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LITERATURE REVIEW OF TREATMENT TECHNOLOGIES TO REMOVE SELENIUM FROM MINING INFLUENCED WATER

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LIST OF ABBREVIATIONS

ABSR - Algal-bacterial selenium removal

BCR- Biochemical reactors

BATs - Best available technologies

BDAT – Best Demonstrated Available Technology

CCME - Canadian Council of Ministers of the Environment

DMSe - Dimethylselenide

DMDSe - Dimethyldiselenide

EES - Enhanced evaporation systems

FGD - Flue gas desulfurization

FWS - Free water surface wetlands

GAC - Granular activated carbon

gpm - Gallons per minute

MIW - Mining influenced water

NF - Nanofiltration

PEI - Polyethyleneimine

RO - Reverse osmosis

SSF - Subsurface flow wetlands

TSS - Total suspended solids

UASBR - Upflow anaerobic sludge blanket reactors

USEPA - U.S. Environmental Protection Agency

ZVI -Zero valent iron

1.0 EXECUTIVE SUMMARY

Elevated aqueous selenium concentrations have been detected at multiple mine sites in Alberta and British Columbia. The waterbodies containing elevated concentrations, which exceed the Canadian Council of Ministers of the Environment (CCME) guideline for total selenium of 1 μg/L, range from creeks and rivers to large endpit lakes. The purpose of this paper is to provide a review of the literature for advances in the treatment of selenium in mining influenced water (MIW) and other waters containing selenium derived from non-mining sources. This review focuses on the types of technologies available, discusses the advantages and disadvantages of various treatment options, and identifies the stage of development of each technology, i.e., laboratory studies, pilot scale tests, or full scale treatment facilities. This review is limited to water treatment, which is one of three selenium management tools (Chapman et al. 2009). The other two management tools, prevention of selenium release and control of selenium in the environment, are not reviewed.

Significant research and development of selenium treatment technologies has occurred over the past two decades. The challenge of treating selenium to meet the stringent applicable standards of a few micro-grams per liter has led to testing of multiple physical, chemical, and biological treatment methods. Among these methods, proven full-scale treatment is currently being conducted by reverse osmosis, reduction by iron, active and passive microbial reduction, *in situ* microbial reduction, and wetlands. These methods are capable of meeting applicable standards, and provide a suite of tools to tackle the increasingly important issue of selenium in the environment. Some Canadian mine site discharge flow rates pose a significant design challenge. These rates can be on the order of 250,000 m^3/day (45,863 US gallons per minute), significantly greater than the highest selenium treatment plant flow rate of 7,630 m^3/day (1,400 US gallons per minute). Although full-scale treatment of selenium is proven, it has not been demonstrated for flow rates typical of the Canadian mine sites.

In the past five years, biological treatment has emerged as a leading technology for selenium treatment. Biological treatment offers a low cost alternative to more expensive physical and chemical treatment methods and is effective in cold climates. Additionally, it has the proven ability to meet regulatory selenium limits. Several different types of active microbial reduction biological systems are currently in operation, including Upflow Anaerobic Sludge Blanket Reactors and Anaerobic Fixed Film Bioreactors. Passive and *in situ* microbial reduction biological treatment systems have the lowest operating costs but have not been developed at full-scale to the same extent as active microbial systems.

2.0 INTRODUCTION

Elevated aqueous selenium concentrations have been detected at multiple mine sites in Alberta and British Columbia. The waterbodies containing elevated concentrations, which exceed the Canadian Council of Ministers of the Environment (CCME) guideline for total selenium of 1 μg/L, range from creeks and rivers to large endpit lakes. The purpose of this paper is to provide a review of the literature for advances in the treatment of selenium in mining influenced water (MIW) and other waters containing selenium derived from non-mining sources. This review focuses on the types of technologies available, discusses the advantages and disadvantages of various treatment options, and identifies the stage of development of each technology, i.e. laboratory studies, pilot scale tests, or full scale treatment facilities. Particular attention is paid to case studies demonstrating the potential of different technologies. Consideration is also given to technologies that are appropriate for the cold climate of the mine sites. This review is limited to water treatment, which is one of three selenium management tools (Chapman et al. 2009). The other two management tools, prevention of selenium release and control of selenium in the environment, are not reviewed.

3.0 SELENIUM CHEMISTY

Selenium is a metalloid found in Group VIA of the periodic table, below sulfur. It has similar chemical properties to sulfur due to its analogous electron distribution, which can make remediation in the presence of sulfur challenging. Selenium is present in the environment in both inorganic and organic forms, and in the solid, liquid, and gas phases. Although it can exist in six oxidation states, the II+ state is not known to exist in nature (Lenz 2008). The four most common, naturally occurring oxidation states are as follows:

- II- H_2Se, HSe^- , metal selenides, alkyl selenides, seleno-amino acids, seleno-proteins
- 0 Se^0 including trigonal (grey) and monoclinic (red) crystalline forms
- IV+ SeO_3^{2-}, $HSeO^{3-}$ and H_2SeO_3
- VI+ $SeO4^{2-}$ and $HSeO_4^-$

Inorganic forms include SeO_3^{2-}, SeO_4^{2-}, Se^0, H_2Se, and metal selenides (MeSe). Organic forms include alkyl selenides such as dimethylselenide (DMSe) and dimethyldiselenide (DMDSe), seleno-amino acids, and seleno-proteins including selenocysteine and selenomethionine. Selenocystein and selenomethionine are analogues of the sulfur-containing proteins methionine and cystein. Both DMSe and DMDSe are volatile, sparingly soluble, and relatively non-toxic, although both are bioavailable (Shrestha et al. 2006). The formation of organic selenium is typically biologically mediated.

Oxidized inorganic forms of selenium exist as highly soluble oxyanions in aqueous systems. Neither Se(VI) (selenate) nor Se(IV) (selenite) anions react with common cations such as calcium or magnesium, therefore they tend to remain in solution. Se(IV) species are more reactive than Se(VI) species and are easier to reduce to elemental selenium (Chapman 2000). Selenium oxyanions frequently associate with particles (e.g., sediments) and can be transported in particle-associated forms. Both selenate and selenite are bioavailable and have high potential for bioaccumulation and toxicity.

Elemental selenium exists in seven different crystalline forms and at least three amorphous forms. Elemental selenium is relatively insoluble and not readily bioavailable, making formation desirable during selenium remediation (Frankenberger and Karlson 1994). Nevertheless, elemental colloidal selenium particles are easily transported through aqueous systems (Haygarth 1994). Inorganic reduced selenium species include insoluble metal selenides and the highly toxic hydrogen selenide (H_2Se), an analogue to hydrogen sulfide only formed under strongly reducing conditions. Hydrogen selenide is highly reactive and forms metal selenides or is substituted into metallic sulfide minerals such as chalcopyrite ($CuFeS_2$) and pyrite (FeS_2).

3.1 Oxidation-Reduction Reactions

Selenium speciation and therefore remediation is highly dependent on pH and redox potential (Eh). A simplified selenium-water system Pourbaix diagram showing major thermodynamically stable selenium species as a function of pH and Eh is shown in Figure 1 (Microbial Technologies 2005). This diagram assumes thermodynamic equilibrium; however, selenate and selenite are often found outside their predicted thermodynamically stable zones (Microbial Technologies 2005). Because selenite is more reactive than selenate, many treatment processes depend on the reduction of selenate to selenite. This process is energetically favored, but occurs slowly in natural systems.

