

# Geochemistry of Selenium in the Residual from Biologically Treated Mine-Impacted Waters

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## Introduction

Although selenium (Se) is an essential element for human, animal and vegetation health, an over- or underabundance may cause adverse health effects and ecological problems. Due to the onset of industrialization, Se has become a contaminant of concern in many parts of the world, including North America. It is naturally occurring in many environments and can become mobile under the right chemical conditions, potentially affecting aquatic habitats and drinking-water sources. While Se occurs naturally at elevated concentrations in sediments, soils and rocks, many anthropogenic activities have been shown to facilitate its mobility. Mining, agriculture and nuclear-power generation have all been demonstrated to increase the potential for mobilizing Se into both groundwater and surface water (Chapman et al., 2010). Of particular importance to British Columbia (BC), elevated Se concentrations in the environment as a result of mining practices have been documented in both Canada and the United States.

Once Se reaches the aquatic environment, it can quickly attain high concentrations due to rapid bioaccumulation within food chains (Lemly, 2004). Selenium in high concentrations can be fatal and, even in lower doses, has the potential to negatively affect human health and reproduction in fish, birds, amphibians and reptiles (Chapman et al., 2010). For example, larval deformities in northern pike were attributed by Muscatello et al. (2006) to exposure to Se in mining effluent from a uranium operation in Saskatchewan. Holm et al. (2003) described harmful impacts of elevated Se from active coal mining on wild rainbow trout and brook trout. Moreover, Se deficiencies can result in humans experiencing growth retardation and impaired bone metabolism (Kang et al., 2013).

Selenium mobility is directly related to the redox state, which controls the speciation in aqueous solution; the sorption properties of the coinciding solid state; and the stability of Se minerals (White and Dubrovsky, 1994). In general, the more oxidizing the environment is, the more mobile Se can be, with the solid-state species of Se occurring under reducing conditions (White et al., 1991). A significant control on Se mobility is the tendency for the element to adsorb onto mineral surfaces. The extent of adsorption is largely dependent on pH, redox conditions and adsorption-site density, with either a decrease in pH or the presence of mildly oxidizing conditions causing a higher rate of Se adsorption (Balistrieri and Chao, 1990). In the aqueous phase, Se species consist of selenate (Se VI) and selenite (Se IV). Selenite adsorbs much more strongly than selenate, with the presence of each species dependent upon the redox conditions of the system (Neal and Sposito, 1989). The reduction and oxidation of Se can occur in the absence of microbes, but the reaction rates are often faster when microbially mediated (Dowdle and Oremland, 1998).

Although the release of Se from industrial wastes to natural waterways and associated impacts are documented (Muscatello et al., 2006; Chapman et al., 2010), technology exists to actively remove Se from industrial effluents. Suspended-growth biological wastewater-treatment systems are currently being used as a way to remove Se from contaminated waters (Lenz et al., 2008; Jain et al., 2015). While wastewater treatment has been proven effective in removing Se from the water, it produces a sludge residual with high concentrations of Se that requires disposal or tertiary treatment. Due to the recent emergence of this technology, there has been little research into the potential for Se to remobilize from a biologically fixed state (i.e., in sludge), and the risks associated with landfilling of this material are not understood.

The purpose of this research is to determine the Se speciation within the solid-phase fraction of the residual produced from biological wastewater treatment, and to advance the understanding of mobilization mechanisms

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within this residual. By addressing both aspects, it will be possible to determine the conditions under which the risk of remobilization is elevated and precisely which Se species are the most vulnerable. Understanding the geochemistry of Se mobility and transport is essential to the development of strategies for mitigating the negative effects of Se in the environment.

The specific objectives of this research are to

- characterize the occurrence of Se in the solid phase of the sludge/residual, specifically the oxidation state(s);
- gain an understanding of the mobility controls on Se within the residual by conducting a suite of aqueous geochemical batch experiments; and
- relate the solid-phase fraction of Se to the results of the batch experiments, to learn if preferential species mobilization occurs under different oxidation pathways when multiple species are present in the residual.

