

In Situ Attenuation of Selenium in Coal Mine Flooded Pits

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ABSTRACT

Suboxia is a prerequisite for the bioremediation of selenium (Se), whereby Se is removed from solution as reduced species (*e.g.*, elemental Se). In this regard, flooded open pits offer suitable repositories for the bioremediation of Se given the tendency of these systems to develop suboxic conditions through either passive or active means. Specifically, the geometry of flooded pits and their water column density characteristics often make them conducive to permanent stratification (meromixis) and the development of bottom water suboxia. In order to assess the potential for Se bioremediation in a coal mine flooded pit in northern Canada, a combination of high resolution physical profiling (temperature, dissolved oxygen and conductivity) and water quality sampling was conducted. Vertical profiling revealed a stratified water column with respect to both temperature and salinity, with the pycnocline occurring at a depth of 5 m. Dissolved oxygen was absent below a depth of 20 m, suggesting that the water column stratification is permanent. Profiles of other redox-sensitive species (dissolved manganese and nitrate) further support the presence of bottom water anoxia below 20 m. The data for nitrate, for example, show evidence of denitrification immediately below the oxic-suboxic boundary. Dissolved Se shows evidence of attenuation in response to the vertical redox gradient in the water column, with surface values (12 to 20 µg/L) decreasing to <3 µg/L in the suboxic zone. Overall, the data reveal evidence of both denitrification and Se reduction, with Se being removed from solution presumably as either selenite (Se⁺⁴) (via adsorption to settling particles) or as precipitation of elemental Se (Se⁰) or selenide (Se²⁻). The implications of the data with respect to mine water management and Se bioremediation are discussed.

Keywords: coal, mining, bioremediation, passive treatment

INTRODUCTION

For coal mine districts throughout North America, selenium (Se) is a water quality parameter of concern with respect to environmental compliance and the protection of aquatic resources. The common occurrence of elevated Se concentrations in coal source rocks (*e.g.*, wasterock, pit walls, tailings, coal reject, *etc.*), and leaching through natural weathering, can increase levels of Se in mining-influenced drainages to well over background levels. Due to potential environmental consequences aquatic taxa exposure to Se in mine-affected settings, considerable effort has been placed on the development and evaluation of active and passive treatment systems for Se removal (CH2MHILL, 2010, 2013). In particular, the potential for the passive removal of Se through various forms of bioremediation has received considerable attention due to the favourable cost implications and the ineffectiveness of traditional chemical precipitation methods for reducing Se to environmentally-acceptable limits (Frankenberger *et al.*, 2004).

Engineered passive and active treatment systems designed to remove Se from solution generally rely upon the development of suboxia. Under suboxic conditions, the potential for Se attenuation is enhanced by a suite of microbially-mediated processes that favour the reduction of selenate (Se⁺⁶) and removal of dissolved Se from solution via adsorption and precipitation reactions. Such suboxic mechanisms include: 1) reduction of selenate (Se⁺⁶) to selenite (Se⁺⁴) followed by adsorption of selenite to particles; 2) precipitation of elemental Se (Se⁰); 3) precipitation of Se as inorganic/organic selenides (Se⁻²); and 4) co-precipitation of Se with reduced sulfur (Masscheleyn and Patrick, 1993). Suboxia is also required to reduce nitrate (through denitrification), the presence of which can inhibit Se reduction and hence its potential for attenuation (Oremland *et al.*, 1991).

Mine settings offer significant opportunities for the bioremediation of Se through the natural and/or engineered development of suboxia within mine facilities. Specifically, large-scale zones of suboxia may occur in pit lakes (Castro and Moore, 2000), within the pore spaces of saturated wasterock (Bianchin *et al.*, 2013), and in some cases, within unsaturated zones of large wasterock dumps (Kuo and Ritchie, 1999). Further, such suboxic zones have the potential to be incorporated into water management strategies designed to reduce Se loadings from mine operations.