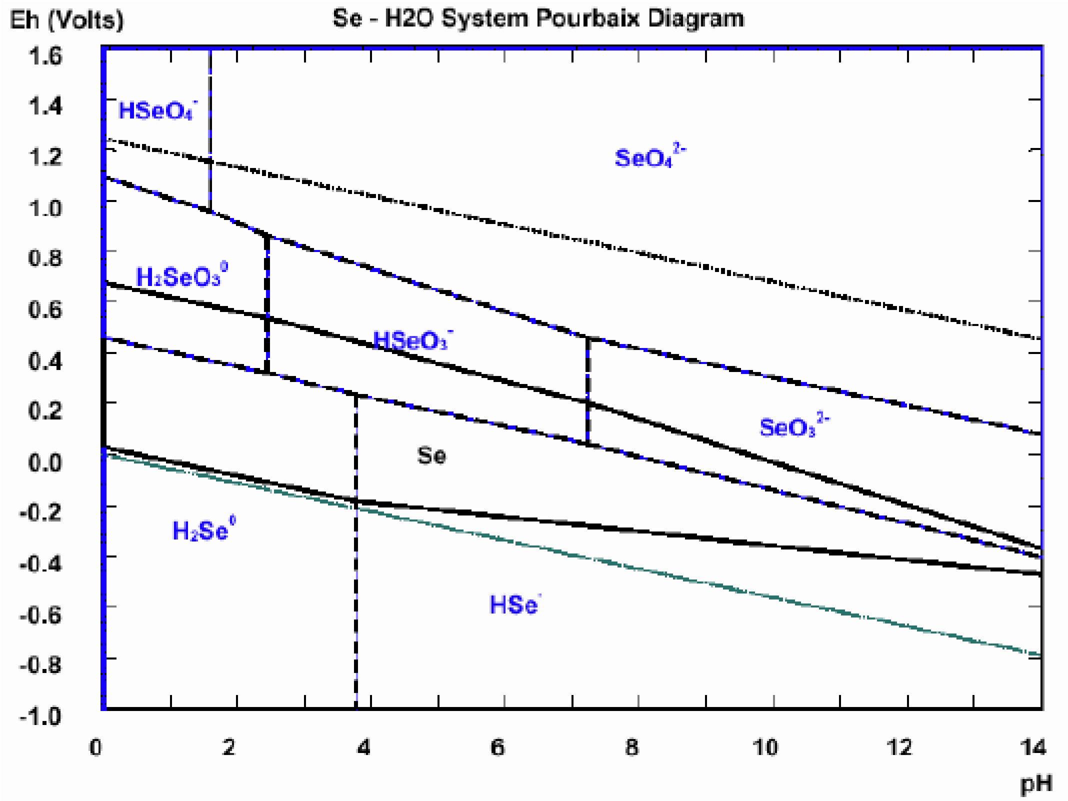

Figure 1. Eh-pH Diagram For The Se-H_2O System. From Microbial Technologies 2005.

3.2 Biologically-Mediated Reactions of Selenium

Biological systems can catalyze the reduction of selenium under normal environmental conditions. Anaerobic and aerobic bacteria, algae, fungi, and plants have all been shown to mediate these reactions (Masschelyn and Patrick 1993). Selenate can be reduced to selenite, and both selenate and selenite can be reduced to elemental selenium or alkyl selenides. These reactions are desirable because elemental selenium is less soluble and therefore less bioavailable and alkyl selenides such as DMse and DMDSe are highly volatile and only sparingly soluble in aqueous systems. These reactions have been encouraged for selenium remediation by creating conditions favorable to microbial growth, constructing wetlands, and applying selenium-bearing wastes or waters to plant-soil systems, a process known as phytoremediation (e.g., Zhang and Frankenberger 2003; Azaizeh et al. 2006; Bañuelos et al. 2005). Temperature, pH, moisture, time, season, concentration and speciation of selenium, and the addition of a carbon source all affect these reactions (Masschelyn and Patrick 1993; Lenz 2008).

Historically, these biologically-mediated reactions have been poorly understood, but recent advances have increased our understanding of these processes. Figure 2 illustrates the biochemical cycling of selenium in the environment by bacteria (adapted from Lenz 2008). Selenate and selenite can be reduced to elemental selenium, a process known as dissimilatory metal reduction, by anaerobic selenium respiration and non-specific selenium reduction by nitrate reducers, sulfate reducers, and archaea. Lenz (2008) suggests inhibition and competition with other anions such as nitrate (which prevent the reduction of selenium in their presence) can be overcome by including anaerobic selenium respirers in the microbial community. Selenium respirers will selectively reduce only selenium and are not affected by competing anions. This process is termed bioaugmentation when specific bacteria are added to an existing microbial population or biostimulation when conditions are manipulated to promote the growth of targeted microbial populations. Oxidation of elemental selenium back to soluble oxyanions can also be mediated by bacteria under oxidizing conditions. Generally, rates of re-oxidation are three to four orders of magnitude slower than microbial reduction (Tokunaga et al. 1994). Solubilization of selenium can occur when elemental selenium is reduced to selenides; however, selenides readily react with metal cations, forming microbiologically induced metal selenide precipitates. Microorganisms can also re-oxidize metal selenides.

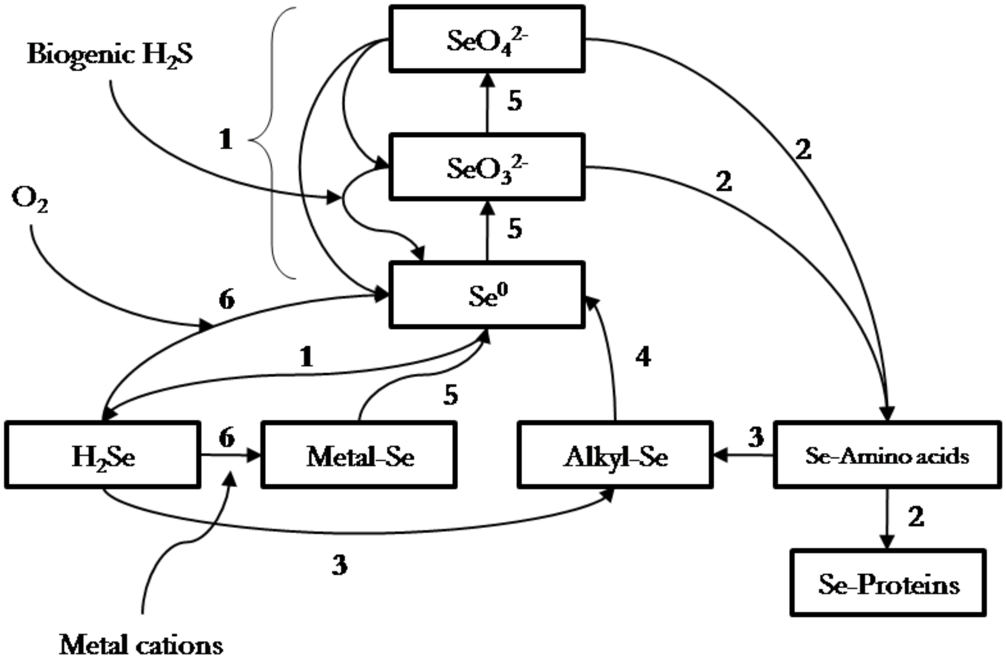

Figure 2. Biochemical selenium cycling with 1) Dissimilatory Reduction, 2) Assimilatory Reduction, 3) Alkylation, 4) Dealkylation, 5) Oxidation, and 6) Bio-induced Precipitation. Adapted From Lenz 2008.

4.0 TREATMENT TECHNOLOGIES

Since attention was first focused on selenium over 25 years ago at Kesterson National Wildlife Refuge, California a number of treatment technologies have been developed. These technologies can be divided broadly into three categories: physical treatment (e.g., reverse osmosis, ion exchange); chemical treatment (e.g., iron precipitation, cementation); and biological treatment (e.g., bioreactors, wetlands). An overview of treatments is provided in Table 1.

Physical treatment technologies include reverse osmosis, nanofiltration, ion exchange, and evaporation. All of these technologies are well understood and have been applied to water treatment in other industries; however, with the exception of reverse osmosis, these technologies have only been developed at a laboratory or pilot scale for selenium removal. Ion exchange is strongly affected by the presence of other ions and in many mining applications sulfate is present at concentrations several orders of magnitude greater than the selenium. This increases the secondary waste volume and reduces the selenium removal efficiency. Other considerations include the production of a selenium concentrated waste stream that requires disposal or further treatment and high capital and operational costs.

