforts are being undertaken to understand the nature and extent of selenium in water discharges in order to develop prevention, source control, and treatment methods to minimize discharges of selenium in water. Extensive sampling of mining-influenced water is being conducted for the influent and effluent of sedimentation ponds to characterize selenium (including speciation) and other key constituents that may impact wastewater treatment technology selection. Sampling is also being carried out during storm events to better understand the range of water flows from a targeted outfall that would require treatment.

Characterization of selenium speciation in targeted rock formations in the surface mining area are being performed to understand the impact of the resulting form and concentration of selenium found in the water runoff. The results of this characterization effort will be used to develop alternative methods of source material management and/or treatment at the source of the waste rock or overburden to reduce the quantity of selenium leached to water that comes in contact with it.

Results indicate that generally the majority of the selenium is within 2 feet of the upper and lower part of the coal seam which is mostly carbonaceous shales (Vesper et al., 2004). There is almost no selenium associated with the sandstone waste rock. The presence of selenium is specific to the geology of the local area and each coal formation. Sequential extraction studies indicated that most of the selenium is organically bound and will not leach with approximately 25% of the selenium on average in environmentally mobile forms (Vesper et al., 2008). Most of the selenium is associated with sulfides likely replacing sulfur in pyrite. There also are some adsorbed phases with clays and ferrihydrites.

Selenium in the upper and lower strata of the coal seam behaves similar to pyrite oxidizing and dissolving upon contact with water. There typically are the following forms of selenium: selenide that is susceptible to oxidation and leaching, elemental insoluble forms of selenium, selenite and selenate (Vesper et al., 2004; Vesper et al., 2008).

If selenium is predominately in the oxidized form in waste rock fills there may be an opportunity to implement *in situ* treatment in the valley fills to create and maintain a reduced environment and prevent oxidation of selenium and resulting leaching to water. Early bench-scale studies indicate that selenium is not mobile in the rock formation, rather it is oxidized to selenite and then selenate in the valley fill once exposed to water and air and then leaches to water that infiltrates the porous valley fill. Petrographic analyses, including x-ray diffraction, quantitative electron microprobe and quantitative scanning electron microscopy analyses are being conducted to provide an understanding of the mineralogy hosting the selenium and its impact on selenium behavior in the environment. Samples of the valley fill cores and fresh "channel samples" from recently exposed high wall areas representative of the stratigraphic column are being collected for soil characterization and selenium leaching evaluation.

5.2.2.3 Metal Ore Extraction and Processing

Selenium can be found within the mineral matrix of ore deposits and can be released to the environment during the extraction and processing of the ore from hard rock mining. Selenium is present in water associated with mining processes from precipitation entering waste rock impoundments, tailings ponds, and the solutions used during processing of the ore. Physical/chemical treatment of the ore often releases selenium and other constituents into the process water. For example, the heap leach process consists of placement of crushed mined ore on an impermeable plastic and/or clay lined leach pad where it can be irrigated with a leach solution to dissolve the valuable metals. The solution percolates through the heap and leaches out the desired metal. Selenium is primarily in the oxidized selenate form.

5.2.2.4 Bitumen Mining

Bitumen is a tar-like form of petroleum or heavy oil. Canada has one of the world's largest supplies of bitumen, with close to 17 million acres (7 million hectares) located in Alberta. Bitumen typically contains sulfur and inorganic elements such as nickel, vanadium, and selenium among others. The oil sand reservoirs contain bound formation water known as connate water, which surrounds individual sand grains as a layer. Oil sands are typically removed by strip mining. The heavy oil containing sands are typically processed from the base mine dump pocket by conveyor and enters large rotating tumblers where the ore is slurried by steam, hot water (185 °F [85 °C]) and caustic soda to condition it for bitumen separation (National Energy Board, 2000). The tailings produced as a result of the separation process consist of a mixture of water, sand and fine clay particles. Tailings are pumped into large holding ponds. Heavy oil is then further processed in upgraders.

5.2.3 Prevention and Source Control Strategies in the Mining Industry

Water treatment is one of three approaches for control of selenium; others include prevention of release and control of the source (Brienne et al., 2009; Chapman et al., 2009b; United States Department of the Interior: Bureau of Land Management, 2005). Treatment of mining-influenced water is difficult due to the large volume of water that may require treatment and the large fluctuations in flow seasonally and with storm events. Prevention and source control practices are more desirable alternatives than treatment because they reduce the volume and concentration of selenium in affected mine-influenced waters. Prevention or mitigation practices can occur at various stages, including pre-mining activities (e.g., road construction with low seleniferous materials), activities during active mining (e.g., institutional controls during mining activities), or reclamation activities (e.g., capping areas that have selenium-containing materials).

A successful site-specific management strategy for selenium in mining-influenced water involves identification of target goals, identification of potential ecological receptors, characterization to understand the nature and extent of selenium in water discharges and understand pathways to receptors, identification of mitigation and source control strategies to prevent receptors from coming into contact with selenium, and development of treatment strategies if mitigation and source control strategies are not applicable (Chapman et al., 2009b; United States Department of the Interior: Bureau of Land Management, 2005). Treatment strategies can be implemented either at the source or prior to discharge to receiving waters.

Chapman et al. (2009b) developed a comprehensive conceptual model that provides a framework to approach management of selenium pertaining to coal extraction in Western Canada. The paper describes an assessment tool for management options, including management at selenium source inputs, geochemical interventions to reduce organic selenium formation, institutional controls, environmental enhancement (i.e., mitigation measures), and treatment. The principal components of this model can be applied to the broader category of managing selenium in mining. Model development includes identifying data quality objectives to determine the decisions that need to be made and the information required to make those decisions. The model reviews the sources of selenium present within a mining operation due to mining activities and identification of water inputs (i.e., surface water, groundwater, precipitation) that come into contact with materials (e.g., waste rock) from mining activities that release selenium into the water by various transport mechanisms. Potential ecological receptors that may be exposed to selenium through various media (e.g., water, sediments) and their habitats as well as pathways of exposure to selenium are identified to determine management options to minimize the release of selenium into the environment.

Table 5-2 provides a summary of various mitigation strategies that can be used to prevent the release of selenium into the environment or minimize exposure to ecological receptors. The examples provided in the table below are not exhaustive and are not applicable to all scenarios, but are presented as examples of mitigation and source control practices in the mining industry.

TABLE 5-2
Examples of Mitigation and Source Control Practices Used Within the Mining Industry to Minimize Selenium Exposure

Mitigation/Source Control Practice	Description
• Mine Planning/Design	• Involves planning of the geometric shape of waste rock storage areas or spoil, reducing areal disturbance or footprint of the mining area, and maximizing backfill opportunities. Backfilling opportunities can include various innovative methods of construction of pit/spoil

TABLE 5-2
Examples of Mitigation and Source Control Practices Used Within the Mining Industry to Minimize Selenium Exposure

Mitigation/Source Control Practice	Description
	design to reduce air/water infiltration and to try to prevent release at the source by reducing the leaching rate of selenium. Other pit design considerations include placement of pit wall dewatering wells in sequence in advance of pit development.
• Submerge waste rock to minimize oxidation	• Submerging the sulfide minerals in waste rock is one of the most effective ways to prevent selenium release to the environment and is practiced to minimize sulfide oxidation and selenium oxidation. This practice will reduce but not eliminate oxidation of selenium (Sobolewski, 2005). This practice can be performed by backfilling waste rock into abandoned pits and subsequently flooding the backfilled pits.
• Capping/Covers	• Capping systems can be designed with natural or synthetic low permeability materials. Covering an area such as a waste rock impoundment with a soil layer can prevent vegetation from coming into contact with selenium. Waste rock storage areas can be covered with impermeable clays, low permeability geologic materials, or synthetic covers to reduce infiltration from precipitation and contact with air to minimize oxidation of selenium. This practice will reduce but not eliminate oxidation of selenium (Chapman, 2006; Chapman et al., 2009b). Covers are designed based on material availability, climate, anticipated life, and desired performance (Sobolewski, 2005). Leachable material should be deep enough to avoid penetration by deep rooting vegetation to prevent uptake of selenium in vegetation that may be a food source for grazers (United States Department of the Interior: Bureau of Land Management, 2005).
• Vegetation Cover	• The use of aggressive vegetation species to promote high biomass production in reclamation can maximize interception of precipitation by vegetation and through various mechanisms such as evaporation, transpiration, absorption, and utilization by the plant can reduce infiltration and therefore leaching from the waste rock areas.
• Progressive Reclamation	• Reclamation is performed as mining proceeds instead of waiting until the end of the mine life to perform reclamation.
• Source Removal	• Removal of source materials involves excavation and disposal of selenium-impacted material. This may be a viable option for small volumes of material (NewFields, 2006).
• Clean Water Diversion	• Diversion ditches are implemented to divert surface water or stormwater around areas that would result in introduction of selenium into the surface water. This can be used to divert surface water around waste rock disposal areas or backfilled pits (NewFields, 2006). Also, runoff can be diverted around mining areas to reduce the risk of contamination.

TABLE 5-2
Examples of Mitigation and Source Control Practices Used Within the Mining Industry to Minimize Selenium Exposure

Mitigation/Source Control Practice	Description
• Stream Alteration	• Stream alteration involves obstructing, diminishing, modifying, or otherwise relocating the natural shape or direction of flow of a stream to prevent infiltration through disturbed material and leaching to groundwater or surface water (United States Department of the Interior: Bureau of Land Management, 2005; NewFields, 2006). Stream alteration is an option when a flow needs to be diverted away from a mine pit, overburden pile, sedimentation pond, or other materials that may leach selenium into the stream (NewFields, 2006). Stream alteration design should provide for an adequate supply of water to downstream aquatic habitat and ensure there is no leaching from seeps from waste rock areas (United States Department of the Interior: Bureau of Land Management, 2005).
• Habitat Management	• Habitat management may involve practices such as selecting vegetation for reclamation planting with low uptake of selenium. Planting low accumulators of selenium as reclamation plants minimizes exposure of selenium to grazing receptors (C.E. Jones & Associates, 2006; NewFields, 2006). An example of a habitat enhancement is creation of a new wetland to encourage wildlife in areas with low levels of selenium, or to create habitat improvements to fisheries (Chapman et al., 2009b).
• Institutional Controls to Minimize Access	• Institutional controls such as erecting fencing around areas that pose a potential risk of selenium exposure. This is not applicable for large areas where maintaining fencing is prohibitive. Other examples of controls include providing an alternative water source to wildlife impacted by mining activities, construction of steep sides on ponds to discourage wildlife feeding there, opting not to stock pit lakes with fish; and installation of fish migration barriers (NewFields, 2006; Chapman et al., 2009b). Vegetation mitigation includes but is not limited to mowing, farming, exclusion fencing, and fences to divide areas of influence containing excess selenium.
• Pit Water Management	• Prevent pit water in active pits from coming into contact with surface water by diverting to inactive pits or pit backfill (United States Department of the Interior: Bureau of Land Management, 2005).
• Backfill Operations	• Practices such as placing the partial backfill of final pit to cover ore outcrop and shales and developing runoff recharge areas away from high seleniferous materials within pits (United States Department of the Interior: Bureau of Land Management, 2005).
• Monitoring for Selenium	• Monitoring can be conducted to determine low seleniferous materials to use for cover, road materials, etc. (United States Department of the Interior: Bureau of Land Management, 2005). Selenium in overburden and backfill can be monitored based to determine whether special handling is required.

TABLE 5-2
Examples of Mitigation and Source Control Practices Used Within the Mining Industry to Minimize Selenium Exposure

Mitigation/Source Control Practice	Description
• Chemical Stabilization	• For concentrated sources of selenium or where waste rock quantities are manageable and the selenium has not been completely oxidized to selenate the addition of a chemical adsorption agent such as ferrihydrite has shown promise in adsorption of selenium and reducing the mobility or leachability to water (J. McHale, personal communication, March 5, 2010).
• Selective Handling of Waste Rock	• Geologic materials containing elevated concentrations of selenium are separated from other run-of-mine overburden and managed differently so as to minimize the “weathering effect” and thereby reducing the potential for mobilization of selenium into the environment. Often these materials containing elevated concentrations of selenium are placed back into a pit.

Examples of various mitigation and source control practices are presented below.

5.2.3.1 Stream Alteration, Smoky Canyon Mine (Idaho)

An example of a mitigation technique implemented to prevent exposure of selenium to downstream ecological receptors is diversion of the Pole Canyon Creek at J.R. Simplot’s Smoky Canyon mine, which involved construction of a 30-inch pipeline to divert Pole Canyon Creek around the waste rock overburden disposal area to prevent the creek from following through an overburden pile and thereby leaching selenium into the downgradient discharge. The project also involved construction of an infiltration basin and a run-on control channel to prevent water from coming into contact with the disposal area (Kaufmann, 2009).

5.2.3.2 Pit Backfill Operations, Powder River Basin (Wyoming)

Powder River Basin Coal Company’s Caballo Mine is a coal mine located outside of Gillette, Wyoming in the Powder River Basin. Monitoring wells have been installed in the backfill areas to monitor selenium levels over time (Murphree, 2005). Selenium concentrations have generally been highest in the shallow backfill wells where mining took place in or adjacent to stream channels with a thin overburden layer. Selenium concentrations have ranged from below detection to 878 µg/L (Murphree, 2005). As mining progressed in areas farther away from the natural alluvial areas, it was observed that backfill area wells showed an improvement in water quality for selenium. Selenium concentrations have been observed to decrease as more saturated and reducing conditions develop and have decreased to below detection limits in some areas. A spike in selenium concentration was observed when drying of the reclaimed stream channel occurred, where selenium concentrations in backfill wells increased from approximately 100 µg/L up to 800 µg/L before decreasing again in subsequent sampling (Murphree, 2005).

5.2.3.3 Sediment Leach Testing, Coal Mine (British Columbia)

Sediments from Coal Mountain (Corbin Pond) and Elkview Operations at Teck Coal Limited were investigated to determine whether selenium has the potential to leach from the sediments cleaned out of their settling ponds. Two laboratory leach tests were performed, with and without recirculation. Recirculation simulated percolation through many layers in a waste rock dump. Selenium was leached from the decant pond sediments only during the "no recirculation" scenario. The results of this study indicate that sediments may require placement in a manner to mitigate direct release of selenium to the watershed (Brienne et al., 2009).

5.2.3.4 Chemical Stabilization, Coal Mine (West Virginia)

Source control of selenium through chemical stabilization and capping (tested by Patriot Coal working in conjunction with the West Virginia Water Research Institute at West Virginia University) has shown promise for management of selenium by reducing mobility. Chemical stabilization of overburden from Patriot Coal's Appalachian-based surface mines has been pilot tested on processed waste rock that has not been fully oxidized. Chemical stabilization with ferric iron based materials appears to result in adsorption of the selenite, thereby preventing further oxidation to selenate, as well as significantly reducing the mobility of the selenium when exposed to water (J. McHale, personal communication, March 5, 2010).

5.2.4 Treatment Approaches

This section illustrates various treatment approaches the mining industry is pursuing in an effort to treat selenium in mining-influenced waters and related process waters. This section focuses on case studies of pilot studies to achieve an effluent concentration of less than 5 µg/L of total selenium. The information presented within this section is based on a combination of questionnaire responses from NAMC-SWG members on their selenium treatment systems and literature on the treatment systems. Full-scale implementation of treatment for selenium has been implemented at several facilities for biological treatment, reverse osmosis, and iron co-precipitation. These have been described in Section 4.

5.2.4.1 Case Study: Pilot Studies for Various Technologies, Coal Mine (West Virginia)

Several pilot studies have been conducted at Patriot Coal for selenium removal at two of their surface mining sites (Site A and B), including:

- Reverse Osmosis
- ABMet® Biological Treatment
- VSEP® Membrane Technology
- ZVI

Reverse Osmosis. At Site A, a pilot study was conducted on the effluent from a valley fill sedimentation pond at a surface coal mining operation to better understand selenium removal by RO. The 20-US gpm (75 Lpm) RO system was run at a recovery of 75% and selenium concentrations were reduced from 30 µg/L in the influent to 2.5 µg/L in the effluent, within the target effluent concentration of 5 µg/L. However, within three days of operation, significant fouling was observed in the cartridge filters upstream of the RO stream and they had to be replaced with new filters. With time, the RO system had to be operated at a higher inlet pressure in order to maintain membrane flux, indicative of membrane surface fouling due to scaling or particulate matter. The pilot was run only for a two-week period because of the fouling issues and it was concluded that an UF or MF system or similar pretreatment would be prerequisite for using RO treatment for selenium at this site. The other main limitation with this option is management of the resulting RO brine concentrate in selenium and other constituents.

ABMet® Biological Treatment Technology. At Site A, a pilot study was conducted on mining-influenced water to better understand selenium removal by the ABMet® technology. The ABMet® pilot system was tested for a 3-month period for flow rates of 1-, 2-, and 3-US gpm (3.8 to 11-Lpm) and selenium concentrations were consistently reduced from average influent concentration of 43 µg/L to less than 5 µg/L in the effluent. The main conclusions of the pilot study were that the ABMet® system was able to meet the selenium treatment requirements and no major process or operational limitations were observed during the pilot test. However, operational issues that may be encountered during scale-up of the system are unclear.

VSEP® Membrane Technology. At Sites A and B, a 4-month pilot study was conducted by New Logic Research on mining-influenced water to test selenium removal by their RO system using a unique vibratory sheer enhanced process (VSEP®). The 2-stage pilot VSEP® units were tested for a flow of 1-US gpm (3.8 Lpm) at the two outfalls with an average influent selenium concentration of 50 µg/L. At an average overall recovery of 95%, the initial results showed that the system was able to remove the effluent concentration to below the target concentration of 5 µg/L. However, with time, membrane fouling issues were observed even with the addition of proprietary anti-scalant and pH adjustment to an acidic pH. This resulted in reduced permeate-specific flux but also caused the selenium concentrations in the effluent to gradually increase. A third-stage conventional spiral wound RO system was utilized to provide polishing to the VSEP® permeate from the first two stages. Fouling issues also resulted in more frequent replacement and cleaning of the membrane units than expected. Similar to conventional RO, this option requires management of the resulting VSEP® brine and spent cleaning solution concentrated in selenium and other constituents.

Zero Valent Iron. At Patriot Coal's Site A, a pilot study was conducted on mining-influenced water to better understand selenium removal by a ZVI system. The 12-US gpm (45 Lpm) pilot system was a 3-stage system with each stage consisting of a tank containing iron fiber media (e.g., steel wool) with a capacity to remove 40% of the influent selenium in 4.5 hours. The pilot was run for a period of one year at different conditions and the optimized system was able to remove selenium to below the target effluent concentration of 5 µg/L from an influent concentration of 20 µg/L. The main operational issues were the elevated levels of soluble and insoluble iron in the effluent that had to be oxidized and separated from the discharge and the replacement of the iron media every 3 to 4 months. TCLP tests on the spent iron media showed that the solids were not hazardous. Issues associated with full-scale implementation of this technology include effectiveness at higher influent selenium concentrations, presence of other competing oxyanions and large footprint. Figure 5-5 shows the Matric Research foam impregnated with ZVI pilot-scale system. Figure 5-6 shows the Shipshaper, LLC pilot-scale ZVI system using steel wool. The rust-colored sedimentation pond water with curtain baffles shown in Figure 5-5 is in part due to the presence of iron from the discharge of the ZVI pilot system.

FIGURE 5-5
ZVI Pilot Test using Iron-Impregnated Foam as ZVI Media
Source: Patriot Coal

FIGURE 5-6
ZVI Pilot Test using Steel Wool as ZVI Media
Source: Patriot Coal

5.2.4.2 Case Study: Pilot Study for Passive Biochemical Reactor Treatment for Gravel Pit Seepage (Colorado)

Golder Associates conducted a 12-month pilot study between 2008 and 2009 for a single solid-phase passive biochemical reactor cell. The study took place in western Grand Junction, CO at a sand and gravel operation along the Colorado River. Seleniferous soils are present due to the Mancos shale within the area. Groundwater is naturally basic and saline in the Grand Valley of Colorado. The study focused on treating seleniferous groundwater from a groundwater interception trench at the sand and gravel facility.

A study was initially conducted from July to November 2006 to test various conditions. Four 55-gallon (208-liter) bioreactors were constructed with varying amounts of cow manure, hay, sawdust, wood chips, limestone, and ZVI (Pahler et al., 2007). The flow rate varied but was approximately 2-US gpm (7.5 Lpm). The highest removal rates were observed using a HRT of 12 hours. Of the four reactors tested, one of them contained no ZVI. This reactor maintained the highest removal efficiency during testing after an initial four weeks of testing. As the ambient temperature decreased during testing, selenium efficiency dropped to below 90% in some reactors but remained above 95%in the reactor without ZVI. The influent contained approximately 28 µg/L of selenium with 57% as selenite, 14% selenate and 29 µg/L organoselenium compounds. Figure 5-7 contains a photo of the study.

FIGURE 5-7
Passive Biochemical Reactor Test
Source: Pahler et al., 2007

Based on the results of this testing, a 12- month pilot study was conducted between 2008 and 2009. The approximate footprint of the pilot-scale system was 2,500 square feet (232 square meters). The flow rate of the pilot study varied between 2 to 24-US gpm (7.5 to 90 Lpm) and the hydraulic residence time varied between 12 to 72 hours. The influent selenium concentration ranged between 5 and 80 µg/L with an average concentration of 34 µg/L. Effluent selenium removal varied between 31% and 98% with an average 85% removal. An observation during pilot testing was that 4 to 6 weeks of incubation time is required and a low flow rate was required to achieve a microbial population to adequately remove selenium at a higher flow rate.

The advantage of this system is minimal operational requirements. A total 80 hours of operational labor was required outside of sampling and analysis to maintain the system during the 12-month pilot study. The only energy requirement was for an influent pump to pump groundwater from the interceptor trench to the pilot cell. Labor associated with maintenance centered on servicing of the pump. The media is removed at the completion of the test for disposal. This is the only waste disposal requirement for this test.

5.2.4.3 Case Study: Pilot Study for Passive Biochemical Reactor Treatment for Mining-Influence Water, Coal Mine (Alberta)

A pilot-scale study was performed by Golder Associates at Teck Coal Limited's Cardinal River Operations mine in Alberta, Canada. The pilot-scale system was designed based on results of bench-scale testing performed. The 0.3-US gpm (1-Lpm) bench-scale biochemical reactor was constructed upstream of the West Jarvis Pond at Cardinal River Operations mine. Results of bench-scale testing performed over 12 weeks (April to June) showed that selenium was removed up to 80 to 90% through the biochemical reactor set-up, depending on the types of organic carbons sources used.

Based on the positive results from the bench-scale test, a 5.79-US gpm (22 Lpm) pilot-scale system was designed and constructed at another location just upstream of Leyland Pond at the former Luscar Mine site at the Cardinal River Operations. Figure 5-8 shows a conceptual block diagram for the pilot-scale test. The seepage flow was captured from the toe of mined rock spoil. It was trenched underground to feed into the bioreactor which is in an up-flow design. The cell is located approximately 600 feet (183 meters) from the toe of the waste dump. The bioreactor is composed of various amounts of local sources of organic carbon and nutrients. A total of 265 cubic yards (203 cubic meters) of organic material is contained within the passive biochemical reactor cell. The average influent temperature is 43 °F (6 °C).

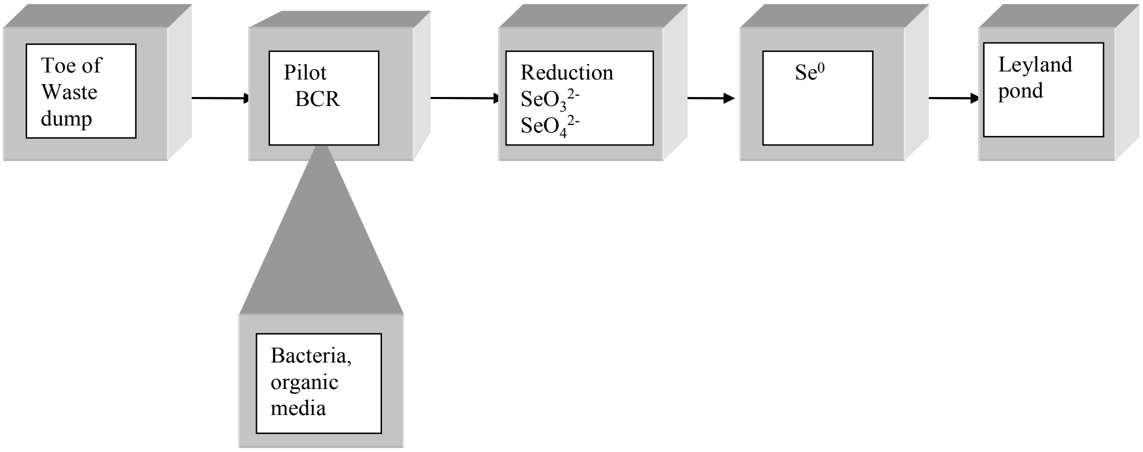


FIGURE 5-8
Pilot-Scale Passive Biochemical Reactor Flow Diagram Seep Flowing into Pond
Source: Teck Coal Limited

Greater than 90% of the total selenium present within the seepage flow is in the selenate form. Monthly sampling was conducted on the influent and effluent of the pilot-scale system and is shown in Figure 5-9. The pilot test was operated from November 2008 through November 2009. At the time of this report, 40 weeks of data was available for the pilot-scale system.