In this paper, the potential utility of flooded open pits as bioremediation cells for Se is discussed through examination of water quality data from a mine in northern Canada. Mine pit lakes often differ from natural lakes in that they are typically deeper, more saline, and less susceptible to wind mixing (due to small fetch and topographic sheltering from pit walls). These features can lead to the development of permanent stratification (meromixis), resulting in the development of suboxic bottom waters. Specific objectives this study are as follows: 1) describe the physical and chemical limnological setting of the flooded pit; 2) delineate the biogeochemical processes governing the behaviour of Se and other mine-related parameters; and 3) discuss potential applications of flooded pits for Se bioremediation through passive and engineered methods.

ENVIRONMENTAL SETTING AND METHODOLOGY

The study site is situated at a closed coal mine in northern Canada at an elevation of ~1,500 m. The open pit was developed between ~1987 and ~1995 and partially backfilled with spoils from ~1995 to ~1998. Passive flooding of the pit began in 1998, reaching a static water level in 2002. The maximum water depth in the pit is 72 m, encompassing a total water volume of 2.35 million m³. Due to the generally low total sulfur content (generally <1%) and high abundance of carbonate minerals in

host rocks, waste materials in the region are not acid generating. Environmental concerns relating to Se are typically associated with neutral to basic-pH leaching from subaerial (unsaturated) wasterock.

On July 31, 2013, the flooded pit was sampled through a combination of *in situ* profiling and water sample collection. *In situ* vertical profiling (20 cm vertical resolution) of conductivity, temperature, pH, dissolved oxygen (DO) and fluorescence was conducted over the deepest portion of the pit using a Sea-Bird Electronics™ conductivity-temperature-depth (CTD) profiler (SBE 19plus SEACAT Profiler, Bellevue, Washington). The CTD was configured with a WETLABS ECO Fluorometer™ to measure vertical variations in chlorophyll concentration in the water column (proxy for photosynthetic algal biomass). Water quality samples were collected at depths of 1, 2, 4, 6, 8, 10, 12, 15, 20, 30, 40, 50 and 60 m, and analyzed for physical parameters, anions, nutrients and total/dissolved trace elements. Trace element concentrations were determined via inductively-coupled plasma mass spectrometry (ICP-MS), while anions were analyzed via ion chromatography (Dionex).

RESULTS AND DISCUSSION

Water column physical structure

High resolution profiles of temperature and conductivity show the presence of a stratified water column in the flooded pit, with a pronounced thermocline observed between 3 and 6 m (Figure 1). The thermocline overlaps with a sharp gradient in salinity as revealed by the profile of specific conductivity. The combined effect of the temperature and salinity gradients result in a pronounced density gradient (pycnocline) that is spatially consistent with the temperature and conductivity gradients observed in the uppermost 6 m of the water column (Figure 1).

Salinity gradients in the flooded pit are dominantly governed by vertical variations in the concentrations of sulfate, calcium and alkalinity, all of which represent products of mine waste weathering (wasterock and pit walls) (Figure 2). Sulfate is liberated through the oxidation of reduced sulfur minerals (*e.g.* pyrite) while calcium and alkalinity represent the products of carbonate mineral dissolution which are abundant in the host Cretaceous sedimentary rocks. Sulfate concentrations in the water column (750 to 1,000 mg/L) are strongly elevated above background values, and illustrate the pronounced mine-related signature in pit waters. The range in sulfate concentration is comparable in magnitude to values observed in wasterock seepages in the region.