The most common types of chemical treatment involve selenate reduction to selenite or elemental selenium, adsorption of selenite, and precipitation of the sorbed and elemental species. Other chemical treatments include cementation, electrocoagulation, and photoreduction. Electrocoagulation and photoreduction have not been demonstrated beyond the laboratory level. Ferrihydrite precipitation with concurrent adsorption of selenium on the ferrihydrite surface is a U.S. Environmental Protection Agency (USEPA) Best Demonstrated Available Technology (BDAT). Since chemical treatment depends on the reactivity of selenite, a step to reduce selenate to selenite is required. Chemical treatment can be expensive, and requires the disposal of chemical sludges or solids that contain selenium.

Biological treatment is emerging as a cost-effective treatment option to remove selenium by either reducing or volatilizing the oxyanions. Several pilot demonstration projects indicate biological systems can treat both selenate and selenite to below regulatory standards. Biological treatments include volatilization of selenium, both passive biochemical reactors (BCRs) and active bioreactors, and constructed wetlands. Historically, there have been problems with the biological removal of selenium in the presence of elevated nitrate concentrations found in agricultural waters; however, recent research suggests the need for pre-treatment of nitrate can be overcome by proper selection of microbial communities. While advances have improved the understanding of biologically-mediated selenium treatment, the processes governing selenium removal are still not completely understood. Additionally, care must be taken to prevent re-oxidation and mobilization of reduced selenium after treatment.

These technologies are discussed in greater detail below. Additionally, summaries of the technologies presented are listed in Tables 1-7. Table 1 contains an overview of the treatment technologies. Tables 2, 3, and 4 provide additional detail on physical, chemical, and biological treatment methods, respectively. Tables 5, 6, and 7 provide a summary of case studies for physical and chemical, active microbial, and passive microbial treatment, respectively.

4.1 Physical Treatment

4.1.1 Membrane Filtration

Membrane separations rely on semi-permeable membranes to purify the fluid being treated. During membrane separation, a pressure gradient is applied across the membrane, forcing water through the membrane while retaining the contaminants. Both reverse osmosis (RO) and nanofiltration (NF) are membrane filtration processes, but they require different membranes. Unlike RO, NF utilizes a hydrophobic membrane layer to reject multivalent ions. Because of this, NF is operated at much lower pressures than RO. Recently, low pressure (low energy) membranes for RO have been developed, lowering operating costs significantly.

For both processes, pre-treatment may be required to prevent membrane fouling, particularly if the water contains elevated levels of hardness (Ca, Mg) or total suspended solids (TSS). Membranes are typically expected to last two to three years. In addition, both processes produce a concentrated waste stream that must be disposed of properly. Disposal options include evaporation, deep well injection, and biological treatment.

Membrane filtration is a reliable, well understood treatment option for the removal of selenium. Historically, high operating costs have been a drawback to the implementation of membrane filtration processes; however, recent advances in NF and low pressure RO have lessened this concern. Likewise, fouling has been addressed with new flow regimes that continually clean the membrane surface during operation, although fouling can remain a problem depending on water chemistry.

Other disadvantages of membrane filtration include waste disposal and pre-treatment requirements. The pre-treatment requirements include filtration to remove fines and colloidal material and also preheating. For most efficient operation of the RO system, the water temperature must be increased to greater than 70 °F, preferably to 85 °F. The brine produced is typically 20% to 30% of the influent flow depending on the influent water quality.

RO has been implemented successfully for both drinking water and industrial wastewater treatment, and the USEPA currently lists RO as one of the best available technologies (BATs) for selenium removal (Twidwell et al. 2000). RO has also been used successfully to treat MIW, both at Barrick's Richmond Hill Mine (Microbial Technologies, 2005) and at an undisclosed metal mine in the Western US (Gusek et al. 2008).

At the Barrick Richmond Hill Mine, RO is used to polish selenium from mine water after treatment by iron reduction and precipitation. Selenium is reduced from 12-22 ppb to about 2 ppb at flows of 200 US gallons per minute (gpm). The RO unit is operated at pressures of 250 psi and greater. As of 2005, filtration pre-treatment was required to remove TSS. During winter months, water is heated to 15 °C to prevent crystallization caused by depressed salt solubilities that are a result of cold temperatures. Additionally, a softening plant is being considered for the treatment of gypsum scaling resulting from elevated calcium concentrations.

To date, no known pilot or operational studies have been published on selenium removal by NF. Kharaka et al. (1996) used NF at a laboratory scale to remove selenium from agricultural drainage. Results showed greater than 95% selective removal for selenium and more than 90% removal for other multivalent anions. NSMP (2007b) also tested a thin-filmed composite RO membrane for the removal of 15 µg/L selenium and 5 mg/L nitrate using water from the Warner Channel, CA. RO removed 97% of the selenium, but only 46% of the nitrate.

Chellam and Clifford (2002) also demonstrated NF for the removal of uranium, molybdenum, selenium (both selenite and selenate), and thorium on a laboratory scale using groundwater contaminated by uranium mill tailings. RO and low pressure RO were tested as well. Water was pretreated using ferric coagulation, flocculation, settling, and filtration at a pH of 10. Ferric coagulation was effective at removing radium and thorium. Molybdenum, selenium, and uranium were highly retained by RO and NF membranes. In particular, selenium demonstrated a 96-98% removal rate at pH 10 for all three membranes tested.

Golder Case Study (Closed Gold Mine, California, US)

Golder has implemented RO treatment for selenium at multiple sites with success including a former uranium mill closure, a chemical plant closure, and a gold mine closure. At a former historic gold mine site in California, Golder utilized RO to treat impounded water for reduction of selenium from approximately 60 µg/L to < 5µg/L. The RO treatment system was implemented on an emergency basis to prevent the impounded water from overto`pping into a drinking water reservoir located below the mine. Trailer-mounted RO systems were leased along with prefiltration and manganese removal columns. The flow to the system was greater than 100 US gpm and was operated for approximately four months. The system was operated at approximately 40% selenium recovery due to the high TDS of the influent water. The brine was returned to the impoundment and the system was operated until the levels in the impoundment were reduced to acceptable levels.

Golder also evaluated implementation of a permanent RO facility to treat the waste rock leachate. The permanent facility was designed at 60 US gpm and included an evaporator for brine management. The capital cost of the system was estimated at $5,200,000 (US dollars [USD]) and the O&M cost at $18 (USD) per thousand gallons of water treated.

4.1.2 Ion Exchange

During ion exchange, a contaminant ion from solution is reversibly exchanged for a more desirable, similarly charged ion attached to an immobile solid surface. Frequently the solid surface is a synthetic resin, but natural, inorganic zeolites can also be used. Depending on the ion exchange resin selected, the process can be used to remove a suite of ions from solution or to preferentially remove only specific ions. Once the resin becomes saturated, it can be regenerated and placed back into service for further contaminant removal. Regeneration involves washing the resin with a solution to remove sorbed contaminant ions and produces a concentrated contaminant waste stream that may require further treatment before disposal. Selective ion exchange is generally considered to be more cost effective than RO (Frankenberger et al. 2004).

Ion exchange is a well established process commonly employed to treat industrial wastewater, but until recently, ion exchange has not been successful in removing selenium from MIW due to the competition between sulfate and selenate. Sulfate and selenate have very similar chemical properties but sulfate levels in MIW are frequently elevated compared to selenate concentrations. (Sulfate is typically reported in the parts per million range while selenate is usually reported in the parts per billion range.) Thus, ion exchange resins quickly become saturated with sulfate and stop removing selenate.

Advantages of ion exchange include selective removal of selenium using a well understood technology. The disadvantages include competition with sulfate anions, the need for backwashing and regeneration of the resin, fouling, and secondary waste disposal.

Polyamine-type weakly basic ion exchange resin has been shown to effectively remove selenate over a wide pH range of 3-12; however, increases in sulfate concentrations significantly reduced selenate adsorption (Nishimura and Hashimoto 2007). During laboratory studies, a 0.3 molar ratio of sulfate to selenate showed a decrease in the amount of selenate adsorbed to the resin. A 50 % decrease in adsorbed selenate was detected when the molar ratio of sulfate to selenate was increased to 2. To overcome this problem, $BaCl_2$ was used to reduce aqueous concentrations of sulfate and selenate by precipitation as $BaSO_4$ and $BaSeO_4$, respectively. Ion exchange was then used as a polishing step to further reduce selenate concentrations. The combination of precipitation followed by ion exchange polishing reduced initial total selenium concentrations from 1 g/L to below 0.1 mg/L. Adsorbed selenate could be eluted from the resin using small volumes of 1 M HCl.

