SELENIUM RELEASE FROM COAL MINES IN THE ELK VALLEY, AND TREATMENT R&D PLANS

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ABSTRACT

Teck Coal Limited operates five coal mines in the Elk River Valley in southeastern British Columbia. Selenium concentrations were found to be elevated in some mine-influenced waters in the area. The major sources of selenium are the large rock spoils present in the drainage area. Removal of selenium by water treatment is being researched to decrease loadings on the Elk River. The focus of the treatment program is biological reduction and volatilization methods, which are more effective for selenium removal in high flow, multiple discharge and low concentration scenarios typical at the sites. Bench-scale testing of active, passive and hybrid bioreactors is currently underway at Teck’s Applied Research and Technology (ART) research centre in Trail, British Columbia. Six active bioreactors were operated using a variety of parameters for eight months, achieving up to 98% selenium removal. Mobilization experiments were also conducted in humidity cells to determine the potential for selenium to leach from sediment samples. Results indicated that selenium was being mobilized from sediment at some of the sites tested. Future testing will continue in the future using a variety of methods.

KEY WORDS: Water treatment, biological removal, sediments

INTRODUCTION

Selenium mobilization in coal operations occurs due to oxidative processes. The mean Elk River selenium concentration has been increasing over time downstream from Elk River Valley mines. The Elk Valley Selenium Task Force (EVSTF) is a multi-government agency/industry scientific team advising and overseeing selenium-related activities at the Teck’s coal operations in British Columbia. These operations are located in the Elk River Valley, in southeastern British Columbia. Teck Coal Limited is owned by Teck Resources Ltd. As part of ongoing discussions with the EVSTF, Teck is proactively researching selenium removal methods (EVSTF, 2008). There are three management approaches for control of selenium: prevention of release, reported in the literature to be effective (Sobolowski, 2005); control of selenium in the environment; and, the third is water treatment (Chapman et al., 2009). Although all three approaches are being actively investigated by Teck, this paper is focused on research and development of water treatment alternatives and mobilization of selenium from settling pond sediments.
Selenium removal technologies have been reviewed (Gusek et al., 2008; NSMP, 2007; MSE, 2001). Microbial-based selenium removal technologies were identified as being applicable to the Elk Valley coal operations (Sobolowski, 2005). Microbial methods to decrease selenium concentrations in Elkview Operations water, investigated at ART on a laboratory scale, were effective in decreasing the selenium concentrations over a range of conditions that could be encountered in the field. Indigenous microbial selenate and selenite reducers were identified in Elkview Lagoon D sediments (Siddique, 2007). The current work evaluates active biological treatment methods to remove selenium from Teck Coal operations’ streams.

STREAM IDENTIFICATION

Teck Coal has 5 coal operations in British Columbia and each operation exhibits complicated water drainage systems. The streams are generally characterized as exhibiting high flows and contain low concentrations of selenium. The main form of selenium in the streams is selenate, which is a difficult form of selenium to remove due to its higher oxidation state (Frankenberger et al., 1998).

The major sources of selenium from operations are the waste rock dumps present in the drainage area. Solution-based biological treatment methods include passive bioreactors, active bioreactors, hybrid systems, anaerobic and aerobic wetlands and combinations of these systems. Biological treatment methods were selected for evaluation due to their effectiveness, general ease of operation, and ability to concentrate the selenium into selenium-containing residues. Volatilization is another biologically based selenium removal method which is being investigated separately (Martin et al., 2008).

Elkview Operations’ Bodie Creek was selected as the candidate stream to evaluate biological selenium removal based on the following key parameters:

- Stream flow;
- Stream selenium concentration and estimated loading;
- Stream location; and
- Availability of infrastructure for treatment evaluation on a larger scale.

SELENIUM REMOVAL

Selenium removal from Elkview Operations Bodie Creek water was evaluated using active biological treatment over a number of years on a laboratory scale. Selenium removal from Bodie Creek water was microbially mediated and occurred on a variety of support materials. The best selenium removal occurred with the reactor operating in an up-flow configuration. Ethanol was used as the nutrient in these investigations.
Experimental

Four 2-m columns and two 1-m columns (7.6 cm in diameter) were used in the experiments. The columns were constructed from clear PVC. The columns operated in an up-flow configuration and were filled with approximately 11 kg of support material. The fine coal rejects known as high frequency screen oversize (HFSO), had a particle size of ~1 mm and were used as the support material. Water from Bodie Creek was collected by Elkview personnel during the test program.

Each column was inoculated using indigenous microorganisms in a lactate medium before water treatment started. The ratio of chemical oxygen demand to sulphate concentration (COD/SO$_4^{2-}$) in the column feed was important for establishing reducing conditions in the columns. Column shutdown was mainly determined by plugging issues.