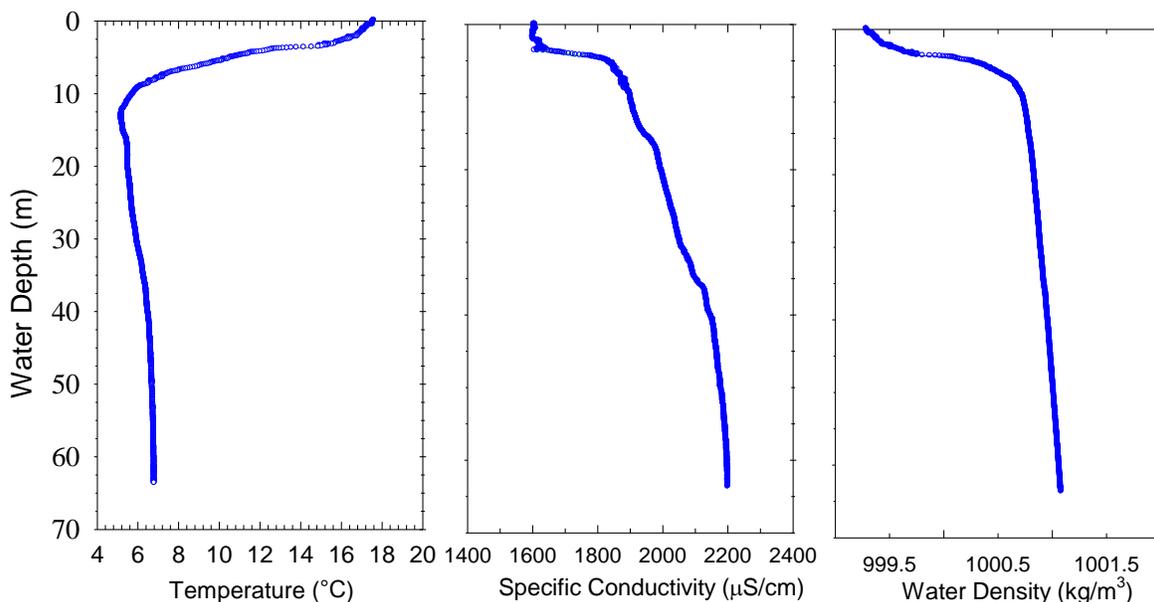
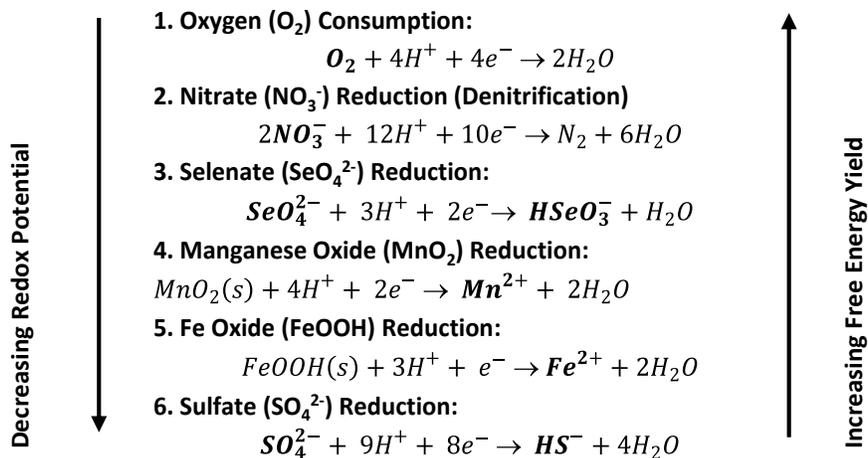


Figure 1 High vertical resolution (20 cm spacing) profiles of *in situ* temperature, specific conductivity and calculated water density in the flooded pit.

Redox conditions

Redox conditions have been shown to be the dominant variable governing Se speciation, precipitation/dissolution, sorption/desorption, methylation and volatilization in water and sediments (Masscheleyn and Patrick, 1993; Zhang and Moore, 1996). Accordingly, an understanding of redox conditions is essential to support interpretations of Se behavior. In natural systems, redox reactions are driven by the oxidation of organic matter, which can be defined by a series of microbially-mediated reactions (Table 1). In the presence of dissolved oxygen, aerobic bacteria will utilize O₂ as a terminal electron acceptor since this redox reaction affords the greatest energy yield. However, in systems where the rate of O₂ consumption exceeds the rate of re-supply, O₂ will become depleted and other secondary oxidants will be utilized by facultative anaerobic bacteria. These, in order of their free energy yield, are nitrate, manganese oxides, iron oxides, and sulfate (Table 1). In this sequence of redox reactions, selenate reduction occurs at a similar redox potential to that of nitrate.

Table 1 Oxidation/reduction reactions associated with the re-mineralization (oxidation) of organic matter. Parameters measured to elucidate redox conditions are highlighted in bold.



