Passive Treatment of Metalloids Associated With Acid Rock Drainage

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ABSTRACT

Passive treatment approaches for metalloids (arsenic, antimony, and selenium) are presented and discussed. Passive approaches are built around utilizing the iron and sulfate inherently present in acid rock drainage (ARD). Arsenic and antimony are effectively removed by co-precipitation and adsorption with iron under acidic pH conditions. The reducing conditions afforded by sulfate reducing bacteria (SRB) in a conventional anaerobic passive system are ideal for the transformation of selenate to selenite and further to elemental selenium; the former being removed by adsorption to iron and organic substrate material and the latter being removed by precipitation and entrapment in the passive treatment media. Problems that can occur when treating metalloids in systems that rely on sulfate reducing bacteria (SRB) are presented and methods to mitigate problems and optimize metalloid removal are discussed. A conceptual design of a passive treatment system to remove arsenic, antimony, and selenium is presented.

INTRODUCTION

Selenium, arsenic, and antimony sometimes occur in acid rock drainage (ARD) from active and inactive mining operations. These metalloids can present a significant environmental and human health risk when released to surface water or groundwater. Selenium poses special risks due to its amorphous chemical characteristics in the environment that allow it to transform into a variety of organo-metallic species and bioaccumulate in plants, aquatic life, and wildlife. Regulatory agencies are continually setting more stringent standards for selenium and other metalloids. U.S. Fish and Wildlife Service is actively pursuing lowering the national selenium water quality criterion to 2 ug/L. U.S. EPA is proposing to lower the Safe Drinking Water Act (SDWA) Maximum Contaminant

Level (MCL) for arsenic from the present limit of 50 ug/L to within the range of 2 to 20 ug/L. The existing MCL for antimony is 6 ug/L.

Passive treatment systems provide an ideal approach for treating ARD because they provide low cost, low maintenance methods for treating waste streams that may exist well beyond end of mine life. Most of the technical literature on passive treatment addresses the removal of common heavy metals such as cadmium, copper, iron, lead, manganese, nickel, and zinc. However, due to the high potential risks caused by metalloids and the ever-tightening regulatory limits, there is a need to develop practical and affordable technologies for their removal. By understanding the chemical and biochemical behavior of metalloids in the environment and applying known and successful concepts of active treatment technologies, passive treatment systems may be developed and engineered to optimize removal of metalloids, while also performing the conventional removal of monovalent and divalent heavy metals.

Arsenic and antimony are effectively removed by co-precipitation and adsorption with iron under acidic pH conditions. These two conditions of high iron and low pH are prevalent in ARD. Selenium is also effectively removed by iron at low pH, provided it is in the reduced form of selenite. The oxidized form of selenium (selenate) is common in surface water and ARD, but is not readily removed by iron. The reducing conditions afforded by sulfate reducing bacteria in a conventional anaerobic passive system are ideal for the transformation of selenate to selenite and further to elemental selenium; the former being removed by adsorption to iron and organic substrate material and the latter being removed by precipitation and entrapment in the passive treatment media. In addition, selenium may be reduced and removed in soil containing naturally occurring *Clostridium* bacteria, provided the necessary nutrients and organic material are present.

The next section discusses the chemistry and treatment of metalloids. The primary chemical and biological removal mechanisms of a passive system are explained and methods to enhance these mechanisms in an engineered passive system are provided. A recent paper published in *Mining Engineering* (Canty, 1999) describes difficulties encountered in attempting to remove arsenic along with heavy metals in a passive treatment system. The paper presents the results of pilot scale testing of the use of sulfate reducing bacteria (SRB) to treat ARD from the mine workings of the Lilly/Orphan Boy Mine near Elliston, Montana. The results of this study will be used to exemplify difficulties that may be encountered when treating a combination of metals and metalloids with a passive system. An alternative conceptual design capable of providing effective removal of both metals and metalloid species is developed and presented.

CHEMISTRY AND TREATMENT OF METALLOIDS

Arsenic

Arsenic is usually present as an oxyanion in mining wastewater. The valence state and species of arsenic depend on the pH and redox conditions of the water (Bodeck, 1988). In reducing, highly acidic water, arsenic may be found primarily in the reduced form of arsenite, As(III). Under oxidizing conditions and a wide pH range, from mildly acidic to basic, arsenic may exist predominantly in the oxidized form of arsenate, As(V). In the natural environment, arsenate is strongly sorbed onto soils and sediments. The process comprises three mechanisms: (1) specific adsorption onto Fe and Al hydrous oxides, clays, and carbonates; (2) co-precipitation with hydrous iron oxides; and (3) isomorphic substitution of arsenic with phosphorous in minerals (Bodeck, 1988). Co-precipitation with iron is probably the most common mechanism under most environmental conditions.