A novel silica polyamine resin made from polyethyleneimine (PEI) impregnated with zirconium was recently tested in the laboratory for selenium removal using process solutions from the Kennecott Mining Company (Hughes et al. 2006). The Zr-WP-2 resin was found to remove selenate and selenite up to pH 8. The Kennecott process solution contained 0.93 mg/L selenium as both SeO_4^{2-} and SeO_3^{2-} and 80 mg/L SO_4^{2-} at pH 4. Zr-WP-2 removed selenium to less than 1 µg/L. Sulfate co-loading was observed on the resin, but selectivity over sulfate was calculated as 67:1 and 103:1 for selenate and selenite, respectively. Zr-WP-2 can be regenerated using 1 M H_3PO_4.

4.1.3 Evaporation

Solar evaporation has been considered for selenium treatment in California (NSMP 2007a). Both simple evaporation ponds and enhanced evaporation systems (EES) have been examined. EES accelerates evaporation rates by spraying water in the air. In a study cited by NSMP, evaporation ponds reduced selenium concentrations by only 25% in the San Joaquin Valley. Solar evaporation utilizes large, shallow ponds that provide a potential avenue for exposure and bioaccumulation of selenium in birds. In addition, sediments accumulated during evaporation require disposal. Advantages include no pre-treatment requirements and insignificant energy requirements. (EES will have higher energy requirements). Solar evaporation is likely unsuitable for selenium removal from MIW due to the prevailing cold climate where operations are typically located and the high potential for selenium exposure to wildlife. An alternative to solar evaporation is the use of mechanical evaporators to produce concentrated brine followed by crystallization, drying, and solid waste disposal. This process typically has high operational costs and has not been investigated for selenium removal from MIW.

4.2 Chemical Treatment

4.2.1 Selenium Reduction using Iron

Zero valent iron (ZVI) is used to reduce selenium oxyanions to elemental selenium. Ferrous cations can also reduce selenate to selenite and subsequently remove selenite by adsorption to iron hydroxides. In an aqueous environment, ZVI can be oxidized to ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions. These ions react with hydroxyl ions present in water to form ferric and ferrous hydroxides. Selenate is reduced to selenite while ferrous iron is oxidized to ferric iron. Selenite then adsorbs to the ferric and ferrous hydroxide surfaces and is removed from solution. Iron reduction removal mechanisms are as follows:

$$SeO_4^{2-} + ZVI \rightarrow Se^{\circ} + Fe^{2+}/Fe^{3+}$$
$$SeO_3^{2-} + ZVI \rightarrow Se^{\circ} + Fe^{2+}/Fe^{3+}$$
$$SeO_4^{2-} + 2Fe(OH)_2 + H_20 \rightarrow SeO_3^{2-} + 2Fe(OH)_3$$

Lovett (2008) used fibrous ZVI (steel wool) to remove selenium from MIW at Catenary Post in a continuous flow reactor. Inlet concentrations of selenium varied from 5 µg/L to 14 µg/L. Over 250 days, effluent concentrations of selenium did not consistently achieve the regulatory limit of 5 µg/L. Results indicated a minimum 5 hour contact time is required to remove selenium to regulatory levels. Additionally, selenium removal may be temperature dependent. Problems with the treatment process included formation of iron oxides, passivation of the iron, exhaustion of the iron, and cost.

In 2007, the NSMP (2007b) ran a pilot scale reactor to remove selenium from drainage water collected from Warner Channel in California using the principles described above; however, rather than using ZVI, ferric and ferrous chloride were added. The pilot system was built by Kemira/ORCA and included flocculation and filtration, with equal doses of 2.5 mg/L ferric and ferrous chloride. The system treated 10 US gpm with a mean selenium concentration of 15 µg/L. Approximately 95% of the total selenium was present as selenate, with the remainder as selenite. The system did not remove any selenium; however, the pilot system was only available for one day, preventing the process from being optimized on site due to time limitations.

Iron or zinc reduction is also used at three operational facilities to remove selenium from MIW (Microbial Technologies 2005). At Barrick's Richmond Hill Mine, ZVI is used to reduce selenate to selenite, followed by ferric sulphate precipitation at pH 4.5. The process is only able to remove selenium to concentrations of 12-22 ppb, and RO is used as a polishing step to reduce selenium to effluent regulations. Meridian Dry Valley Mine use zinc powder to reduce selenate to selenite, followed by iron salt precipitation at an acidic pH. At another mine site, ZVI and ferrous sulphate at pH 4.5 are used to reduce selenate to selenite. Ferric chloride is then added to form ferric hydroxide, which co-precipitates the selenite.

While iron reduction can significantly decrease selenium concentrations, it has been applied with varying success for meeting regulatory standards. Morever, high operational costs and sludge disposal are disadvantages of this process. Treatment may also be temperature dependent.

4.2.2 Ferrihydrite Co-Precipitation

Ferrihydrite co-precipitation of selenium is a USEPA BDAT for the removal of selenium from wastewater. Selenium is removed by adsorbing to the iron surface and subsequent precipitation of ferrihydrite from solution. The reaction is as follows:

$$Se^{4+} + FeCl_3 + 4H_2O \rightarrow Fe(OH)_3 \bullet Se + 8H^+$$

Twidwell et al. (2000) reviewed ferrihydrite co-precipitation and concluded that:

- Selenite is adsorbed much more effectively than selenate; therefore selenate should be reduced to selenite before ferrihydrite co-precipitation.
- Adsorption of selenite depends on having oxyhydroxide present; amorphous ferrihydrite appears to be more effective than crystalline ferrioxyhydroxides.
- The higher the selenite concentration, the more effective the process appears to be.
- Available data suggest the best pH for selenite adsorption ranges between 4 and 6, producing 85-95 % removal of selenite; pHs greater than 7 show drastic decreases in adsorption.

- Selenate adsorption may be strongly affected by the presence of sulfate, bicarbonate, and aqueous silica species.

Only one pilot study has been undertaken to demonstrate ferrihydrite co-precipitation and long term studies of the stability of ferrihydrite co-precipitation waste have not been performed. In 2001, the USEPA conducted a 1 US gpm pilot demonstration at the Kennecott Utah Copper Corporation's Garfield Wetlands-Kessler Springs site (MSE 2001). The water contained 1,950 µg /L selenium, primarily as selenite. Using an iron concentration of 4,800 mg/L, the mean effluent selenium concentration was 90 µg/L. The minimum reported selenium concentration was 35 µg/L.

Although ferrihydrite co-precipitation is a USEPA BDAT, consistent removal to regulatory levels of selenium has not been proven. Additional disadvantages include sludge disposal, uncertainty with respect to the long term stability of the sludge, and high operational costs typical of chemical treatment.

4.2.3 Catalyzed cementation

Catalyzed cementation is a treatment process that removes selenium by cementation to the surface of iron particles (MSE 2001). During treatment, proprietary catalysts are added to enhance cementation to the iron surface at a lowered pH. Catalyzed cementation can remove both selenate and selenite from solution.

Advantages of catalytic cementation include its ability to reduce selenium below 5 µg/L. Additionally, the process does not appear to be highly temperature dependent. Unfortunately, the process has not been widely tested. Other disadvantages include high chemical costs and solid waste disposal requirements. Additionally, no long term studies of the stability of the cementation waste have been undertaken.

Catalyzed cementation was tested as part of the USEPA demonstration project for selenium removal at Kennecott's Garfield Wetlands-Kessler Springs site (MSE 2001). Water with total selenium concentrations of 1,950 µg/L (primarily as selenate) was tested at a flow rate of 1 US gpm. Even after extensive optimization in the field, the lowest effluent concentration achieved was 26 µg/L. Continued optimization in the laboratory achieved a mean effluent selenium concentration of 3 µg/L.

