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**Temperature-Dependent Selenium Sorption to Mine Drainage Solids:
Implication for Diel Cycling**

- Task 1. Refine methods, with new instrumentation purchased with funds from this project, to speciate inorganic (selenite, selenate) and organic selenium.
- Task 2. Determine sorption-desorption parameters for selenite as a function of temperature to iron oxides formed during mine drainage treatment and other common minerals found in acid and alkaline mine drainage impacted waters.

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TABLE OF CONTENTS

INTRODUCTION: PURPOSE OF STUDY	1
TASK 1. METHOD DEVELOPMENT	2
1 SUMMARY	2
2 APPARATUS, MATERIALS, AND EXPERIMENTAL PROCEDURES	2
2.1 Equipment and supplies	2
2.2 Method development	3
2.3 Sample stability on the autosampler	3
2.4 Detection limits	3
2.5 Labware evaluation for Se labwork	4
2.6 Photolysis evaluation	5
2.7 Influence of competing ions	5
3 RESULTS OF METHOD DEVELOPMENT AND QA/QC.....	6
3.1 Method development	6
3.2 Stability of samples on autosampler	9
3.3 Determination of detection limits	9
3.4 Labware evaluation	10
3.5 Photolysis evaluation	11
3.6 Interference of competing ions	12
4 DISCUSSION	13
5 CONCLUSIONS	14
TASK 2. TEMPERATURE DEPENDENT SELENITE SORPTION TO FOUR MINE DRAINAGE SOLIDS AT THREE TEMPERATURES	15
1 SUMMARY	15
2 APPARATUS, MATERIALS, AND EXPERIMENTAL PROCEDURES	15
2.1 Experimental apparatus	15
2.2 Sample collection	16
2.3 Sample characterization.....	17
2.4 Solution pH and electrical conductivity	17
2.5 Moisture content	18
2.6 Elemental composition	18
2.7 Determination of solid:solution ratios	19
2.8 Determination of equilibration time	19
2.9 Isotherm construction and analysis.....	19
3 RESULTS OF SORPTION EXPERIMENTS	20
3.1 Sorbent characterization	20
3.2 Determination of solid:solution ratios	21
3.3 Determination of equilibration time	21
3.4 Isotherms	23
4 DISCUSSION	28
5 CONCLUSIONS	29
6 LITERATURE CITED	29
APPENDIX.....	31

LIST OF TABLES

Table 1	Instrumental operating conditions for selenite determination by HG-AFS for the Full Range and Low Range methods.	7
Table 2	Calculated detection limits for the full range and low range selenite determination by HG-AFS.	10
Table 3	ANCOVA results for labware evaluation at three nominal Se(IV) concentrations.	11
Table 4	ANCOVA least squares means (LSM) and standard error (St Error) for labware evaluation at three nominal Se(IV) concentrations.	11
Table 5	Temperature and light intensity in the two locations used to evaluate the effects of light on Se(IV) recovery.	11
Table 6	Average error and standard deviation in Se(IV) determination from dissolved iron and sulfate, alone and in combination. Negative numbers indicate that measured Se(IV) was less than expected.	13
Table 7	Description and origins of solids used as sorbents for Se(IV) sorption.	17
Table 8	Properties of the sorbents used in the isotherm experiments.	21
Table 9	Elemental composition of sorbents used in the sorption experiments.	22
Table 10	Sorption constant (K_D) and confidence interval (CI) for each solid at each temperature. Different superscripted letters on K_D s within a sorbent indicates a significant ($\alpha=0.05$) difference.	27
Table 11	Mean pH change and standard deviation for each solid at each temperature. A negative pH change indicates a pH decrease during the experiment.	28

LIST OF FIGURES

Figure 1	Typical calibration curve for the Full Range method (0 – 50 $\mu\text{g L}^{-1}$). Instrument settings are provided in Table 2.	8
Figure 2	Typical calibration curve for the Low Range method (0 – 10 $\mu\text{g L}^{-1}$). Instrument settings are provided in Table 2.	8
Figure 3	Concentration of standards held on autosampler with time. Error bars (one standard error) were typically smaller than the marker indicating the data.	9
Figure 4	Effect of location (greenhouse or laboratory) and light condition (dark or light) on mean percent Se(IV) recovery.	12
Figure 5	Linear sorption isotherms for the gray sandstone (O-1) at 10, 20 and 30°C.	23
Figure 6	Linear sorption isotherms for the brown sandstone (O-2) at 10, 20 and 30°C.	24
Figure 7	Sorption isotherms for the passive treatment solid (AMD-1) at 10, 20 and 30°C.	24
Figure 8	Sorption isotherms for the active treatment solid (AMD-2) at 10, 20 and 30°C.	25
Figure 9	Sorption constant (K_D) and 95% confidence interval (CI) for each solid at each temperature.	26
Figure 10	Langmuir isotherms for the passive treatment solid (AMD-1) at 10, 20, and 30°C.	27

LIST OF ABBREVIATIONS

AMD	acid mine drainage
ANCOVA	analysis of covariance
BDHCL	boosted discharge hollow cathode lamp
BDL	below detection limit
CI	confidence interval (95%)
DDI	distilled deionized water
EC	electrical conductivity
HG	hydride generation
HG-AFS	hydride generation-atomic fluorescence spectroscopy
ICP-OES	inductively coupled plasma-optical emission spectroscopy
IDL	instrument detection limit
LSM	least squares mean
LOI	loss on ignition
LLOQ	lower limit of quantitation
MDL	method detection limit
OSMRE	Office of Surface Mining Reclamation and Enforcement
OM	organic matter
PP	Polypropylene
PTFE	polytetrafluoroethylene
PSA	PS Analytical
St Dev	standard deviation
St Error	standard error
pH	hydrogen ion activity as determined by electrode
QA/QC	quality assurance/quality control
r^2	coefficient of linear determination
WV	West Virginia
WVU	West Virginia University

LIST OF CHEMICAL SPECIES

Al	Aluminum
C	Carbon
Ca	Calcium
Fe	Iron
Fe(III)	Ferric iron
HCl	Hydrochloric Acid
HNO ₃	Nitric acid
Mg	Magnesium
Mn	Manganese
N	Nitrogen
Na	Sodium
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NaNO ₃	Sodium nitrate
NaBH ₄	Sodium borohydride
S	Sulfur
Se	Selenium
Se(-II)	Selenide
Se(IV)	Selenite. This is a general reference to Se in the +IV state without indicating the specific chemical species (H ₂ Se ^(IV) O ₃ , HSe ^(IV) O ₃ ⁻ , Se ^(IV) O ₃ ⁻²) present.
Se(VI)	Selenate. This is a general reference to Se in the +VI state without indicating the specific chemical species (HSe ^(VI) O ₄ ⁻ , Se ^(VI) O ₄ ⁻²) present.

UNITS OF MEASUREMENT

°C	degrees Celsius
g	grams
hr	hour
kPa	kilopascals
L	Liter
<i>M</i>	molarity
mA	milliampere
mg	milligram
mg kg ⁻¹	milligram per kilogram
mg L ⁻¹	milligram per liter
mL	milliliter
mm	millimeter
min	minute
μg	microgram
μg L ⁻¹	microgram per liter
ng L ⁻¹	nanogram per liter
nm	nanometer
psi	pounds per square inch
rpm	revolutions per minute
s	second
v/v	volume-volume (ratio of two volumes)
%	percent
% (m/v)	mass-volume percentage (ratio of mass to volume)
% (v/v)	volume-volume percentage (v/v expressed as a percentage)

INTRODUCTION: PURPOSE OF STUDY

Selenium (Se) has a complex biogeochemical cycle driven by microbially-mediated reactions, multiple oxidation states, sorption-desorption reactions, and slow transformation kinetics. Understanding this cycle is critical for predicting toxicity, bioavailability, natural distribution, mobility, and long-term Se storage. However, many critical aspects of the biogeochemical cycle remain poorly understood. For example a study conducted on the Great Salt Lake (Dicataldo et al., 2011) found Se cycled in diel pattern in August but not in May or September. Short-term changes in Se concentration, combined with seasonal variability in cycles, may account for the inconsistent concentrations of Se reportedly measured at electrical plants and mining operations. It may also inform standard practices for sampling when Se is a regulated element.

The overall goal of our research was to determine the role of temperature in Se(IV) sorption to materials common in systems impacted by mine drainage. We hypothesized that temperature and selenite sorption are inversely related. To test this, we conducted selenite sorption experiments to four solids commonly found in mining impacted areas (gray sandstone, brown sandstone, active acid mine drainage (AMD) treatment solids and passive AMD treatment solids) at three temperatures (10°, 20°, and 30°C). The two sandstone samples are representative of the solids in contact with the alkaline mine drainage typical in the southern West Virginia (WV) coal fields. The two AMD treatment solids were from two common AMD treatment methods for acidic mine drainage typically found in northern WV.

Although Se can occur as selenide (Se(-II)), selenite (Se(IV)), selenate (Se(VI)), and as a part of organic compounds (seleno-proteins) this study focused on Se(IV) because

- It is the first Se species to be oxidized from reduced mining-associated sources.
- It binds (sorbs) to solids more strongly than the more oxidized selenate (Se(VI)) and thus is more likely to cycle based on sorption interactions.

We approached this project with two tasks. Selenium is a notoriously difficult element to determine, especially at low concentrations. Task 1 was to develop a robust, reproducible analytical procedure for selenite determination using Hydride Generation-Atomic Fluorescence Spectrometry (HG-AFS). This included instrument acquisition and setup, method development, quantitation limits, an evaluation of suitable labware, and other relevant quality assurance/quality control (QA/QC) procedures. Once we were confident in our analytical approach, Task 2 was to conduct sorption experiments for the four solids at three temperatures. This task included collection and characterization of the solids, determination of the appropriate solid-to-solution ratios, and the sorption isotherms for each solid at each temperature.

TASK 1. METHOD DEVELOPMENT

1 SUMMARY

Task 1 included six activities; (1) acquiring and receiving training for PS Analytical (PSA) for the hydride-generation atomic fluorescence spectroscopy system (HG-AFS), (2) determining detection limits for developed HG-AFS methods, (3) determining stability of samples on the autosampler, (4) evaluating labware for suitability, (5) evaluating photolysis as a degradative pathway, and (6) investigating the impact of interfering ions on selenite quantitation.

The purchased instrument was a PSA 10.055 Millennium Excalibur HG-AFS (Orpington, Kent, United Kingdom), a Se boosted discharge hollow cathode lamp (BDHCL), and a PSA 20.400 autosampler. Following vendor training method development and QA/QC procedures were completed between November 2015 and December 2016.

