Report as of FY2007 for 2007WV105B: "WRI 99 Selenium Speciation & Removal"

Publications

Project 2007WV105B has resulted in no reported publications as of FY2007.

Report Follows

WRI-99 Selenium Speciation and Removal
Final Report

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Introduction/Background

Selenium (Se) has been detected in mine drainage waters in southern West Virginia above the current water quality limit of 5 μg L^{-1} total Se. Although an essential element, Se has a very small threshold between essentiality and toxicity. The common dissolved forms of Se are free or complexed selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}). Because toxicity and treatment strategy depend on speciation, a robust, reliable method for the quantification of selenite and selenate is needed. Relatively little work has been done on Se determination in mine drainage waters.

A Zero Valent Iron-Steel Wool (ZVI-SW) treatment technology has emerged as a promising technique to remediate selenium contaminated waters. Field scale studies have shown near complete removal of selenium within 24 hrs. However, a more complete understanding of the removal kinetics, especially the effects of initial Se speciation and other influent water quality parameters is needed to design site-specific treatment systems. There is also a need to know the forms of Se following treatment. Two selenium removal mechanisms can be postulated. First, selenate/selenite reduction to elemental selenium, coupled to the oxidation of iron in the steel wool, and second, selenite (and to a lesser extent, selenate) adsorption to iron oxide corrosion products on the steel wool. Synchrotron-based spectroscopy can provide molecular evidence for the oxidation state of elements in environmental samples (Hayes et al., 1987; Manceau and Charlet, 1994; Myneni et al., 1997) and thus can be used to determine the reaction products of treatment reactions.

Research Objectives

1. Develop and validate a method to determine trace levels of selenate and selenite in mine drainage waters.

2. Quantify the effects of solution properties and initial selenium species on the kinetics of removal by ZVI-SW in bench-scale experiments.

3. Use synchrotron-based spectroscopy to determine the forms of selenium following reaction with ZVI-SW.

Methodology

Inorganic Selenium Speciation

A flow injection – hydride generation – inductively coupled plasma spectroscopic (FI-HG-ICP) method was used to determine selenite. Selenite is reduced to the volatile hydride form in an acidic medium, swept into the ICP with an inert carrier gas and determined at 196.026 nm. To speciate selenite and selenate (in a sample containing both) two determinations are required. Selenite is determined in one aliquot as described above. A second aliquot is digested in hot, concentrated HCl to reduce selenate to selenite (total Se). Selenate is then calculated by difference.

Selenium Removal Kinetics

All experiments were conducted in a water-jacketed, glass reaction flasks designed to allow for control of gas partial pressures and periodic sample collection. Constant mixing speed was maintained by overhead stirring with Teflon coated paddles. All experiments were conducted at 30^{o}C in duplicate. Treatments were salt type ($Ca(NO_3)_2$ or $CaCl_2$) and ionic strength (0.01 to 25 mM), selenite or selenate, and open or N_2 purged systems. All chemicals were of at least reagent-grade quality. Selenium was added as either Na_2SeO_3 or Na_2SeO_4 and ionic strength was adjusted using either $Ca(NO_3)_2$ or $CaCl_2$. Samples were collected with time, filtered (0.45 μm) and selenite concentrations determined as described above.

Synchrotron-Based Spectroscopy

Untreated, fine grade (#0) steel wool (0.1 g) was reacted with 50 mL of 5 mg L^{-1} Se (as Na_2SeO_3 or Na_2SeO_4) in screw cap centrifuge tubes. There were two factors, selenium species at two levels, Se(IV) or Se(VI), and aeration at two levels, nitrogen-purged or unpurged, for a total of four samples. For the unpurged samples, no attempt was made to exclude any gases from the solution. For the N_2-purged samples, wool was added to the Se-containing solutions and then purged for 5 minutes. Tubes for all treatments were capped tightly and those that were purged were wrapped with parafilm to minimize gas exchange. Preliminary experiments and previous studies have shown nearly complete selenium removal by steel wool within 24 hours and within 5 hours with iron powders (Mondal et al., 2004). Therefore, after at least 24 hours, steel wool samples were removed from tubes and placed into specially prepared Plexiglass sample holders. Supernatant solution was added to fill the cell completely and immediately sealed on both sides with Kapton tape. Samples were prepared individually and placed immediately in the X-ray sample compartment. It was not possible to keep samples from being exposed to air during preparation, and Kapton tape is not gas tight. The time period from the start of sample preparation to the first exposure to synchrotron radiation was less than three minutes.