Water column redox conditions in the flooded pit were assessed through examination of various redox-sensitive indicators including dissolved oxygen (DO), nitrate, ammonia, dissolved Fe and dissolved Mn (Figure 2). Overall, the presence of lake stratification has a pronounced effect on water column redox conditions. DO levels show a progressive decline below the thermocline, from a maximum of 12 mg/L (at 5 m) to undetectable concentrations below a depth of 22 m. The absence of DO below 22 m provides strong evidence to indicate that the flooded pit is permanently stratified. If a mixing event had occurred in the previous months, some residual DO would be expected to persist in lake bottom waters.

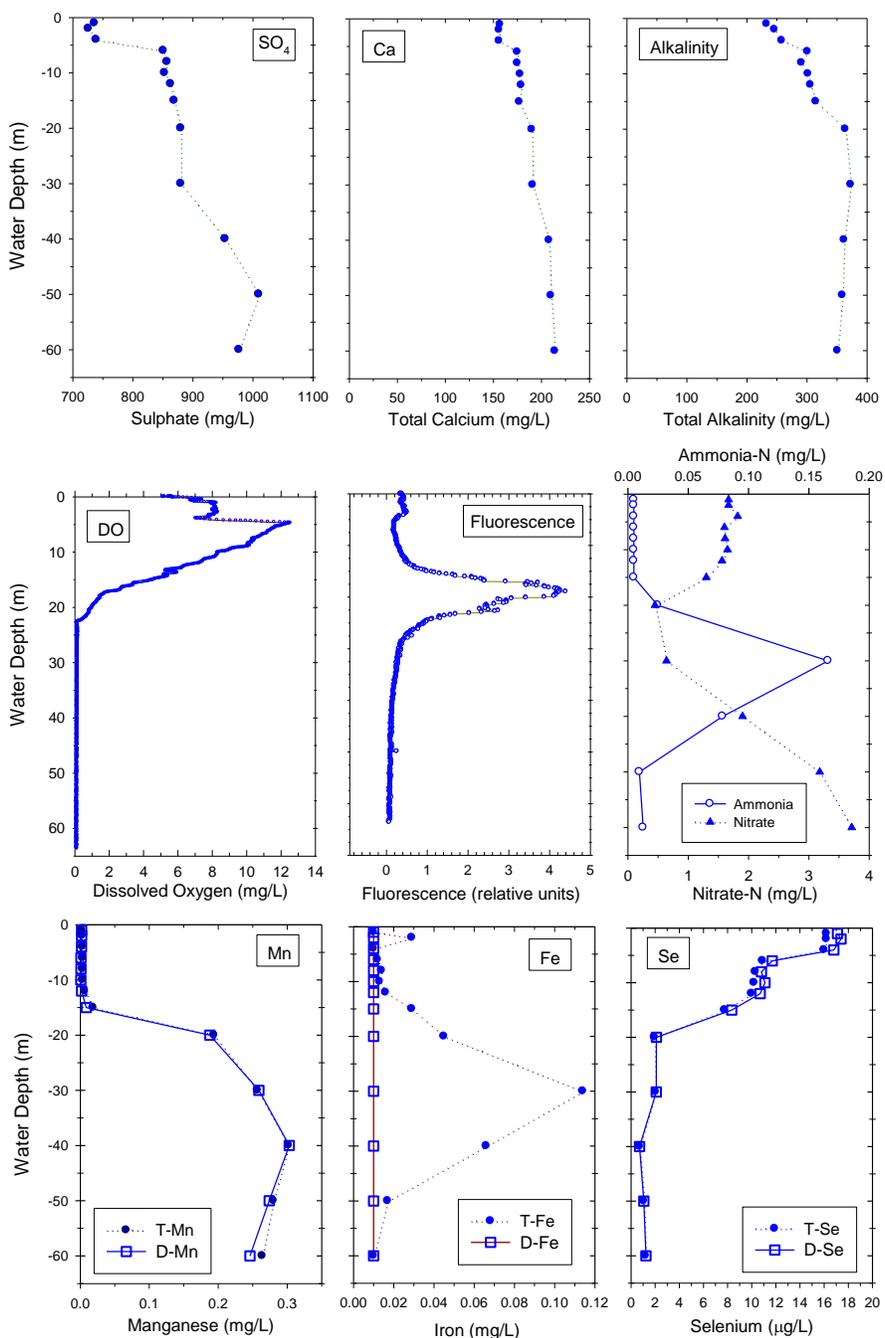


Figure 2 Vertical profiles of sulfate, total calcium, total alkalinity, dissolved oxygen, fluorescence, nitrate-N, ammonia-N, manganese, iron and selenium in the flooded pit. Data for fluorescence and dissolved oxygen were collected via high vertical resolution *in situ* profiling.