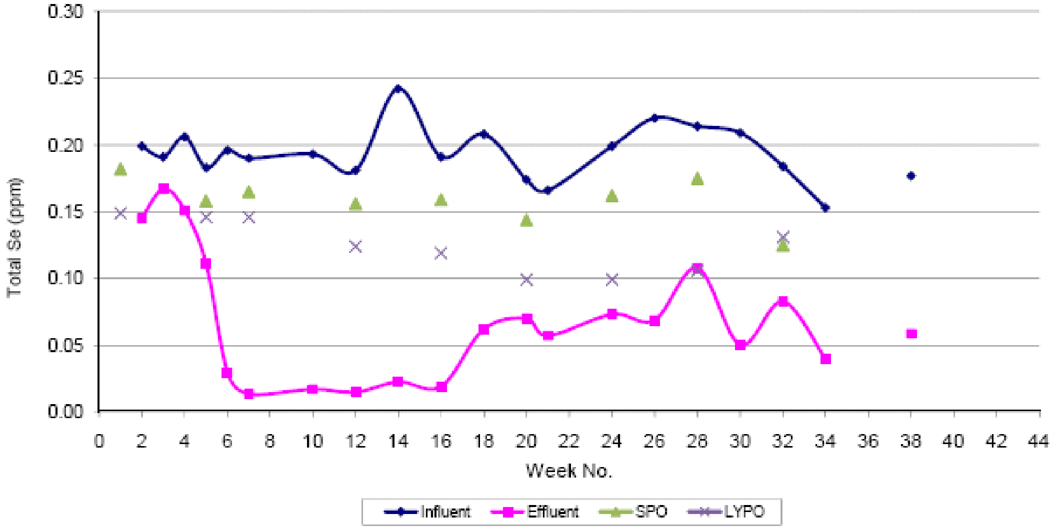


FIGURE 5-9
Pilot-Scale Passive Biochemical Reactor Selenium Concentrations (Preliminary Data)
Source: Teck Coal Limited/ Golder Associates

Figure 5-10 includes flow and HRT information. The test began in early November where the ambient temperature at Cardinal River Operations was approximately -20 °F (-29 °C).

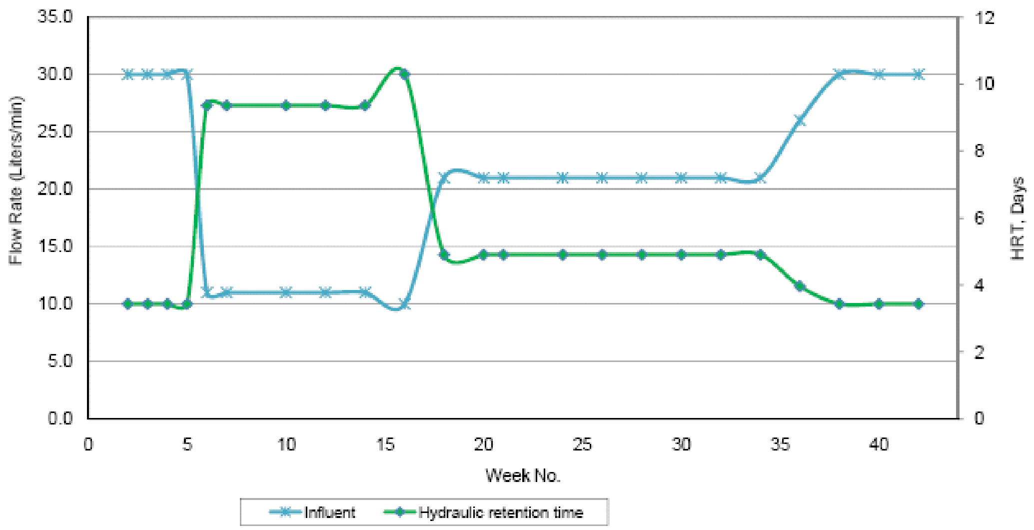


FIGURE 5-10
Pilot-Scale Passive Biochemical Reactor Flow and Hydraulic Retention Time (Preliminary Data)
Source: Teck Coal Limited/ Golder Associates

High nitrate levels were encountered in the influent during the pilot study that were not encountered during the bench-scale study since the pilot study was located in a different area of the Cardinal River Operations. Selenium removal is affected by nitrate removal. Nitrate removal is microbially favored over selenium removal so selenium was not removed until nitrate was reduced.

5.2.4.4 Case Study: Full-Scale Chemical Treatment System, Zinc Refinery (Quebec, Canada)

A full-scale treatment system was installed in 1998 at an Xstrata zinc refinery to treat a weak sulfuric acid bleed stream from three sulfuric acid plants. Zinc concentrates contain selenium, which is released in the offgas at a roaster plant. Selenium is retained in a weak sulfuric acid solution during offgas treatment (Monteith et al., 2000). The treatment system is designed to treat selenite, and does not effectively treat selenate. The selenium in the weak acid solution is present in the selenite form.

The system is a patented two-stage process CEZinc (Geoffrey et al., 2008). In the first stage, sodium sulfide is added to remove dissolved mercury. In the second stage, sodium dithionite is added to remove selenite. The effluent from the plant is then combined with other plant effluents and treated in a facility wastewater treatment using lime addition before discharge. The flow rate of the system is 110-US gpm (415 Lpm) and the hydraulic residence time is up to 20 hours. The footprint of the treatment system is about 4,000 square feet (372 square meters), excluding sludge storage. Figure 5-11 shows a process flow diagram of the process.

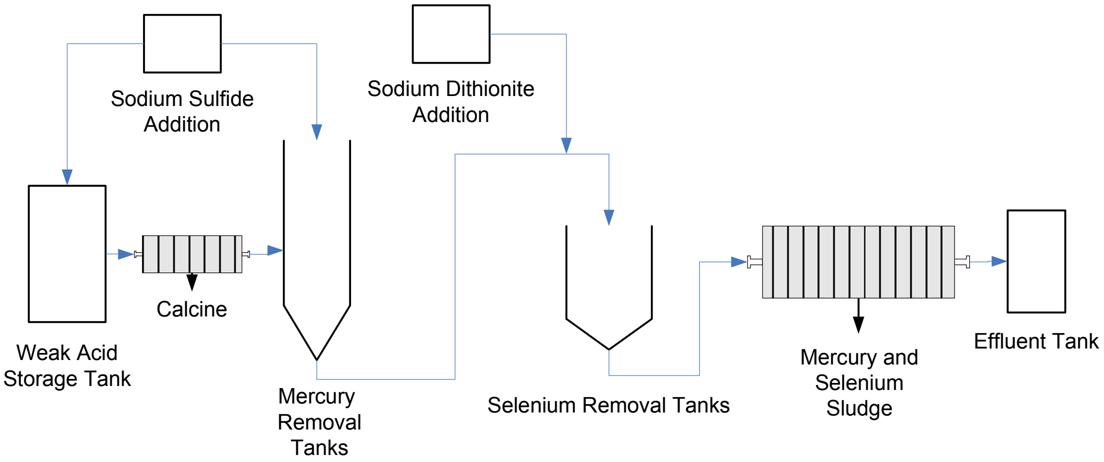


FIGURE 5-11
Process Flow Diagram for Treatment of a Weak Acid Solution Containing Mercury and Selenium
Source: Adapted from Geoffrey et al., 2008

Equation 5-1 illustrates the reaction between selenite and sodium dithionite in a sulfuric acid solution that precipitates to elemental selenium.

$$H_2SeO_3 + 2H_2SO_4 + 2Na_2S_2O_4 \rightarrow Se(s) + 4SO_2 + 2Na_2SO_4 + 3H_2O \quad \text{(Equation 5-1)}$$

The influent selenium concentration ranges from 20 to 450 mg/L, with an average concentration of 200 mg/L. The maximum effluent of the system is 3.5 mg/L. Selenite is reduced to its elemental state using sodium dithionite as long as the dithionite to selenium ratio is in excess of 2 and the pH < 1.7 (Geoffrey et al., 2008). Sodium sulfide can also be used in place of sodium dithionite to precipitate selenite from single metal solutions. However, if mercury is present, selenite removal is less efficient (Geoffrey et al., 2008).

The capital and operating costs of the full-scale treatment system are shown in Table 5-3. The treatment system is labor intensive due to the lack of automation for the sludge dewatering system.

TABLE 5-3
Capital and Operating Costs of the Selenium Removal System at Xstrata Zinc

Costs
• Capital Cost: $ 10 to 12 million
• Labor: $300,000 per year
• Chemical: $700,000 per year
• Maintenance: $50,000 per year
• Energy: unknown
• Sludge Handling and Disposal: $60,000

Note: Costs are in United States Dollars (2008)
Source: Xstrata Zinc

5.2.4.5 Case Study: Full-Scale Chemical Treatment System, Uranium Mine (Saskatchewan, Canada)

A full-scale treatment system that employs chemical treatment at a mining facility in Canada has observed selenium removal. Although the system was not designed for selenium removal, selenium removal is achieved through the treatment system. Figure 5-12 shows a process flow diagram of the tailings neutralization circuit and Figure 5-13 shows a process flow diagram of the main wastewater treatment plant. The flow rate of the tailings neutralization circuit treats about 370-US gpm (1,400 Lpm) and the main treatment plant treats a flow of 750 to 925-US gpm (2,800 to 3,500 Lpm). The HRT of the plant is 2 to 3 hours. The tailings neutralization circuit treats raffinate and spent regenerant solution. The main water treatment plants treats process flows consisting of the tailings thickener overflow and tailings management facility pond water. Selenium removal efficiency is very sensitive to residence time, ORP, and pH. Surging conditions can also cause complications. The tailings neutralization facility treats an influent selenium concentration of 90 µg/L to an effluent concentration of 20 µg/L, with a removal efficiency of almost 80%.

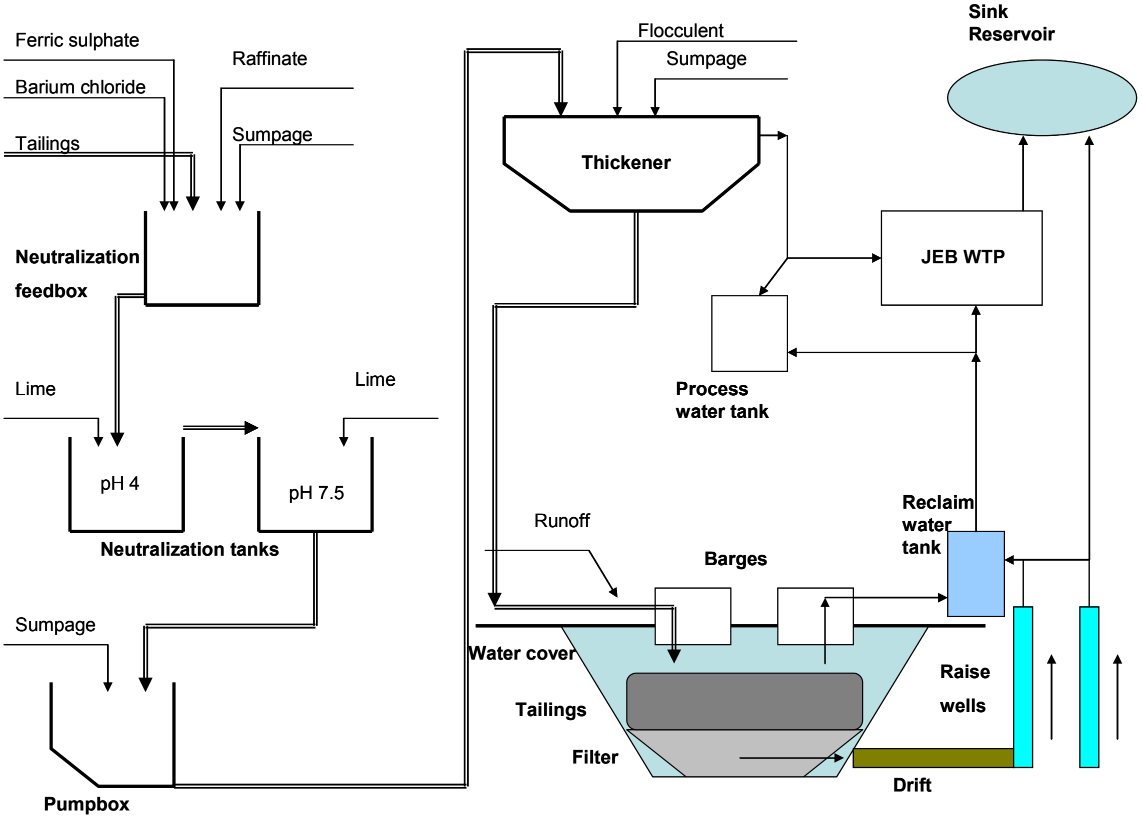


FIGURE 5-12
Tailing Neutralization Circuit Process Flow Diagram
Source: Areva Resources Canada

The main water treatment plant flow diagram is shown in Figure 5-13. Lime slurry is added to a pH of approximately 11 to precipitate metals such as nickel. Air is added to oxidize and strip radon gas. The effluent of the hydroxide precipitation tanks flows to a clarifier, where the overflow flows to radium/arsenic reaction tanks. Sulfuric acid is added to achieve a pH of 4.5 and barium chloride is added to precipitate radium. Ferric sulfate is then added to precipitate arsenic, molybdenum and selenium. The effluent of the reaction tanks flows to a clarifier, where a coagulant is added. The overflow from the clarifer flows to radium polishing tanks where barium chloride is added to precipitate residual radium. Lime is added to raise the pH to approximately 8 to precipitate residual metals. The effluent of the reaction tanks flows to a clarifier where a coagulant is added to enhance precipitation. The overflow from the clarifier flows to monitoring ponds. The sludge from the clarifiers is handled separately.

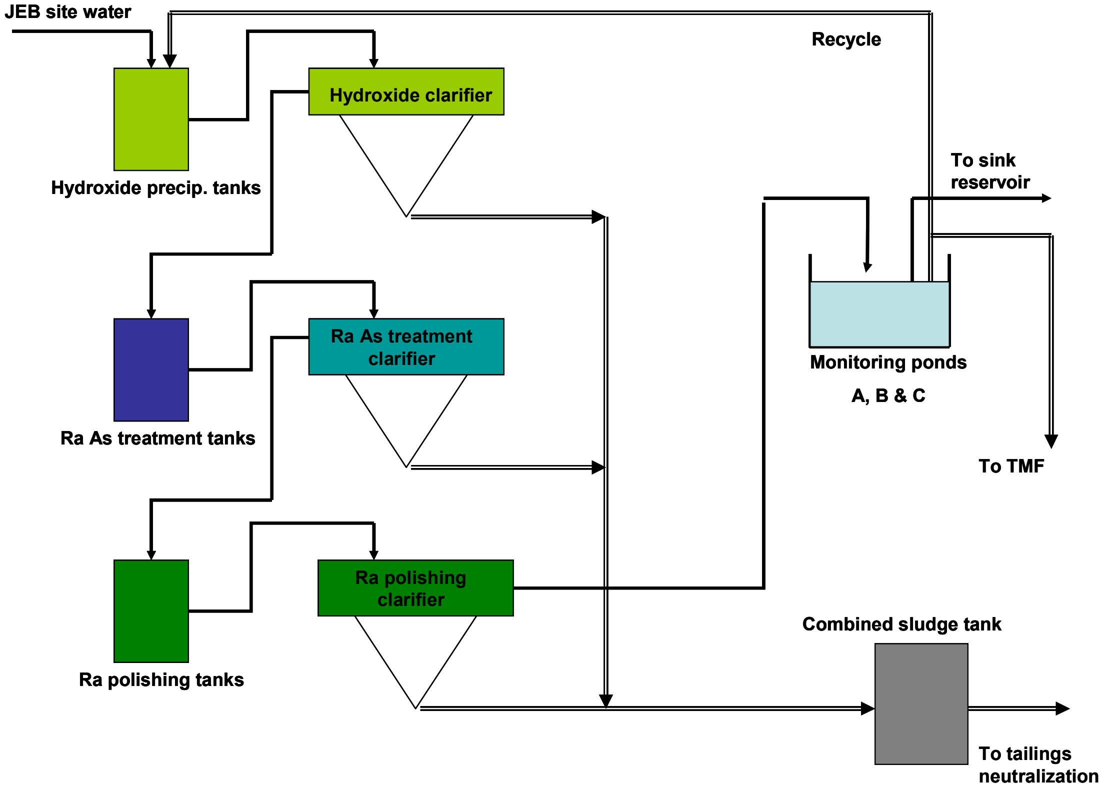


FIGURE 5-13
JEB Water Treatment Plant Process Flow Diagram
Source: Areva Resources Canada

The main treatment plant treats an influent selenium level of 7 µg/L to an average effluent selenium level of 4 µg/L (43% removal efficiency). Complications at start up included inadequate mixing of waste streams with added reagents. A lesson learned from start up of the system is that selenium removal is fundamentally linked to the addition of iron.

5.2.4.6 Case Study: Biochemical Reactor Treatment for Mining-Influenced Water, Smoky Canyon Mine (Idaho)

Various bench-scale and pilot-scale studies have been conducted at J.R. Simplot's Smoky Canyon mine to treat selenium in water from operations. Phosphate ore at the Smoky Canyon mine is milled at the mine site, processed into concentrated slurry, and pumped 86 miles (138 kilometers) to a fertilizer manufacturing facility. The mine has been in operation since 1982. Concentrations of selenium in a French drain which underlies the Pole Canyon

Overburden Disposal Area (ODA) vary from below detection limits at the inlet to near 680 µg/L at the outlet (Bond, 2000).

Based on successful bench-scale testing, a series of field studies were completed on the Pole Canyon ODA. Munkers (2000) added cheese whey (carbon source) and granular iron to the surface of test fields in the overburden area. Although initially selenium removal was observed in samples collected using lysimeters, removal decreased over time. Munkers (2000) also amended the subsurface (approximately 10 feet below ground surface) of this ODA with a mixture of granular iron and potato waste. Up to 80% removal of selenium was observed in pore water concentrations in comparison with the control. A 200-foot (60-meter) long trench lined with powdered ZVI was also installed just above the toe of the ODA. Approximately 10,000 gallons per day (37,850 liters per day) of cheese whey were added to a trench installed for one week and selenium concentrations exiting the ODA decreased to approximately 50 µg/L. Concentrations quickly rebounded when addition of whey was stopped, indicating a need for a continuous source of carbon to maintain treatment of selenium.

A second pilot study was performed in 2001 at the same Pole Canyon ODA (NewFields, 2006). A 4,000-gallon (15,000-liter) bioreactor was loaded with approximately 100 pounds (45 kilograms) of seep sediment for a selenium-reducing bacteria source, 400 pounds (180 kilograms) of powdered iron, and filled with plastic bio-rings (Möller, 2002). The flow rate of the seep into the bioreactor was 0.5-US gpm (1.9 Lpm) and the residence time of the bioreactor was roughly 5 days. During the first 3 months of operation, cheese whey was used as a carbon source while compost was used during the latter 3 months. Approximately 10 gallons (38 liters) of cheese whey were added once each day during the first 3 months of operation. Cheese whey achieved roughly 75% reduction of selenium in seep water while the compost achieved greater than 90% reduction (NewFields, 2006). Inlet seep concentrations were between 500 to 2,000 µg/L of selenium throughout the six-month test. The test was conducted at approximately neutral pH, with an inlet alkalinity of 380 mg/L and a temperature of approximately 50 °F (10 °C). BOD levels entering and exiting the bioreactor were measured. The influent BOD concentration was approximately 10 mg/L whereas the effluent was approximately 650 mg/L, indicating the cheese whey was completely consumed by microbes within the bioreactor (Möller, 2002).

5.2.4.7 Case Study: Constructed Wetlands, Powder River Basin (Wyoming)

The North Antelope Rochelle Mine is a coal mine located on the eastern flank of the Powder River Basin in Campbell County, Wyoming. The mine was required to reclaim the alluvial valley floor of Porcupine Creek based on their permit with the Wyoming Department of Environmental Quality/Land Quality Division. The reclamation took place at several stages. The first stage occurred in 1985-1986 and including re-construction using salvaged alluvial material (Murphree, 2003). The native material and topsoil placed on the channel limited infiltration. In addition, monitoring wells were constructed in the area and high TDS and selenium concentrations were observed in monitoring wells. Selenium concentrations as high as 932 µg/L have been observed in monitoring wells but have generally ranged from below detection to 200 µg/L. TDS levels range from 3,800 to 25,320 mg/L. The pH ranges from 6.2 to 7.9 and the alkalinities are high (411 to 944 mg/L), typical of wells in the Southern Powder River Basin (Murphree, 2003). In 2002-2003, a diversion which bypassed Porcupine Creek was removed and pools, counter-weirs and constructed wetlands were added which significantly reduced selenium levels within Porcupine Creek. Boron levels initially spiked upward but decreased soon afterwards. Selenium levels have significantly decreased since April 2002 (Murphree, 2003).

Groundwater levels within the area have risen since the construction of the pools and counter-weirs. Previously, selenate was the main species of selenium observed in monitoring wells. Since construction of the pools and wetlands, selenite has been observed in monitoring wells, indicating reduction of selenate occurring within the wetlands. Sulfate-reducing bacteria have been detected in backfill monitoring wells (Murphree, 2003).

6.0 Industry-Specific Approaches to Managing Selenium: Power Generation Sector

6.1 Overview of Sources and Fate of Selenium in Coal-Fired Power Plants

Selenium is a naturally occurring trace element in coal. As coal is combusted, selenium can partition into solid, liquid and vapor phases. Figure 6-1 illustrates the fate of selenium at coal-fired power plants.

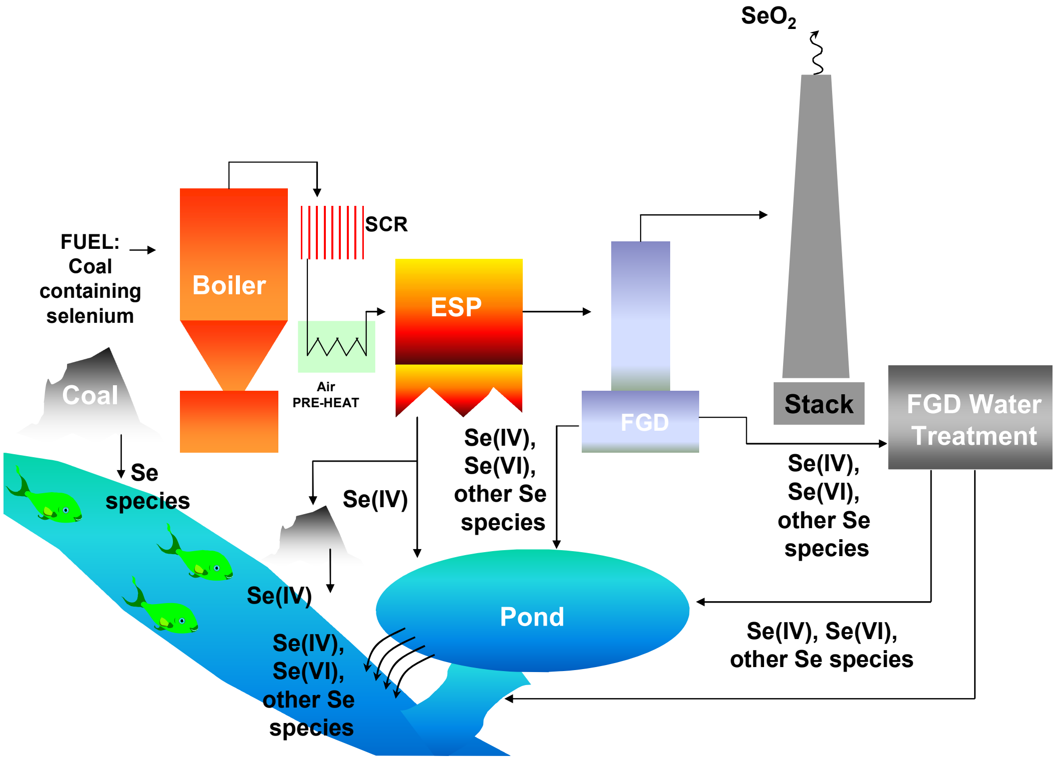


FIGURE 6-1
Fate of Predominant Selenium Species in Coal-fired Power Plants
Source: Electric Power Research Institute

In solid form, selenium is found primarily in fly ash, most of which is separated from the flue gases by electrostatic precipitators (ESPs) prior to flue gas desulfurization (FGD). In vapor form, selenium is likely present as a volatile metal in flue gas as selenium dioxide (SeO_2) and may be captured by the wet FGD system. Selenium may be present in the liquid phase in various water streams throughout a plant, including the following:

- **Wet flue gas desulphurization:** Most wet FGD scrubber systems periodically blow down or purge a portion of the absorber slurry to limit buildup of chlorides and suspended solids. For many of these systems, the blowdown represents a new liquid stream that requires some treatment for solids removal and, in some cases, removal of potentially toxic trace elements such as selenium.