4.2.4 Electrocoagulation

During electrocoagulation, water is treated using electrolysis with graphite or stainless steel cathodes in conjunction with a metal anode (e.g., Al, Fe, Zn, Ni, etc.). Anode material selection is dependent on the wastewater composition. When a voltage is applied across the electrodes, insoluble precipitates are formed from ions of the metal electrode and selenium, arsenic, or other metals present in the water. Contaminant removal depends on the composition of the water, the material and configuration of the electrodes, and the electric current. Electrocoagulation can reduce sludge production significantly compared to other chemical processes such as iron reduction. A disadvantage of this process is that it has not been tested at the pilot or full scale and the process has high capital and operation and maintenance costs.

A hybrid electrocoagulation-microfiltration process was tested in the laboratory using industrial wastewater from copper production to remove selenium, arsenic, copper, lead, zinc, and cadmium (Mavrov et al. 2006). Water was pretreated using lime neutralization and sedimentation followed by electrocoagulation. After electrocoagulation, water was filtered using a microfiltration flat sheet ceramic membrane and it then underwent a final lime neutralization step. During experiments, good adsorption and co-precipitation of selenium with iron hydroxides generated during electrocoagulation were observed. The iron hydroxide fines were completely removed by microfiltration. Selenium was reduced by 98.7 % from 2.32 mg/L to 0.03 mg/L using an anodic current density of 4.8 mA/cm^2. Arsenic (99.9 % removal), copper (> 98 %), lead (> 98 %), zinc (> 99.9 %) and cadmium (> 99.9 %) were also removed from the wastewater.

4.2.5 Photoreduction

Photoreduction has been studied on a laboratory scale for the removal of selenium (Nguyen et al. 2005). During photoreduction, UV light is used to generate electron-hole pairs on the surface of a photocatalyst. Contaminants absorbed to the surface of the photocatalyst undergo redox reactions induced by the electrons and holes created by the exposure to UV light. The treated species are then desorbed and the surface of the photocatalyst is regenerated.

TiO_2 has been found to be an effective photocatalyst for the reduction of both selenate and selenite in solution. Nguyen et al. (2005) found that using UV light at wavelengths less than 380 nm at a pH of 3.5 in the presence of TiO_2 and formic acid will reduce Se(VI) and Se(IV) to Se(0). Concentrations of 20 – 40 µg/L of selenate and selenite were tested with UV exposure times ranging between 2 and 8 hrs producing final effluent concentrations between 31 and 1 µg/L total selenium. The reduction of Se(VI) proceeded more slowly than Se(IV), presumably due to poorer adsorption of Se(VI) onto the surface of TiO_2. The formation of toxic H_2Se was observed during photoreduction, and was removed by a scrubber containing CuSO4 and NaOH in series.

4.2.6 Selenium Adsorption on Peanut Shells

Selenium removal by adsorption to peanut shells has been studied on a laboratory scale (El Shafey 2007). This process has only recently been developed and is not well characterized, but peanut shells are readily available at low cost. Before treatment, peanut shells are treated with strong sulfuric acid to carbonize the shells while partially oxidizing the cellulose and hemicelluloses and fragmenting the lignin. The sulfuric acid treatment results in a carbonaceous material with functional groups for both the sorption and reduction of selenium. Selenite sorbed to the material at an optimal pH of 1.5. As pH increased, sorbtion capacity decreased. Sorption was also found to be temperature dependent. Removals as high as 63% percent were observed for 25 mg/L selenide solutions.

4.3 Biological Treatment

4.3.1 Algal Volatilization of Selenium

Selenium can be removed from sediments or water through biological volatilization by plants, algae, and microbes (Bañuelos et al. 2005). The biological conversion of inorganic selenium to methylated species (i.e., dimethyl selenide, dimethyl diselenide) is termed biomethylation. The methylated species are lost from soils and water through volatilization to the atmosphere. This is considered a favorable remedial pathway as the volatile selenium species are far less toxic (Bañuelos et al. 2005). Depending on the location, volatilization to the atmosphere can remove the selenium from an area of high soil or aqueous concentrations to an area that is selenium deficient.

Algal treatment has been demonstrated on bench, pilot, and demonstration scale levels. Algal treatment occurs via enhanced cyanobacterial and algal growth through nutrient addition. These additional nutrients increase algal biomass, thereby increasing selenium volatilization rates (Fan et al. 1998). Cyanobacterial mats and the green algae Chlorella 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). In addition to treatment by volatilization, the algal biomass generated also serves as a carbon source to support microbial selenium reduction processes. In essence, the algae volatilize selenium while alive, and once the algae die, the algal detritus supports microbial selenium reduction. Additional selenium removal also likely occurs via algal uptake of selenium (Yu and Wang 2004).

A demonstration scale algal-bacterial selenium removal (ABSR) facility in California operated from 1997 to 2003 and treated between 2.5 US gpm and 19 US gpm of agricultural drainage water. The system included nutrient addition to promote algal growth as well as carbon addition (e.g., molasses) to promote microbial selenium reduction. In 2003, the algal component was discontinued because experiments showed the algal component did not significantly increase the overall selenium removal rate (Fisher 2004). Carbon addition alone was continued as the primary treatment.

Algal treatment has also been shown to be effective in concert with in situ carbon treatment of pit lakes (Harrington 2002). After the initial carbon amendment decreases the bulk of the selenium via dissimilatory microbial reduction, algal blooms in subsequent years provide enough biomass to keep the lake under reducing conditions and thereby retain elemental selenium in its reduced, insoluble form.

The advantages of algal treatment are low cost and the ability to implement the process *in situ* on existing water bodies or as a unit process in an active treatment plant. The disadvantages include the difficulty of generating sufficient biomass to promote biological reduction and the inability to treat selenium to regulatory levels. As with any biological process, the rate of algal treatment will decrease with decreasing temperatures and the process therefore may not be suitable for cold sites.

4.3.2 Microbial Reduction Treatment

Microbial reduction of selenium is well-documented (Quinn et al. 2000; Oremland et al. 1989; Fujita et al. 2002; Zhang and Frankenburger 2003; Cantafio et al. 1996) and has been implemented successfully in full-scale treatment plants. This process is commonly referred to as biological treatment. The process consists of the reduction of soluble, oxidized selenium ions (selenate, selenite) to insoluble elemental selenium. The microbial reduction of selenium depends on oxidation-reduction reactions in which the treatment substrate (e.g., molasses, wood chips, dried distiller’s grain solids) serves as the electron donor and selenate and selenite serve as the electron acceptors. The generalized formula for this process is (Oremland et al. 1989):

$$4CH_3COO^- + 3SeO_4- \rightarrow 3Se^\circ + 8CO_2 + 4H_20 + 4H^+$$

This process can be carried out in an active plant which typically requires feed pumps for nutrient addition, tanks, and water heaters. The process can also be in a passive bioreactor which can operate without electricity or continuous nutrient inputs. A more detailed description of these two technologies follows.

4.3.2.1 Active Microbial Reduction Treatment

Active microbial reduction can be accomplished by utilizing a variety of reactor configurations the selection of which is dependent upon a number of factors including flow rate, selenium concentration, and the matrix of other contaminants. Simple systems such as ponds have been utilized and more complex systems capable of higher loading rates such as fixed film systems have also been successful is reducing selenium levels.

Upflow anaerobic sludge blanket reactors (UASBRs) have been pilot tested for the removal of selenium. UASBRs anaerobically treat contaminants using dense, granulated sludge particles suspended in the reactor. Wastewater is distributed at the bottom of the reactor and flows vertically up through the sludge particles where microbial treatment occurs. The effluent is collected at the top of the reactor, and may undergo further treatment (e.g., settling and recycling of sludge particles) before discharge. When selenium is treated by UASBRs, a carbon source such as molasses or ethanol is required to act as electron donor and effectively reduce oxidized selenium to elemental selenium. Precipitated selenium particles can be incorporated into granular sludge particles or suspended in the water, where they are recovered in a post-treatment filtration or settling step.

Considerations for the design of UASBRs include water composition, loading, the upflow velocity, and pH. Advantages include the ability to treat high loading rates to regulatory limits using a smaller footprint than passive systems. Disadvantages include the need for pre-treatment removal of suspended solids that inhibit floc formation, sludge retention, post-treatment capture of suspended elemental selenium particles present in the effluent, and temperature dependence.

