Selenium leaching kinetics and in-situ control

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Abstract Selenium leached from coal tailings and spoil is a challenge for mining operations in southern West Virginia. Selenium discharges are regulated at 5 µg/L and discharges are commonly in the range of 10 to 25 µg/L. Once oxidized to selenate ion, removal is extremely difficult and expensive, particularly in the narrow valleys and highly variable flow regimes of southern West Virginia. This study attempts to understand the potential to control selenium at source, through special handling and treatment of selenium rich rock units. Earlier study has indicated that the bulk of selenium in a given overburden sequence is associated with organic shales, primarily located adjacent to the coal seams. Rock units with greater than 1 mg/kg of total selenium are generally considered a risk for producing selenium leachate This study reports on the first 72 weeks of a humidity cell leaching study. After an initial rapid leaching of the exchangeable fraction, selenium leaching rate stabilized at about 0.07%/day for 32 weeks after which it declined gradually. After 60 weeks about 25% of the total selenium had leached. Selenite is known to bind to ferrihydrite and a series of leaching cells included ferrihydrite. It has kept [Se] at or below the regulatory limit of 5 µg/L throughout the experiment confirming selenite as the initial, mobile selenium species during weathering and ferrihydrite's potential as a sorbent.

Key Words Coal tailings, selenium, kinetics, is-situ control

Introduction

Selenium is a naturally occurring element and one of its important features is the very narrow margin between nutritionally optimal and potentially toxic dietary exposures for vertebrate animals (Wilber, 1980). Recently, elevated concentrations of selenium due to mining activities and irrigation have been found in the western US and the Appalachian region. Se in drainage water was reported in concentrations of 140 to 1400 µg/L in the San Joaquin Valley of California (Cantafio et al., 1996; Amweg et al., 2003). An environmental impact study of mountain top mining and valley fills in Appalachian region found selenium concentrations greater than the 5 µg/L USEPA chronic aquatic life standard, in streams below coal mines (USEPA, 2005). These elevated concentrations of Se have caused concern for its potential impacts on aquatic ecosystems and human health.

Inorganic selenium usually exists in four states in the environment, selenate [Se (VI)], selenite [(Se (IV)], elemental selenium [Se^0], and selenide [Se^{2-}]. In aquatic environments, selenite and selenate are the predominant inorganic forms of selenium. Both selenite and selenate occur as oxyanions. Selenite exists under moderate redox potentials and at wide pH ranges. Its chemical forms vary with pH, such as H_2SeO_3 in acidic solution, $HSeO_3^-$ in neutral solution and SeO_3^{2-} in alkaline solution (Séby et al., 1997). Selenate is a weakly basic group VI oxyanion and commonly present either in a fully deprotonated form (SeO_4^{2-}) or singly protonated biselenate ($HSeO_4^-$) (Shriver et al., 1994).

A variety of treatment technologies have been reported to remove selenium from contaminated waters (Mariñas and Selleck, 1992; Gallup, 1996; Frankenberger et al., 2004; Mavrov et al., 2006). Some advanced techniques (e.g., ion-exchange, reverse osmosis, nanofiltration) are not economically feasible for treating large scale discharges that are often in excess of 4,000 L/min (Zhang et al., 2005). Zero valent iron is one of the more widely used and promising methods in removing selenium from solution by reducing selenate to selenite or elemental selenium. Su and Suarez (2000) found that ferrihydrite (amorphous $Fe(OH)_3$) sorbs selenium and that selenite binds to ferrihydrite to a greater extent than selenate. They also reported that ferrihydrite is more effective than goethite in sorbing selenium.

Pumure, et al. (2010) used both sonication and sequential extraction to estimate that roughly 25 to 33% of the total selenium in coal associated rock was extractable. Given the technical and financial burdens of treating selenium discharges, the potential for controlling selenium at source is an attractive option. That will require understanding 1) the proportion of selenium that is potentially mobile, 2) the kinetics of its release, 3) identification of in-situ treatment methods, 4)

their application rates and 5) long-term performance at operational scale. This paper discusses early steps for understanding items 2, 3 and 4.