Overall, we confirmed that HG-AFS is a sensitive technique for selenite quantification; our detection limits were comparable to those reported in other HG-AFS studies and for other analytical methods. A labware evaluation study determined that silanized glass was the most appropriate material and was used in all other procedural work except when samples were in strong (4-6 *M*) acid (i.e. when on the autosampler). Both light and competing ions were evaluated as possible sources of analytical error. Although the experiment to evaluate the effect of light was inconclusive, all experimental samples were wrapped in aluminum foil prior to acidification for analysis to minimize exposure to light. The presence of multiple ions (Fe^{3+} and sulfate) in solution caused a small decrease in the instrument signal (measured selenite concentration), all samples were subsampled and analyzed for these ions to ensure analytical accuracy. Our work was conducted with selenite concentrations observed in nature, suggesting that similar QA/QC procedures are necessary for selenite quantification of natural samples for accurate reporting.

2 APPARATUS, MATERIALS, AND EXPERIMENTAL PROCEDURES

2.1 Equipment and supplies

All samples were analyzed with a PSA 10.055 Millennium Excalibur HG-AFS (Orpington, Kent, United Kingdom) operating with a Se boosted discharge hollow cathode lamp (BDHCL) and according to conditions listed in Table 1. A PSA 20.400 autosampler was used in all analyses. Homologous polytetrafluoroethylene tubes provided by PSA (Environmental Express; SC, US) were used to hold all samples on the autosampler.

Glassware was cleaned according to standard laboratory protocols using a two stage acid bath. Glassware was first soaked in 7.0 *M* nitric acid (HNO₃) for a minimum of twenty-four hours. Glassware was rinsed with distilled deionized water (DDI) before soaking in 1.0 *M* hydrochloric acid (HCl) bath for a minimum of twenty-four hours. Glassware was rinsed with DDI water and air-dried prior to use.

All reagents used were of analytical grade. Acid baths were prepared with standard reagent grade HCl and HNO₃. Trace metal grade HCl (11.65 *M*) was used for sample acidification, instrumental blank solution, and autosampler wash solution. Sodium hydroxide pellets and sodium borohydride powder (99% pure, nitrogen flushed) were purchased from Acros Organic (NJ, USA). A 0.7% m/v sodium borohydride (NaBH₄) solution was prepared daily and was stabilized with 0.1 *M* NaOH. All samples were prepared in 0.1 *M* sodium nitrate from Fisher Scientific (CO, USA). Anhydrous sodium sulfate was purchased from Fisher Scientific (CO, USA).

2.2 Method development

Instrumental methods were developed for selenite by hydride generation - atomic fluorescence spectrometry (HG-AFS) in consultation with PSA. A complete instrument method included settings for instrument gain (electronic signal amplification), and times for delay, analysis and memory. The requirements for a method were reproducible, linear ($r^2 > 0.99$) calibration slopes and intercepts on different days (within 5%). In anticipation of analyzing a wide range of selenite concentrations, two methods were developed. The full range method was suitable for samples from 0 to 50 $\mu\text{g L}^{-1}$. For when it was necessary to determine very low selenite concentrations, a low range method was developed for samples between 0 and 10 $\mu\text{g L}^{-1}$.

2.3 Sample stability on the autosampler

The autosampler holds 63 samples. Because the analysis time is approximately three (3) minutes per sample, the last sample can be on the autosampler for three hours before analysis. To determine if selenite concentrations decreased with sample time on the autosampler, a stability test was performed. Known standards of 0, 12.5, 25.0, 37.5, and 50.0 $\mu\text{g L}^{-1}$ were prepared using a 1,000 mg L^{-1} selenite standard (AccuStandard (CT, USA) in 0.1 *M* sodium nitrate (NaNO₃) to adjust for ionic strength and 5% v/v HCl. After instrument calibration, standards were analyzed every twenty minutes until lack of volume prevented further measurement.

2.4 Detection limits

The detection limit is defined as the smallest quantity of analyte that is statistically different from the blank. The instrument detection limit (IDL) was determined by analyzing a single sample seven times.

The IDL was determined by analyzing one sample seven times. The IDL was calculated as (Harris, 2010a)

$$\text{IDL} = \frac{3s}{m} \quad (1)$$

where s was the standard deviation of the seven measurements on one sample and m was the slope of the calibration equation.

The method detection limit (MDL), which is greater than the instrument detection limit, was determined by analyzing seven samples one time each. The MDL, which is greater than the IDL, was determined by analyzing seven samples one time each. The MDL was then calculated as (Harris, 2010a)

$$\text{MDL} = \frac{3s}{m} \quad (2)$$

where s was the standard deviation of the seven samples and m was the slope of the calibration equation.

The lower limit of quantitation (LLOQ) is the smallest concentration that can be measured with reasonable accuracy and is defined as the signal that is ten times greater than the background noise. The LLOQ was determined by analyzing seven samples one time each. The LLOQ was determined by analyzing seven samples one time each. The LLOQ was calculated as (Harris, 2010a)

$$\text{LLOQ} = \frac{10s}{m} \quad (3)$$

where s was the standard deviation of the seven samples and m was the slope of the calibration equation.

Samples were prepared from the selenite standard in 0.1 M NaNO₃ and 0.2 v/v HCl. Following calibration, a prepared sample of 0.20 μg L⁻¹ for the low range method (0-10 μg L⁻¹) and a prepared sample of 2.0 μg L⁻¹ for the high range method (0-50 μg L⁻¹) were analyzed seven times for IDL determination for each method. Seven samples of 0.2 μg L⁻¹ (0-10 μg L⁻¹ method) and 2.0 μg L⁻¹ (0-50 μg L⁻¹ method) selenite were analyzed once each to compute LLOQs and MDLs for the developed methods.

2.5 Labware evaluation for Se labwork

To determine the material most suitable for selenite sorption experiments, four types of materials were assessed: glass, silanized glass, polytetrafluoroethylene (PTFE), and polypropylene (PP). Varying selenite stock solutions (0, 10, 25, and 50 μg L⁻¹) were prepared in 0.1 M sodium chloride (NaCl) in triplicate. Each sample was 40 mL in volume. Samples were placed on a rotary shaker (Glas-Col; IN, USA) at 30 revolutions per minute (rpm) for 6, 12, 24, or 48 hours to evaluate the ability of the material to suitably hold samples for sorption studies. Samples were prepared for each individual time point. After

equilibration time, samples were transferred to homologous polypropylene tubes (Environmental Express; SC, USA) and immediately acidified for selenite determination by HG-AFS as described above. Samples were prepared in triplicate in a randomized design (n=180).

2.6 Photolysis evaluation

Light intensity measurements in the greenhouse were recorded with a data logger installed in each room. Light intensity measurements in the laboratory were analyzed with an Apogee MQ-301 ceptometer (Logan, UT).

Varying selenite stock solutions (0, 10, 40 $\mu\text{g L}^{-1}$) were prepared in 0.1 M NaNO_3 . Each sample was 40 mL in volume. Samples were contained in silanized glass vial and sealed with Teflon-faced septum. Samples were prepared in triplicate. Two series of samples were prepared for the light treatment and dark treatment. The dark treatment samples were placed in amber glass and the entire vial was wrapped in aluminum foil. The light treatment samples were placed in clear glass. Two locations were selected for this experiment: the laboratory and greenhouse. A light and dark series of samples was placed in each location for twenty-four hours. Light samples were laid on a table in each location rather than standing with or without a test tube rack. Samples in the dark treatment were placed in amber glass vials and wrapped in aluminum foil. After the twenty-four hour hold period, samples were analyzed for selenite by HG-AFS. Samples were prepared in triplicate (n=48). The effect of light on percent selenite recovery was determined using single factor analysis of variance (ANOVA).

2.7 Influence of competing ions

Samples were prepared from the selenite standard in 0.1 M NaNO_3 and 0.2 v/v HCl to a concentration of 25 $\mu\text{g L}^{-1}$ with and without common ions present in mine drainage solids, ferric iron and sulfate. Ferric iron was added to samples at a level of 0, 2.5, and 5.0 $\mu\text{g L}^{-1}$ using a 1,000 mg L^{-1} Fe(III) standard. Sulfate was added to samples at a level of 0, 125, and 250 $\mu\text{g L}^{-1}$ using a prepared standard made from sodium sulfate. All samples were prepared in silanized glass vials and were wrapped in aluminum foil. Samples were placed on a rotary shaker at room temperature (20 °C) for twenty-four hours and analyzed for selenite by HG-AFS.

Error was calculated according to equation 4 (Huang, 2010):

$$e = \frac{C - \mu}{\mu} \quad (4)$$

where e was the error, C was the reading of the sample with the interfering ion, and μ was the reading of the control sample with no interfering ions. All samples were prepared in duplicate (n=18).

3 RESULTS OF METHOD DEVELOPMENT AND QA/QC

3.1 Method development

To ensure the highest possible precision and accuracy for all selenite determinations and to make the best possible use of resources, two instrumental methods were developed and used (Table 1). The Full Range method is suitable for higher concentrations, up to 50 micrograms per liter ($\mu\text{g L}^{-1}$) as delivered to the instrument. A typical calibration curve equation for the Full Range method ($r^2 = 0.992$) was

$$S = -1.528 + 1.196 [\text{Se}] \quad (5)$$

where S = Signal (instrument response) and $[\text{Se}]$ is selenite concentration in $\mu\text{g L}^{-1}$ (Figure 1).

For samples with low selenite concentrations ($< 10 \mu\text{g L}^{-1}$) a second method (Low Range) with a larger gain and longer analysis time was developed (Table 1) and was linear to $10 \mu\text{g L}^{-1}$. A typical calibration curve equation for the Low Range method ($r^2 = 0.998$) was

$$S = -5.273 + 144.78 [\text{Se}] \quad (6)$$

where variables are as defined above (Figure 2).

The analytical protocol is to analyze all samples using the full range calibration. When higher precision is needed for low selenite concentration ($< 10 \mu\text{g L}^{-1}$) samples, the Low Range method is used.

Table 1. Instrumental operating conditions for selenite determination by HG-AFS for the Full Range and Low Range methods.

