SELENIUM, URANIUM, AND NITRATE: TREATMENT OF TROUBLESOME CONTAMINANTS IN MINING WASTEWATERS – EBR CASE STUDIES[1]

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Abstract: Selenium (Se), uranium (U), and nitrate (NO_3) are widespread in many North American mining environments and related industrial waters. These contaminants are often particularly difficult or expensive to remove using conventional water treatment methods, such as chemical coagulation/precipitation, reverse osmosis filtration, ion exchange, etc. Treatment system capital and operating expenses combined with additional costs of sludge or concentrate stream disposal, are driving research and application of biotreatment methods for removal of these contaminants from mining and industrial wastewaters.

This paper discusses application of the Electro-Biochemical Reactor (EBR) technology for Se, U, and NO_3 bio-reduction and removal from mining wastewaters. Three case studies are presented, based on laboratory bench- and on-site pilot-scale trials with significantly different mining waters (flotation-influenced base metals mine water, leach solution from a gold mine, and coal mine seepage water), each contaminated with varying concentrations of Se, U, and NO_3. Average concentrations of these contaminants were 2,712 µg L^{-1} Se, 2.0 µg L^{-1} U, and 1.53 mg L^{-1} NO_3-N (Site A); 2.9 µg L^{-1} Se, 92.5 µg L^{-1} U, and 189 mg L^{-1} NO_3-N (Site B); and 105 µg L^{-1} Se, 18.4 µg L^{-1} U, and 50 mg L^{-1} NO_3-N (Site C). The EBR technology was demonstrated on all three sites to treat the waters to <0.5 – 3.2 µg L^{-1} Se, <0.1 – 0.8 µg L^{-1} U, and <0.02 – <2 mg L^{-1} NO_3-N.

The high combined Se, U, and NO_3 removal efficiency achieved with EBR treatment, at both laboratory and field scale, has positive implications for future treatment system design at many sites. The EBR process would be applicable and beneficial at sites facing the challenge of mixed contaminant treatment to low discharge standards, simplifying the treatment train to one primary process, and eliminating the need for sludge or concentrate stream treatment/disposal.

Additional Key Words: bio-treatment, electro-biochemical reactor

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Introduction

Selenium, Uranium, and Nitrate in Mining Waters

Selenium, U, and NO_3 are widespread in many North American mining environments and related industrial waters. Both Se and U are naturally occurring trace elements that are also toxic at low concentrations, although due to different reasons (Conley et al., 2009; Besser et al., 1996). Elevated Se exposure affects growth, reproduction, mortality, and causes embryo deformities in aquatic life and birds (Hamilton, 2004). Aggravating the issue is the bioaccumulative nature of Se in food chains (Ohlendorf, 2002). The health effects of uranium exposure for humans and animals include renal disorders, neurobehavioral effects, mutagenic effects, skin irritation and reduced fertility (Brugge et al., 2005; Lourenço et al., 2017). In addition to these two elements, nitrogen species, such as nitrate and ammonia, are often found in the mining waters mainly due to leaching of residual blasting compounds and/or cyanide degradation.

Treatment to remove NO_3 and either Se or U or combinations of all three contaminants from mining waters has proven to be challenging for conventional water treatment methods (Sorg, 1991). Uranium is most often removed via lime softening and enhanced coagulation/filtration or ion exchange (Katsoyiannis and Zouboulis, 2013). However, Se and NO_3 are not susceptible to conventional coagulation methods. Anaerobic biological treatment and ferric precipitation are most commonly used for Se removal (Sandy and DiSante, 2010), whereas NO_3 is best targeted by biological denitrification treatment methods but it can also be removed by ion exchange systems with ion-specific resins (Dahab, 1991). Additionally, all three contaminants can be targeted to some extent by reverse osmosis (RO) membrane filtration but this is expensive and produces brines that require additional treatment or disposal.

Sites that face water contamination with all three contaminants either resort to complex treatment trains with multiple unit processes targeting each compound or turn to more expensive solutions like RO. Many conventional treatment methods generate a concentrated waste stream (e.g., brine from RO treatment) that must be properly disposed of or treated further. The application of these treatment methods is fairly common in the drinking water market; however, the elevated capital and operating expenses and proper sludge or brine disposal, is driving research and application of biotreatments methods for concurrent removal of nitrate with Se and/or U from mining and other industrial waters.

Electro-Biochemical Reactor

Electro-microbiology is a developing scientific discipline that studies microbial extracellular electron utilization and transfer mechanisms (Franks, 2012; Lovley, 2012). Synthesis of adenosine triphosphate (ATP), the molecule responsible for energy transfer in all living organisms, is dependent on electron flows and electrochemical gradients. Microbes have been demonstrated to utilize metals and minerals as the terminal electron acceptor for energy synthesis in anaerobic environments (El-Naggar and Finkel, 2013). Cytochromes located on and near microbial cell membranes and flagella are capable of gathering and exchanging electrons with their environment. This in turn allows these microbes to interact directly with electrons and electron acceptors in their extracellular environment for energy exchange (Reguera et al., 2005).

Biological denitrification and reduction of selenate/selenite and soluble U(VI) species are well known and documented processes. In recent years, multiple laboratory studies have demonstrated improved denitrification and metals reduction kinetics when electrodes were used as electron donors for the bioreactor and the microbes (Gregory et al., 2004; Park et al., 2005). However, the concepts of electro-microbiology have not yet been applied to large-scale water treatment systems simultaneously targeting Se, U, and NO_3.

We have demonstrated improved Se, U, and NO_3 transformation kinetics through an Electro-Biochemical Reactor (EBR), a patented technology applying the concepts of electro-microbiology to mine water biotreatment. By directly supplying electrons to the microbes throughout the bioreactor system, the EBRs attain more controlled and stable oxidation-reduction environments, resulting in reduced nutrient requirements and better performance at lower temperatures (Adams et al., 2012; Opara et al., 2014; Opara et al., 2016; Fudyma et al., 2018). In conventional biological treatment systems, electrons are supplied from nutrients and chemicals added to the system that require metabolism to access the electrons. An excess of nutrients/chemicals is typically required to compensate for inefficient and variable electron availability needed to adjust reactor chemistry and provide energy for microbial growth and contaminant removal. The EBR system provides a low voltage potential (1-3 V) at a low milli-Amp current that directly supplies electrons to the microbes without the added energy expense of nutrient metabolism or excess microbial growth.

