Column Tests of Selenium Biomineralization in Support of Saturated Rockfill Design

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Abstract Biological reduction of oxidized selenium to less mobile forms within mine waste rock can reduce the cost of protecting water quality. Batch and column studies of native microbial capacity to reduce Se in waste rock show that oxygen and nitrate inhibition is overcome via carbon addition. Biofilm in aerobic columns showed 50 to 99% nitrate reduction followed by 40 to 95% selenium removal; selenium was sequestered as selenite. Microaerophilic nitrate and selenate removal increased to 75 and 98%, with 25% sulfate removal. Suboxic denitrification and selenium reduction to elemental selenium was most rapid and efficient, as high as 99%.

Key words biological reduction of selenium, column tests, biomineralization.

Introduction

Enviromin, Inc. and the Center for Biofilm Engineering (CBE) at Montana State University have jointly conducted column studies of selenium and nitrate reduction in saturated rock fills (SRF) on behalf of Teck Resources Limited (Teck). Waste rock is produced during mining and can release selenium into the environment upon exposure to water and air. Selenium is recognized as an "essential toxin," as it is an essential nutrient which has potential to be toxic with increased concentration (Lenz and Lens, 2008). Saturated backfills have been identified as a priority research target for *in situ* reduction of selenium from mine-affected water at Teck operations.

The oxygen-dependent reduction of nitrate, selenium, and other electron acceptors common in mine waste are illustrated in the conceptual model shown in Figure 1. Nitrate from blasting during the mining process can potentially serve as an electron acceptor coupled to the oxidation of reduced iron sulfide minerals that contain selenium, and both oxygen and nitrate may inhibit selenium reduction by competing as electron acceptors.

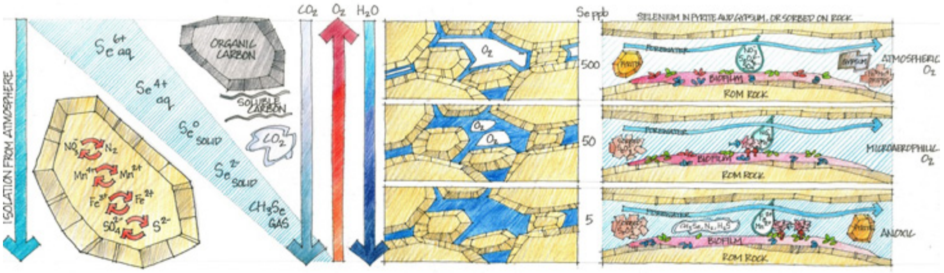

Figure 1 *Conceptual Model of Selenium Biogeochemistry for Waste Rock Deposits.*

Decreased solubility of Se resulting from incremental Se reduction. Elemental cycling of N, Mn, Fe, S, and C dominates the biogeochemistry. As sediment becomes progressively saturated with water and oxygen content decreases, and carbon dioxide accumulates. Shifts in the microbial ecology occur, as shown at right, with the mixed community of aerobic (red), facultative (green) and anaerobic (blue) microbes in the aerobic biofilm transitioning to a community of facultative and obligate anaerobes under anoxic conditions. Changes in solutes, pore gases, and minerals in equilibrium under progressively reduced conditions are illustrated. Selenium concentration is shown to change, as a rough approximation, by an order of magnitude between each condition shown.

Column-based rate experiments were used to explore biogeochemical strategies for decreasing selenium and nitrate release from waste rock facilities. Under realistic flow conditions within saturated fills, oxygen and growth substrate were varied to assess the rate and extent of selenium and nitrate reduction and the associated microbial activity (see Hwang et al. 2017, this volume). This work was conducted in support of pilot scale demonstration tests of this innovative *in situ* biological treatment technology (see Mayer and Yost 2017, this volume).

Methods

Six 3.7 L column reactors packed with waste rock were run in an upflow configuration under aerobic, microaerobic, and suboxic conditions, respectively; 18 columns were run in total. For each oxygen exposure condition, experiments were run in duplicate using three growth substrates: no-added carbon, glycerol, and methanol. Dissolved oxygen was controlled in the influent groundwater by sparging with nitrogen gas to achieve microaerophilic and suboxic conditions, respectively. Influent groundwater was amended to a concentration of 1.0 mg/L Se-SeO_4 (1.81 mg/L selenate) with NO_3-N between 1 and 10 mg/L depending upon the experiment.

Experiments were conducted until desired biogeochemical conditions were attained, generally within 60 days. Tests were designed to represent realistic conditions for multiple “stream tubes” inside saturated backfilled mine panels, as shown in Figure 2. These column experiments were conducted under darkness and were temperature-controlled at 10°C (+/- 1 °C), with an influent flow rate of 0.85 mL/min. These conditions were intended to simulate conditions relevant to the mine site.

