Advancement in Non-Biological Selenium Removal Treatment Systems – Results of Continuous Pilot Scale Operations

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ABSTRACT

Recent changes in regulations and scientific advances concerning selenium bioaccumulation have led to greater interest in non-biological treatment systems for selenium control in mine impacted and industrial waste water. BQE Water's Selen-IX™ process removes selenate from waste water to reach modern ultra-low selenium regulatory targets. Selen-IX™ combines selective ion exchange with electro-reduction of selenate in electrocells while producing a stable residue byproduct. This paper summarizes four years of pilot scale demonstration on a wide range of water chemistries and shows how Selen-IX™ and other non-biological technologies can be combined to remove inorganic tetravalent and hexavalent selenium as well as organoselenium species from impacted water to reach discharge targets ranging from 0.001 to 0.005 mg/L. A key aspect of cost effective removal of selenium via Selen-IX™ is the deportment of selenium in stable residue that does not require complicated handling or dedicated repositories.

KEYWORDS: Selenium, selenate, ion exchange, electrocoagulation, electroreduction, co-precipitation, organoselenium, mine waste water, treatment residue (up to 10 in order of importance)

INTRODUCTION

Sources and speciation of selenium in industrial effluents

In the mining and metal production sector, selenium contamination of waste water results from the release of selenium from the mineral deposit. In this case, selenium contamination is linked to water contact and seepage through waste rock and tailings. Selenium contamination is relevant to coal fired power generation as selenium contained in coal being burned is volatilized and then captured through scrubbing of flue gas. The blow down water from flue gas desulphurization contains selenium and other constituents captured by the scrubber. In the oil and gas sector, selenium can be present with sulphur in sour gas. In such a case, the sweetening of gas leads to the co-removal of selenium and sulphur, ultimately generating selenium bearing waste water for discharge.

The speciation of selenium varies significantly depending on the source and solution chemistry of the selenium bearing water. The following section describes different species of selenium and characteristics relevant to treatment.

Elemental selenium in suspended solids

Solid particles of elemental selenium can be found in waste water resulting from dust or particulate scrubbing. This form of selenium can be removed from water by filtration or gravity separation in clarifiers, often assisted by flocculants and/or coagulants. As most water treatment plants involve solid liquid separation and/or filtration of some variety or another, elemental selenium particulate is not typically a major concern in water treatment. Once solid particulate is removed, the only species of selenium that remain in the raw untreated water are the dissolved forms of selenium including inorganic selenite and selenate as well as organoselenium species.

Dissolved tetravalent selenium

There are several forms of dissolved tetravalent selenium that may be present in waste water depending mainly on pH. This is due to the fact that selenious acid (H_2SeO_3) carries two protons that can dissociate according to the following two reactions (Holleman and Wiberg, 2001):

$$H_2SeO_3 = H^+ + HSeO_3^- \qquad\qquad (1) \qquad pK_{a1} = 2.6$$

$$HSeO_3^- = H^+ + SeO_3^{2-} \qquad\qquad (2) \qquad pK_{a2} = 8.3$$

The pK_{a1} of reaction (1) signifies that at pH 2.6 approximately 50% of tetravalent selenium is present in the undissociated acid form (H_2SeO_3) which is non-ionic, and the other 50% is present as the monovalent biselenite ion $HSeO_3^-$. Similarly, pK_{a2} of reaction (2) signifies that at pH 8.3, 50% of tetravalent selenium is present as biselenite and 50% is present as the selenite ion SeO_3^{2-}. It is well established that tetravalent selenium is readily removed from water by using ferric iron co-precipitation at pH > 4 (NAMC, 2011). The pH set point > 4 is required for two reasons including:

- Ferric iron precipitates as ferric hydroxide/ferrihydrite solids that act as the adsorbent for tetravalent selenium

- Tetravalent selenium needs to be converted into one of the ionic forms of biselenite or selenite in order to attach to the surface of the ferric solids

Because the removal of tetravalent selenium by ferric co-precipitation is highly efficient, tetravalent selenium removal is generally not an issue and is often easily incorporated into water treatment systems using lime neutralization or through addition of ferric as a coagulant.

Dissolved hexavalent selenium

Similar to tetravalent selenium, dissolved hexavalent selenium can exist in several different forms. However, since the values of pK_{a1} and pK_{a2} of the dissociation reactions (3) and (4) are much lower than those of reactions (1) and (2), respectively, the single most dominant hexavalent selenium species in waters at pH > 1.7 is the divalent selenate SeO_4^{2-}.

$$H_2SeO_4 = H^+ + HSeO_4^- \qquad\qquad (3) \qquad \text{Strong acid } pK_{a1} \sim -3$$

$$HSeO_4^- = H^+ + SeO_4^{2-} \qquad\qquad (4) \qquad pK_{a2} = 1.7$$

In contrast to tetravalent selenium, hexavalent selenium cannot be removed from water by ferric co-precipitation. This means that advanced water treatment is required for the removal of hexavalent selenium. This advanced treatment typically involves the reduction of hexavalent selenium into more reduced forms such as selenite and elemental selenium and subsequent separation of these reduced forms of selenium from the treated water.

Organoselenium species

Organoselenium species refers to the class of compounds consisting of selenium bound to organic molecules such as selenomethionine and dimethyl selenide. These compounds form when inorganic selenium species are metabolized by microorganisms such as bacteria, phytoplankton, algae, and aquatic plants in the natural environment or in the strongly reductive environment generated by microbial populations residing in biological treatment systems (LeBlanc and Wallschläger 2016). The rates of bioaccumulation of the inorganic species of selenium are much lower than those of organoselenium species such as selenomethionine and its derivatives (Phibbs et al., 2011).

This means that water containing even trace levels of organoselenium is much more likely to cause chronic toxicity and environmental impacts in the receiving environment than water containing more elevated levels of inorganic selenium. As organoselenium is generated by bacterial action, biological water treatment systems may in some cases increase the rate of selenium bioaccumulation in the receiving environment despite the fact that they remove the majority of the total selenium from the feed water (LeBlanc & Wallschläger, 2016, Sandy, 2016).

Selenium regulations

New stringent selenium regulations have been implemented or proposed (US EPA, 2016; BC WQG, 2017) to minimize the risk of chronic toxicity caused by selenium bioaccumulation in fish and other aquatic organisms. The water based limits for total selenium vary from 1.6 to 3.1 µg/L.

In terms of treatment, biological selenium reduction which was identified as the Best Available Technology (BAT) as recently as 2013 (NAMC SWG, 2013) cannot meet these ultra-low limits.