The Adams Avenue Agricultural Drainage Research Center operated pilot tests for the removal of selenium in San Joaquin Valley agricultural drainage by UASBRs over three years in the early l990s (Owens 1998). Influent total selenium concentrations were about 500 µg/L in the presence of 3 mg/L nitrate as nitrogen. Methanol was fed to the system at approximately 250 mg/L. Complete nitrogen removal was observed, while selenium removal varied from 58% to greater than 90%. Lenz (2008) also operated a series of pilot scale UASBRs over the course of several years. Among his conclusions were:

- For non-specific selenium reduction, the ratio of selenate to sulfate should be greater than 1.92×10^{-3} to reduce competition with sulfate and maintain complete selenate removal.
- High concentrations of sulfide did not interfere with selenate removal; therefore it may be possible to combine sulfide precipitation of metals with selenium removal in MIW.
- Selenium respiring microorganisms were able to efficiently reduce selenate even in the presence of elevated sulfate and nitrate concentrations.
- Selenium reduction is temperature dependent, and decreases in temperature can induce production of alkylated selenium species (e.g., DMSe or DMDSe).

General Electric's ABMet® (formerly Applied Bioscience's BSeRTM process) is another active microbial reduction process used to treat selenium. ABMet® has been demonstrated at both pilot and full scale operational levels in MIW and flue gas desulfurization (FGD) wastewaters, respectively (MSE 2001; Sonstegard et al. 2008). ABMet® is a plug-flow, anaerobic bioreactor in which a selenium-reducing bacterial biofilm is supported on granular activated carbon (GAC). The system is inoculated with a mixture of proprietary and indigenous microorganisms, and reducing conditions are maintained by feeding a molasses-based nutrient mixture to the system. Advantages of ABMet® include a small footprint and proven performance. Disadvantages include the need for pre- and post-treatment steps to remove suspended solids, backwashing to prevent plugging and short-circuiting of flow, and temperature dependence. In addition, capital costs can be high due to the large volumes of GAC required.

ABMet® was a pilot demonstration technology at the USEPA Kennecott demonstration program (MSE 2001). During six months of operation, the process was able to lower the concentration of selenium from 1,950 µg/L to below 2 µg/L with hydraulic retention times as low as 5.5 hours. ABMet® is also used to treat selenium in FGD wastewaters at Duke Energy and Progress Energy in North Carolina (Sonstegard et al. 2008). At Progress Energy, during 9 months of operation, average selenium removal was 99.3%, with consistent removal of selenium from 1,500 µg/L to less than 10 µg/L in the presence of high dissolved solids levels.

Golder Case Study (Undisclosed gold mine, South Dakota, US)

Golder designed and constructed an active treatment system that includes microbiological reduction to remove selenium at closed mine site in South Dakota, U.S (Gusek et al. 2008). The treatment system is designed to treat pH-neutral, waste rock leachate characterized by high TDS (approximately 5,000 to 15,000 mg/L), high hardness, and high sulfate concentrations. The average influent selenium concentrations are approximately 70 μg/L, the discharge limit is 4.6 μg/L, and the maximum design flow is 700 US gpm. The process flow includes the following systems:

- Conventional multimedia filtration with polymer addition for TSS removal;
- Reverse Osmosis (RO) for TDS management and volume management during peak flows. The RO system includes influent water heating (including a boiler and heat exchanger), anti-scalant addition, and membrane cleaning; and,
- Active microbial reduction treatment to remove selenium from the RO reject stream. Treated biological effluent is recombined with RO permeate to meet the discharge limit for TDS and is discharged to surface water. Any excess bio-treated brine is discharged to the local municipal wastewater treatment system.

The microbial reduction treatment system achieves removal of selenium to residuals less than 10 μg/L and the discharge limit is achieved by blending with the RO permeate prior to stream discharge. The approximate O&M cost is $6 (2005 USD) per thousand gallons of water treated, although the majority of this cost is for the RO process and sewer surcharge for the brine discharged to the sewer. Cost evaluations completed to determine the optimal treatment strategy estimated that the O&M cost would increase to $13 (USD) per thousand gallons of water treated if disposal of the excess brine to the local sewer system were not available and additional treatment of the brine were required. At the time of the development of the treatment process, the client was utilizing a chemical reduction process for selenium control at an O&M cost greater than $15 (USD) per thousand gallons of water treated. The combination of RO and a microbial reduction treatment system is beneficial because it meets stringent selenium surface water discharge limits while allowing the installation of a treatment system with a large range of treatment capacity, from 70 to 700 US gpm (average 250 US gpm), in a 1 acre treatment facility relatively small space.

The advantages of active biological treatment include the ability to meet regulatory limits, a small footprint, and lower operating costs compared to stand-alone RO and chemical treatment. The disadvantages include high capital costs and the need for pre-treatment.

4.3.2.2 Passive Microbial Reduction Treatment

Passive microbial reduction of selenium typically consists of a gravity flow reactor containing a solid organic media. The organic media slowly degrades and provides a carbon source to sustain the microbial reduction of selenate and selenite to elemental selenium. Examples of successfully-implemented organic media include hay, wood chips, sawdust, rice straw (Pahler et al. 2007; Zhang et al. 2007). The media can also contain an alkalinity buffer such as limestone. These systems, also known as biochemical reactors (BCRs), have been successfully inoculated with selenium reducing bacteria or with a generic inoculum such as cow manure. BCR effluent can contain elevated levels of biochemical oxygen demand and total coliforms and may require a polishing step in order to comply with regulatory standards. Because this is a relatively new technology that has been developed over the past 20 years, the long-term performance of BCRs, including the required media replacement interval, is not well understood. BCRs are typically used to treat contaminants that precipitate or are biologically removed under reducing conditions, such as metals, nitrate, and sulfate. Full-scale BCRs have been constructed in the US, Canada, Europe, and South Africa. Golder has designed and/or constructed one full-scale and two pilot BCRs for selenium removal in addition to performing multiple bench studies.

Golder Case Study (Undisclosed gold mine, Montana, US)

A BCR is being used at an undisclosed gold mine in Montana to treat selenium (Blumenstein et al. 2008). The first of two modules of a full-scale BCR was constructed in fall 2007 with a design flow rate of 10 US gpm, to treat waste rock seepage. The BCR cell typically reduces influent selenium concentrations of 20 μg/L to below the laboratory detection limit (1 μg/L), which is below the applicable regulatory standard. An additional module is planned to expand the total treatment capacity to 20 US gpm.

The advantages of passive microbial reduction treatment are low capital and O&M costs; BCRs operate virtually unattended. The disadvantages include the large area required to treat high flows and the lack of understanding of long-term performance, particularly at cold sites. The design and construction cost of the first module was about $200,000 (USD). The annual operating costs are estimated at $0.30 (USD) per thousand gallons.

4.3.3 In Situ Microbial Reduction Treatment

In situ treatment of pit lakes with a carbon amendment is another type of passive microbial reduction treatment which consists of amending a pit lake with nutrients, including a carbon source, to remove selenium. The carbon amendment often consists of soluble organic compounds (e.g., molasses, ethanol) that serve as an energy source (i.e., electron donors) which promote the growth and activity of selenate- and selenite-reducing microorganisms indigenous to the site. The goal of the carbon amendment approach is to create and maintain geochemically reducing conditions in the deeper portions of the water column to achieve reduction and subsequent sequestration of selenium within the lake sediments. It is vital that anaerobic conditions are maintained on the lake bottom to prevent re-oxidation and mobilization of selenium.

Depending on site conditions such as the lake mixing regime, it may be necessary to reapply the amendment to maintain anaerobic conditions throughout the water column and prevent the remobilization of elemental selenium. The process, ostensibly patented by Alexco Resources Inc., results in anoxic conditions that are lethal to aquatic life. Therefore, the process is suitable only to waterbodies that do not contain aquatic life. This treatment method has effectively reduced selenium concentrations in pit lakes at the Sweetwater uranium mine in Wyoming (Harrington 2002) and the Gilt Edge Superfund Site in South Dakota (Harrington et al. 2004). The Sweetwater mine pit lake has an average depth of 60 feet, a surface area of 60 acres, and a total volume of 1.25 billion gallons. The initial selenium concentration was 0.45 mg/L. The lake was treated in 1999 with 1.1 million pounds of carbon and other nutrients and within six weeks the selenium concentrations were reduced to levels below the applicable standard of 0.05 mg/L. Selenium concentrations remained below the standard two years after the initial application.