Sorption of arsenate by iron follows the Langmuir isotherm, while the reduced form, arsenite, is less strongly sorbed by iron with removal varying linearly with iron concentration (Bodeck, 1988). Oxi-ferric hydroxide surfaces are positively charged under acidic pH conditions and negatively charged under alkaline pH conditions. Thus, to facilitate adsorption and removal of oxyanions such as arsenic, antimony, and selenium, iron coprecipitation should be conducted under acidic pH conditions (EPRI, 1990). Alkaline conditions are necessary for coprecipitation of cationic metals such as copper, zinc, nickel, and cadmium.

Insoluble ferric arsenate ($FeAsO_4$) may be reacted by maintaining the Fe/As molar ratio at 4 or greater (Mirza and Ramachandran, 1996). At this molar ratio, the optimal pH for reaction is 5. However, by increasing the Fe/As ratio, the optimal pH range can be widened and the removal efficiency of arsenic increased. Thus, when using iron for treatment, there are two removal mechanisms for arsenic: (1) adsorption to the surface of oxi-ferric hydroxide, which for anions is improved under acidic pH conditions; and (2) precipitation of insoluble ferric arsenate, assuming that the ratio of iron to arsenic is sufficiently high.

There are various opinions on the form of the iron-arsenic compound that is precipitated during arsenic removal with iron salts. These compounds are amorphous and cannot be identified reliably by x-ray diffraction (XRD) techniques. The amorphous form of $FeAsO_4$ at Fe/As = 1 is not stable and therefore not suitable for disposal as a sludge (Mirza and Ramachandran, 1996). Arsenic containing sludges are regulated by USEPA Toxicity Characteristic Leaching Procedures (TCLP), which defines whether or not a solid waste is hazardous. However, basic ferric arsenate with Fe/As = 4 or greater is extremely insoluble and readily meets regulatory limits when subjected to TCLP analysis (Broadhurst, undated; Mirza and Ramachandran, 1996).

Antimony

Similar to arsenic, antimony commonly exists in two oxidation states: the reduced form, Sb(III) and the oxidized form, Sb(V). Antimony Sb(V) is the most prominent oxidation state under oxidizing conditions and at a pH of greater than 3 (Bodeck, 1988). Antimony is commonly complexed with OH^- ligand as $Sb(OH)_6^-$. This form of antimony is readily adsorbed to iron under acidic pH conditions. At low pH (below neutral), the surface charge of oxi-ferric hydroxide is positive and thus capable of adsorbing anions.

Factors that effect antimony adsorption include iron concentration [as Fe(III)], pH, and contact time. Figure 1 shows the effect of iron dose and pH on antimony removal. The data for Figure 1 were derived from bench-scale treatability tests performed by Parametrix, Inc. Experiments were conducted on mine drainage in beaker tests using varying doses of ferric sulfate. The solution pH was adjusted with sulfuric acid and sodium hydroxide. The starting concentration of antimony was 50 ug/L. Beaker samples were allowed to settle and were filtered prior to analysis of antimony.

The mechanism for antimony removal is adsorption and, accordingly, Figure 1 shows that removal efficiency is improved with increasing iron dose. Additionally, low pH favors removal as a result of the charge that is placed on the adsorbent, oxi-ferric hydroxide. Arsenic (not shown on the figure) was also present in these tests at an initial concentration of 190 ug/L. Arsenic was removed to below 1 ug/L at all iron doses and pH values above 3.5. Both arsenic and antimony were analyzed by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) with a detection limit of 1 ug/L.

Contact time also influences antimony removal efficiency as shown on Figure 2. Figure 2 was also developed with data from bench-scale treatability tests conducted in stirred beakers at a constant iron dose of 34 mg/L and constant pH of 5. As shown, most of the antimony is adsorbed and removed within a contact time of 10 minutes. Longer contact times provide some additional removal.