Se K-Edge XANES spectra were collected at Beamline X18B at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, using a multi-element Ge detector, at room temperature with 0.3 eV step size through the XANES region. Selenium foil was used for the Se(0) standard; liquid Se(IV) and Se(VI) standards were prepared as 10 mM solutions of Na_2SeO_3 and Na_2SeO_4. Data (two to three scans) were averaged normalized, and background subtracted using standard procedures in the program ATHENA (Newville, 2001).

Principal Findings

Inorganic Selenium Speciation

The FI-HG-ICP selenite calibration curve was linear (R^2 > 0.999 up to 3 mg L^{-1}) although greater precision and lower detection limits could be achieved with lower concentration standards. For the range 0 to 500 μg L^{-1} (R^2 = 0.9999) the detection limit was 5.2 μg L^{-1} with a relative standard deviation (RSD) of 7.2 % at 1 μg L^{-1} and an average RSD of 1.9% (range 0.98 – 3.1%) above 1 μg L^{-1}. The detection limit could be reduced to 1.2 μg L^{-1} by calibrating from 0 to 50 μg L^{-1}. Selenate was quantitatively reduced to selenite and recovered.

Selenium Removal Kinetics: Salt Type and Concentration Effects

Selenate removal appeared to proceed in two phases (Figure 1). There was a lag phase of approximately 12 hrs when no selenium was removed from solution, followed by a rapid removal phase lasting from 12 to 24 hours. Neither the length of the lag phase and the rapid removal rate appear to be affected by ionic strength.

In contrast, selenite removal was dependent on ionic strength (Figure 2), and at constant ionic strength (Figure 1 and 2), much slower (longer lag phase). This result is not what was expected and deserves more study; typically selenite removal is much faster than selenate. Selenite removal rate appears to be dependant on salt type, with faster removal in $CaCl_2$ (Figure 3) than in $Ca(NO_3)_2$ (Figure 2).

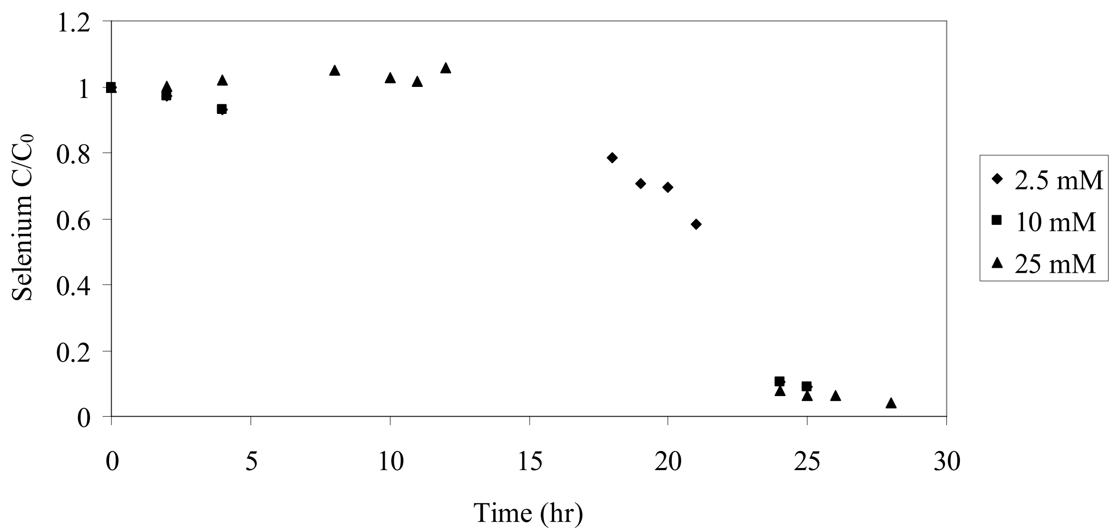

Figure 1. Selenate removal with ZVI-SW as a function of salt concentration in an open system. Initial selenate concentration 2 mg L^{-1}; background salt $Ca(NO_3)_2$.