Furthermore, the US EPA regulations measure the success of water treatment not only by the concentration of total selenium in treated effluent but also by selenium levels in fish tissue sampled from the receiving environment. This more sophisticated method of water quality regulation is becoming more common as the variability of bioaccumulative potential of different metal species is explored by researchers.

NON-BIOLOGICAL TREATMENT METHODS FOR SELENIUM

The interest in non-biological treatment options for selenate removal has increased over the last two years due to the risks and limitations of biological treatment systems namely:

- Inability to reach < 3.1 µg/L limits consistently and without dilution
- Residual biosolids containing selenium requiring disposal in lined impoundments with leachate collection and treatment
- Risk of creating chronic effluent toxicity because of bioaccumulative potential of organoselenium
- Risk of creating acute effluent toxicity through release of plumes of nutrients causing low dissolved oxygen in receiving environment (Teck Coal Limited 2015)
- High capital and O&M costs of integrated biological treatment systems (Utility Water Act Group 2017)

Non-biological treatment processes most often considered for selenium removal include ferric co-precipitation, reverse osmosis (RO) and nanofiltration (NF) membrane treatment, limited-use sorbents and Selen-IX™.

Ferric co-precipitation and electrocoagulation

Ferric can be dosed into water either as liquid products such as ferric sulphate or ferric chloride. Ferric iron introduced to water acts as a coagulant and helps settle suspended solids and colloids by overcoming repulsive forces between charged particles. Some metals and metalloids species co-precipitate or adsorb onto the surface of hydroxylated coagulants. Selenite behaves in this way and is readily removed through ferric co-precipitation. However, selenate is not amenable to this treatment method.

Ferric iron can be added to water electrolytically through electrocoagulation. Electrocoagulation is a useful method of maximizing the efficiency of coagulation, but it does not change the oxidation state of selenium from 6 to either 4 or 0 and so is not an effective method of removing selenate from water.

While ferric co-precipitation may reduce the concentration of selenate in some streams, it cannot be applied broadly to remove selenium to reach limits below 3 µg/L unless the stream only contains selenium as selenite.

RO membrane treatment

Reverse Osmosis (RO) is a non-selective approach to water treatment and will remove a broad spectrum of dissolved species from water including selenium. The extent of removal ranges from 95-99%. The main residual stream from RO treatment is the retentate, or brine stream. As selenium and other ionic species contained in the retentate are still dissolved, they are highly labile and their re-release to environment is a major risk. While evaporation and crystallization methods can be applied to brine, this results in generating water soluble salts.

The volume of retentate generated is driven by the overall salt content and level of saturation of the influent stream. For most industrial applications, the volume of retentate brine would be 20-40% of the volume of the influent stream. This high volume, low stability residue brine represents a major liability for operations that choose to use RO treatment. However, RO may be useful as a method of concentrating selenium into brine that is treated chemically to produce a more stable selenium bearing by-product.

Limited-use sorbents

Most single-use sorbent products that are commercially available for the removal of selenium are iron based including but not limited to Zero Valent Iron (ZVI) and iron/steel wool. The major issue with elemental iron-based sorbents such as ZVI and iron wool is that the surface of the material will passivate through generation of iron oxide surface layers, reducing the selenium removal efficiency. In addition, the kinetics of selenate removal using iron-based sorbents is slow. Generally, sorbent materials have to be in contact with selenium containing water for a long time (2-12 hours) in order to remove selenium effectively. As a result, reactor vessels are sizable and a large inventory of sorbent is required. Once utilized, spent sorbent materials require disposal or landfill. One approach to mitigating the weaknesses of iron-based sorbents such as ZVI is that used by the Lewatit FO 36 material. This product is an iron doped ion exchange resin developed for removal of trace oxyanions from drinking water that can be regenerated.

In general, the major challenge of selenium removal with sorbents is how to maximize sorbent life span through regeneration and surface rejuvenation. If a frequent replacement of large volume of material is required for the application then it is unlikely to be a cost effective method of removing selenium from waste water.

Selen-IX™

The Selen-IX™ process developed by BQE Water to remove a range of selenium species from industrially impacted water. The integrated process comprises three units: pretreatment filtration, ion exchange (IX) and electroreduction circuit (ERC). A schematic block flow diagram of the process is shown in Figure 1.
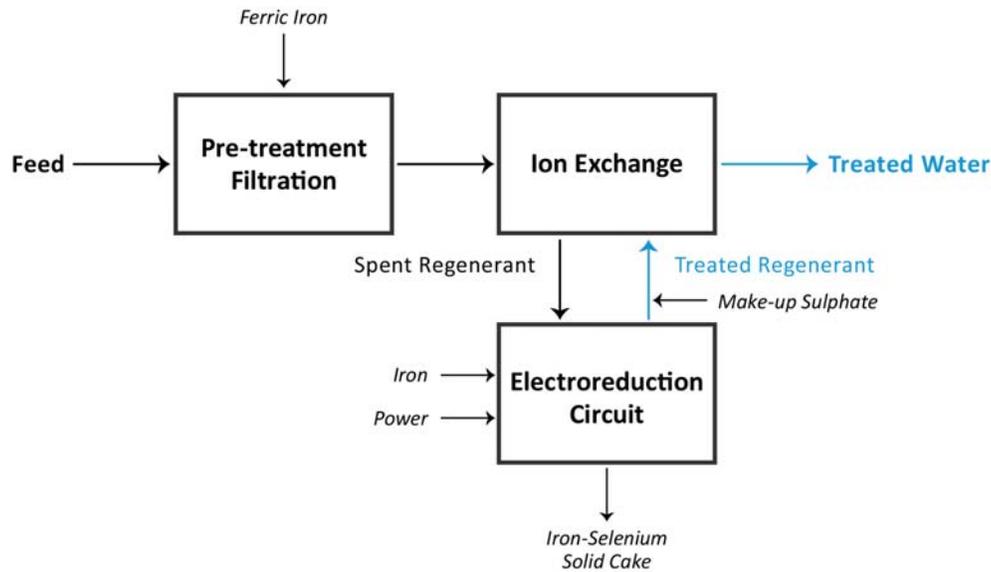
Figure 1. Selen-IX™ block flow diagram

The purpose of pretreatment is to coagulant and remove suspended solids from influent water. In doing so, this removes selenite from feed water as well as TSS that would otherwise negatively impact the ion exchange circuit. The role of the IX circuit in Selen-IX™ is twofold: to remove selenium from feed water to level as low as less than 0.001 mg/L and to concentrate the removed selenium up by at least an order of magnitude into a small volume of regenerant that is then processed through the ERC circuit. The role of the ERC circuit is similarly twofold: to remove selenium from the IX spent regenerant into a stable solid that can be easily separated from solution and to enable recycle of selenium free regenerant back to the IX circuit. The removal of selenium in the ERC involves a series of reactions between selenate contained in the brine and iron released from anodes inside the ERC resulting in the reduction of selenate to elemental selenium and simultaneous encapsulation of the said selenium into mixed iron oxide solids matrix.