Selenium

Knowing the species of selenium is critical for identifying the appropriate treatment method. Selenate, Se(VI), is the predominant species in oxygenated waters and ARD but it is not readily removed, regardless of the treatment technology employed. The key to successful treatment is to reduce selenate to selenite, Se(IV), by chemical or biological processes. Selenite is readily removed by sorption to soils, organics, cellular material, ferric iron, etc. (Bodeck, 1988). As shown in Figure 3, selenite can be reduced to very low levels by ferric iron adsorption at a pH below neutral (Merrill et al., 1986 and 1987).

Selenium is effectively removed in passive, anaerobic biological treatment units where sulfate reducing bacteria (SRB) are present. ARD provides the necessary sulfate for the bacteria to feed upon. The basic biochemical process involves the employment of common sulfate reducing bacteria, which are responsible for converting species such as sulfate to sulfide and selenate to selenite or elemental selenium. The process works under anaerobic biological conditions, thus providing a reducing environment. Reduced selenium is subsequently removed by entrapment in the substrate or by ligand exchange and adsorption to biomass and organic substrate, which usually consists of composted livestock manure. Sulfides formed in the process combine with heavy metals such as copper, cadmium, lead, mercury, and zinc to precipitate insoluble sulfide minerals. SRB systems are capable of providing greater than 95 percent removal of selenium and effluent concentrations ranging from 10 to 20 ug/L selenium (Mudder and Botz, 1997).

Additional selenium polishing after the anaerobic (reducing) cells may be provided by a number of innovative approaches. Laboratory studies (Khalafalla, 1990) indicate that selenite undergoes a fast exchange reaction with pyrite to form an insoluble mineral, FeS.Se. On a laboratory scale, the process has been shown to remove selenium to very low levels. Thus, sulfide-containing tailings or waste rock may have the potential to remove selenium once reduced to selenite. This discovery has potential application in a passive system containing pyrite tailings or crushed ore material in a subsurface, reducing filter drain. Additionally, it may have application in tailings ponds, in situ, if the appropriate conditions for microbiological reduction of selenium can be fostered in subsurface zones of the pond.

Another new, innovative method involves the use of iron-oxide-coated sand to adsorb selenite in a process similar to ferric iron adsorption. Selenium, once converted to selenite, is readily adsorbed and removed by ferric iron. This new process employs the same removal mechanisms as iron adsorption, but the iron is fixed to granular material, which can be operated in a passive drain configuration. Iron-oxide-coated sand has been shown in pilot scale studies to have high capacities for selenium and other metalloids, with effluent levels typically less than 10 ug/L with corresponding contact times of only 10 minutes (Benjamin, 1996). An additional advantage to this polishing steps is that it can significantly reduce the size of the preceding SRB system by treating trace amounts of selenium that are allowed to breakthrough the SRB cell.

Land treatment is another potential alternative for selenium removal. Naturally occurring soil bacteria (e.g., *Clostridium*) have the ability to reduce selenate to selenite and to elemental selenium under anaerobic conditions (Baldwin et al., 1985). The reduced selenium species are more effectively adsorbed (in the case of selenite) or precipitated (in the case of elemental selenium) within the subsurface of the soil layer.

Natural or engineered wetlands are also known to provide significant removal of selenium. In aquatic wetland systems, selenium is introduced via the water and is accumulated in sediments to varying degrees depending on the selenium form in the water and the redox conditions within the system. Once in the sediments, varying amounts are converted to organo-selenium compounds which are then accumulated by aquatic invertebrates and wetland plants, which are in turn consumed by fish and wildlife. Organo-selenium compounds are highly bioaccumulative and toxic. The amount of selenium conversion is largely a function of biological productivity, with more productive systems such as wetlands converting a greater percentage to the bioaccumulative organo-selenium compounds. Because of the potential risks to wildlife, treatment wetlands are not recommended for selenium removal. Additionally, conditions that might promote wildlife habitat should be avoided when designing passive treatment systems to remove selenium.

It is to be noted that there are practical limitations even with the most advanced and expensive methods of selenium treatment. Relatively inexpensive, passive methods of treatment are capable of removing selenium to levels comparable to more advanced technologies such as ion exchange and reverse osmosis. Today's treatment technologies, when operated on a large scale, are only capable of achieving a selenium discharge concentration of around 10 to 20 ug/L (Mirza and Ramachandran, 1996; Mudder and Boltz, 1997). The selenium levels attainable with any practical means of treatment are thus expected to be higher than the proposed freshwater quality criterion of 2 ug/L.