## Methods

### Bulk Characterization

Residual samples were collected from a suspended-growth biological treatment system for mine-impacted waters and were submitted to ALS Laboratories in Vancouver, BC for analysis of 35 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Th, Ti, Tl, U, V, W, Zn) by aqua-regia digestion and for Se content by four-acid digestion. Organic content was estimated by measuring S as  $\text{SO}_4$  using a carbonate-leach analysis, and S as  $\text{S}_2$  and C concentrations by LECO combustion analysis. By having a bulk chemical characterization of the residual, more detailed characterization methods could be further refined in order to optimize the characterization process. Figure 1 is a photo of the residual sample.

### Sequential-Extraction Procedures

Sequential-extraction procedures (SEP) were carried out in order to determine which Se species were present in the residual and their relative abundances. The method used was based on a study by Wright et al. (2003), who compared two different methods of sequential extraction for Se in soils and sediments. The method identified as most relevant was originally developed by Zhang and Moore (1996); it was then modified for this study by adding a step to target acid-volatile sulphide compounds, which was identified by Chao and Sanzalone (1989) to also remove selenide compounds. The need for the selenide step was motivated by a study by Lenz et al. (2008) that used X-ray absorption near-edge structure (XANES) analysis to critically evaluate the accuracy of the sequential-extraction procedure and found that elemental Se was overestimated due to the concurrent mobilization of selenide with the intended mobilization of elemental Se.



**Figure 1.** Residual from biological treatment of mine-impacted waters, showing evidence of Fe oxidation on the edges.

Residual samples were stored in resealable plastic bags at  $4^\circ\text{C}$  until analysis to limit microbial activity. All reagents used were analytical grade and, due to the oxidation sensitivity of the residual, all solutions used were prepared in 1 L polyethylene bottles under an  $\text{N}_2$  atmosphere and bubbled with  $\text{N}_2$  gas for 10 minutes to ensure that all oxygen was removed from solution. All sample preparation and handling was conducted under  $\text{N}_2$  atmosphere to prevent oxidation of the residual. Six replicates of each sample were prepared by placing 6 g of residual in separate 50 mL centrifuge tubes. Following each extraction step, the solid fraction from one replicate was set aside and preserved for solid-state characterization. After each step, the samples were centrifuged at 10 000 rpm for 10 minutes and the supernatant decanted to a 50 mL test tube. Following this, the samples were diluted with 10 mL of de-ionized water, stirred for 5 minutes and centrifuged a second time. The second supernatant was combined with the first in the 50 mL test tube. The supernatant was then filtered using a  $0.45\ \mu\text{m}$  syringe filter, diluted with 2% nitric acid to reach a 1 in 10 dilution factor and stored at  $4^\circ\text{C}$  until analysis. Table 1 provides a summary of the five steps used and the Se species targeted by each step.

**Table 1.** Reagents used and targeted Se species for each of the fractions in the sequential-extraction procedure.

Fraction	Concentration	Reagent	Targeted Se species
F1	0.25 M	KCl	Selenate
F2	0.1 M	$\text{K}_2\text{HPO}_4$	Selenite
F3	4 M	HCl	Selenide
F4	0.25 M	$\text{Na}_2\text{SO}_3$	Elemental Se
F5	5%	NaOCl	Organoselenium

**Fraction F1:** 0.25 M KCl was added to each 6 g sample at a 1 in 8 solid:solution ratio and the sample stirred with a glass rod for 2 minutes, capped, placed on the shaker bench at 300 rpm for 5 minutes and left at room temperature for 2 hours.

**Fraction F2:** 0.1 M  $K_2HPO_4$  was added to each 6 g sample at a 1 in 8 solid:solution ratio and the sample adjusted to a pH of 8 using 6 M HCl, stirred with a glass rod for 2 minutes, placed on the shaker bench at 300 rpm for 5 minutes and left at room temperature for 2 hours.