Since the brine processed through the ERC is recycled quantitatively back to the IX, there is no liquid waste stream produced by Selen-IX™ and only a small amount of salt (Na_2SO_4) is added to maintain the brine strength. With these circuits working in tandem, selenium is removed from a large volume of impacted water and is converted into a low volume, stable solid by-product. Additionally, as an entirely physico-chemical process, there is no potential for organoselenium to be generated by the system and no need for effluent polishing of nutrients or otherwise toxic by-products in the treated water.

SUMMARY OF FOUR YEARS OF PILOT SCALE DEMONSTRATION OF SELEN-IX™

Since 2013, BQE Water has completed four pilot demonstration campaigns using a mobile Selen-IX™ plant treating a wide range of mine impacted waters. The plant is housed in a 40-ft sea container comprising all unit operations and is fully automated enabling 24/7 continuous operation. Over the course of 4 pilot campaigns, BQE Water has treated approximately 400 m³ and operated the system for 6 months, cumulatively. The key takeaways from the four years of piloting and process demonstration include the following:

- Discharge limits below 0.001 mg/L can be achieved on waters with relatively wide range of quality including gypsum saturated wastewater as is typical in mining effluent;
- Solid residue produced by Selen-IX™ exhibits characteristics that allow multiple management options to be considered including co-disposal with tailings, landfilling and potential offtake by steel producers; and
- Regulatory agencies accept Selen-IX™ as the method of selenium control built into mining projects.

Table 1 summarizes the four years of pilot experience including source of mine water, project objectives, feed water quality, lessons learned and solids residue disposal.

Table 1. Summary of Selen-IX™ pilot demonstrations – objectives & lessons learned

#	Company/ project	Feed water	Se in pilot feed (mg/L)	Se in pilot effluent (mg/L)	Pilot objective	Lessons learned
1	Teck/ Elk Valley	Gypsum saturated waste rock seepage	0.456	< 0.005	Technology evaluation	Selenium is removed selectively, Opex increased by NO_3, ~ 4 mg/L NO_3 converted to $N-NH_4$
2	Seabridge Gold/ KSM	Acidic waste rock seepage	0.12 – 0.32	< 0.001	Permitting /permits issued	Opex insensitive to Se level in feed. Process adapts quickly to step changes in selenium level in feed
3	AuRico/ Kemess U/G	Neutral tailings supernatant	0.082	< 0.002	EA certificate issued/ currently in permitting	Opex decreased at low sulphate level in feed
4	Canadian mine/ existing operation	Treated tailings supernatant	0.015 – 0.1	< 0.005	Technology evaluation	At sulphate level > 4 g/L, direct treatment in ERC may become cost-effective

The following sections will go into more detail of results of two pilot studies and one lab study that exemplify how different elements of non-biological treatment can be integrated to achieve high levels of removal of various species of selenium from water.

CASE 1: REMOVAL OF INORGANIC SELENIUM FROM MINE WATER

Background

The AuRico Kemess Underground project is a brownfield mine (Cu-Au-Ag) project in British Columbia, Canada that is currently in permitting. Selenium was identified as an important constituent of concern for regulatory authorities and local communities with respect to the impact of the project on the downstream aquatic environment. As part of the Environmental Assessment process, BQE Water was engaged to conduct a pilot demonstrating the removal of selenium to reach the BC Water Quality Guideline for Aquatic life of 2 µg/L. A key reason why BQE Water was brought on for this project is the ability of Selen-IX™ to achieve discharge targets below 3 µg/L at end of pipe, thus removing the reliance on dilution to maintain water quality in the receiving environment. This significantly reduces the risk of non-compliance due to lack of rainfall or inaccuracy in hydrological modelling.

In this project, initial laboratory work was conducted in early 2015 followed by a 2 month pilot later in the same year. Approximately 100 m3 of water was shipped from the existing pit lake to the pilot site in Vancouver where it was spiked with gypsum and selenate to match water chemistry predicted by geochemical modeling. Table 2 shows the chemistry of the Kemess feed water following the chemical spiking.

Table 2. Chemistry of Kemess feed water requiring treatment for selenium

pH	TDS (mg/L)	Se(IV) (mg/L)	Se(VI) (mg/L)	SO_4 (mg/L)	N-NO_3 (mg/L)	Alkalinity (mg/L)	Cl (mg/L)
6.5	2,740	0.02	0.08	1,430	12	40	329

Of the total 0.1 mg/L of selenium, the ratio of selenite to selenate is 1:4. Prior to treatment for selenate using Selen-IX, the water was treated with ferric iron to precipitate selenite. Table 3 shows the removal of selenite as a function of ferric iron dose. In this case approximately 10 mg/L of ferric iron was used to precipitate selenite.

Table 3. Impact of ferric iron dose on selenium removal

Ferric Iron Dose (mg/L)	0	5	10	23	37	100	300
Total Dissolved Selenium (mg/L)	0.1	0.08	0.078	0.076	0.077	0.08	0.073

It can be seen that even when very large doses of ferric iron are applied to solution that selenate is poorly removed. In this case, approximately 9% of the selenate present when 300 mg/L of ferric iron was applied.

Selen-IX™ continuous pilot results

The Kemess pilot was divided into 3 phases. During the first phase the system was run while various system operating parameters were optimized and design criteria data generated. Following this, the system parameters were fixed and the system was run to demonstrate removal of selenium to satisfy the project's EA condition. Finally, a third phase involved treatment of feed water that was spiked to match lower TDS feed expected earlier in the project lifespan. This

was done to better inform operating expenses of the circuit over time. Table 4 shows the duration and volume of water treated for each of these phases.