Changes in various conditions including T (°C), pH, oxidation reduction potential (ORP, mV), concentrations of dissolved oxygen (DO), total organic carbon (TOC), dissolved (non-purgeable) organic carbon (NPOC), total inorganic carbon (TIC), total Se, selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}), sulfide (S^{2-}) and dissolved metal(loid)s (As, Sb, Al, Ba, Be, Ca, Cd, Cr, Cu, Co, Fe, Mg, Na, Mn, Mo, K, Ni, Ag, Pb, U, V, Zn) were measured using relevant probe-based, ion chromatography and/or ICP-MS methods. Furthermore, periodic microbial cell counts were conducted. The microbial community and biomineralization was characterized in samples from each column; microbial community characterization results are presented by Hwang, et al. this volume.

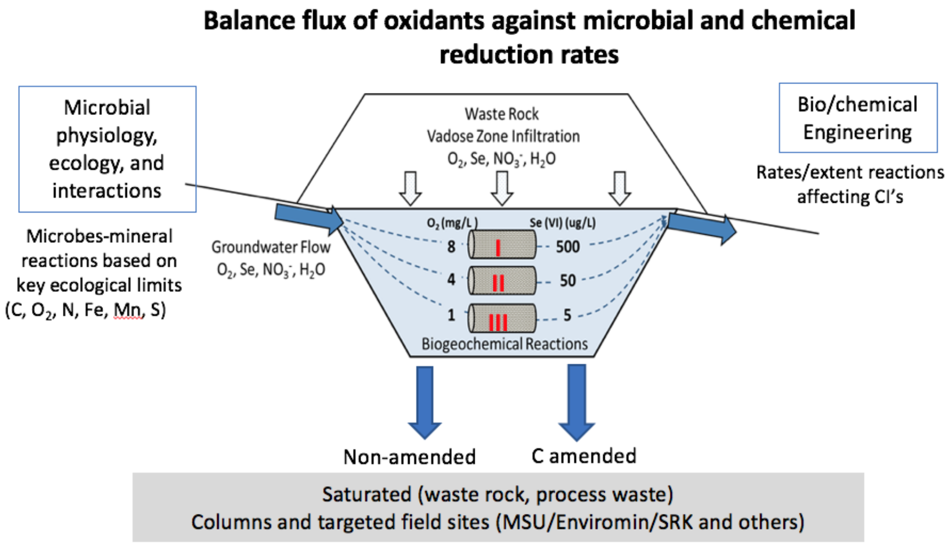

Figure 2 *Experimental Model of Saturated Fill Biogeochemistry*

Stream tubes as envisioned within a saturated fill environment, with oxygen conditions changing with depth as represented by the three phases of experimentation.

Results

Aerobic Column Tests

The aerobic biofilm in no–carbon control columns reduced less than 80% of nitrate and only 20% of selenium. In the carbon-amended columns, following a 20-day acclimation period, up to 99% of nitrate was reduced, with 40 and 95% selenium removal, despite the presence of moderate levels of oxygen. The methanol-amended column showed better nitrate and selenate removal than the glycerol-treated column. Consistent with the observed nitrate reduction during the aerobic tests, low nitrite concentrations were measured in the columns by day 54. Carbon was detected in outflow from the glycerol and methanol-treated columns, but was very low from the no-carbon control. The number of biological cells in the effluent increased when carbon was first introduced into the columns and then declined as the biofilm became established. No sulfate reduction was observed.

Microaerophilic Column Tests

The microaerobic biofilm in the no–carbon control columns was more efficient at nitrate and selenium reduction than under aerobic conditions: ultimately, as much as 95% of nitrate and 80% of selenate was removed after 30 days. In the carbon-amended columns, following a 21-day acclimation period at 10°C, up to 99% of nitrate was reduced with over 95% selenium removal. Nitrite was detected initially, and then intermittently following a period of denitrification.