The FGD purge stream contains a slurry of water, dissolved solids, and suspended solids (mainly calcium sulfate [gypsum] or calcium sulfite solids), fly ash, and inert constituents from limestone. The purge is separated into coarse (typically > 0.1 mm) and fine solid fractions (< 0.1 mm), usually using hydrocyclones, and the coarse fraction is dewatered by vacuum belt filters or settling ponds. Figure 6-2 shows an example of a limestone forced oxidation FGD scrubber system, which is one of many possible configurations.

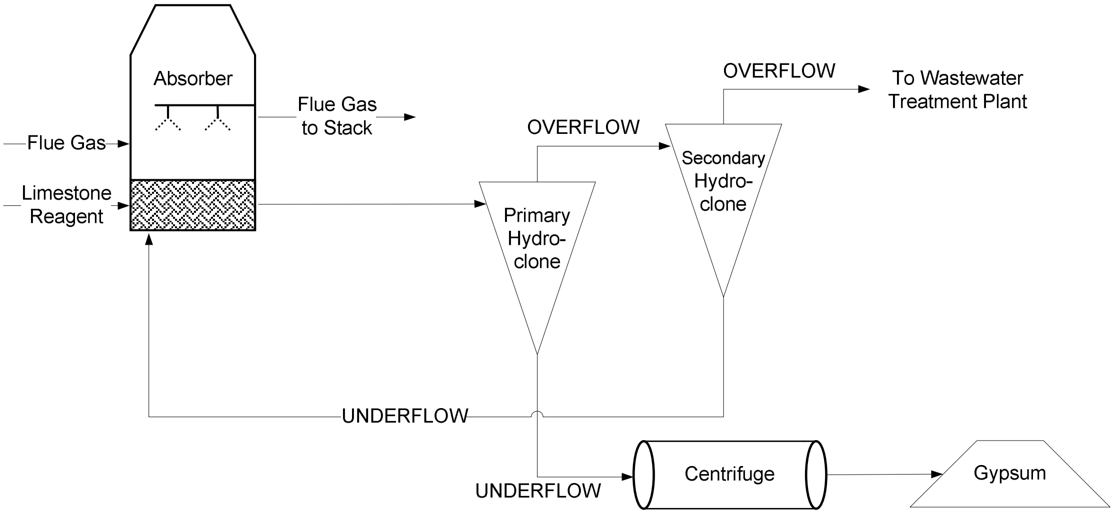


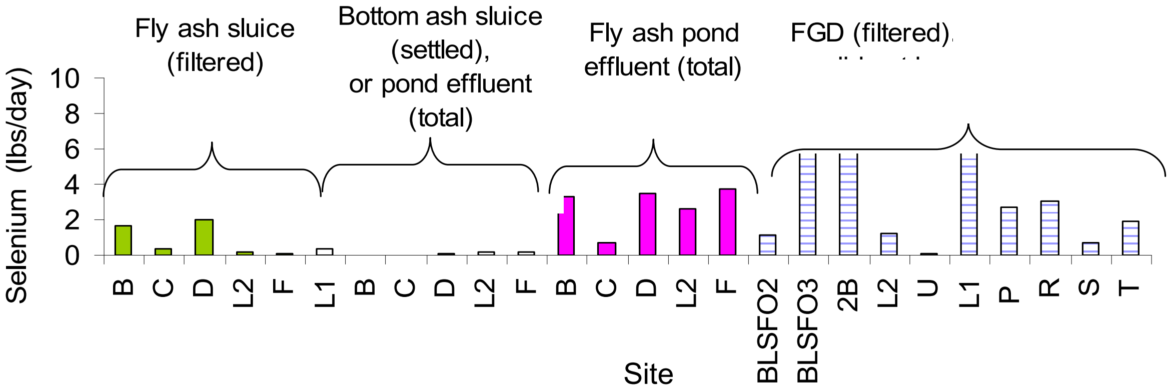
FIGURE 6-2
Limestone Forced Oxidation Flue Gas Desulphurization System Example Configuration

- **Fly ash sluice water and ash pond water:** Selenium in coal is volatilized during combustion to SeO_2 in the flue gas (EPRI, 2007b). As the flue gas cools, a portion of the selenium condenses onto the fly ash. Wet fly ash handling operations involve sluicing fly ash with water to a pond for disposal. The fly ash sluice water is sent to a pond to settle suspended solids and metals prior to discharge. A fly ash pond may receive other process liquid streams such as untreated or treated FGD water that may also contain selenium.

- **Other streams:** Other wastewater streams that contain selenium include bottom ash ponds, fly ash leachate (at plants that handle fly ash, dry and send it to on-site landfills), FGD landfill leachate, coal pile runoff, economizer ash sluice water, and other low-volume water streams. These streams contribute a smaller mass load of selenium as compared to fly ash ponds or untreated FGD water at a typical coal-fired power plant.

Facilities surveyed during this study use various sources of coal, with one facility reporting using coal from approximately 40 sources. Selenium levels in coal used in coal-fired power plants vary widely and range from 0.5 to 10 mg/kg with a median typically in the 1 to 3 mg/kg range (EPRI, 2005).

Figure 6-3 illustrates a range of dissolved selenium mass load by various streams for various coal-fired power plants. As shown in Figure 6-3, untreated FGD water can significantly increase a site's overall wastewater loading of solids and trace elements such as selenium.



Note: Many sites did not have flow data, so assumed to be 0.2mgd.

FIGURE 6-3
Dissolved Selenium Load in Untreated FGD Water Compared to Other Streams for Power Plants with FGD Systems Installed
Source: EPRI, 2008a.

Untreated FGD water has a highly variable composition and is high in dissolved salts (e.g., total dissolved solids [TDS] typically 2 to 6%) and scale-forming ions (e.g., calcium and magnesium typically in excess of 500 mg/L, sulfate in excess of 1,500 mg/L). Selenium is volatile at the elevated temperatures of flue gasses, and therefore is not efficiently captured by particulate air pollution control devices (electrostatic precipitators or bag houses).

Figure 6-4 shows the partitioning of selenium in untreated FGD water among various power plants. The figure shows the variation in selenium concentrations and partitioning between particulate and dissolved (i.e., operationally defined as < 0.45 µm) forms (EPRI, 2009d; EPRI, 2009e). Particulate selenium may be removed by solids separation processes. However, dissolved selenium may need to be removed by additional chemical or biological treatment, selection of which would depend on the species of the dissolved selenium.

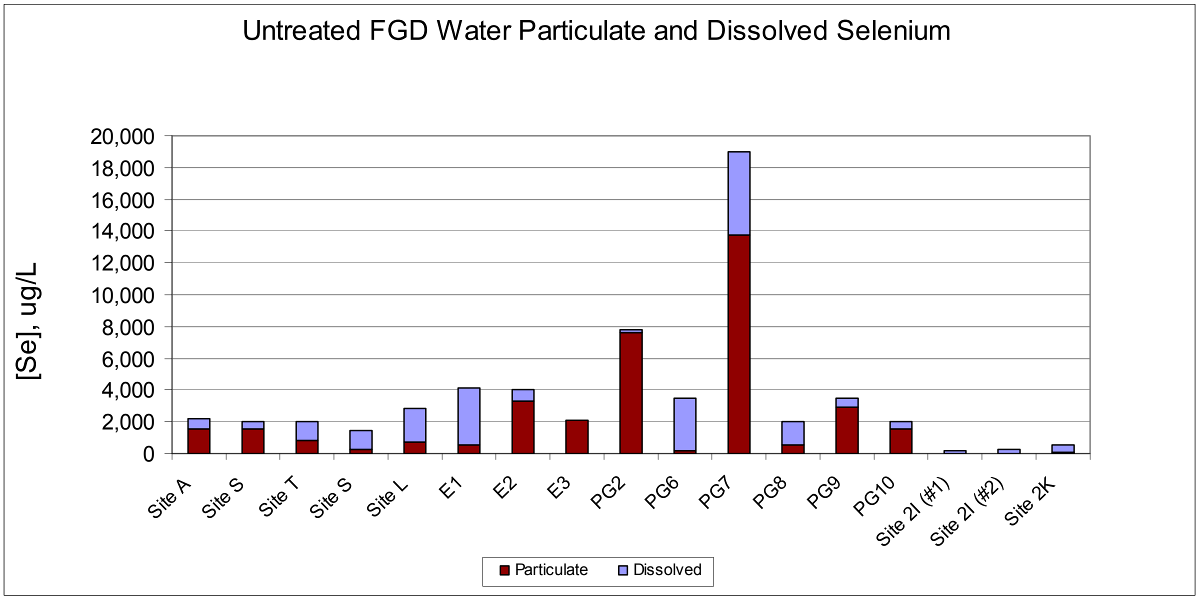


FIGURE 6-4
Dissolved and Particulate Selenium in Untreated FGD Water

The design of an FGD absorber affects the speciation of selenium present in untreated FGD water. There are three main types of wet FGD systems: natural, inhibited, and forced-oxidation systems. Of the wet FGD systems currently in operation in the United States, approximately half are forced-oxidation systems. In addition, the majority of planned FGD systems will also be forced-oxidation systems (USEPA, 2009). While the predominant species of selenium in natural or inhibited oxidation systems appears to be selenite and selenosulfate, selenate is often formed in forced oxidation. Figure 6-5 shows a range of selenium species present for sites that employ forced oxidation.

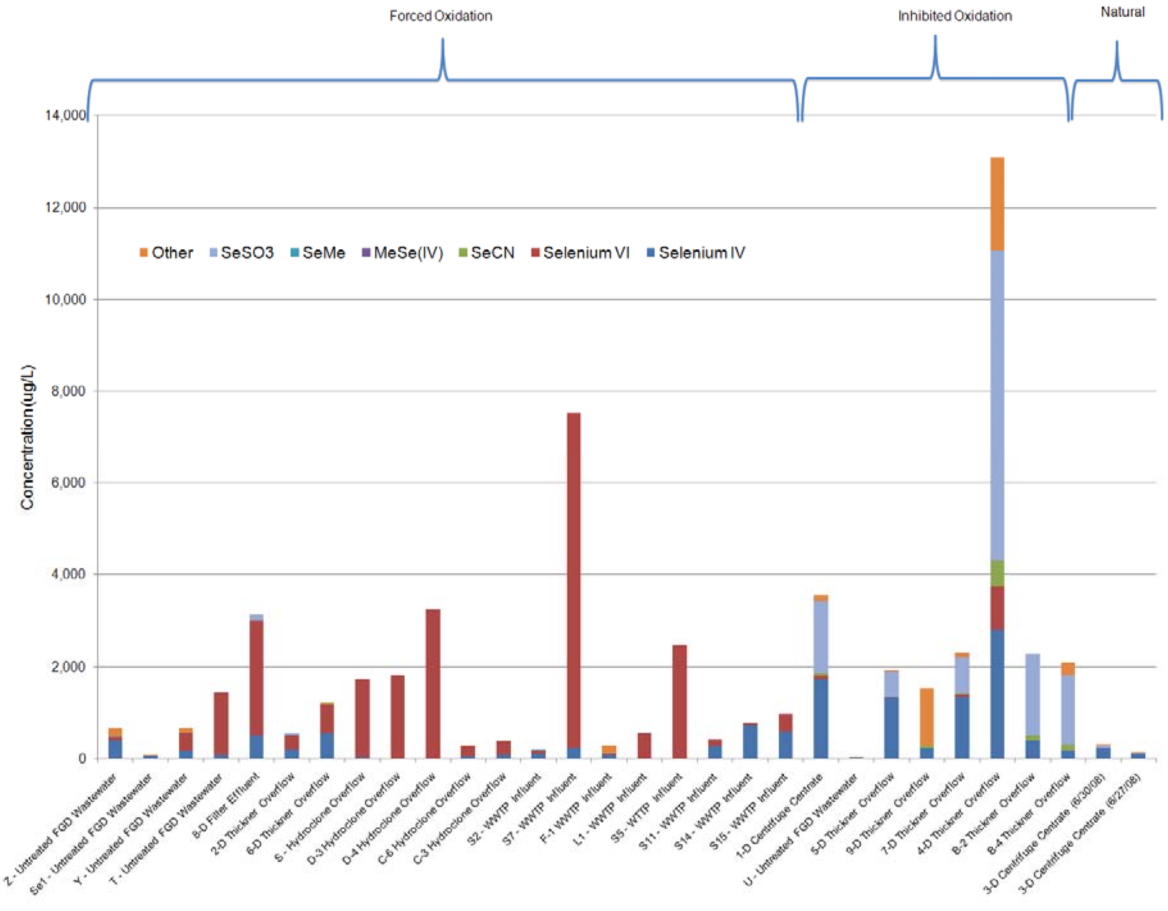


FIGURE 6-5
Effect of Forced Oxidation on Selenium Speciation in FGD System Liquid

The range of oxidation to selenate in the forced-oxidation samples was measured in a previous EPRI study, and was found to vary from very low percentages (<5%) of the total dissolved selenium to 100% (EPRI, 2008a). Factors that may affect selenate conversion within an absorber may include operating conditions of the scrubber such as liquor residence time under forced oxidation conditions, concentrations of metallic catalysts or adsorbents in the scrubber slurry, scrubber operating pH, and ORP of the FGD water (EPRI, 2008a).

6.2 FGD Water Characteristics that Affect Selenium Removal

The predominant form of selenium in fly ash sluice water or in wet FGD systems with natural or inhibited oxidation is selenite, which either forms particulate with metal (predominately iron) oxides present in the wastewater and can be removed through solids separation processes or can be precipitated and removed using iron co-precipitation at slightly acidic pH. However, selenate which is formed in forced oxidation FGD systems is not removed by iron co-precipitation. As significant concentrations of selenate can be present in the purge water from limestone forced oxidation systems, alternatives to iron co-precipitation, such as anoxic biological treatment, are needed. Site-specific knowledge of the selenium species present and species variability as operating conditions of the FGD absorber change is needed to select the appropriate selenium treatment technology.

Table 6-1 shows the range of FGD water characteristics, including parameters that may affect removal of selenium and therefore treatment technology selection (Higgins et al., 2009). The water is supersaturated with calcium sulfate and is hot, mildly acidic and corrosive. Each facility's FGD system is designed to operate at a certain maintained chloride concentration. As a result, the influent of FGD wastewater into the wastewater treatment plant will be at a chloride concentration equal to the design concentration. While chloride concentration of the wastewater may not directly affect selenium removal, it will affect the efficiency and requirements of each technology studied.

TABLE 6-1
Typical Composition of FGD Water

Parameter	Typical Range
Flow	30 gpm to 2,300 gpm
Temperature	125 ºF to 140 ºF (52 ºC to 60 ºC)
pH	4.5 to 9 (typically <7)
Total suspended solids	1.4% to 17%
Sulfate	1,500 to 35,000 mg/L
Chloride	1,000 to 28,000 mg/L
Calcium	750 to 4,000 mg/L
Magnesium	1,100 to 4,800 mg/L
Sodium	670 to 4,800 mg/L
Nitrate	10 to 1,000 mg/L
Total Kjeldahl Nitrogen	2.5 to 58 mg/L as nitrogen

Source: Higgins et al. 2009.

6.3 Prevention and Source Control Strategies for Coal-fired Power Plants

As described in Section 3.0, there are various prevention and source control strategies to reduce or eliminate selenium in effluent discharges at power plants. These practices are summarized within this section.

6.3.1 Conversion from Wet to Dry Fly Ash Handling

Wet sluicing of fly ash to ash ponds is a significant source of selenium to ash pond water. EPRI evaluated four sites and found 85 to 95% of selenium in ash pond influent was contributed by fly ash sluice water (EPRI, 1997a; EPRI, 1997b; EPRI, 1998; EPRI, 1999). This measurement applies to the clarified ash pond water after settling of solids in the ash delta. Conversion to dry fly ash handling will largely, but not completely eliminate this load of selenium. After conversion, there will be some offsetting the reduction due to washdown of fly ash in the ash handling areas and ash landfill leachate (if the landfill is onsite). Other minor contributions to ash pond selenium levels may also continue as a result of bottom ash handling.

It should be noted that these sites did not have FGD systems, which can also be a significant additional source of selenium (EPRI, 2007a; EPRI, 2008a). The loading of selenium from FGD wastewater relative to fly ash handling varies between sites.

6.3.2 Zero Liquid Discharge

In 2008, EPRI compiled an inventory of zero liquid discharge (ZLD) water management systems currently operating at U.S. power generating stations (EPRI, 2008b). The study was not limited to coal-fired facilities but included a large number of gas-fired combined cycle facilities (57% of the facilities documented were gas-fired). Also, the study was not limited to systems treating FGD wastewater. Many of the ZLD systems listed were used for cooling tower blowdown and other waste streams. The report also documented some planned installations that may or may not be completed. The study included the following main ZLD technologies:

- Brine concentrators
- Conventional and specialized reverse osmosis systems
- Evaporation ponds
- Staged cooling towers
- Dry cooling towers

Additional ZLD operations included feeding plant wastewater to the plant's FGD operations, discharging to the sewer, land applications, or deep well injection. No significant correlations were found between power plant fuel type (gas or coal) and the ZLD technologies in use.

Some plants completely recycle their FGD water without creating a purge stream that needs to be treated. Plants that do not produce gypsum for re-sale may be able to operate their FGD systems such that the moisture retained with the landfilled solids entrains sufficient chlorides that a separate purge stream is not required (USEPA, 2009). The ability to purge the untreated FGD water with the gypsum is dependent on the chloride to sulfur ratio of the coal. Most plants do not have the ability to purge the chlorides stream with the unwashed gypsum, particularly if the sulfur levels in the coal are relatively low and the chlorides are high.

Evaporation ponds are typically constructed in a warm, dry climate such as that of the southwestern part of the United States where the evaporation rate of ponded FGD wastewater is greater than the rate of combined wastewater and precipitation inputs (USEPA, 2009).

An underground injection well has been constructed at one facility to discharge FGD wastewater. However, there have been operational difficulties associated with this system.

Fly ash conditioning is performed for dry fly ash handling systems to prevent fly ash from blowing away when it's trucked. EPA's study indicated that only one facility uses FGD wastewater to condition ash, and one other facility uses this in combination with an evaporator (USEPA, 2009).

One facility in the United States currently employs evaporator/crystallizer technology to treat FGD wastewater, with the treatment plant having gone online in 2009. The first step involved is pre-treatment of the FGD wastewater using physical/chemical treatment including clarification, chemical treatment such as with iron and/or sodium sulfide or other organosulfide, and softening to reduce suspended solids, calcium, magnesium, and metals.

The second step involves the use of a falling film evaporator or brine concentrator. Evaporators operate by transferring latent heat from condensing steam across a tube surface to evaporate the FGD wastewater. The influent wastewater is preheated using a heat exchanger that is typically made of titanium plates. Fluoride is typically a problem with ZLD systems employing titanium heat exchangers, due to corrosion of the titanium when in contact with hydrofluoric acid, which is produced when acidifying water containing fluoride.

Brine concentrators are specific types of falling-film evaporators used to treat wastewaters saturated or supersaturated with calcium sulfate or silica (USEPA, 2009). The brine concentrator or falling-film evaporator employs calcium sulfate seed crystal in the circulating brine in the evaporator. This process produces a concentrated wastewater stream and salts. The brine concentrator can typically concentrate the FGD wastewater by 5 to 10 times, which reduces the inlet FGD scrubber purge water volume by 80 or 90%.

6.4 Overview of Technologies Implemented at FGD Water Treatment Facilities

Several technologies have been implemented full-scale at FGD water treatment facilities in the United States to remove particulate and/or dissolved selenium from the wastewater stream. These technologies, which are discussed in detail within this section, fall into three main categories:

- Physical/Chemical Treatment Technologies, in which various configurations are possible:
  - Solids settling (tank-based or settling pond, generally removes particulate selenium).

  - Lime and iron (ferrous chloride or ferric chloride) addition (removes particulate and dissolved selenium predominantly in the form of selenite at pH below 7).

- Biological Treatment:
  - Fixed-film anaerobic/anoxic reactor-based biological treatment (generally removes various selenium species including selenate, as well as other trace elements).
  - Passive treatment: surface-flow wetlands (can remove various selenium species).
- Zero Liquid Discharge Technologies (eliminates FGD water discharge), which includes evaporation, complete recycle, conditioning dry fly ash, and underground injection.

In order to achieve low levels (<50 µg/L) of selenium in the treated FGD effluent, selenium removal is typically required at two stages of the entire wastewater treatment train. Initial physical/chemical treatment can generally achieve selenium concentrations in the low one hundreds µg/L. Follow-up treatment by biological treatment systems is implemented at power plants where lower effluent concentrations are required. The biological systems, which can attain in some cases attain much lower effluent concentrations, require physical/chemical pretreatment for FGD water.

Some facilities have installed tank-based treatment systems to remove solids and metals prior to discharging the FGD water, while others use settling ponds. The USEPA estimates that more than 192 plants will be operating wet FGD scrubbers by 2020 and that 158 of these plants will have water discharges (USEPA, 2009). Of the 53 facilities in USEPA's survey that currently discharge FGD wastewater (USEPA, 2009) 4% use anoxic/anaerobic biological treatment and 2% use constructed wetlands for selenium removal, as shown in Figure 6-6. The other treatment technologies were designed for either solids or metals removal, with some facilities optimized for removal of selenium.

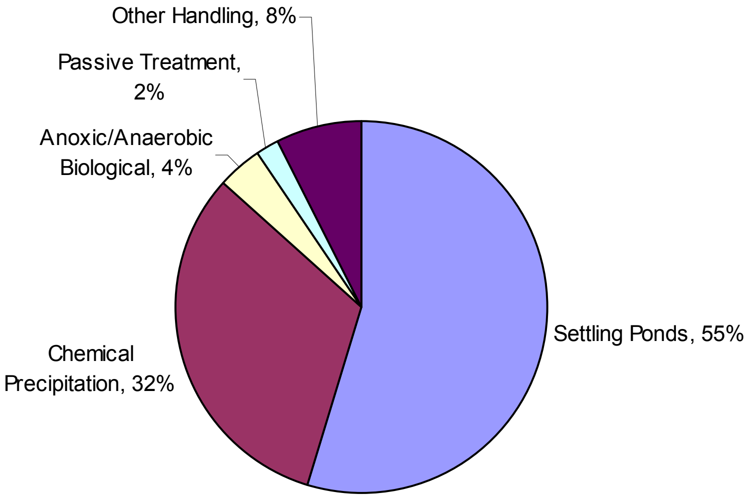


FIGURE 6-6
Types of FGD Water Treatment Technologies Implemented in the United States
Note: Data obtained from USEPA survey of existing FGD water treatment facilities (USEPA, 2009).

Of the 10 case studies (identified here as Sites PG1 through PG10) presented within this section on FGD water treatment, one physical/chemical treatment plant, two biological treatment plants, and one passive treatment system were designed for selenium removal. The biological treatment plants and passive treatment system were built in 2007/2008. In addition, there are six sites for which case studies are presented that have physical/chemical treatment plants that remove selenium as part of their solids and metals removal targets.

