# Mine Design for In-Situ Control of Selenium and Nitrate

Soren Jensen[1], Jennifer Foster[1], Marie-Christine Noel[1], Mike Bartlett[2]

[1]*SRK Consulting, 1066 West Hastings Street, Vancouver, British Columbia, Canada, sjensen@srk.com*

[2]*Millennium EMS Solutions Ltd. Suite 325, 1925 18 Avenue NE, Calgary, AB T2E 7T8*

## Abstract

This paper describes an approach for designing and developing a coal project for in-situ control of selenium and nitrate in contact water from the mine as an alternative to engineered water treatment plants. The design integrates water management, pit design and sequencing such that completed open pits can be backfilled and used as in-situ bioreactors for attenuating selenium and nitrate. The attenuation process is well established and proven at different scales but the hydraulic design of the backfilled pit and operational control of carbon dosing will have to be developed through phased field tests carried out concurrently with full-scale design. Results of the initial on-site pilot test are presented.

**Keywords:** coal, selenium, nitrate, in-situ, biological, treatment, suboxic, anaerobic

## Introduction

Selenium (Se) is a naturally occurring substance and an essential element required for the health of humans, animals, and some plants. However, selenium has also become a contaminant of potential concern throughout the world. Mining, power generation and agriculture are among the largest emitters of selenium world-wide (Lemly 2004).

Selenium management at mining operations typically involves:

- Source control measures to limit release from oxidizing sulphide minerals such as subaqueous disposal and low permeability covers; and
- Interception and collection of contact water for passive or active selenium water treatment.

Selenium concentrations in mine water are project specific and vary widely. Concentrations can approach 1 mg/L at sites with pronounced selenium leaching (Dockrey 2012). In comparison, the freshwater ambient chronic water quality criterion for selenium recommended by the United States Environmental Protection Agency is 0.0031 mg/L for lotic (flowing) waters (US EPA 2016). In some cases, the recommended water quality criterion for selenium could therefore be exceeded if seepage or discharge from a mine exceeds 0.5% of the total streamflow. The orders-of-magnitude difference between selenium concentrations in mine water and receiving water quality criteria means that some mining projects are required to achieve near-complete capture and treatment of all mine water from a project area to comply with instream selenium criteria.

Over the last three decades, the growing understanding of ecological effects that can be caused by selenium in aquatic environments has prompted industry to develop better and more reliable selenium water treatment technologies. Historically, selenium water treatment processes have relied on chemical reduction of selenate to selenite or elemental selenium using reducing agents such as zero-valent iron followed by ferric-coprecipitation for removal of residual selenite (CH2M Hill 2013). However, chemical processes are costly and tend to increase concentrations of dissolved components, which must subsequently be removed. In addition, the processes were not able to reliably achieve effluent concentrations required by discharge permits (Golder 2009). In the 1990s, several selenium water treatment technologies that rely on biological reduction for removal of selenium were developed and have been adopted by the mining industry (CH2M Hill 2013).

Biological removal of selenium from water relies on anaerobic microorganisms, which reduce oxidized forms of selenium, such as selenate, to more reduced forms (selenite) or to elemental selenium, which can then be removed from water by co-precipitation or precipitation. The process occurs naturally in wetlands and in suboxic lake sediments and has also been observed to occur in backfilled open pits at a closed coal mine (de Souza 1999, Bianchin 2013). The biological water treatment process also removes nitrate, which is another water quality parameter of potential concern for the mining industry. Nitrate in mine water is primarily due to dissolution of ammonium nitrate-based explosive residuals.

Although biological treatment has been proven on an industrial scale, the treatment process is relatively costly to implement and operate, particularly since water treatment often is required in-perpetuity. Lower cost treatment options, such as gravel reactors or in-pit anaerobic biological treatment, are emerging as real alternatives to mechanized treatment plants. In addition to lower cost, the in-situ treatment systems may also improve treatment performance.

This paper presents the approach used for integrating mine design and in-situ selenium management for the proposed Grassy Mountain Coal Project located in Southern Alberta and discusses design and operational control of in-situ treatment systems.