Parameter	Full Range Method	Low Range Method
Gain	1	10
Filter	16	32
Wavelength	196.0 nm	196.0 nm
Primary Current	20.0 ± 0.5 mA	20.0 ± 0.5 mA
Boost Current	25.0 ± 0.5 mA	25.0 ± 0.5 mA
Delay Time	10 s	10 s
Analysis Time	5 s	15 s
Memory Time	40 s	40 s
Probe Rinse Solution	40% v/v HCl	40% v/v HCl
Probe Rinse Flow Rate	8 mL min ⁻¹	8 mL min ⁻¹
Sample Flow Rate	8 mL min ⁻¹	8 mL min ⁻¹
Sample Acidity	5% v/v HCl	5 % v/v HCl
Blank Flow Rate	8 mL min ⁻¹	8 mL min ⁻¹
Reductant	20% v/v HCl	20% v/v HCl
Reductant Flow Rate	4.5 mL min ⁻¹	4.5 mL min ⁻¹
Carrier Gas	Argon	Argon
Carrier Gas Flow Rate	0.60 L min ⁻¹	0.60 L min ⁻¹
Drier Gas	Argon	Argon
Drier Gas Flow Rate	2.5 L min ⁻¹	2.5 L min ⁻¹

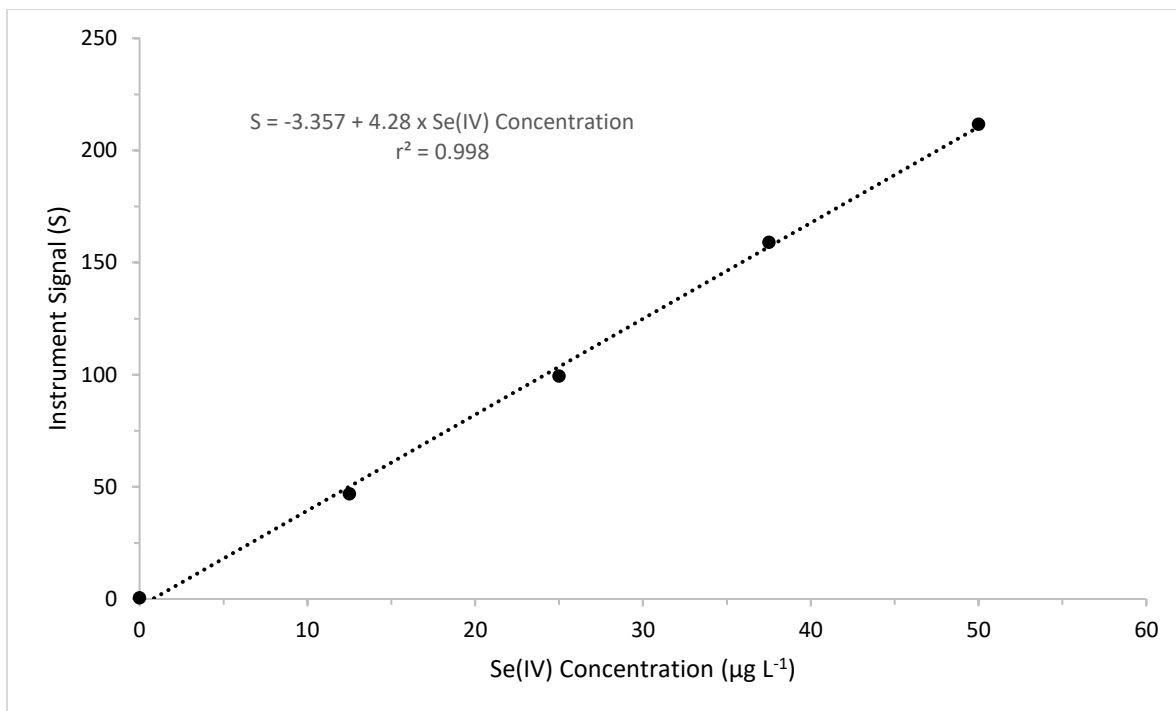


Figure 1. Typical calibration curve for the Full Range method (0 – 50 µg L⁻¹). Instrument settings are provided in Table 1.

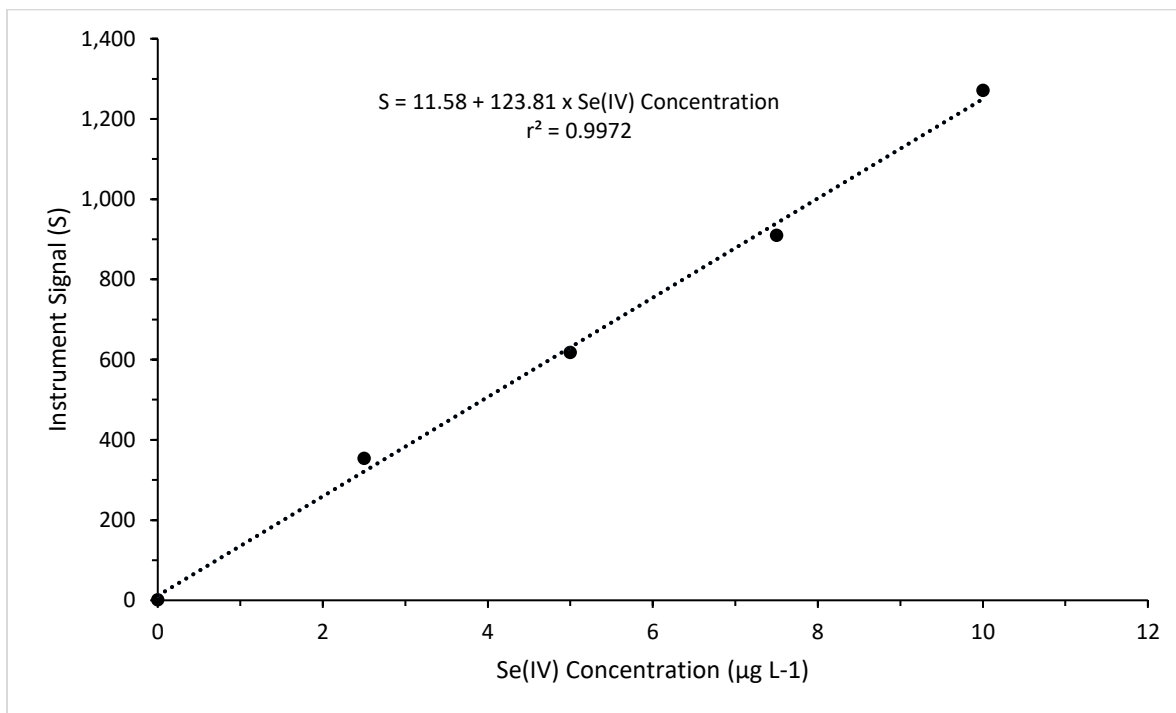


Figure 2. Typical calibration curve for the Low Range method (0 – 10 µg L⁻¹). Instrument settings are provided in Table 1.

3.2 Stability of samples on autosampler

The analyzed concentration of each calibration standard was plotted against time (Figure 3). The average loss was $0.025 \mu\text{g L}^{-1} \text{min}^{-1}$ or $0.2\% \text{hour}^{-1}$ which suggests that for a minimum acceptable precision rate of 5% at most 25 samples can be analyzed in a single instrumental run. For analyses in which there are more than 25 samples, samples will be placed on the autosampler at different times to minimize loss.

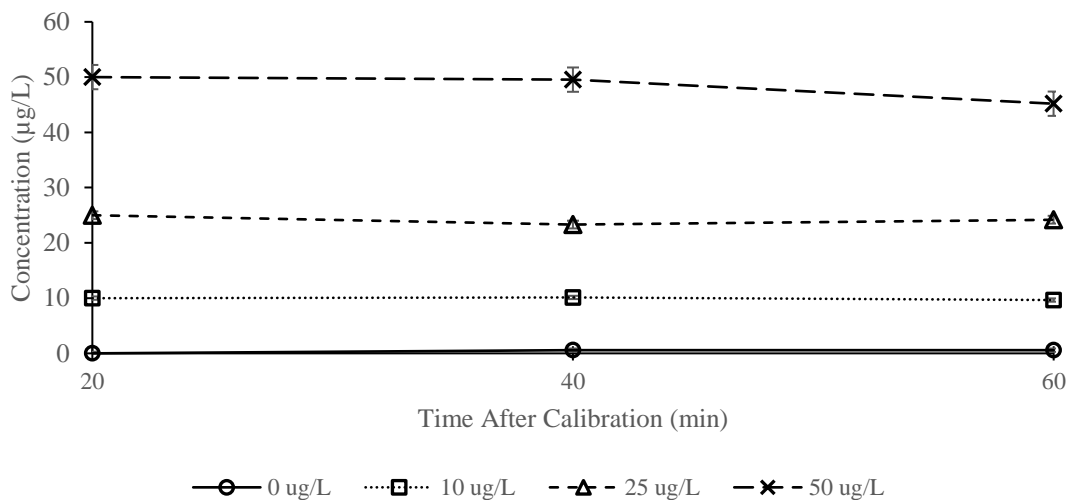


Figure 3. Concentration of standards held on autosampler with time. Error bars (one standard error) were typically smaller than the marker indicating the data.

3.3 Determination of detection limits

The two developed methods have different instrument detection limits (Table 2) because of different calibration equation slopes and instrumental settings, most notably the gain setting and filter value. For the low range method, the gain was set to 10 whereas the gain setting was 1 for the high range method. The gain setting establishes the amplification of the detector. The higher the gain setting, the greater the sensitivity of the method (PSA, 2010). The gain ranges are determined based on the concentration range of samples being analyzed. The filter value for the low range method was 32 and 16 for the high range method. The filter value smooths the signal using Box Car integration to dampen the displayed signal (PSA, 2010). The filter value set was the number of points averaged to plot as a single point along the signal curve. The larger the filter value, the greater the amount of smoothing applied to the curve. The filter value was determined by the concentration of samples analyzed. While the methods are capable of

detecting $0.001 \mu\text{g L}^{-1}$ and $0.02 \mu\text{g L}^{-1}$ respectively, sample concentrations reported below the LLOQ were reported as below detection limit (bdl).

Table 2. Calculated detection limits for the full range and low range selenite determination by HG-AFS.

	IDL (Eq. 1)	MDL (Eq. 2)	LLOQ (Eq. 3)
	----- $\mu\text{g L}^{-1}$ -----		
Full Range Method	0.02	0.02	0.05
Low Range Method	0.0008	0.0001	0.0005

3.4 Labware evaluation

Analysis of covariance (ANCOVA) was used for statistical analysis with a response variable of normalized concentration and an interval variable of time. Normalized concentration was used for analysis because the trace metal grade hydrochloric acid used for acidification contains trace levels of Se ($\leq 1 \mu\text{g L}^{-1}$ per manufacturer specification). The variable time was a covariate and reflects conditions under which the experiment was carried out, in this case time points at which samples were allowed to equilibrate. The time for which the samples equilibrated was assumed not to be impacted by the factor levels of the experiment, in this case the normalized concentration. Time alone was not statistically significant for any concentration analyzed with all p-values greater than 0.05 (Table 3). The interaction of treatment (labware used) and time was statistically significant for both the 25 and $50 \mu\text{g L}^{-1}$ model. Silanized glass was statistically different from all other labware tested. Silanized glass, demonstrated a greater ability to maintain concentration over time at all selenite concentrations analyzed and corresponded to the greatest least squares means and smallest standard error. (Table 4). Although the measured concentrations increased over time for samples in silanized glass and polypropylene plastic, the increase was less than 5% and thus within the precision of the instrument.