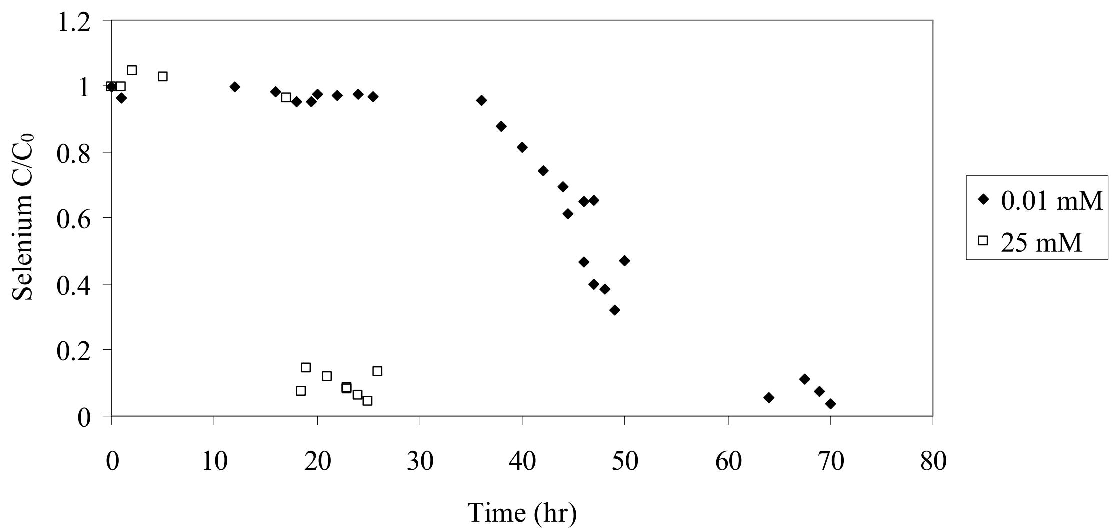

Figure 2. Selenite removal with ZVI-SW as a function of salt concentration in an open system. Initial selenite concentration 2 mg L^{-1}; background salt $Ca(NO_3)_2$.

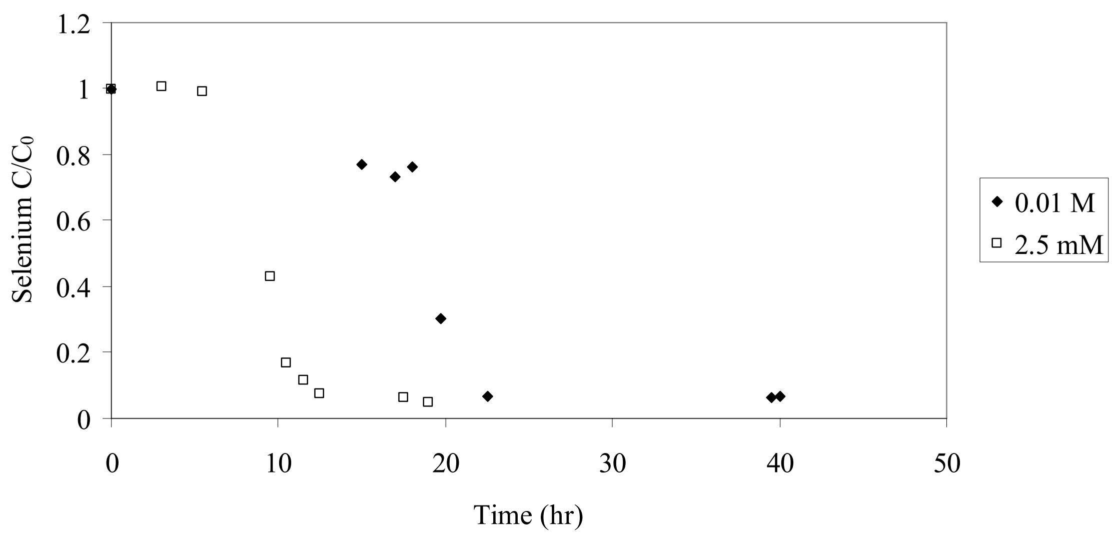

Figure 3. Selenite removal with ZVI-SW as a function of salt concentration in an open system. Initial selenite concentration 2 mg L^{-1}; background salt $CaCl_2$.

