

## Subsurface Sequestration of Leached Waste-Rock Selenium in Reactive Ferrihydrite Beds

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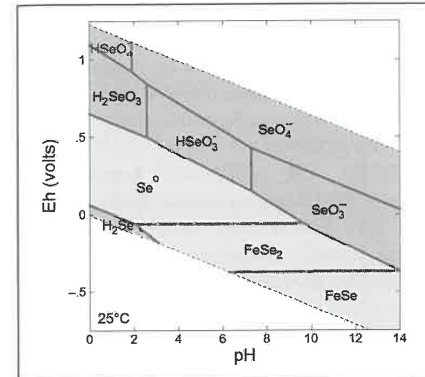
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### ABSTRACT

Thirty lysimeters were installed at a large surface mine in southern West Virginia in Spring 2010 to test for transport rate of selenium in mine-run interburden as well as selenium removal by adsorption to layered ferric oxyhydroxide (ferrihydrite). Each 488 × 732 cm cell contained about 55 tons (122 to 183 cm thickness) of interburden, overlaying various thicknesses (0.6, 5.7, 22.9 and 45.7 cm, plus a zero-amendment control cell) of fine-grained ferrihydrite from a limestone-treated AMD wetland. The mass of ferrihydrite was 0 to 2.2% weight percent of the spoil. The control and each amendment were replicated six times, for estimation of uncertainty in reproducibility of results. Rainfall was collected on and infiltrated through these cells to create a leachate that drained to individual central collection tanks. Sampling was performed 46 times at approximate two week intervals from 2010 to 2012. Basal ferrihydrite layers in the three highest amendment categories successfully removed up to 76.9% selenium (in comparison to the unamended piles) from leachate by an adsorption mechanism. Results were somewhat variable for replicates. The higher amendment concentrations were demonstrably more effective, while the very thin ferrihydrite-treated piles showed no significant reduction from unamended piles. Selenium estimates were sufficiently precise to discriminate mean values among treatments. Work now focuses on continuing the time series to assess long-term persistence of Se fluxes, examine the ultimate capacity of the ferrihydrite beds, and to geochemically model the adsorption and transport processes.

### INTRODUCTION

It has been widely observed that selenium (Se) fate and transport in coal overburden materials may be influenced by mining and reclamation operations (Dreher and Finkelman 1992). Predicting the fate and transport of Se mobilized from within coal mine spoil requires an understanding of the amount, form, and redox state of the element present; the rate and mechanism(s) of solubility; and the tendency for adsorption within the spoil mass post-dissolution (Naftz and Rice 1989). Se concentrations in southern West Virginia coal overburden lithologies range from 0.84 mg/kg in sandstone to 4.10 mg/kg in organic shale, with high Se concentrations covarying with high sulfur levels (Vesper et al. 2008). The proportion of mobile Se was estimated by Roy (2005) using extreme sequential extraction methods to accelerate and maximize its dissolution rate. She estimated that roughly 50% of total Se in overburden is non-extractable while another 25% is bound in non-mobile organic form. Most of the remaining 25% potentially mobile Se was inferred in this study to occur either within sulfide minerals or as adsorbed ions. Similar estimates were obtained for mobile Se (35% and 38% of total Se) using extraction by sonication of two similar organic shales from southern West Virginia (Pumure et al. 2010). All these sequential extraction estimates should be considered upper limits on field Se solubility, obtained under more intense weathering conditions than found in nature. Emerson et al. (2009) determined the more-reactive fine fraction (<2 mm) as 34% for southern West Virginia coal mine spoil that had been exposed to weathering for one to two years.



**Figure 1. Eh-pH diagram for soluble Se species (blue) and insoluble solid phases containing Se (tan); calculations are for  $10^{-6}$ M total Se and  $10^{-3}$ M total Fe at 25°C**

Diehl et al. (2005) determined Se in pyrite in southern Appalachian coals by a variety of micro-analytical techniques. Whole-coal values for Se ranged from 25 to 247 mg/kg, while 670 mg/kg Se was found in pyrite alone, roughly 2 to 20% of the Se in the coal. This Se percentage for pyrite correlates well with the fraction found in sulfides by Roy (2005) (8% in the pyrite fraction of coal, 13% in shale).

Thus the most likely primary solid-phase occurrence of Se is in sulfide minerals, either in pyrite or ferroselite ( $\text{FeSe}_2$ ), its Se-bearing analog. An Eh-pH diagram for Se species (Figure 1) shows areas of thermodynamic stability for elemental zero-valent Se ( $\text{Se}^0$ ) as well as more reduced iron sulfidic. The principal soluble species are selenate and selenite, obtained by oxidation of these source solid phases. The oxidation of selenite to selenate, the more mobile aqueous species, requires higher oxidation potential than for sulfide dissolution. Vesper et al. (2008) showed that the proportion of selenate to selenite only gradually increased downstream of source coal mines. Selenite is generally the most abundant Se species reported in various power plant ash materials (Huggins et al. 2007), although Hyun et al. (2006) also found significant selenate. Zhang and

Sparks (1992) observed that while both aqueous phases are amenable to adsorption on crystalline iron oxides, selenite is less rapidly adsorbed, but more tightly held, than selenate.