PASSIVE TREATMENT DESIGN CONSIDERATIONS TO PROMOTE REMOVAL OF METALLOIDS

Passive treatment methods are often the most economical and favorable for management of ARD, particularly in post closure situations, where low cost and low maintenance is desired. Passive treatment technology takes on a variety of forms including: oxic and anoxic limestone gravel filters; oxic and anoxic settling ponds or sumps; aerobic and anaerobic processes, such as, as SRB contactors; and constructed wetlands. The choice of treatment technology depends on the water chemistry and the specific contaminants to be removed as well as other factors including land availability, topography, and weather conditions.

ARD inherently provides iron as Fe (III), which may be utilized to remove arsenic and antimony. ARD also provides sulfate, which may be utilized to promote reducing conditions in an SRB contactor. As discussed in the previous section, reducing conditions are necessary in order to remove selenium to low levels. ARD results when sulfide minerals, particularly pyrite (FeS), come in contact with oxygen and water. Acid generation occurs when sulfide minerals are oxidized according to the following overall reaction:

$$\mathrm{FeS_2} + 15/4\ \mathrm{O_2} + 7/2\ \mathrm{H_2O}\ \_\ \mathrm{Fe(OH)_3} + 2\mathrm{SO_4^{-2}} + 4\mathrm{H^+}$$

A recent paper (Canty, 1999) illustrates problems that can occur when attempting to remove metalloids in an SRB contactor. The paper is based on pilot studies conducted on portal drainage from the Lilly/Orphan Boy (LOB) Mine, near Elliston, Montana. The pilot SRB system, an upflow contactor with organic substrate, successfully removed zinc, aluminum, manganese, cadmium and copper. However, the system was less effective at removing iron and arsenic. The poor removals of iron and arsenic were attributable to the reducing conditions achieved in the SRB system to promote removal of heavy metals. Under reducing conditions, insoluble Fe(III) is converted to soluble Fe(II). The soluble form of iron is not removed in the SRB contactor. In addition, arsenic, previously adsorbed to Fe(III) would be expected to be released along with Fe(II). Some arsenic should be retained by adsorption onto the organic substrate. However, under reducing conditions, As(V) is converted to As(III), which has lower adsorption affinity.

Conceptual Design Example

The pilot study at the LOB mine portal is instructional and we use it here as an example to show how the passive treatment system could have been designed to facilitate removal of metalloids as well as heavy metals. As a basis for conceptual design, we use the influent water characteristics of the LOB portal as shown in the Table 1 below. Antimony and selenium were either not present or not measured in the drainage. For this design example, it is assumed that both selenium and antimony are present in the portal ARD.

TABLE 1 LOB portal water quality characteristics(1)

Parameter	Units	Value
Flow Rate	gpm (lpm)	2 (7.6)
pH	Standard	3
As	mg/L	1.07
Al	mg/L	9.69
Cd	mg/L	0.33
Cu	mg/L	0.32
Fe	mg/L	27.7
Mn	mg/L	6.21
Zn	mg/L	26.1
SO_4	mg/L	277
Fe/As	Molar ratio	35

(1) Source: Canty, 1999

As shown in the table, ARD from the LOB portal contains the necessary quantities of iron to promote efficient removal of arsenic and antimony. As shown in Figure 1, the level of iron [Fe(III)] present in the portal drainage is sufficient to achieve very low levels of antimony. The Fe/As ratio in the ARD is greater than 4 and thus sufficiently high to form insoluble ferric arsenate ($FeAsO_4$). The water also contains more than the requisite amount of sulfate to promote SRB and thus anaerobic conditions to reduce selenate to selenite. In summary, the portal drainage already contains the reagents necessary to provide highly effective removal of metalloids. No additional reagents need to be added.

An alternative treatment configuration for the portal drainage is shown in Figure 4. The ARD would first flow into an oxic limestone channel to increase the water pH from three to approximately five. The limestone drain would be open to the atmosphere and contain crushed limestone rock. The water would then flow into an open settling pond for removal iron floc containing coprecipitated arsenic and antimony.