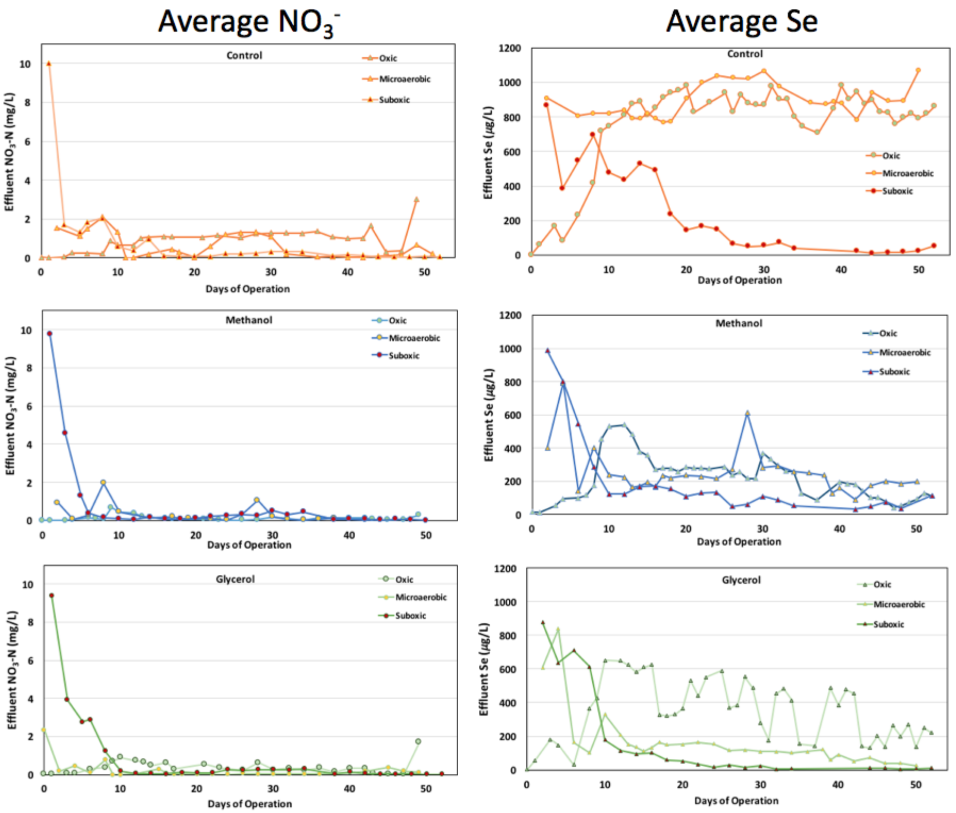

Figure 3 *Average nitrate and selenium for the three oxygen treatments and three carbon treatments*

Carbon was released by no-carbon control columns at low levels, while carbon was released by the glycerol and methanol columns at higher concentrations. None of the columns were carbon limited. Minor (up to 25%) sulfate reduction was observed and the no-carbon control columns showed an ability to release carbon extracted from carbonaceous rock when oxygen was low conditions. Selenite was detected in low concentrations following reduction of selenate.

Suboxic Column Tests

The suboxic biofilms in no-carbon control columns achieved nitrate and selenium reduction more slowly than in the glycerol-treated columns, but ultimately, both reduced most nitrate and removed more than 95% of selenate. As in the microaerobic columns, the glycerol-treated column more efficiently reduced nitrate and selenium to low concentrations than the methanol-treated column, which showed between 80-90% efficiency. Significantly more sulfate reduction was observed in Phase III, but little sulfide was measured; this may reflect the precipitation of sulfide minerals. Approximately equal masses of selenite and elemental selenium were detected following reduction of selenate.

Conclusions

This study characterized the conditions under which native microbial communities promote nitrate and selenium reduction/attenuation in saturated column flow reactors. Results are summarized in Figure 3. The microbial communities associated with biomineralization of N, Fe, Se and S have been identified and vary in rate and efficiency in response to changes in oxygen, nitrate, and carbon availability (see Hwang et al. this volume). These results were used to address the following two questions that inform the design and operation of pilot and full scale SRF facilities.

1. **How do varied dissolved oxygen levels influence selenium reduction rates?** As dissolved oxygen drops and becomes more consistent, nitrate and selenium reduction is initiated more rapidly and becomes more efficient in removing mass from solution. Review of Figure 3 shows that denitrification happens more readily than selenium reduction. Both processes were relatively noisier in the no-carbon control column, but could reach efficient removal at steady state for water with a 16-hour residence time under suboxic conditions, following a period of biofilm growth on the order of weeks. Reduction was more efficient in methanol-treated biofilms when oxygen was present, and in glycerol-treated biofilms when oxygen was low. Reducing conditions were established most quickly, and were most stable, when oxygen was low.

2. **Is carbon amendment necessary? Can coal from waste rocks provide enough carbon for selenium reduction?** Under suboxic conditions, no-carbon control columns were able to release carbon into solution, presumably through biological degradation of the carbonaceous waste rock. Under microaerophilic and suboxic conditions, the available native carbon appears to be sufficient to drive reduction with adequate residence time. This may not be true during upset conditions, however, such as seasonal spikes in oxygen or nitrate.

Acknowledgements

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