

SELEN-IX™: ION EXCHANGE AND ELECTROCHEMISTRY AT WORK TO COST EFFECTIVELY REMOVE SELENIUM FROM MINE IMPACTED WATERS TO ULTRA-LOW CONCENTRATIONS

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ABSTRACT

With more rigorous regulations being enacted in the mining industry, a need exists for cost effective and environmentally compliant technologies to remove selenium from mine impacted waters to ultra-low concentrations. Existing selenium treatment methods have high life cycle costs, introduce risks of acute fish toxicity, and produce biological waste residues that represent future liabilities. Furthermore, achieving selenium discharge limits of less than 4 ppb is a challenge for existing technologies. Selen-IX™ is a technology developed by BioteQ that selectively removes selenium from mine impacted waters to less than 1 ppb. The technology is purely physico-chemical and takes advantage of the basic principles of ion exchange and electrochemistry. Unlike conventional electrocoagulation that removes suspended solids and breaks emulsions or oxidizes heavy metals, the electrochemical process employed by Selen-IX™ relies on creating conditions where iron acts as a highly effective reducing reagent transforming selenium from a dissolved species into elemental selenium bound in a solid phase. The iron-selenium by-product of Selen-IX™ is an inorganic, non-hazardous and chemically stable solid (Figure 1). Due to their high iron content, the solids produced by Selen-IX™ are of interest to the steel making industry as a low cost feedstock. This offtake potential can not only reduce the life cycle cost of selenium removal by reducing disposal costs but more importantly, eliminate the risk of future environmental liabilities. In this paper, the basics of Selen-IX™ technology are presented along with results of successful piloting on streams from coal and copper-gold deposits.

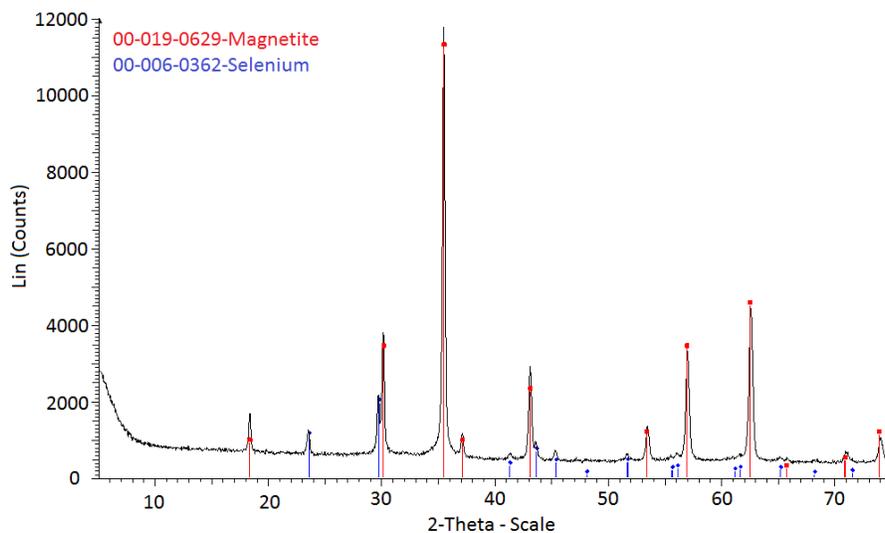


Figure 1 - XRD spectra of iron-selenium solids produced during pilot campaign

KEYWORDS

Selenium, cost effective treatment, mine impacted waters, ion exchange, electrochemistry, iron

INTRODUCTION

Various contaminants are released into mining wastewater during the extraction and processing of metals. One such contaminant is selenium. A naturally occurring element found in rocks and minerals, mining activities accelerate its release into the environment. Selenium in trace quantities is essential to all life forms but at higher concentrations it can be harmful, especially to aquatic life where selenium bioaccumulation can lead to reproductive deficiencies.

Water coming into contact with mining waste rock becomes contaminated with selenium from mineralization. Selenium species present in mine impacted waters are typically inorganic forms such as selenite (SeO_3^{2-}) and selenate SeO_4^{2-} . Elemental selenium associated with finely suspended solids can also be present in mine impacted waters in very small quantities. Filtration or gravity separation in clarifiers assisted by flocculants and/or coagulants can be used to remove selenium associated with fines.

Depending on the pH, tetravalent selenium can be present in mine water as selenious acid (H_2SeO_3), biselenite (HSeO_3^-) and selenite (SeO_3^{2-}) (Holleman & Wiberg, 2001). At $\text{pH} > 4$, tetravalent selenium can be co-precipitated readily with ferric iron (NAMC, 2011). Removing tetravalent selenium with ferric iron is very efficient and is often incorporated into lime neutralization circuits used for removing other metals. Hexavalent selenium also has three forms: selenic acid (H_2SeO_4), biselenate (HSeO_4^-) and selenate (SeO_4^{2-}). Selenate is the dominant hexavalent selenium species present in mine water at $\text{pH} > 1.7$. Common adsorption/precipitation methods are not effective for selenate removal. Removing hexavalent selenium from water typically involves reducing selenate into selenite or elemental selenium followed by the removal of the reduced species.