Table 4. Pilot operational phases and duration

Phase	Objective	Days of operation	Volume treated
1	Generation of design data and optimization of operating parameters	21	45 m^3
2	Demonstration of consistent selenium removal to <0.002 mg/L from 95th percentile predicted water quality	20	40 m^3
3	Treatment of low TDS (~500 mg/L) water to better inform operating cost estimate	10	20 m^3

Following the commencement of pilot operations, the system demonstrated consistent removal of selenium, reaching the 2 µg/L target 98% of the time during the campaign. The one exception was a day early in the program during the optimization phase. Figure 2 shows the removal of selenium on a daily composite basis over the course of the program.
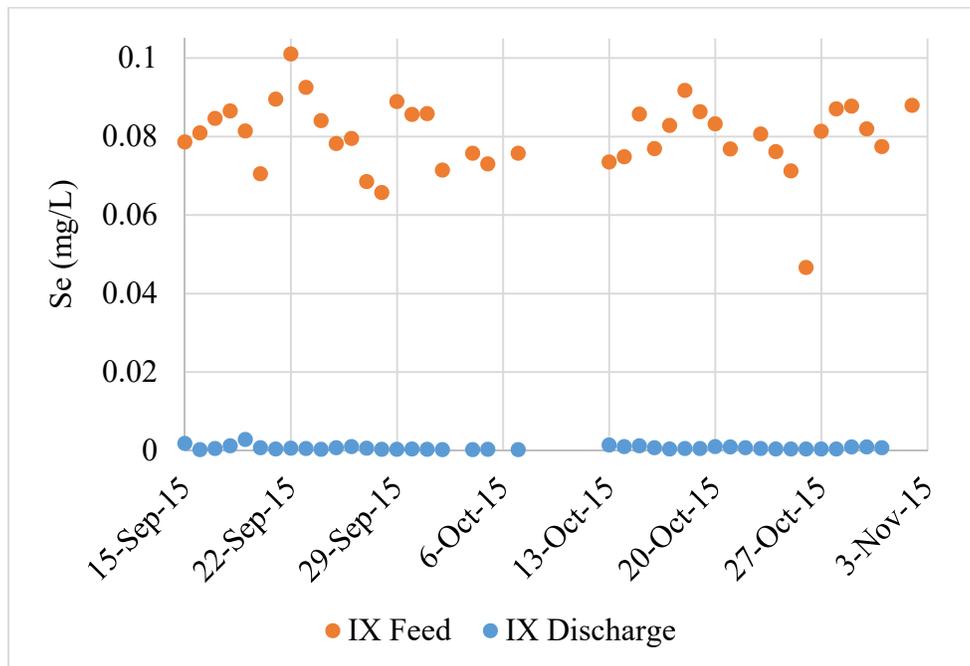

Figure 2. Selenium removal across Selen-IX™ circuit during Kemess pilot

Simultaneously, the electroreduction circuit was operating as required to precipitate selenium from the regenerant brine. It can be seen that the regenerant brine was typically in the range of 1.5-1.75 mg/L of selenium. As the feed selenium to the plant was in the range of 0.08-0.1 mg/L selenium, this indicates a concentration factor of approximately 15-20 across the IX system. The removal of selenium from brine in this system is pictured in Figure 3. The treated regenerant typically contained selenium in the range of 0.01 mg/L selenium.
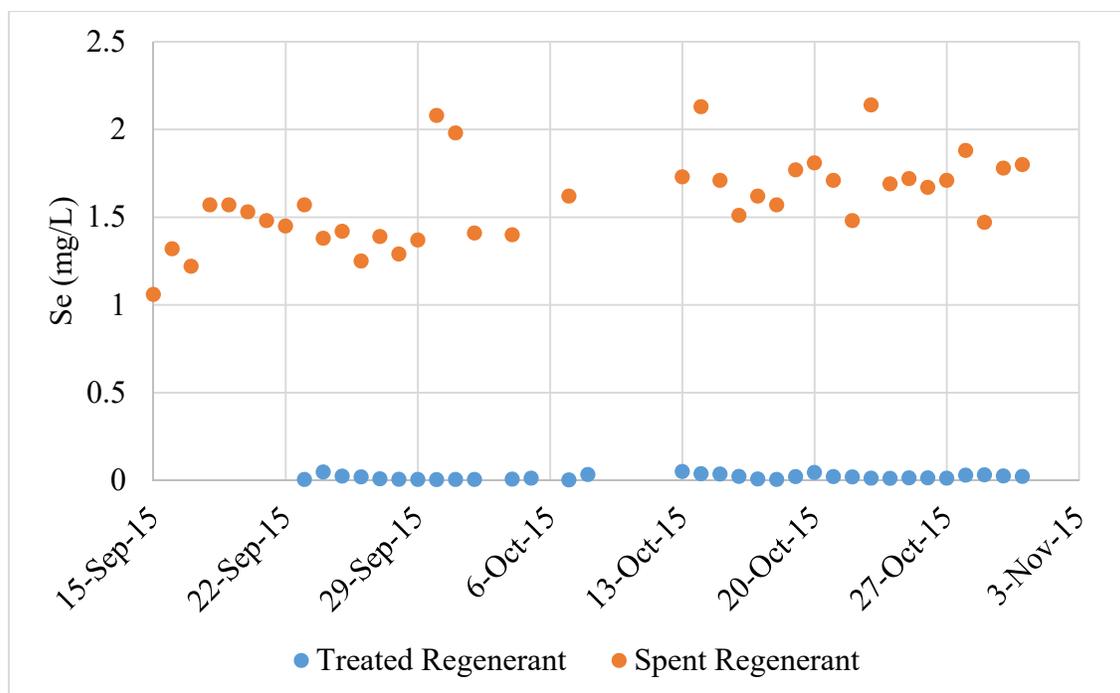
Figure 3. Selenium removal from IX regenerant via electroreductive treatment during Kemess pilot

As this pilot was geared to develop design information for full scale implementation, one of the program objectives was to demonstrate consistent precipitation of selenium in the electroreduction circuit while incorporating the start-up/shut-down procedures that would be required for full scale. This goal was achieved.

Residue stability

The stability and character of treatment residue is of major importance both for overall lifecycle cost and to regulatory authorities concerned about long term project impacts. As such, one of the Kemess pilot objectives was to characterize the treatment residue and determine cost effective methods of managing it. The goal here was to avoid the need for dedicated lined impoundments or shipment of residue for offsite landfill as has been required for other selenium removal projects in the province.

In the Kemess project, the Selen-IX™ treatment system is expected to generate approximately 9,000 tonnes of residue over the 21 year project life. During this time, the mine and mineral processing operations will generate approximately 109,000,000 tonnes of tailings. Co-mingling of water treatment solids with tailings was identified as the most cost effective method of managing water treatment residue.