The objectives of this study were to determine the efficacy and efficiency of the EBR technology for Se, U, and NO_3 bio-reduction and removal from mining wastewaters. Three case studies are presented, based on laboratory bench- and on-site pilot-scale trials with significantly different mining waters (flotation-influenced base metals mine water, leach solution from a gold mine, and coal mine seepage water), each contaminated with varying concentrations of Se, U, and NO_3.

Methods

Site Test Waters

Wastewaters from three confidential Canadian mine sites were evaluated (Table 1). Water A was from an underground mining project producing Zn, Cu, Pb, Ag, and Au, using flotation circuits. Water and solids from the flotation process were discharged to a tailings pond where solids were allowed to settle with subsequent water re-circulated to the ore processing facility. A complex flotation process and the water recirculation practice made the water chemistry a moving target, with many difficult to treat constituents. Positive water balance dictated that excess water from the tailings pond needed to be treated before being discharged to the environment. An on-site pilot-scale EBR system was installed at the tailings pond.

Table 1. Characteristics of three mining waters tested for selenium, uranium, and nitrate removal using the EBR technology.

	Source	Ave. total Se [µg/L]	Ave. total U [µg/L]	Ave. NO_3-N [mg/L]	Bench Testing	Pilot Trial
Water A	Underground metals mine, flotation-influenced process waters	2,712	1.99	0.8	✓	✓
Water B	Open pit coal mine, seepage waters	105	18.4	49.8	✓	✓
Water C	Prospect gold mine, leach solutions	3.17	92.5	189	✓	

Water B was from an open pit coal mine. The weathering of coal mine waste rock releases selenium and other co-contaminants, such as sulfate and iron, into the seepage waters. The site seepage waters were collected in a sedimentation pond and treated in an on-site pilot-scale EBR operation. The operation was conducted during fall months, providing an opportunity for cold weather testing (Fig. 1).

Figure 1. EBR pilot system location by a sedimentation pond at a confidential coal mine during warm and cold weather, Water B.

Water C was from a gold drilling exploration project. The leachate was generated from a mixture of cyanide-leached ore mixed in portions thought to represent run of mine ore. The cyanide neutralized leach solution was treated in a bench-scale EBR operation for a three-month period. Results of this laboratory-scale test were used as a proof-of-concept to demonstrate treatment feasibility to obtain mining operations permits and will be used to provide baseline data for future pilot-scale work and potential process adjustments.

System Setup and Operation

Each on-site pilot-scale trial was preceded by laboratory bench-scale feasibility tests with the goals of demonstrating Se, U, and NO_3 removal from mining waters and identifying key pilot-scale test parameters. Mine waters were collected from the three sites described above and shipped to the Inotec laboratory for evaluation. Se-, U-, and nitrate-reducing microorganisms from Inotec repository and native to the three mine sites were screened in these waters. The microbial consortia best capable of desired contaminant transformations were selected. Bench tests were conducted to develop design and operational parameters for pilot test systems. This testing helps ensure a high probability of successful on-site pilot treatment demonstration. Pilot-scale testing was conducted on-site to validate treatment efficiencies under conditions of larger flows, fluctuating water chemistries, and other varying site conditions, such as temperature. The data gathered at this testing phase allows better development of design, operation, and costing parameters for the full-scale facilities.

Both laboratory bench-scale and on-site pilot-scale systems consisted of plug-flow, fixed bed, up-flow bioreactors, in a two-stage configuration. All tests were performed under continuous flow conditions; bench-scale systems were operated at flowrates of 0.5-2.0 mL/min, while the pilot systems were operated at 1-3 L/min. The bioreactors were filled with activated carbon as microbial support media and inoculated with site-specific Se-, U-, and nitrate-reducers. A 1-3 V potential was applied across each reactor using adjustable DC power supplies connected to Ti rod electrodes. EBR reactors were operated with hydraulic retention times (HRT) of 6-24 hours and provided with agricultural-grade molasses as a nutrient (C, N, and P source). No additional post-treatment (e.g., sedimentation, filtration, etc.) was used. Pilot-scale systems were fully automated and PLC controlled.

Monitoring and Analytical

Inotec personnel monitored lab and field parameters daily (dissolved oxygen, temperature, pH, ORP, conductivity, flowrate, molasses additions, and applied voltage/current) using an Orion Star A329 Portable Multiparameter Meter. Samples were sent to ALS Environmental in Vancouver, Canada (an independent analytical laboratory) for full-suite analysis. Metals and inorganics analyses were performed using ICP-MS (method EPA 6020A) and IC (method EPA 300.1), respectively. Unless noted otherwise, all Se and U data presented are expressed as total values; i.e., samples were not filtered prior to ICP-MS analysis.

Results and Discussion

Water A: Flotation-Influenced Process Waters

The main contaminant of interest in mine water A was Se. Complex water chemistry stemming from multiple ore flotation circuits used for recovery of five different metals and continuous water reuse rendered this water difficult to treat using conventional physical, chemical, and/or biological processes. Chemical oxygen demand (COD) of the water averaged 700 mg/L, with only 240 mg/L attributed to biological oxygen demand (BOD). Most of the COD was due to complex organics used in the processing plant, such as xanthates used as collectors in the froth flotation process. Initial evaluation tests with industry leading conventional chemical and biological processes were unsuccessful in meeting the required discharge criteria, and none were within an order of magnitude of meeting the total Se discharge limit of 20 µg/L.