Current commercially available selenium treatment options cannot always satisfy all treatment objectives which are highly site specific, introduce new potentially long term project risks and have high life cycle costs. Over the last three years, there have been a number of pilot and full scale installations of selenium treatment using biological selenium reduction applied primarily at coal mine sites. The performance of these biological systems has demonstrated a number of weaknesses from the inability to consistently meet Se concentrations lower than $\sim 3.5 \mu\text{g/L}$, increased risk of acute fish toxicity and other long term impacts on the receiving environment, and the lack of adaptability to sudden changes in hydraulic flow and/or mass load of selenium. The biological systems are also sensitive to water temperatures which increases either the capital or operating cost for large flows of cold water typically encountered by mines in North America. Furthermore, little is known about the long term stability of selenium contained in the biological waste residues which affects the options for long term storage and/or safe disposal. As a result, the risk-adjusted life cycle cost of biological selenium removal is high and the mining industry continues to seek alternate non-biological treatment options.

Selen-IX™ is one of the technologies that can fill this need. A combination of ion exchange and electrochemical reduction, Selen-IX™ is a physico-chemical process that removes selenium from mine water selectively and can reach end of pipe discharge limits $< 1 \mu\text{g/L}$ on a consistent basis. The process eliminates the risk of acute fish toxicity and environmental impacts caused by BOD, COD and phosphorus which are often problematic for biological systems. Furthermore, Selen-IX™ is not sensitive to water temperature and is better equipped to respond to fluctuations in both hydraulic flow and mass load of selenium. Additionally, Selen-IX™ generates an inorganic residue composed of well-defined iron oxides and elemental selenium. All this translates into significantly reduced selenium treatment life cycle costs (Mohammadi, Littlejohn, West & Hall, 2014; Baker, Kratochvil & Murphy, 2015; Kratochvil, Littlejohn & Lopez, 2015).

SELEN-IX™ PROCESS DESCRIPTION

Selen-IX™ is comprised of two main process steps: ion exchange (IX) to remove selenium from mine water and eluate treatment to precipitate the selenium as a stable iron-solid. A block diagram of the Selen-IX™ process is provided in Figure 2.

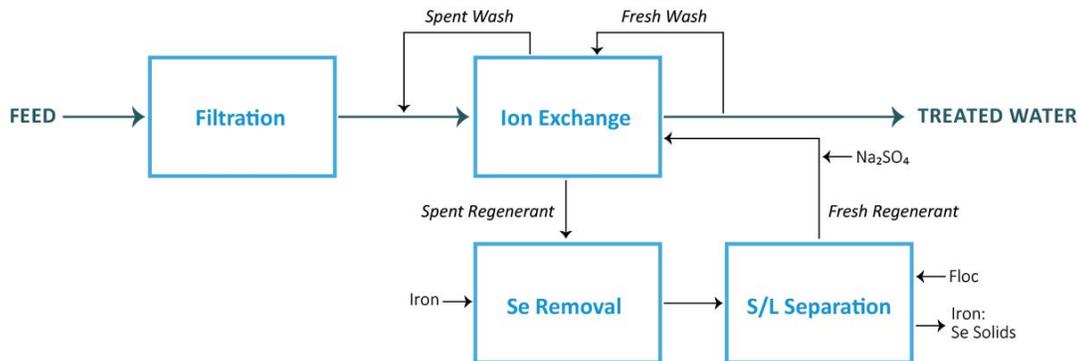


Figure 2 Selen-IX™ block flow diagram

Ion Exchange

In the first stage of the Selen-IX™ process, the ion exchange circuit selectively removes selenate from the feed water to achieve $< 1 \mu\text{g/L}$ Se in the treated water for discharge. The process starts by first filtering the feed water to decrease total suspended solids (TSS) to less than 10 mg/L. The feed is then pumped through three ion exchange columns in series where selenate is selectively adsorbed on to a strong base anion (SBA) resin. The columns operate in a lead-middle-lag configuration where at any given time three columns are in load while the fourth is in regeneration/wash mode. Figure 3 shows a picture of the ion exchange columns in the Selen-IX™ mobile pilot plant.



Figure 3 Ion exchange columns in Selen-IX™ mobile pilot plant

With selenate removed from the feed, the treated effluent is compliant with selenium regulatory requirements and can be safely discharged to the environment. Similar to other IX processes a small portion of the treated effluent is used as wash water for the ion exchange column operation. Loading continues until the resin reaches its specified loading cycle duration. At this point the selenate captured by the resin bed is stripped from the resin using a brine solution. Overall, this process step concentrates the

selenium into a small volume of selenium-rich brine solution, the spent eluate, which is then treated downstream with electrocells. After the regeneration/wash cycle the resin is available for further cycles of selenate loading.