Ferrihydrite or similar iron oxyhydroxides, a common neutralization product of treated metal-rich mine drainage, is thought to be a principal adsorbent for sequestering Se dissolved from coal waste rock. Ferrihydrite removed 95% of selenite at pH 4 and 80% at pH 9 (Merrill et al. 1985). Su and Suarez (2001) reached similar conclusions for amorphous iron oxide and its more crystalline phase goethite ( $\alpha\text{-FeOOH}$ ), although the amorphous phase showed less capacity for adsorption. Zhang and Sparks (1990) examined the reaction rates of selenate and selenite sorption on goethite and concluded that selenite formed an inner sphere complex, whereas selenate formed a less strongly-bound, but more rapidly formed, outer sphere complex. Ziemkiewicz et al. (2011) added ferrihydrite to Se-bearing mine spoil in batch reactors and found that roughly 70% of available Se was immobilized by adsorption compared to untreated controls.

While laboratory leaching results provide insight into weathering and leaching mechanisms, the more salient issue to the mining and regulatory sectors is the concentration of total Se that will discharge from operating mines over time. Se discharge dynamics under field conditions are poorly understood, largely due to the slow nature of field weathering processes, the low concentrations of Se involved, and the relatively short time for which Se has been monitored in mined areas. Se was not considered a pollutant in Appalachian coal mining until about 2003, after which several large surface mines were required to sample and report Se discharged via their regulated water outlets. Ziemkiewicz and Lovett (2012) developed a chronological sequence relating the age of various coal mine spoil units to selenium concentrations in outlets monitored over an eight year period. They reported that selenium concentrations ranged from 25 to 100  $\mu\text{g/L}$  in young spoil to less than 5  $\mu\text{g/L}$  in spoil that was more than about 25 years old, indicating a relatively rapid selenium



Figure 2. Location map of the study site, Lincoln County, WV

removal rate. Nonetheless, there has been insufficient opportunity to develop a regional sense for how long or at what concentrations Se will discharge from mined spoil materials via leachate. Due to close rock-water interaction, and the variation of selenium concentrations within spoil units, the regulated discharges integrate selenium rich sources like organic shales, diluted by water from selenium-poor rock units and surface runoff. So it is pivotal to find techniques to isolate selenium-rich rock units and then minimize the leaching of selenium from them.

Another complicating factor at field scales of leaching is the compositional heterogeneity of spoil materials and how this might influence its Se leaching characteristics. Large-scale surface coal mining in the dissected Appalachian plateau involves multiple coal seams, overburden and interburden sequences, as well as a mixture of sedimentary lithologies. However, spoil created and emplaced by mining methods is generally well-mixed within individual sequences. Roughly half the overburden/interburden at a modern mine is moved by cast-blasting and the other half by dragline or shovel/truck haulage. Excavated spoil is generally replaced by backfill along an advancing sloped face from 10 to 50 m long. Such handling methods result in a high degree of overburden blending. Weathering begins immediately after disaggregation of the rock by mining. Spoil age refers to the length of time since a rock unit was mined. While each lithology within a

sequence will behave differently with regard to Se mobility, spoil units are highly mixed composites of the overburden lithologies. Segregation of the Se-rich rock units opens the possibility of treatment directed at specific lithologies to strategically limit Se release.

Finally, the well-known heterogeneous nature of fluid flow systems that develop in coal-mine spoil adds another aspect of variability. Double-porosity characteristics, flow through conduit-like networks, and linear-flow characteristics have been observed and documented in the Appalachians (Maher and Donovan 1997; Hawkins 2004). In field trials, the vagaries of different fluid flowpath networks may cause differences in leaching intensity to be observed between spoil piles. In summary, for reasons of inherent variability in spoil composition and in the resulting fluid flow systems through spoil piles, field-scale experiments must incorporate adequate replication to verify the significance of chemical fluxes observed at the discharge.

## PURPOSE AND OBJECTIVES

The purpose of this study is to provide some initial estimates of selenium mobility in the presence of varying amounts of absorbent materials, as well as to test for the variability of spoil-pile chemistry and hydrology at field leaching scale, rather than laboratory scale. This particular investigation focuses strictly on Se leaching behavior over a period of three years of initial exposure of fresh waste-rock spoil to infiltration and weathering. The study area is a large (6,000 ha) surface mine in Lincoln County, WV (Figure 2). This is an area where surface mining has been practiced for about 30 years and is ongoing. Discharges from the mine enter the Little Coal and Mud River basins.

