Biogeochemical Attenuation of Selenium and Nitrate in Mine Contact Waters

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Abstract

Conuma Resources Ltd. (Conuma) operates three mines that produce steelmaking coal. These mines are in northeast British Columbia, Canada in Treaty 8 Territory. The main parameters of potential concern (POPC) identified in the mine contact water that require treatment include selenium (Se) and nitrate ($N0_3$-). Selenium originates primarily from weathering of exposed mine waste materials (i.e., waste rock) while nitrate is released via leaching of blasting residues associated with ammonium nitrate-based explosives. Elevated concentrations of these POPCs, particularly selenium, have the potential to impact the health of the aquatic ecosystem. To treat and reduce concentrations of Se and $N0_3$- in the mine contact waters, in-situ anaerobic semi-passive biological treatment systems commonly referred to as biochemical reactors (BCRs) were constructed. Design and operational controls that were incorporated in the mitigation measures included lateral water flow within the in-situ anaerobic bioreactors to allow for attenuation of Se and $N0_3$-. The results show evidence of effective denitrification (up to 100 %) with concentrations of $N0_3$- decreasing from 49 mg/L to <10 µg/L in the outflow of the anaerobic bioreactors. Selenium shows pronounced removal (up to 94%) with concentrations decreasing from ~200 µg/L to 20 µg/L. The reduction in Se concentration was accompanied by a shift in Se speciation from dominantly selenate (SeVI) to selenite (SeIV) and/or to elemental selenium via dissimilatory microbial reduction under anaerobic conditions. The data also suggest that Se remobilization via direct oxidation pathways may be occurring after the treated water has gone through the aeration process, however, the rate is insignificant to be of concerns. Collectively, the water chemistry results indicate that the biochemical reactors are an effective technology for the bioremediation of Se and $N0_3$- in coal mine affected waters under suboxic conditions. Optimization of the operational design of the biochemical reactors currently underway are expected to improve Se and $N0_3$- removal performance and achieve greater outcomes of water treatment.

The engagement and involvement of First Nations in the design, implementation, and operations of water management systems; as well as environmental monitoring is ongoing, and information gathered will are shared in a coordinated manner through multiple forums including the environmental monitoring compliance committee (EMCC).

Introduction

Discharges from coal mines into receiving waters downstream of mine sites are required to meet applicable ambient water quality guidelines for constituents of potential environmental concern (*i.e.,* national, (CCME), federal (ECCC), and provincial). In British Columbia (BC), guidelines can be modified on site-specific bases into "in-stream" water quality objectives to address specific receiving water issues (*e.g.,* high background). Science-based environmental benchmarks (SBEBs) are developed into Site Performance Objectives (SPOs) that are specified in environmental management permits and are established with associated monitoring frequency and reporting requirements (BCMOE, 2016).

Selenium (Se) and nitrate (NO_3) are parameters of potential concern (POPC) at coal mine operations throughout the world. Selenium is a naturally occurring substance and an essential element required for the health of humans, animals, and some plants. Selenium is released to the environment via weathering of exposed surfaces of mine waste materials (e.g., waste rock, pit walls, coarse rejects, and tailings). Nitrate is released primarily via dissolution of blasting residues associated with ammonium nitrate-based explosives (Mahmood et al., 2014).

In the environment, Se is present in five oxidation states including Se(IV), Se(VI), Se(0), Se(-1) and Se(-II). Among these species, the reduced forms of selenium (i.e., Se(0), and Se(-II)) are insoluble in water and less bioavailable while selenate (SeO_4^{2-}) and selenite (SeO_3^{2-},) are highly soluble oxyanions and predominant in most industrial wastewaters and mine contact waters. Both selenate and selenite are bioavailable and have the potential to bioaccumulate.

Several technologies including, physical, chemical, and biological are available for selenium and nitrate treatment. Selenate removal has been reported to be typically not feasible using conventional physical/chemical technologies. Removal of selenite can occur using iron co-precipitation, a conventional physical/chemical technology. However, meeting stringent regulatory discharge limits (in µg/L) may not be possible (NAMC-SWG, 2020). Over the past two decades, technology development for selenate removal has progressed and biological treatment has emerged as the most promising method (NAMC-SWG, 2020). Microbial reduction of Se oxyanions to insoluble elemental selenium has been applied successfully for removal of selenium from wastewater or process water using diverse types of bioreactors (Rittmann, 2006; van Hullebusch et al., 2003).