Silanization of glass creates a hydrophobic barrier that is resistant to most chemicals. The possibility of this barrier scratching in the presence of solids for sorption experiments was a concern. A non-silanized glass vial, a freshly silanized glass vial, and a used silanized glass vial were filled with Gentian violet indicator for twenty-four hours. After this period, the vials were visually assessed for purple staining indicating that dye had sorbed to ion-exchange centers on the glass surface. The non-silanized vial was stained, whereas neither silanized vials were stained. Therefore, we concluded that the silanized layer does not scratch or degrade during sorption experiments with the solid sorbents used in this study.

Table 3. ANCOVA results for labware evaluation at three nominal Se(IV) concentrations.

Nominal Concentration	Model	Time	Treatment	Treatment x Time
----- $\mu\text{g L}^{-1}$ -----	----- p-value -----			
10	0.17	0.34	0.07	0.45
25	<0.0001	0.06	0.005	<0.0001
50	0.02	0.51	0.20	0.001

Table 4. ANCOVA least squares means (LSM) and standard error (St Error) for labware evaluation at three nominal Se(IV) concentrations.

Nominal Concentration	Glass		PP		PTFE		Silanized Glass	
	LSM	St Error	LSM	St Error	LSM	St Error	LSM	St Error
10 $\mu\text{g L}^{-1}$	6.57	-0.02	6.41	0.01	6.41	-0.02	6.99	0.00
25 $\mu\text{g L}^{-1}$	20.67	-0.20	17.56	0.003	17.23	0.03	19.42	0.02
50 $\mu\text{g L}^{-1}$	37.32	-0.18	32.52	0.08	34.78	-0.03	35.63	0.05

PP = polypropylene; PTFE = polytetrafluoroethylene

3.5 Photolysis evaluation

The measured experimental conditions are given in Table 5. The Se(IV) percent recovery was significantly larger ($p = <0.0001$) for samples in the laboratory (102.0%) than for samples in the greenhouse (89.6%), but the presence or absence of light did not have a significant effect ($p = 0.51$). The results of the experiment are considered inconclusive because there was no effect of light on samples in the greenhouse (Figure 4). However, as a precaution all vials were wrapped in foil.

Table 5. Temperature and light intensity in the two locations used to evaluate the effects of light on Se(IV) recovery.

Location	Temperature	Light Intensity
	$^{\circ}\text{C}$	$\mu\text{mol m}^{-2}\text{s}^{-1}$
Laboratory	24	5
Greenhouse	23.5	696

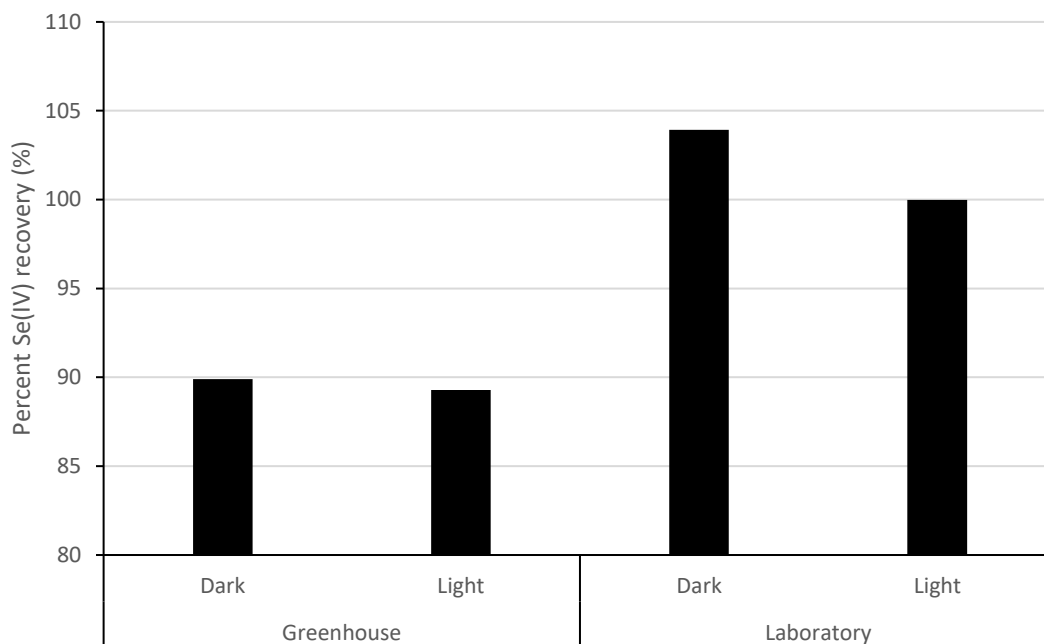


Figure 4. Effect of location (greenhouse or laboratory) and light condition (dark or light) on mean percent Se(IV) recovery.

3.6 Interference of competing ions

The presence of ferric iron and sulfate resulted in suppressed Se(IV) recovery. The average error of all samples with only one interfering ion was less than $0.1 \mu\text{g L}^{-1}$ (Table 6). Hence, the presence of these ions at trace levels was not of analytical concern. Samples with more than one interfering ion had an error of between 0.2 and $0.3 \mu\text{g L}^{-1}$ and may be of concern analytically when selenite concentrations are very small.

Table 6. Average error and standard deviation in Se(IV) determination from dissolved iron and sulfate, alone and in combination. Negative numbers indicate that measured Se(IV) was less than expected.

Ion	Delivered Concentration	Average Error	St Dev
	----- $\mu\text{g L}^{-1}$ -----		
Fe ⁺³	2.5	-0.07	0.06
Fe ⁺³	5.0	-0.11	0.05
SO ₄ ⁻²	125	-0.075	0.002
SO ₄ ⁻²	250	-0.12	0.05
Fe ⁺³ , SO ₄ ⁻²	2.5, 125	-0.12	0.02
Fe ⁺³ , SO ₄ ⁻²	2.5, 250	-0.24	0.03
Fe ⁺³ , SO ₄ ⁻²	5.0, 125	-0.26	0.03
Fe ⁺³ , SO ₄ ⁻²	5.0, 250	-0.29	0.02

4 DISCUSSION

HG-AFS is a sensitive and selective technique for selenite determination. The instrument and method used is selective in that only six elements form a gaseous hydride and each of these elements has a characteristic wavelength of excitation and fluorescence. The detection limits determined for the developed high range method are comparable to limits reported by Corns et al. (1993). Detection limits determined for the low range methods are comparable to limits reported by Weir et al. (1998). Sample stability on the autosampler was an issue that had to be addressed as there was a 5% loss in precision per hour. The presence of iron or sulfate alone resulted in a slight negative bias that was within the range of instrumental precision. The presence of iron and sulfate together also resulted in a small negative bias, between 0.2 and 0.3 $\mu\text{g L}^{-1}$ that could be important for some very low selenite concentration samples. The developed methodology was sensitive for Se(IV) quantitation. Precautions such as placing no more than 25 samples on the autosampler at a time, analyzing other ions in solution, and keeping samples in the dark until acidified will further add to the sensitivity of Se(IV) determinations.

Silanized glass was the most suitable material for labwork. Samples contained in silanized glass had the greatest measured concentration across all time points. Silanized glass corresponded with the greatest least squares means as well as the smallest error. The ability of silanized glass to successfully maintain concentration across time with minimal loss was related to the sealing of ion-exchange centers on the glass surface with polysiloxane chains.

5 CONCLUSIONS

- The methods developed were sensitive for Se(IV) detection with MDLs of $0.0001 \mu\text{g L}^{-1}$ (low range method) and $0.02 \mu\text{g L}^{-1}$ (high range method) and LLOQs of $0.0005 \mu\text{g L}^{-1}$ (low range method) and $0.05 \mu\text{g L}^{-1}$ (high range method). These were similar to reported detection limits for other methods.
- Samples were stable on the autosampler for a period of one hour with <5% concentration loss. During analyses that requires more than an hour to complete, samples were placed on the autosampler at different times to minimize loss.
- Silanized glassware exhibited the least retention of selenite at all time points tested and was selected as the most appropriate labware for selenite work. Further, the hydrophobic barrier created through silanization did not abrade in the presence of the tested solids and thus was suitable for sorption work.
- All samples were wrapped in aluminum foil to minimize the possibility of degradation due to light.
- The presence of Fe^{+3} or SO_4^{-2} in samples did suppress selenite recovery, but the small error ($\leq 0.1 \mu\text{g L}^{-1}$) created by low concentrations of the ions was not of analytical concern. The presence of both ions in the same sample caused slightly greater error ($0.2\text{-}0.3 \mu\text{g L}^{-1}$), which may be of concern analytically. Therefore, all samples were also analyzed for ions of concern in the sorption experiments.

TASK 2. TEMPERATURE DEPENDENT SELENITE SORPTION TO FOUR MINE DRAINAGE SOLIDS AT THREE TEMPERATURES

1 SUMMARY

Task 2 included four planned activities; (1) characterizing solids for physiochemical parameters that may influence sorption, (2) determining the appropriate solid:solution ratio, (3) determining the proper equilibrium time, and (4) conducting isotherms for all solids at three temperatures.

Solid characterization, with the exception of Se, carbon (C), nitrogen (N), and sulfur (S) concentrations, was completed in January – March of 2016. The selenite content of solids was determined in February of 2017 and C, N, and S content was determined in April 2017 upon installation of the Elementar VARIO Max cube. The necessary solid:solution ratio and equilibrium times were evaluated in February and March. Preliminary sorption isotherms were determined in March and April until the HG-AFS and associated autosampler malfunctioned. The isotherm experiments were completed in May following instrument repair.

Linear isotherms were found for O-1 and O-2 at all temperatures and Langmuir isotherms for AMD-1 at all temperatures and AMD-2 at 20° and 30°C. We could not confirm the hypothesis that selenite sorption and temperature are inversely related. Increasing temperature corresponded with decreased sorption constants (K_D) only for the AMD solids which is consistent with selenite sorption being an exothermic process. Increasing temperature resulted in increased sorption for the overburden samples.

2 APPARATUS, MATERIALS, AND EXPERIMENTAL PROCEDURES

2.1 Experimental apparatus

Solution pH was determined using a Mettler Toledo SevenEasy pH meter calibrated using three points. (Mettler Toledo International, Inc. Schwarzenbach, Switzerland). Solution electrical conductivity (EC) was analyzed using a Mettler Toledo SevenCompact conductivity meter calibrated using four points (Mettler Toledo International, Inc. Schwarzenbach, Switzerland). A MARS 5 Microwave (CEM Corporation Mathews, NC) was used to digest of samples for elemental determination. Digested samples were analyzed for aluminum, iron, manganese, magnesium, calcium, and sodium by ICP-OES (Perkin-Elmer Optima DV2100, Perkin-Elmer Corp. Norwalk, CT) and for Se(IV) by HG-AFS (PSA 10.055 Millennium Excalibur, PSA, Orpington, Kent, United Kingdom). Solids were also analyzed for carbon, hydrogen, and sulfur using a Vario MAX cube (Elementar, Langensfeld, Germany).