Eluate Treatment in Electrocells

In the eluate treatment circuit, the selenium-rich brine solution is treated to precipitate the selenium. The process works by continuously circulating the eluate through banks of electrocells equipped with iron anodes to allow the formation of solids that are easily separated from solution. As the DC current passes through the cells, iron from the anodes dissolves into solution where it reacts with selenium. The eluate treatment circuit is operated in batch mode. When the treatment of a batch of eluate is complete, the contents are discharged and flocculent is added to help in developing flocs in the downstream clarifier. The settled sludge is then dewatered, forming a small volume of stable, non-toxic iron-selenium cake. This solid by-product is safe for non-hazardous landfill disposal and has potential for re-use in the steel industry. The clarified solution free of selenium is recycled back to the ion exchange circuit for re-use in resin regeneration. More than 99% of the selenium in the eluate is removed during this process.

RESULTS AND DISCUSSION

Selen-IX™ has been piloted with different mining companies on different mine water streams – coal, gold/copper and gold deposits – from 2013 to 2015. Key results from the last two pilot campaigns will be presented and discussed below. For both of these pilot campaigns the target was to treat water to reach less than 1 µg/L selenium. The water composition for these streams was highly variable. The key constituents present in the mine water for each campaign are provided in Table 1.

Table 1 Key constituents in mining waste streams

Key Constituents	Pilot 1	Pilot 2
Dissolved Selenium (mg/L)	0.103 – 0.350	0.082
Chloride (mg/L)	10	329
Nitrate as N-NO ₃ (mg/L)	32	12
Sulphate (mg/L)	1,950	1,428
Alkalinity (mg/L)	0	40
TDS (mg/L)	2,910	2,740
pH	4.1 to 4.5	6 to 6.5

IX Performance

During each pilot program several IX kinetics tests were undertaken to determine the optimal IX loading cycle duration. Cycles were extended as long as possible to make the best use of the IX resin capacity while maintaining the selenium discharge target for each campaign. Figure 5 show the selenium concentration in the daily composite samples collected from the IX feed and effluent during operation in the demonstration phase of the two different pilots. Despite treating variable selenium influent concentrations that ranged between 50 and 350 µg/L, selenium levels below the target of 1 µg/L was always achieved in the treated effluent.

To evaluate the resiliency of the process in responding to feed fluctuations, the selenium concentration in the influent was varied suddenly midway through the first campaign. Duplicate samples of the IX discharge as well as blank samples were collected daily and showed a strong correlation between one another, indicating that the analytical technique employed was reliable even at the sub µg/L level.