This paper presents data derived from using anaerobic biochemical reactors (BCRs) for the in-situ treatment of selenium and nitrate in contact water from the Brule Mine. BCRs are a proven and effective biological technology that is used as an alternative to active mechanized physical/chemical treatment and engineered water treatment plants to meet SPOs. In addition to their effectiveness in removing selenate, the in-situ BCRs are cost effective.

Methods

Site Description and BCR Technology

Consistent with other proponents within the mining industry, Conuma has implemented BCRs as the treatment systems of choice to treat and remove nitrates and selenium from mine contact water before discharge into the environment. Conuma has continued in the five plus years of its operation of Brule, to develop and implement progressive generations of BCRs with the help of industry experts and third-party qualified professionals who have worked successfully with BCRs in North American mining applications. The progression of BCR treatment technology at Brule is consistent with other mining operations in North America, as best practices are adapted to the conditions in Northeast British Columbia.

BCRs utilize organic substrate to create an environment where microbes consume and scavenge oxygen beginning with free oxygen, then nitrates, and then reduce selenate to selenite and eventually to elemental selenium. BCRs are generally operated as a gravity downflow systems although upflow configurations are also possible with hydraulic retention time being a key design parameter. BCRs generally have lower capital and operational costs, although they require daily interaction and adjustment of the systems. With proper design, BCRs can operate with minimal energy or chemicals inputs, and can operate reliably in cold climates without external heat inputs. Conuma currently operates two BCRs at Brule Mine (BCR1 and BCR2). For the purposes of this paper, only BCR1 is discussed.

BCR1 treatment system at Brule Mine was initially designed and constructed in 2015. In 2017, BCR1 was optimized by improving composition and layering of the treatment media. The reactor cell media installed in 2017 for BCR1 consisted of three distinct layers of limestone, sawdust and wood chips, and hay. These two previous BCR1 designs utilized the “horizontal flow” system, where water entered BCR1 through an influent manifold pipe situated in the upper interval of the BCR and nested in mixed media. Water then flowed horizontally through a treatment media layer across the reactor and then downward into an underlying limestone drain layer and discharged through a manifold situated within the limestone layer. Water levels within BCR1 were controlled by stop logs located within the Agridrain. From the Agridrain, the effluent flowed into an aeration pond. Although this system was progressively more functional, uniformity of influent flow (and thus effectiveness of treatment) posed operational challenges and there was increased evidence of water forming preferred flow paths, and thus not receiving full treatment. As a result, BCR1 was optimized for the second time by installing a bottom-up vertical flow system that addressed the flaw observed in the horizontal flow system. Conuma retained Navigator Environmental & Technical Services to optimize BCR1 and incorporate design improvements recommended by Third-Party Independent reviewers who completed an evaluation of BCR Technology and its application to cold climates.

In October 2021, BCR1 was drained (this is an anticipated and planned maintenance function for all BCR and indeed most active treatment systems), and the spent media was removed and ultimately replaced. The following design improvements were implemented: the gravel bed on the bottom of the BCR was extended the full length of the BCR; an extensive underdrain system was installed in the gravel bed; a system of standpipes was installed to introduce water into the BCR at the top of the treatment media in order to conserve heat and provide uniform flow across the BCR; the underdrains were plumbed into manholes to collect treated water; new treatment media with substantially more wood fibre was carefully prepared and installed; new insulating hay was installed on top of the treatment media; and pumps were installed in the manholes to remove treated water from the system. These changes converted BCR1 from a horizontal flow BCR to a vertical downflow BCR. This new configuration promotes more uniform flow and uniform treatment, limiting channelling of contact water and promoting uniform residence time. The changes were completed in mid-November 2021 and the first samples from the optimized BCR1 were collected on November 22, 2021.