Nitrate shows a pronounced mine-related signature in surface waters (1.6 mg/L), and reflects the input of residual nitrogen-based blasting residues. Below the oxic-suboxic boundary at 22 m, nitrate-N values decline to a minimum value of 0.5 mg/L at a depth of 20 m. The horizon of low

nitrate concentration is interpreted to result from denitrification (microbially-mediated nitrate reduction) in the suboxic zone below 20 m. Below the nitrate minimum, nitrate-N values progressively increase to a bottom water maximum of 3.7 mg/L, presumably reflecting the original mine-related signature established post-filling. Overall, the data suggest that the nitrate profile is in non-steady-state, whereby denitrification is progressively depleting the nitrate inventory in the suboxic zone below 20 m.

The occurrence of nitrate reduction near the oxic-suboxic boundary may in part be related to the peak in photosynthetic biomass (*e.g.*, algae) observed between 16 and 23 m, which will supply a source of organic detritus (and oxygen demand) to this portion of the water column. The magnitude of the fluorescence peak is indicative of oligotrophic conditions, which is common to pit lake environments. The influence of the autotrophic peak is also illustrated by the ammonia data, which show a concentration maximum in the upper portion of the suboxic zone (Figure 2). This ammonia peak is inferred to represent a product of organic matter remineralization. The presence of ammonia also provides additional evidence in support of suboxic conditions below water depths of 20 m, given the chemical instability of this species in the presence of DO.

Below the oxic-suboxic boundary at 22 m, dissolved Mn concentrations increase to a maximum of 0.3 mg/L. This is consistent with the reductive dissolution of Mn-oxides in the suboxic water column, which will liberate dissolved Mn²⁺ into solution. In contrast to Mn, dissolved Fe does not show any evidence of bottom water enrichment. Low levels of particulate Fe (as inferred from the total Fe profile) are evident; however, the data do not indicate the occurrence of Fe-oxide reductive dissolution. Collectively, the data for redox proxies are indicative of mildly suboxic conditions below 20 m, as inferred by the absence of DO, evidence of denitrification, presence of ammonia, and elevated levels of dissolved Mn. Indicators of more strongly reducing conditions, as would be revealed by Fe oxide reductive dissolution and/or sulfate reduction, are not observed.

Selenium

Profiles for dissolved and total Se are congruent, indicating that Se is present almost exclusively as dissolved species (Figure 2). Se shows evidence of attenuation in response to the vertical redox gradient in the water column, with surface values (12 to 20 µg/L) decreasing to <3 µg/L in the suboxic zone (Figure 2). The low Se values below the oxic-suboxic boundary, and the strong parallels between Se and DO, suggest that the behaviour and attenuation of Se is tied to vertical variations in redox conditions. Specifically, the data strongly suggest that the decrease in Se concentrations below 20 m reflects the removal of dissolved Se from solution as reduced Se phases, presumably as either selenite (Se⁺⁴) (via adsorption to settling of particles) or as precipitation of elemental Se (Se⁰) or selenide (Se²⁻). The redox-controlled attenuation of Se is supported by the data for other redox proxies, which show evidence of both denitrification and Mn-oxide reductive dissolution. Specifically, the selenate/selenite redox couple occurs between nitrate reduction and Mn-oxide reduction (Table 1) Importantly, these data demonstrate that Se removal is achievable under mildly suboxic conditions in the presence of nitrate, which could be expected to hinder Se reduction.