## Methods

Geochemical characterization of the coal deposit and host rock at the Grassy Mountain Coal Project identified oxidizable and leachable selenium and a high likelihood of selenium concentrations exceeding water quality targets in waste rock seepage at the proposed mine. Located on a mountain ridge near the headwaters of Blairmore Creek and Gold Creek, the Project area occupies a sizable portion of the local catchment areas (Figure 1). Therefore, the capacity of the creeks to assimilate mine water discharge is limited. From the inception of the Project, it was clear that efficient collection of mine water and selenium water treatment would be required to meet receiving water quality guidelines in the downstream environment.

In a traditional approach to mine design, mine engineers are tasked with development, and later optimization, of an economic mine design that includes an open pit or under-

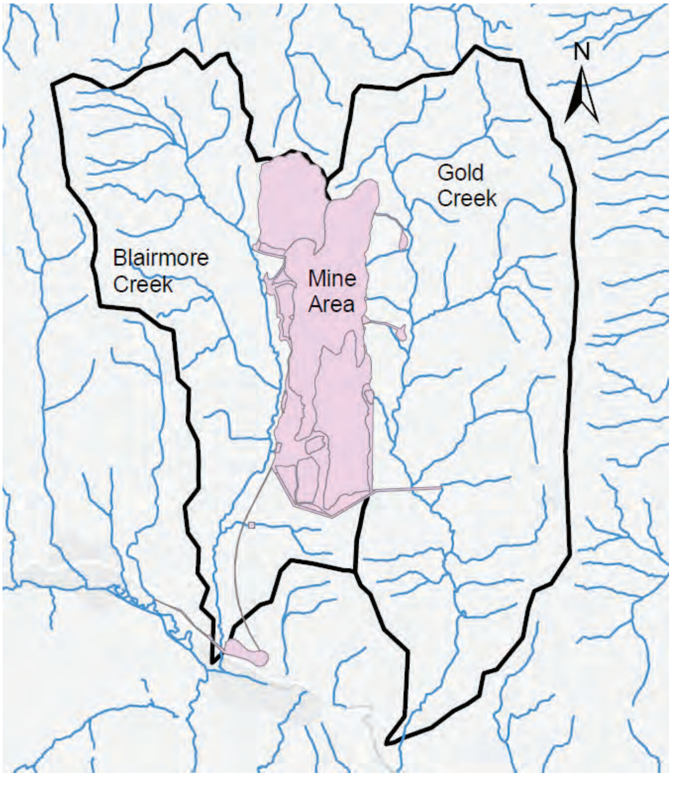


***Figure 1** Ultimate Mine Footprint and Adjacent Catchments*

ground mine development schedule and design of waste rock storage areas. Water management features are then designed to accommodate the most economic mine design. However, the high efficiency capture and water treatment required to manage selenium for the Project meant that the mine design had to accommodate water collection and water treatment for the project to be feasible. Selenium mitigation measures that were incorporated in the mine design included:

- A mining sequence that allowed for timely conversion of mined-out open pits to saturated in-situ anaerobic bioreactors to allow for attenuation of selenium and nitrate.
- Maximizing in-pit placement of waste rock to facilitate seepage capture.
- Design of ex-pit waste rock area foundations for seepage collection.

The conversion of mined-out open pits to anaerobic bioreactors for removal of selenium and nitrate is the key aspect of the proposed mine design and water management approach and therefore the focus of the discussion in this paper. Suboxic conditions in pit water promote the conversion of soluble selenate ions ($SeO_4^{2-}$) to selenite ($SeO_3^{2}$) or elemental selenium metal ($Se^0$). Selenite is less soluble and tends to adsorb to mineral surfaces. Elemental selenium is insoluble. Therefore, the conversion of selenate causes the reduced selenium species to become attenuated. Nitrate ($NO_3^-$) is reduced to nitrogen gas ($N_2$) (Martin 2009). A key requirement is the presence of dissolved organic carbon that provides electrons for these processes. The carbon in turn is oxidized to carbonate as bicarbonate and dissolved carbon dioxide.