## METHODS

### Experimental Array and Design

Thirty pan-type lysimeters of large size (488 × 732 cm; Figure 3) were constructed on a reclaimed section of the mine in spring 2010. The individual lysimeter cells were constructed in a continuous

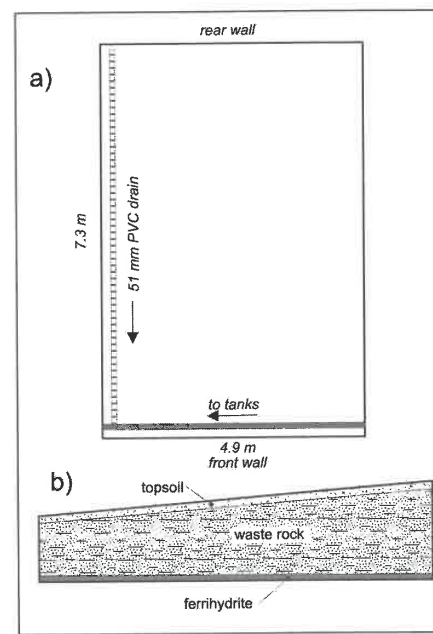


Figure 3. Plan view (a) and cross section view (b) of cell construction

array (Figure 4) of two rows of 15 cells each, separated by a 183 cm high plywood inner wall. The outer walls of both rows were 122 cm high; thus the side partitions between cells and the soil surface were sloped gently from inner to outer walls. The cells were lined along the base and sides with 4-mil polyethylene and filled with (from bottom to top) a thin ferrihydrite layer, shale waste rock, and a ca. 30 cm topsoil layer of weathered brown sandstone (Figure 3). The base of the liner was gently sloped roughly parallel to the soil surface, inducing basal gravity drainage from the inner to outer wall of each cell (Figure 3).

Treatments consisted of five ferrihydrite levels with six replications each. Treatments and replications were completely randomized. Each randomized experimental unit was assigned a number from 1 to 30, with a suffix to identify material composition. Additionally, the slope of the lysimeter array in each row (cells 1 to 15 and 16 to 30) was about 1:20 from north to south,

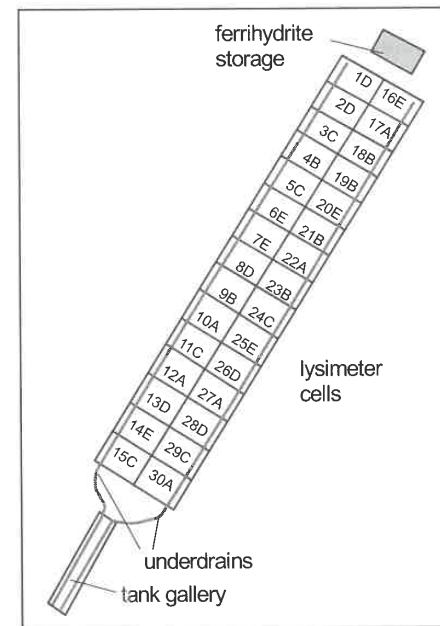


Figure 4. Layout of lysimeter array, with labels showing ID numbers of individual cells

allowing gravity drainage of collected lysimeter leachate in that direction. Each cell contained a two-inch perforated-PVC lateral underdrain in the ferrihydrite layer, located along the down-gradient side wall and sloped from inner to outer wall, where it was collected in a non-perforated 1.9 cm ABS pipe bundled in an array with pipes from all 15 cells in that row. These pipe bundles directed flow continuously under gravity to an array of thirty 1,250 L polyethylene tanks, each receiving water from a single lysimeter (Figure 4).

Precipitation onto the soil of each cell either infiltrated or ran off onto native soil around the array, allowing no runoff between or onto adjacent lysimeters. Perennial grass/legume cover on the surface of each cell induced some evapotranspiration. The difference between surface infiltration and evapotranspiration constitutes recharge into each cell, which seeps deeply into the overburden soils and collects on the bottom liner, flowing into the diversion pipes and each cell's

respective sample tank. The sample tank for each cell thus contained a time-integrated volume of leachate fluids collected during multiple recharge events between sampling dates.

The average depth of all material in each cell was from 122–183 cm (Figure 3), with an average volume of 21.7 m<sup>3</sup>. The total mass was approximately 55 tons for an average field-moisture bulk density of 2.53 g/cm<sup>3</sup>.

### Material Composition

Each cell contained approximately the same volume of waste rock, measured by counting excavator buckets during construction, but various amounts of ferrihydrite, measured as a uniform thickness at the base of the spoil, immediately over the liner. The waste rock was sampled during construction in three 19 L pails and analyzed chemically. The waste rock was freshly-mined organic shale that forms the interval between the Stockton and Coalburg coal seams in the Pennsylvanian Kanawha Formation. The rock was homogeneous in appearance, stockpiled in a single day of mining for use in this project. The ferrihydrite was obtained from a large wetland near Pittsburgh, PA, in which limestone-treated AMD sludge had settled over a period of 30+ years, producing a reaction product with negligible aluminum and of high uniformity. The layer thickness and weight/weight ratio of ferrihydrite to spoil for each treatment (A-E) are as follows.