Table 6-2 summarizes the plant design, coal type, FGD design, and wastewater treatment configuration for each site. The case study wastewater treatment technologies include:

- Physical/Chemical Treatment
  - Solids Separation (Sites PG3, PG4, PG5)
  - Lime addition followed by clarification then iron co-precipitation (Sites PG7, PG10)
  - Lime and iron co-precipitation in same reactor followed by clarification (Sites PG1, PG2, PG6, PG8, PG9)
- Anoxic/anaerobic reactor-based biological treatment (Sites PG2, PG3)
- Passive treatment: constructed wetland (Sites PG4, PG5)

TABLE 6-2
Power Plant Case Study FGD Wastewater Treatment Summary

Site	Coal Type	FGD Design	Wastewater Treatment
PG1	Eastern bituminous	Limestone forced oxidation	Lime addition/ferrous chloride addition/clarification/filtration
PG2	Eastern bituminous	Limestone forced oxidation	Lime addition/ferric chloride addition/clarification/filtration/ anaerobic biological treatment
PG3	Eastern bituminous	Limestone forced oxidation	Settling pond/anaerobic biological treatment
PG4	Eastern bituminous	Limestone forced oxidation	Clarification/equalization and 1:1 service water addition to reduce chlorides/constructed wetland
PG5	Eastern bituminous	Limestone forced oxidation	Clarification/ equalization with 3:1 service water addition to reduce chlorides/constructed wetland
PG6	Eastern bituminous	Limestone forced oxidation	Lime addition/ferric chloride addition/clarification/filtration
PG7	Sub-bituminous	Limestone forced oxidation	Lime addition/primary clarification/ferric chloride addition/ organosulfide addition/secondary clarification
PG8	Eastern bituminous	Limestone forced oxidation	Lime addition/ferric chloride and sodium sulfide addition/ clarification/aerobic biological treatment/filtration
PG9	Eastern bituminous	Limestone forced oxidation	Two stages of lime addition/ferric chloride addition/ clarification; aerobic biological treatment/filtration
PG10	Eastern bituminous	Limestone forced oxidation	Lime addition/ primary clarification/ferric chloride addition/ secondary clarification

The treatment technologies in each case study were evaluated in the following areas to assess factors associated with implementation, effectiveness, and operability of each technology:

- Treatment effectiveness based on removal achieved from plants for which data are available.
- Extent and significance of any confounding factors (e.g., sulfate, nitrate, other metals, etc.).
- Main advantages and disadvantages.
- Space required for treatment system.
- Capital and operating costs, if available.

6.5 Case Studies: Physical/Chemical Treatment Technologies for Selenium Removal

The physical/chemical treatment cases are presented within this section because these facilities have either optimized their existing treatment to enhance selenium removal or are evaluating options for removal of selenium from their FGD water.

6.5.1 Case Study Site PG1

Site PG1 burns a mixture of petroleum coke and eastern bituminous coal in each of its generating units and operates a wet limestone forced oxidation FGD system. Figure 6-7 includes a process flow diagram for the FGD water treatment plant. The FGD water treatment plant was designed for selenium removal and the processes employed are as follows:

- Equalization
- Lime addition/pH adjustment
- Chemical precipitation—ferrous chloride addition
- Clarification
- Multimedia filtration
- Solids handling

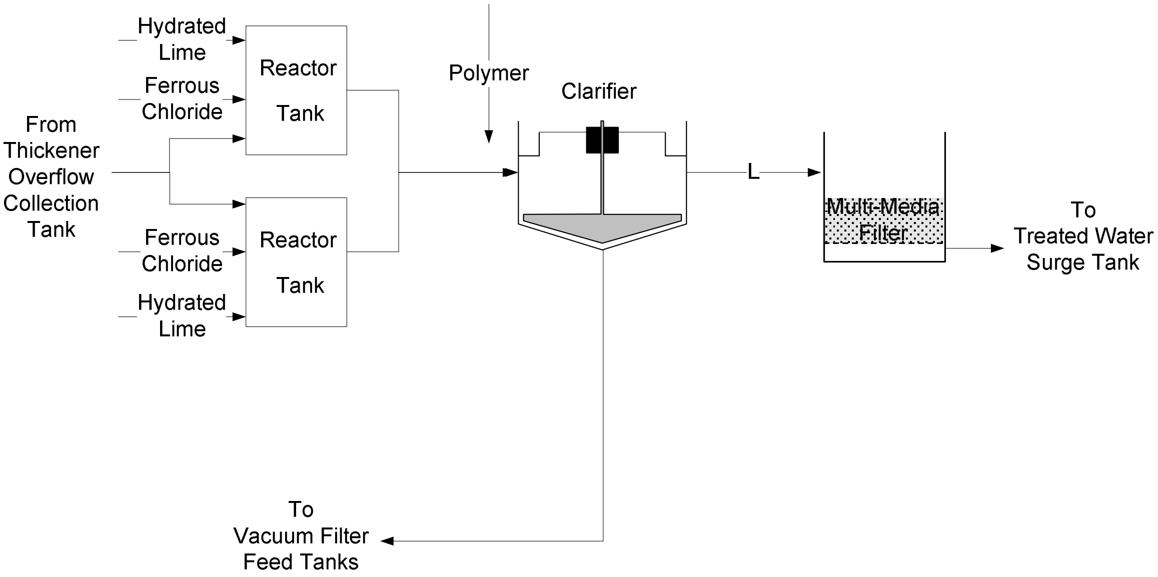


FIGURE 6-7
Site PG1 FGD Water Treatment Process Flow Diagram

The overflow from the thickeners is transferred to a collection tank where a percentage of the water is transferred to the FGD water treatment plant. The FGD water treatment plant operates at a flow rate of 300 gpm. The reactors operate in parallel as a batch process: one reactor is filled and operating, while the other finishes operation and drains. The pH is adjusted by lime addition to a pH of approximately 8.0. Once the pH is adjusted, the agitator speed is reduced in the reactor and ferrous chloride is added to enhance selenium removal. Site PG1 adds ferrous iron (as ferrous chloride) to enhance selenate treatment, as compared with most FGDs that add ferric iron. Polymer is added to the effluent of the reactors and the effluent from the reactors flows to a clarifier for solids settling. The clarifier residence time is approximately 3 days. The overflow from the clarifier flows to a multimedia filter containing gravel and sand. The sand filter effluent mixes with other process water streams in a surge tank prior to being discharged.

Table 6-3 demonstrates the removal efficiency across the treatment system for Site PG1. This is based on median concentrations from three sample events. Staff at site PG1 observed that 90% selenium removal is achieved with their batch treatment system with ferrous chloride as long as chloride levels in the FGD water remain below 15,000 mg/L. If the chloride level is above 18,000 mg/L, selenium removal drops to around 60%. The variation in removal may also be linked to the variation in predominant selenium species observed at Site PG1; both selenite and selenate have been observed as the predominant selenium species at different times. PG1 plant staff indicated that seleno-nitrogen and selenocyanate species are present as well.

TABLE 6-3
Site PG1 Selenium Removal

Treatment	Influent Total Selenium (µg/L)	Mid-point Total Selenium (µg/L)	Effluent Total Selenium (µg/L)	Removal Efficiency
Lime addition/pH adjustment/ chemical precipitation—ferrous chloride addition/ clarification/ multi-media filtration	337	Not available	55	84%

6.5.2 Case Study Site PG6

Site PG6 burns eastern bituminous coal. Secondary hydrocyclone overflow discharges to the FGD water treatment plant continuously at a flow rate of approximately 200 to 225 US gpm (750 to 850 Lpm). The residence time of the treatment plant is 24 to 32 hours. The chlorides concentration of the FGD influent is approximately 15,000 to 30,000 mg/L and the effluent also contains approximately 1 to 3% solids. Figure 6-8 presents a process flow diagram of the Site PG6 FGD water treatment system. The FGD water treatment system contains the following operations:

- Equalization
- Lime and ferric chloride addition
- Polymer flocculation
- Clarification
- Final pH adjustment (hydrochloric acid addition)
- Filtration
- Solids handling

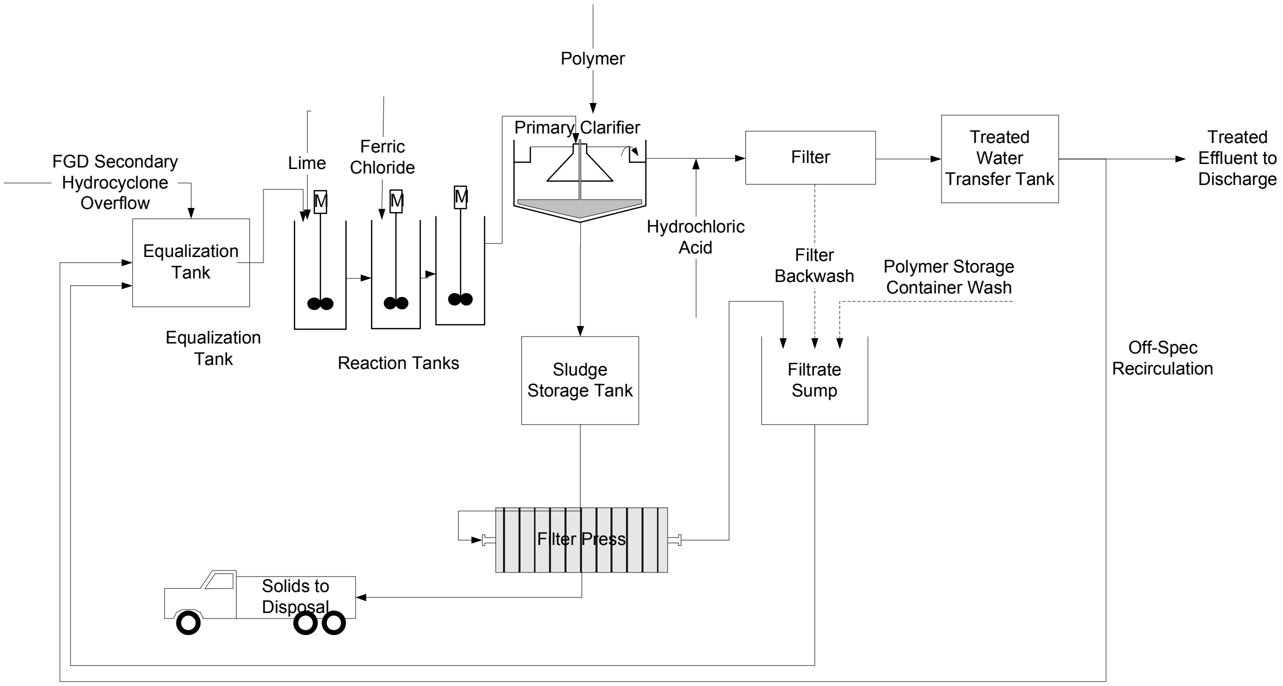


FIGURE 6-8
Site PG6 FGD Water Treatment Process Flow Diagram

The FGD water influent has a pH of approximately 6.0. At Reaction Tank 1, the pH is raised to 9.0 using hydrated lime. From Reaction Tank 1, the FGD water flows to Reaction Tank 2, where ferric chloride (55 to 65 gallons per day) is added to co-precipitate metals. The overflow from Reaction Tank 2 is transferred to Reaction Tank 3, which provides an environment to build floc to enhance metals precipitation. From Reaction Tank 3, the wastewater is transferred to the clarifier. A flocculating polymer is added to the clarifier feed pump discharge.

The overflow from the clarifiers flows to sand gravity filters. As the wastewater is pumped to the gravity filters, the plant adds hydrochloric acid to the wastewater to ensure the pH is between 6.0 and 9.0.

From the gravity filters, the wastewater is transferred to the treated water transfer tank and discharged from the plant. The plant commingles the effluent from the FGD water treatment system with the plant's once-through cooling water prior to discharge.

The underflow from the clarifiers is transferred to the sludge storage tank and from there is pumped through one of two filter presses.

Total selenium removal efficiency was characterized across the system based on a one-time sample event (Table 6-4). The data likely do not represent the average or the potential range of removal efficiency of selenium across the system. Of the 3,470 µg/L total selenium present within the influent sample, 3,280 µg/L was dissolved selenium. The total selenium concentration measured in the effluent of the treatment system was 2,500 µg/L, of which 2,460 µg/L was selenate.

TABLE 6-4
Site PG6 Selenium Removal

Site	Treatment	Influent Total Selenium (µg/L)	Mid-point Total Selenium (µg/L)	Effluent Total Selenium (µg/L)	Removal Efficiency
PG6	Lime addition/ferric chloride addition/clarification/filtration	3,470	Not Available	2,500	28%

6.5.3 Case Study Site PG8

Site PG8 burns eastern bituminous coal. Secondary hydrocyclone overflow enters the FGD water treatment plant on an intermittent basis with a chlorides concentration of approximately 20,000 mg/L. Site PG8 uses dibasic acid (DBA) at the scrubber for improved sulfur dioxide removal. Figure 6-9 presents a process flow diagram of the FGD water treatment system. The FGD water treatment system contains the following operations:

- Surge tank
- pH adjustment (lime addition)
- Ferric chloride/sodium sulfide addition
- Clarification
- Final pH adjustment (hydrochloric acid)
- Aerobic sequential batch reactor for organics removal
- Filtration
- Solids handling

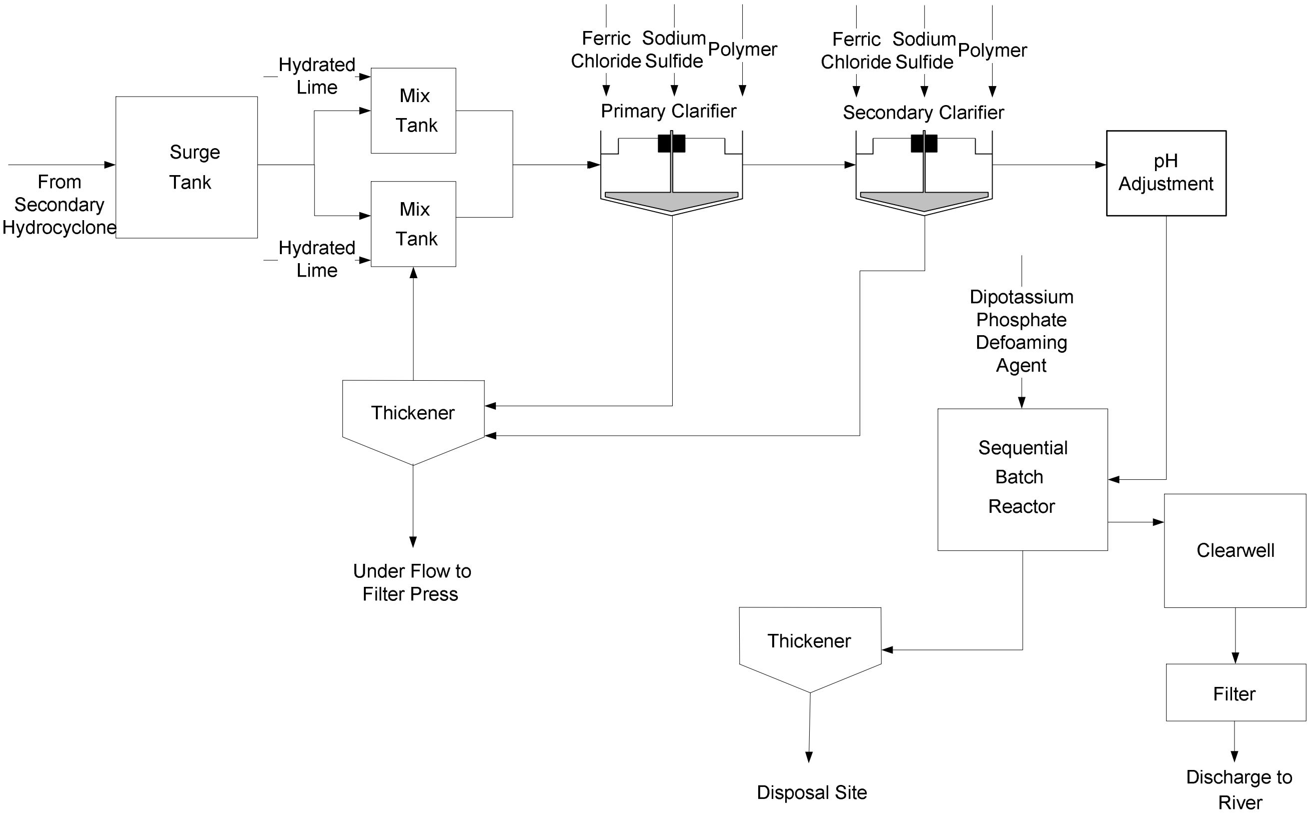


FIGURE 6-9
Site PG8 FGD Water Treatment Plant Process Flow Diagram

The flow rate from the surge tank is 150 to 175 US gpm (550 to 650 Lpm). From the surge tank the pH is raised to 8.6 using hydrated lime addition. From the pH adjustment tank, the FGD water flows to both primary and secondary clarifiers, where ferric chloride, sodium sulfide and polymer are added at each clarifier. The secondary clarifier overflow is routed to a pH adjustment tank where the pH is adjusted from the range of 8.6 to 7.8. From the pH adjustment sump, the FGD water flows to two sequencing batch reactors (SBRs) for aerobic biological treatment to remove organics present in the water from DBA addition. Dipotassium phosphate is added as a nutrient for bacteria that break down DBA. The treated FGD water flows from the SBRs to a clearwell and through pressure filters before being discharged. The total residence time of the system is approximately 2.5 days.

The solids from the primary and secondary clarifiers are sent to a thickener followed by a filter press for dewatering of solids. Solids from the SBRs are dewatered using a thickener and sent to the ash disposal site.

Personnel at Site PG8 noted that there has been an improvement in selenium removal performance in 2008/2009 which correlates in part with a switch in coal supply. The plant uses approximately 15 to 20 sources of coal and selenium levels within the coal may affect the levels seen at the influent of the FGD water treatment plant. The plant staff noted that they have an average of 50% selenium removal efficiency. Table 6-5 includes results from a one-time sampling event and shows efficiency of removal of total and dissolved selenium. More than half the selenium was in the dissolved form and approximately 55% was removed by physical/chemical treatment. Selenium speciation data were not available for this sample event.

TABLE 6-5
Site PG8 Selenium Removal

Form of Selenium	Influent Selenium (µg/L)	Selenium After Physical/Chemical Treatment (µg/L)	Removal Efficiency
Total Selenium	2,025	785	65%
Dissolved Selenium	1,500	645	55%

6.5.4 Case Study Site PG9

Site PG9 burns eastern bituminous coal units and operates a limestone forced oxidation FGD system. The plant previously added DBA to enhance sulfur dioxide removal efficiency but switched to formic acid which resulted in improved selenium removal efficiency. The slurry is purged to maintain a chloride concentration of approximately 15,000 to 20,000 mg/L (Eastern Research Group, 2007).

Addition of secondary hydrocyclones reduced the solids content of FGD purge water and improved selenium removal. The FGD water treatment plant is operated on a continual basis but receives secondary hydrocyclone overflow intermittently, typically 12 to 18 hours per day. The HRT of the FGD wastewater treatment system is approximately 3.5 days. Figure 6-10 is a process flow diagram for the system. The processes employed in the FGD water treatment plant are as follows:

- Equalization
- Lime, ferric chloride, cationic polymer addition, and aeration
- Anionic polymer addition
- Clarification
- Lime, ferric chloride and cationic polymer addition and aeration
- Clarification
- Nutrient/phosphoric acid/substrate addition
- Cooling
- Aerobic biological treatment
- Sand filtration
- Solids handling

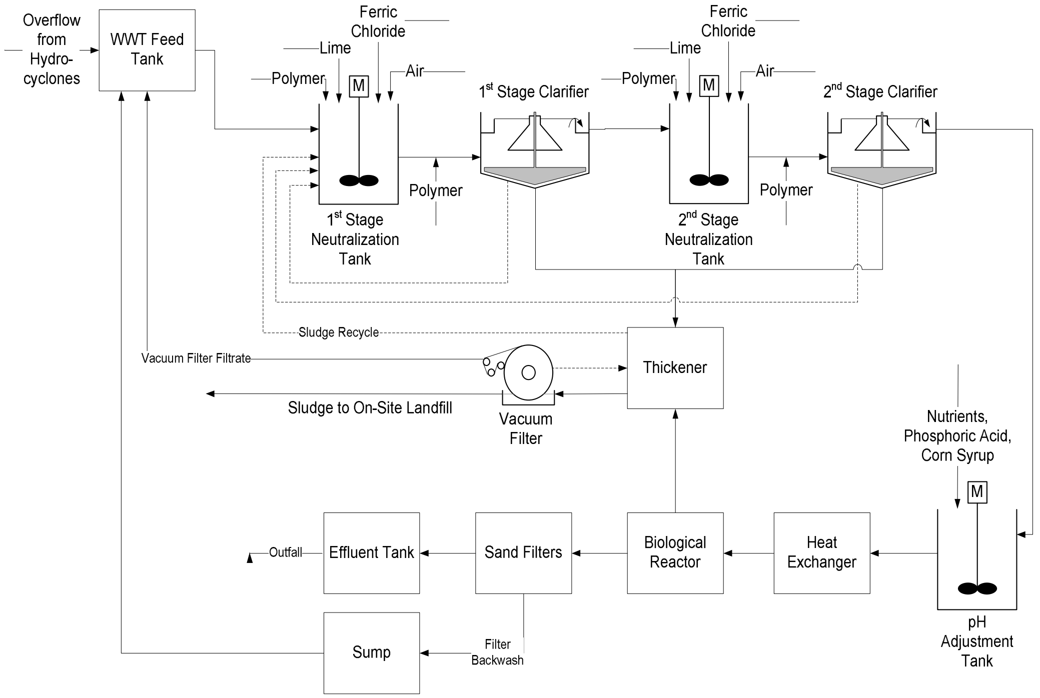


FIGURE 6-10
Site PG9 FGD Water Treatment Plant Process Flow Diagram

With the secondary hydrocyclones operating, the wastewater entering the FGD water treatment system contains less than one percent solids. After equalization, water enters the first stage chemical precipitation, where lime is added to adjust the pH to 8.1. Ferric chloride, air, and cationic polymer are added to enhance precipitation of metals. After first-stage clarification, the FGD water enters a second-stage chemical precipitation/clarification step, before nutrients and corn syrup are added in a pH adjustment tank. The pH of the FGD water entering the biological reactor is generally 7.5 to 8.0. The biological treatment system was also designed to remove BOD from the FGD water. BOD is present in FGD water at Site PG9 because formic acid is added at the FGD scrubber. Afterwards, the FGD water is transferred to sand filters. Solids from the biological reactor and the clarifiers are dewatered in a thickener and vacuum filter. The filtrate from the solids dewatering is sent through the start of the treatment process and solids are landfilled (USEPA, 2009).

Table 6-6 includes results from a one-time sampling event at Site PG9 and shows efficiency of removal of total and dissolved selenium. Most of the selenium is in the particulate form and effectively removed through treatment.

TABLE 6-6
Site PG9 Selenium Removal

Form of Selenium	Influent Selenium (µg/L)	After Physical/Chemical Treatment-Selenium (µg/L)	Removal Efficiency
Total Selenium	3,530	238	93%
Dissolved Selenium	584	241	58%

6.5.5 Case Study Site PG7

Site PG7 is a sub-bituminous coal-fired power plant with a selective catalytic reduction and a limestone forced-oxidation FGD system. Figure 6-11 shows a process flow diagram of the FGD water treatment plant. The FGD water treatment plant consists of the following processes:

- Equalization tank
- Desaturation/pH adjustment (lime addition)
- Polymer addition
- Primary clarification
- pH adjustment (hydrochloric acid)
- Organosulfide addition
- Ferric chloride addition
- Polymer addition
- Secondary clarification
- Solids handling

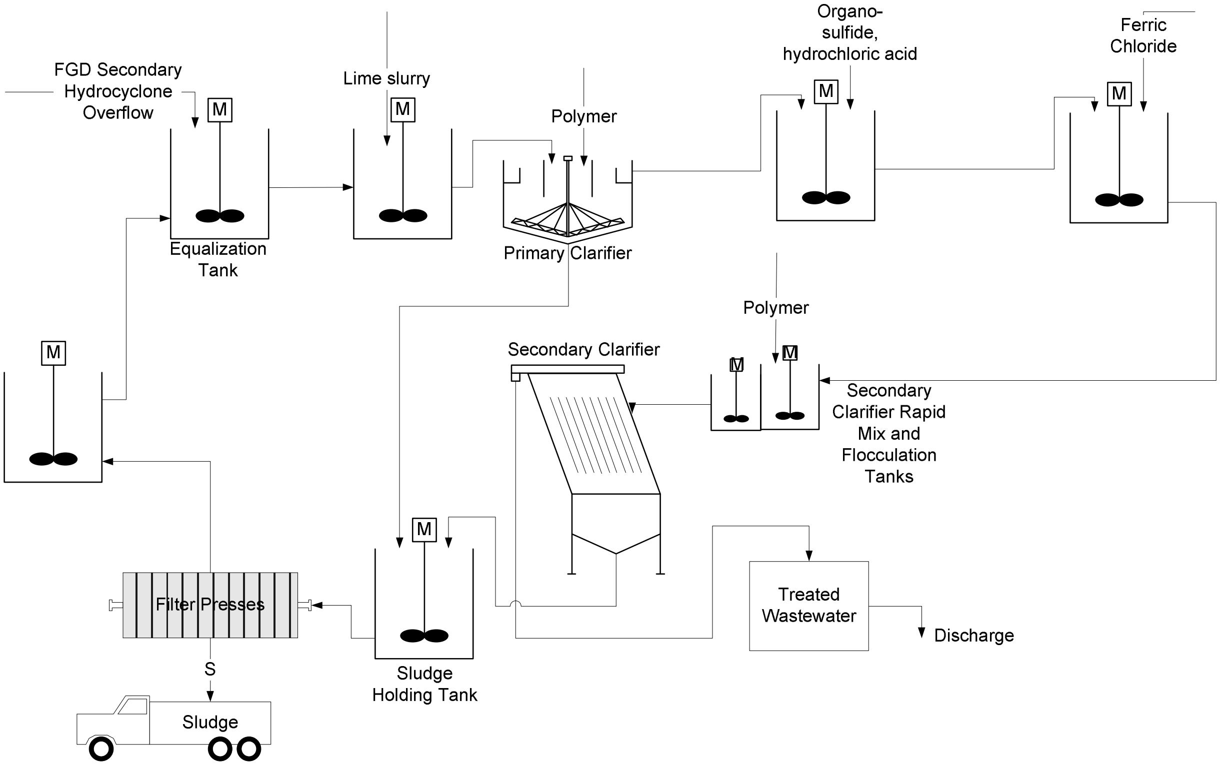


FIGURE 6-11
Site PG7 FGD Water Treatment Plant Process Flow Diagram

FGD blowdown is routed through primary hydrocyclones to separate gypsum solids from fines. Underflow is routed to a vacuum belt filter for gypsum dewatering. Overflow from the primary hydrocyclones passes to secondary hydrocyclones. Secondary hydrocyclone overflow is routed to the treatment plant equalization tank.