With this in mind, solids generated during the Kemess pilot were characterized using a number of analytical techniques including: elemental analysis, X-ray diffraction, and toxicity characteristic leaching procedure (TCLP). The solids passed the TCLP test, indicating that they are non-hazardous. Furthermore, the solids analysis showed that the Selen-IX™ solids are composed of mainly iron oxides with iron alone accounting for close to 50% of the solids dry

weight. In addition to these relatively simple characterization methods, approximately 15 kg of Selen-IX™ residue solids were set aside for the purpose of long term assessment of co-disposal of these solids with tailings.

Following the pilot, a third party environmental engineering firm conducted longer term solid stability testing using the residue generated in the pilot. In this program, Kemess mineral processing tailings and Selen-IX™ residue were mixed and contacted with simulated tailings water in flow-through, saturated cells for a period of 9 months. Saturated cell effluent was monitored to assess the release of metals from the solid material. The ratio of Selen-IX™ residue to mine tailings in the solid mixtures was approximately one hundred times greater than would be expected on the basis of total tailings and total water treatment residue generated in order to better represent non-homogenous mixing in the tailings storage facility.

The primary conclusion of this work was that there was no additional release of selenium or other metals in the mixed solids compared to the tailings alone, indicating an exceptionally high degree of Selen-IX™ residue stability in the tailings environment. This supports the plan to co-dispose of residue with tailings.

Further, when the cumulative release of metals from the saturated cell tests was analyzed, there were indications that not only did the Selen-IX™ residue not leach metal, but that the tailings mixture amended with Selen-IX™ solids released lower levels of oxyanions commonly captured by iron co-precipitation than the tailings that contained no Selen-IX™ solids. Table 5 shows the cumulative amount of key metals released over the course of 9 months of saturated cell testing in terms of total micrograms of metal per kilogram of tailings.

Table 5. Cumulative release of metals from saturated cell testing of tails mixtures

| | µg metal released per kg solids | | | | | |
	Sb	As	Mo	Se	Sn	V
Tails without Selen-IX™ solids	0.017	0.077	14.0	0.065	0.007	0.033
Tails with Selen-IX™ solids	0.013	0.067	13.2	0.048	0.006	0.028
Difference	-23%	-12%	-5%	-26%	-14%	-15%

Current project status

The EA for the Kemess project was accepted in part on the basis of the Selen-IX™ pilot campaign. Since then, the project is moving through permitting. BQE Water did detailed design engineering for a full scale water treatment plant treating 65 L/s (1.5 MGPD) to treat selenium and other metals in Q1-Q2 of 2017. Figure 4 shows a 3D rendering of the facility to be built.
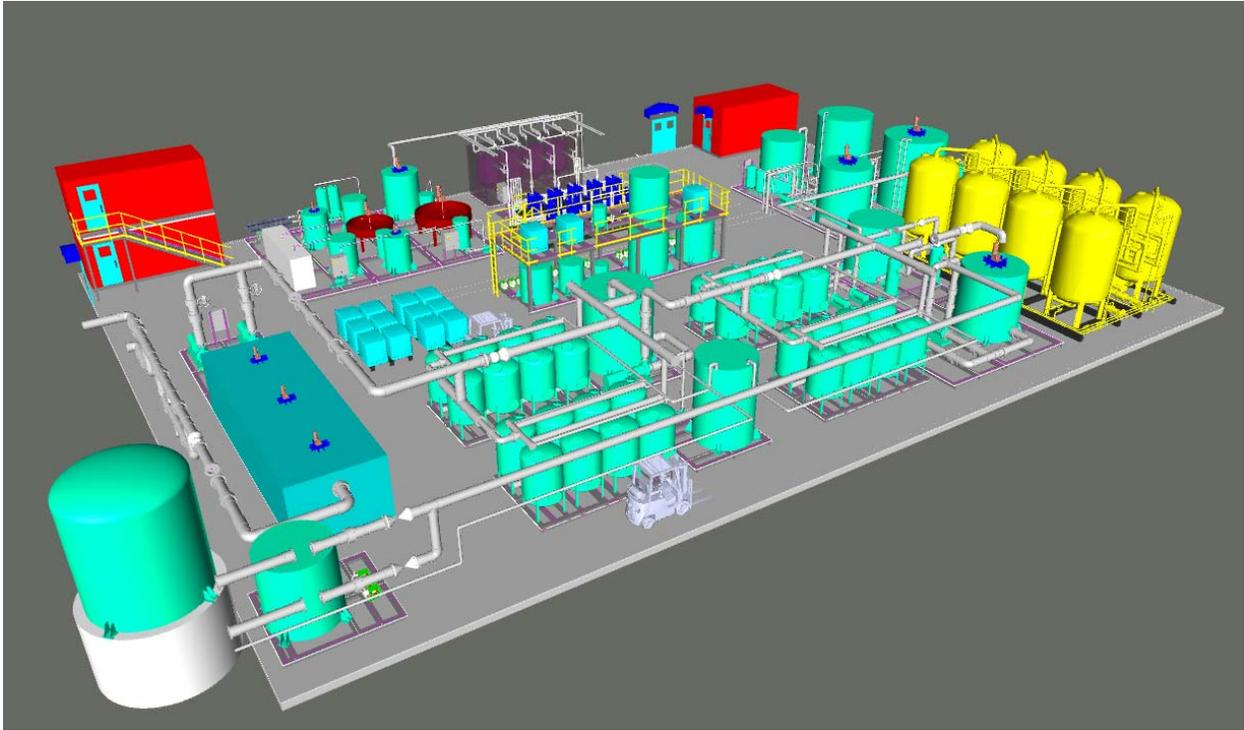
Figure 4. Rendering of 65 L/s Aurico WTP

The construction of the Aurico WTP is expected to take place in 2018 and BQE Water will commence operating the plant in 2019.

CASE 2: COST BENEFIT ASSESSMENT OF ION EXCHANGE COMBINED WITH ELECTROREDUCTION COMPARED TO DIRECT ERC TREATMENT

Background

An existing Canadian mining operation has a water treatment plant that uses ferric co-precipitation to effectively remove selenite and a host of other metals from tailings supernatant. However, this system does not remove selenate from impacted water to a sufficient degree to reach water quality targets and so additional treatment on the stream is required. BQE Water worked with the site to conduct a pilot demonstration of Selen-IX™ on the stream in 2016.

The mine owner is faced with the uncertainty about future water quality specifically involving selenium and sulphate concentrations in tailings supernatant. Therefore, one of the pilot objectives was to demonstrate effective removal of selenium to below 0.005 mg/L on a wide range of feed water quality. This was accomplished by operating the Selen-IX™ pilot plant on three different feed waters in three consecutive phases listed in Table 6.