Following an extensive bench-scale testing program that included additional evaluations to develop an EBR system design that effectively treated the complex wastewater containing high concentrations of flotation organics with a broad spectrum of metals, a pilot-scale EBR unit was deployed on site to treat water A. Influent waters showed highly variable water chemistry, with an average Se concentration of 2,712 µg/L, that varied up to 3,420 µg/L. The EBR system reduced Se to an average concentration of 5.4 µg/L, never exceeding the discharge limit of 20 µg/L after the system start-up period. Due to the development of a site microbial population during laboratory-scale testing, EBR inoculation and start-up periods are considerably shorter than conventional systems; pilot system start-up for water A lasted about a week (Fig, 2).

Uranium was not regulated under current mine site's discharge permit; U concentrations in the tailings pond's water typically did not exceed several µg/L but was a requested monitoring parameter. The pilot-scale EBR system demonstrated consistent U removal to below the detection limit of 0.1 µg/L throughout the duration of the pilot trial, even though the influent U levels rose 6-fold by the end of the test (Fig. 3).

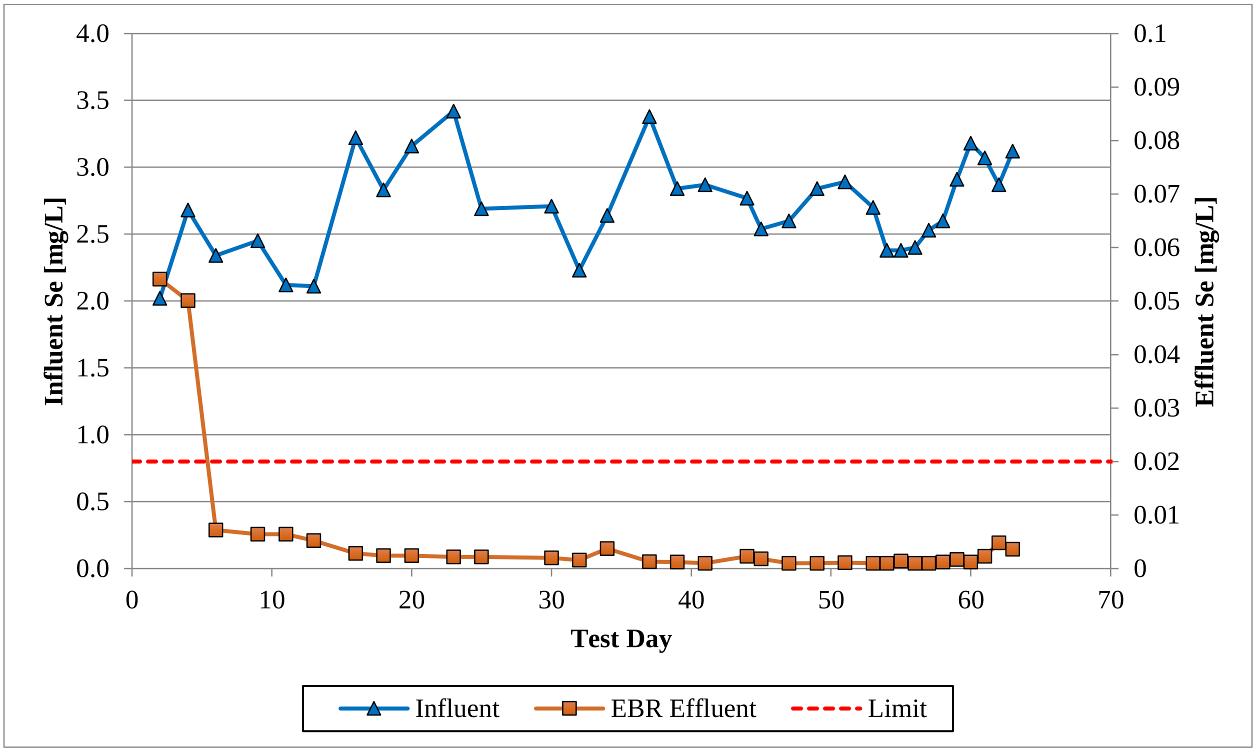

Figure 2. Selenium removal by the pilot-scale EBR system; mine water A. Note different y-axes for the influent and effluent concentrations.

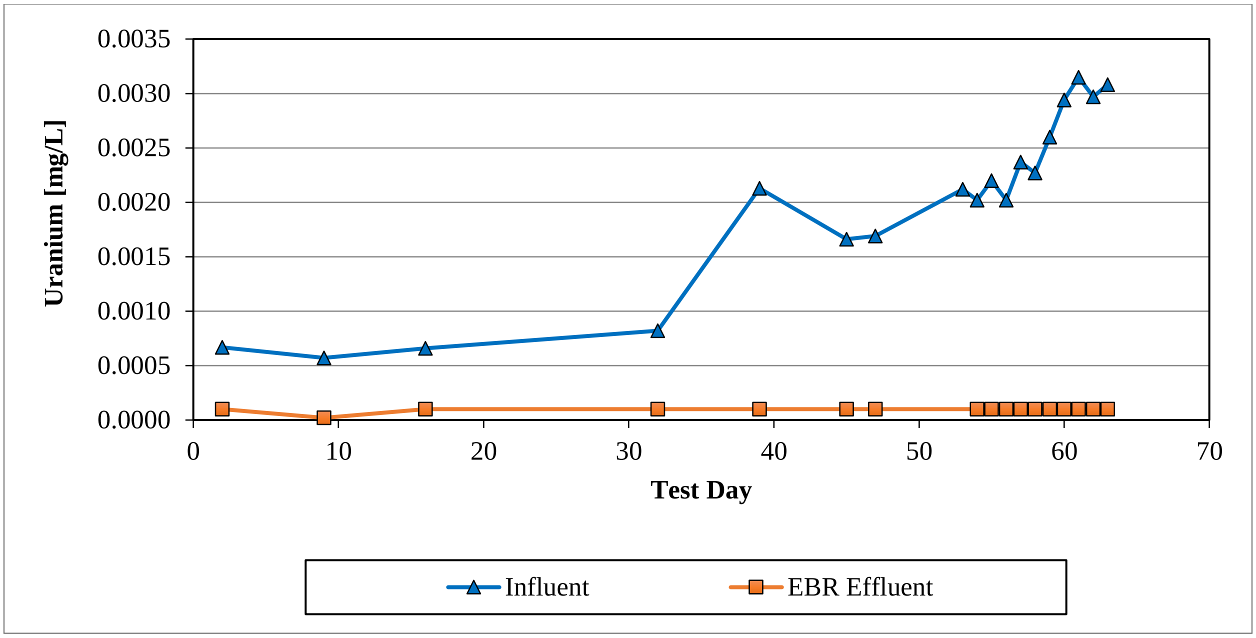

Figure 3. Uranium removal by the pilot-scale EBR system; mine water A.