Selenite was determined with a PSA 10.055 Millennium Excalibur HG-AFS (Orpington, Kent, United Kingdom), a Se boosted discharge hollow cathode lamp with primary and secondary discharges of 20.0

and 25.5 mA respectively, and a PSA 20.400 autosampler as described in Task 1. The full range method was used for all determinations. Homologous polytetrafluoroethylene tubes provided by PSA were used to hold all samples on the autosampler. Supernatants from the sorption experiments were analyzed for iron, aluminum, sulfur, and calcium by ICP-OES (Perkin-Elmer Optima DV2100, Perkin-Elmer Corp. Norwalk, CT) and pH (Mettler Toledo International, Inc. Schwarzenbach, Switzerland).

Glassware was cleaned according to laboratory standards before cleaning in a two stage acid bath. Glassware was first soaked in 7.0 *M* nitric acid for a minimum of twenty-four hours. Glassware was rinsed with distilled deionized water before soaking in 1.0 *M* hydrochloric acid bath for a minimum of twenty-four hours. Glass was rinsed with distilled deionized water and air-dried prior to use.

Glassware was silanized by filling each vial with Sigmacote[®] once the vial was completely dry. After ten seconds, the vial was emptied by pouring all Sigmacote[®] back into its original container. Vials were allowed to air dry before use for a minimum of twenty-four hours.

All reagents used were of analytical grade. Trace metal grade hydrochloric acid (11.65 *M*) for sample acidification and for instrumental blank and wash solutions was purchased from Fisher Scientific (CO, USA). Sodium hydroxide pellets and sodium borohydride powder (99% pure, nitrogen flushed) were purchased from Acros Organic (NJ, USA). A 0.7% m/v sodium borohydride solution was prepared daily by dissolving sodium borohydride powder in distilled deionized water and was stabilized with 0.1 *M* sodium hydroxide prepared with sodium hydroxide pellets. All samples were prepared in 0.1 *M* sodium chloride (Fisher Scientific; CO, USA). A 1,000 mg L⁻¹ selenite standard was purchased from AccuStandard (CT, USA). Sigmacote[®] was purchased from Sigma-Aldrich (MO, USA).

2.2 Sample collection

Two sandstone overburden samples were obtained from a previous study. Sample O-1 was a gray sandstone collected from the Catenary Mine in Eskdale, West Virginia. Sample O-2 was a brown sandstone collected from the Birch River Mine in Cowen, West Virginia. These two samples were selected to represent two common rock types that could come in contact with Se containing alkaline mine water, especially in the southern WV coalfields (Table 7). Gray sandstone is generally unweathered and is used in durable rock fills. The more weathered brown sandstone is the preferred topsoil material during reclamation.

Two solids formed from acid mine drainage treatment were also collected. Sample AMD-1 was collected in October 2015 from a passive wetland treatment system (Wetland 1) from Saint Vincent College in Westmoreland County, PA. The solids were dredged from the wetland in summer of 2015 and were left to

dry in a pile. Samples were collected in five gallon buckets and from various points within the pile. The second solid (AMD-2) was collected for a previous study from an active hydrated lime treatment system from an abandoned mine in Upshur County, WV (Table 7).

Table 7. Description and origins of solids used as sorbents for Se(IV) sorption.

Sample ID	Sample Description	Origin
O-1	Gray Sandstone	Eskdale, WV
O-2	Brown Sandstone	Cowen, WV
AMD-1	Passive Treatment Solid	Latrobe, PA
AMD-2	Active Treatment Solid	Upshur County, WV

2.3 Sample characterization

AMD-1 was air-dried in the West Virginia University (WVU) greenhouse. The solid was passed through a 2-mm sieve before storage. Samples were stored in five gallon plastic buckets at room temperature. All other previously collected samples had been dried and stored in plastic bags at room temperature. All solids were characterized after passing a 2-mm sieve.

Solids were further sieved for use in sorption experiments. Four plastic sieves were stacked in order of decreasing mesh size and placed on an 8" sieve shaker for five minutes (Gilson Company, Inc., OH). The sieve containing the greatest amount of material was selected for each solid. Sieves were washed and dried between each solid to avoid contamination.

2.4 Solution pH and electrical conductivity

Suspension pH was used to determine pH of all solids. A mass of 5.00 ± 0.05 g of material was placed in a plastic soufflé cup. A volume of 5.0 mL of distilled deionized water was added to the soufflé cup. Samples were placed on an oscillating shaker for one hour. After equilibration, samples were analyzed for pH using a Mettler Toledo SevenEasy pH meter. (Mettler Toledo International, Inc. Schwerzenbach, Switzerland). pH was determined for each solid in duplicate.

Solution EC for all solids was determined by adding an additional 5.0 mL of distilled deionized water to the soufflé cup processed for pH. Samples were allowed to equilibrate for one hour. Solution EC was analyzed using a Mettler Toledo SevenCompact conductivity meter. EC was determined for each solid in duplicate.

2.5 Moisture content

Crucibles used in this analysis were heated at 105 °C for two hours and allowed to cool to room temperature in a desiccator. After cooling, crucibles were weighed. A mass of 5.0 ± 0.05 g of material was placed into a crucible. Samples were placed into a drying oven at 105 °C for twelve hours. Samples were removed from the oven and were placed into a desiccator to cool to room temperature. Samples were weighed again, and the percent moisture was calculated by difference. Moisture content was determined for each sample in duplicate.

2.6 Elemental composition

Elemental composition of samples was determined via acid-assisted microwave digestion according to EPA Method 3051A. A mass of 0.50 ± 0.005 g of solid was transferred to a HP-500 Plus™ Teflon digestion vessel. The digestion vessel was held horizontally and the weigh paper was inserted; the vessel was returned to vertical to transfer the solid. This was done to prevent solid from coating the sides of the vessel, which can result in uneven heating during digestion. A volume of 9.0 mL of trace-metals grade 16 *M* HNO₃ and 3.0 mL of trace-metals grade 12 *M* HCl were added to each digestion vessel in a fume hood. The combination of these acids, known as aqua regia, is necessary for proper digestion of samples with high concentrations of iron and aluminum. Vessels were covered with a watch glass and allowed to predigest in the fume hood overnight. This period allowed any vigorous oxidation due to the presence of organic matter to vent before digestion. After pre-digestion, vessels were sealed and digested with microwave heating in a MARS 5 Microwave (CEM Corporation Mathews, NC). The sealed vessels were placed into the microwave six at a time and reached 175 °C in a ten-minute ramp time and were held at constant temperature for 5 minutes. After cooling to room temperature, samples were vented in a fume hood. Samples were filtered (Fisherbrand grade Q2) and diluted to 100.0 mL using distilled deionized water in acid-washed volumetric flasks. Samples were analyzed for aluminum, iron, manganese, magnesium, calcium, and sodium by ICP-OES (Perkin-Elmer Optima DV2100, Perkin-Elmer Corp. Norwalk, CT). Elemental composition was determined using six replicates for AMD-1 and AMD-2. Elemental composition data for the overburden samples were taken from Odenheimer (2015) and used the same procedure.

Selenite content of all solids was determined using the microwave procedure described above. Following digestion samples were analyzed by HG-AFS using the high range method. Samples were digested in duplicate.

2.7 Determination of solid:solution ratios

Before completing the final sorption experiment at varying temperatures, the appropriate solid:solution ratio for each solid and equilibrium time were determined. Following the procedure described in Roy (1991), five solid:solution ratios were tested: 0.2, 0.4, 0.6, 0.8, and 1.0 grams of sorbent per one liter of 0.1 M NaCl solution. While the solids were suspended in solution, 40 mL of solution was transferred to silanized glass vials. The initial Se concentration of solution was prepared to 50 $\mu\text{g L}^{-1}$ using a secondary standard prepared from sodium selenite. Replicate samples (n=12 per solid) were wrapped in aluminum foil and were placed on a rotary shaker for twenty-four hours. Samples were analyzed for selenite by HG-AFS using the high-range method. The percent selenite sorbed was calculated as

$$\% \text{ Sorbed} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (7)$$

where C_i was initial concentration and C_e was the measured equilibrium concentration.

2.8 Determination of equilibration time

Replicate samples (n=8 per solid) containing the proper mass of solid as determined through the solid:solution ratio were prepared to 50 $\mu\text{g L}^{-1}$ Se using a secondary standard prepared from sodium selenite in 0.1 M NaCl. Samples were wrapped in aluminum foil and were placed on a rotary shaker for a 1, 24, 48, and 72 hours. Samples were analyzed by HG-AFS after each equilibration time for total Se using the high-range method. The rate of change was calculated as

$$\% \text{ Change} = \frac{(C_t - C_{t-1})}{C_t} \times 100 \quad (8)$$

where C_t was the equilibrium concentration at the measured time point and C_{t-1} was the equilibrium concentration at the previous time point.

2.9 Isotherm construction and analysis

A 0.1 M NaCl solution was prepared, and the appropriate amount of sorbent as determined by the solid:solution ratio was added. The solution was agitated with a stir bar, and while the solids were suspended in solution, 40 mL of solution was transferred to silanized glass vials. Varying initial selenite concentrations (0, 10, 20, 30, 40 and 50 $\mu\text{g L}^{-1}$) were established in each vial using a secondary standard prepared from sodium selenite in triplicate (n=15 per solid). Each sample was 40 mL in volume.

All vials were wrapped in aluminum foil and were placed on a rotary shaker (Glas-Col; IN, USA) at 30 revolutions per minute for 48 hours. Samples for the 10 $^{\circ}\text{C}$ isotherm were kept in a refrigerator at 8 $^{\circ}\text{C} \pm$

1 °C. Samples for the 20 °C isotherm were kept on the laboratory counter with the room temperature at 20 °C ± 1 °C. Samples for the 30 °C isotherm were equilibrated in an oven kept at 30 °C ± 1 °C.

After equilibration, samples were transferred to homologous polypropylene tubes (Environmental Express; SC, USA) and acidified for selenite determination by HG-AFS. An aliquot was transferred to a polypropylene centrifuge tube and was refrigerated until analysis by ICP-OES for iron, aluminum, sulfur, and calcium content. The pH of all samples was determined before and after equilibrium.

Blank vials without solid underwent the same process. The measured concentration of these vials was used as the initial concentration. The measured concentration of all samples was the equilibrium concentration. Sorbed concentration was calculated as

$$C_S = \frac{(C_I - C_E)}{m} \times V \quad (9)$$

where C_S was the concentration sorbed ($\mu\text{g L}^{-1}$), C_I was the initial concentration determined from the blanks ($\mu\text{g L}^{-1}$), C_E was the equilibrium concentration ($\mu\text{g L}^{-1}$), m was the mass of sorbent (kg), and V was the volume of solution (L). Regression analysis on the initial, linear portion of the isotherm was used to calculate K_D as

$$y = K_D x + b \quad (10)$$

where sorbed concentration was the independent variable (y-axis) and equilibrium concentration was the dependent variable (x-axis). Sorbents were not corrected for moisture content.