In the optimized BCR1, water enters the BCR through an influent manifold pipe situated in the upper interval of the BCR and nested in mixed media (BCR1-IN). Water then flows vertically through a mixed-treatment media layer across the reactor and then downward into the underlying limestone drain layer. Treated water (i.e., effluent) discharges from BCR1 through Agridrain1 or is pumped from the manholes into an aeration pond where the anaerobic effluent is aerated prior to discharge into the main sediment pond via an open channel into the southwestern corner (MSP-IN1), where it flows towards the discharge end of MSP (MSP-D) and then to the downstream receiving environment (Blind Creek) before reaching the Compliance point BC-01a. Figure 1 shows the location of the BCRs, and Figure 2 presents the water management through the BCR and surrounding infrastructures. The breakdown of the organic media over time provides electron donors to support the development of reducing conditions required for the reduction of nitrate to nitrogen gas and selenium to SeO_4^{2-} and SeO_3^{2} and then to Se(0) which is precipitated within the BCR through microbially-mediated processes.

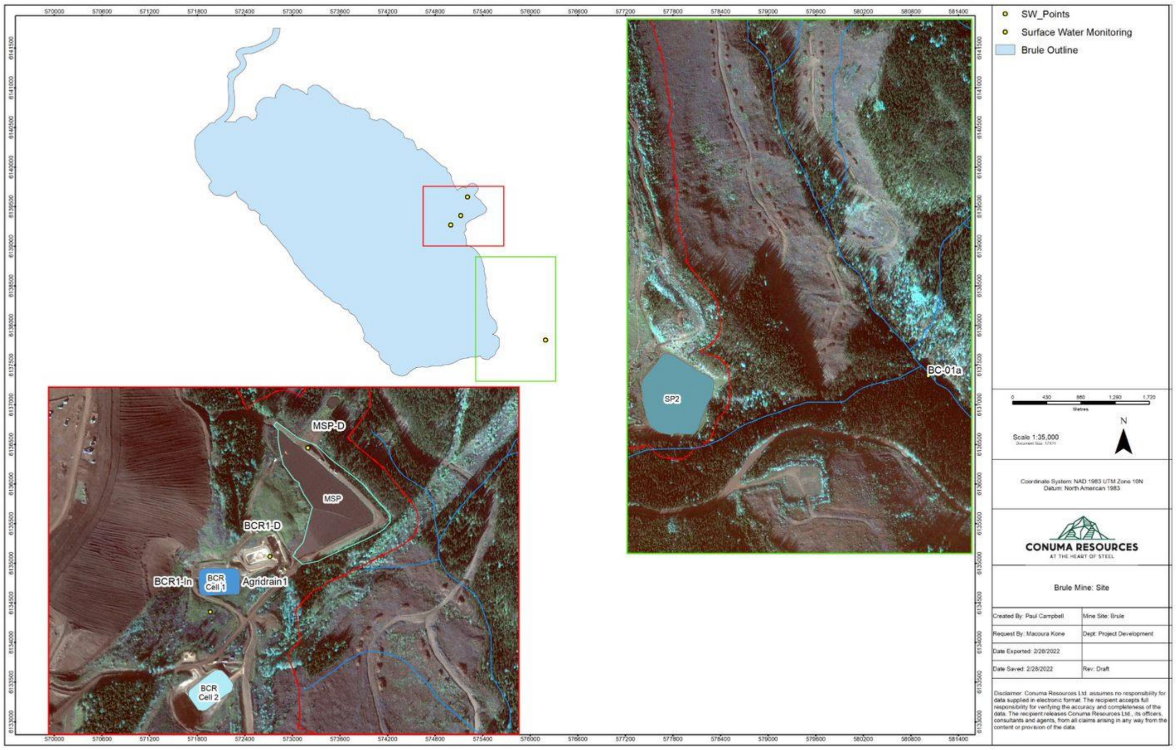

Figure 1: Location of the BCRs

Figure 2: Water Management Through the BCRs

Monitoring

Water samples were collected from monitoring sites described in Figure 2 and sent to an accredited laboratory for comprehensive analysis of geochemical parameters including physical parameters, nutrients, sulphide, anions, total/dissolved trace elements metals and selenium species. Trace element concentrations were determined via inductively coupled plasma mass spectrometry (ICP-MS), while anions were analyzed via ion chromatography. Solid and water samples were analyzed for microbial community by DNA sequencing and quantification of specific bacteria by qPCR tests.

Results

Results are presented in the following sections.