The advantages of this process are its low cost, and the ability to treat a large volume of water while meeting stringent regulatory limits. The disadvantages include the generation of toxic, anoxic conditions, and uncertainty with respect to the long-term stability of precipitated selenium.

4.3.4 Wetlands

Engineered treatment wetlands are divided into two categories: subsurface flow wetlands (SSF) and free water surface wetlands (FWS). In an SSF system, water flows below the surface of a crushed media, such as gravel or sand, and the media surface is planted with aquatic plants. A FWS system is similar to a natural wetland or marsh, with water flowing over the surface of a planted treatment cell.

Wetlands are complex systems characterized by multiple processes including aerobic and anaerobic biological activity, settling and filtration, volatilization, and phytoremediation. The principle selenium removal mechanisms are volatilization and plant uptake (Frankenburger et al. 2004; Azaizeh et al. 2006). A secondary wetland removal mechanism is biological reduction in anaerobic sediments.

Lab-scale SSF treatment of selenium has demonstrated removal of selenium to below 0.2 μg/L (Azaizeh et al. 2006). SSF testing for selenium removal on a larger scale has not been reported. Selenium removal in full-scale FWS wetlands has been well-documented. A 36-hectare constructed wetland near San Francisco, CA receives oil refinery wastewater from Chevron's Richmond refinery with selenium concentrations between 20 and 30 μg/L. The wetland treats 10,000 m^3/day and achieves effluent selenium concentrations of less than 5 μg/L. Volatilization accounts for 10 -30% of the total selenium removal (Frankenburger et al. 2004). A primary concern with FWS systems is that wildlife are drawn to these systems and are thus likely exposed to toxic levels of selenium. The oil refinery wetland led to elevated selenium concentrations in birds (Lemly 2003) and consequently steps were taken to reduce its attractiveness to wildlife. SSF treatment largely avoids any exposure to wildlife because of the subsurface water flow.

The advantages of wetland treatment are low capital and O&M costs and the ability to treat high flows and achieve effluent concentrations that comply with regulatory standards. The disadvantages include the large area required, removal mechanisms that are not completely understood, and the risk of creating a wildlife hazard. Furthermore, the performance of these systems at cold sites has not been documented.

5.0 CONCLUSIONS

Significant research and development of selenium treatment technologies has occurred over the past two decades. The challenge of treating selenium to meet the stringent applicable standards of a few micro-grams per liter has led to testing of multiple physical, chemical, and biological treatment methods. Among these methods, proven full-scale treatment is currently being conducted by reverse osmosis, reduction by iron, active and passive microbial reduction, *in situ* microbial reduction, and wetlands. These methods are capable of meeting applicable standards, and provide a suite of tools to tackle the increasingly important issue of selenium in the environment. Some Canadian mine site discharge flow rates pose a significant design challenge. These rates can be on the order of 250,000 m^3/day (45,863 US gpm), significantly greater than the highest selenium treatment plant flow rate of 7,630 m^3/day (1,400 US gpm). Although full-scale treatment of selenium is proven, it has not been demonstrated for flow rates typical of the Canadian mine sites. This review is limited to water treatment, which is one of three selenium management tools (Chapman et al. 2009). The other two management tools, prevention of selenium release and control of selenium in the environment, are not reviewed.

In the past five years, biological treatment has emerged as a leading technology for selenium treatment. Biological treatment offers a low cost alternative to more expensive physical and chemical treatment methods. Additionally, it has the proven ability to meet regulatory selenium limits. Germane summary statistics of these methods are provided in Tables 6 and 7 for active and passive biological-based systems, respectively. For cold climate sites, BCRs and *in situ* microbial reduction appear to be treatment processes worthy of additional study which is currently underway. A brief summary of this effort follows.

Golder conducted pilot testing of algal volatilization and bench and pilot testing of BCR treatment at the Cardinal River Operations site in 2008. The algal volatilization testing resulted in total selenium removal rates of up to 30% (Golder 2009) at a relatively low cost. Bench testing of the BCR technology demonstrated 90% removal of total selenium (Golder 2008). The results of the pilot BCR will help determine the cold weather performance of the technology and provide greater insight to passive microbial treatment methods.

The treatment of endpit lakes presents a unique situation which may allow certain methods to be effective that would not otherwise be considered. Treatment of endpit lakes by *in situ* microbial reduction appears to be an effective, low-cost option, although the process may be subject to patents.

Additionally, endpit lakes could be used as deep-water disposal for RO brine. Limnological studies at the Cardinal River Operations site indicate that some pit lakes may be stratified; the hypolimnion does not mix with upper layers of the lakes (Wolanski 1999). Thus, the hypolimnion of a permanently stratified lake could provide ideal conditions under which to store RO brine. Another option may be to continuously treat endpit lake water with a BCR cell which discharges back to the lake. A relatively small BCR (20 US gpm) could treat over 10 million gallons of lake water per year. Furthermore, the high organic load in the BCR effluent would likely generate anaerobic conditions in the hypolimnion which would result in partial *in situ* microbial reduction and subsequent stabilization of elemental selenium on the lake bottom. These lake treatment options would probably temporarily degrade lake water quality in order to treat selenium or stabilize reduced selenium in the hypolimnion. If degradation of the lakes is not permitted, these options may not be feasible.

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TABLES

Table 1
Overview of Treatment Technologies

Treatment Type	Technology
Physical	Reverse Osmosis Nanofiltration Ion Exchange Evaporation
Chemical	Iron Reduction and Precipitation Ferric Coagulation and Filtration Cementation Electrocoagulation Photoreduction
Biological	Volatilization Active Microbial Reduction Passive Microbial Reduction In Situ Microbial Reduction Wetlands

Table 2
Advantages and Disadvantages of Physical Treatment Processes for Selenium Removal

Treatment Technology	Technology Description	Advantages	Disadvantages	Development Stage
Reverse Osmosis	Pressure-driven separation through a semi-permeable membrane that allows water to pass through while rejecting contaminants	Reliable, well understood process that is scalable; can achieve regulatory limits	Membrane fouling; may require pre-treatment; high operating pressure; brine disposal	Full Scale
Nanofiltration	Low pressure membrane separation based on molecular size and ionic charge that allows water to pass through while rejecting contaminants	Reliable, well understood process that is scalable; low operating pressures; can achieve regulatory limits	Membrane fouling; may require pre-treatment; brine disposal	Laboratory
Ion Exchange	Reversible exchange of contaminant ions from a process stream with more desirable ions of a similar charge adsorbed to a solid surface	Selective removal of selenium using a reliable, well understood process that is scalable; can achieve regulatory limits	Backwashing and regeneration of resin are required; waste disposal; sulfate competition; inability to remove selenate	Laboratory
Evaporation	Vaporization of pure water to concentrate contaminants as a solid or in a brine stream	Insignificant energy requirements; no pre-treatment requirements	Large footprint; dependent on solar radiation levels and temperature; disposal of accumulated sediments; pathway for Se exposure to wildlife; regulatory limits may not be achievable	Pilot

Table 3
Advantages and Disadvantages of Chemical Treatment Processes for Selenium Removal

Treatment Technology	Technology Description	Advantages	Disadvantages	Development Stage
Selenium Reduction Using Iron	Use of ZVI or Fe(II) for SeO_4^{2-} and SeO_3^{2-} reduction and subsequent precipitation	Proven technology to reduce Se concentrations	High chemical consumption; waste disposal; long term stability of waste is unknown; may be temperature dependent; does not consistently achieve regulatory limits	Full Scale
Ferrihydrite Co-Precipitation	Removal of Se by adsorption to amorphous ferrihydrite	EPA best available demonstrated technology	High chemical consumption; waste disposal; long-term stability of waste is unknown; most effective with selenite	Pilot
Catalyzed Cementation	Removal of Se by cementation onto an iron surface and subsequent settling	Effective removal of both selenate and selenite	High chemical consumption; waste disposal; long-term stability of waste is unknown; does not consistently achieve regulatory limits	Pilot
Electrocoagulation	Formation and removal of selenide precipitates by electrolysis	Effective removal of selenate and selenite; low sludge production	High capital and operational costs; may require pre- and post-treatment; technology not proven to reduce Se below regulatory limits	Laboratory
Photoreduction	Reduction of SeO_4^{2-} and SeO_3^{2-} to elemental Se using UV light in the presence of a TiO_2 catalyst	Minimal sludge production; recoverable elemental selenium fraction	High energy requirements; process not well characterized; production of toxic H_2Se gas	Laboratory