3 RESULTS OF SORPTION EXPERIMENTS

3.1 Sorbent characterization

The pH of the brown sandstone (O-2) was a little higher than expected for weathered material (Table 8). The higher pH of the active treatment solid (AMD-2) was likely because this type of solid typically contains unreacted lime coated with iron oxides. This explanation is consistent with the larger EC of AMD-2 (Table 8) and with the elemental concentrations of Ca (Table 9). The un-weathered gray overburden (O-1) had a higher EC than the weathered brown overburden. Both overburden samples had lower moisture contents than did the AMD samples. Sieve size classes for each solid type are also given in Table 8.

Table 8. Properties of the sorbents used in the isotherm experiments.

Sample ID	pH		EC		Moisture Content		Sieve Size
	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean
	standard unit		$\mu\text{S cm}^{-1}$		%		----- mm -----
O-1	7.69	0.02	229	8	0.23	0.01	<0.063
O-2	6.99	0.01	38	1	0.23	0.07	<0.063
AMD-1	6.57	0.06	635	4	12.5	0.7	0.125 - 0.063
AMD-2	8.78	0.01	2,390	42	3.64	0.07	0.125 - 0.063

3.2 Determination of solid:solution ratios

A solid:solution ratio that resulted in 45-55% sorption was used for all sorption experiments (McDonald and Evangelou, 1997). Based on this criteria, a mass of solid per 40 mL vial was 1.9 g for O-1, 1.0g for O-2, 0.05g for AMD-1 and 0.4g for AMD-2.

3.3 Determination of equilibration time

The equilibration time was operationally defined as the minimum amount of time needed to establish a rate of change in solute concentration less than or equal to 5% per 24 hour interval (Roy, 1991). The least reactive solids — O-1 and AMD-1 were used to select an appropriate equilibration. An equilibration time of 48 hours was chosen because there was less than a 5% change at in selenite concentration and to match the labware evaluation experiment.

Table 9. Elemental composition of sorbents used in the sorption experiments.

	Al		Ca		Fe		Mg		Mn		Na		Se(IV)	
	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev
	----- mg kg ⁻¹ -----													
O-1	27,000	4,000	2,300	700	30,000	8,000	4,300	800	300	100	700	200	0.9	0.8
O-2	39,000	19,000	1,800	400	34,000	8,000	4,200	200	400	100	740	70	5	6
AMD-1	11,200	800	1,900	300	67,000	3,000	630	30	314	9	260	60	0.6	0.5
AMD-2	35,000	1,000	128,000	7,000	82,000	4,000	9,000	200	2,800	100	290	90	0.4	0.2

3.4 Isotherms

Linear isotherms were observed for O-1, O-2 AMD-2 at all temperatures; Langmuir isotherms were observed for AMD-1 at all temperatures and for AMD-2 at 20° and 30°C. In order to compare sorption across all solids tested, only the linear portion of each isotherm was plotted for analysis (Figures 5-8). For the Langmuir isotherms, all equilibrium data less than the intersection of the linear increase with the flat, plateau region of the isotherm. The plateau was calculated as the mean of the last five data points. Regression analysis was used to estimate the slope (K_D) and confidence interval for the slope estimate of the linear isotherms (Table 9).

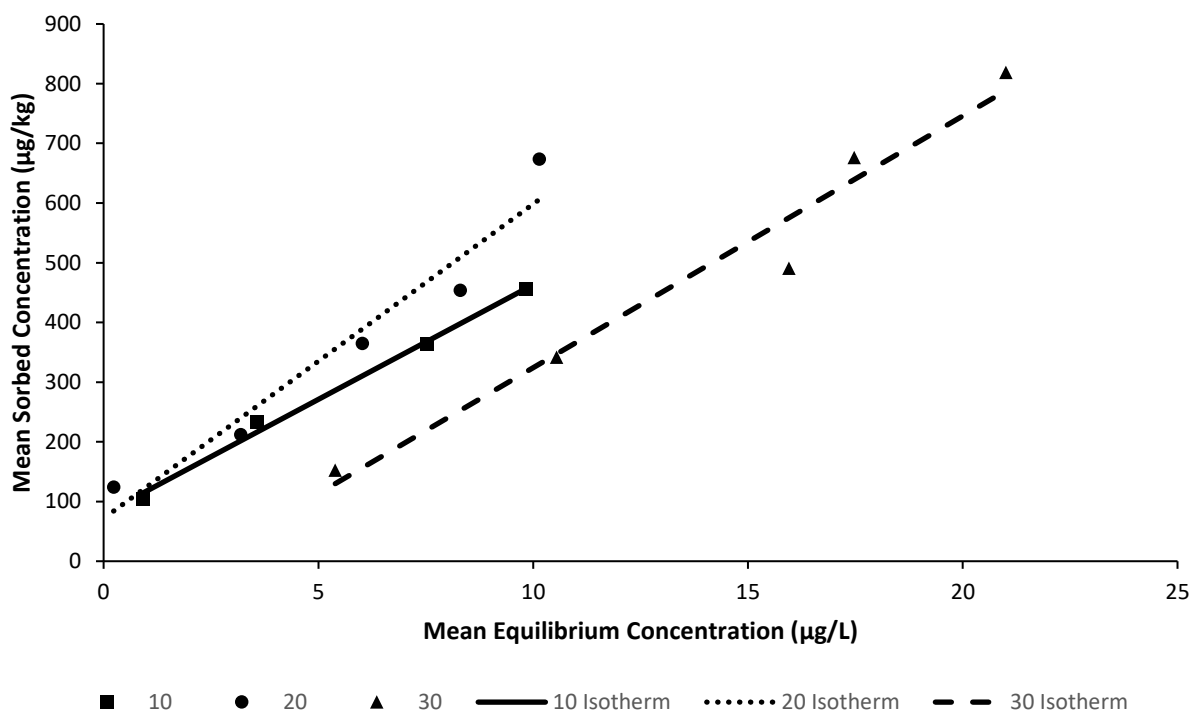


Figure 5. Linear sorption isotherms for the gray sandstone (O-1) at 10, 20 and 30°C.

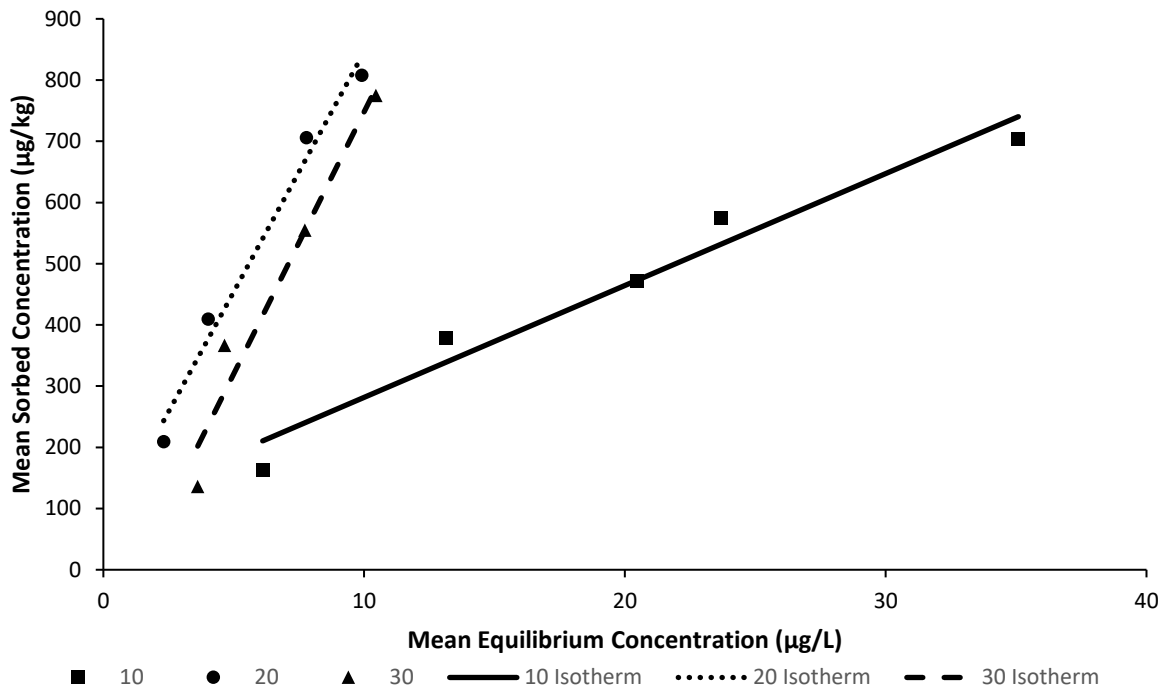


Figure 6. Linear sorption isotherms for the brown sandstone (O-2) at 10, 20 and 30°C.

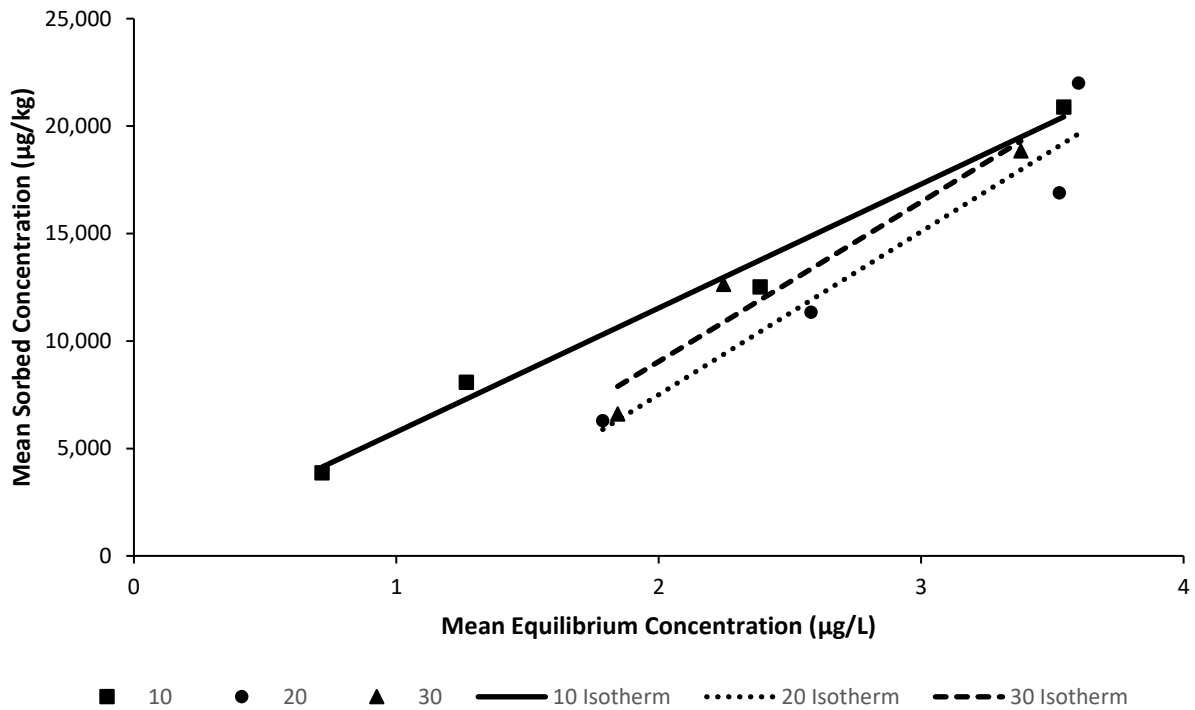


Figure 7. Sorption isotherms for the passive treatment solid (AMD-1) at 10, 20 and 30°C.