- A—no (0% w/w) ferrihydrite (6 lysimeters ferrihydrite)
- B—0.6 cm (0.2%) ferrihydrite (6 lysimeters)
- C—5.7 cm (1.5%) ferrihydrite (6 lysimeters)
- D—22.9 cm (6%) ferrihydrite (6 lysimeters)
- E—45.7 cm (12%) ferrihydrite (6 lysimeters)

Therefore, the array includes 6 identical replicates of each treatment, to allow for assessment of sampling error and uncertainty in material variation/hydrologic conditions.

### Water Sampling and Chemical Analysis

Sampling was performed biweekly beginning on May 14, 2010, through June 1, 2012. On each

date, the fluid volumes in the collection tanks were measured, samples collected, and each tank drained. Field pH, temperature, and conductivity were measured and the filtered samples were immediately taken to a state-certified analytical laboratory (REI Consultants, Beaver, WV) and analyzed for total Se, SO<sub>4</sub>, alkalinity to pH 4.5 endpoint, acidity, Fe, Al, Ca, Mg, Mn, Na, and Cl. The water in the tanks and collection drains was found to be frozen on December 10, 2010 (week 30). Sampling resumed on April 8, 2011 (week 48). There were several sampling events in fall 2010 when some tanks were dry due to lack of infiltration and no samples could be collected. Also, when tanks and lines thawed in April to May 2011, there were some tanks/lines which took longer to re-establish flow than others. Therefore, the number of replicates for each treatment was usually, but not always, six. During exceptionally dry periods, most if not all tanks were dry. Thus on some dates, as few as one sample per replicate set was collected, affecting precision estimates.

## RESULTS

### Time Series of Results

Figure 5 shows time series of selenium for the five treatments. Each plot shows a set of six different replicate time series for total selenium concentration in one treatment class, with each replicate obtained from a different lysimeter. The ferrihydrite addition increases from top (zero ferrihydrite) to bottom (maximum ferrihydrite, 45.7 cm). This plot shows general coherence in concentration between individual replicate sets, although the confidence intervals indicate variance within treatments as well. In particular, the first and second replicates in all treatments but especially C, D, and E—the circles and triangle symbols in these plots—were notably and in some cases markedly higher than the other replicates in their sets. It is conceivable that this could represent systematic natural variability in the refuse; all these cells are in the same portion of the array, from cells 1–12 (Figure 4) and were the first installed. It may also be that there was some difference in the installation of these lysimeters, either in the composition of the refuse used for