Nitrate-N was typically present in site A's tailings pond's waters below the permitted 10 mg/L. However, the site's nitrite-N discharge limit was 0.6 mg/L and the tailings pond waters typically exceeded this concentration. The pilot-scale EBR system consistently reduced the variable tailing pond NO_3-N and NO_2-N water concentrations to below the detection limits of 0.1 mg/L and 0.02 mg/L, respectively (Fig. 4 and 5).

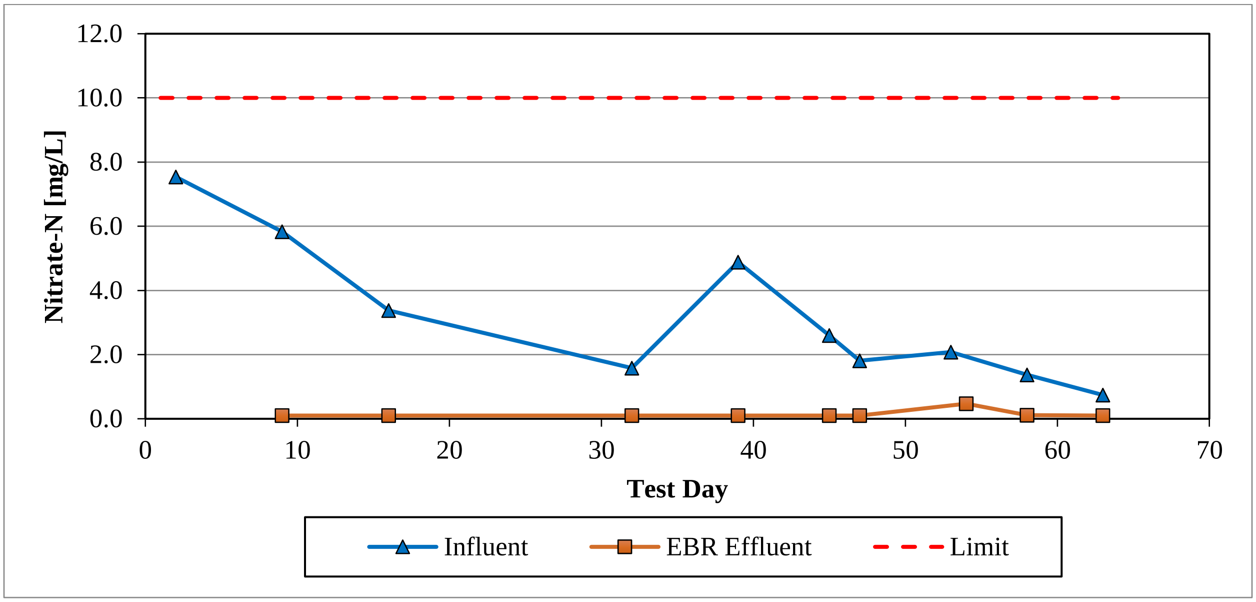

Figure 4. Nitrate-N removal by the pilot-scale EBR system; mine water A.

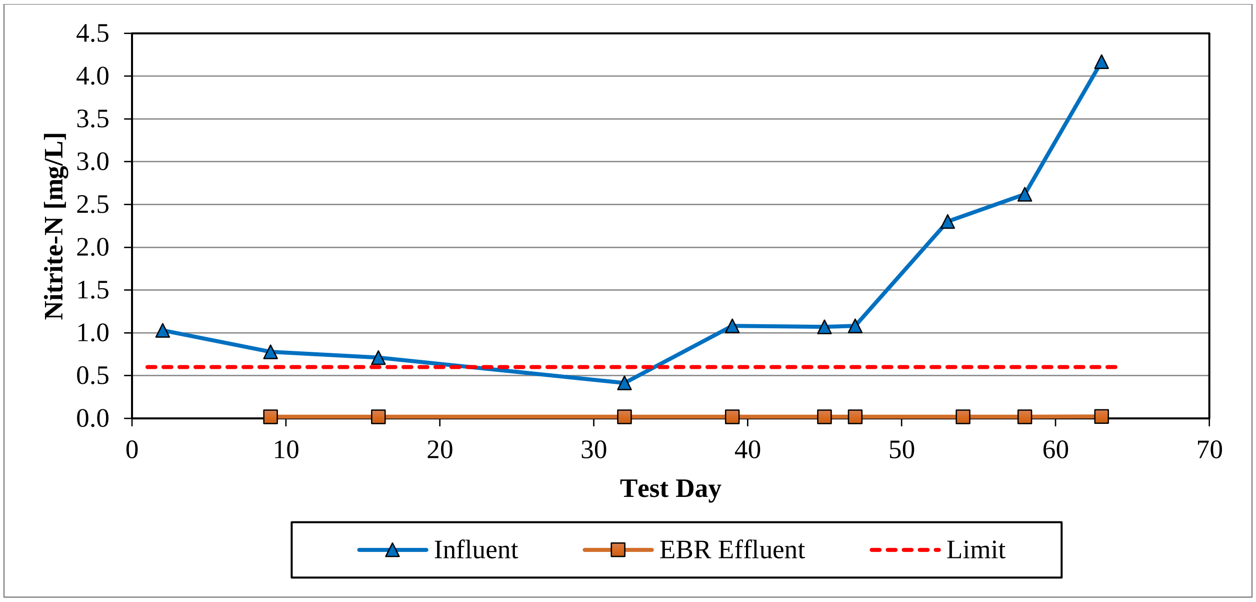

Figure 5. Nitrite-N removal by the pilot-scale EBR system; mine water A.