In-situ attenuation of selenium using suboxic or anaerobic biological processes is well researched and has been demonstrated at different scales in various configurations. Luek (2012), for example, describes a pilot-scale biological reactor with a media comprising mulch, manure and gravel. In-situ biological treatment was used in a batch configuration for removal of dissolved selenium and uranium from a pit lake at the Sweetwater Mine in Wyoming in 1999 (Paulson 2004). However, there are to date no publicised examples of backfilled open pits that have been specifically designed and operated as biological reactors for removal of selenium. For the Grassy Mountain Project, the approach was therefore to develop an understanding of the process kinetics and process control strategy in parallel with the mine development by implementing on-site field trials at increasing scales.

Conversion of the open pits to anaerobic bioreactors involves some of the same design considerations as in mechanical reactor design used for active water treatment plants:

- At least one pit with sufficient hydraulic retention time must be available for water treatment early in the mine life by the time selenium and nitrate impacted mine water is produced on site.
- Subsequent open pits should ideally be hydraulically connected to the downstream-most open pit such that selenium and nitrate treatment can occur in a series of in-situ pit reactors with a single discharge point.
- The combined volume of the in-situ bioreactor (i.e. open pits backfilled with waste rock) must provide sufficient residence time for complete selenium and nitrate attenuation to occur for a range of flow and temperature conditions.
- Placement of backfilled waste rock should be planned in a way that would facilitate hydraulic control of mine water passing through the in-situ bioreactors in the open pits.

Suboxic conditions required for the attenuation process are generated by microorganisms that consume oxygen and other electron acceptors such as nitrate as they metabolize carbon. Therefore, unless existing concentrations of dissolved organic carbon are sufficient, addition of organic carbon and nutrients in the mine water is required for the process to work and is also the main process variable for controlling in-situ bioreactors. Molasses and methanol are readily available and relatively low-cost sources of organic carbon that have been used in similar in-situ treatment applications and in active water treatment plants (Martin 2009). The dose of organic carbon required depends primarily on the concentration of dissolved oxygen and nitrate in the mine water. Approximately 3 g of methanol is stoichiometrically required to attenuate 1 g of nitrate.

The rate at which suboxic conditions develop determines the time required for attenuation and consequently the hydraulic residence time required for the in-situ bioreactor. In an active water treatment plant, the residence time required is in the order of hours. The residence time required to achieve complete attenuation of selenium and nitrate in an in-situ bioreactor at the Grassy Mountain site is unknown; however, case studies of full-scale treatment systems using similar processes indicate that the hydraulic residence time required is on the order of a few weeks (Poulson 2004, Martin 2009).

Implementation of in-situ bioreactors requires an understanding of the process stoichiometry, kinetics and performance response to varying carbon types and doses. The goal of the first small-scale field trial was to evaluate these factors.

The first field test was conducted in the summer of 2017 and was intended as simple, small-scale reactors that would yield basic information on the stoichiometry and kinetics of the treatment process for a limited set of conditions. Another objective was to establish and test operating and monitoring procedures that could be transferred to subsequent larger-scale tests and eventually to full-scale operations.

Seven 45-gallon (170 Litre (L)) plastic barrels were used as small-scale reactors. Each barrel was filled with coarse waste rock and coal reject from historical mining activities in the project area. No organic material or microbial seed was added. A 1,000 L tote elevated above the barrels was used as a feed tank for the test. Feed water flowed by gravity through the test barrels. Feed flow rates were controlled by adjusting drip valves installed at the inlet on each barrel. The test setup required no power.

The barrel setup was first tested hydraulically by feeding a sodium chloride tracer solution through each barrel and monitoring the conductivity of the effluent. The tracer test demonstrated that feed flow could be controlled reliably to yield a hydraulic retention time of approximately two weeks. Reactive tests were conducted next. The feed water tote was filled with water and charged with nitrate (80 mg/L as nitrate-N) and selenate (1.3 mg/L as sodium selenate). Pails with dissolved carbon or water (for the controls) were connected to the feed water inlet of each barrel. The flow of dissolved carbon or water from the pails were also controlled by drip valves. Flow from the feed tote and from the carbon (or water) totes were approximately equal, which resulted in a combined feed with approximately 40 mg/L nitrate-N and 0.650 mg/L of selenium.