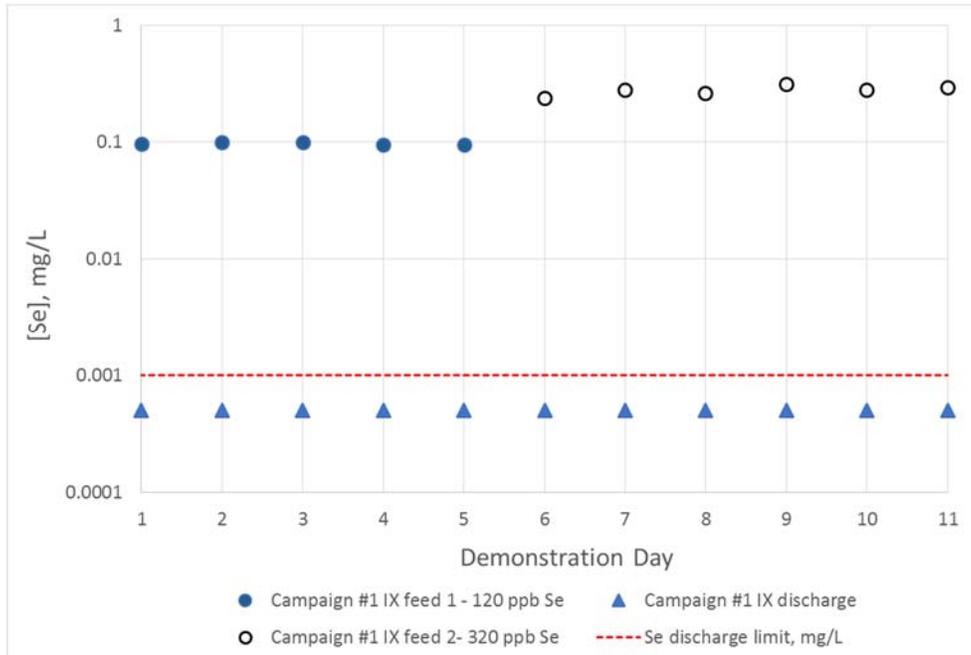


Figure 4 Selenium daily composite sample - pilot 1

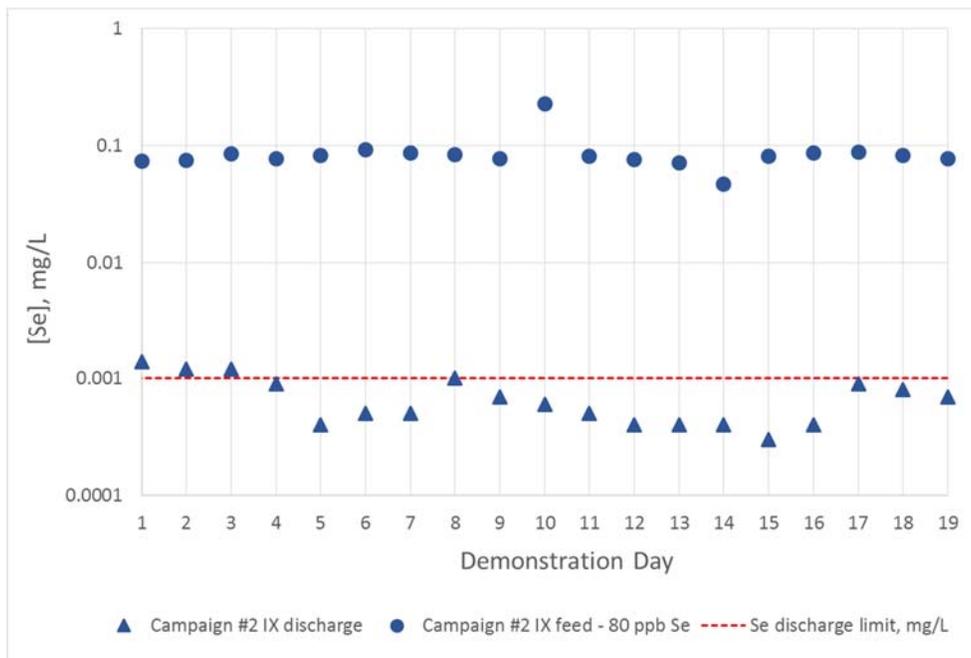


Figure 5 Selenium daily composite sample - pilot 2

Figure 6 illustrates how the selenium concentration in the IX discharge is linked to the selenium concentration in the recycled regenerant. The graph was constructed using data from both piloting campaigns and identifies the target selenium concentration in the eluate treatment circuit.

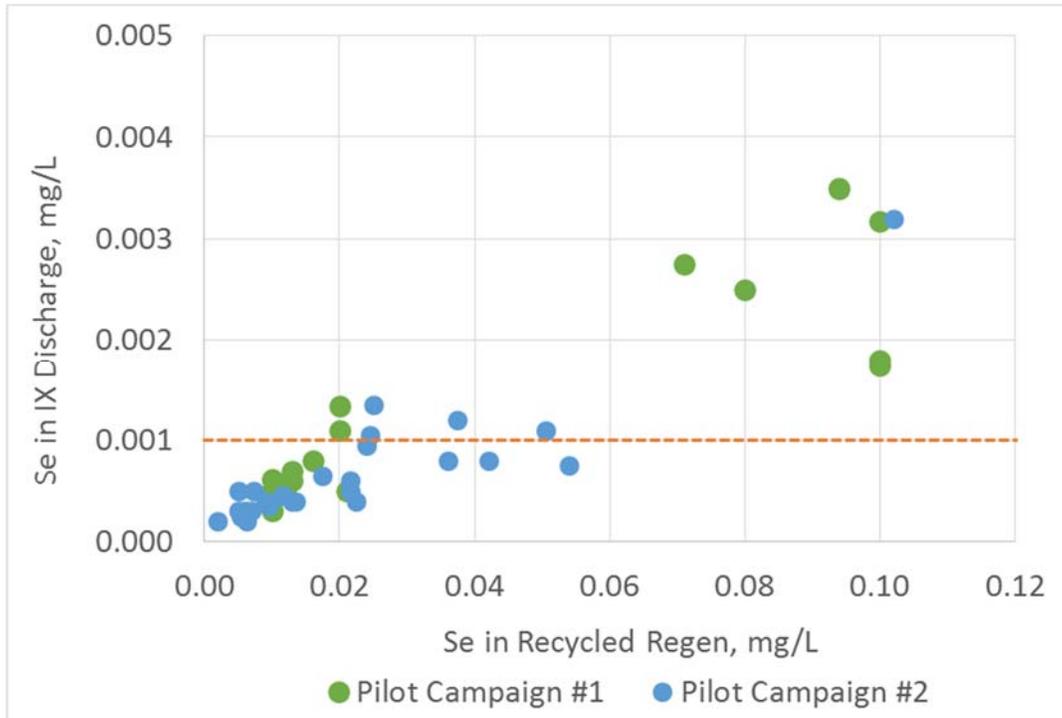


Figure 6 Dependence of Se in IX discharge on Se in recycled regenerant

According to the graph, if the recycled regenerant contains 30 $\mu\text{g/L}$ of selenium, the IX discharge will contain 1.2 $\mu\text{g/L}$ of selenium. Similarly, a selenium concentration of 15 $\mu\text{g/L}$ in the recycled regenerant results in < 1 $\mu\text{g/L}$ selenium in the IX discharge. The fact that missing the eluate treatment target by a significant margin results in a minor deviation from target in the IX discharge speaks to the overall adaptability and resiliency of the process.