Water B: Coal Mine Seepage Waters

After a successful 6-month laboratory bench-scale evaluation and pilot system design, the pilot EBR unit was deployed for an on-site trial at a British Columbia (BC) coal mine, where Se and NO_3 were the main contaminants of interest. Elevated Se concentrations are a ubiquitous occurrence in coal mining environments in western Canada, with values ranging from below 50 to over 500 µg/L in site waters. Mining of seleniferous coals in Canada has resulted in pronounced increases in Se in receiving waters in recent years.

Unlike site A's fluctuating water chemistry, the coal waste seepage waters were characterized by stable chemistry. Selenium in site B's waters averaged 105 µg/L during on-site testing, varying between 97 and 116 µg/L. The pilot-scale EBR system consistently removed Se to an average of 0.5 µg/L throughout the testing, significantly below the site discharge limit of 10 µg/L (Figure 6).

Uranium, a secondary contaminant at site B, was also relatively constant and averaged 18.4 µg/L. The EBR pilot system effluent averaged 0.7 µg/L total U throughout the test (Fig. 7).

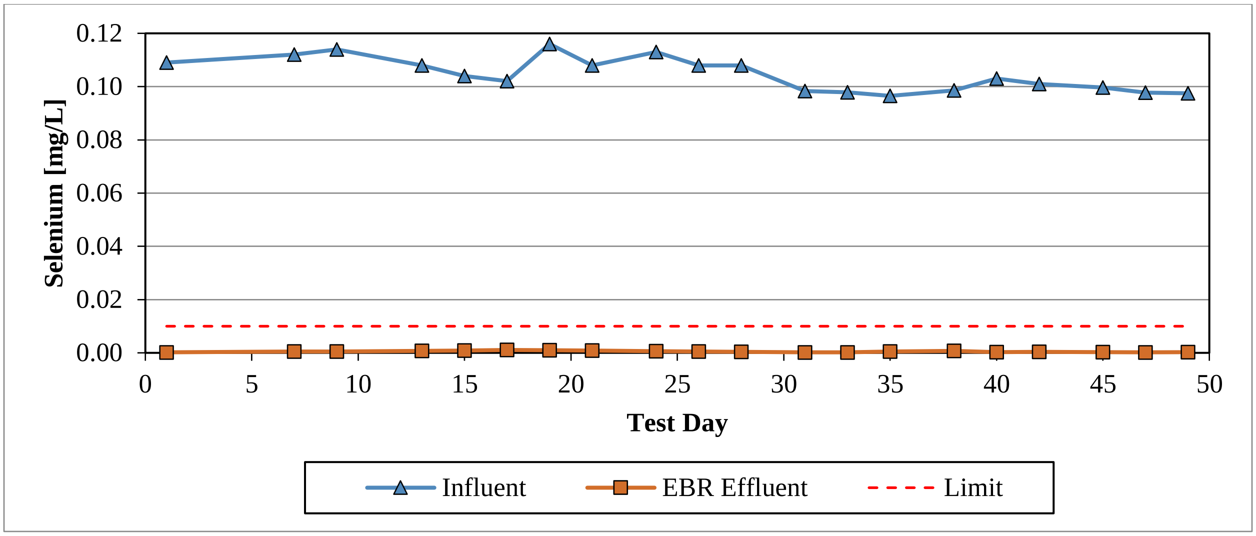

Figure 6. Selenium removal by the pilot-scale EBR system; mine water B.

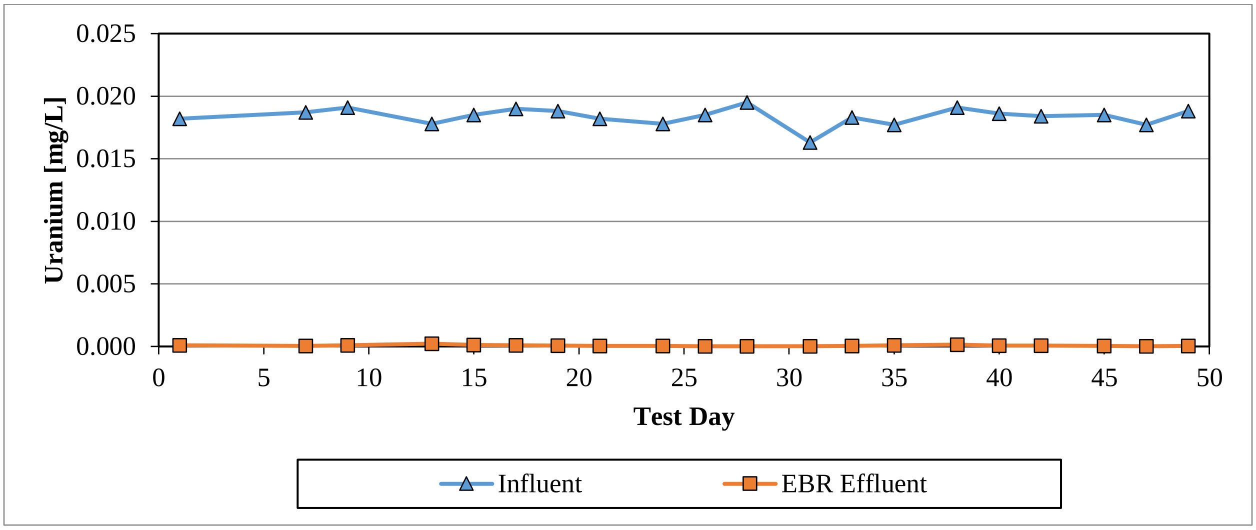

Figure 7. Uranium removal by the pilot-scale EBR system; mine water B.