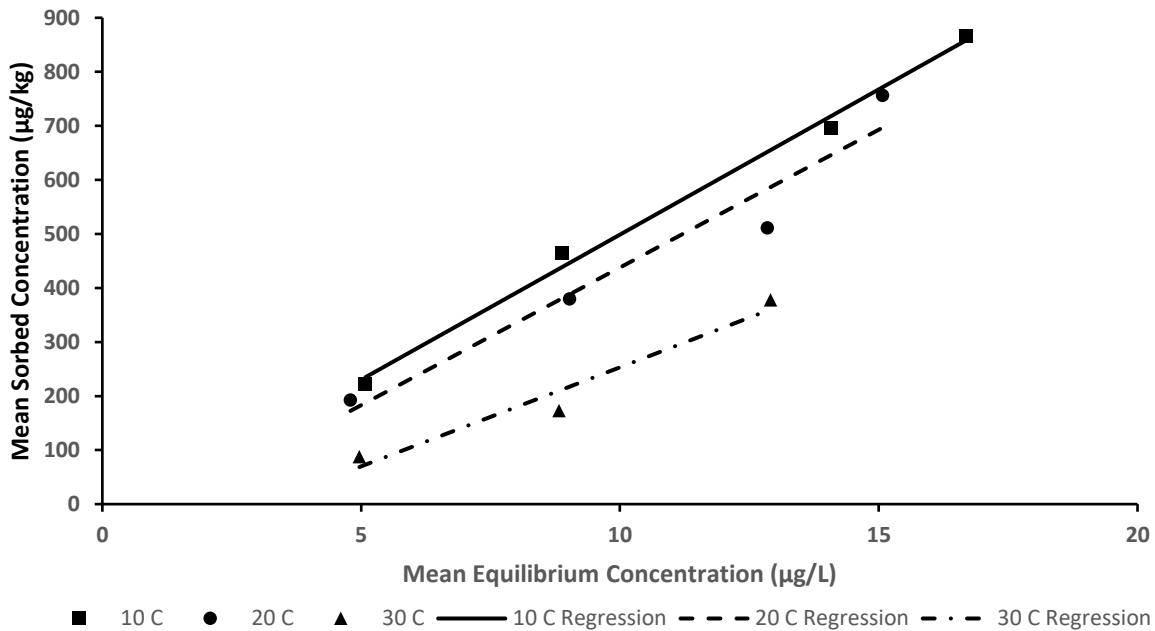


Figure 8. Sorption isotherms for the active treatment solid (AMD-2) at 10, 20 and 30°C.

There was a slight tendency for an inverse relationship between temperature and K_D for O-1, and a strong inverse relationship for AMD-1 (Table 9, Figure 9). Increased temperature leads to a weak increase in K_D for O-2 and there was no relationship between temperature and K_D for AMD-2 (Table 9). The sorption constant for AMD-1 was two orders-of-magnitude larger than for any other solid. The Langmuir plateau corresponds to selenite sorption capacity and which increased as temperature increased (Figure 10). Selenite sorption capacity increased from 20,300 µg/kg at 10°C to 21,400 µg/kg at 20°C to 25,700 µg/kg at 30°C although only 30°C was significantly different from 10°C and 20°C ($\alpha=0.05$).

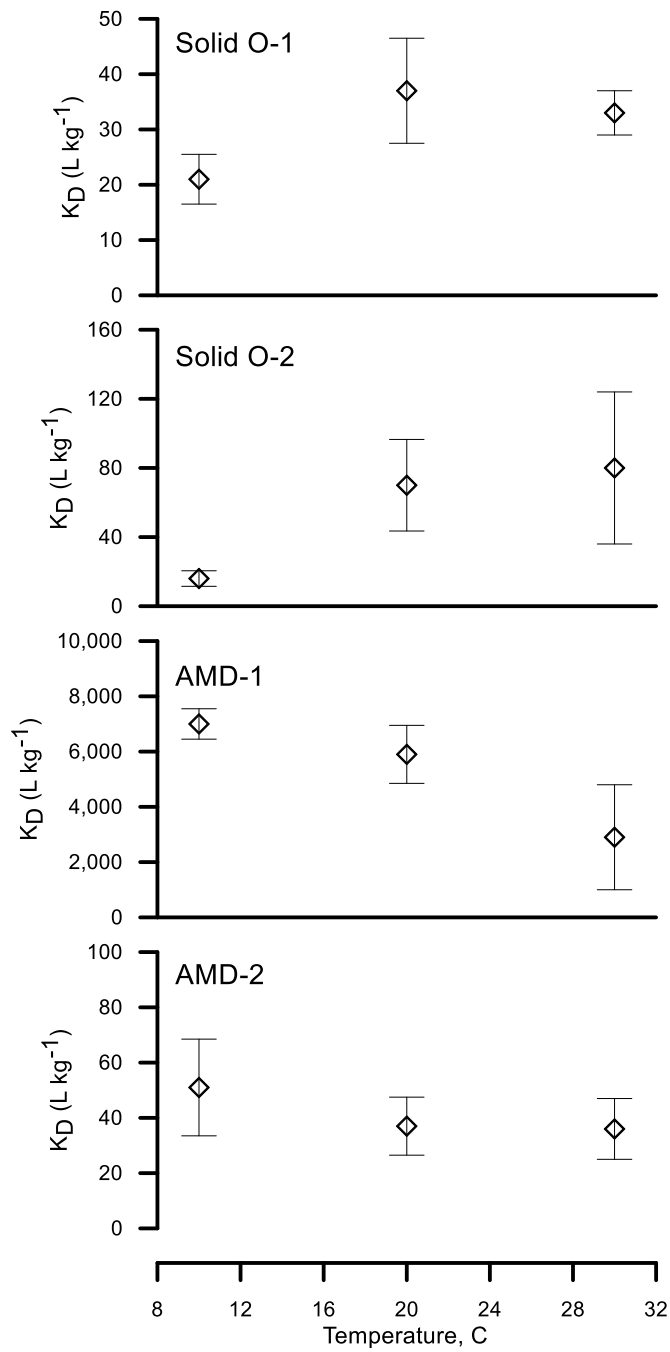


Figure 9. Sorption constant (K_D) and 95% confidence interval (CI) for each solid at each temperature.

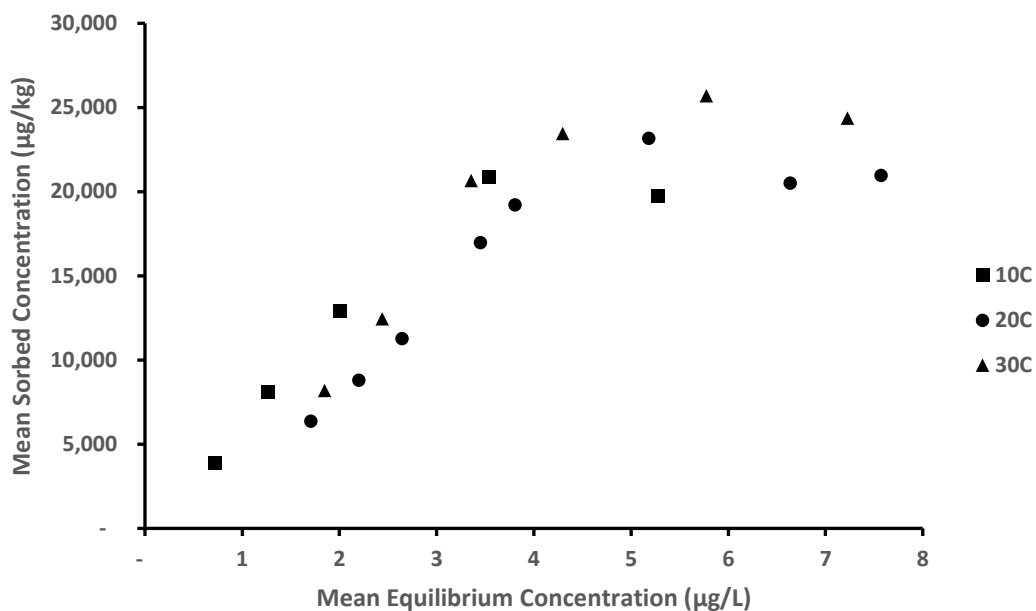


Figure 10. Langmuir isotherms for the passive treatment solid (AMD-1) at 10, 20, and 30°C.

Table 10. Sorption constant (K_D) and confidence interval (CI) for each solid at each temperature. Different superscripted letters on K_D s within a sorbent indicates a significant ($\alpha=0.05$) difference.

	O-1		O-2		AMD-1		AMD-2	
	K_D	C.I.	K_D	C.I.	K_D	C.I.	K_D	C.I.
°C	-----L kg ⁻¹ -----							
10	21 ^b	9	16 ^b	9	7,000 ^a	1,100	51 ^a	35
20	37 ^a	19	70 ^a	53	5,900 ^b	2,100	37 ^a	21
30	33 ^a	8	80 ^a	88	2,900 ^c	3,800	36 ^a	22

There were changes in pH during the sorption experiments (Table 11). For all solids with the exception of AMD-2, these were small (<0.4) but not unimportant because selenite sorption is a pH-dependent process. The largest pH decrease was -0.24 pH units for AMD-2 at 20°C but again was not related to the extent of selenite sorption. Additional study of AMD-2 found that the pH change was a result of the solid itself rather than selenite sorption or artifacts from the vial.

Table 11. Mean pH change and standard deviation for each solid at each temperature. A negative pH change indicates a pH decrease during the experiment.