Table 1: Hydrochemistry of influent, effluent and receiving waters

	DO (mg/L)	ORP (mg/L)	pH	Se (mg/L)	Nitrate (mg/L)	Sulphate (mg/L)	Ammonia (mg/L)
BCR1-In	0 -15	0 - 176	6 – 8	0.009 - 0.199	0.013 – 49.2	317 - 712	246 - 605
Agridrain	<0 - 5	-482 – 39	6 – 8	0.002 - 0.1	0.001 - 28	306 - 721	288 - 732
BCR1-D	<0 - 18	-187 – 169	7 – 9	0.006 - 0.089	0.001 – 28.7	322 - 728	294 - 802
BC-01a	0 -124	0 -169	8 -9	0.001 – 0.061	1.01 – 47.9	41 - 618	116 - 530

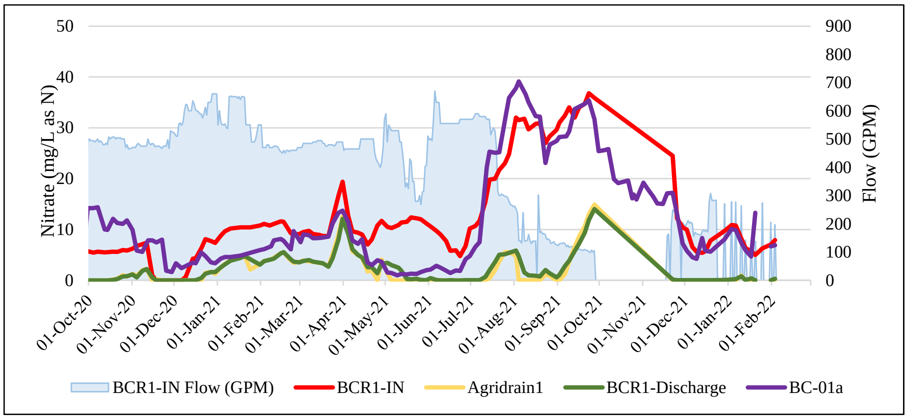

Figure 3: Time series of nitrate in influent, effluent and receiving environment

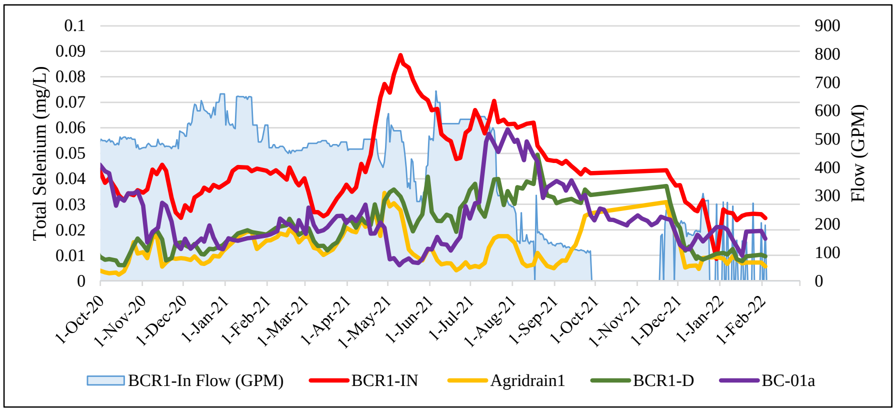

Figure 4: Time series of total selenium in influent, effluent and receiving environment

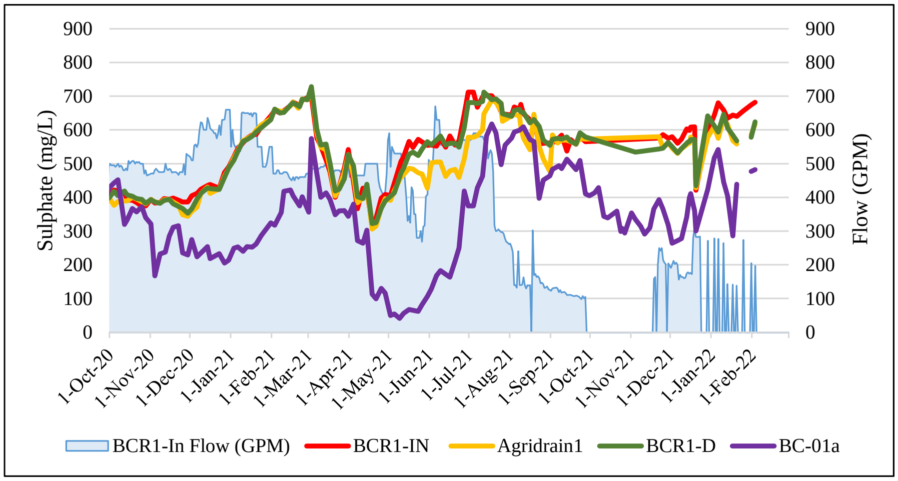

Figure 5: Time series of sulphate in influent, effluent and receiving environment