The plant was designed to treat 70 US gpm (265 Lpm) of wastewater with a TSS concentration of less than 1.5%. It typically operates at about 35 US gpm (132 Lpm). After equalization, wastewater flows to Reaction Tank 1. Wastewater pH is adjusted from approximately 5.6 to 8.5 by adding hydrated lime to de-saturate the wastewater. Effluent from Reaction Tank 1 flows by gravity to a primary clarifier. Polymer is added to aid solids removal and sludge is recycled back to Reaction Tank 1.

The pH is lowered to approximately 7 and an organosulfide is added to Reaction Tank 2 to precipitate mercury. The effluent from Reaction Tank 2 flows by gravity to Reaction Tank 3, where ferric chloride is added for coagulation and for iron co-precipitation. Effluent from Reaction Tank 3 passes to a Flash Mix tank where polymer is added, and to a flocculation tank followed by a parallel plate clarifier. Sludge from this clarifier is recycled back to Reaction Tank 3 to aid floc formation and settling.

Solids from the primary and secondary clarifiers are sent to a sludge holding tank and dewatered using a filter press. The treatment system at Site PG7 is located in an approximately 80-foot by 80-foot building.

Results from a one-time sampling event at Site PG7 provide a limited characterization of efficiency of removal of total and dissolved selenium (Table 6-7). Most of the selenium was in the particulate form and effectively removed through treatment. Some particulate selenium was solubilized, likely as selenite, during lime addition. This solubilized selenium along with a portion of the originally dissolved selenium was subsequently removed (after the pH was lowered) through iron co-precipitation and secondary clarification. The remaining selenium in the effluent was 100% dissolved. Selenium speciation data were not available for this sampling event, but are known to vary over time in the untreated FGD water at Site PG7 such that selenate is sometimes the predominant species, and selenite at other times.

TABLE 6-7
Site PG7 Selenium Removal

Form of Selenium	Influent Selenium (µg/L)	After Primary Clarification-Selenium (µg/L)	Effluent Selenium (µg/L)	Removal Efficiency
Total Selenium	19,000	8,500	3,000	84%
Dissolved Selenium	5,200	8,600	3,000	42%

6.5.6 Case Study Site PG10

Site PG10 burns eastern bituminous coal. Primary hydrocyclone overflow is discharged to the FGD purge water treatment plant continuously at a flow rate of approximately 500 US gpm (1,900 Lpm). The chloride concentration of the FGD water treatment plant influent is approximately 5,500 to 8,000 mg/L and contains 5.7% solids (USEPA, 2009). Figure 6-12 presents a process flow diagram of the FGD water treatment system. The FGD water treatment system contains the following operations:

- Lime desaturation
- Primary clarification
- Equalization
- Ferric chloride addition
- Polymer addition
- Secondary clarification
- Solids handling

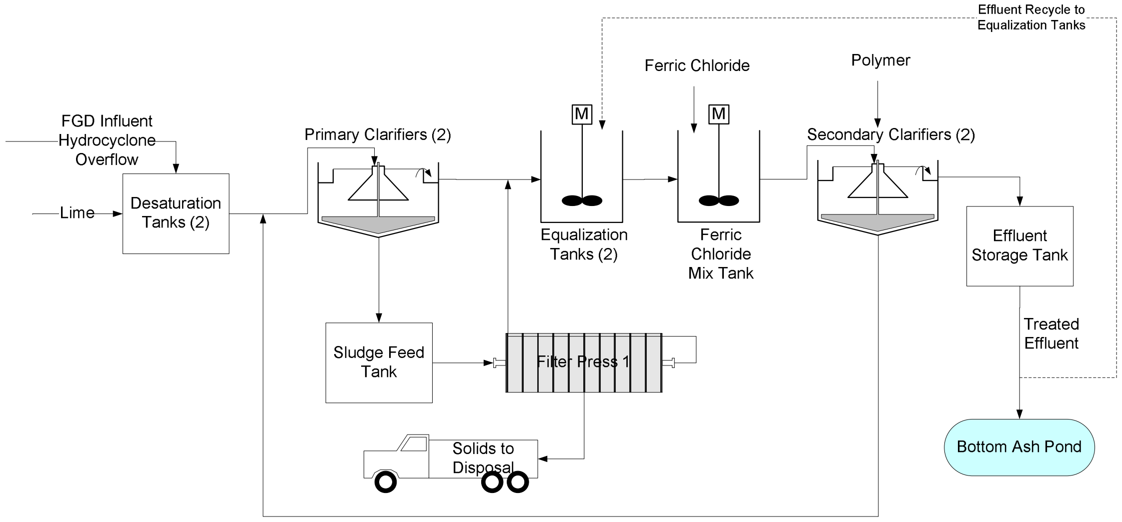


FIGURE 6-12
Site PG10 FGD Water Treatment Plant Process Flow Diagram

The FGD influent has a pH of approximately 6.5 to 7.0. At the desaturation tank, the pH is raised to a value between 8.2 and 8.7 using hydrated lime addition. From the desaturation tank, the FGD water flows to the primary clarifier. The overflow of the primary clarifier containing approximately 0.1% solids, flows to a ferric chloride mix tank where ferric chloride is added to enhance solids removal. The effluent from the ferric chloride mix tank flows to a secondary clarifier where polymer is added to promote floc formation and settling. The effluent of the secondary clarifier flows to an effluent tank prior to discharge to the bottom ash pond.

Results from a one-time sampling event at Site PG10 provide a limited characterization of removal efficiency for total and dissolved selenium (Table 6-8). Most of the selenium is in the particulate form and is effectively removed through treatment. Dissolved selenium is not effectively removed through this facility's physical/chemical treatment process. This is to be expected, as the iron addition is carried out at elevated pH, which is not likely to result in selenite removal by iron co-precipitation. The remaining selenium in the effluent was almost 100% dissolved. Selenium speciation data were not available for this sampling event.

TABLE 6-8
Site PG10 Selenium Removal

Form of Selenium	Influent Selenium (µg/L)	After Primary Clarification-Selenium (µg/L)	Effluent Selenium (µg/L)	Removal Efficiency
Total Selenium	1,990	234	431	78%
Dissolved Selenium	443	472	407	8%

6.5.7 Effect of pH on Iron Co-precipitation for Case Study Sites

Each of the case study sites operates at a pH above the optimal pH range of 4 to 6 for selenium removal with iron co-precipitation. Among these, site PG7 has been optimized for mercury removal and operates at a pH below 7 which is better for selenite removal than the higher pH maintained at other sites. However, Site PG7 wastewater also has a large selenate fraction, and total selenium removal through iron co-precipitation is therefore reduced.

Site PG8 performed a study using their FGD water to determine the optimal pH for selenium removal and found that selenium removal was most effective at pH 5 to 5.5. Another lesson learned from the pilot study conducted at Site PG8 was that optimization of selenium removal occurred when solids were removed prior to final pH adjustment. Total selenium was approximately 250 µg/L in the effluent during this study. It has been observed at Site PG1's FGD water treatment plant that pH may vary over the year, which is likely to affect selenium removal efficiency.

6.5.8 Operational Considerations for Physical/Chemical Treatment Case Studies

Operational issues that are typically observed within a physical/chemical treatment plant include issues with plugging of media used in filtration and scaling of equipment and piping. FGD water tends to be supersaturated with calcium sulfate which can cause scaling. Even after desaturation, FGD water has a tendency to scale and cause plugging of lines or scale formation on equipment, and plugging of media used for filtration. The sand filter at Site PG7 was plugged by scale and solids during its first year of operation and was removed from service. Scale buildup in the underground discharge piping has restricted flow and requires periodic mechanical cleanout. Site PG7 burns sub-bituminous coal and utilizes a relatively high magnesium (~2%) limestone, which results in a much higher sulfate concentration in the purge water and exacerbates their scaling problems.

Solids dewatering can be an issue for Site PG1 at times and the sludge from the ferrous chloride precipitation process is sometimes mixed with fly ash to stabilize the sludge prior to disposal in a landfill.

Safety issues at physical/chemical treatment plants arise from the operations of mechanical equipment and handling of corrosive chemicals such as hydrochloric acid and ferric chloride.

6.5.9 Capital and Operations and Maintenance Costs for Physical/Chemical Treatment

The capital costs of the treatment systems presented in the case studies above ranged from $15-$30 million dollars, with operations and maintenance costs of approximately $450,000 to

$2 million per year. The greatest portion of the operations costs are attributed to chemical usage and disposal of dewatered solids. For example, one facility reported chemical usage costs of $140,000 per year and sludge (non-hazardous) disposal of $100,000 per year out of their $450,000 total annual costs. Additional operations costs include labor for operations of the FGD water treatment system, utilities, and maintenance labor and materials. Labor needed to run the FGD water treatment systems are typically 1 to 2 full-time equivalents.

6.6 Biological Treatment Technologies for Selenium Removal

6.6.1 Case Study Site PG2: ABMet® System

Site PG2 burns eastern bituminous coal and operates a wet limestone forced oxidation FGD system, selective catalytic reduction (SCR), and ESPs. The units blow down intermittently to maintain a chloride concentration in the scrubbers between 8,000 and 10,000 mg/L. The limestone slurry is made from limestone pulverized in onsite ball mills. Primary and secondary hydrocyclones are used for solids separation.

Site PG2 employs physical/chemical FGD water treatment prior to anaerobic biological reduction treatment. The flow rate of the FGD wastewater treatment plant is 600 US gpm (2,270 Lpm) and is designed to receive intermittent flows. The FGD water treatment plant is laid out on approximately 5 acres (2 hectares), although 2.5 of those acres are dedicated for truck access and turnarounds to the facility. Figure 6-13 presents a process flow diagram for the system. The FGD water treatment system consists of the following processes:

- Physical/chemical treatment
  - Equalization
  - Lime addition
  - Organosulfide addition (the system is designed for organosulfide addition to Reaction Tank #2 for enhanced mercury removal; however, at present, organosulfide is not added as mercury removal can be achieved with solids removal and polishing by the bioreactor)
  - Ferric chloride addition
  - Polymer addition for improved flocculation
  - Clarification
  - Filtration
- Biological treatment
  - Cooling
  - Nutrient addition
  - First stage biological reaction
  - Nutrient addition
  - Second stage biological reaction

- Solids handling

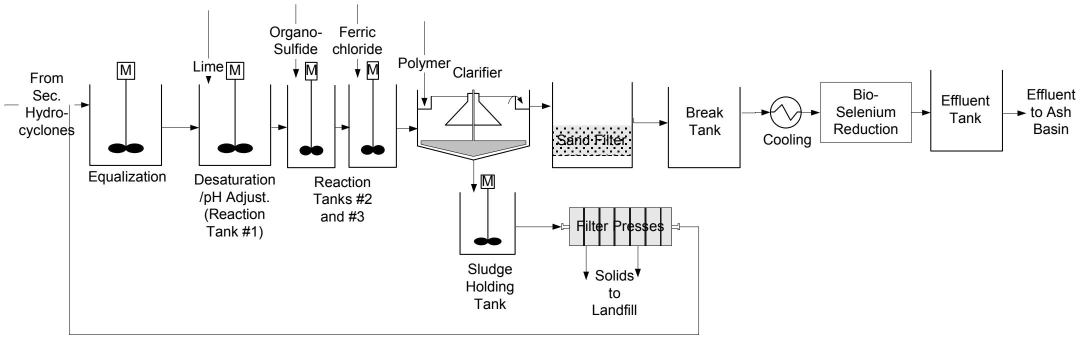


FIGURE 6-13
Site PG2 FGD Water Treatment Plant Process Flow Diagram
Note: Organosulfide can be added to Reaction Tank #2 as shown in the schematic to enhance mercury removal, although this is not done at present because mercury removal can be achieved with solids removal and polishing by the bioreactor.

The secondary hydrocyclone overflow enters the equalization tank and flows to Reaction Tank #1. Lime slurry is added to this tank to raise the pH of the water to between 8.5 and 9.2. As noted above, organosulfide was designed to be added to a second reaction tank (Reaction Tank #2) to enhance mercury removal, but is not currently added. Ferric chloride is added in Reaction Tank #3, which serves to generate ferric hydroxide which aids in the precipitation of a number of metals of interest. Polymer is added for floc formation and solids are settled in clarifiers. The overflow from the clarifiers flows to a bank of sand filters. Prior to reaching the filters, hydrochloric acid is added to neutralize the pH.

Sludge from the clarifier is transferred to a Sludge Holding Tank. When there is sufficient volume in the tank the sludge is processed through one of four filter presses. The solids concentration in the sludge typically ranges from 15 to 20%.

The treatment efficiency across the physical chemical treatment system is expressed in Figure 6-14. An average 97% of the total selenium is removed through the physical/chemical treatment process. Figure 6-15 shows the dissolved selenium before and after physical treatment, which shows that in addition some dissolved selenium likely present as selenite is removed in the physical/chemical treatment plant. Selenium speciation results indicate that there is generally slightly more selenate than selenite in the dissolved fraction of the untreated FGD water. The selenate present in the FGD water was not removed by physical/chemical treatment.

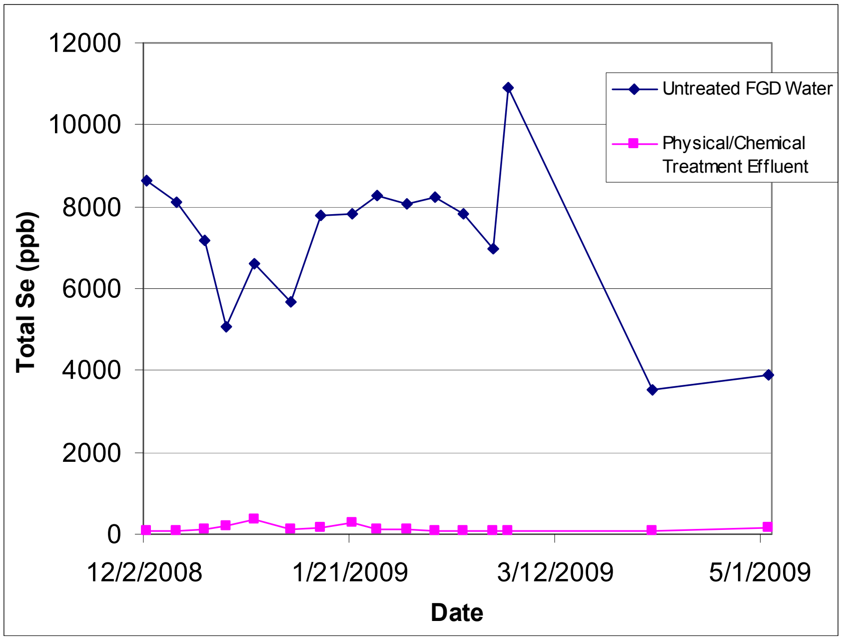


FIGURE 6-14
Site PG2 Total Selenium Removal by Physical/Chemical Treatment

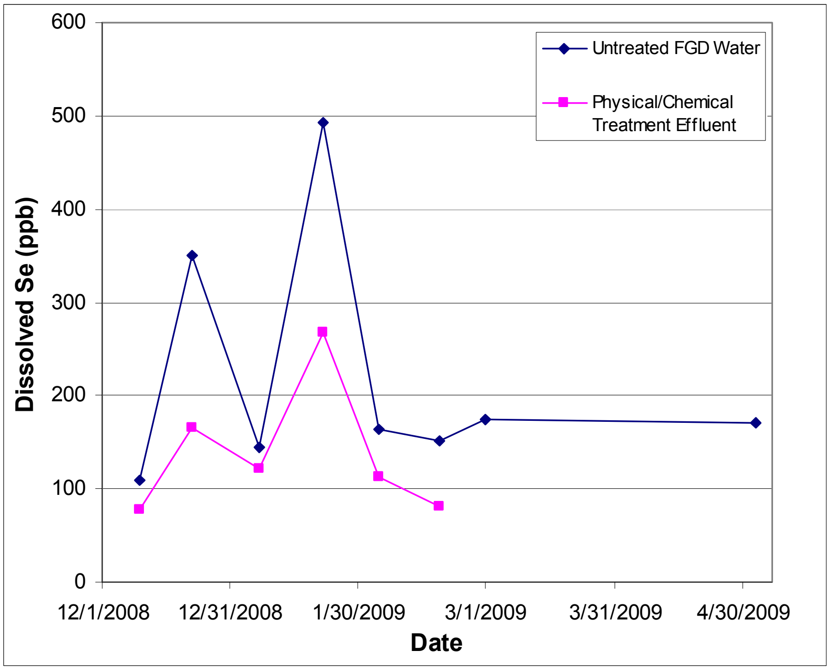


FIGURE 6-15
Site PG2 Dissolved Selenium Removal by Physical/Chemical Treatment

The FGD water is cooled with a heat exchanger that uses service water discharged as once-through cooling water which is mixed with the effluent of the FGD water treatment system. The GE ABMet® treatment system consists of two-stage bioreactors in series. The biological treatment system at Site PG2 consists of sixteen bioreactor cells configured in a two-stage arrangement of eight cells each. Each stage is further broken down into two trains. The system is equipped with recycle pumps, allowing for multiple configurations of the system, including the transfer of effluent back to the front end of the system for seeding or plant outages (EPRI, pending(a)).

A proprietary molasses-based nutrient is added prior to the water entering the first stage bioreactor cells. The cells use a down-flow design. The influent is distributed across the top of a granulated activated carbon (GAC) bed through a system of sixteen sparger nozzles. The effluent from the first stage bioreactor cells flows into a large holding compartment prior to flowing into the second stage of equipment. The second stage is similar to the first stage, and includes nutrient addition and an additional eight bioreactor cells (EPRI, pending(a)).

The backwash system is used to remove precipitated solids and excess biomass from the media. In addition to backwashing, a degas sequence is employed periodically to release gases that build in the bioreactor. The trapped gases reduce flow through the cells. The backwash water is pumped back to the equalization tank for solids removals and re-processing (EPRI, pending(a)).

Figure 6-16 and 6-17 show total selenium over time at Site PG2 before and after biological treatment. The physical/chemical treatment plant removed an average of 98% of the total selenium in the FGD water, which reduced total selenium levels to the low 100s µg/L. The biological treatment plant resulted in consistent removal over a six-month period to below detection levels (<10 µg/L), resulting in greater than 99% overall removal for the overall system on a consistent basis. The biological treatment system was also able to treat other parameters to low levels such as mercury (average 8.3 ng/L), arsenic, copper, and nickel. The biological treatment system also treated nitrate to below detection (<32 mg/L) but did not on average effectively remove ammonia or organic nitrogen (EPRI, pending(a)).

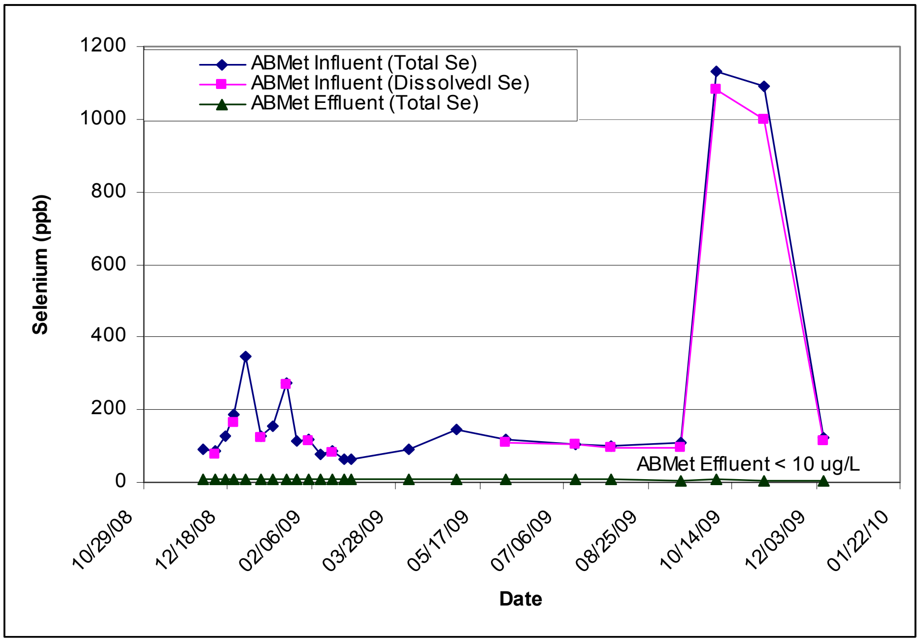


FIGURE 6-16
Site PG2 Total Selenium Removal by ABMet® Treatment

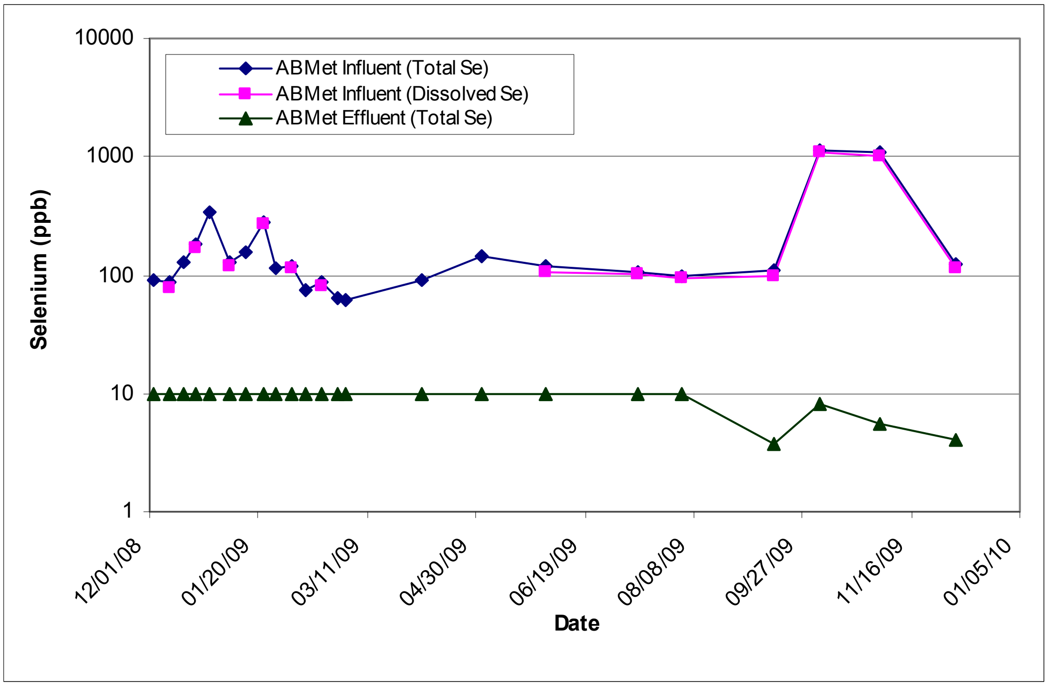


FIGURE 6-17
Site PG2 Total Selenium Removal by ABMet® Treatment (Logarithmic Scale)

Figures 6-18 and 6-19 illustrate selenate and selenite removal through treatment, respectively.

