PASSIVE AND SEMI-PASSIVE TREATMENT ALTERNATIVES FOR THE BIOREMEDIATION OF SELENIUM FROM MINE WATERS

[1]A.J. Martin
[2]R. Jones
[1]M. Buckwalter-Davis

[1]Lorax Environmental Services Ltd., 2289 Burrard St., Vancouver, BC, V6J 3H9
[2]Teck Coal Limited, Suite 1000, 205 - 9th Avenue S.E., Calgary, AB, T2G 0R4

ABSTRACT

The bioremediation of selenium (Se) from mine waters using passive systems (those requiring negligible management) and semi-passive systems (those requiring active management to sustain desired conditions and processes) is reviewed. Examples of passive systems include natural wetlands, constructed surface-flow wetlands, constructed subsurface-flow wetlands and permeable reactive barriers (PRB). Examples of semi-passive systems, such as *in situ* pit lake treatment, require active management that may involve periodic amendments (*e.g.*, organic carbon, nutrients) to stimulate desired microbial mechanisms. In all cases, Se bioremediation relies primarily upon microbial and/or biological processes to remove Se from solution, including plant uptake, precipitation (*e.g.*, *in situ* formation of elemental Se), adsorption, microbial/algal assimilation and biological volatilization (*e.g.*, release of dimethyl selenide to atmosphere). Case studies that describe field-scale examples of passive and semi-passive bioremediation for Se are presented. Considerations for Se bioremediation in interior temperate climates (*e.g.* Elk River Valley region) as they relate to constructed/natural wetlands, pond environments (*e.g.*, sedimentation ponds), pit lakes and PRBs are discussed.

KEY WORDS: selenium, bioremediation, passive, semi-passive, mining

INTRODUCTION

Selenium (Se) is a naturally occurring metalloid that is widely distributed at low concentrations in crustal rocks, surface waters and groundwaters. However, anthropogenic activities such as irrigated agriculture, fossil fuel combustion, petroleum refining and mining operations can greatly increase Se loadings to the environment. The common occurrence of elevated Se concentrations in coal source rocks, for example, can greatly increase levels of Se in mining-influenced drainages over background levels, where the primary mode of Se input is through the weathering and leaching of exposed Se-bearing rocks (waste rock, pit walls, tailings, coarse coal reject, *etc*.). In aquatic settings, the major pathway for Se toxicity is through ingestion and associated Se accumulation in the tissues of reproductive egg-laying organisms (*e.g.*, fish, birds, amphibians). Toxicity is manifested as reproductive impairment due to maternal transfer resulting in juvenile abnormality or embryo death (Chapman *et al.*, 2009).

Due to existing and potential environmental consequences of Se exposure to aquatic taxa in freshwater settings, considerable effort has been placed on the evaluation and development of active and passive treatment systems for Se removal. In particular, the potential for the passive removal of Se through various forms of bioremediation has received considerable attention owing to the favourable cost implications and the ineffectiveness of traditional chemical precipitation methods for reducing Se to within environmentally-acceptable limits (Frankenberger *et al*., 2004).

In this paper, alternatives for the bioremediation of Se from mine waters using passive and semi-passive systems are reviewed. Case studies of field-scale treatment systems are described where data permit. Systems requiring extensive infrastructure, power and/or temperature control are not considered. The relevance of the various bioremediation alternatives to cold temperate climates (*e.g.*, interior Canada) is also discussed.

BACKGROUND

The speciation of Se in aquatic environments is highly dependent on reduction-oxidation (redox) potential, pH, ionic strength (salinity), biological/microbial interactions and kinetic limitations (rates of reactions). In particular, redox potential has been shown to present a dominant variable governing the speciation of Se in aquatic systems (Masscheleyn and Patrick, 1993; Zhang and Moore, 1996). In oxygenated surface waters at circumneutral pH, selenate (Se^{6+}) is predicted to dominate the Se species assemblage. At lower redox potentials, selenate is reduced to selenite (Se^{4+}) (Oremland *et al*., 1990). Selenite has a greater tendency for adsorption and therefore exhibits reduced mobility in comparison to selenate. In reducing environments, elemental Se (Se^0) and various selenides (Se^{2-}) become important, and their formation can present a dominant accumulation pathway in organic-rich sediments (Zhang and Moore, 1996). The formation of volatile methylated species such as dimethylselenide (DMse) by fungi, bacteria and algae and subsequent volatilization of gaseous Se to the atmosphere can be important mechanism of Se loss from aquatic environments (Hansen *et al*., 1998; Dungan and Frakenberger, 1999).