Pails containing carbon solution were replaced weekly to prevent degradation of the organic carbon in the pail. Each barrel was equipped with three inlet ports, which allowed operators to switch ports in the event biofouling blocked the flow of influent – a common problem in fixed-bed bioreactors.

Table 1 shows the test conditions used for the seven barrels. The control barrel (1) was filled with waste rock and received feed from the tote but no carbon (only water) was added to the pail. Barrels 2 through 5 received low (75% of stoichiometric demand) or high (110% of stoichiometric demand) doses of either methanol or a 50:50 mixture of methanol and molasses (by weight). In barrels 6 and 7, 5% and 20% the waste rock had been replaced by coarse coal material. The purpose of these barrel tests was to evaluate whether organic carbon leaching from coal would be sufficient to generate suboxic conditions.

Results of the reactive test are illustrated in Figure 2. Chloride concentrations in the barrel effluent (residual from the tracer test) decreased relatively uniformly for all barrels, except for the control barrel, which saw higher feed flow from the feed tote than the other six barrels. Selenium concentrations in the effluent from the four barrels that were dosed with methanol or methanol and molasses were reduced to less than 0.015 mg/L compared to a concentration of 0.200 mg/L in the control after approximately two weeks. The barrels with coal reject (6 and 7) appeared to show some attenuation when compared to the control barrel (1). However, a concentration increase in the control barrel was considered a consequence of the greater rate of flow from the feed tote as evidenced by the greater nitrate and selenium concentration. When normalized for flow, the reactive response of the coal reject barrels is the same as the response of the control barrel. Nitrate-N concentrations in the barrels dosed with carbon were less than 0.1 mg/L after two weeks compared to approximately 20 mg/L in the control barrels. The dose or type of organic carbon did not appear to affect the rate or extent of degradation.

*Table 1* Test Barrel Carbon Type and Dose

| Barrel # | Carbon Type | Carbon Dose |
|---|---|---|
| 1 | Control | None |
| 2 | Methanol | Carbon 1, Low Dose |
| 3 | Methanol | Carbon 1, High Dose |
| 4 | Methanol + Molasses | Carbon 2, Low Dose |
| 5 | Methanol + Molasses | Carbon 2, High Dose |
| 6 | Coal Reject | 5% of Barrel Volume |
| 7 | Coal Reject | 20% of Barrel Volume |