The pilot system at LOB did not have this pretreatment step; ARD flowed directly from the mine to the SRB contactors. As a result, iron and arsenic became reduced in the SRB and were subsequently discharged untreated. A pretreatment settling pond allows the majority of iron and coprecipitated arsenic and antimony to be removed before the SRB step. Pretreatment also reduces the likelihood of the SRB becoming plugged by iron slime.

Following pond settling, the pretreated water would flow upward through an anaerobic SRB contactor (an anaerobic pond in this case) containing composted cow manure amended with inert materials to maintain sufficient hydraulic conductivity. The contactor would have an empty-bed hydraulic retention time of approximately 20 days and a total substrate volume of approximately 8,000 cubic feet (227 m^3). A longer retention time is needed for selenium conversion as compared to typical retention times necessary for precipitation and removal of metal sulfides (20 days versus 2 days) (Cohen, 1996; Mudder and Botz, 1997). The anaerobic contactor would provide the necessary reducing conditions (by SRB) to convert selenate to selenite and elemental selenium. Sulfate reducing bacteria would also generate sulfide ions for the precipitation and removal of heavy metals. Biological sulfate reduction would also increase pH and buffer the water through consumption of hydronium ion and production of bicarbonate.

Water exiting the SRB contactor would have near neutral pH and residual iron in the reduced form of Fe(II). As a polishing step, water from the SRB contactor would be allowed to gravity flow through a stepped channel to provide aeration and oxidation/precipitation of residual iron as $Fe(OH)_3$. The water would then flow by gravity into a shallow oxidation pond to provide additional aeration and settling of the iron floc. The iron would coprecipitate residual metals and metaloids in the effluent water. As a precautionary measure, the pretreatment and post-treatment settling ponds should be netted to prohibit contact by wildlife.

The aforementioned treatment configuration would be expected to provide very low discharge concentrations (e.g., ug/L levels) of antimony, arsenic, and selenium. Additional treatment of selenium could be provided, if necessary, by applying the final discharge to land (e.g., infiltration or irrigation). As mentioned earlier, indigenous soil bacteria have the ability to reduce selenate to selenite and to elemental selenium under anaerobic conditions. Selenium is thereby removed by adsorption to soil minerals (in the case of selenite) or trapped by filtration (in the case of elemental selenium).

CONCLUSIONS

Due to the high potential risks caused by metalloids and the ever-tightening regulatory limits, there is a need to develop practical and affordable technologies for their removal. As shown, passive treatment methods may be developed and employed to take advantage of the iron and sulfate already present in ARD. If antimony and arsenic are present in ARD, they should be removed with iron prior to any sort of anaerobic treatment. The reducing conditions within an SRB contactor are unfavorable for the adsorption of antimony and arsenic. Arsenic and antimony are effectively removed by co-precipitation and adsorption with iron under acidic pH conditions. Very low (ug/L level) concentrations may be achieved by adjusting the water pH to near five and allowing the metalloids to coprecipitate and settle with ferric iron. This may be accomplished with a limestone rock channel followed by open-pond settling.

If selenium is present in ARD, it will likely be in the oxidized form of selenate. Selenate should be reduced to selenite for successful treatment. The reducing conditions afforded by SRB in an anaerobic passive system are ideal for the transformation of selenate to selenite and further to elemental selenium; the former being removed by adsorption to iron and organic substrate material and the latter being removed by precipitation and entrapment in the passive treatment media. Post treatment of SRB effluent may be provided with an oxidation pond to coprecipitate metals and metaloids with residual iron. Additional selenium treatment may be provided if necessary by land applying the effluent.

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Figure 1 Effects of pH and iron dose on antimony removal