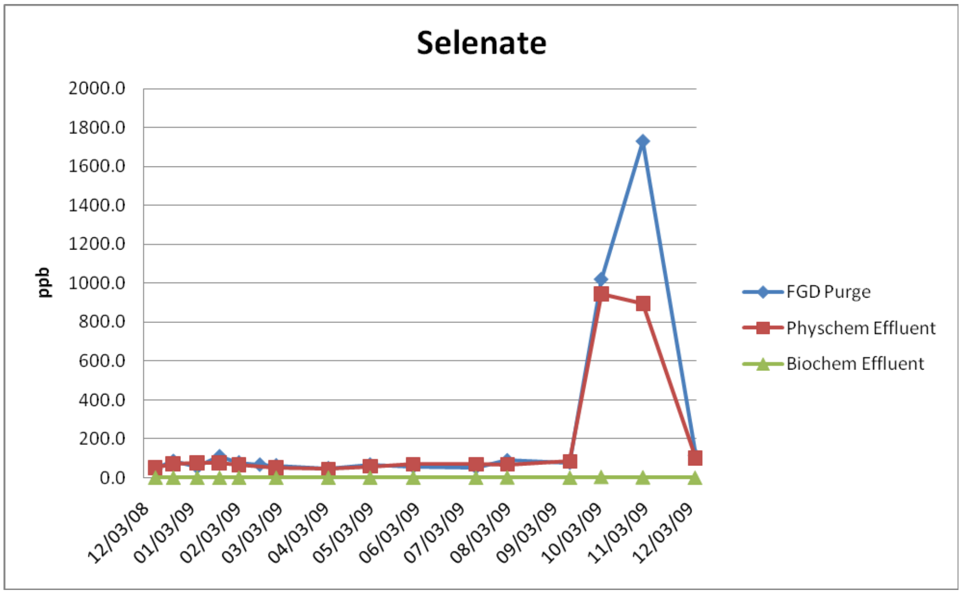


FIGURE 6-18
Site PG2 Selenate Removal by ABMet® Treatment
Source: EPRI, pending(a)

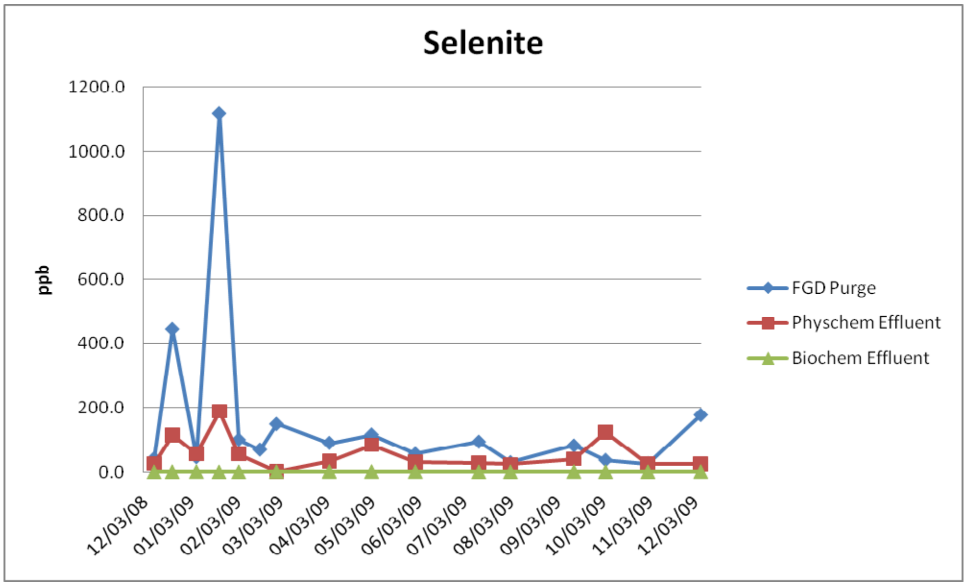


FIGURE 6-19
Site PG2 Selenite Removal by ABMet® Treatment
Source: EPRI, pending(a)

6.6.2 Case Study Site PG3: ABMet® System

Site PG3 burns eastern bituminous coal and operates a selective catalytic reduction (SCR), ESP, and wet limestone forced oxidation FGD system, and operates both primary and secondary hydrocyclones to dewater the gypsum produced in their scrubbers. The FGD water flows from the secondary hydrocyclones to a settling pond. Figure 6-20 contains a process flow diagram of the Site PG3 FGD water treatment system. The purpose of the settling pond is to remove TSS and lower the temperature of the water to below 105 °F (40 °C). The FGD water treatment system consists of the following processes:

- Physical treatment
  - Settling pond (lined, 16-acre [6.5-hectare])
- Biological treatment
  - Nutrient addition
  - First stage biological reaction
  - Nutrient addition
  - Second stage biological reaction
  - Flush pond

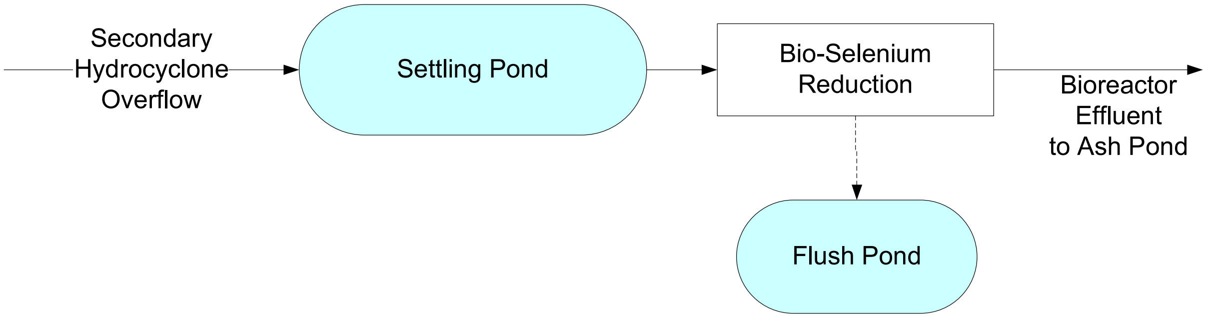


FIGURE 6-20
Site PG3 FGD Water Treatment Plant Process Flow Diagram

The ABMet® system at Site PG3 consists of four parallel trains that contain two bioreactors in series each and treat an FGD water flow rate of 1,400 US gpm (5,300 Lpm). A molasses-based nutrient is added as part of the biological treatment system. The bioreactors are designed for 4-hour retention time. The bioreactor must be flushed periodically to remove solids from the system. The source of water for backwashing is the FGD settling pond. Backflush wastewater is transferred to the flush pond, which is located directly next to the settling pond.

Solids separation across the settling pond resulted in an average 38% removal of total selenium from pond influent to effluent Figure 6-21. Levels fluctuate over time, due to both varying levels of total selenium as well as varying levels of particulate versus dissolved selenium over time. It should be noted, however, that the total selenium levels after in-pond settling are still considerably higher than levels that would be permitted at a regulated outfall. Particulate and dissolved selenium data for effluent of the settling pond (Figure 6-22) show that selenium is almost 100% in the dissolved form, indicating that the pond effectively removes the particulate selenium. During an interview with staff at Site PG3, it was noted that selenate is generally the predominant species of selenium present in the dissolved form within FGD water at the plant.

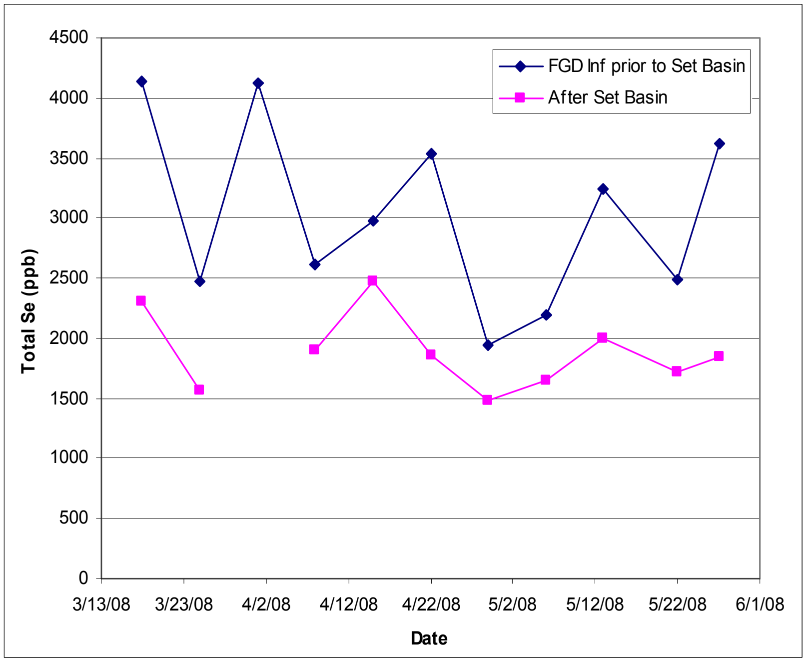


FIGURE 6-21
Site PG3 Total Selenium before and after Solids Settling

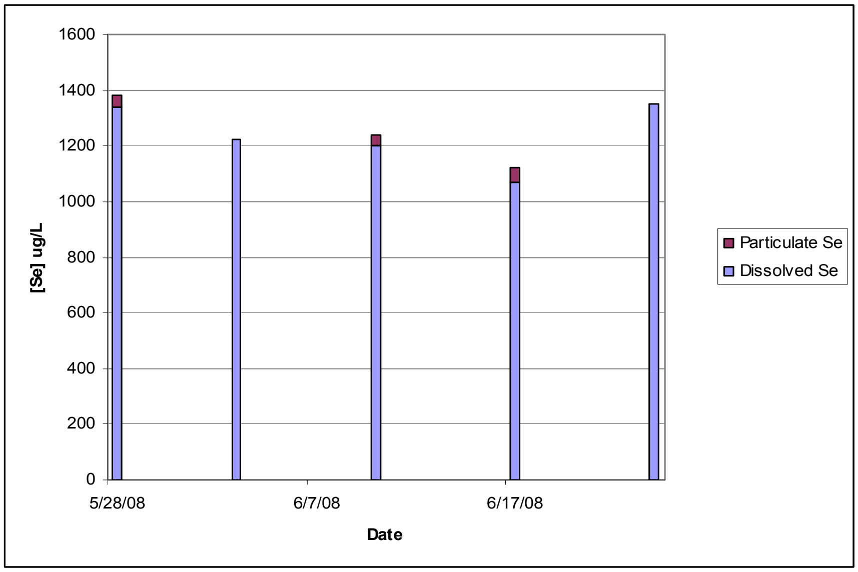


FIGURE 6-22
Site PG3 Particulate and Dissolved Selenium after Solids Separation

Figure 6-23 shows median values of particulate and selenium removal across each of the biological treatment cells at over a 5-week period in 2008 at Site PG3. The data indicate that approximately one-third of the total selenium removal from the FGD water took place within the settling pond. The effluent of the biological treatment system had selenium concentrations less than 50 µg/L. Selenium speciation data collected indicate that the effluent of the settling pond contains almost 100% dissolved selenium at levels greater than

1,000 µg/L. These levels were reduced to low concentrations in the biological treatment system.

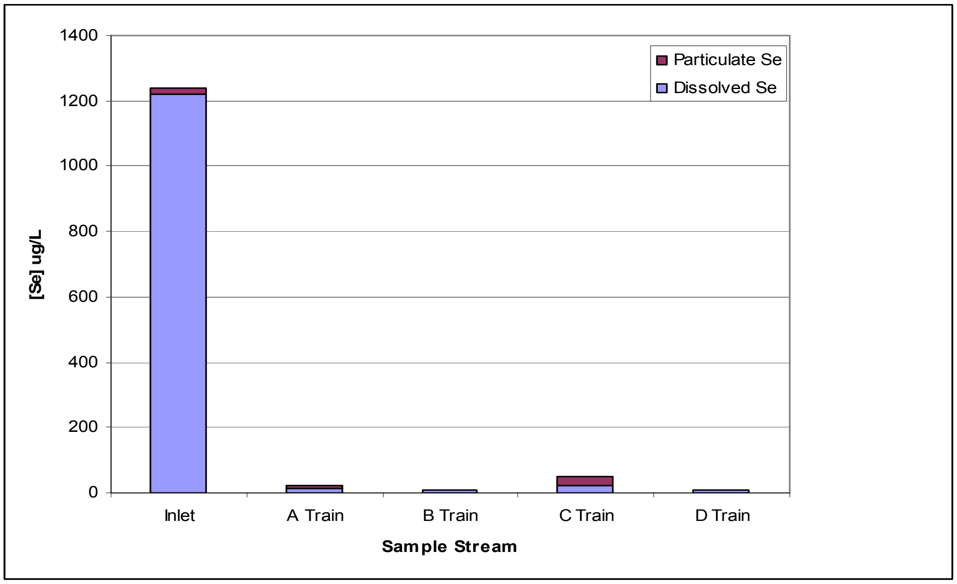


FIGURE 6-23
Site PG3 Particulate and Dissolved Selenium through Biological Treatment

6.6.3 Anoxic/Anaerobic Biological Treatment: Operations and Safety Considerations

The staff at Sites PG2 and PG3 stated that operational issues during routine operations have not been observed to date regarding the bioreactors. Site PG2 reported backwashing of the bioreactor cell twice per month. Site PG2 pumps the backwash water after backwashing to the equalization tank at the head of the biological treatment plant. The solids from backwashing are minimal in volume and are disposed of along with the solids from the filter press operations at the physical/chemical treatment plant. At Site PG3, the forward flush pond is used to store backwash water. Hydrogen sulfide may be produced within the bioreactors so hydrogen sulfide monitoring is conducted as a safety precaution at both sites.

6.6.4 Anoxic/Anaerobic Biological Treatment: Capital and Operations and Maintenance Costs

The capital cost for the FGD water treatment plant including the settling pond at Site PG3 is approximately $33 million, of which approximately $22 million is for the biological treatment system. Operations costs are unknown as the systems have not been in operation long enough to determine what the long-term operations costs are for the system. Costs to re-seed the system with microbes if needed at Site PG3 were estimated to be approximately $200,000 (2006 $USD). However, this re-seeding was not required. The cost of biological treatment systems varies greatly from site to site and a site-specific estimate is recommended.

6.7 Passive Biological Treatment: Constructed Wetlands

Sites PG4 and PG5 use constructed wetlands for removal of metals. Site PG4's constructed wetlands are designed for selenium and mercury removal and Site PG5's constructed wetlands are designed for mercury removal. Organic matter additions are not currently made at either of the wetlands.

6.7.1 Case Study Site PG4: Surface-Flow Wetland

Site PG4 burns eastern bituminous coal and operates a wet limestone forced oxidation FGD system. Primary and secondary hydrocyclones are used for solids separation. The chloride purge stream from the scrubber is blown down approximately four of every six hours. The overflow from the secondary hydrocyclones is sent to a holding tank and then sent to the FGD water treatment plant. Figure 6-24 shows a process flow diagram of the Site PG4 FGD water treatment system. The FGD water treatment system consists of the following processes:

- Physical treatment
  - Equalization
  - Polymer flocculation and clarification
- Constructed wetlands
  - Equalization/cooling
  - Wetlands
- Solids handling

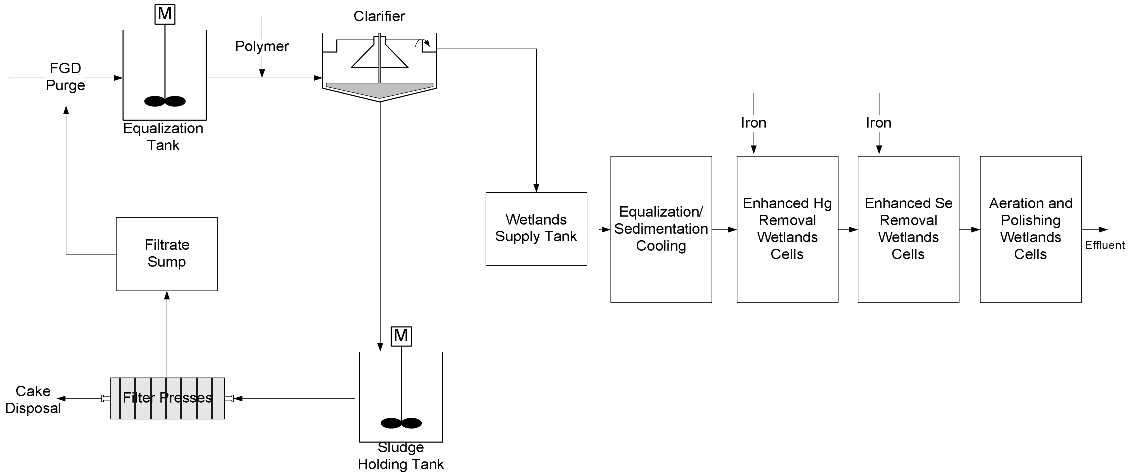


FIGURE 6-24
Site PG4 FGD Water Treatment Plant Process Flow Diagram

The FGD water flows continuously from the equalization tank to the clarifier. A cationic polymer is used to promote floc formation and solids settling. The solids from the clarifier are sent to a sludge holding tank and then dewatered using a filter press. The constructed wetlands system is discussed in a later section.

Total selenium before and after clarification for Site PG4 is shown in Figure 6-25. The data indicate that an average of 85% of the total selenium is removed in the clarifier. This suggests that selenium is largely in the particulate form at Site PG4, a contrast to Site PG3 where selenium was largely in the dissolved form. Selenium speciation and dissolved selenium data are not available from this plant.

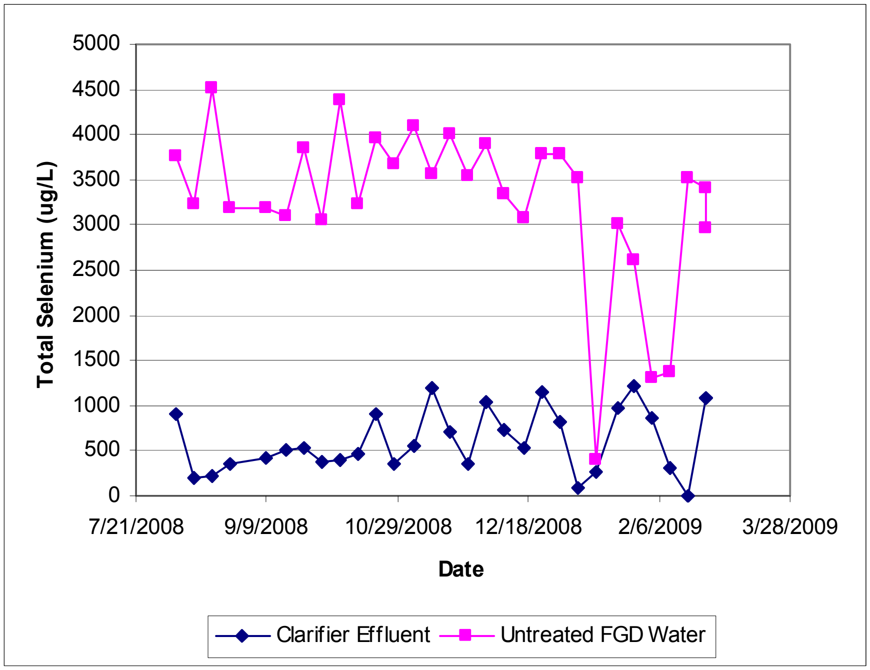


FIGURE 6-25
Site PG4 Total Selenium before and after Solids Separation

Pretreatment is required for the wetlands to reduce suspended solids. Service water is also added at a 1:1 ratio to reduce levels of chlorides, boron, and high temperature. The FGD water is cooled with the service water to temperatures below 95°F (35°C) and boron levels are maintained below 50 mg/L to protect wetland vegetation. The overall footprint of the treatment system at Site PG4 is approximately 12 to 15 acres (5 to 6 hectares).

The site PG4 constructed wetlands consists of nine surface-flow treatment cells arranged in three parallel banks of three cells each. Each train consists of two cells of bulrush, a third aeration cell containing cascading rocks, and a fourth cell containing cattails. Average total selenium removal at Site PG4 is generally 20%. Figure 6-26 shows influent and effluent selenium data for the Site PG4 constructed wetland. ORP readings taken across the system indicated that reducing conditions conducive to selenium removal are present within some of the cells, but there are also areas with oxidizing conditions which do not promote selenium removal. Reduction of oxidized forms of selenite and selenate to their elemental form cannot occur without anoxic conditions. Varying oxidizing and reducing conditions may result in alternating periods of selenium sequestration and remobilization at Site PG4 (EPRI, pending(b)).

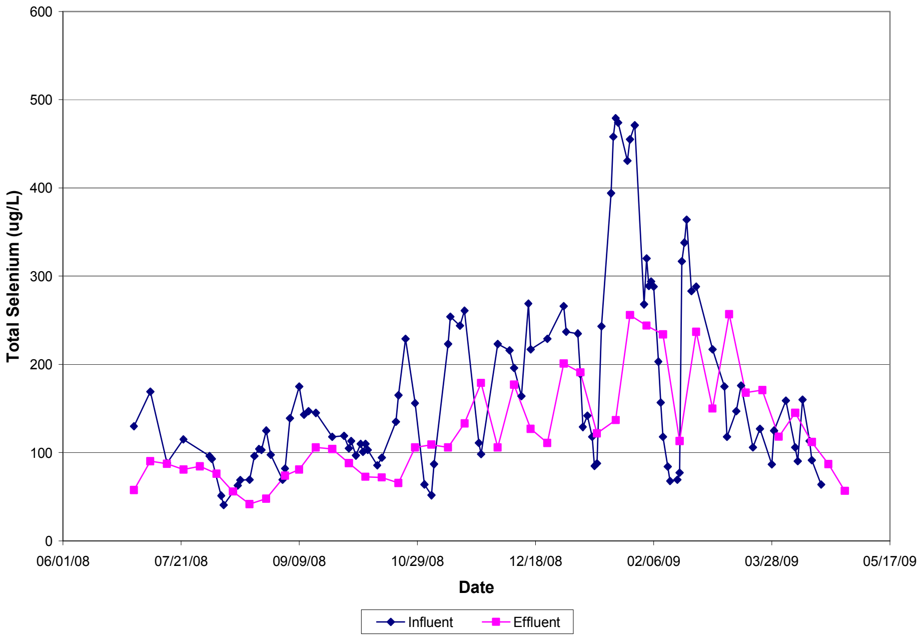


FIGURE 6-26
Site PG4 Total Selenium through the Constructed Wetland

A study was conducted at Site PG4 that tested organic addition for one of the treatment trains of the constructed wetland. The test consisted of yeast and sugar addition at varying amounts over the course of a seven-month period. The train treated with the sugar/yeast addition achieved up to 40% selenium removal while 19% removal of selenium was observed for the wetland train that did not have additions.

6.7.2 Case Study Site PG5: Surface-flow Wetland

Site PG5 burns eastern bituminous coal and operates a wet limestone forced-oxidation FGD system. Figure 6-27 shows a process flow diagram of the FGD water treatment system. The FGD water treatment system consists of the following processes:

- Physical Treatment
  - Polymer flocculation and clarification
  - Equalization
- Constructed Wetlands
- Solids Handling

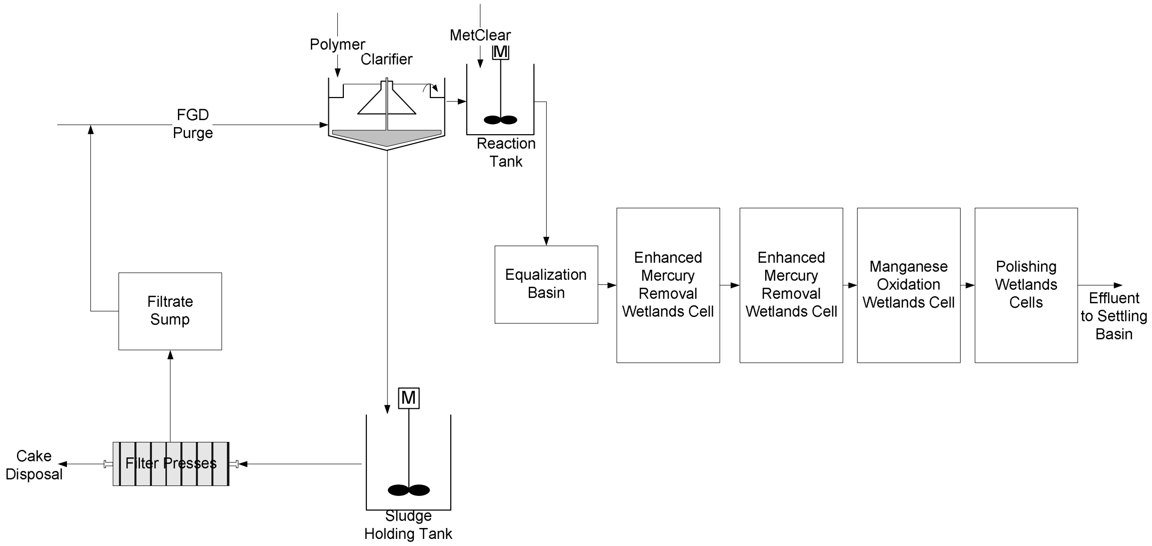


FIGURE 6-27
Site PG5 FGD Water Treatment Plant Process Flow Diagram

The FGD water flows into a clarifier where polymer is added to promote floc formation and settling, followed by a reaction tank where MetClear® is used to promote metals removal in the equalization basin. The solids from the clarifier are sent to a sludge holding tank and are then dewatered using a filter press.