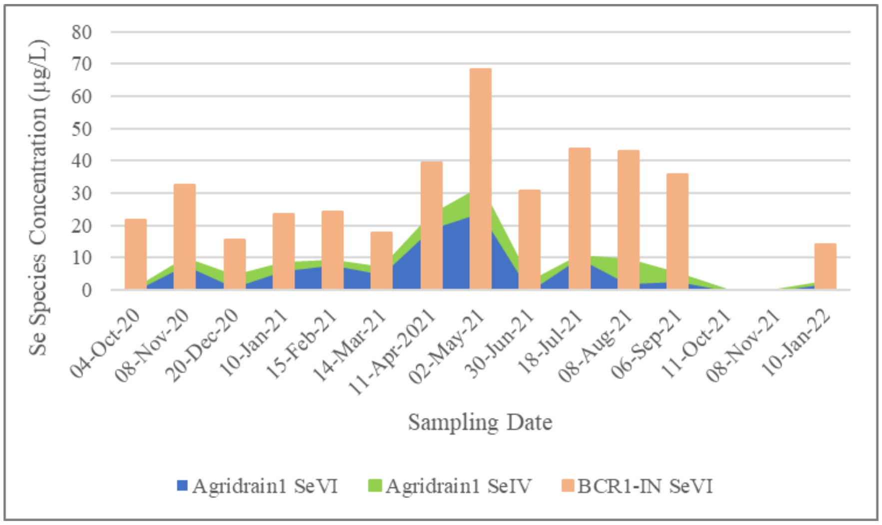

Figure 6: Selenium speciation species in influent and Agridrain effluent

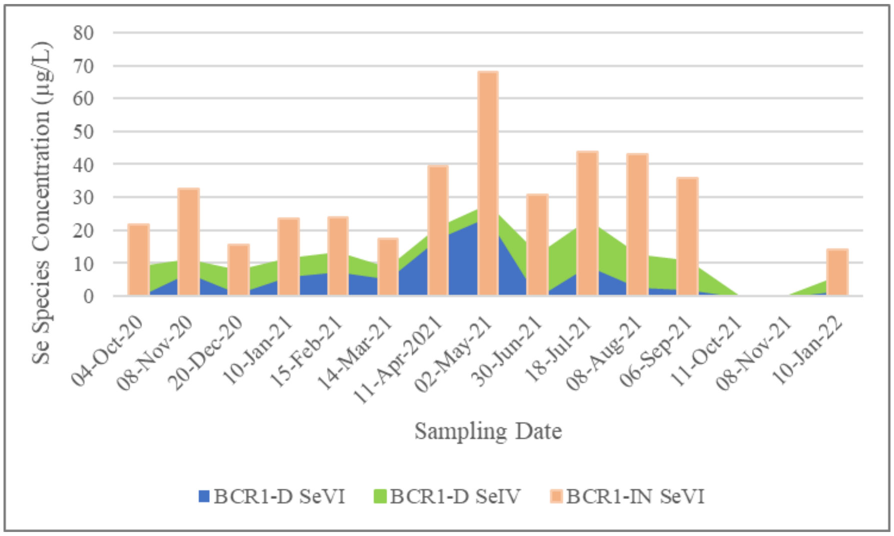

Figure 6: Selenium speciation species in influent and BCR1-D effluent

Discussion

The data for redox proxies in the Agridrain are indicative of mildly suboxic conditions, as inferred by absence of DO, values of oxidation-reduction potential (ORP), and presence of ammonia (Table 1). Indicators of more strongly reducing conditions, as would be revealed by sulphate reduction and/or reductive dissolution of Fe oxide were not observed. Concentrations of Fe were below the detection limits, and no decreases were observed for sulphate (Figure 5).