Passive and semi-passive treatment systems for the bioremediation of Se from waste waters rely upon various biogeochemical processes that are mediated by microbes (*e.g.*, bacteria) or plants (*e.g.*, algae, macrophytes). The mechanisms relevant to Se bioremediation in passive and semi-passive systems reflect processes that result in the removal dissolved Se from solution via adsorption, precipitation, biological uptake and volatilization, and include:

1. Microbially-mediated reduction of selenate (Se^{6+}) to selenite (Se^{4+}) in suboxic conditions followed by adsorption of selenite;
2. Precipitation of reduced Se species (elemental Se, selenides) through microbially-mediated reduction of Se oxyanions (selenate+selenite) in anoxic environments;
3. Microbial, fungal or biological methylation of Se to volatile methylated species (*e.g.*, DMSe) and release to the atmosphere (volatilization);
4. Uptake of Se oxyanions (selenate+selenite) into cells of microorganisms followed by assimilatory reduction to selenide and incorporation into metabolic machinery (*e.g.*, cellular proteins); and
5. Immobilization of Se through plant uptake.

TREATMENT ALTERNATIVES

In the following sections, descriptions are provided for the following passive and semi-passive bioremediation systems:

- Wetlands (natural and constructed surface-flow and subsurface-flow systems)
- Permeable reactive barriers
- *In situ* treatment of pit lakes/ponds; and
- *In situ* treatment of mine workings.

These emerging technologies have been selected based on their application at field scales, their success in removing Se from surface and/or groundwaters, and the availability of data in support of case study evaluation. In the context of this paper, wetlands (natural and constructed) and permeable reactive barriers (PRBs) are considered to represent passive systems for which minimal management and maintenance is required following initial commissioning. *In situ* Se removal in pit lakes, ponds and mine workings are considered semi-passive as these systems typically require on-going management (*e.g.*, fertilization or addition of organic amendments) to sustain desired processes in the long-term.

Wetlands: Wetland treatment systems offer a practical alternative for the bioremediation of Se due to the relatively-low costs with respect to construction, operation and maintenance. Removal through precipitation/adsorption of reduced species, immobilization into plant tissues, and release of volatile compounds to the atmosphere (volatilization) represent the dominant sinks for Se in wetland systems (Masscheleleyn and Patrick, 1993). The uptake of Se by plant roots is influenced by the chemical form and concentration of Se, soil redox conditions, pH of the rhizosphere, and the presence of competing ions such as nitrate, sulphate and phosphate The generation of volatile Se in sediments and plants can be bio-stimulated with the addition of organic amendments including saccharides, amino acids, and proteins (Losi and Frakenberger, 1997).

Wetlands can comprise surface-flow wetlands (natural or constructed) or subsurface-flow (SSF) constructed wetlands (Frakenberger *et al.*, 2004). In contrast to surface-flow wetlands, SSF wetlands typically consist of engineered gravel beds that serve as a rooting medium for salt-tolerant emergent wetland plants such as cattails (Typha spp.) and bulrushes (Scirpus spp.) (Shardendu *et al.*, 2003). In SSF systems, the influent stream flows through the gravel/root system where biogeochemical reactions within the plant root zone (rhizome) promote the removal of Se through a combination of Se uptake, *in situ* precipitation and volatilization (Figure 1).

An ecological risk associated with the use of surface-flow wetlands for Se bioremediation is the potential for increased transfer of Se into invertebrate and vertebrate food chains (Dungan and Frakenberger, 1999). However, deterrents such as barriers and noise can be used to reduce the attractiveness of wetland systems to wildlife. A primary advantage of SSF treatment is the capacity to minimize the potential for food-chain transfer of Se through physical isolation of the waste stream from biological receptors. Other limitations of wetland systems include their limited capacity to treat high-flow waste streams and seasonal changes in performance in temperate climates associated with annual temperature fluctuations and plant growth/decay cycles (Lin and Terry, 2003).