The Site PG5 passive treatment system covers 6.5 acres (2.6 hectares). Service water is added at a 3:1 ratio with the FGD water prior to entering the wetlands to reduce chlorides to acceptable levels (below 4,000 mg/L). The FGD water is also cooled with the addition of service water, keeping temperatures below 95 ºF (35 ºC) and boron levels below 50 mg/L. The wetland is designed as a free water surface wetland and contains two trains where each train consists of two cells of bulrush, a third manganese oxidation cell, and a fourth cell containing cattails. Currently, organic substrate is not added to the wetland to enhance selenium removal.

Based on the data set provided from 2007 through June 2009, there is a 17% average removal of total selenium by clarification as pretreatment to the wetland (Figure 6-28). This suggests that there is relatively little particulate selenium within the FGD water and most of the selenium is in the dissolved or fine particulate form.

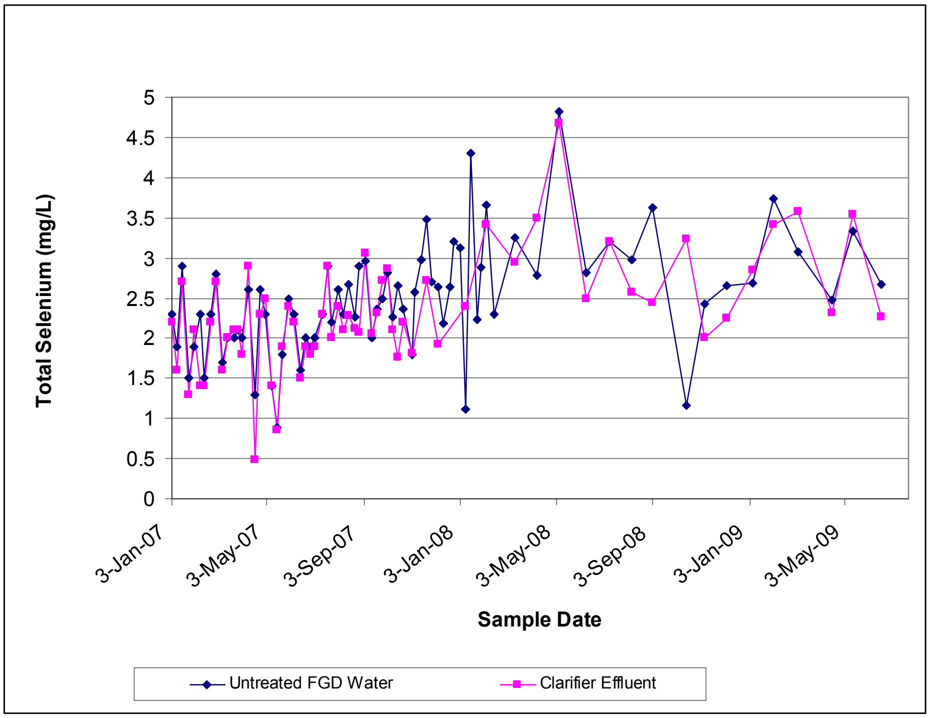


FIGURE 6-28
Site PG5 Total Selenium before and after Solids Separation

Table 6-9 shows the median selenium concentrations and speciation of untreated FGD water at Site PG5. The selenium present in the FGD water is predominantly dissolved selenium as selenate. Selenate is not removed well using physical/chemical treatment methods, as evidenced by the little or no removal observed.

TABLE 6-9
Selenium Speciation for Untreated FGD Water at Site PG5

Form of Selenium	Concentration (µg/L)
Total Selenium	2,720
Dissolved Selenium	2,500
Selenate	2,460
Selenite	7

Selenium removal has been variable at the constructed wetland at Site PG5 (Figure 6-29). Average total selenium removal achieved through the constructed wetland for the time period shown below is approximately 10% at Site PG5.

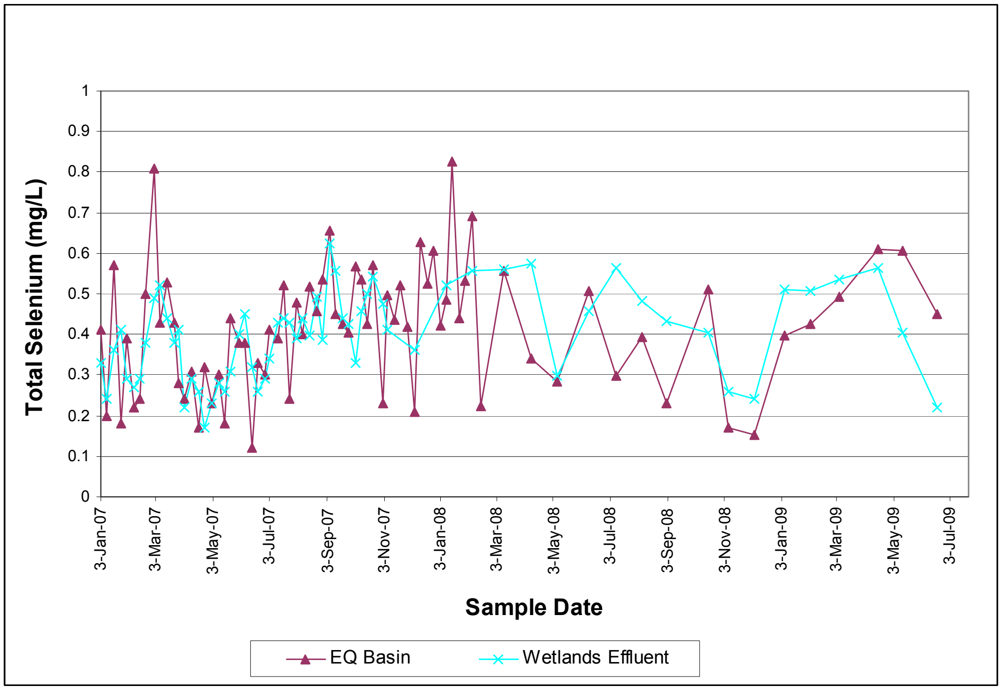


FIGURE 6-29
Site PG5 Total Selenium Removal through Constructed Wetland

6.7.3 Operations and Safety Considerations: Constructed Wetlands

Operational difficulties at Site PG4 have been observed at startup due to the presence of boron in the FGD water. Effects of boron on wetlands plants have been observed where the tips of the plants have turned brown. Service water is now added to maintain boron to ≤50 mg/L. At Site PG4, the wetlands plants have taken a long time to grow to cover the entire treatment cells, which may affect selenium removal. Maintenance costs of the wetlands treatment system is low with no O&M required to date for either of the systems constructed in 2007/2008, other than routine inspections.

6.7.4 Capital and Operating Costs: Constructed Wetlands

Capital costs of the Site PG5 constructed wetland are approximately $13 million. Operating costs of the constructed wetlands are low, with costs mainly due to chemical polymers used during pretreatment and disposal of solids.

6.7.5 Pilot Testing of Passive Treatment System at Coal-Fired Power Plant

Site PG4 has been piloting a vertical flow wetland at their site as part of a long-term pilot study. The vertical flow wetland pilot study has shown removal of selenium to low µg/L levels with removals of 85% across the wetland pilot test cell for total and dissolved selenium as part of a long-term pilot test (EPRI, pending (b)). The test cell received a portion of the discharge from the equalization basin (Figure 6-24). Subsequent monitoring in 2008/2009 evaluated three organic substrate configurations (Test Conditions 1 through 3 shown on Figure 6-30).

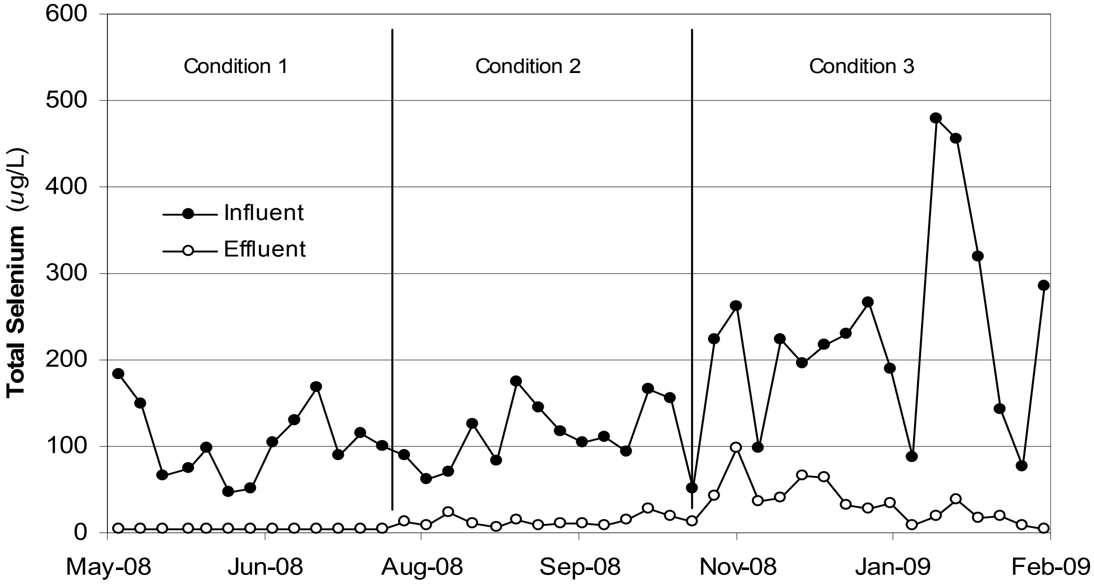


FIGURE 6-30
Vertical Flow Wetland Pilot Test Results for Total Selenium
Source: EPRI, pending(b).

The test cell was composed of organic substrate consisting of spent mushroom compost placed over a gravel bed. Influent total selenium ranged between 47.8 µg/L to 479 µg/L during this timeframe. Selenite:selenate ratios in the influent were 2:1 or greater.

Strongly reducing conditions favoring selenium and mercury removal, as indicated by ORP measurements, are developed within the first foot of the VFW substrate. It should be noted that influent water contained relatively low concentrations of selenium, as much of the selenium was removed in the solids removal step, upstream of the pilot. Also, though most selenium in the pilot influent was present as the more easily treated selenite, the smaller selenate fraction was also effectively captured in the pilot VFW (EPRI, pending(b)). Site PG4 recently decided to install a full-scale VFW which is expected to be operational by 2012.

6.8 Full-scale Treatment of Selenium for Coal Ash Leachate

Various studies have been performed for the treatment of selenium from coal ash leachate. A 28-month study was conducted on various trace elements at the Allegheny Power Services utility at Springdale, Pennsylvania. The Springdale coal ash leachate treatment system is a surface-flow constructed wetland comprising an equalization basin, four vegetated wetland cells, two rock drains, an organic upflow cell, and an algal treatment cell. An EPRI study concluded that there are five surface-flow constructed wetlands treatment systems in operation for coal ash leachate treatment, although none of these wetlands is designed specifically for selenium removal (EPRI, 2007b).

A study was conducted on coal ash leachate treatment at Tennessee Valley Authority’s Paradise Fossil Plant. Ammonia, arsenic, selenium, and mercury were measured during the study. The 125,000-gallon-per-day demonstration project consisted of two treatment processes run in parallel. The first treatment process was a trickling filter followed by a surface-flow constructed wetland. The second treatment system consisted of a trickling filter, ZVI extraction trench, settling/oxidation basin, and constructed wetland. The ZVI extraction trench consisted of a layered rock bed topped by a 6-inch layer of iron filings. The treatment option that included the ZVI extraction trench reduced selenium from 52 µg/L to 8 µg/L (EPRI, 2007b; USDOE, 2007).

7.0 Industry-Specific Approaches to Managing Selenium: Oil and Gas Sector

7.1 Characterization of Downstream Selenium in Refinery Wastewater

As described in Section 2.0, the major source of selenium in refinery wastewater is associated with crude oil from seleniferous deposits such as marine shales. The refining of crude oil requires water. While evaporative losses account for the nearly 50-80% of the water used in crude oil refining nearly 20% of the total water consumed will be discharged and require treatment (CH2M HILL 2003). Because selenium is isomorphous with sulfur it accompanies sulfur during the processing of crude oil in downstream refining processes. The majority of the selenium and sulfur contained in crude oil that is refined to fuels (e.g, gasoline, kerosene, etc.) or other petrochemicals is in the sour water streams from the control of overhead gases associated with the crude distillation, fluidized catalytic cracking and sulfur recovery unit processes in the refinery. The predominant forms of selenium in SSW are hydrogen selenide (H_2Se) and hydrogen selenocyanate (HSeCN) at acidic to neutral pH. Minor amounts of elemental selenium and oxidized forms such as selenite and selenate might also be present. The term “sour water” is derived from the presence of ammonia and hydrogen sulfide in the wastewater. Ammonia and hydrogen sulfide are typically removed from sour water by steam stripping in either a single or multi-stage steam stripping distillation unit operation resulting in the majority of the selenium in the stripper bottoms. Selenium removal by steam stripping is not effective (Montgomery Watson, 1995a).

A secondary and much smaller source of selenium to water discharges from refining is from crude preparation operations including the initial crude dewatering and desalting processing steps prior to refining. Crude oil can contain elevated quantities of inorganic salts, sand, silt, and iron solids. These impurities including water can be emulsified in the crude oil matrix and thereby require removal prior to refining. Crude oil is preheated and mixed with water to remove these impurities. The predominant form of selenium from these operations will be selenite and to a lesser degree selenate depending upon the level of oxidation during washing of the crude.

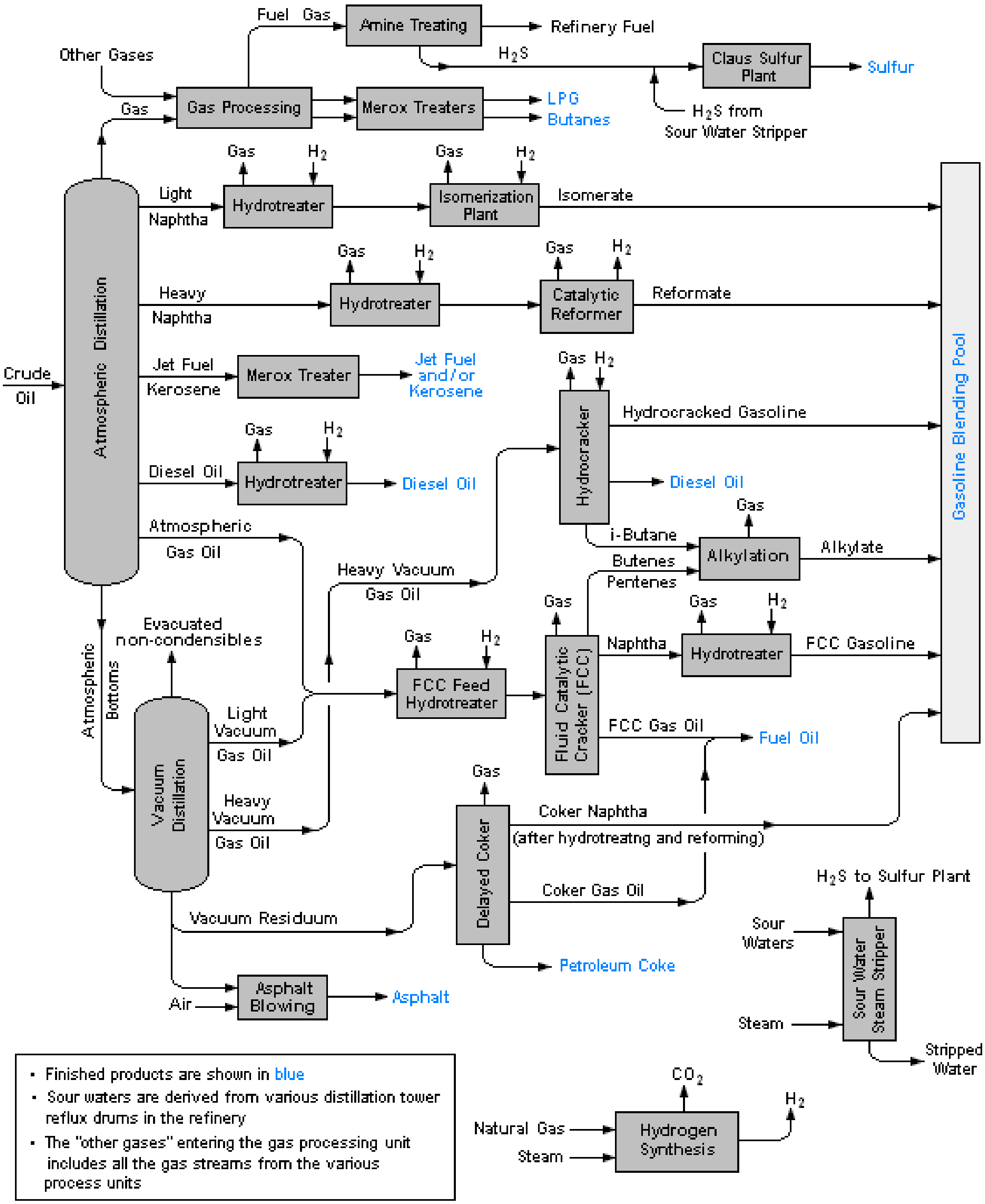
The SSW, crude dewatering and crude desalting streams are typically combined and treated by the refinery’s end of pipe wastewater treatment plant. Desalting or crude washing is used to remove many of the contaminants from the crude oil before further processing. Most refineries provide primary treatment for oil recovery and secondary biological treatment for soluble contaminants removal. During end of pipe treatment with aerobic biological processes the majority of the selenium from these processes will be oxidized to selenite and to a lesser degree selenate.

Table 7-1 presents the distribution of selenium species in the SSW and the wastewater treatment plant effluent of Bay Area refineries performed as part of a study for the WSPA (Brown and Caldwell, 1994). The principal source of selenium in refinery wastewater was identified during the study as SWS bottoms (Brown and Caldwell, 1994). Figure 7-1 illustrates a typical refinery process flow diagram and shows the SSW effluent wastewater stream.

TABLE 7-1
Selenium Speciation in Bay Area Refineries

Selenium Species	Stripped Sour Water (μg/L)	Refinery Wastewater Treatment Plant Effluent (μg/L)[1]
Total selenium	170 – 4,870	11 – 300
Particulate selenium	<5 – 33	<5
Dissolved selenium	141 – 4,700	16 – 290
Volatile selenium	<0.3	0.3 –15
Selenocyanate	84 – 4,800	<10
Selenite	<10	13 – 171
Selenate	<10	<10 – 46

Source: Adapted from Brown and Caldwell, 1994
Notes:
[1] The Refinery Wastewater Treatment Plant Effluent values within this table represent selenium levels that were present prior to introduction of selenium treatment at Bay Area refineries.



- Finished products are shown in blue
- Sour waters are derived from various distillation tower reflux drums in the refinery
- The "other gases" entering the gas processing unit includes all the gas streams from the various process units

FIGURE 7-1
Typical Oil Refinery Process Flow Diagram
Source: en.citizendium.org/images/6/60/RefineryFlow.png

Another stream that may contain elevated levels of selenium is the desalter effluent. The influent to the refinery wastewater treatment plant can consist of the following streams:

- SSW effluent
- Desalter effluent
- Coker effluent
- Boiler blowdown
- Cooling tower blowdown and other wastewater streams
- Extracted groundwater
- Stormwater
- Process condensate
- Spent caustic
- Maintenance/sampling
- Hydrotest water
- Wash water
- Tank bottom draws
- Process water wash streams
- Water treatment/rinse backwash

Upgrading of bitumen or heavy crude oil is a process that removes the heavy oil from the oil sands after bitumen mining and ore processing. Upgrading is a low complexity refining step that typically involves the separation and processing of diluents used to aid in the separation of the bitumen from the sand. It also include further processing of the separated heavy oil including distillation steps to separate naptha and gas oils with hydrotreating and stabilization as well as hydrocracking of the heavy oil and desalting. Much like refineries the selenium will be concentrated in the sour water treatment systems and the desalting water.

7.2 Refinery Wastewater Prevention/Source Control

Prevention and source control options for the oil and gas sector are more limited than for other sectors because of the variability in the feedstock properties and the complexity of the refining process. A lower quality crude oil feedstock translates into additional processing and greater amounts of water use and subsequent waste generation (CH2M HILL, 2003, Higgins, 1995). Prevention/source control methods in refineries focus on recycling and segregation of wastewater streams.

The following may be feasible waste recycling and reuse opportunities for the refining industry on a site specific basis:

- SWS bottoms recycled as Crude Desalter Water
- Boiler blowdown recycled as cooling tower makeup
- Cooling tower side stream softening
- Demineralizer reject as cooling tower makeup
- Wastewater treatment plant effluent recycled as cooling tower makeup water
- Spent catalyst sent for offsite regeneration

The SWS bottoms can be used as wash water in the crude oil desalter. The SWS bottoms may be high in phenol, and using the water for this purpose has the additional benefit of phenol removal (Higgins, 1995). While this reuse will not eliminate the selenium discharge to the effluent wastewater treatment system, it will affect the resulting concentration of the selenium to the end of pipe treatment system.

Segregation and rerouting of wastewater sources within a refinery can be performed to minimize the overall flow of wastewater that is treated at the refinery wastewater treatment plant. Examples of streams that can be segregated and rerouted for direct discharge include uncontaminated stormwater or, in some cases, cooling tower blowdown.

7.3 Refinery Wastewater Treatment for Selenium Removal

Even with water reuse and segregation, water used in crude oil refining may still result in wastewater with elevated levels of selenium. Selenium removal from refinery wastewater can be accomplished at various locations within a refinery:

- Upstream of the refinery wastewater treatment plant at higher selenium concentration waste streams such as SSW effluent or desalter effluent.
- Secondary suspended growth biological treatment of the whole waste stream with specific additional technologies for selenium removal.
- Tertiary treatment of the secondary biological treatment effluent for selenium removal.

7.3.1 Stripped Sour Water Treatment Approaches

The majority of the selenium in stripped sour water is typically selenocyanate. However, this is a function of the refinery configuration and certain other features of refinery processing, and in some stripped sour waters other forms may predominate. Selenocyanate can be treated either by heavy metals precipitation, or through oxidation of the selenocyanate complex to selenite and subsequent adsorption.

Copper precipitation of the selenocyanate complex (e.g., sodium selenocyanate) occurs at elevated pH of 9-10 and results in approximately 95% removal of the selenocyanate (Manceau and Gallup, 1997). Tin and silver salts were found to be equally effective at chemical precipitation of the selenocyanate but even more cost prohibitive. The primary issue with this approach is that it may add excess copper to the refinery effluent, and water quality criteria for copper may be lower than for selenium. Other issues include the efficacy of the treatment – what level can be consistently achieved in the effluent.

Oxidation and adsorption of selenocyanate is complicated by the wastewater matrix given the waste stream also contains higher levels of COD and ammonia-nitrogen. Controlling the oxidation of the selenocyanate to selenite only (not allowing to oxidize to selenate) can be difficult and therefore may either be incomplete given other chemicals that can consume the oxidant or proceed completely to selenate. Chemical oxidation can be accomplished by the addition of hydrogen peroxide, chlorine dioxide, potassium permanganate and ozone. If the reaction is controlled to produce selenite it can be adsorbed through ferrihydrite iron co-precipitation.

There are two issues with this treatment approach. First, in the full-scale system, it is very difficult to control the chemical oxidation reaction to stop at selenite formation and the oxidation reaction proceeds to formation of selenate. Selenate is very poorly removed by chemical adsorption in iron co-precipitation systems. Secondly, because of high levels of

COD, and reduced sulfur the chemical consumption rate will be high and can be cost-prohibitive. Assuming that the oxidation reaction can be controlled to form selenite, the iron requirement for selenium precipitation will be high due to the presence of high COD, and the sludge production will also be very high, may be as high as several tons of sludge (considered a hazardous waste) generated per pound of selenium removed, resulting in very high disposal cost. In addition, the commercial uses typically achieve concentrations of 50 µg/L, significantly higher than the recent regulatory proposed limit of 5 µg/L.

As an example, a SSW bottom selenium removal treatment system was one considered alternative for selenium discharge compliance for a Suncor refinery. The treatment system would require significant capital investment but still not remove enough of the total mass of selenium considering other sources to meet the targeted 4.6 µg/L discharge requirement. Additionally pilot tests confirmed the difficulty in controlling the oxidation of selenium. The approximate 12,000 pounds per day of iron residuals that would be produced would also result in additional operating and disposal costs (Davis et al., 2009).