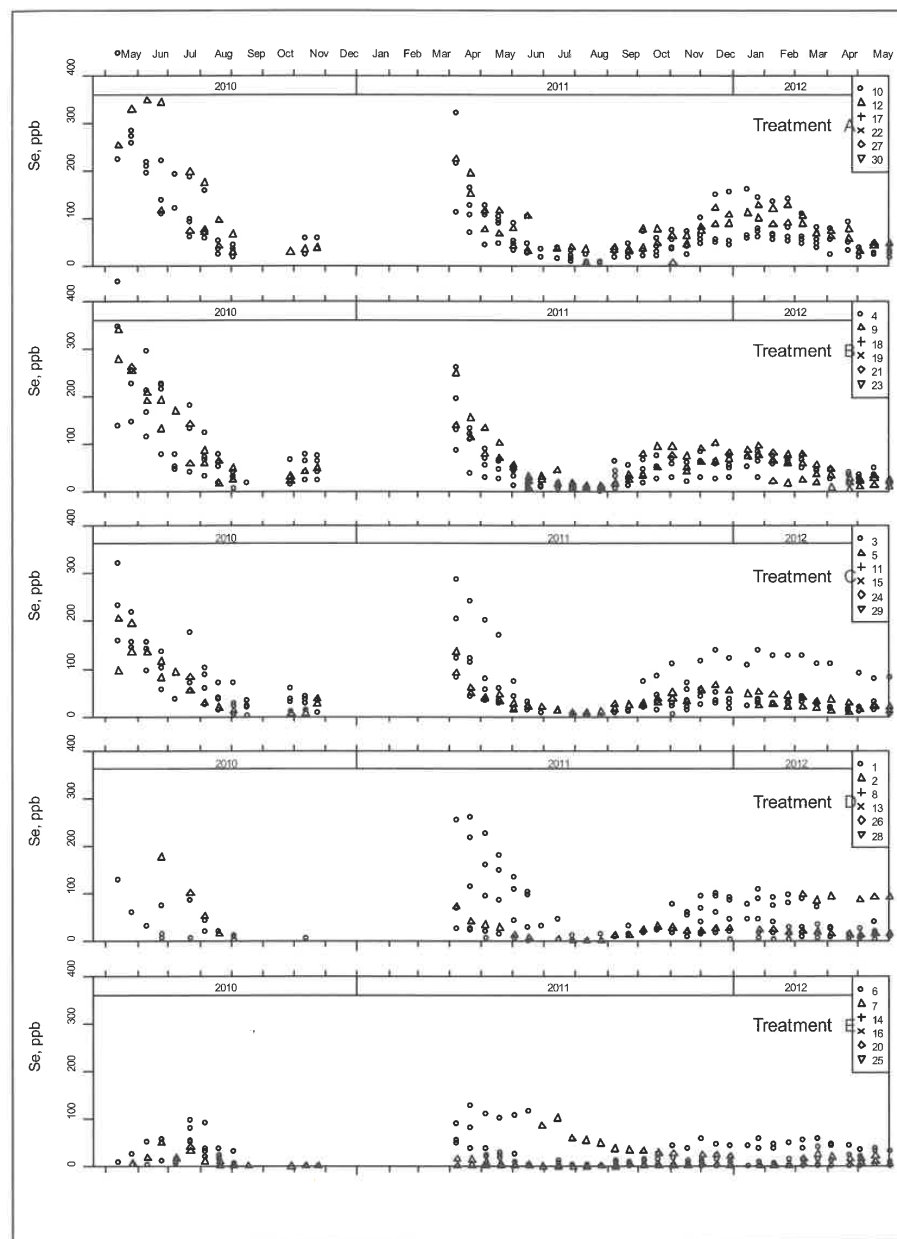


Figure 5. Raw time series of Se concentrations arranged by treatment. Each plot shows replicates for different treatments.



those cells, in the compaction method, or in the technique used for leveling the PVC drain line within the ferrihydrite layer. Excepting this variability, there is generally minor variance between replicates within treatments, and variance within treatments seems greatest at times of highest Se concentration, which occurred in spring of both 2010 and 2011. Nonetheless, the estimates were reasonably precise. The ratio of the standard deviation of the mean/mean was: 0.06, 0.07, 0.08, 0.12, and 0.08 for treatments A, B, C, D and E respectively.

There was a gap in sampling between late November 2010 and early April 2011, caused by freezing of line drainage between the lysimeters and the tanks. During winter 2011–12, no freeze-up occurred. As a result, in addition to the winter 2010–11 data gap, several sampling events in fall 2010 and spring 2011 had fewer than six replicates per treatment, as some drain lines thawed before others. Also, there were some periods in 2010 when some lysimeters produced no water during dry conditions.

#### Statistical Analysis of Mean Concentrations

Figure 6 shows the mean concentrations of the up to 6 replicates within each treatment (X symbols) and the 95% confidence limits on these concentrations calculated from sample standard errors and Student's *t* values (based on *n*–1 degrees of freedom) for up to six replicates. The fitted line in all plots represents the means of Treatment A replicates (no ferrihydrite). Some error brackets are significantly larger than others, either due to more variability within replicates for that date (larger standard error) or due to fewer samples than six due to freezing or dry conditions (smaller sample size and larger *t* statistic). Treating the zero-ferrihydrite mean as an unbiased estimate, the confidence range for the means of other treatments exceeding the zero-treatment mean curve decreases from Treatment B (0.6 cm ferrihydrite) to Treatment E (45.7 cm ferrihydrite). For treatment E, there are extensive periods when the confidence range for Se lies completely below the untreated mean Se curve. It is clear from these results that the mean Se concentrations decline in

comparison to the Treatment A (control) values as the mass of ferrihydrite increases.

#### Se Fluxes

Figure 7 shows time series of Se fluxes calculated as the product of average discharge volume between sampling dates and the Se concentration at the end of the sampling period. The units are in g total Se/day. There appears to be no significant difference in flux between Treatments A and B, and in fact Treatment B was higher in Se flux in the initial three months of leaching, becoming more similar in 2011 and 2012 sampling. There is substantial decrease in Se loads for Treatments C, D, and E compared to both the Treatment A and B values. To a higher degree than the mean concentration plots, the fluxes demonstrate that Se fluxes are significantly lower in the Treatment C, D, and E lysimeters than in the untreated or lightly-treated spoil piles.

Figure 8 compares cumulative Se fluxes for the five treatments, again averaged for all replicates. Treatments A and B are, again, the highest in Se loads (112.8 and 149.8 g Se, respectively), with Treatment B being the highest based on elevated concentrations in the first three months of sampling. In later sampling, the A and B piles show no significant difference in their mean fluxes. Treatment C (76.8 g Se) is slightly lower in flux than treatment A and much less than B. Treatments D and E are both substantially lower (45.4 and 26.1 g, respectively). The mean Se flux for Treatment E at the end of the sampling period in 2012 was 76.9% lower than that of the untreated lysimeters.