Nitrate-N was another major contaminant at site B, resulting from residual blasting compounds in the waste coal heaps. Its concentrations averaged nearly 50 mg/L, as N. Initially, complete denitrification was achieved by the EBR unit but as the temperature dropped to below 5^0C, EBR denitrification kinetics slowed down (Fig. 8). Interestingly, even though NO_3 was the preferred electron acceptor, lower temperatures did not affect Se or U removal (Fig. 6 and 7). Furthermore, there was no accumulation of nitrite, which is an intermediate product of denitrification (Fig. 9). The obtained trial results dictate that for a full-scale EBR facility to meet the 10 mg/L nitrate-N discharge limit, influent waters must be at temperatures above ~5^0C.

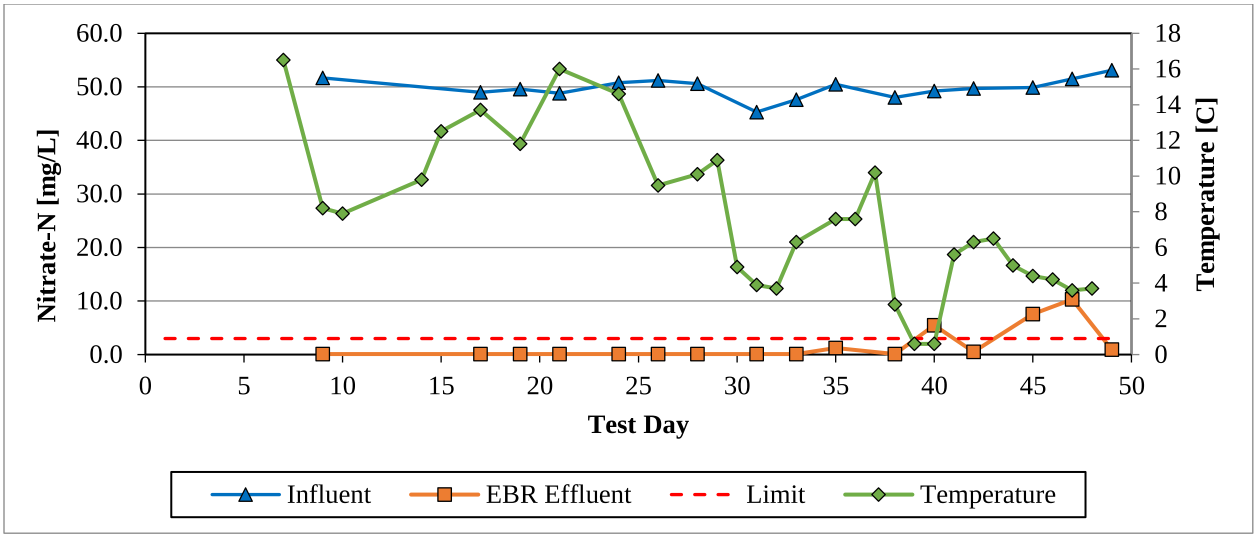

Figure 8. Nitrate-N removal by the pilot-scale EBR system and influent water temperature; mine water B.

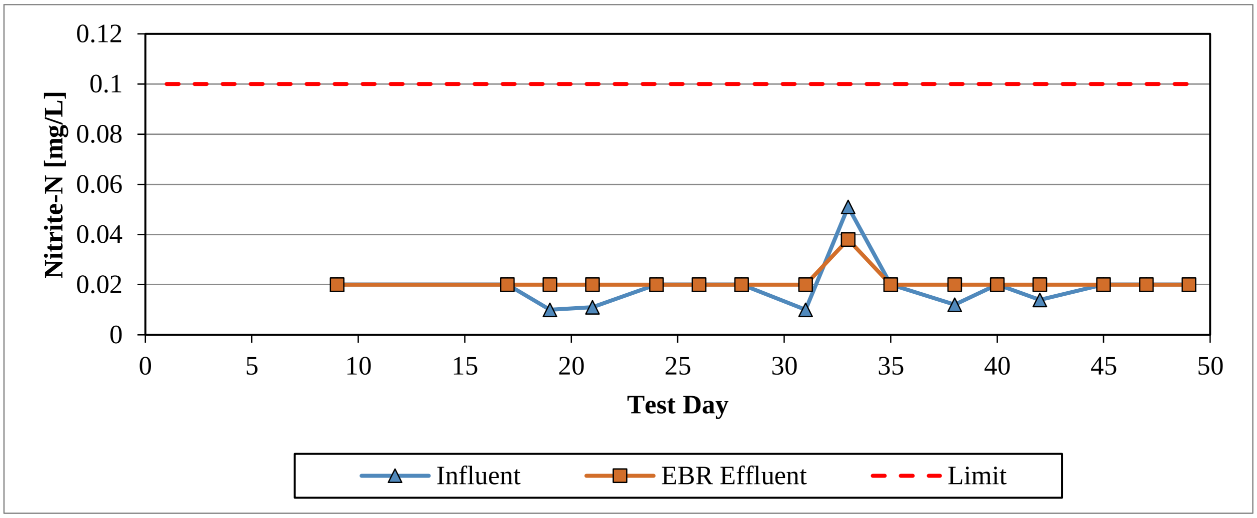

Figure 9. Nitrite-N removal by the pilot-scale EBR system; mine water B.

Water C: Gold Mine Leach Waters

A prospective gold mine, in site permitting stages, performed gold leaching testing on the ore samples. Barren leach solutions were evaluated at laboratory bench-scale for EBR treatment of contaminants of interest, mainly nitrate-N at 150-250 mg/L and uranium at 40-160 µg/L.