Selenium Removal Kinetics: Initial Selenite Concentration Effects

Selenite removal at the lowest initial concentration (1 μg L^{-1}) tested was dependent on ionic strength (Figure 4), but not at the higher initial concentrations of 2 or 4 μg L^{-1} (Figures 5 and 6).

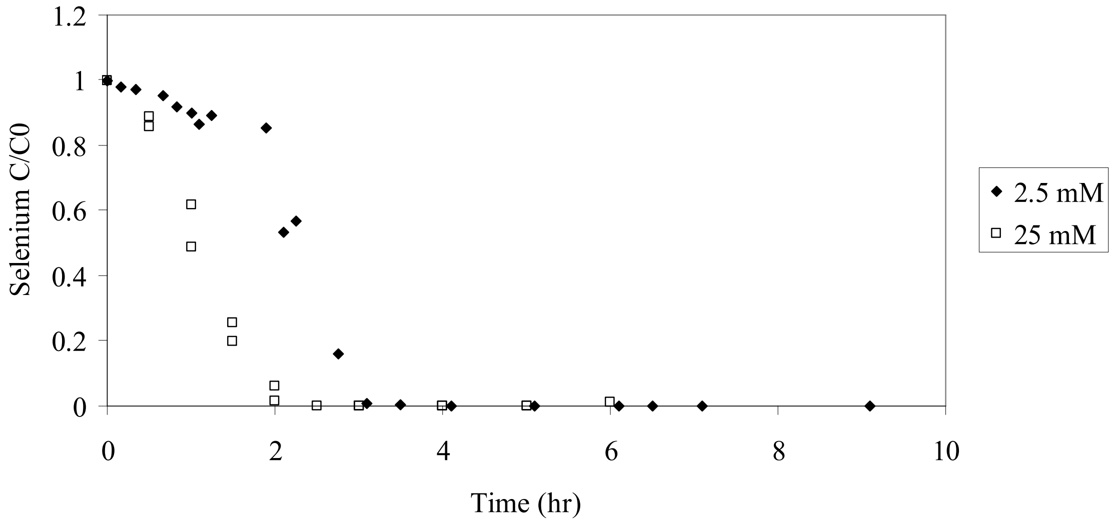

Figure 4. Selenite removal with ZVI-SW as a function of salt concentration in N_2 purged system; 1 mg L^{-1} initial Se, background salt $Ca(Cl)_2$.