**Fraction F3:** 4 M HCl was added to each sample at a 1 in 8 solid:solution ratio and the sample placed on the shaker bench at 300 rpm for 5 minutes and then in a hot-water bath at 95°C for 45 minutes. Due to the presence of iron sulphides in the residual, considerable volatilization of sulphur gas was observed after the addition of HCl. Because of this, stirring was not required and the 50 mL centrifuge tubes were capped immediately following the addition of the reagent.

**Fraction F4:** 0.25 M  $Na_2SO_3$  was added to each sample at a 1 in 8 solid:solution ratio and the sample adjusted to a pH of 7 using 6 M HCl, stirred with a glass rod for 2 minutes and placed on the shaker bench at 300 rpm for 4 hours.

**Fraction F5:** 4% NaOCl was added to each sample at a 1 in 20 solid:solution ratio and the sample stirred with a glass rod for 2 minutes and placed in a hot-water bath for 1 hour. Zhang and Moore (1996) originally used a 1 in 4 solid:solution ratio for this step, but not all of the organoselenium was thought to have mobilized after a trial run of this method. Consequently, the solid:solution ratio was decreased in this study so more reactant was available.

Following the SEP, the supernatant was analyzed for Se and 41 additional elements (Li, Be, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hg, Tl, Pb, Th and U) using inductively coupled plasma–mass spectrometry (ICP-MS) in the 4D Laboratories at Simon Fraser University.

### Batch Experiments

Geochemical batch experiments were conducted on the residual (RES) and four Se standards ( $Na_2SeO_3$ ,  $SeS_2$ ,  $Se^0$  and ZnSe) to evaluate Se oxidation. The RES and  $SeS_2$  experiments were conducted simultaneously for 64 and 46 days, respectively. The experiments for the remaining standards were conducted approximately 10 weeks later for a total of 25 days. Batches were sampled on a 2 or 3 day interval for the first 2 weeks and then approximately every 4 days for the remainder of the experiments.

Three oxidants were used ( $O_2$ ,  $Fe^{3+}$  and  $NO_3^-$ ) to simulate mildly oxidizing or highly oxidizing conditions. For each

of the redox conditions, the pH was either left at the natural pH of the solution or controlled with HCl at pH 2.5. Table 2 provides a summary of the redox and pH conditions simulated for each sample. Iron III and nitrate solutions were prepared in an  $N_2$  atmosphere and then bubbled with  $N_2$  gas for 10 minutes to ensure the intended oxidant was isolated

**Table 2.** Summary of the samples subjected to batch experiments, the oxidant type and concentration associated with each one, and the corresponding pH of each batch reactor.