The results of the 1994-1995 study (Brown and Caldwell, 1995; Montgomery Watson, 1995a) conducted for WSPA also stated similar concerns as above. The study also stated that the kinetics of oxidation pretreatment is important for effective selenium removal. The completeness of the oxidation reaction is dependent on dose, temperature, pH, and contact time. The optimal pH for iron co-precipitation was reported to be 5.5. The optimal pH for hydrogen peroxide and ozone oxidation was reported to be 11, and the optimum pH for chlorine dioxide was 7.

The results of another 1994-1995 study (Aware Engineering Inc., 1995.) for WSPA indicated that ion exchange treatment technology is not effective for the removal of selenium from SSW effluent. High sulfur (all species) and TDS were reported to reduce its effectiveness.

7.3.2 Combined End of Pipe Refinery Wastewater Treatment Approaches

Combined refinery wastewater discharges are typically treated biologically after primary removal of oil in suspended growth biological treatment processes. Selenium removal can be accomplished in both conventional activated sludge and biological nutrient removal configurations for end of pipe treatment. In these biological treatment systems, selenocyanate can be oxidized through aerobic heterotrophic biological treatment to selenium and subsequently oxidized to selenite and in part selenate. The selenite and selenate can be reduced to elemental selenium under anoxic conditions in biological nutrient removal configurations, where it is an electron acceptor similar to nitrates in the absence of oxygen and presence of carbon in the anoxic zone. The biological nutrient (e.g. nitrogen) removal treatment flow schematic typically consists of an anoxic reactor followed by an aerobic reactor and secondary clarification with internal recycle from the aerobic reactor to the anoxic reactor. This configuration is known as the Modified Ludzack-Ettinger process and will typically result in at most 80% total nitrogen removal and similarly partial reduction of selenium. However, this process has not been demonstrated on a commercial scale in a refinery. Figure 7-2 provides a simplified process flow diagram for this process.

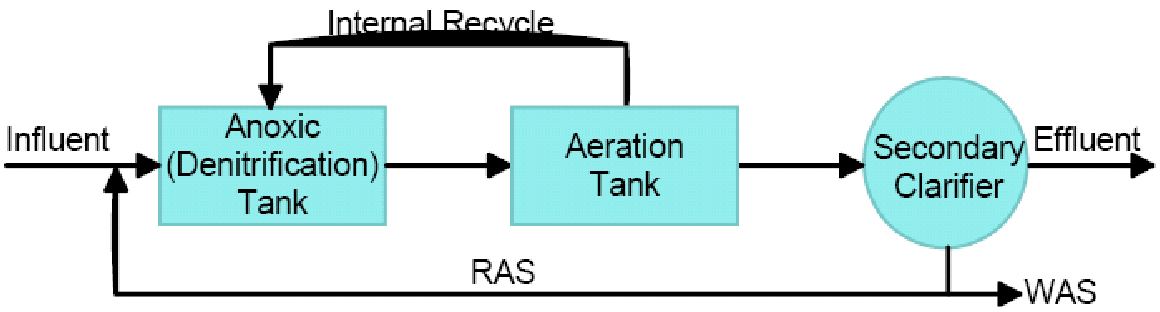


FIGURE 7-2
Typical Biological Nutrient Removal Treatment System

If the effluent biological treatment system is a conventional activated sludge system then selenite and to a lesser degree selenate will be produced through the biological oxidation of the selenocyanate. Without adsorption or reduction, these soluble forms of selenium will pass through the secondary clarifier and be discharged with the effluent. Figure 7-3 provides a simplified process flow diagram for a conventional activated sludge process.

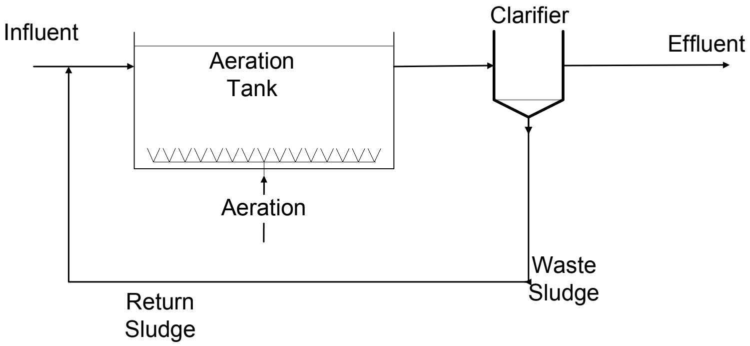


FIGURE 7-3
Conventional Activated Sludge Treatment System

If the discharge limitations dictate further removal of selenium from these two typical end-of-pipe biological wastewater treatment systems, then tertiary treatment or polishing will be required. These can consist of either biological or chemical treatment processes. In order to achieve low levels of selenium, a polishing anoxic reactor after the aerobic reactor can be introduced with the addition of a small amount of external organic carbon source such as methanol as electron donor. Alternatively, polishing treatment technologies such as anoxic filter, ABMet®, and FBR can be used on the secondary clarifier effluent to reduce the selenium concentration to acceptable levels. The effluent from the SSW treatment system can be either combined to the other refinery waste streams for further treatment or can be discharged directly to the outfall depending on the effluent quality.

Biological treatment with *in-situ* iron addition for selenite adsorption through ferrihydrite coprecipitation is also possible. However, this will reduce the operating pH of the biological treatment system and produce excessive sludge for disposal. Also, the effectiveness of iron co-precipitation to consistently achieve low levels (less than 5 µg/L) has not been demonstrated (San Francisco Bay Area refineries using iron co-precipitation typically achieve <50 µg/L, not 5 µg/L), and this approach may also be cost-prohibitive.

The results of the 1994-1995 study (Brown and Caldwell, 1995; Montgomery Watson, 1995b) conducted at Shell Oil Company for WSPA indicated that the anoxic/aerobic suspended growth process can achieve a selenium removal efficiency of approximately 62% under normal operating conditions without increasing the total sludge production. The average selenium concentration was reduced from an influent value of 263 µg/L to an effluent value of 94 µg/L. The aerobic suspended growth process with ferric addition reduced the average selenium from an influent value of 311 µg/L to an effluent value of 63 µg/L. However, the sludge production was increased significantly, and the operating pH was reduced.

7.3.3 Tertiary Treatment of Biologically Treated Effluent

The biologically treated effluent can be further treated for selenium removal using polishing treatment technologies such as anoxic filters, ABMet®, FBR, iron co-precipitation, and ion exchange. However, iron co-precipitation may not reduce the selenium concentration to low levels (less than 5 µg/L) because it doesn’t effectively remove the fraction of selenium in selenate form. Any technology that is selected needs to be pilot-tested for effectiveness to remove selenium to low levels.

The results of the 1994-1995 study (Brown and Caldwell, 1995; Montgomery Watson, 1995b) conducted at Shell Oil Company for WSPA indicated that the anoxic fixed-film process can achieve a selenium removal efficiency of approximately 68% under normal operating conditions, reducing the average selenium concentration from an influent value of 153 µg/L to an effluent value of 46 µg/L. The effluent target value for selenium removal in this study was 50 µg/L. Additional pilot testing needs to be conducted at various refineries’ wastewater treatment plants to confirm the effectiveness of the selenium polishing treatment technologies.

7.4 Case Studies for Selenium Removal in Wastewater

7.4.1 Refinery A

An example of selenium removal at various stages of treatment is the case study for treatment studies conducted at various Refinery A. Selenium removal is employed at the following stages within a refinery:

- SSW effluent
- Biotreater effluent
- Dissolved air flotation unit feed

SSW Treatment. Figure 7-4 contains a process flow diagram for the treatment system at the SSW effluent. The treatment system consists of oxidation with potassium permanganate followed by iron co-precipitation. Potassium permanganate is used to oxidize selenocyanate to selenite. A 70 US gpm (265 Lpm) system was built to treat 4,800 µg/L total selenium (mainly consisting of selenocyanate) to approximately 500 to 1,000 µg/L to reduce the selenium load downstream. Cost information is not available for this system.

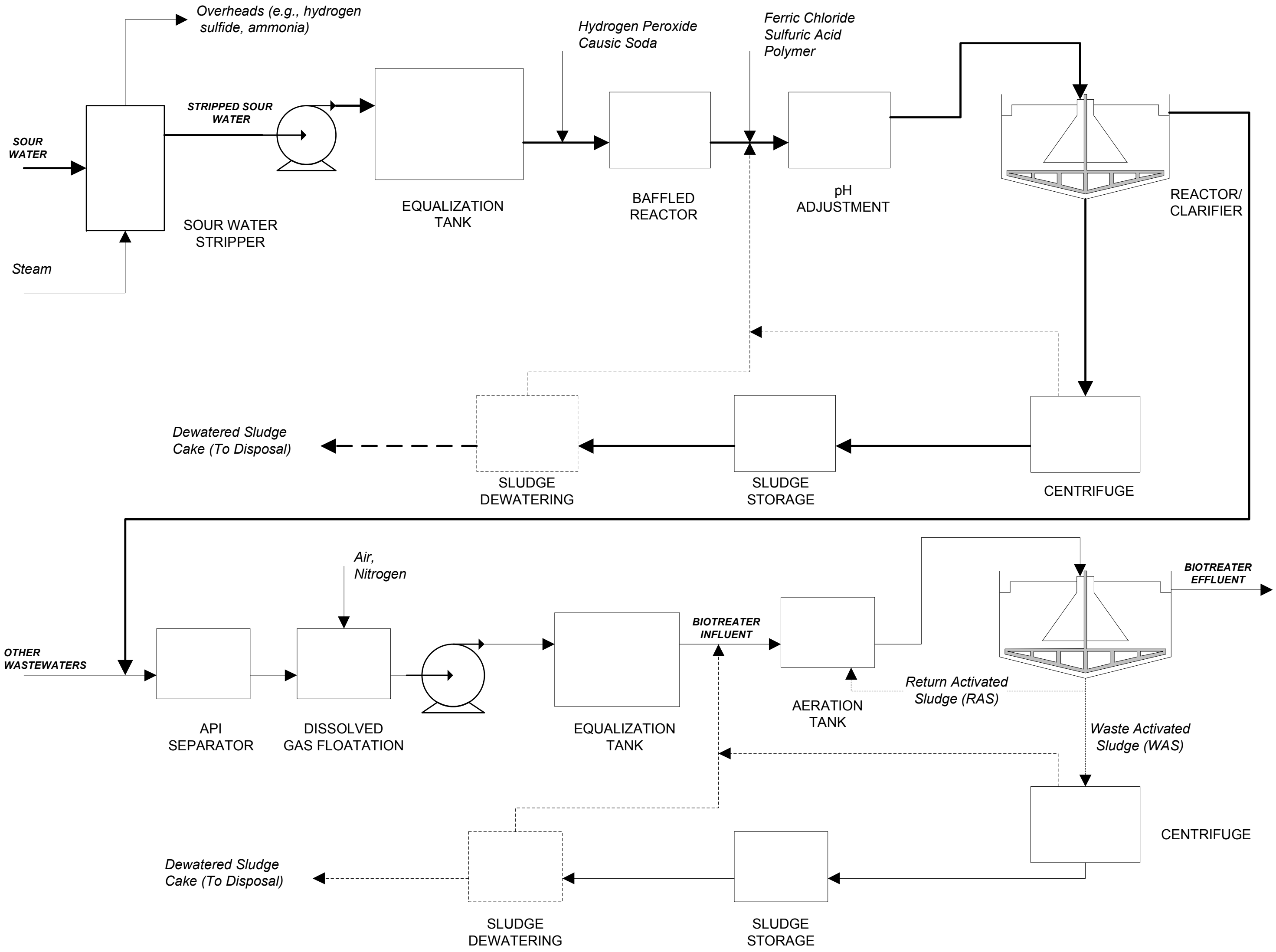


FIGURE 7-4
Refinery Stripped Sour Water Effluent Treatment System Process Flow Diagram

A pilot study was conducted at Refinery A over a 2-week period for the SSW effluent using the VSEP® technology. The flow rate of the pilot study was 0.64 US gpm (2.4 Lpm). The first stage recovery was 92%, and second stage recovery was 70%. The average influent to the pilot was approximately 480 µg/L and achieved an average effluent of 73.4 µg/L. The reject selenium concentration was 5,160 µg/L. Pretreatment would be required to reduce membrane fouling for a full-scale system. The costs of disposal of the reject from the VSEP® technology would be higher than the disposal costs compared to a UF/RO unit because of pretreatment chemicals added. A full-scale system was estimated to require weekly cleaning and to include high operating costs due to labor and chemicals.

Dissolved Air Flotation Unit Feed Treatment. The process flow diagram for the treatment system shown in Figure 7-4 also shows the treatment system at the dissolved air flotation unit feed. The 600 US gpm (2,270 Lpm) treatment system consists of ferric chloride addition oxidation. The chemical feed system has about a 1,000-square-foot footprint. The system treats an influent concentration of 450 µg/L to 200 µg/L. The capital cost of the system was $2 million (2005 USD). The costs included a combination of the chemical feed system and an upgrade of the existing dissolved air flotation system. Operating costs are not available.

Biotreater Effluent Treatment. Figure 7-5 includes a process flow diagram of the refinery wastewater treatment system. The footprint of the system is approximately 20,000 square feet (1,850 square meters), including the settling ponds. The flow rate of the wastewater treatment system is 6 million US gallons per day or approximately 4,167 US gpm (15,775 Lpm). The influent to the treatment system is approximately 176 µg/L, and the effluent of the system is approximately 36 µg/L (based on a 2-year average with ±20% variability). Selenite is the predominant species to be treated, with over 70% of the selenium attributable to selenite. The iron co-precipitation system shown in Figure 7-5 treats selenium only in the selenite form. Another disadvantage of the system is the high volume of sludge generated from the use of iron. The cost of the system is $15 million (1995 USD).

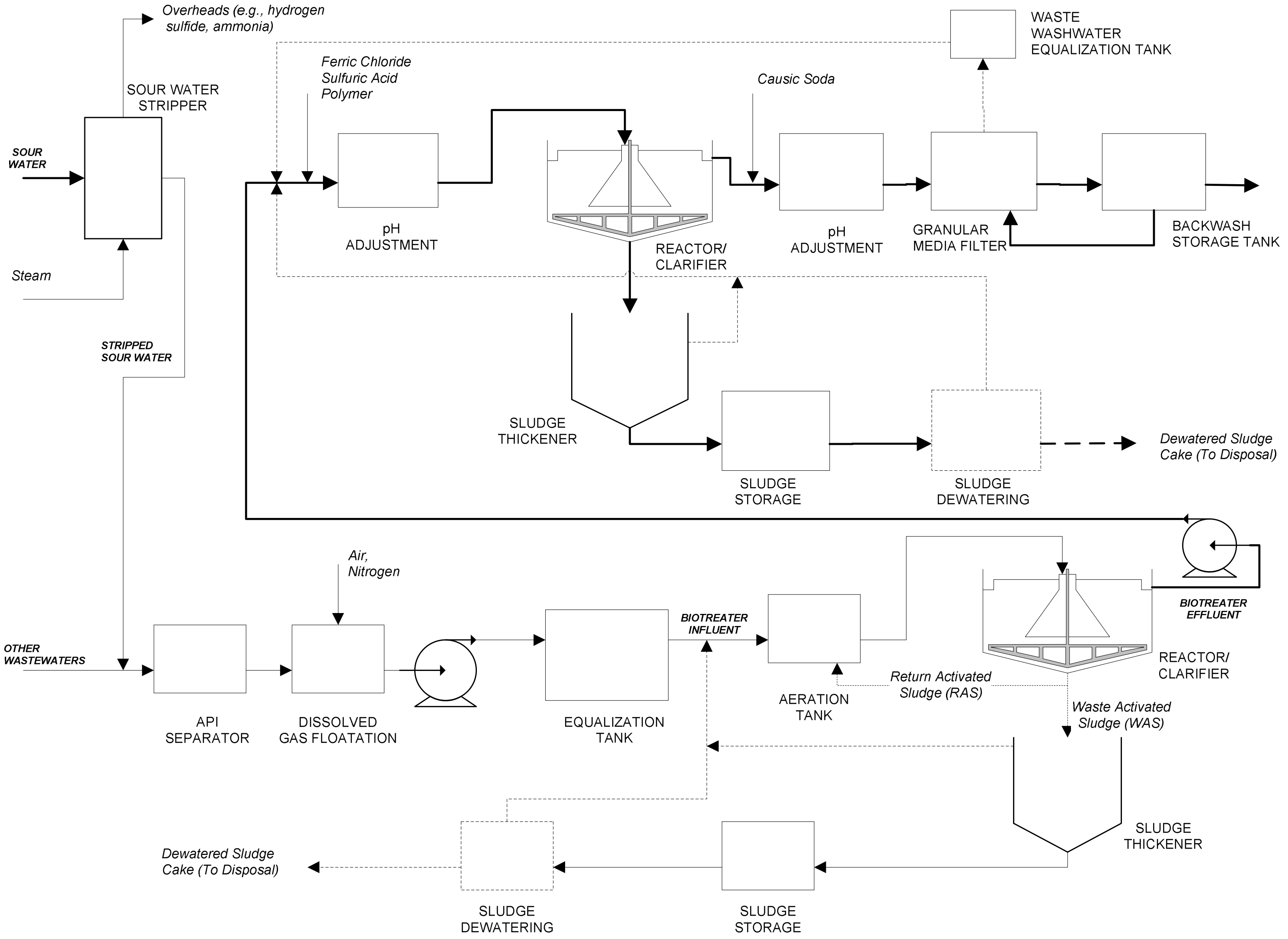


FIGURE 7-5

Refinery Biotreater Effluent Treatment System Process Flow Diagram

A pilot study has been performed on the final effluent at a refinery using UF/RO treatment. A 15.67 US gpm (59 Lpm) study was performed with a UF recovery of 90% and RO recovery of 75%. The influent to the unit was 600 µg/L and achieved an effluent concentration of 6 µg/L. The disadvantages of UF/RO are that pretreatment is required, fouling of the membrane is an issue, there are high operational costs due to labor and chemicals, and the treatment is energy-intensive.

7.4.2 Refinery B

Iron co-precipitation treatment has been installed at Refinery B to remove selenium from wastewater treatment plant effluent. A pilot-scale Actiflo® process (Siemens Water Technologies licensed from Kruger, Inc.) was tested and installed full-scale at the refinery (McCloskey and Jettinghoff, 2009). The full-scale system has been in operation since May 2008. Refinery B is required to meet an outfall limit of 12 µg/L for total recoverable selenium for their facility. The major source of selenium is the SSW effluent. Originally, membrane treatment of the SSW effluent was considered but not carried forward because of concerns of high temperature and high organic loading on membranes such as RO.

The existing wastewater treatment system consisted of primary and secondary treatment. The Actiflo® process was installed prior to the final sand filter to precipitate and remove selenite within the biotreatment effluent. The sand filter removes particulate selenium that has been precipitated as part of the Actiflo® process. The Actiflo® process is a clarification process that combines ballasted flocculation with microsand and lamellar tube settling (McCloskey and Jettinghoff, 2009). The footprint of an Actiflo® is up to 20 times smaller than a conventional clarifier and has a high overflow rate (40 US gpm per square foot) and short HRT (McCloskey and Jettinghoff, 2009).

Figure 7-6 shows a conceptual drawing of the Actiflo® process. Ferric chloride is added as a coagulant for iron co-precipitation. Polymer is added to improve flocculation and settling of particulate selenium adsorbed to microsand. Sludge that is settled at the bottom of the clarifier is sent to a hydrocyclone to separate the microsand from the sludge for reuse. The clarified water exits the system and flows to the final sand filters (McCloskey and Jettinghoff, 2009).

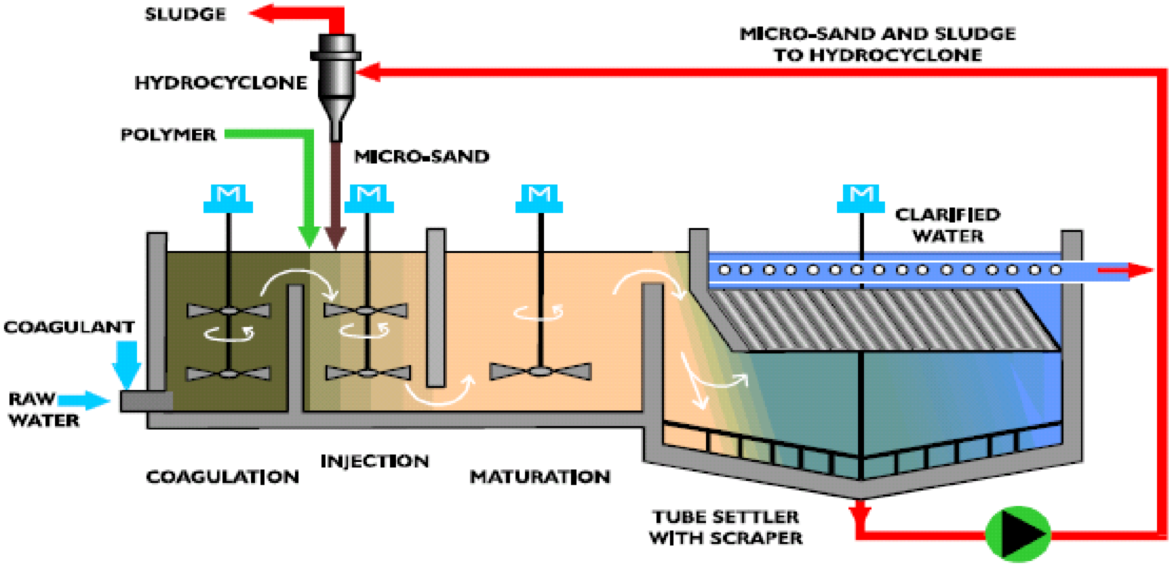


FIGURE 7-6
Actiflo® Process
Source: McCloskey and Jettinghoff, 2009

Pilot testing was conducted in early 2008 for 3 months at a flow rate of approximately 900 gpm. Pilot study measurements of total selenium resulted in overall selenium removal of 61.4%. All effluent readings were below 12 µg/L (McCloskey and Jettinghoff, 2009).

The full-scale system has been in operation since May 2008 and treats 4,000 to 5,000 usgpm. The full-scale system consists of five pilot-scale mobile units. The system was installed in a building for weather protection (McCloskey and Jettinghoff, 2009).

The refinery has performed a study on the use of clean metals sampling techniques (USEPA Method 1669) and ICP-DRC-MS on refinery wastewater effluent that resulted in significantly reduced interferences with a MDL that is several orders of magnitude lower (<0.01 µg/L) than conventional methods (2 µg/L). This method was used to determine upstream concentrations for re-evaluation of the permit limit for the facility (Redman et al., 2009).

8.0 Conclusions

The development of low cost, reliable technologies to remove selenium from water is a priority for the agriculture, mining, power generation, and oil and gas industries as environmental standards and criteria applicable to their surface water discharges are currently very low with a potential for them to be even lower given pending guidance by regulatory agencies.

Water treatment for the removal of selenium will likely be a component of a successful selenium management strategy for industry to achieve selenium discharge requirements of 5 µg/L in the United States or 1 µg/L in Canada. It should be considered in conjunction with water reuse, prevention and source control measures for selenium. Prevention of release and source control strategies for selenium may be more, or less desirable depending upon the industrial activity and their associated costs compared to end of pipe water treatment. Generally, complete source control will not be possible, or practical for many process-affected waters from the various industry sectors.

Achieving selenium levels of less than 5 µg/L in the United States (1 µg/L in Canada) in water discharges from the various industry processes poses a challenge 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 chemicals);
- Treatment generally results in a concentrated by-product or residual; and,
- Re-release from the residuals can occur.

Significant variation in selenium levels and forms exist among the different industry types, within each industry type, and even sometimes within the same facility over time. 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, there is no treatment technology that is a “one-size fits all” solution. Adequate characterization of selenium that captures seasonal variation and speciation of selenium should be performed to determine the applicable technology for removal. Selection of the technology is highly dependent on the speciation of selenium and the competing and interfering water chemistry of industry-specific waters. The flows for some discharges vary greatly over the course of time and selection of the technology will be limited by the minimum and maximum feasible ranges of design flows for a treatment system to function properly.

There are a variety of physical, chemical and biological treatment technologies that 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 treatment technology process. Because the performance of each technology is flow based, the system may require flow equalization infrastructure as well. The end result is a treatment plant that can have a significant total installed and operations and maintenance cost. While these physical, chemical and biological treatment technologies have the potential to remove selenium, there are very few technologies that have successfully and/or consistently removed selenium in water to less than 5 µg/L at any scale. There are still fewer technologies that 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. There are no technologies that have been demonstrated at full-scale to cost-effectively remove selenium to less than 5 µg/L for waters associated with every one of the industry sectors. Therefore, performance of the technology must be demonstrated on a case-specific basis.

Information exchange among and within industries is needed to advance technologies for selenium removal, including the need to consider process engineering principles applied to both the science behind the physical, chemical treatment technology, and an overall system configuration for the core treatment technology.

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