## DISCUSSION

### Sequestration Mechanism

These results show conclusively that there was a very large reduction in Se flux for the lysimeters employing higher masses/thicknesses of ferrihydrite compared to the untreated or lightly-treated cells. We attribute the reduction to adsorption of selenite and possibly selenate ions, although no redox estimates were obtained due to the batch method of sampling. There was not a proportional difference between the flux reduction of the

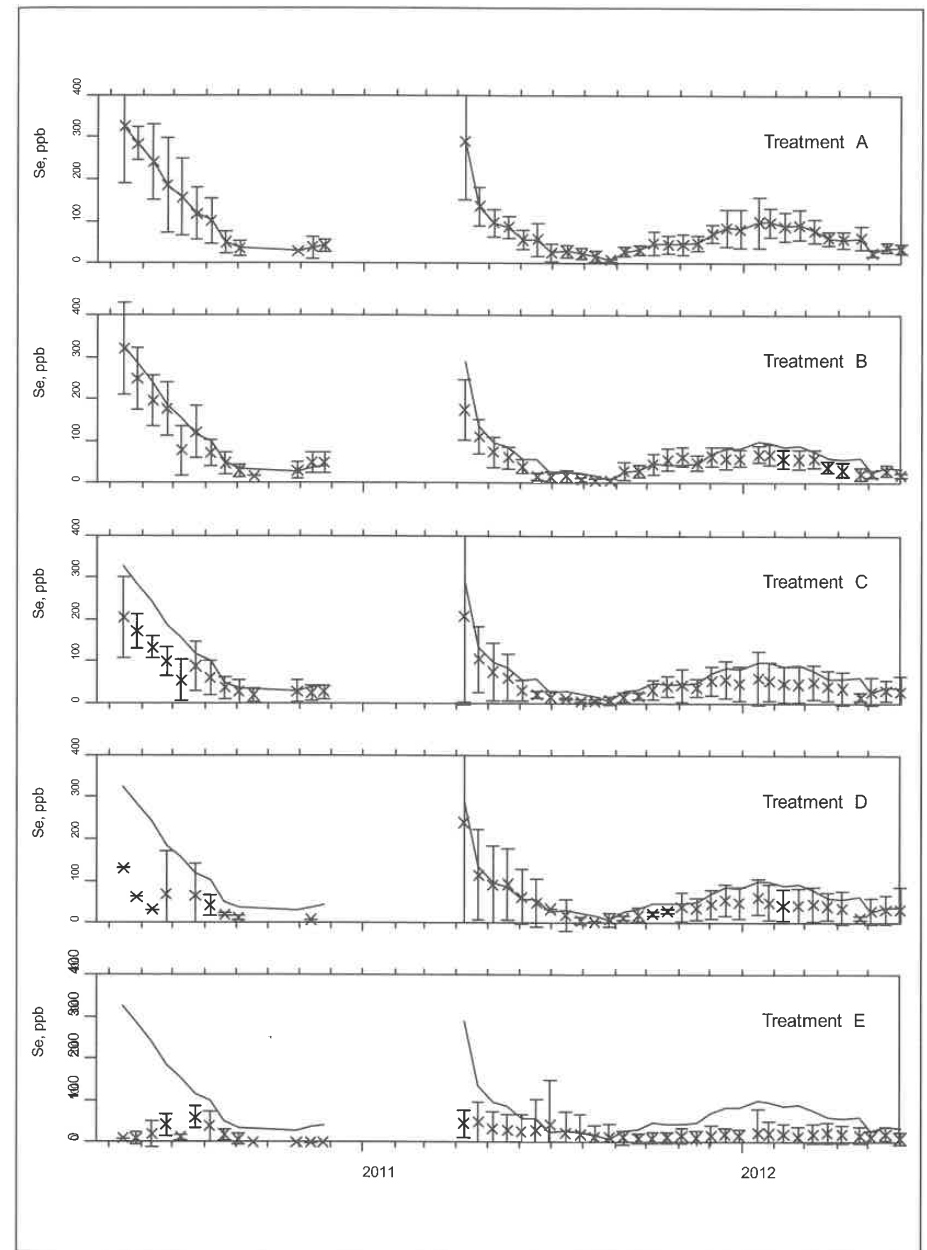


Figure 6. Time series of mean (X's) and confidence intervals (95%) for Se concentrations of all replicates within treatment classes (*n*=6 or less)