Sample	Oxidant	Concentration	pH
RES	$O_2$	Open to atm.	Natural
RES	$O_2$	Open to atm.	2.5
RES	$O_2$	Closed to atm.	Natural
RES	$O_2$	Closed to atm.	2.5
RES	$NaNO_3$	1.0 mmol	Natural
RES	$NaNO_3$	1.0 mmol	2.5
RES	$NaNO_3$	100 mmol	Natural
RES	$NaNO_3$	100 mmol	2.5
RES	$FeCl_3$	0.1 mmol	Natural
RES	$FeCl_3$	0.1 mmol	2.5
RES	$FeCl_3$	10 mmol	Natural
RES	$FeCl_3$	10 mmol	2.5
$SeS_2$	$O_2$	Open to atm.	Natural
$SeS_2$	$O_2$	Open to atm.	2.5
$SeS_2$	$O_2$	Closed to atm.	Natural
$SeS_2$	$O_2$	Closed to atm.	2.5
$SeS_2$	$NaNO_3$	1.0 mmol	Natural
$SeS_2$	$NaNO_3$	1.0 mmol	2.5
$SeS_2$	$NaNO_3$	100 mmol	Natural
$SeS_2$	$NaNO_3$	100 mmol	2.5
$SeS_2$	$FeCl_3$	0.1 mmol	Natural
$SeS_2$	$FeCl_3$	0.1 mmol	2.5
$SeS_2$	$FeCl_3$	10 mmol	Natural
$SeS_2$	$FeCl_3$	10 mmol	2.5
$Na_2SeO_3$	$O_2$	Closed to atm.	Natural
$Na_2SeO_3$	$O_2$	Closed to atm.	2.5
$Na_2SeO_3$	$NaNO_3$	1.0 mmol	Natural
$Na_2SeO_3$	$NaNO_3$	1.0 mmol	2.5
$Na_2SeO_3$	$FeCl_3$	0.1 mmol	Natural
$Na_2SeO_3$	$FeCl_3$	0.1 mmol	2.5
$Se^0$	$O_2$	Closed to atm.	Natural
$Se^0$	$O_2$	Closed to atm.	2.5
$Se^0$	$NaNO_3$	1.0 mmol	Natural
$Se^0$	$NaNO_3$	1.0 mmol	2.5
$Se^0$	$FeCl_3$	0.1 mmol	Natural
$Se^0$	$FeCl_3$	0.1 mmol	2.5
ZnSe	$O_2$	Closed to atm.	Natural
ZnSe	$O_2$	Closed to atm.	2.5
ZnSe	$NaNO_3$	1.0 mmol	Natural
ZnSe	$NaNO_3$	1.0 mmol	2.5
ZnSe	$FeCl_3$	0.1 mmol	Natural
ZnSe	$FeCl_3$	0.1 mmol	2.5

Abbreviations: 'Closed to atm.', closed to atmosphere; 'Open to atm.', open to atmosphere; 'RES', residual.

in solution. For the oxygen experiments, de-ionized water was used and either left open to the atmosphere to simulate highly oxidizing conditions or sealed to limit the oxygen available and simulate mildly oxidizing conditions.  $\text{FeCl}_3$  was used to prepare 0.1 mmol (mildly oxidizing) and 10 mmol (highly oxidizing) iron solutions, and  $\text{NaNO}_3$  was used to prepare 1.0 mmol (mildly oxidizing) and 100 mmol (highly oxidizing) nitrate solutions. All chemicals used were analytical grade. Following the first round of experiments, the highest Se mobilization was observed under mildly oxidizing conditions; therefore, only the lower concentration of the two oxidants was used for the remaining experiments.

Residual samples were prepared by freezing with liquid nitrogen and grinding to approximately 10  $\mu\text{m}$ . Each batch reactor was prepared using a 500 mL resealable polyethylene bottle. The batch reactors can be seen in Figure 2. A 1:10 solid:solution ratio was prepared by adding 30 g of sample to 300 g of oxidizing solution. For the Se standards, the weight used was calculated to equal the molarity of Se present in 30 g of the residual, and 300 g of oxidizing solution was used to ensure the same Se:solution ratio. The batch reactors were left at room temperature for the duration of the experiment and hand shaken after each sampling event.



**Figure 2.** Selection of batch reactors used to evaluate Se oxidation.

**Table 3.** Summary of the residual samples analyzed using X-ray absorption near edge structure (XANES) analysis at the Canadian Light Source and the Advanced Photon Source, their associated valence state and the corresponding experiments.