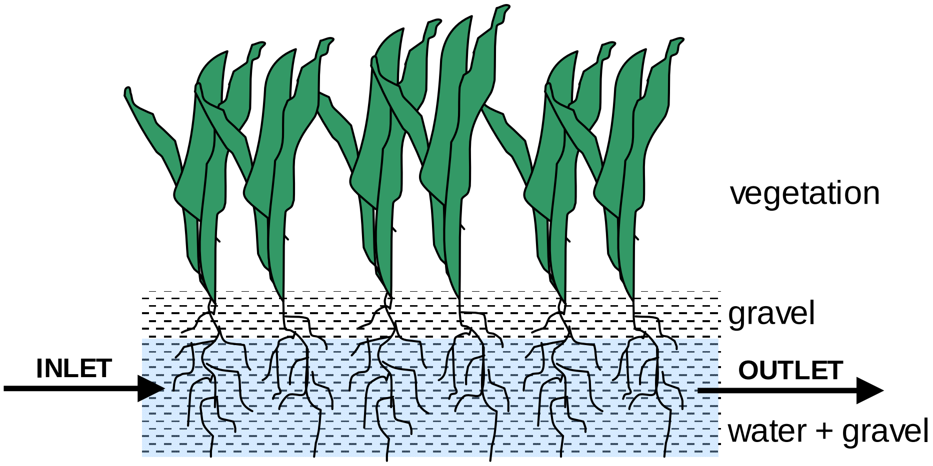

Figure 1. Conceptualized schematic of subsurface-flow wetland

Permeable Reactive Barriers: Permeable Reactive Barriers (PRBs) present a passive, *in situ* technology that has a high potential to treat shallow aquifers at a lower cost than traditional pump-and-treat methods (Blowes et al., 2000). In these systems, a permeable barrier is constructed to intercept a contaminated groundwater plume, with the barrier amended with one or more materials to create a reactive media for contaminant removal (Figure 2). Zero valent iron (ZVI) has proven to be an effective reactive material for the treatment of Se using PRBs, where ZVI facilitates the reduction and precipitation of Se as reduced forms, including elemental Se and Fe-selenides (Morrison et al., 2001). PRBs are most effective for the remediation of lower-flow and highly-concentrated waste streams which report to groundwater. PRBs are also more cost effective for well-constrained groundwater flows with relatively-small cross-sectional flow paths. With proper design and application, PRBs can perform to design standards for several decades. The major limitations of PRBs relate to their finite life span and potential to become clogged through precipitation of secondary minerals which can impede flow and performance (Blowes *et al*., 2000).

Pit Lakes/Ponds: Pit lakes are a common feature at closure for many mine sites and are often repositories for large volumes of mine-impacted water. Pit lakes offer viable opportunities for the bioremediation of Se given the tendency of these systems to develop suboxic conditions through either passive or active means. For Se bioremediation to be effective in pit lakes, suboxic conditions must be achieved to allow precipitation of reduced species (*e.g.*, elemental Se). Suboxic conditions are more easily sustained in stratified lakes due to the reduced influence of atmospheric interaction with pit bottom waters. The geometry and density characteristics of pit lakes often make them more conducive to lake stratification. Pit lakes differ from natural lakes in that they are often deep, steep sided, and sheltered from wind by pit walls. Further, given the saline features of pit wall runoff and other mine-related inputs that may enter the pit, pit lakes are often more saline than natural lakes. These features contribute to an increased tendency for seasonal and/or permanent stratification (meromixis). The depletion of oxygen and onset to Se/sulphate reduction in pit lakes can be accelerated through the addition of nutrients and/or organic amendments (Martin *et al*., 2003). Such amendments have also been successful in promoting oxygen depletion and maintaining stratification in initially oxygenated pit lakes (Harrington *et al*., 2004; Harrington, 2002).

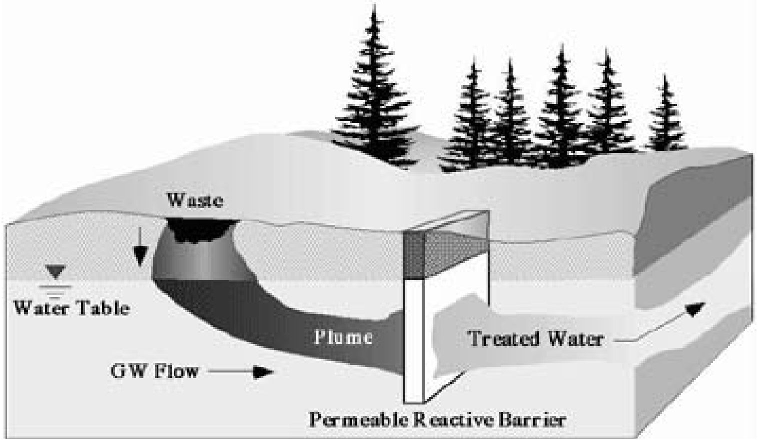

Figure 2: Schematic of permeable reactive barrier (from Bronstein, 2005)

The features described above for pit lakes can also apply to ponds, although suboxia is harder to sustain in such systems given their typically shallow water depths and tendency for wind-induced mixing. However, there is evidence to suggest that Se volatilization from pond environments can be effective in removing Se in the absence of anoxic conditions through the stimulation of volatilization by nutrient addition (Fan et al., 1998).