Methods

This paper reports the initial 72 weeks of leaching coal tailings in humidity cells. Freshly processed tailings were taken from a coal preparation plant in southern West Virginia. The cells consisted of nested plastic containers with removable, sealed lids. The smaller (1L) container was drilled with six holes and lined with aquarium pre-filter and standard fiberglass window screen material to prevent the loss of fine particles. Twelve treatment cells were constructed; six were untreated controls and six were treated with ferrihydrite. The ferrihydrite application (13% dry weight basis) was blended with approximately 555 grams of coal tailings. After initial leaching, these cells were placed on 1 cm thick spacers, to allow free drainage, inside 2 L plastic containers, also with removable, sealable lids.

An initial leaching was conducted immediately following construction of the treatment cells and every two weeks thereafter for a period of 33 weeks (November 2008-July 2009). Thereafter, leaching was conducted every two or four weeks (July 2009 – April 2010). Even distribution of leaching water was achieved by preparing a distributor cell. It consisted of an empty 1L container with twelve holes drilled in the bottom. It was placed on top of a 1L treatment cell containing tailings and/or amendment. Then, 1L of deionized water (DI H_2O) was poured into the top, empty 1L container. By holding these stacked containers above the empty 2 L container, DI H_2O leached evenly through the treatment cells and leachate was collected in the 2L container. Half of the leached water (500 mL) was poured into a labeled sampling bottle, measured for pH, and refrigerated pending transportation to the analytical laboratory for analyses of acidity and alkalinity. The remaining 500 mL was filtered through 0.45 µm filter via a Millipore Filtration unit. The filtered water was collected in a labeled sampling bottled and acidified with nitric acid for analyses of Al, Fe, Mn, SO_4 and Se. All chemical analyses were conducted by REIC Labs, Beckley WV, a State-certified analytical laboratory. This process was identical for each of the twelve treatment cells.

At the preparation plant, the tailings are placed in a valley where the discharge is routinely monitored. The disposal site contains in excess of one million cubic meters of tailings. We found that the concentration of chloride, a conservative ion, leaching out of the pile was 7.2 times greater than that leaching through the humidity cells. Presumably this accounts for the lower solids/liquid ratio of leaching under field scale conditions. When this factor of 7.2 was applied to humidity cell leachate concentrations, selenium concentrations from the control leaching cells also fell within the range observed in the field (2 to 32 µg/L, averaging 12 µg/L). All aqueous Se concentrations in this paper have been adjusted to reflect estimated field values. The total Se concentration of the tailings was 1.55 mg/kg. For hypothetical purposes, it was assumed that 33% of the total selenium in the tailings sample was mobile (from Pumure, et al. 2010). This yielded an estimated, initial 280 µg of mobile selenium in each humidity cell. The mass of Se leached in each cycle was recorded and subtracted from the previous leach cycle's remaining Se.