Light source	Sample name	Experiment description
CLS	RES 2_1	Starting residual sample
CLS	RES 2_2	Starting residual sample - duplicate
CLS	RES 2_3	Starting residual sample - duplicate
CLS	O2-O	$\text{O}_2$ oxidant - open to atmosphere
CLS	O2-O 2.5	$\text{O}_2$ oxidant - open to atmosphere with pH at 2.5
CLS	O2-C	$\text{O}_2$ oxidant - closed to atmosphere
CLS	O2-C 2.5	$\text{O}_2$ oxidant - closed to atmosphere with pH at 2.5
CLS	NO3 1.0	$\text{NO}_3$ oxidant using 1.0 mmol $\text{NaNO}_3$
CLS	NO3 1.0 2.5	$\text{NO}_3$ oxidant using 1.0 mmol $\text{NaNO}_3$ with pH at 2.5
CLS	NO3 100	$\text{NO}_3$ oxidant using 100 mmol $\text{NaNO}_3$
CLS	NO3 100 2.5	$\text{NO}_3$ oxidant using 100 mmol $\text{NaNO}_3$ with pH at 2.5
CLS	Fe 0.1	Fe oxidant using 0.1 mmol $\text{FeCl}_3$
CLS	Fe 0.1 2.5	Fe oxidant using 0.1 mmol $\text{FeCl}_3$ with pH at 2.5
CLS	Fe 10	Fe oxidant using 10 mmol $\text{FeCl}_3$
CLS	Fe 10 2.5	Fe oxidant using 10 mmol $\text{FeCl}_3$ with pH at 2.5
APS	RES 2	Starting residual sample
APS	RES 2_B	Starting residual sample - duplicate
APS	RES 3	Starting residual sample - duplicate
APS	F1	Residual following Fraction 1 of the SEP (targets selenate)
APS	F2	Residual following Fraction 2 of the SEP (targets selenite)
APS	F3	Residual following Fraction 3 of the SEP (targets selenides)
APS	F4	Residual following Fraction 4 of the SEP (targets elemental)
APS	F5	Residual following Fraction 5 of the SEP (targets organic)

Prior to each sampling event, the pH and the oxidation-reduction potential (ORP) of the solution were measured and recorded. In the controlled pH experiments, HCl was added prior to sampling to adjust the pH to 2.5. The solution was then sampled using a syringe and a 0.45 µm filter. Following this, three separate 1 mL aliquots of the supernatant were transferred to 15 mL test tubes and diluted to a ratio of 1 in 10 with either 2% nitric acid for analysis of cations by inductively coupled plasma–emission spectrometry (ICP-ES) and ICP-MS, or de-ionized water for analysis of anions by ion chromatography. At the end of the experiments, the solid-phase fraction was retained for Se-species characterization.

## X-ray Absorption Near Edge Structure

X-ray absorption near edge structure (XANES) analysis was performed at the Canadian Light Source (CLS) in Saskatoon, SK and the Advanced Photon Source (APS) in Chicago, IL to characterize the Se speciation in the residual before and after the batch and SEP experiments. The first run was performed at the CLS and included the starting residual and the samples associated with the batch experiments. The second run was performed at the APS and included samples associated with the SEPs and replicate samples of the starting residual. Table 3 provides a summary of the samples analyzed at each light source and their associated experiments.

In addition to the samples, a series of Se standards was run for the purpose of linear combination fitting. This method fits the known spectra of the standards to the unknown composition of the residual in order to determine the relative amounts of each Se species in the residual. While this method can identify the composition of an unknown sample accurately, it requires that the general composition of the material be known, to account for the major Se species, so that the appropriate standards are selected. Based on the bulk characterization performed, ten Se standards were identified to be of interest and were run at the CLS and the APS. Table 4 provides a summary of these standards.

In both cases, samples were shipped to the light source at a temperature of 4°C and kept at that temperature until analysis to limit biological activity and subsequent sample oxidation. Samples were prepared using Teflon® washers sealed in Kapton® tape, and the standards were prepared by grinding the sample to a fine powder that was spread on and sealed between layers of Kapton tape.