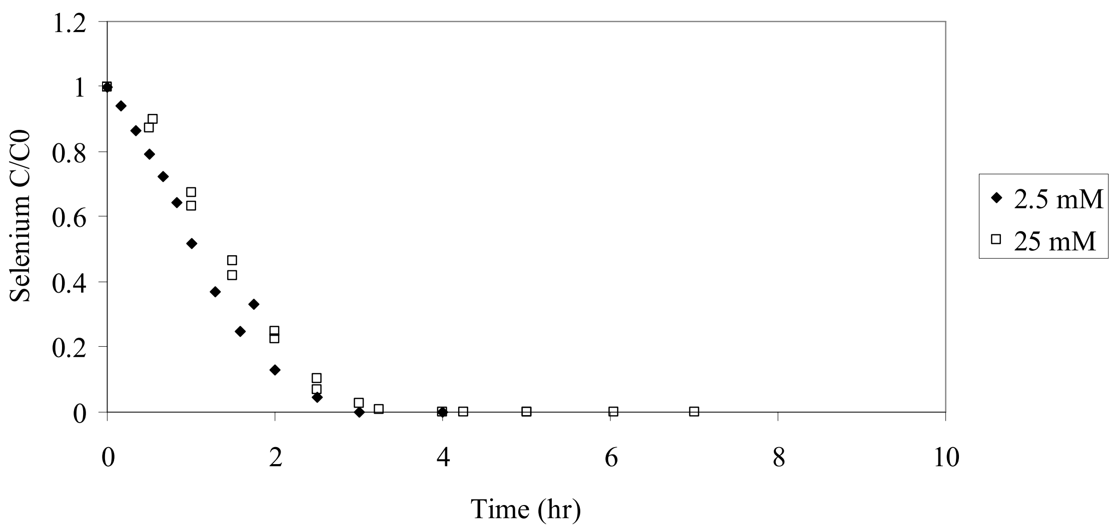

Figure 5. Selenite removal with ZVI-SW as a function of salt concentration in N_2 purged system; 2 mg L^{-1} initial Se, background salt $Ca(Cl)_2$.

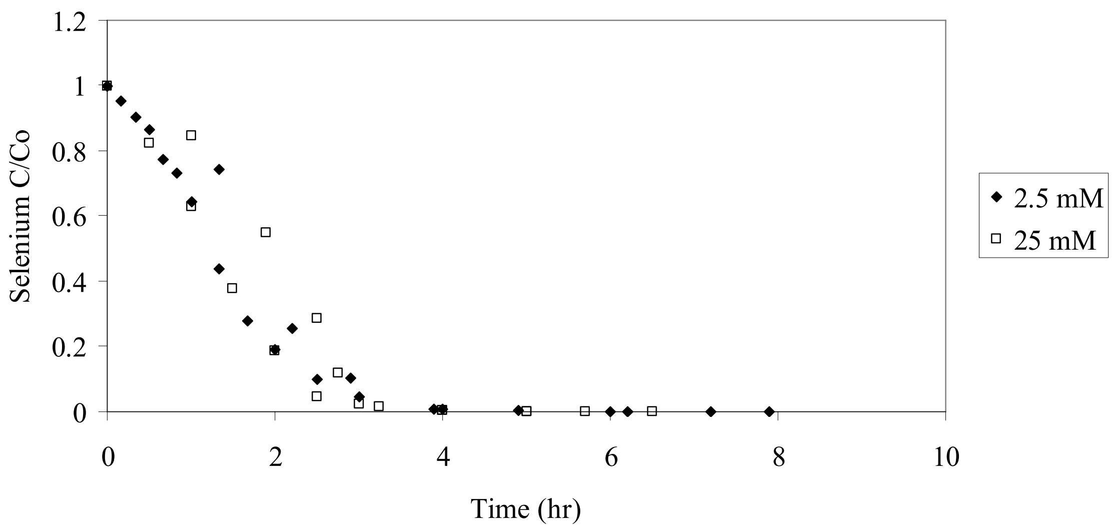

Figure 5. Selenite removal with ZVI-SW as a function of salt concentration in N_2 purged system; 4 mg L^{-1} initial Se, background salt $Ca(Cl)_2$.

Synchrotron-Based Spectroscopy

Spectra for Se all standards were comparable to published Se spectra. For simplicity, spectra white line positions (peaks) are used for comparison rather than edge positions (near edge inflection points). Both Se(VI) treatments (purged and unpurged) showed evidence of elemental Se (Figure 1). The stronger elemental Se peak for the purged sample may be the result of the removal of oxygen from the solution. The peaks at eV less than that for Se(VI) may indicate the presence of selenite sorbed to the iron oxide produced during the reaction. Selenite has been shown to bond to iron oxides (Neal and Sposito, 1991).

That elemental Se was formed in both the purged and unpurged samples is consistent with previous studies that indicated that there was no effect on Se removal from chloride (100mM), nitrate (10 mM), sulfate (5 mM), or bicarbonate (5 mM) in solution, and only small effects from sulfate at 50 and 100 mM, and bicarbonate at 10 mM (Zhang et al., 2005).

