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1. INTRODUCTION

Selenium has the potential to be extremely toxic in high concentrations and is of particular concern due to its propensity to bioaccumulate within food chains. Mining activities can result in elevated levels of selenium in surrounding surface water bodies due to runoff from waste rock piles. Bacterially-mediated redox based methods are used to treat the mine-impacted water but produce a solid state residual which contains elevated selenium concentrations. **This research aims to understand how selenium occurs within the solid phase of the residual from wastewater treatment, and under what conditions it may remobilize.**

2. GEOCHEMISTRY OF SELENIUM

Four major selenium species in nature:

- Se⁶⁺ - Selenate (SeO₄²⁻)
- Se⁴⁺ - Selenite (SeO₃²⁻)
- Se⁰ - Elemental (multiple allotropes)
- Se²⁻ - Selenide (metal selenides and organics)

Selenium mobility is directly related to the redox state of the environment: **OXIDIZING = MOBILE**

Selenite has a higher affinity for adsorption, and will form inner-sphere complexes with the adsorption surface. Selenate adsorbs weakly as an outer sphere complex, held to the surface by electrostatic attraction.

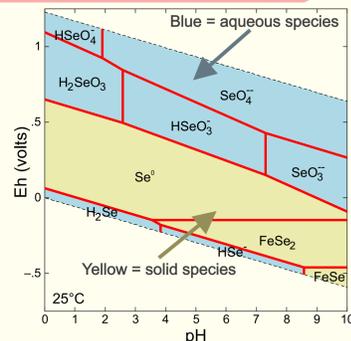


Figure 4. Thermodynamic stability diagram for selenium in a system with iron present. The y-axis represents the oxidation-reduction potential of the system.

3. RESEARCH GOAL & OBJECTIVES

Characterize the occurrence of selenium in the solid-phase of the residual (oxidation states)

Gain understanding of the mobility controls on selenium within the residual by conducting aqueous geochemical batch experiments

Relate the speciation in the solid-phase to the batch experiments and learn if preferential species mobilization occurs under different oxidation pathways

4. METHODOLOGY

Batch Experiments

Three oxidants were used to simulate mildly or highly oxidizing conditions and either the natural pH of the system or a controlled pH of 2.5 (Figure 5). For the oxygen experiments, mildly oxidizing conditions were simulated by sealing the batch reactor and highly oxidizing by leaving it open to provide an unlimited amount of oxygen.

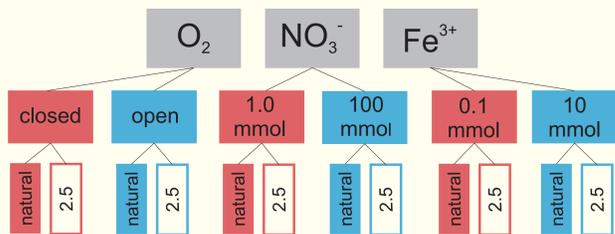


Figure 5. Simulated redox and pH scenarios for the batch experiments. For each oxidant, 1 mildly oxidizing and 1 highly oxidizing situation was simulated at 2 different pH's

X-ray Absorption Near Edge Structure (XANES)

Experiments were performed at the Canadian Light Source and the Advanced Photon Source using the VESPERS and 9BM beamlines, respectively. In addition to residual samples, 10 selenium standards were run for the purpose of comparison: BaSeO₄, Na₂SeO₃, Se⁰ (grey), SeS₂, FeSe, ZnSe, CuSe, seleno-DL-cystine, seleno-L-methionine and seleno-cystamine.

Data collected in fluorescence mode using a 4-element Vortex detector.

Energy range (200eV to 250eV above the Se K-edge absorption edge) selected using a silicon (111) double crystal monochromator.

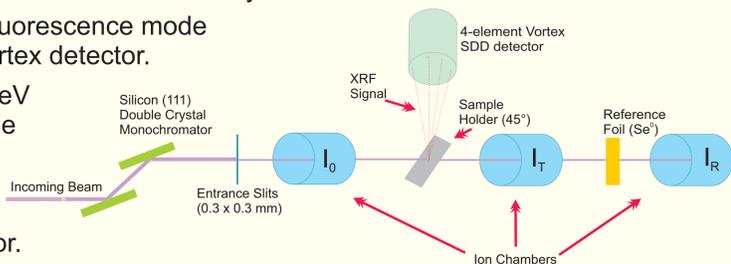


Figure 6. Schematic of the experimental set up used on 9BM at the APS. Experimental configuration at the Canadian Light Source was similar, but lacked the third ion chamber (I_R).



Figure 1. Residual sample taken from the biological treatment plant.

Figure 2. Batch reactors for select redox-pH experiments.

Figure 3. Experimental set up on 9BM at the Advanced Photon Source.

5. PRELIMINARY RESULTS & DISCUSSION

Batch Experiments

Highest concentrations of selenium were observed under mildly oxidizing conditions using all three oxidants (O₂, NO₃⁻ and Fe³⁺) (Figure 7).

Low pH (2.5) may inhibit the mobility of selenium in the residual with very little fluctuation observed under both mildly and highly oxidizing conditions using all three oxidants (Figure 7).