### Se K-Edge Data Collection

#### Canadian Light Source

Bulk Se K-edge XANES spectra were collected on the very sensitive elemental and structural probe employing radiation from a synchrotron (VESPERS) 07B2-1 beamline at the Canadian Light Source. Samples were positioned in

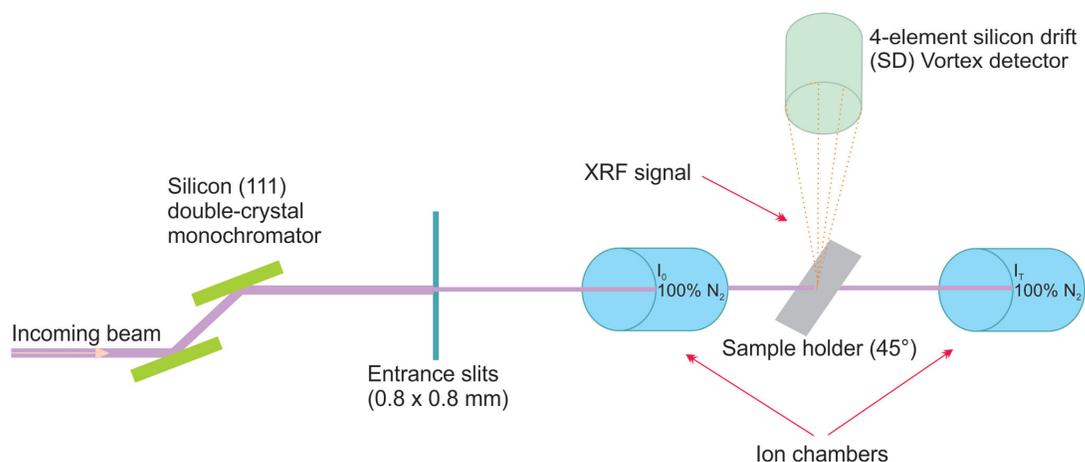
front of the X-ray beam at an angle of 45°. The XANES spectra of the samples were collected in fluorescence mode using a four-element silicon drift (SD) Vortex detector. The spectra of the Se standards were collected in both transmission and fluorescence modes. Spectra were collected from ~200 to ~250 eV above the Se K-edge absorption edge (12658 eV), with a step size of 0.5 eV near the edge. The energy range was selected using a silicon (111) double-crystal monochromator, which provided a monochromatic flux of ~10<sup>10</sup> photons/sec. The beam size was set to 0.8 mm wide and 0.8 mm tall. A Se reference standard was run periodically between samples for beamline energy calibration. Ion chambers were filled with 100% N<sub>2</sub> gas. Samples were initially measured by performing three scans on three separate spots, for a total of nine scans. Due to evidence of beam damage in some samples, a second run was performed with one scan at nine separate spots, for a total of nine scans. Figure 3 provides a schematic representation of the experimental set-up that was used for XANES analysis on the VESPERS beamline.

#### Advanced Photon Source

Bulk Se K-edge XANES spectra were collected on a bending magnet beamline (9BM) at the Advanced Photon Source. Samples were positioned in front of the X-ray beam at an angle of 45°. XANES spectra of the samples were collected in fluorescence mode using a four-element silicon drift (SD) Vortex detector. The spectra of the Se standards were collected in both transmission and fluorescence modes. Spectra were collected from ~200 to ~250 eV above the Se K-edge absorption edge (12658 eV), with a step size of 0.5 eV near the edge. The energy range was selected using a silicon (111) double-crystal monochromator, which provided a monochromatic flux of ~10<sup>10</sup> photons/sec. The beam size was set to 0.3 mm wide and 0.3 mm tall. A Se reference standard was run concurrently with samples for beamline energy calibration. Ion chambers were filled with one-third Ar gas and two-thirds N<sub>2</sub> gas. Three layers of

**Table 4.** Summary of the Se standards analyzed using X-ray absorption near edge structure (XANES) analysis at the Canadian Light Source and the Advanced Photon Source, and their associated valence state.