For solutions containing selenite, only the purged samples show evidence for the formation of elemental Se (Figure 3). This suggests that some component of the unpurged solution is interfering with the reduction process. The unpurged spectra is very noisy compared to all other collected spectra because the concentration of Se(IV) in solution is very low; 5 mg Se L^{-1} is too low to obtain reliable spectra; this signal may represent adsorbed but unreacted selenite. Note that once dissolved Se is reduced to and precipitated as Se(0), its effective concentration in the beam is increased.

The most likely component of an unpurged solution to interfere with Se reduction is dissolved oxygen. The formation of an oxidized iron coating on the surface of the wool could prevent the transfer of electrons necessary for the redox reaction to occur and/or selenite sorption to these oxides may slow the reduction process (Neal and Sposito, 1991). However, an inspection of the sample tubes before analysis indicated no evidence of iron oxidation on the surface of the wool or in solution for the unpurged selenite treatment. To minimize the possibility that this observation was an artifact, new samples were prepared as described above, with the same result.

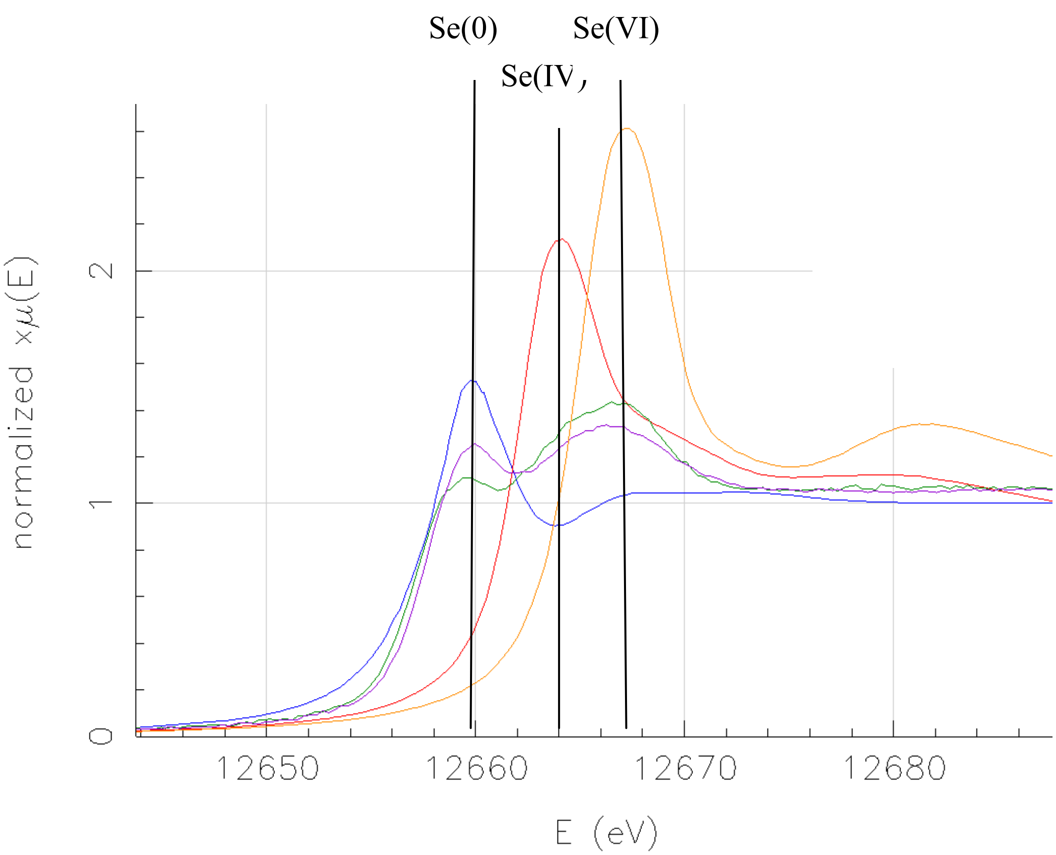

Figure 6. Selenate solutions (Ar-purged, purple and unpurged, green) after reaction with steel wool for 24 hrs. White lines (peaks) are indicated for each Se species. Both purged and un-purged treatments show peaks at 12658 eV indicating the presence of elemental Se.