The mechanism of Se attenuation described here is consistent with other forms of passive and engineered Se removal systems that rely on suboxic conditions, including passive wetland treatment (Martin *et al.*, 2011), passive removal in saturated wasterock (Bianchin *et al.*, 2013),

constructed permeable reactive barriers (Morrison *et al.*, 2001), and active biological treatment systems (CH2M HILL, 2010, 2013).

A conceptual model for Se bioremediation is shown in Figure 3. The required elements to support selenate reduction and removal from solution include: 1) a stratified water column, which allows the development of bottom water suboxia; and 2) a source of oxygen demand, which in this case is provided by *in situ* photosynthetic activity. The input of terrestrial organics via surface runoff likely also provides a source of organic carbon (and oxygen demand) to the system.

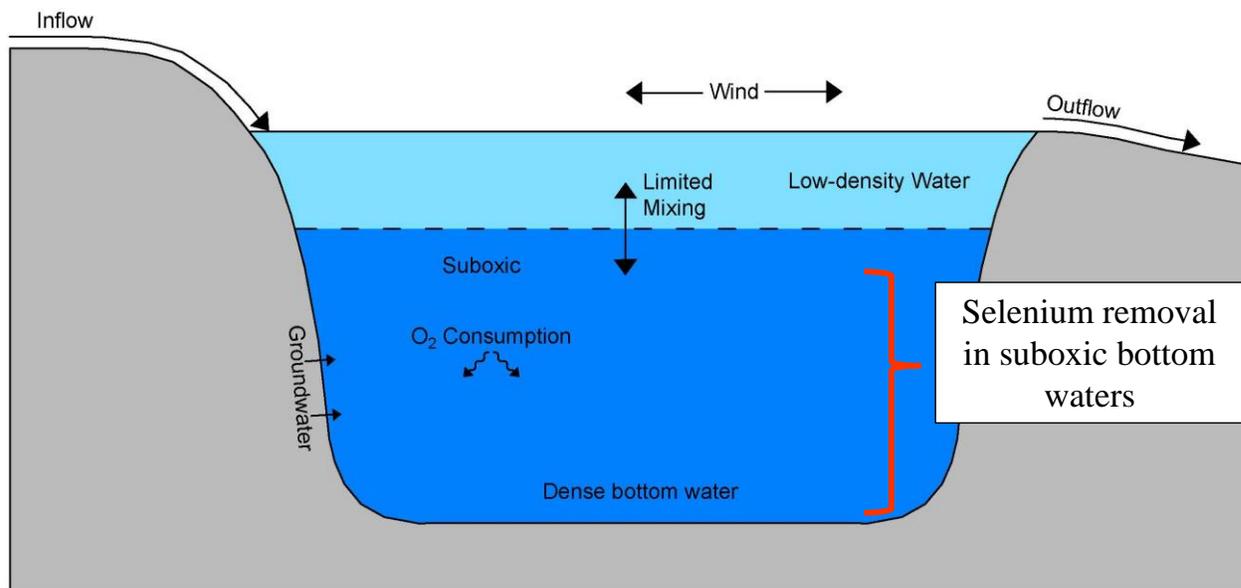


Figure 3. Conceptual model for selenium removal in a stratified flooded pit.

CONCLUSIONS AND IMPLICATIONS FOR MINE WATER MANAGEMENT

Overall, the data provided here illustrate the potential utility of flooded pits as *in situ* bioremediation cells for the removal of Se. The scale of Se removal can be illustrated by the volume of water in this system showing Se concentrations <5 µg/L, which equates to approximately 1 million m³ (below a depth of 20 m). There is also the potential to enhance rates of Se removal via the addition of organic amendments. Lake fertilization, for example, can provide an effective means to increase rates of *in situ* algal production and associated carbon generation (Dessouki *et al.*, 2005; Martin *et al.*, 2009). Such methods rely upon the well-established links between phosphorus limitation and algal growth (Schindler *et al.*, 1980). This form of amendment is very cost effective, given that only small additions of phosphorus can promote extensive carbon production. Alternatively, successful Se removal has been achieved via the direct addition of organic amendments to flooded pits (as liquid or solid forms) (Park *et al.*, 2006).