Table 6. Pilot operational phases and duration

Phase	Water chemistry	Days of operation	Volume treated
1	Existing tailings supernatant containing about 0.015 mg/L selenate and 2 g/L sulphate	23	55 m^3
2	Tailings supernatant spiked with Se to 0.100 mg/L selenate	6	13 m^3
3	Tailings supernatant spiked with SO_4 to 4,000 mg/L sulphate	8	15 m^3

Table 7 shows the detailed water quality of the plant feed used during the three pilot phases. As can be seen from Table 7, the only three constituents that varied significantly in the plant feed during the campaign included sulphate, selenium, and sodium.

Table 7. Concentrations of major constituents in plant feed during the three phases of pilot campaign

Analyte (mg/L)	Phase 1 Existing feed water	Phase 2 High selenium feed water	Phase 3 High sulphate feed water
Sulphate	1,750	1,790	3,990
Selenium	0.0144	0.105	0.0166
Sodium	207	254	1,340
Chloride	83	87	80.9
Ammonia as N	8.9	9.1	8.7
Hardness as $CaCO_3$	1,590	1,640	1,680
Antimony	0.0003	< 0.0010	< 0.0010
Arsenic	0.0256	0.0212	0.023
Calcium	624	645	658
Copper	0.0039	0.0053	0.003
Magnesium	8.68	7.89	8.71
Molybdenum	0.016	0.0018	0.0017
Nickel	0.0281	0.0193	0.0173

It is important to note that in all previous pilot demonstrations, the concentration of sulphate was less than 2,000 mg/L as determined by the solubility of gypsum. This was due to the fact that sodium concentrations in those waters were very low. In contrast, in the most recent campaign, one of the plant feed streams contained approximately 4,000 mg/L sulphate as a result of the fact that the majority of sulphate was balanced by sodium.

Selen-IX™ performance

From day #1 of the campaign and throughout all three phases, the plant operated with complete IX regenerant recycle, i.e. in "closed loop" without any interruptions. Figure 5 shows the removal of selenate from feed water during the three campaign phases.
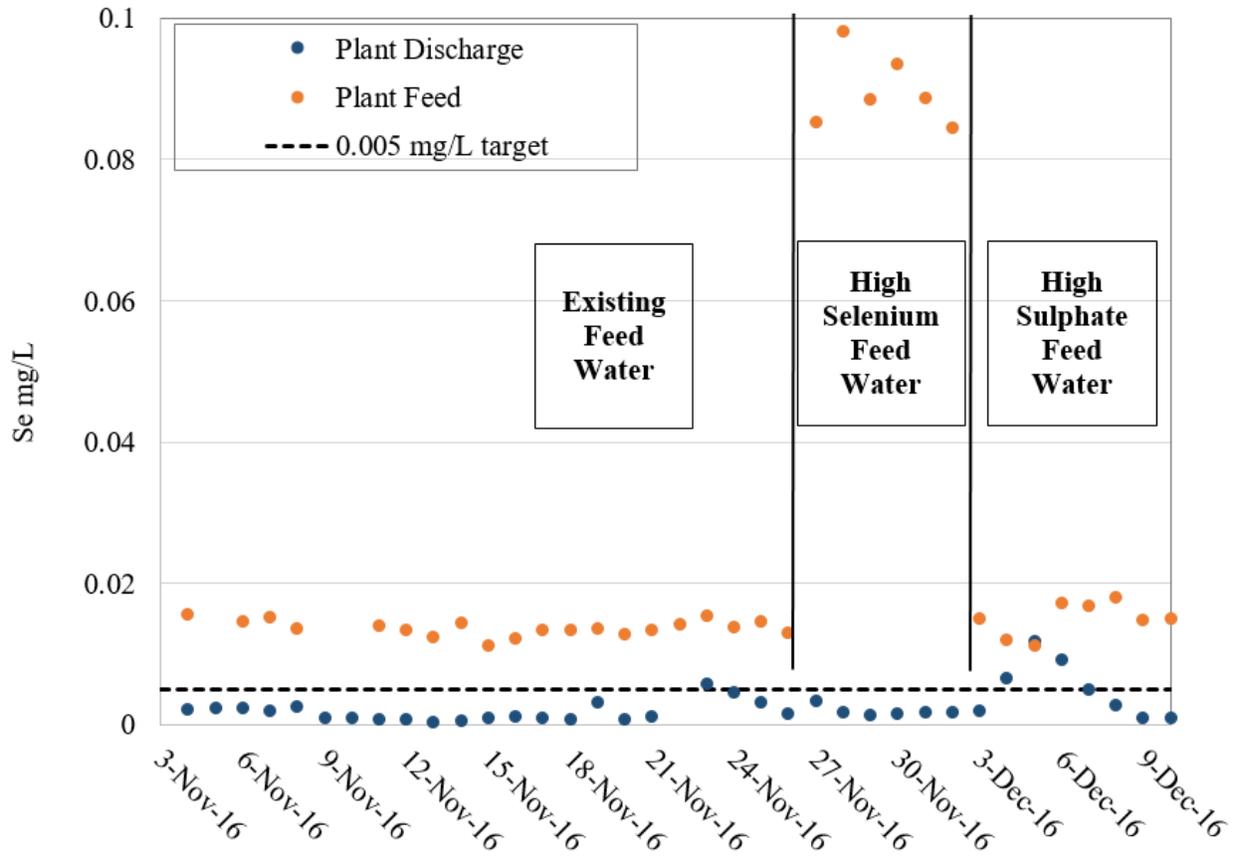
Figure 5. Selenium removal achieved during pilot

As can be seen from this figure, selenium was effectively removed to below the 0.005 mg/L end-of-pipe target throughout the campaign except for the first three days of switching to high-sulphate feed operation. The pilot plant had never treated water with TDS > 3,500 mg/L prior to this and the settings in the IX circuit which worked well for feed water with lower TDS proved inadequate for the high TDS water during the third phase of the campaign. Once the IX loading cycle setting was adjusted and reduced, the end-of-pipe concentration dropped back below the 0.005 mg/L target and remained there during the rest of the campaign.