The IX columns were operated using a lead-middle-lag configuration. The freshly regenerated column is first in the lag position where the barren resin polishes the last few micrograms of selenium from the effluent of the other two columns. From there, the column moves into the middle position where it treats the effluent of the lead column. Finally, the column moves into the lead position where the resin is filled to capacity to treat the influent water high in selenium. The data generated in kinetics tests were used during each pilot campaign to tune the system to make the best use of the resin capacity. The following table shows the discharge values of each IX loading stage for the second pilot campaign.

Table 2 IX load inter-stage composite averages for pilot 2

Average composite for pilot program (mg/L Se)	
IX Lead	0.027
IX Middle	0.0028
IX Discharge	0.0010

Figure 7 shows a typical IX regeneration curve obtained during the second pilot. The diamond markers show the concentration of selenium across the regeneration profile as a function of regeneration bed volumes, with blue diamonds representing wash, red for rich eluate and purple for lean eluate. The green and blue lines indicate the set-points for the lean and rich eluate fractions. The dashed grey line shows the concentration of selenium in the rich and lean composite.

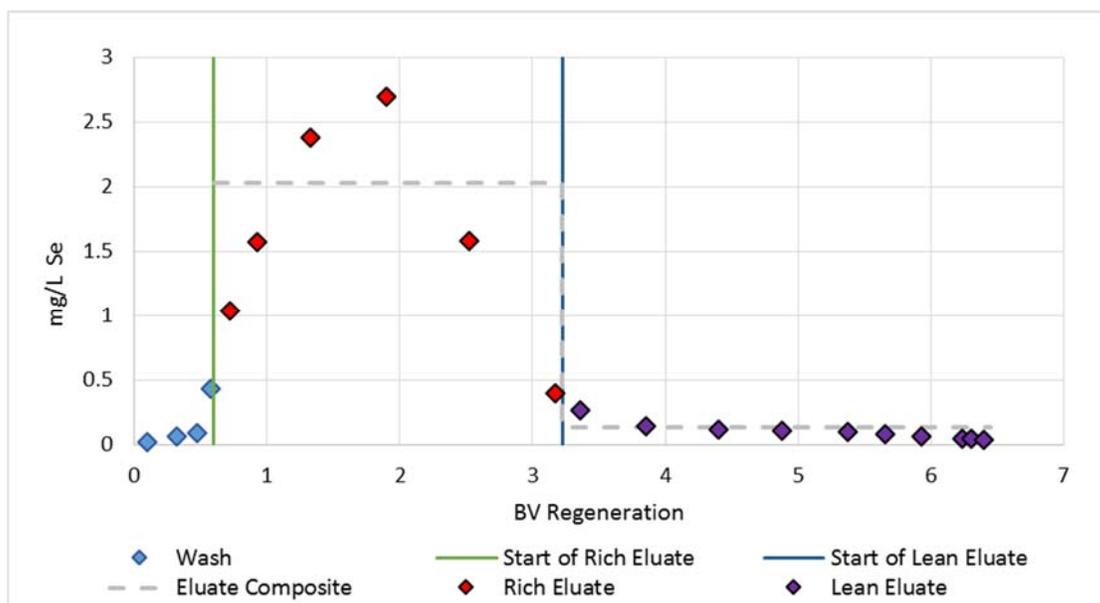


Figure 7 Sample kinetic curve of regeneration cycle for pilot 2

Several kinetic curves of this variety were generated over the course of each pilot. They were used to better define the necessary regeneration duration and the split between lean and rich eluate. This informs the size of the eluate circuit and allows optimization of the process with respect to reagent consumption and solid by-product generation.

Depending on the IX discharge target and according to Figure 6, not all the spent regenerant from the IX columns required treatment in the downstream eluate treatment circuit. Therefore, for each pilot campaign the spent regenerant stream was divided into two parts, the rich and lean eluate. Rich eluate contains the vast majority of selenium and is sent downstream for eluate treatment where selenium is precipitated out of solution. Lean eluate is relatively low in selenium and does not require further treatment, and is recycled through the column to regenerate the resin and elute more selenium in the subsequent regeneration cycles.