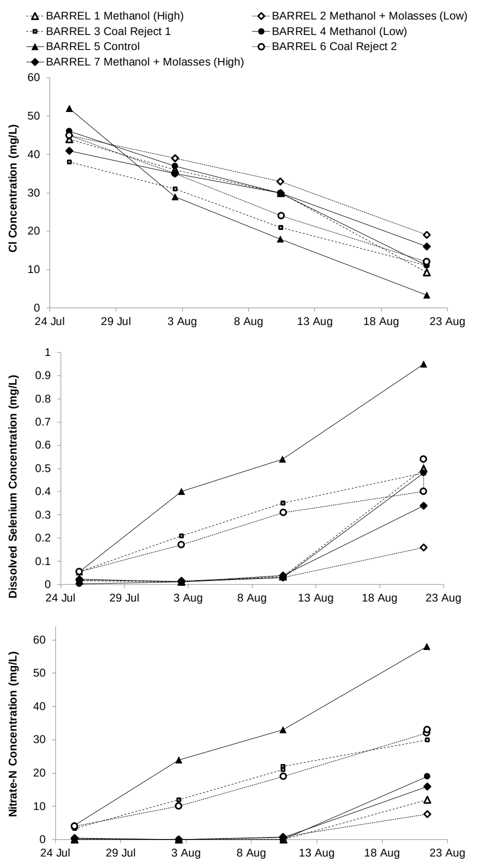


***Figure 2*** *Chloride, Diss. Selenium and Nitrate-N Concentrations in Test Barrel Effluent*

Attenuation of selenium and nitrate was sustained in the barrels for approximately two weeks after which concentrations of selenium and nitrate rebounded. This occurred due to a loss of carbon in the feed solution. Despite efforts to prevent carbon degradation in the pails with carbon solution, a biofilm formed on the inside of the tubing that supplied carbon to the barrels. The biofilm likely metabolized the readily degradable carbon before it reached the barrel inlet. This unintended loss of organic carbon illustrates the importance of maintaining anaerobic conditions in the in-situ bioreactors. Subsequent, larger-scale tests will use 100% methanol as a carbon source, which in its pure form is toxic to microorganisms, to circumvent this problem.

The barrel test demonstrated that attenuation of selenium and nitrate can be accomplished in a simple flow-through reactor using a rock media and a simple organic carbon source. The test also validated the operability of the bioreactor system, demonstrated that two weeks of resident time is a reasonable starting point for future tests and showed the importance of maintaining sufficient carbon supply to sustain suboxic conditions. Larger-scale field-tests are required to evaluate process kinetics and control at a wider range of temperatures and residence times.

## Conclusions

Selenium management for the Grassy Mountain Coal Project requires that mine water capture and treatment considerations are integrated in the mine design. The conversion of mined-out open pits to anaerobic bioreactors for attenuation of selenium and nitrate is the key aspect of the proposed mine design and water management approach. The attenuation process is well established and proven at different scale but the hydraulic design of the backfilled pit and operational control of carbon dosing will have to be developed through phased field tests carried out concurrently with full-scale design.

## Acknowledgements

The authors thank the Riversdale Resources Limited and Millennium EMS Solutions Ltd. for their support and cooperation in the planning and execution of the work presented in this paper.

## References

Bianchin M, Martin A, Adams J (2013) In-Situ Immobilization of Selenium within the Saturated Zones of Backfilled Pits at Coal-Mine Operations. BC Mine Reclamation Symposium, September 2013.

CH2M Hill (2013a) Review of Available Technologies for the Removal of Selenium from Water – Addendum. Prepared for North American Metals Council. Prepared by CH2MHILL, March 2013.

de Souza M, Huang C, Chee N (1999) Rhizosphere bacteria enhance the accumulation of selenium and mercury in wetland plants. Planta 209: 259. https://doi.org/10.1007/s004250050630 DOI

Dockrey J, Martin A, Stockwell J (2012) Potential Rose of Nitrate in the Release and Attenuation of Selenium in Coal-Mine Environments. Proceedings of 19th Annual BC MEND ML/ARD Workshop, presentation 25, 2012.

Golder Associates (2009) Literature Review of treatment Technologies to Remove Selenium from Mining Influenced Water. North American Metals Council, http://www.namc.org/docs/00057713.PDF

Lemly DA (2004) Aquatic selenium pollution is a global environmental safety issue. Ecotoxicology and Environmental Safety 59, 2004, p. 44-56

Martin A, Jones R, Buckwalter-Davis M (2009) Passive and Semi-Passive Treatment Alternatives for the Bioremediation of Selenium from Mine Waters [C]. doi:http://dx.doi.org/10.14288/1.0042571

Paulson O, Harrington J (2004) Bioremediation of the Sweetwater Pit Lake – Four Years Following Treatment. Proceedings of the US EPA Meeting: Pit Lakes 2004, November 16 – 18, Reno, Nevada, Washington, D.C.

Luek A, Brock C, Rowan D, Rasmussen J (2014) A Simplified Anaerobic Bioreactor for the Treatment of Selenium-Laden Discharges from Non-acidic, End-Pit Lakes. Mine Water Environment, 2014, 33:295–306. DOI 10.1007/s10230-014-0296-2

United States Environmental Protection Agency (US EPA) (2016) Aquatic Life Ambient Water Quality Criterion for Selenium – Freshwater. EPA 822-R-16-006, June 2016, Washington, DC, USA.