Selenium was a tertiary contaminant, present below 5 µg/L. The laboratory EBR system initially removed Se to below 0.5 µg/L but as the system was optimized for NO_3 and U reduction (both present at higher concentrations and both being more energetically favorable electron acceptors than selenium), Se removal efficiency dropped (Fig. 10). Since the mine is in permitting stages, discharge limits have not been assigned yet but it is believed Se standard will be set around 5-10 µg/L, well above the predicted leach water concentrations. Should the limit be set lower or should the actual leach water's Se concentrations be higher than predicted, the EBR system can be optimized for higher Se removal efficiency, as demonstrated in the first month of testing.

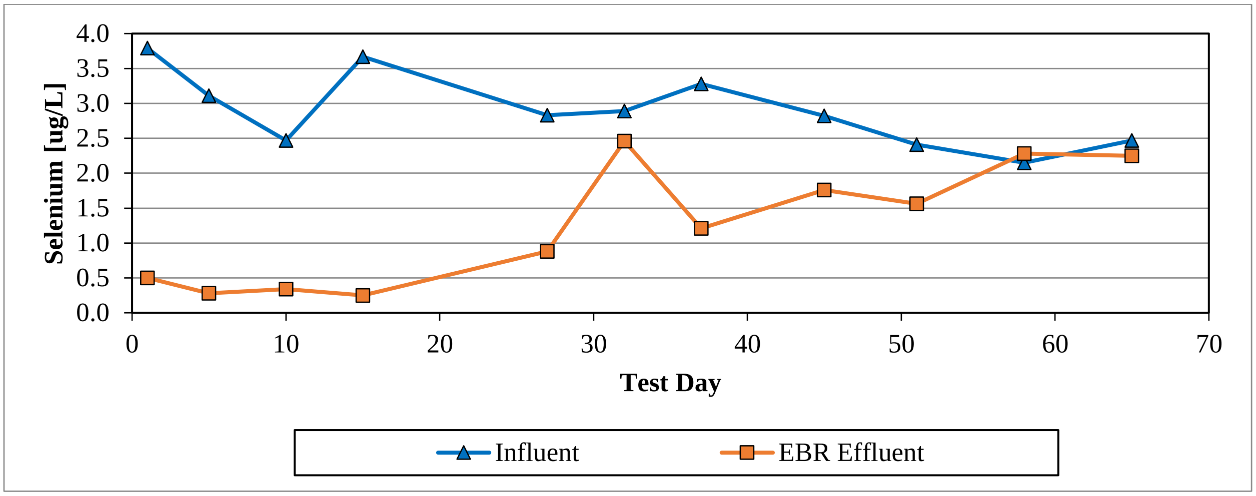

Figure 10. Selenium removal by the bench-scale EBR system; mine water C.

Uranium averaged 92.5 µg/L in the tested leach waters and was consistently removed by the bench-scale EBR system to an average of 0.8 µg/L (Fig. 11). Nitrate and nitrite were both elevated, as would be expected from gold mining leach waters. Complete denitrification was demonstrated with the bench-scale EBR system (Fig. 12 and 13).

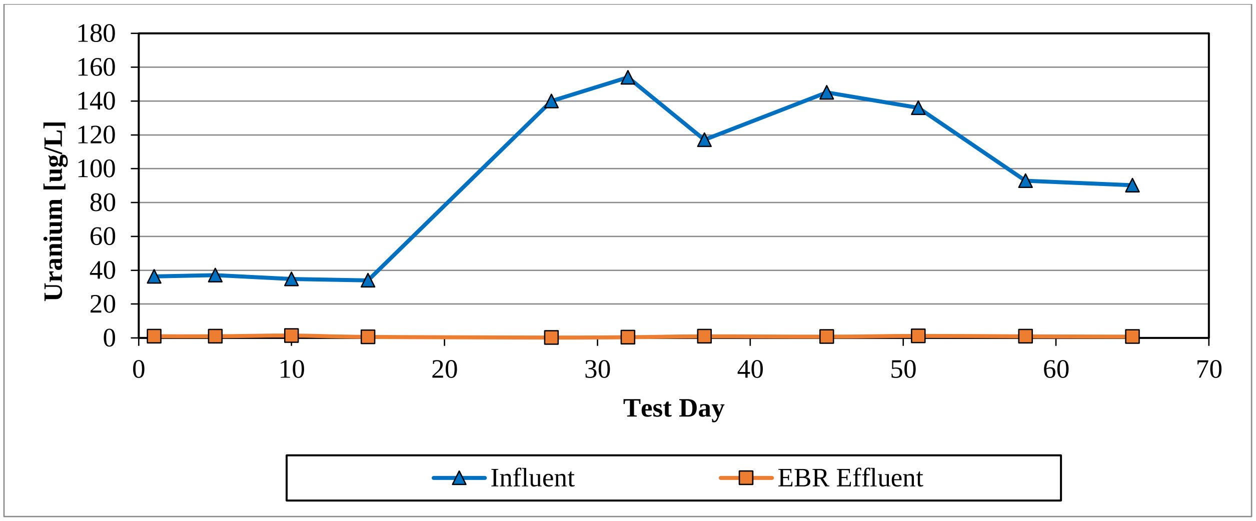

Figure 11. Uranium removal by the bench-scale EBR system; mine water C.