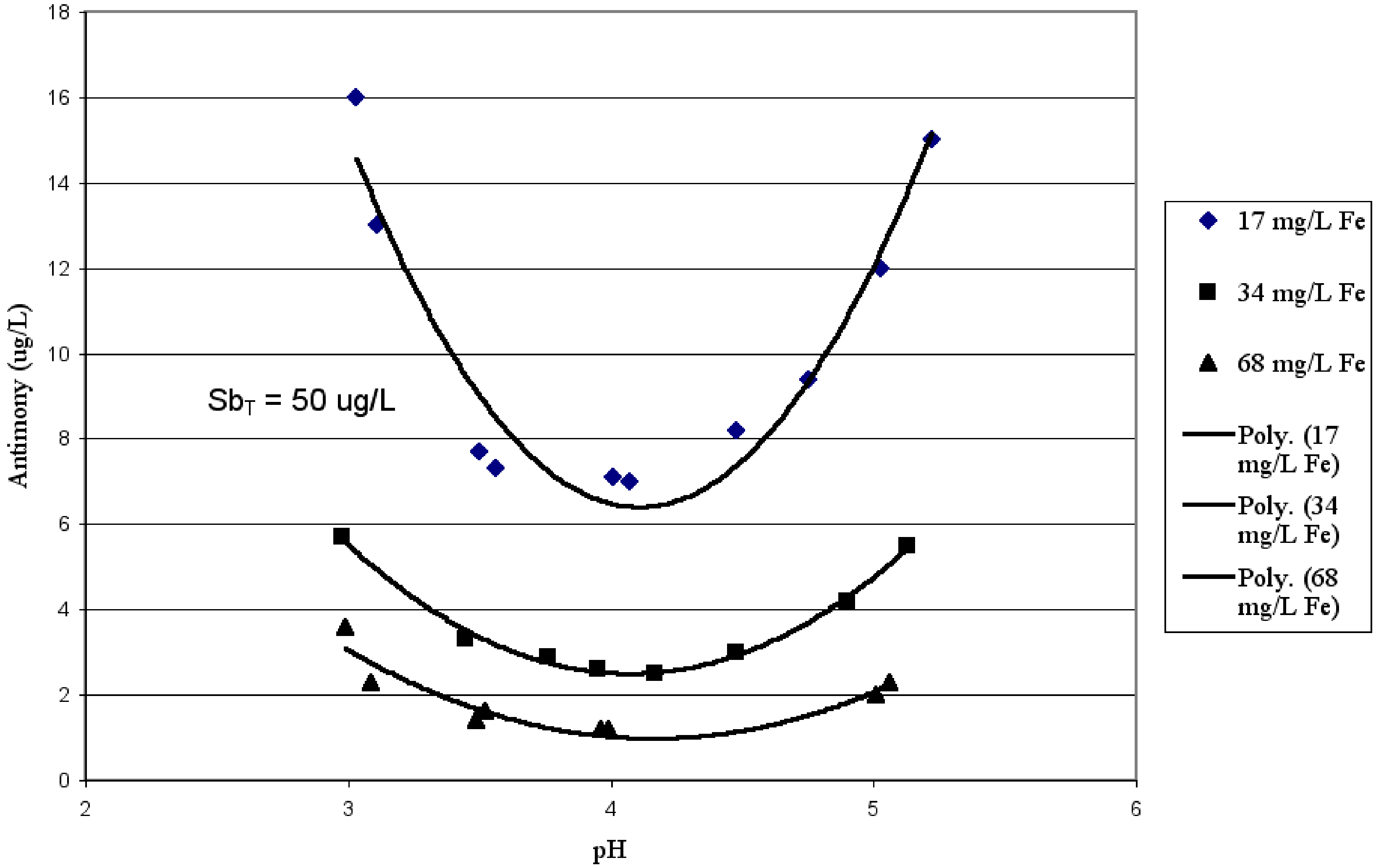


Figure 2 Effect of contact time on antimony removal