Highly oxidizing conditions may also inhibit the mobility of the selenium with only a slight increase observed. (Figure 7).

Under mildly oxidizing conditions, peak selenium concentrations were observed after 16-18 days, followed by a sudden decrease until 31 days when concentrations stabilized near background levels. The decrease could be due to either absorption of selenite back onto the surface of the residual or the consumption of available reactant and the subsequent reduction of selenium to a stable form.

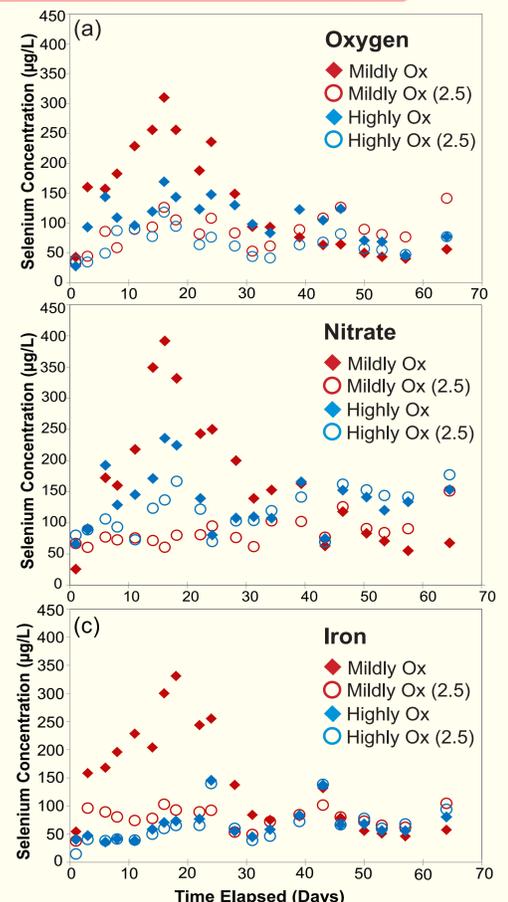


Figure 7. Se concentrations during batch experiments. O₂ (a), NO₃⁻ (b) and Fe³⁺ (c) experiments with mildly oxidizing conditions represented by red markers and highly oxidizing by blue. Low pH (2.5) represented by open circles.

Selenium Speciation (XANES)

Starting residual sample thought to consist primarily of FeSe, Se⁰ and SeS₂ (Figure 8).

The scenario that mobilized the most selenium (mildly oxidizing) had the least effect on speciation change within the residual (Figure 9).

Highly oxidizing and low pH scenarios showed oxidation of Se²⁻ to Se⁰ or SeS₂ (Figure 9).

SeS₂ and the red allotrope of Se⁰ have similar spectra, the latter will be measured in December to confirm which of the two are present in the residual.

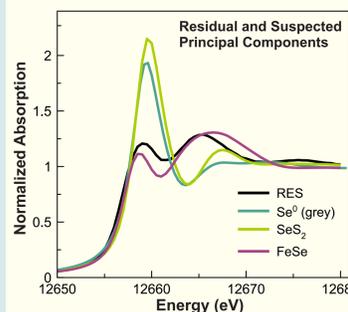


Figure 8. Se XANES spectra for starting residual sample and suspected principle components.

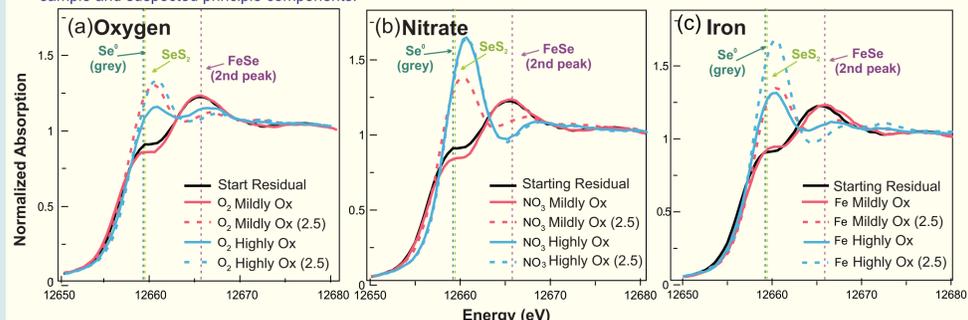


Figure 9. Se XANES spectra for the starting residual sample compared to post-experiment samples for O₂ (a), NO₃⁻ (b) and Fe³⁺ (c) batch experiments. Dashed vertical lines represent white line positions for suspected principal components.

6. CONCLUSIONS & FUTURE WORK

Mildly oxidizing conditions mobilized the most Se but had the least effect on speciation change.

Highly oxidizing and low pH conditions inhibits the mobility of Se but show speciation change, signifying the occurrence of oxidation.

The decline in Se after 16-18 days under mildly oxidizing conditions may be due to adsorption of selenite or total consumption of the reactant and subsequent reduction of the Se.

Red Se⁰ will be measured at the APS to determine its contribution to the composition of the starting residual.

Geochemical modelling will be conducted to obtain reaction rates and additional aqueous chemistry will be analyzed to further evaluate the oxidation mechanisms.

7. ACKNOWLEDGEMENTS

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