Flooded pits that exhibit stratified and suboxic water columns also offer the potential to passively treat other site contact flows. This is illustrated in Figure 4 which shows a conceptual model depicting the injection of contact waters (*e.g.*, wasterock seepage) into the suboxic (bottom) zone of a flooded pit. Following mixing and Se attenuation in pit bottom waters, waters are then withdrawn from the pit for final discharge, which may require aerobic polishing prior to release to

receiving streams. The input of contact waters to the pit bottom will introduce DO, which has the potential to push the system to a less favourable redox regime (more oxic). In this regard, the addition of fertilizer and/or inoculum (*e.g.*, Se and nitrate reducing microbes) could be used to sustain suboxia and the desired redox state conducive to Se removal (also illustrated in Figure 4). This form of semi-passive treatment has been implemented at the Island Copper Mine, which uses a combination of ARD injection to bottom waters and surface water fertilization to promote more reducing conditions in the lower water column (Polling *et al.*, 2003).

With regards to mine water management, the data presented here also highlight the merits of maximizing saturated storage volumes in the design of mine waste facilities, which can passively, or through augmentation, form large-scale zones of suboxia. This requires consideration during mine planning (pit morphometry), potential use of in-pit berms to maximize in-pit water levels, mine waste management and water management.

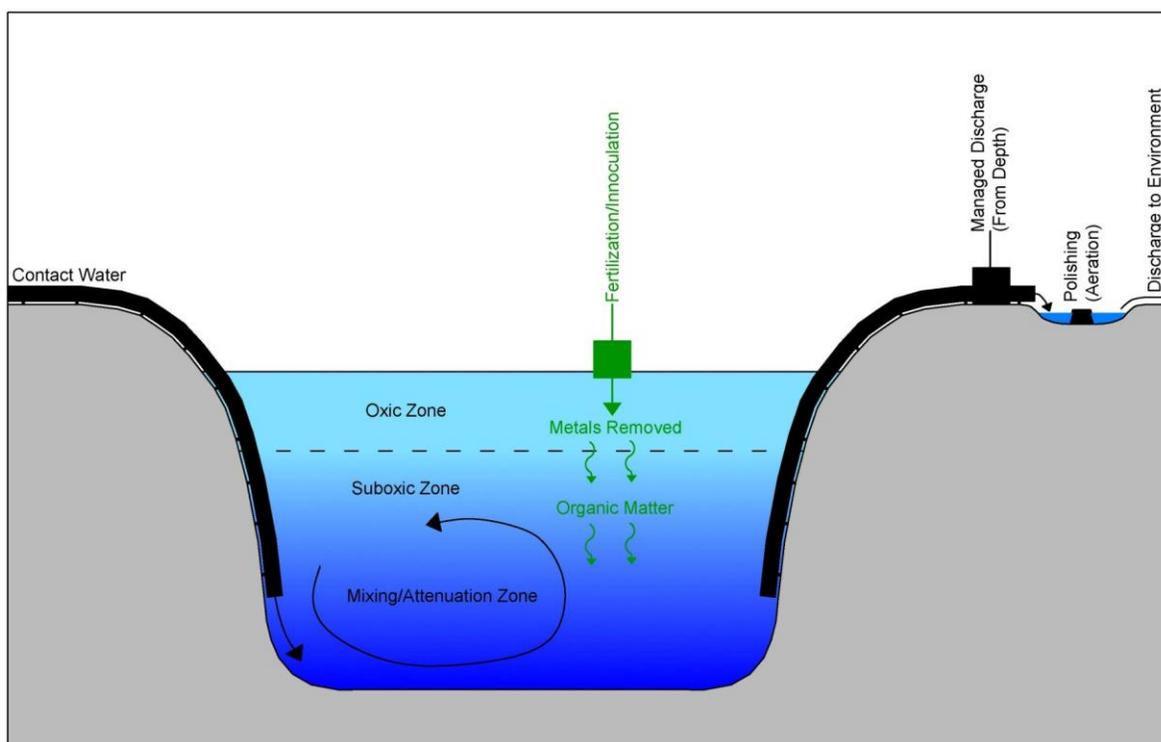


Figure 4. Conceptual model that describes a contact water injection system to pit bottom waters and associated removal in support of engineered Se removal system. Fertilization and polishing components

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