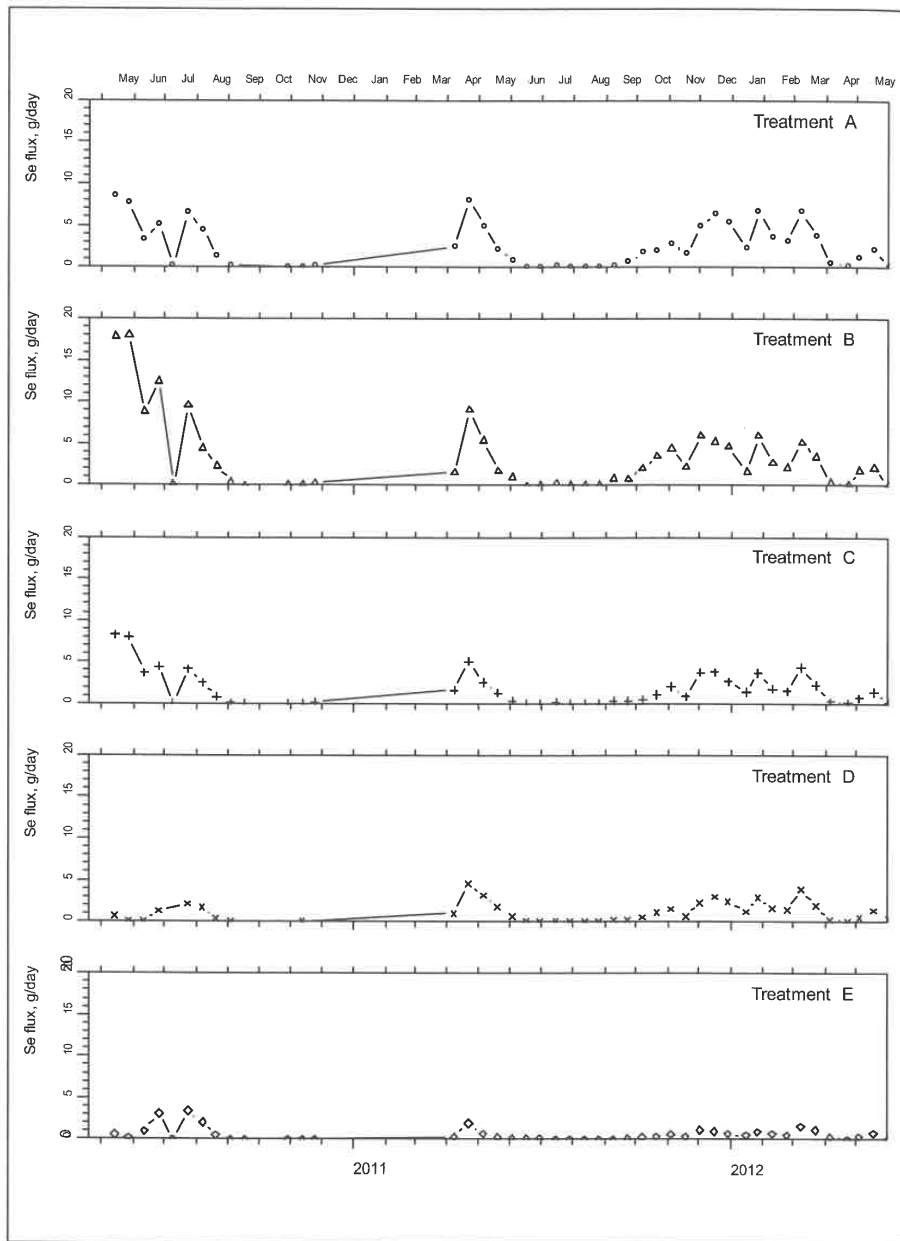


Figure 7. Time series of mean Se flux (g/day) per cell for each treatment class (n=6 or less)

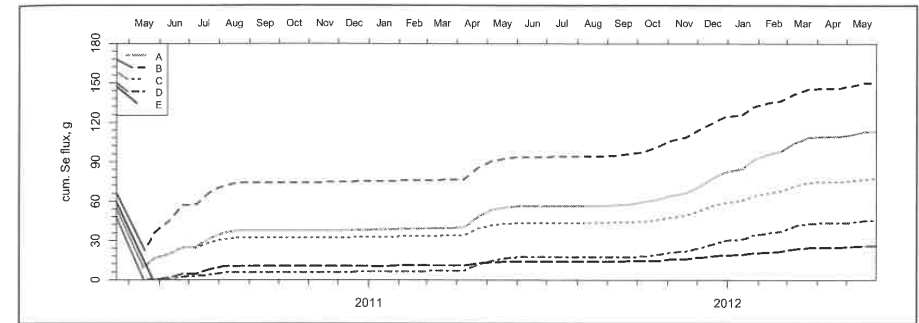


Figure 8. Cumulative Se fluxes for the five ferrihydrite treatments

22.9 cm (59.8% reduction) and 45.7 cm (76.9% reduction) ferrihydrite layers. The use of thin ferrihydrite layers appeared to have little adsorption effect, and in fact early fluxes from the Treatment B piles were much higher than the controls.