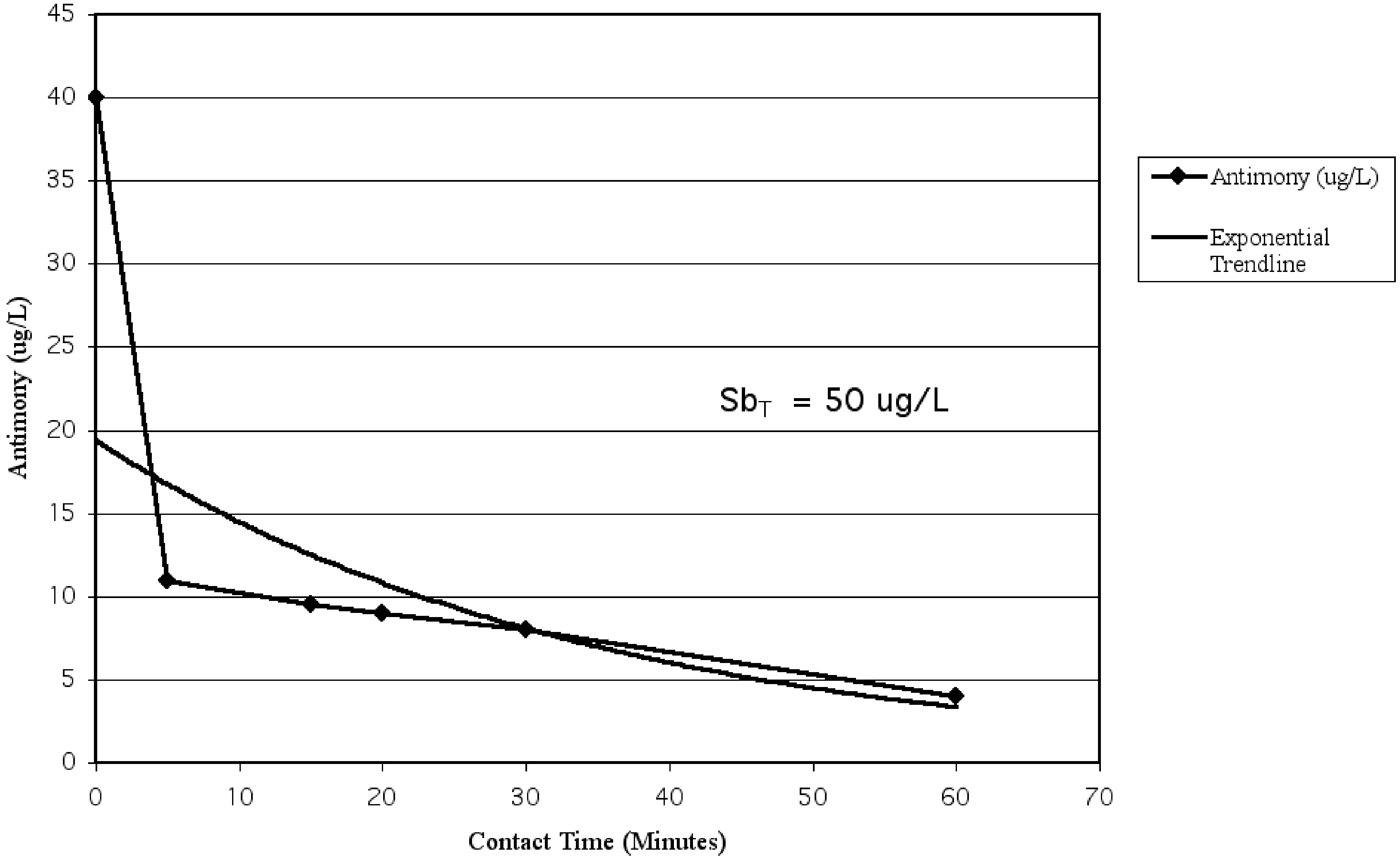
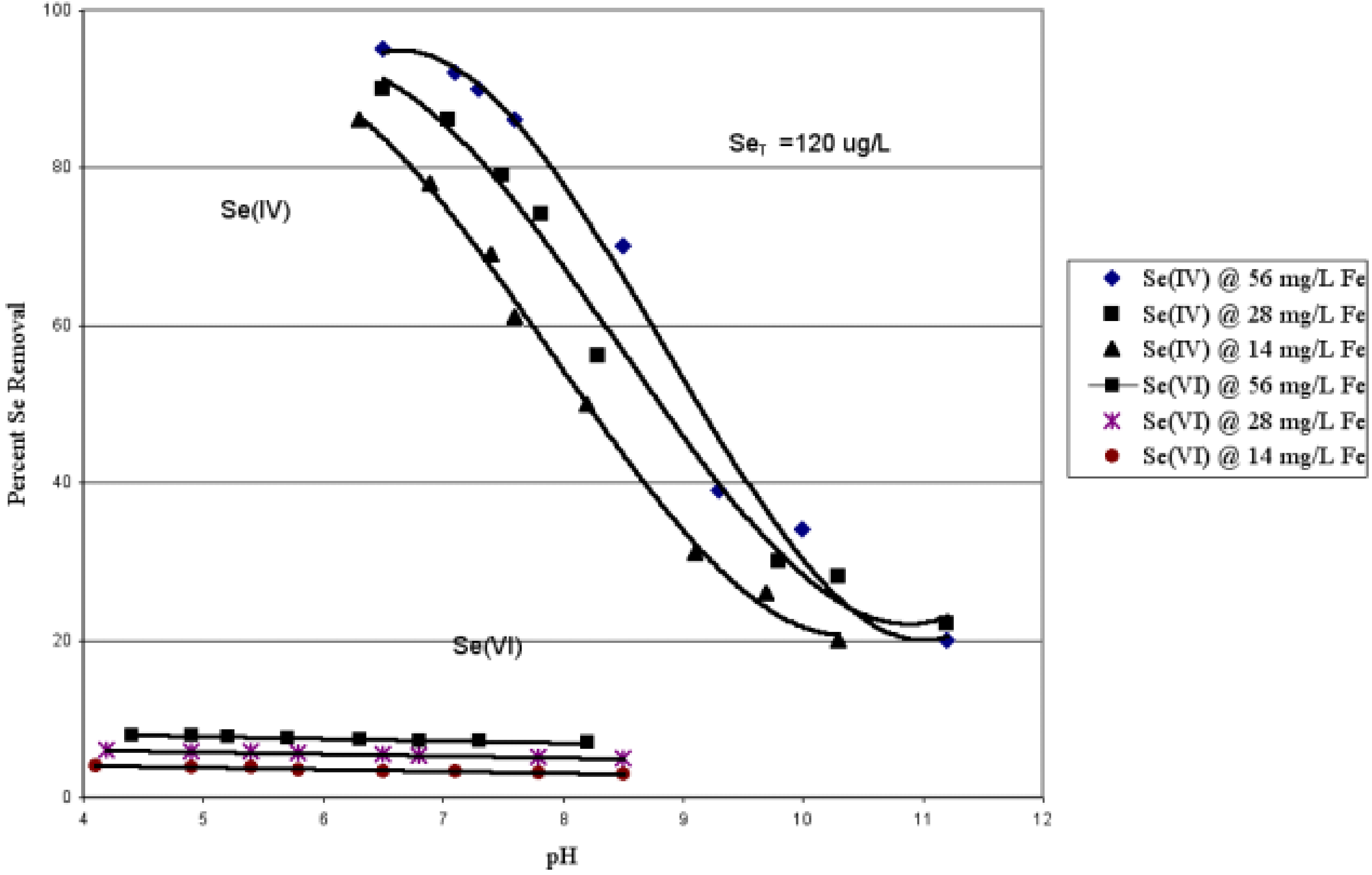