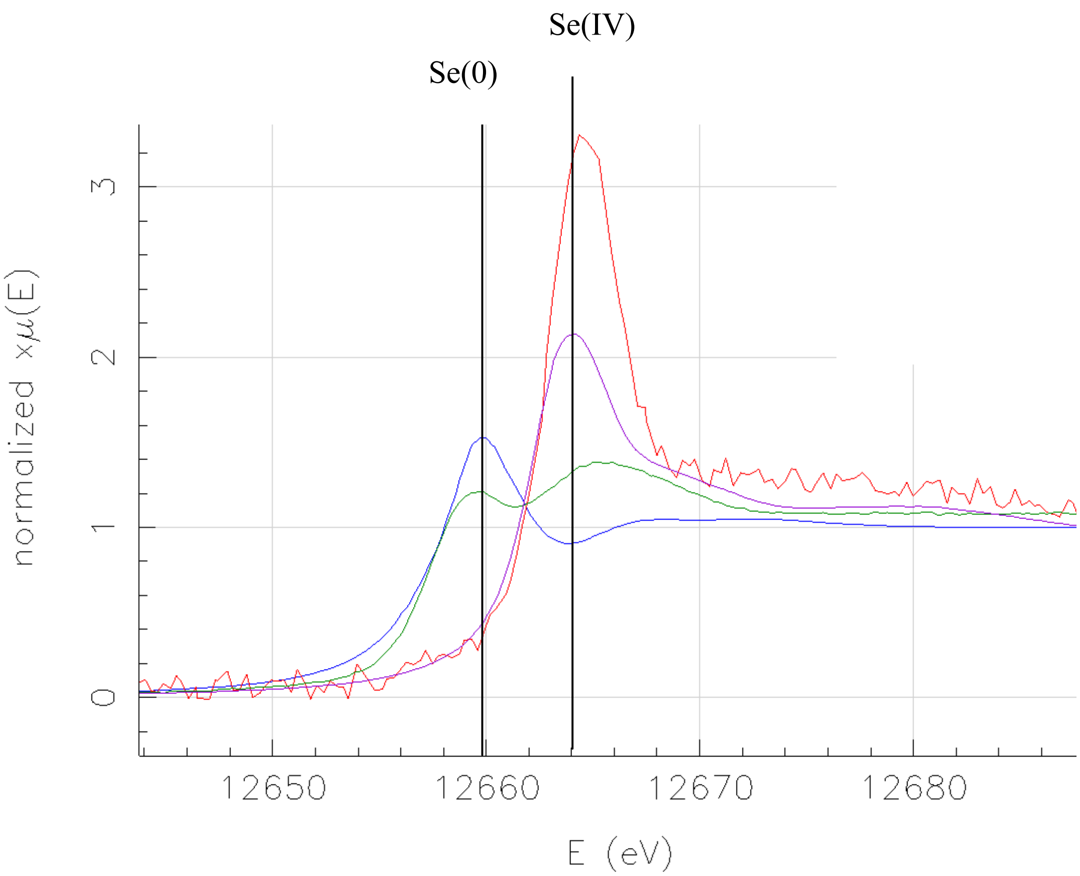

Figure 7. Selenite solutions (Ar-purged, green and unpurged, red) after reaction with steel wool for 24 hrs. White lines (peaks) are indicated for each Se species. Only the purged solution has a peak at 12658 eV indicating the presence of elemental Se.

Significance of the Project

Because the current water quality standard for Se is written as total Se, that is what commercial laboratories provide. However, because toxicity and treatment system design and efficiency will depend on Se speciation, the implementation of a relatively inexpensive, reliable FI-HG-ICP method to speciate Se will be valuable for research, regulatory, and treatment design needs.

The observation that selenite removal was slower than selenate removal (batch kinetic and spectroscopic results) is opposite of what is typically observed. The most likely explanation for this is the overall reaction dependence on ionic strength and salt type (Cl vs NO_3). Removal rate dependence on initial selenite concentration and open or closed system indicates that selenium reduction by ZVI-SW is a complex process and that additional research is needed to understand the effects of other water quality parameters on removal rates.

Student Support:

Donglin (Lynn) Huang Ph.D. Student (1st year)

Publications

In Preparation

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