Table 4
Advantages and Disadvantages of Biological Treatment Processes

Treatment Technology	Technology Description	Advantages	Disadvantages	Development Stage
Algal Volatilization	Volatilization of methylated Se by stimulating algal growth through the addition of nutrients, including carbon	Low cost, *in situ* treatment process	Difficulty stimulating sufficient algal growth; inability to reduce Se below regulatory limits; temperature dependent	Pilot
Active Microbial Reduction	Microbial Se reduction to Se° by the active addition of nutrients, carbon, and/or energy	Proven technology to meet regulatory limits; small footprint; lower operating costs compared to physical and chemical treatment	High capital costs; pre-treatment may be required; plugging by Se precipitates; re-oxidation and mobilization of Se possible	Full Scale
Passive Microbial Reduction	Passive flow system constructed with materials promoting microbial reduction of Se without the active addition of chemicals or energy	Low capital and O&M costs; little to no active supervision required; ability to meet regulatory limits	Long term performance not well understood; large footprint; may require effluent polishing; temperature dependent; re-oxidation and mobilization of Se possible	Full Scale
In Situ Microbial Reduction	Microbial reduction of Se by the *in situ* addition of a carbon source to promote reducing conditions	Low cost; *in situ* treatment of large volumes of water; ability to meet regulatory limits	Generation of anoxic conditions toxic to wildlife; long term stability of precipitated Se is unknown; multiple applications of carbon may be required; lake turnover can be problematic; patented process	Full Scale
Wetlands	Engineered system constructed using wetland vegetation, soils, and associated microbes to promote biological removal of Se by reduction or volatilization	Low capital and O&M costs; ability to treat high flow rates; ability to meet regulatory limits	Potential wildlife exposure to elevated Se levels; large footprint; incomplete understanding of removal mechanisms; may be temperature dependent; re-oxidation and mobilization of Se possible	Full Scale

Table 5
Physical and Chemical Case Study Details

Source	Description	Scale	Length of Operation	Location	Flow Rate	Water Quality			Cost (USD)	Reference
						Parameter	Influent	Effluent		
MIW	Se reduction by steel wool	Pilot	8 mo	Catenary Post	NA	Se	5 - 14 µg/L	> 5 µg/L	NA	Lovett 2008
MIW	Ferrihydrite co-precipitation	Pilot	6 mo	KUCC Garfield Wetlands-Kessler Springs	1 US gpm	Se	1,950 µg/L	90 µg/L	NA	MSE 2001
MIW	Catalytic cementation	Pilot	6 mo	KUCC Garfield Wetlands-Kessler Springs	1 US gpm	Se	1,950 µg/L	26 µg/L	NA	MSE 2001
MIW	Reverse Osmosis	Full Scale Temporary	4 mo	Closed gold mine, California	100 US gpm	Se	60 µg/L	<5 µg/L	NA	Golder case study
MIW	Iron reduction and precipitation Reverse Osmosis	Full Scale	NA	Barrick Richmond Hill Mine	200 US gpm	Se	100 µg/L	2 µg/L	Capital: $1.5 million (2005 dollars) Operating: $10 - $18/1,000 gal.	Microbial Technologies 2005
MIW	Selenium reduction w/ zinc powder and iron co-precipitation	Full Scale	NA, ongoing	Meridian Dry Valley Mine	NA	NA	NA	NA	NA	Microbial Technologies 2005

Note: MIW - mining influenced water.
NA - information is unavailable

Table 6
Active Microbial Reduction Case Study Details

Source	Description	Scale	Length of Operation	Location	Flow Rate	Water Quality			Cost (USD)	Reference
						Parameter	Influent	Effluent		
Agricultural	Upflow Anaerobic Sludge Blanket Reactor (UASBR)	Pilot	2 yr	California	NA	Se	500 µg/L	50 µg/L	Operating: $1.23-1.48/1,000 gal (2005 dollars)	Owens 1998
MIW	BSeR^{TM} (GE ABMet®)	Pilot	6 mo	KUCC Garfield Wetlands-Kessler Springs	1 US gpm	Se	1,500 µg/L	< 2 µg/L	Operating: $1.32/1,000 gal (2001 dollars)	MSE 2001
MIW	Anaerobic fixed film bioreactor using activated carbon support	Full Scale	2 yr, ongoing	Goldcorp's former Wharf Resources Mine, Lead, SD	40-300 US gpm	NO_3^- SeO_4^{2-} As	30 mg/L 15 µg/L 70 µg/L	<1 mg/L <5 µg/L <1 µg/L	Capital: $1 million Operating: $0.57/1,000 gal (2005 dollars)	Microbial Technologies 2005
MIW	Anaerobic fixed film bioreactor using activated carbon support	Full Scale	NA, ongoing	Zortman-Landusky gold mine, MT	75-300 US gpm	NO_3^- SeO_4^{2-} CN^-	200 mg/L 500-700 µg/L 300-400 µg/L	<10 mg/L 100 µg/L 200 µg/L	Capital: $3 million Operating: $2.38/1,000 gal (2000 Dollars)	Microbial Technologies 2005
Flue-Gas Desulfurization	GE ABMet®	Full Scale	9 mo, ongoing	Progress Energy Roxboro Station	1400 US gpm	Se	1,500 µg/L	< 10 µg/L	NA	Sonstegard et al. 2008
MIW	Anaerobic fixed film bioreactor using high surface area media support	Full Scale	2 yr, ongoing	Undisclosed gold mine, Western US	250 US gpm	Se TDS	70 µg/L 16,000 mg/L	< 10 µg/L	Operating: $5.71/1,000 gal (2008 dollars)	Gusek et al. 2008

Note: MIW - mining influenced water.
NA - information is unavailable

Table 7
Passive Microbial Reduction, *In Situ* Microbial Reduction & Wetlands Case Study Details

Source	Description	Scale	Length of Operation	Location	Flow Rate	Water Quality			Cost (USD)	Reference
						Parameter	Influent	Effluent		
MIW	Free Water Surface (FWS) wetland	Pilot	NA	Undisclosed gold mine, Nevada	10 US gpm	Se pH	40 µg/L 7.5	16 µg/L	NA	Gusek et al. 2008
MIW	Biochemical Reactor (BCR) with FWS wetland polishing	Pilot	NA	Undisclosed gold mine, Nevada	6 US gpm	Se pH	22 µg/L 2.7	< 5 µg/L	NA	Gusek et al. 2008
MIW	BCR	Pilot	18 mo	Brewer Mine, South Carolina	1 US gpm	Se	1,500 µg/L	50 µg/L	NA	Gusek 2000
MIW	BCR	Pilot	6 months, ongoing	Sand and Gravel Pit, Colorado	10 US gpm	Se	20 µg/L	2 µg/L	Capital Cost: $80,000 Operating: $0.30/1,000 gallons (2008 dollars)[1]	Pahler et al. 2008
MIW	BCR with FWS wetland polishing unit	Full Scale	1.5 yrs, ongoing	Undisclosed gold mine, Montana	10 US gpm	Se	20 µg/L	< 1 µg/L	Capital Cost : $225,000 Operating $0.30/1,000 gallons (2008 dollars)[1]	Blumenstein et al. 2008
Oil Refinery Wastewater	FWS wetland	Full Scale	NA, ongoing	Chevron Oil Refinery, Richmond, CA	1,835 US gpm	Se	20 - 30 µg/L	< 5 µg/L	NA	Frankenburger et al. 2004

Note: MIW - mining influenced water.
NA - information is unavailable

[1] - BCR operating costs assume 2 hours of labor per month at $60/hr for system operation and maintenance.