Figure 6 shows the removal of selenium from IX brine in the ERC circuit. It can be seen that when the plant started treating the feed with the high selenium concentration, the selenium concentration in IX brine increased but that had no impact on the removal of selenium from the brine in the ERC. It is evident from the results that the removal of selenium in the ERC was consistent throughout the campaign and not impacted by changes in plant feed composition.
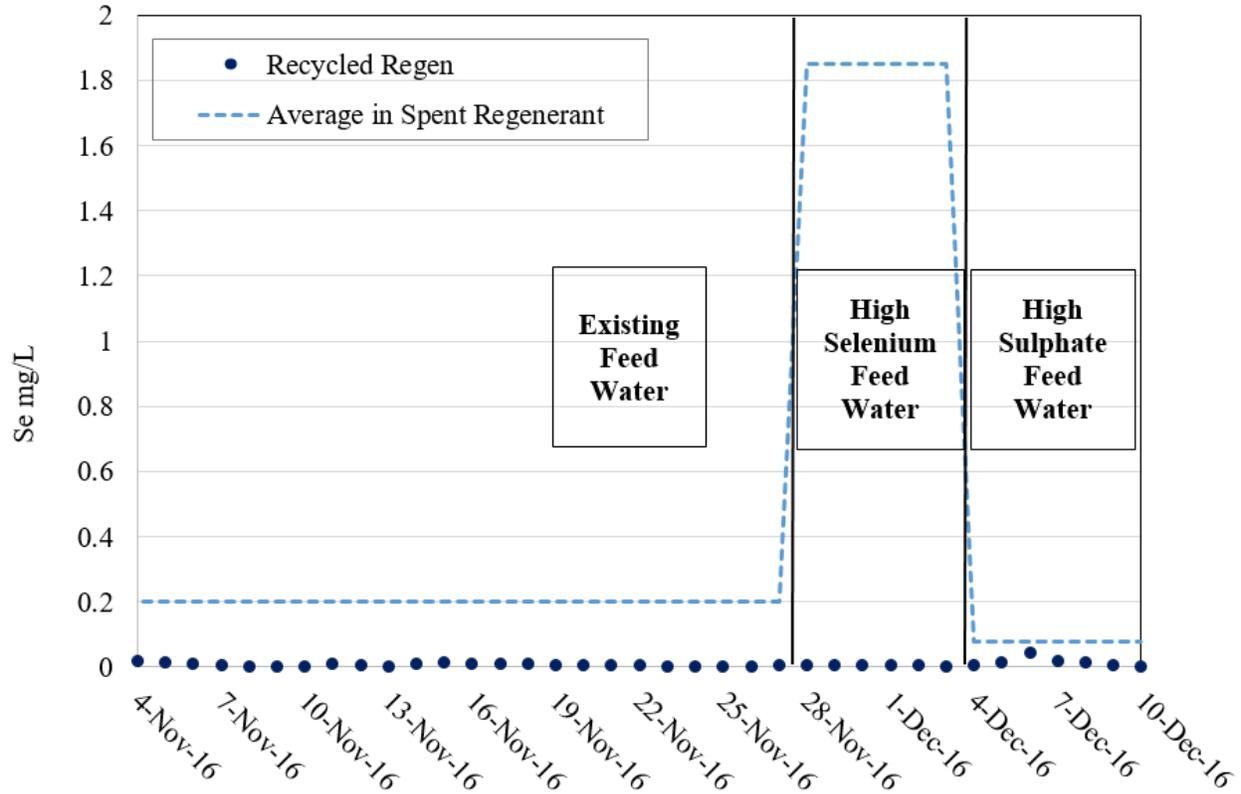
Figure 6. Selenium removal by ERC across the three phases of piloting campaign

BQE Water has reported previously (Mohammadi et al, 2016) that the IX performance in the Selen-IX™ process is influenced by the concentration of sulphate in the feed water. While there is no effect from sulphate on the ability of Selen-IX™ to meet < 0.001 mg/L selenium discharge targets, there is an impact on the treatment cost due to diminished IX resin capacity for selenium at high TDS levels. This can be seen indirectly from Figures 5 and 6 by comparing concentrations of selenium in the IX feed and spent regenerant. Table 8 provides the summary of this for the three phases of the recent pilot campaign.

Table 8. Selenium in feed and spent regenerant along with IX concentration factor in Selen-IX™

Phase	Water chemistry	Average Se in feed (mg/L)	Average Se in spent regenerant (mg/L)	Concentration factor	Hydraulic flow through ERC as % hydraulic flow through the plant
1	As received	0.015	0.200	13.5	7.4%
2	Spiked with more selenium	0.100	1.850	18.5	5.4%
3	Spiked with more sulphate	0.015	0.082	5.5	18.1%

Table 8 shows that the concentration factor achieved by the IX circuit is enhanced from 13.5 to 18.5 when selenium concentration is increased but is reduced from 13.5 to 5.5 when the TDS level is increased from 3,000 to 5,000 mg/L. Note that the hydraulic flow through the ERC is a small fraction of the hydraulic flow through the plant. When feed TDS increased to 5,000 mg/L the hydraulic loading to the ERC almost doubled.

It follows that as the sulphate concentration in the feed water increases, the pre-concentration furnished by the IX portion of Selen-IX™ becomes less and less efficient and a direct electro-reduction treatment with no selenium pre-concentration by IX, may become more cost effective. Therefore, several tests were completed to assess the technical and economic feasibility of treating feed water with high TDS/sulphate level directly in the ERC, i.e. completely by-passing IX, and compare the results of those tests to the ones obtained using the combination of IX and ERC in Selen-IX™.