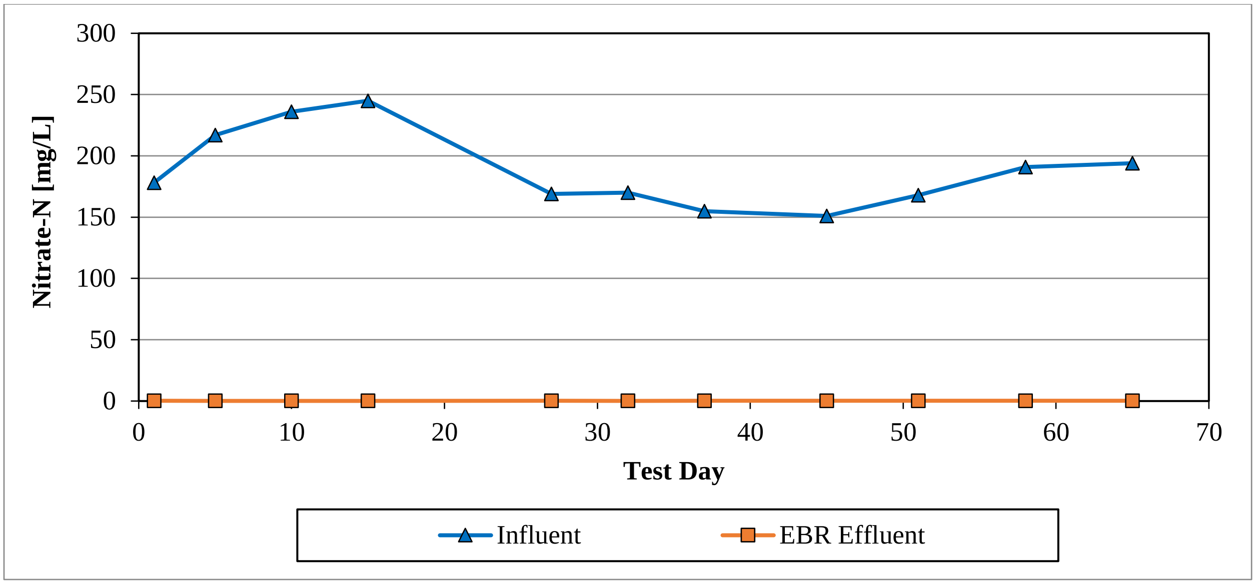

Figure 12. Nitrate-N removal by the bench-scale EBR system; mine water C.

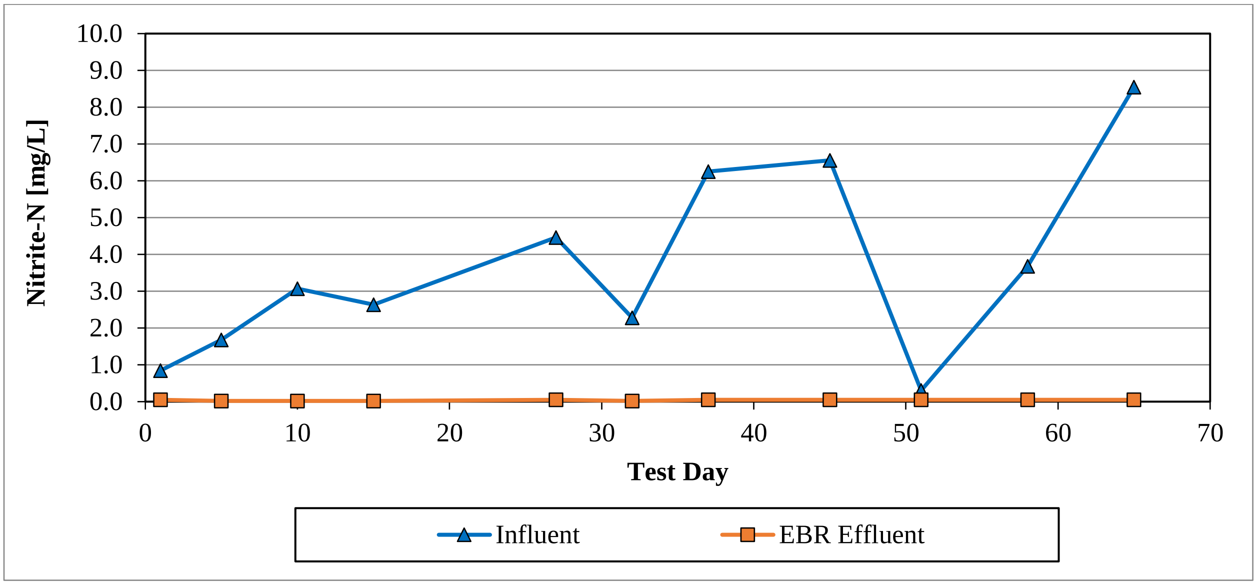

Figure 13. Nitrite-N removal by the bench-scale EBR system; mine water C.

Positive EBR treatability results have aided the mine in review meetings and will be used with further testing in obtaining the site permit. The EBR technology will be evaluated on site in pilot trials to demonstrate treatability of actual leach waters, assess the effects of on-site environmental factors, such as temperature, on treatment efficiencies, and to develop operational and design parameters for a full-scale facility.

Conclusions

The EBR technology has been demonstrated to successfully and simultaneously target Se, U, and nitrate/nitrite in three very different mining waters. The summary of the EBR efficiencies during these three trials are provided in Table 2. These successful trials have positive implications for mine sites facing challenges of simultaneous treatment of multiple contaminants to low discharge levels. Since other existing technologies either must be combined to target all three contaminants simultaneously, creating a complex treatment train, or are expensive to operate (e.g., RO), and/or produce concentrated waste streams that need additional treatment or storage, the EBR technology offers an effective, simplified, and more affordable solution.

Table 2. Summary of EBR removal efficiencies of selenium, uranium, and nitrate/nitrite.

		Water A	Water B	Water C
$Se_{,tot.}$	Influent [µg/L]	2,712	105	3.17
	EBR Effluent [µg/L]	5.44	0.52	1.25
	Removal [%]	99.8%	99.5%	60.6%
$U_{,tot.}$	Influent [µg/L]	1.99	18.4	92.5
	EBR Effluent [µg/L]	<0.1	0.07	0.83
	Removal [%]	>95.0%	99.6%	99.1%
NO_3-N	Influent [mg/L]	0.8	49.8	189
	EBR Effluent [mg/L]	<0.1	<3.1	<0.2
	Removal [%]	>87.5%	>93.8%	>99.9%
NO_2-N	Influent [mg/L]	1.53	<0.02	3.66
	EBR Effluent [mg/L]	<0.02	<0.02	<0.04
	Removal [%]	>98.7%	N/A	>98.9%

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