By dividing the eluate into a rich and lean, the volume of eluate requiring treatment is decreased, thereby reducing the capital and operating costs associated with the eluate treatment circuit. This also reduces the amount of solid by-product generated per cubic metre of water treated.

Eluate Treatment Circuit Performance

The eluate treatment circuit is operated using sequential batch reactors (SBR). During the demonstration phase of each pilot campaign, daily composite samples were created by mixing equal volumes of treated eluate from the end-point samples of each batch performed during the day. Additionally, a detailed kinetics test was conducted on the day's second batch as a diagnostic and predictive measure. An example of a kinetic test conducted during the second pilot campaign is shown in Figure 8. As illustrated in the graph, the total reaction time of 1.3 hours in the SBR was sufficient to reach the treated eluate target concentration of 0.015 mg/L selenium which corresponds to a power consumption of ~ 3,200 kWh/kg of selenium removed.

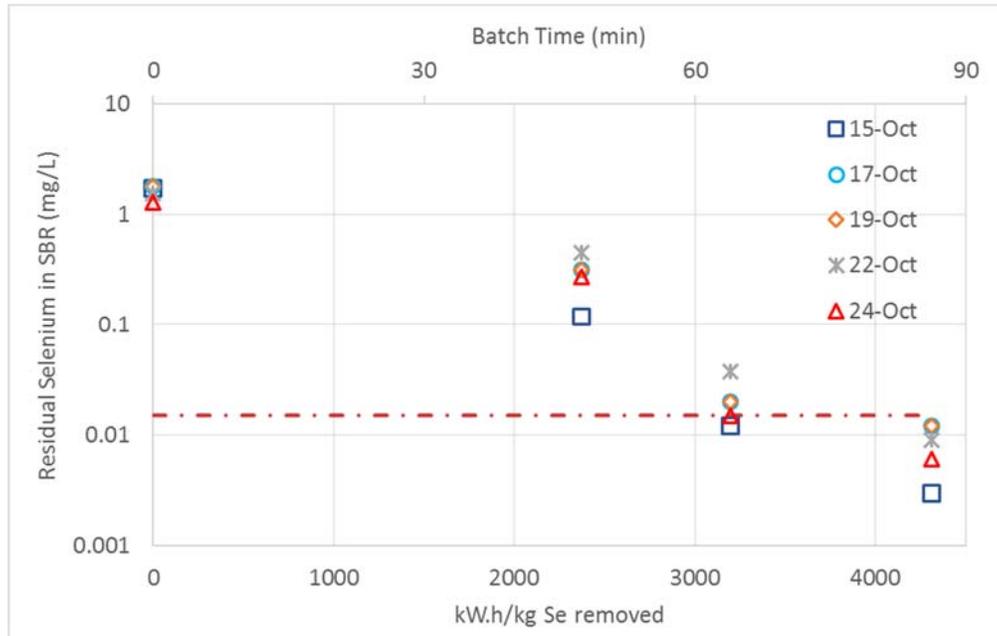


Figure 8 Sample SBR kinetics curves for pilot 2

Daily composite results for selenium in the SBR discharge are charted below in Figure 9 using logarithmic axis in order to emphasize the data corresponding to low selenium concentrations.

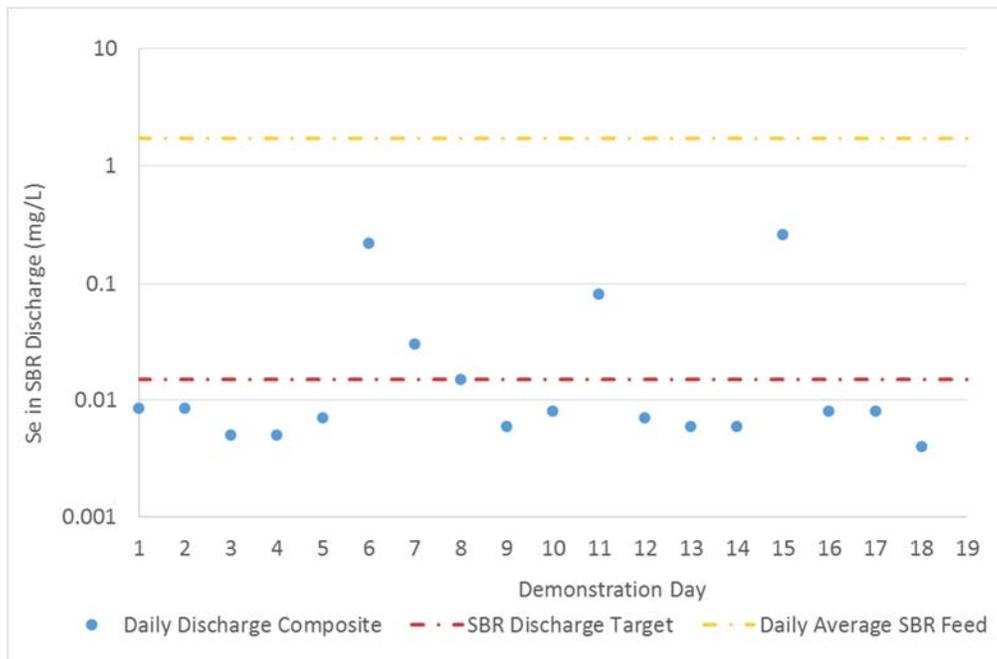


Figure 9 SBR performance for pilot 2

Figure 9 shows that except for four days during the demonstration phase, selenium in the treated eluate from the SBR circuit was below the target of 0.015 mg/L. The off-spec results reported in Figure 9 were due to either operator error or deviation from operating protocol.