Conclusions

Selenium leaching rate. It is assumed that, much like ARD generation, Se mobilization involves a weathering (oxidation) step followed by leaching. Collectively the processes will be referred to as leaching. Initially the Se leached at a rate of 0.2%/day, quickly stabilized at about 0.06%/day then, after week 36, it began a gradual decline to 0.04%/day by week 72. The initially high leaching rate is likely due to accumulated oxidation products between the wash plant and laboratory leaching. Initial leachate pH of the control cells was 9.7. During the 72 week leaching period average pH steadily declined to about 7.2 where it has remained for the last ten weeks. Figure 1A shows the cumulative Se leached from the control cells and prediction curves generated by three models. The empirical model uses the observed rate of 0.06%/day (0.42%/week) decay rate to estimate Se lost during each leach cycle. The sum of those values represents the cumulative Se leached at any given week. Polynomial and power curves were also evaluated. The polynomial model gave the higher R^2 of the two tested models (0.9931 vs. 0.9667). If it correctly predicts cumulative selenium leaching, the polynomial model would, in fact, become a horizontal line at its zenith. The power curve better predicts the decreasing rate of Se leaching after week 35.
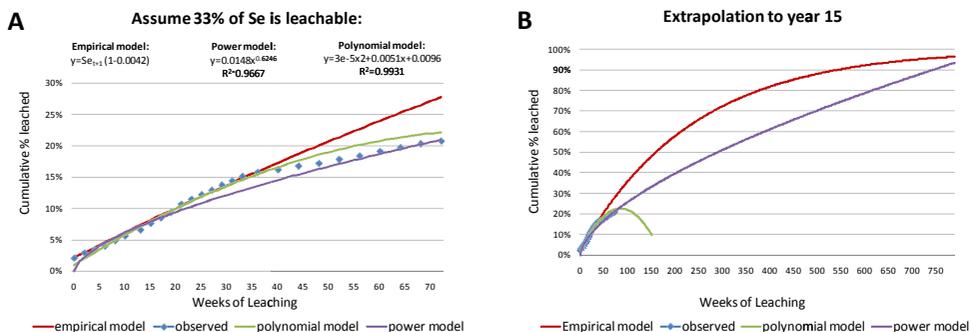
Figure 1 *Cumulative Se leached from the control humidity cells during the first 72 weeks was compared to three prediction models: an empirical model based on a leaching rate of 0.42%/week, a power curve and a polynomial curve. Figure 1A shows the prediction curves within the range of observations and 1B extrapolates those curves to 15 years.*

Figure 1B extrapolates the three curves beyond the range of observations. If the polynomial model is correct, Se will stop leaching around week 90, having leached only about 7.6% of the rock's total Se (23% x 33%). That is unlikely. On the other hand, the empirical model predicts 90% exhaustion of 'leachable Se' in about 10 years while the power model predicts 90% exhaustion in about15 years. Continued monitoring of these cells will be undertaken to better predict the long term leaching behaviour of Se in coal tailings.

In-situ Se control

In the control (untreated) humidity cells, Se concentrations ranged from a high of 43µg/L to about 8 µg/L (Figure 2). These values were similar to those observed at discharge of the field site, a 1,000,000+ tonne refuse facility. These estimated Se concentrations were generated by multiplying the humidity cell leachate concentrations by 7.2. It appears that this adjustment factor yields a reasonably good approximation to field concentrations. Mindful that these are estimates and that extrapolating from humidity cells to field concentrations has its limitations, it is clear that selenium kinetics can be clarified through this process. It is also clear that ferrihydrite has successfully maintained a selenium concentration near or below 5 µg/L for the first 72 weeks of the test and that it has strong potential as a method for in-situ control of selenium in coal related rock.
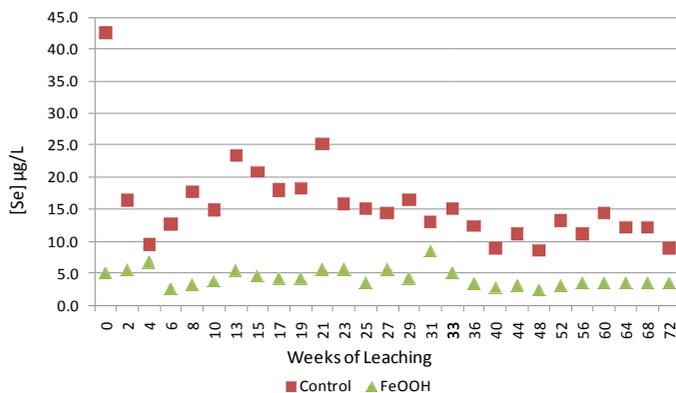

Figure 2 *Ferrihydrite treated humidity cells maintained [Se] near or below 5 µg/L for the first 72 weeks of the leaching experiment. Control values were similar to those observed in the field*

The effectiveness of ferrihydrite in capturing Se strongly suggests that upon initial oxidation of selenium bearing rock, selenite is the first soluble species produced and that its oxidation to selenate is sufficiently slow to allow sorption to ferrihydrite before selenate is generated in appreciable quantities.

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