The main advantage of *in situ* pit lake treatment is the semi-passive feature and the ability to remediate large volumes of water at relatively low cost. The disadvantages include the generation of anoxic and potentially toxic waters that may require secondary treatment (*e.g.*, aeration and settlement) prior to discharge to receiving water courses.

Mine Workings: The methods described above for the *in situ* bioremediation of Se in pit lakes also have relevance to the *in situ* treatment of mine workings. The long residence times of waters in flooded underground settings present an ideal environment for the establishment of reducing conditions and removal of Se through reduction and precipitation mechanisms. Although no case studies for Se were available for review, the addition of organic carbon and nutrients to mine workings has been shown to promote conditions conducive to Se removal (Harrington, 2002).

CASE STUDIES

Chevron Surface Flow Wetland (San Pablo Bay, California): The Chevron Wetland is a 36 ha surface-flow constructed wetland that was commissioned to treat Se-rich oil refinery wastewaters (Hansen *et al*., 1998). The wetland comprises a combination of dense saltmarsh vegetation and open water. Se concentrations in the inflow of 20 to 30 μg/L decrease to <5 μg/L in the outflow, representing a loading reduction of ~89% (flow = 50 to 80 L/s) (Table 1). Mechanisms contributing to Se removal include adsorption/precipitation, plant uptake, and volatilization. Most of the Se removal has been attributed to immobilization in sediments and plant tissues, with volatilization estimates accounting for 10 to 30% of the Se removed (Hansen *et al*., 1998). The major disadvantage of surface flow wetlands in the increased potential risk for Se accumulation in organisms such as birds and fish. Indeed, development of the Chevron system resulted in an increase in Se body burdens in birds, leading to measures to reduce the attractiveness of the wetland to wildlife.

Benton Lake Wetland (Great Falls, Montana): Benton Lake is a shallow seasonal lake that was divided into six ponds through the construction of dikes to facilitate water management and habitat for waterfowl (Zhang and Moore, 1996). The system comprises a combination of perennial and seasonal wetlands, with water depths ranging from 0.5 to 1 m. Surface waters that enter the wetland system host elevated levels of dissolved Se (as selenate) in response to the weathering of Se-rich marine shales underlying the basin. Total dissolved Se concentrations decrease through the pond system from 26 to <1 μg/L (Table 1). Detailed analysis of Se partitioning demonstrated that Se removal to sediments (as elemental Se and organic-Se) could account for the bulk of Se removal (Zhang and Moore, 1996). Similar to the Chevron wetland, there have been concerns over increased Se transfer to waterbirds.

***In Situ* Pit Lake Treatment (Sweetwater Uranium Mine, Wyoming):** The Sweetwater Pit Lake, an oligotrophic lake located in Sweetwater County (Wyoming), was formed by the flooding of the Sweetwater open pit uranium mine following cessation of dewatering activities in 1983. The lake (4.5 million m^3) was treated by Kennecott Uranium Company with ~550 tons of sugars, fats, proteins, alcohols, phosphates and nitrates over a two month period in 1999 (Paulson *et al*., 2002; Harrington, 2002). Bacterial metabolization of the nutrient/carbon amendments promoted the development of suboxic conditions which led to the removal of dissolved Se from an initial concentration of 460 μg/L to values <10 μg/L. Removal is presumed to have occurred through adsorption/precipitation of reduced Se species (*e.g.*, elemental Se). The treatment process was efficient, requiring minimal equipment (a hydroseeder) at an estimated cost of <$0.16/$m^3$. Phosphate addition maintains the growth of algae which provides a continuous source of organic carbon to maintain desired conditions in the water column.

***In Situ* Treatment of Backfilled Pit (Beal Mountain Mine, Montana):** Closure of the Beal Mountain Mine, located near Butte Montana, involved backfilling the open pit with wasterock (Harrington, 2002). Inputs of seepage, pit wall runoff and precipitation filled the voids of the backfilled pit. In order to ameliorate elevated levels of nitrate (~2 mg/L) and Se (42 to 47 μg/L) in pit waters, organic carbon was added to the pit during the filling period to allow the distribution of carbon throughout the wasterock pore spaces. Organic carbon was added at a rate sufficient to reduce Se levels to between 2 and 3 μg/L.

***In Situ* Pit Lake Treatment (Gilt Edge Mine Superfund Site):** The Gilt Edge Mine near Lead, South Dakota, was the site of *in situ* treatment of the Anchor Hill Pit Lake (Park *et al*., 2006; Harrington *et al*., 2004). Prior to treatment in 1991, the pit lake (235,000 m^3) was characterized by low pH (pH=3) and elevated concentrations of TDS, nitrate, sulphate and several trace elements, including Se (~20 μg/L).