Standard	Se species
Barium selenate	Se <sup>6+</sup>
Sodium selenite	Se <sup>4+</sup>
Elemental Se	Se <sup>0</sup>
Selenium sulphide	Se <sup>4+</sup>
Iron selenide	Se <sup>2-</sup>
Zinc selenide	Se <sup>2-</sup>
Copper selenide	Se <sup>2-</sup>
Seleno-DL-cystine	Se <sup>2-</sup> (organoSe)
Seleno-L-methionine	Se <sup>2-</sup> (organoSe)
Seleno-cystamine	Se <sup>2-</sup> (organoSe)



**Figure 3.** Schematic of the experimental set-up used on the VESPERS beamline at the Canadian Light Source, Saskatoon, SK.

thick aluminum foil were placed over the detector to mitigate detector saturation from high Fe content in the samples. Residual samples were measured by conducting two scans on three separate spots on each sample to avoid beam damage. Figure 4 provides a schematic representation of the experimental set-up that was used for XANES analysis on the 9BM beamline.

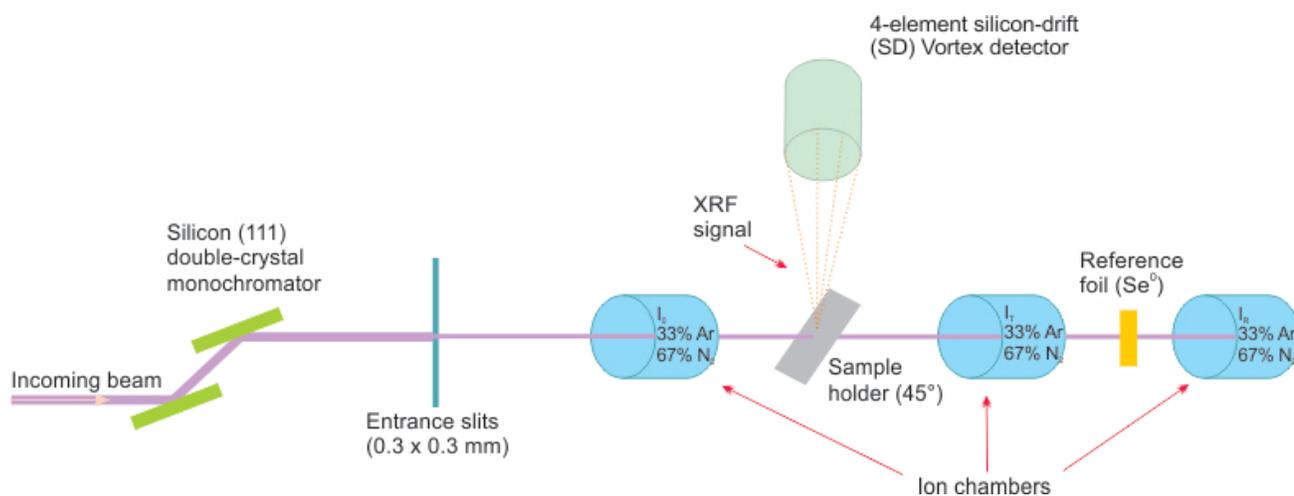
### Future Work

The experimental portion of this study is complete and analysis of the supernatant from the batch experiments for cations and anions is underway. The data obtained from the XANES work will be analyzed using a technique known as linear combination fitting (LCF), where the spectra from known Se standards will be fitted to the unknown residual samples to determine the relative proportions of each Se species. Modelling of the batch experiments will be done in Geochemists Workbench to determine reaction rates for the

oxidation of Se in the residual. Conclusions can then be drawn with regards to which Se species are most vulnerable to mobilization under the specific conditions of the experiments. Once the speciation and mobilization mechanisms are better understood, this information can be used to develop an optimal sludge-management plan to minimize associated potential environmental risks. The increased understanding of Se behaviour can also aid in the development of further remediation technologies and support the decision-making process where risk-based management is optimal.

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**Figure 4.** Schematic of the experimental set-up used on the 9BM beamline at the Advanced Photon Source, Chicago, IL.

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