Solids Residue Characterization and Stability

The Selen-IX™ process generates a solid by-product stream resulting from the treatment of the IX brine in electrocells. This by-product is stable iron oxyhydroxide laden with the selenium removed from the impacted water. These are solids generated through precipitation of iron and selenium from the regenerant brine. In the second pilot campaign 15.6 kg of dry solids were generated during the treatment of 36 m³ of water for a solids generation rate of 430 g/m³. Figure 10 shows the solids cake formed after processing the slurry through a filter press.

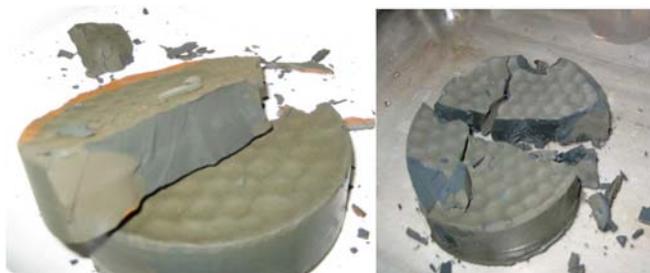


Figure 10 Iron-selenium solids by-product cake (pressed)

The solids generated by Selen-IX™ during the two campaigns were characterized with elemental analysis, X-ray diffraction (XRD) analysis, and Toxicity Characteristic Leaching Procedure (TCLP) analysis. Elemental analysis yields the elemental composition of the material, XRD gives insight into the compounds that make up the solids, and TCLP analysis shows whether the material is considered safe for non-hazardous landfill.

Elemental analysis of the solids by-product from both pilots is shown in Table 3. The majority species in the solid by-product is iron. The remainder of the material is oxygen and hydrogen present in hydroxide and waters of hydration. The elemental analysis of this material was conducted using ALS Minerals' ME-MS61 4 acid digestion procedure, which involves contacting the material with perchloric, hydrofluoric, nitric and hydrochloric acid. This rather involved acid leach procedure is necessary to close the selenium mass balance. Simple contact with sulphuric or hydrochloric acid is insufficient to dissolve the selenium bearing material. The aggressive nature of the leaching procedure required to dissolve the Selen-IX™ solids is indicative of their refractory and stable nature.

Table 3 Elemental assay of Selen-IX™ solids from pilot 1 and 2

Constituent	Unit	Pilot 1 average washed solids	Pilot 2 average as-is solids
H ₂ O	%	60	70
Al	%	0.03	0.02
Ca	%	0.22	0.19
Fe	%	43.8	41.1
K	%	0.02	0.01
Mg	%	0.04	0.04
Mn	%	0.30	0.28
Mo	%	<0.1	<0.1
Na	%	2.04	6.65
S	%	4.3	7.36
Se	%	< 0.1	< 0.1

XRD analysis of the Selen-IX™ solids was carried out by researchers at UBC Earth and Ocean Science. The resulting spectra was software matched to a database of solids, the outcomes of which are shown in Table 4.

Table 4 XRD analysis of Selen-IX™ solids from pilot 1 and 2

Mineral	Ideal Formula	Percentage Pilot 1	Percentage Pilot 2
Goethite	$\alpha\text{-Fe}^{3+}\text{O(OH)}$	57.0	60.5
Magnetite	Fe_3O_4	4.1	15.0
Melanterite	$\text{Fe}^{2+}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	-	7.5
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1.5	0.8
Lepidocrocite	$\gamma\text{-Fe}^{3+}\text{O(OH)}$	35.5	13.31
Bloedite	$\text{Na}_2\text{Mg(SO}_4)_2 \cdot 4\text{H}_2\text{O}$	1.9	2.89
Total		100.0	100.0

As anticipated from the elemental analysis, the majority of the material consists of various iron oxyhydroxide compounds, including magnetite. In previous solid characterization work done by BioteQ, magnetite has been found to be associated with precipitated selenium. Magnetite is a refractory compound that is difficult to dissolve and adds to the overall stability of the Selen-IX™ solids.