Table 1. Case Study Summary for Passive and Semi-Passive Bioremediation Systems for Selenium

Project	**Location**	**System Type**	**Treatment**	**Initial [Se] (µg/L)**	**Final [Se] (µg/L)**	**Flow Rate (L/s) or Volume**	**Reference**
Chevron Marsh	San Francisco Bay, California	Constructed surface-flow wetland	Adsorption/precipitation, biological uptake by plants, and volatilization to the atmosphere.	20-30 µg/L	<5 µg/L	50-80 L/s	Hansen et al., 1998
Benton Marsh	Great Falls, Montana	Engineered natural system comprising perennial and seasonal wetlands	Adsorption/precipitation, biological uptake by plants, and volatilization to the atmosphere.	26 µg/L	0.7 µg/L	Flow not reported	Zhang and Moore, 1996
Sweetwater Pit	Sweetwater County, Wyoming	Pit lake	*In situ* removal through addition of nutrients and organic amendments	443 µg/L	<5 µg/L	4.5 million m^3	Paulson et. al., 2002
Anchor Hill Pit Lake	Gilt Edge Mine, South Dakota	Pit lake	Lime addition followed by i*n situ* removal through addition of nutrients and organic amendments.	20 µg/L	<1 µg/L	235,000 m^3	Park et al., 2006
Beal Mountain Mine Pit Lake	Butte, Montana	Back-filled pit lake	*In situ* removal through addition of organic carbon during pit filling	42-47 µg/L	2-3 µg/L	Volume not reported	Harrington, 2002
Monticello Mill Tailings Site	Monticello, Utah	Permeable reactive barrier	PRB using zero valent iron, in conjunction with impermeable funnel walls to funnel contaminated groundwater	18.2 µg/L	0.1 µg/L	0.3 to 0.6 L/s	Bronstein, 2005

Following lime addition to neutralize acidity, the lake was amended with various sources of organic carbon (methanol, molasses and wood chips), fertilizer (phosphoric acid) and further base additions (sodium hydroxide). Following complete neutralization of the water column and subsequent to organic/nutrient amendments, reducing conditions developed as indicated by the onset of sulphate reduction. Pronounced decreases in Se concentration occurred commensurately with the shift to reducing conditions to values <1 μg/L in 2004. For release to the environment, pit waters have been extracted from an intermediate depth, filtered to remove particulate metals, and pumped to a holding pond to allow removal of hydrogen sulphide prior to discharge to a local creek system.

Monticello Permeable Reactive Barrier (Monticello, Utah): A PRB system using zero-valent iron (ZVI) was commissioned in 1999 to remediate contaminated groundwater at a former uranium and vanadium ore-processing mill at Monticello, Utah (Carpenter *et al.*, 2000; Bronstein, 2005). The remediation system includes a PRB used in conjunction with impermeable funnel walls to funnel contaminated ground water to the PRB for treatment. The barrier was built by driving steel sheet piling into the bedrock forming a rectangular box approximately 100 feet long by 8 feet wide. The native soils inside the box were replaced with ZVI and gravel packs upgradient and downgradient of the ZVI. The impermeable walls are composed of a bentonite and soil slurry mix. Water quality data for an array monitoring wells indicated that initial concentrations of Se (40 µg/L) were reduced to non-detectable levels for influent flows ranging from 0.3 to 0.6 L/s. Losses in PRB performance have occurred in response to a decrease in hydraulic conductivity associated with the precipitation carbonate and oxide minerals within and adjacent to the barrier.

SUMMARY

This paper demonstrates that, for certain environments, passive and/or semi-passive systems can present potentially cost-effective options for the bioremediation of Se. With regards to wetlands, surface-flow systems can afford significant Se removal for relatively low-flow applications. However, such systems have been shown to create a potential wildlife hazard primarily through increased Se transfer to waterbirds. In this regard, subsurface-flow wetlands offer considerable promise given that influent waters are physically isolated from the surface environment. Wetlands are also limited in cold climates that experience large seasonal flow and temperature fluctuations. *In situ* pit lake treatment for Se through fertilization and/or organic amendments is clearly a viable option to treat large volumes of water at relatively-low cost. The Sweetwater, Beal Mountain, and Anchor Hill pit lake case studies are all examples of Se bioremediation in cold-temperate interior climates where water temperatures are less than 4ºC for several months of the year. Permeable reactive barriers also offer a viable strategy to treat Se in cold-temperate interior climates due to the perennial nature of groundwater flows and the maintenance of performance at low temperatures.

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