Nitrate concentrations in the untreated influent water (BCR1-IN) show mine-related signature, attributed to residual ammonia-nitrogen-based blasting residues. Concentrations ranged from (<1 to 49 mg/L). After treatment in the bioreactor, concentrations of nitrate in the outflow of the bioreactors (Agridrain) decreased to less than 1 mg/L with pH ranging from 6 to 8 (Table 1). These results show evidence of effective denitrification (i.e., microbially-mediated nitrate reduction) up to 100 % by nitrate reducing bacteria (NRB) such as *Thiobacillus*, *Acinetobacter*, *Pseudomonas*, *Sulfuricumonas* identified in the bioreactor and the Agridrain. These results support earlier findings that demonstrated the use of these bacteria for the reduction of nitrate (Lortie et al., 1992; Torrento et al., 2010). Similarly, concentrations in the discharge effluent water (BCR1-D) were below the regulatory limit of 10 mg/L (Figure 3).

Selenium shows removal rate of up to 94% with concentrations decreasing from ~200 µg/L to less than 20 µg/L at pH 7-9 (Table 1), attributed to selenium reducing bacteria (SeRB) such as *Pseudomonas*, *Bacillus*, identified in the bioreactor and the Agridrain. These results are consistent with earlier findings that demonstrated the use of these bacteria for the reduction of selenium oxyanion, selenate (SeVI) and selenite (SeIV) (Lortie et al., 1992) and production of insoluble elemental selenium (Stolz et al., 2006; Lenz and Lens, 2009) (Figure 4). The reduction in Se concentration was accompanied by a shift in Se speciation from dominantly selenate (SeVI) to selenite (SeIV) and/or to insoluble elemental selenium (Figures 6 and 7) via dissimilatory microbial reduction under suboxic to anaerobic conditions. The influent is characterized by selenate (SeVI) while selenite (SeIV) is predominant in BCR treated waters. Both selenate and selenite yielded lower concentrations in BCR effluents (Agridrain and BCR1-D) than influent (BCR1-IN), indicating that the BCRs can reduce selenate to selenite and then to insoluble elemental selenium believed to be adsorbed into mixed media in the BCRs. Other forms of Se evaluated, include organic Se compounds and selenocyanate, which were at trace levels (i.e., selenocyanate, dimethylselenide, methylselenic acid, and unknown selenium compounds) or with concentrations less than analytical detection limits (i.e., selenomethionine and dimethyl diselenide).

The results presented here show simultaneous and significant selenate and nitrate reduction within the bioreactors under suboxic to anoxic conditions, consistent with findings reported earlier by Oremland et al. (1999) and Bianchin et al. (2013). Nitrate in the treated effluent (Agridrain) were near complete consumption and below the regulatory limits, while selenium concentrations, though below the regulatory limits in most instances perform less than nitrate. These results also support findings by Zhao et al (2014) who demonstrated that near complete removal of nitrate may be required for significant selenate reduction to occur. Concentrations of nitrate have mostly been below the SPO limit at the compliance site (BC-01a) for the last three months. However, selenium in the receiving environment (BC-01a) remain above the SPO limit. Recent optimization of BCR1 and the proposed construction of additional water management structures are expected to improve contact water management, influent, and downstream receiving water quality.

Conclusion

The use of biochemical reactors for the attenuation of selenium and nitrate are integrated in the Brule Mine design and water management plans. The results presented in this paper demonstrate that BCRs can be used as in situ bioremediation technology for effective reduction of Se and NO_3 in mine contact waters and meet regulatory limits.

There is an opportunity to enhance Se removal and meet rapidly regulatory limits via the addition of organic substrates (i.e., molasses) or defined organic amendments (i.e., acetate and lactase) to the bioreactors as carbon source and electron donors to facilitate growth and reduction of Se oxyanions to elemental selenium. (USEPA, 2001, Park et al., 2006).

Certainly, improvement of water management structures for the interception and collection of contact water for treatment and source control measures will limit release of constituents of concern into the environment.

The engagement and involvement of First Nations in the design, implementation, and operations of water management systems; as well as environmental monitoring is ongoing, and information gathered are shared in a coordinated manner through multiple forums including the environmental monitoring compliance committee (EMCC).

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