#### Replication and Variability

The variability of fluxes in all treatment replicates was not negligible, but within a limited range. There were minor outliers in Se concentration in both treatments C and D. However, at most sampling events for which a full number of replicates could be sampled, the standard errors were reasonably low. The largest sampling errors occurred when one or more of the replicates could not be sampled due to frozen plumbing or dry conditions. In general, the replication provides convincing evidence for reproducibility of both the Se-generating potential of untreated spoil and for its sequestration by adsorption using increasing masses of ferrihydrite.

The most surprising outcome was the elevated flux in the Treatment B piles compared to the control. Closer examination of these data indicates the leachate chemistry was similar between treatments, but more than twice the flow was collected in the B lysimeters than the A set. The reason for this difference is not understood, as the flows were much more similar for these two sets for the duration of the experiment. Sampling error of some type in flow measurement is a possibility.

#### Se Mobility Observations

In all treatments, strong seasonality was observed in both Se concentrations and in flow rates. The “stair-step” appearance of Figure 8 underscores the episodic nature of Se fluxes. It may be speculated that, during winter conditions, infiltration into the spoil is at minimum rate but air ingress is continuous and encourages oxidation even while discharge of water is minimal. The “slug” of elevated Se concentrations in spring may therefore represent flushing of over-winter reaction products. Strong Se flushes were observed both in early 2010 and 2011. In 2012, the flush occurred but at lower concentration than in the first two years. During drier seasons, both flow and concentration of Se drop to very low levels. The seasonality of Se discharge may offer water management options for addressing periods of high concentration.

#### Practical Implications

The success of this sequestration trial suggests that an inexpensive waste material (ferric iron-rich mine drainage treatment sludge) could be an effective spoil amendment that could reduce and control dissolved Se outbreaks at mine scale. Organic-rich shale tends to be among the most sulfur- and selenium-rich overburden lithologies. It is often found stratigraphically above coal seams, which, in combination with its diagnostic color, makes it amenable to selective handling during the mining process. Placing layers of ferrihydrite within and at the base of

selectively-handled cells of organic shale may be a practical method for immobilizing a significant proportion of the Se flux for an entire surface mine. Scaling these results to much larger spoil masses will require testing and optimization of the technique. Nonetheless, a simple variant of this method yielded excellent sequestration in this investigation in cells for which the mass of ferrihydrite was sufficient. While many of the mean concentrations observed in Treatment E were higher than the 5 µg/L discharge limit (maximum 59.6 µg/L; mean 19.7 µg/L), these values are four to six times lower than in unamended spoil, and after July 2011, all values remained below 20 µg/L. While monitoring continues at this site, it may be hypothesized that many of the higher concentrations occurred in the first year or so of leaching. Given that such unamended spoil generates such extreme Se concentrations in leachate, the amenability of surface mine waters to Se management without active treatment may depend on such special handling techniques to control Se concentrations.

## CONCLUSIONS

This investigation was an experiment at field scale to test the effectiveness of a single basal ferrihydrite layer at reducing Se mobility in leachate derived from organic-rich shale spoil. Thirty 488 × 732 cm lysimeters of identical construction, composition, and design, except for various thicknesses of ferrihydrite added, were monitored for 2.4 years on a biweekly basis. Key results include that:

- Time series of Se concentration and flux are highest during late winter and spring months, attributed both to spring flush of overwinter reaction products and to elevated recharge. Se fluxes are strongly seasonal, and winter/spring measurements of flux are critical to long-term accurate estimation.
- In a trial of four different layer thicknesses of ferrihydrite and one control (no ferrihydrite), the three thickest ferrihydrite amendments showed significant reduction in Se fluxes from the control, while the

thinnest layer showed no reduction. The two thickest layers (22.9 and 45.7 cm) showed 59.4% and 76.9%, respectively, cumulative reduction in Se flux.

- All results were couched in terms of mean results for six replicates in each treatment class. The uncertainty due to variability in materials, construction, and hydrology of individual lysimeters was quantitatively assessed and considered within acceptable limits. The reported confidence intervals indicate that differences found in mean Se concentration and flux are considered to have a high probability of significance.

## ACKNOWLEDGMENTS

This study was sponsored by the Appalachian Research Initiative for Environmental Science (ARIES). The views, opinions and recommendations expressed herein are solely those of the authors and do not imply any endorsement by ARIES employees, other ARIES-affiliated researchers or industrial members. Information about ARIES can be found at <http://www.energy.vt.edu/ARIES>.

This work was also supported by funding from the US Office of Surface Mining to the senior author. The cooperation of Patriot Coal Co. in constructing the lysimeters and providing site access was fundamental to the success of the project. Sampling assistance and laboratory chemical analyses were provided by REI Consultants, Beaver, WV.

The author thanks J.J. Donovan for his contribution to this paper.

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