Solution parameters such as oxidation-reduction potential (ORP), pH, temperature and dissolved oxygen concentrations were measured on the column overflow solutions. Electrode potentials were calculated relative to a saturated silver chloride/silver electrode and converted to $E_h$. Solutions were also assayed weekly for dissolved selenium, sulphur, calcium, magnesium and barium. Sulphide concentrations were determined periodically with a Hach meter. The experimental setup is shown in Figure 1.

Figure 1. Column setup for up-flow experiments.

Column Operation

Six columns were operated for a maximum duration of 239 days. During this time period different operating strategies were conducted such as varying the operating temperature, feed rate and nutrient and sulphate addition rates. Table 1 illustrates the operating conditions for each of the columns.
### Table 1. Operating conditions for columns.

<table>
<thead>
<tr>
<th>Column</th>
<th>Support Material</th>
<th>Inoculation</th>
<th>Flow Rate</th>
<th>Column</th>
<th>Operating Day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HFSO</td>
<td>Slow flow through</td>
<td>1.56</td>
<td>2</td>
<td>239</td>
</tr>
<tr>
<td>2</td>
<td>HFSO</td>
<td>Medium flow through</td>
<td>3.13</td>
<td>2</td>
<td>217</td>
</tr>
<tr>
<td>3</td>
<td>HFSO</td>
<td>Static (biosolids culture)</td>
<td>1.56 initial 6.26 final</td>
<td>2</td>
<td>159</td>
</tr>
<tr>
<td>4</td>
<td>HFSO</td>
<td>Static (biosolids culture)</td>
<td>1.56</td>
<td>2</td>
<td>138</td>
</tr>
<tr>
<td>5</td>
<td>HFSO biosolids /gravel layer</td>
<td>Static (lactate media)</td>
<td>1.56</td>
<td>1</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>HFSO layered with gravel</td>
<td>Static (biosolids culture)</td>
<td>1.56</td>
<td>1</td>
<td>166</td>
</tr>
</tbody>
</table>

Reducing conditions are required for optimum selenium removal. A convenient way to monitor reducing conditions in the columns is ORP. Figure 2 represents $E_h$ measurements taken over the operating period for Columns 1 and 2. The $E_h$ readings became more negative as reducing conditions were established in the columns. The spikes observed in Figure 2 can be attributed to operation upsets, or changes in operating parameters, such as flow rate or nutrient concentration.

![Figure 2. ORP in column overflow solutions during the operating period.](image-url)
Selenium Removal

The feed and overflow selenium concentrations in Columns 1 and 2 are shown in Figure 3. Selenium concentrations in the Bodie Creek water ranged from 27 - 140 µg/L, averaging 61 µg/L. High selenium removals were generally obtained.

![Figure 3](image)

**Figure 3.** Selenium concentrations in column overflow during operating period.

Table 2 illustrates the effect of the flow rate on the selenium removal for Columns 1 – 4. Columns 5 and 6 plugged early and were decommissioned. The average selenium removal from the columns operating at a specific flow of 1.56 m³/(m²d) was 97%. Increasing the specific flow to 3.13 m³/(m²d) slightly decreased selenium removal to 94%. Column 3 was operated at 1.56 m³/(m²d) until day 138 when the flow rate was increased to 6.26 m³/(m²d), and additional sulphate was discontinued. The selenium removal for these two flow rates was 97% and 42%, respectively. While Columns 1 and 2 ran at 1.56 and 3.13 m³/(m²d), the Eh measurements were similar (-100 mV). Increasing the flow rate to 6.26 m³/(m²d) in Column 3 caused the Eh to rise dramatically.

<table>
<thead>
<tr>
<th>Column</th>
<th>Test Descriptor</th>
<th>Flow Rate Range (m³/m²d)</th>
<th>Average Flow Rate (m³/m²d)</th>
<th>Average Selenium Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 x</td>
<td>0.06 – 2.3</td>
<td>1.2</td>
<td>97.1</td>
</tr>
<tr>
<td>2</td>
<td>10 x</td>
<td>0.06 – 3.7</td>
<td>2.2</td>
<td>93.7</td>
</tr>
<tr>
<td>3</td>
<td>5 x</td>
<td>0.88 – 2.6</td>
<td>1.4</td>
<td>97.6</td>
</tr>
<tr>
<td>4</td>
<td>20 x</td>
<td>4.4 – 7.2</td>
<td>5.5</td>
<td>42.4</td>
</tr>
<tr>
<td></td>
<td>5 x</td>
<td>1.1 – 2.6</td>
<td>1.5</td>
<td>97.4</td>
</tr>
</tbody>
</table>

* Ethanol feed concentration 10 mmol/L.