Figure 3 Selenate vs. selenite removal via iron coprecipitation



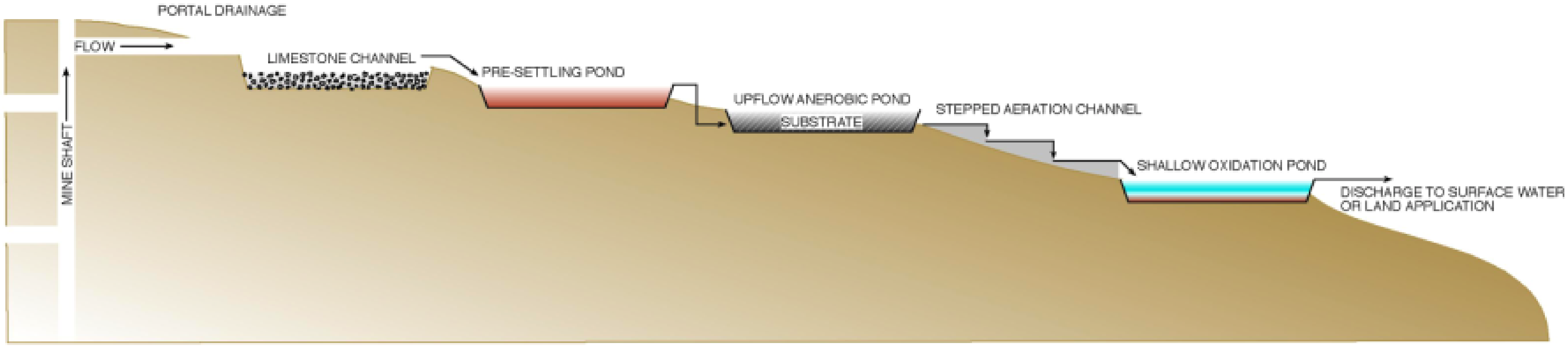


Figure 4
Conceptual Flow Diagram
of a Passive Treatment System to
Remove Antimony Arsenic and Selenium