	O-1		O-2		AMD-1		AMD-2	
	Δ pH	St Dev	Δ pH	St Dev	Δ pH	St Dev	Δ pH	St Dev
$^{\circ}$ C	-----standard units-----							
10	0.26	0.03	0.32	0.04	-0.24	0.07	-1.00	0.2
20	0.23	0.08	0.07	0.06	-0.07	0.05	-1.24	0.03
30	-0.27	0.07	0.03	0.06	0.04	0.04	-1.18	0.03

4 DISCUSSION

Linear isotherms were found for O-1 and O-2 at all temperatures. Langmuir isotherms were found for AMD-1 at all temperatures and AMD-2 at 20 $^{\circ}$ and 30 $^{\circ}$ C. Both linear (Jordan et al., 2013; Kersten and Vlasova, 2009) and Langmuir (Hasan and Ranjan, 2010) isotherm types have been reported. The range of equilibrium concentrations used in this study are comparable to those found where selenium is an element of concern.

We could not confirm our hypothesis that selenite sorption and temperature were inversely related for these mining-related solids. Sorption constants (K_D) decreased with increasing temperature for the two AMD solids, especially for AMD-1 (Table 10, Figure 9), as hypothesized, but tended to increase with increasing temperature for the gray and brown overburden samples (O-1 and for O-2; Figure 8).

Decreased sorption with increased temperature for the AMD solids is consistent with other anion sorption work conducted with other oxides such as goethite (Balistreri and Chao, 1987; Kersten and Vlasova, 2009), anatase (Jordan et al., 2013). It's worth noting that AMD-1 was likely the purest iron phase in our sample set and had the strongest inverse relationship between sorption and temperature. AMD-2 was a mixture of iron oxides and other calcium-containing solids. The two overburden samples were sandstone (quartz) with other unknown iron minerals.

This study is among the first to report on the temperature dependence of Se(IV) sorption to surfaces commonly found in coal mining environments. It suggests that the results from Se(IV) sorption to pure phases (e.g. goethite and anatase) are not readily extrapolated to environments where mixtures of minerals and/or mixed mineral phases are likely to exist. A reasonable next step would be to quantify Se(IV) sorption to actual stream sediments where selenium is known to be a contaminant of concern.

5 CONCLUSIONS

- The sandstone-based overburden samples (O-1, O-2) had smaller sorption constants than the acid mine drainage samples (AMD-1, AMD-2).
- All solids exhibited linear sorption isotherms, except the passive AMD treatment solid which was Langmuir.
- Increasing temperature tended to increase K_D for the overburden samples and decrease K_D for the AMD treatment solids, especially for AMD-1

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APPENDIX

Full Range Method Calibration Means (Figure 1)

Standard (ug/L)	Average Peak Height
0	0.56
12.5	46.88
25	99.48
37.5	159.11
50	211.69

Low Range Method Calibration Means (Figure 2)

Standard (ug/L)	Average Peak Height
0	1.34
2.5	353.28
5	617.99
7.5	909.95
10	1270.68

Stability on Autosampler (Figure 3)

Sample	Time After Calibration	Concentration
Blank	20	0.144101
	40	0.061856
	60	0.062387
10 ppb	20	10.56179
	40	10.48186
	60	9.650047
25 ppb	20	24.71495
	40	23.81396
	60	23.60457
50 ppb	20	48.65789
	40	46.93541
	60	47.32845

Low Range Method (Table 2)

Single 0.2 ppb Sample Analyzed 7 Times	
Rep 1	0.25
Rep 2	0.21
Rep 3	0.19
Rep 4	0.20
Rep 5	0.19
Rep 6	0.19
Rep 7	0.19
Average	0.20
STDEV	0.02

Slope of Calibration	84.49063
Instrument Detection Limit	0.0008
Method Detection Limit	0.0001
Lower Limit of Quantitation	0.0005

Full Range Method (Table 2)

Single 2.0 ppb Sample Analyzed 7 Times	
Rep 1	2.04
Rep 2	2.18
Rep 3	1.81
Rep 4	2.11
Rep 5	1.84
Rep 6	2.01
Rep 7	2.06
Average	2.01
STDEV	0.14

Slope of Calibration	18.87192
Instrument Detection Limit	0.02
Method Detection Limit	0.01
Lower Limit of Quantitation	0.05

Seven 0.2 ppb Samples Analyzed 1 Time	
Sample 1	0.18
Sample 2	0.18
Sample 3	0.19
Sample 4	0.19
Sample 5	0.18
Sample 6	0.18
Sample 7	0.18
Average	0.18
STDEV	0.004

Seven 2.0 ppb Samples Analyzed 1 Time	
Sample 1	1.76
Sample 2	1.82
Sample 3	1.72
Sample 4	1.95
Sample 5	1.67
Sample 6	1.85
Sample 7	1.86
Average	1.81
STDEV	0.09

Lab Ware Evaluation (Tables 3 and 4)

Hour	Treatment	Nominal	Measured
0	Glass	22.67	21.57
0	PP	22.67	21.57
0	PTFE	22.67	21.57
0	Silanize	22.67	21.57
6	Glass	22.67	21.19
6	PP	22.67	19.18
6	PTFE	22.67	19.01
6	Silanize	22.67	20.12
12	Glass	22.67	23.17
12	PP	22.67	18.45
12	PTFE	22.67	19.74
12	Silanize	22.67	21.24
24	Glass	22.67	14.77
24	PP	22.67	17.62
24	PTFE	22.67	17.99
24	Silanize	22.67	22.52
48	Glass	22.67	16.82
48	PP	22.67	22.93
48	PTFE	22.67	21.57
48	Silanize	22.67	22.33

Photolysis Study (Figure 4)

Location	Light	% Recovery
Greenhou	Dark	100.323
Greenhou	Dark	72.942
Greenhou	Dark	92.595
Greenhou	Dark	89.655
Greenhou	Dark	88.599
Greenhou	Dark	95.31
Greenhou	Light	92.35
Greenhou	Light	80.315
Greenhou	Light	93.239
Greenhou	Light	88.629
Greenhou	Light	91.57
Greenhou	Light	89.64
Lab	Dark	104.701
Lab	Dark	107.699
Lab	Dark	103.815
Lab	Dark	103.598
Lab	Dark	105.268
Lab	Dark	98.444
Lab	Light	98.934
Lab	Light	98.7
Lab	Light	97.806
Lab	Light	100.14
Lab	Light	103.559
Lab	Light	100.741

Competing Ions (Table 6)

Ions	Treatment	Measured	BlankCorrected
Se	25	23.49	22.97
Se+Fe	25, 2.5	21.955	21.435
Se, Fe	25, 5.0	21	20.48
Se, SO4	25, 125	21.79	21.27
Se, SO4	25, 250	20.84	20.32
Se, Fe, SO4	25, 2.5, 125	20.71	20.19
Se, Fe, SO4	25, 2.5, 250	17.925	17.405
Se, Fe, SO4	25, 5.0, 125	17.595	17.075
Se, Fe, SO4	25, 5.0, 250	16.885	16.365

Data used to determine optimal solid:solution ratio as described in Section 2.7 page 19.

Passive Treatment Solid	
Solid Solution Ratio	% Sorption
0.2	69.9
0.4	100.07
0.6	100.93
0.8	71.77
1	102.58

Active Treatment Solid	
Solid Solution Ratio	% Sorption
0.2	0
0.4	50.43
0.6	50
0.8	57.56
1	50.37

WV11 Overburden Solid Gray Sandstone	
Solid Solution Ratio	% Sorption
0.2	0.74
0.4	9.39
0.6	13.44
0.8	20.08
1	20.32

WV4 Overburden Solid Brown Sandstone	
Solid Solution Ratio	% Sorption
0.2	4.62
0.4	13.86
0.6	24.89
0.8	33.87
1	45.34

Passive Treatment Solid

Time	Recovery	% Change
1 Hr	31.16	1.155327
24 Hr	30.8	21.07143
48 Hr	24.31	13.20444
72 Hr	21.1	

Active Treatment Solid

Time	Recovery	% Change
1 Hr	35.9	22.11699
24 Hr	27.96	13.26896
48 Hr	24.25	4.28866
72 Hr	23.21	

Brown Sandstone Solid

Time	Recovery	% Change
1 Hr	44.36	24.5266
24 Hr	33.48	27.80765
48 Hr	24.17	3.227141
72 Hr	23.39	

Gray Sandstone Solid

Time	Recovery	% Change
1 Hr	44.36	29.75654
24 Hr	31.16	15.82157
48 Hr	26.23	4.574914
72 Hr	25.03	

Linear isotherm data gray sandstone overburden (Figure 5).

Temp	Mean Equilibrium	Mean Sorbed
C	µg/L	µg/kg
10	0.91	103.86
10	3.57	232.67
10	7.52	363.59
10	9.84	455.22
20	0.23	124.10
20	4.61	181.72
20	6.02	364.60
20	8.31	453.78
20	10.14	673.55
30	5.39	152.48
30	10.54	341.86
30	15.96	490.57
30	17.47	676.12
30	21.00	818.76

Linear isotherm data brown sandstone overburden (Figure 6).

Temp	Mean Equilibrium	Mean Sorbed
C	ug/L	ug/kg
10	6.11	162.83
10	13.13	379.29
10	20.45	472.37
10	23.67	575.02
10	35.09	704.16
20	2.31	209.10
20	4.02	409.25
20	7.79	705.98
20	9.92	807.93
30	3.62	136.11
30	4.64	366.60
30	7.73	554.57
30	10.46	774.88

Linear isotherm data active treatment solid Figure 8.

Temp	Mean Equilibrium	Mean Sorbed
C	ug/L	ug/kg
10	5.08	222.71
10	8.88	463.92
10	14.08	696.37
10	16.70	867.30
20	4.79	192.85
20	9.02	379.94
20	12.85	511.44
30	4.97	87.78
30	8.82	172.85
30	12.91	378.24

Linear isotherm data passive treatment solid (Figure 7),

Temp	Mean Equilibrium	Mean Sorbed
C	µg/L	µg/kg
10	0.72	3857.26
10	1.27	8071.37
10	2.01	12885.64
10	3.54	20882.40
20	1.71	6367.82
20	2.20	8800.00
20	2.65	11278.16
20	3.45	16965.52
20	3.81	19222.99
30	1.85	8195.40
30		6473.56
30	2.44	12450.57
30	3.36	20666.67

Langmuir isotherm for passive treatment solid (Figure 10).

10C		20C		30C	
[Equilibrium]	[Adsorbed]	[Equilibrium]	[Adsorbed]	[Equilibrium]	[Adsorbed]
0.7	3857.3	1.7	6367.8	1.8	8195.4
1.3	8071.4	2.2	8800.0	2.4	12450.6
2.0	12885.6	2.6	11278.2	3.4	20666.7
3.5	20882.4	3.5	16965.5	4.3	23457.5
5.3	19750.2	3.8	19223.0	5.8	25701.1
		5.2	23163.2	7.2	24367.8
		6.6	20514.9		
		7.6	20965.5		