Selen-IX™ solids by-product from pilots 1 and 2 were subjected to the TCLP procedure used to classify solids as either hazardous or non-hazardous for disposal in landfills. The results of this procedure are shown in Table 5. The Selen-IX™ solids showed no release of metals beyond the specified TCLP limits, indicating the material is suitable for disposal as non-hazardous waste.

Table 5 Results of TCLP procedure performed on Selen-IX™ solids from pilot 1 and 2

Metal mg/L	TCLP Regulatory Limit	TCLP Results Solids from Pilot 1	TCLP Results Solids from Pilot 2
As	5	<1.0	<0.010
Ba	100	<2.5	<1.0
Cd	1	<0.050	<0.001
Cr	5	<0.25	<0.050
Pb	5	<0.25	<0.010
Hg	0.2	<0.0010	<0.001
Se	1	<1.0	<0.020

Solid Residue Management

An important aspect of any water treatment process is the management of residues. While TCLP results and overall mineralogy indicate the primary eluate solids generated through the Selen-IX™ process can be treated as non-hazardous waste, the disposal of residue must be considered in analysis of the life cycle cost for water treatment. As such, there is significant benefit to arranging offtake agreements for water treatment by-products.

The by-product generated with Selen-IX™ consists largely of iron oxyhydroxide compounds with minor impurities. The relatively high iron content of this material (40-50 wt% Fe) indicates it may be suitable feedstock for iron ore processing or cement production. The material is fundamentally similar to the magnetite, hematite, goethite and limonite minerals that make up the majority of steel mill feed. The iron oxyhydroxide material could also be used as feed in steel sinter plants, which convert fine particulate into

sinter blocks appropriate for feed in blast furnaces. Portland cement typically contains 2-5% iron by weight, which is generally sourced from iron scrap or iron oxide. The high iron content of the Selen-IX™ solids could provide this iron content in Portland cement. At this stage these applications are still being investigated by BioteQ. Either of these options would convert a by-product waste into a useful product.

In pilot 2 the mass of Selen-IX™ solids by-product generated is expected to be in the order of 500 g/m³ of water treated. These estimates were calculated using the 95th percentile operations base case water composition and the end of pipe Selen-IX™ discharge limit of < 0.001 mg/L. Therefore, the true mass generated over the life of mine are likely to be significantly smaller due to the lower average amount of contaminants in the feed water for treatment. Proper cake dewatering achievable in industrial scale filtration equipment which is not possible at the pilot scale will also contribute to a lower mass of solids generation. Table 6 outlines the amount of solids predicted to be generated in the full scale installation for pilot 2.

Table 6 Solid by-product estimates in full scale installation for pilot 2

Wet mass per water treated (g/m ³)	Total life of mine (t)	% of total tailings/waste rock mass	Iron content wt %	Se content wt %
500	9000	0.008%	41.1	<0.1%

The above table shows the solids generation while treating water to reach < 1 µg/L selenium target at end of pipe. It may be possible to relax that discharge target depending on the amount of dilution water in the receiving environment during certain parts of the year. Table 7 shows the impact of discharge target on total solids generation by the process.

Table 7 Solid by-product as unction of selenium discharge target for pilot 2

Discharge target (mg/L)	Primary Solid Generation (wet mass g/m ³)
0.001	500
0.002	458
0.003	416
0.004	375
0.005	333

If the solids residue offtake by steel or cement producers is not available or practical due to remote mine site location, the next preferred option for managing the Selen-IX™ solids is co-disposal with tailings. Typically, the mass of Selen-IX™ solids will represent a very small fraction of the tonnage of tailings – in one of the case studies presented in this paper, Selen-IX™ solids would account for approximately 0.008% of the mass of tailings expected to be generated and stored in the tailings storage facility over the life of the mine. Disposal of the Selen-IX™ solids by mixing and depositing into the tailings storage facility underwater will keep the by-product under anoxic conditions in a zone of low hydraulic conductivity, further minimizing the potential for metals release.

CONCLUSIONS

As a result of the two pilot campaigns, Selen-IX™ has been selected as the most suitable treatment process for two mining projects in British Columbia. One of these was recently granted their environmental approvals by both federal and provincial regulatory agencies.

Key finding that contributed to Selen-IX™ being selected include:

- Continuous around the clock pilot scale testing demonstrated that Selen-IX™ can reach selenium discharge limits at the end of pipe < 0.001 mg/L from streams containing up to 320 ppb total selenium and 3 g/L TDS.
- A step change in feed selenium concentration from 0.120 mg/L to 0.320 mg/L did not cause any process upsets and the plant maintained the discharge target of less than 0.001 mg/L.
- Key process interdependencies were established, including the link between selenium in plant discharge and selenium in the recycled regenerant. Several significant eluate treatment circuit performance excursions experienced during the second pilot campaign and caused by the nature of pilot scale testing had minimal effect on the final effluent water quality.
- Iron-selenium solids generated by Selen-IX™ were analyzed and passed TCLP rendering them safe for non-hazardous landfill disposal.

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