After 142 days of operation, Column 2 showed signs of plugging. On day 200, the flow rate in this column was reduced from 3.13 m³/m²d to 1.56 m³/m²d. Plugging issues continued and the column was shut down on day 217.
Figure 4 represents the effects of changes in nutrient concentration on selenium and sulphate removals. When the feed ethanol concentration was decreased to 5 mM, selenium removal decreased slightly; however, sulphate removal decreased significantly. Improvement in the selenium removal selectivity was also observed when the specific feed flow rates were increased from 1.56 - 3.13 m$^3$/(m$^2$d) to 6.26 m$^3$/(m$^2$d). This result may reflect the relative rates of selenate and sulphate reduction under these conditions.

**Figure 4.** Effect of changing parameters on sulphate and selenium removal.

**Post Mortem Analysis**

A scanning electron microscope (SEM) investigation identified minerals present in the HFSO and from the decommissioned columns. These SEM micrographs are shown in Figure 5. Selenium was not detected by SEM.

**Figure 5.** SEM study of support material before (left) and after (right) experiment.
A decrease in the pore volume of approximately 20% inhibited solution flow through the columns. The source of the plugging was largely inorganic, with pyrite, siderite, gypsum, goethite and elemental sulphur being identified as secondary minerals. Selenium was not taken up by the HFSO in the absence of micro-organisms.

SELENIUM MOBILIZATION

The ability of selenium to mobilize from decant sediments was investigated in laboratory-scale experiments. Sediments from decant ponds at Coal Mountain (Corbin Pond) and Elkview (Bodie Creek) Operations were investigated in this study. The experimental setup is shown in Figure 6.

Cells were set up using Büchner funnels. Irrigation of the sediments occurred via perforated tubing attached to the upper funnel with caulking. A filter paper was placed in the lower funnel with a 1.5-cm-thick layer of washed and weighed gravel on top. The gravel simulated coarse material in the waste rock dumps. A 1.5-cm-thick layer of weighed sediment was then placed on top of the gravel.

Water was recirculated to simulate percolation through many layers in a waste rock dump (Recirculation). The second leach test (No recirculation) was set up the same as the first except the water dispersed in the humidity cells originated from one common reservoir and was collected. The irrigation rate was based on local precipitation data for Sparwood, British Columbia. Selenium leaching results are presented in Figure 7.

Figure 6. Leach test with recirculation (left) and no recirculation (right).
The initial selenium concentrations in the Corbin Pond and Bodie Creek Decant sediments were 0.94 and 11.3 mg/kg dry weight, respectively. The Corbin Pond sediment samples were generally coarser (9.3 – 1000 µm) than the Bodie Creek Decant samples (19 – 29 µm). The leach test with solution recirculation showed no significant changes in the selenium concentration for Corbin Pond sediment and the Bodie Creek Decant Pond #1 sediment after the first week. In both solution recirculation tests, week 1 leachate selenium concentrations were 0.001 mg/L and were <0.001 mg/L in the remaining test weeks. These results indicate that solution recirculation inhibits selenium mobilization compared to tests without recirculation.

In tests with no recirculation, the selenium release from Corbin Pond sediment occurred via a flushing mechanism where selenium may be present in a soluble form. Selenium release from Bodie Creek Decant Pond #1 indicated a leaching process was occurring from the form of the curves in Figure 7. Over time this release would decrease as the selenium was depleted. Placement of the sediments in such a way to avoid direct release of selenium to the water shed is recommended.
CONCLUSIONS

The following conclusions were reached from this study:

- A target stream was identified for evaluating an active biological selenium removal system by considering loading. The criteria for identifying treatment technologies and streams have subsequently been extended to include all of Teck’s British Columbian coal operations, a wider range of treatment options and streams for each operation.

- A laboratory-based active biological water treatment system successfully demonstrated selenium removal under a variety of conditions for up to 239 days of continuous operation. The ORP was an important control parameter for the selenium removal system. Selenium removal up to 98% was observed in these experiments.

- Plugging of the columns occurred as a result of inorganic solids buildup, impeding column permeability. A coarser support material is suggested for future studies. Some selectivity in selenium removal over sulphate removal was observed by limiting nutrient concentrations and increasing specific flow rates.

- Decant pond sediments released selenium from aerobic processes in laboratory-scale experiments. The selenium release occurred via flushing or from leaching.

FUTURE WORK

Biological treatment methods show promise for selenium removal at Teck’s coal operations. The concepts require evaluation at a larger scale onsite and for an extended period of time. The use of locally available materials is desirable in the treatment systems. An integrated laboratory and field program is already underway to determine the feasibility of various treatment methods as part of a larger selenium study.

The current ART-based laboratory program is evaluating active and passive bioreactor systems in addition to chemical methods for selenium removal. Locally available materials are being used as the support/nutrient system. Water from two of Teck’s coal operations will be tested to determine the general applicability of the methods. The laboratory experiments are on a 20-L scale. Experiments will be run to determine the influence of startup and operating variables on selenium removal.

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REFERENCES