Evaluating direct treatment using ERC only compared to combined IX and ERC

Figure 7 shows examples of kinetics of selenium removal in the ERC from IX brine during the last phase of the campaign when the plant treated high sulphate feed water. The target of selenium removal in the ERC when operating in tandem with the IX circuit was about 0.050 mg/L. When the residual concentration of selenium in treated brine is at or below 0.050 mg/L then the IX circuit achieves the end-of-pipe limit of less than 0.005 mg/L. Figure 7 shows that the ERC was achieving the target of selenium removal at about 0.15 kWh/m^3 of water treated by the pilot plant, and that the kinetics profile was very consistent.
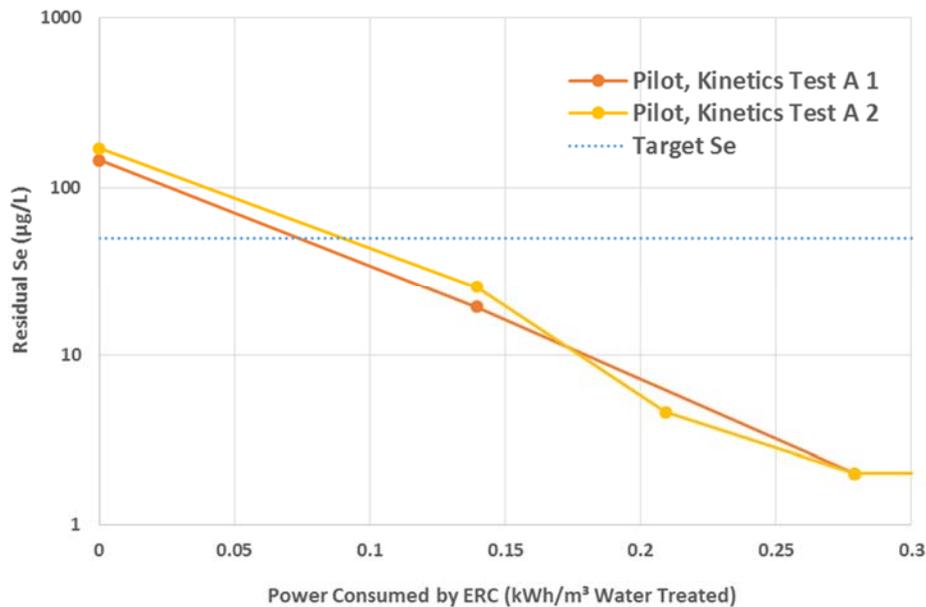

Figure 7. Results for selenium removal from IX regenerant for ERC operation during Phase 3 of the pilot campaign (high sulphate water treatment)

Figure 8 shows results of selenium removal in the ERC when the high sulphate feed water was treated directly through the ERC, i.e. by-passed the IX. Here the target of treatment in the ERC was 0.005 mg/L because the water discharged from the ERC becomes the plant effluent that is

subject to the end-of-pipe selenium removal target. Figure 8 shows that the ERC was able to achieve well below the 0.005 mg/L limit at the power consumption of approximately 2 kWh/m^3 of water treated. One of the advantages of the ERC operating on the IX spent regenerant is the high conductivity of sodium sulphate solution which ensures that the power losses caused by the electrical resistance of solution in the ERC are extremely low. In contrast, the power losses of ERC applied as direct treatment are significant, even at the 4,000 mg/L sulphate concentration of the water tested during the pilot campaign.
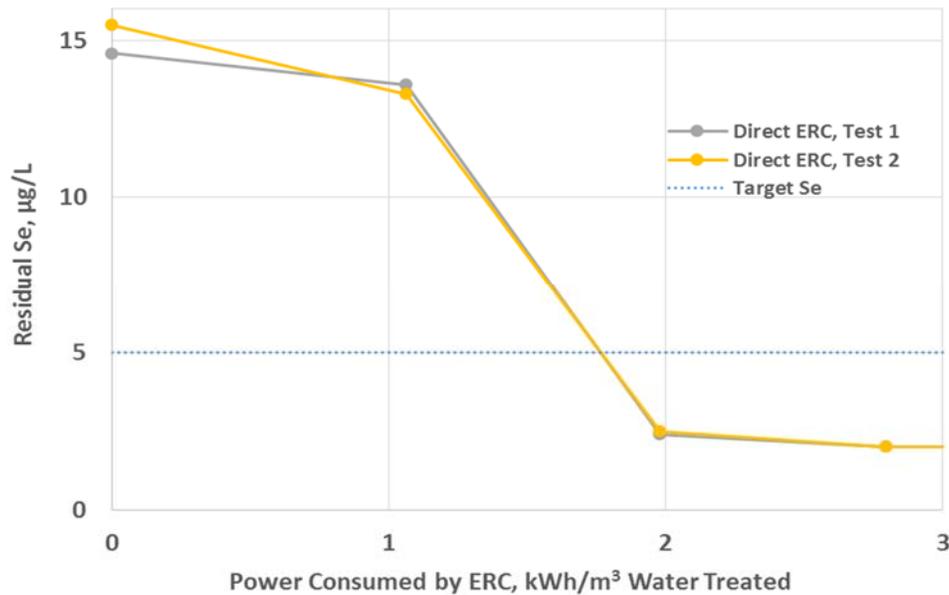

Figure 8. Results for direct selenium removal from high sulphate water in the ERC

Table 9 summarizes the comparison of the direct ERC treatment and the treatment through IX combined with ERC. The total cost of consumables shown in Table 9 includes all operating consumables, i.e. power, iron, and sodium sulphate, expressed per cubic metre of the high sulphate water discharged into the environment subject to the 0.005 mg/L end-of-pipe limit.

Table 9. Comparing direct ERC treatment to IX-ERC treatment for feed water with 4,000 mg/L SO$_4$

Feed with 4,000 mg/L SO$_4$ (5,000 mg/L TDS)	[Se] in solution at start of ERC treatment, (mg/L)	[Se] in solution after ERC treatment, (mg/L)	ERC power input (kWh/m^3)	Total cost of consumables ($/m^3)
IX-ERC	~ 0.200	< 0.010	0.15	0.45
Direct ERC	~ 0.015	< 0.005	2.0	0.53

As can be seen from this table, the cost per cubic metre of water treated is higher with the direct ERC treatment and so for the present case BQE Water recommended that the client consider both the IX and ERC be part of the full scale system. Nevertheless, results of direct ERC treatment show that the direct electroreductive treatment to selenium targets below 0.005 mg/L is technically viable and that for waters with sulphate concentrations somewhat greater than 4,000

mg/L, the unit operating cost of direct ERC treatment is likely to be lower than the cost of a combined IX-ERC treatment in Selen-IX™. This suggests that direct ERC treatment for selenium be considered for high TDS waste waters such as flue gas desulphurization blow down.

Recovery of iron from Selen-IX™ residue for re-use

In this case, the iron oxyhydroxide residue from Selen-IX™ treatment would be blended with tailings and deposited into the existing tailings management facility (TMF). However, as the existing water treatment plant on site uses liquid iron sulphate as a consumable reagent, BQE Water recognized the potential for reprocessing of Selen-IX™ solids to recover iron. An investigation into this topic was included in the pilot campaign by exposing Selen-IX™ residue generated by the pilot plant to sulphuric acid following discharge from the ERC. The release of iron and selenium from the solids was measured by analyzing concentrations of dissolved iron and selenium in the acidic solution. During the tests, the pH of the slurry discharged from the ERC was adjusted to different pH set points from 5 to 9.

Figure 9 summarizes the results of selenium and iron release from the Selen-IX™ residue. This figure shows that acidifying the slurry to pH as low as 5 mobilized little or no selenium (greater than 98% remained bound to solids) while releasing 93% of the total iron contained in the solids.
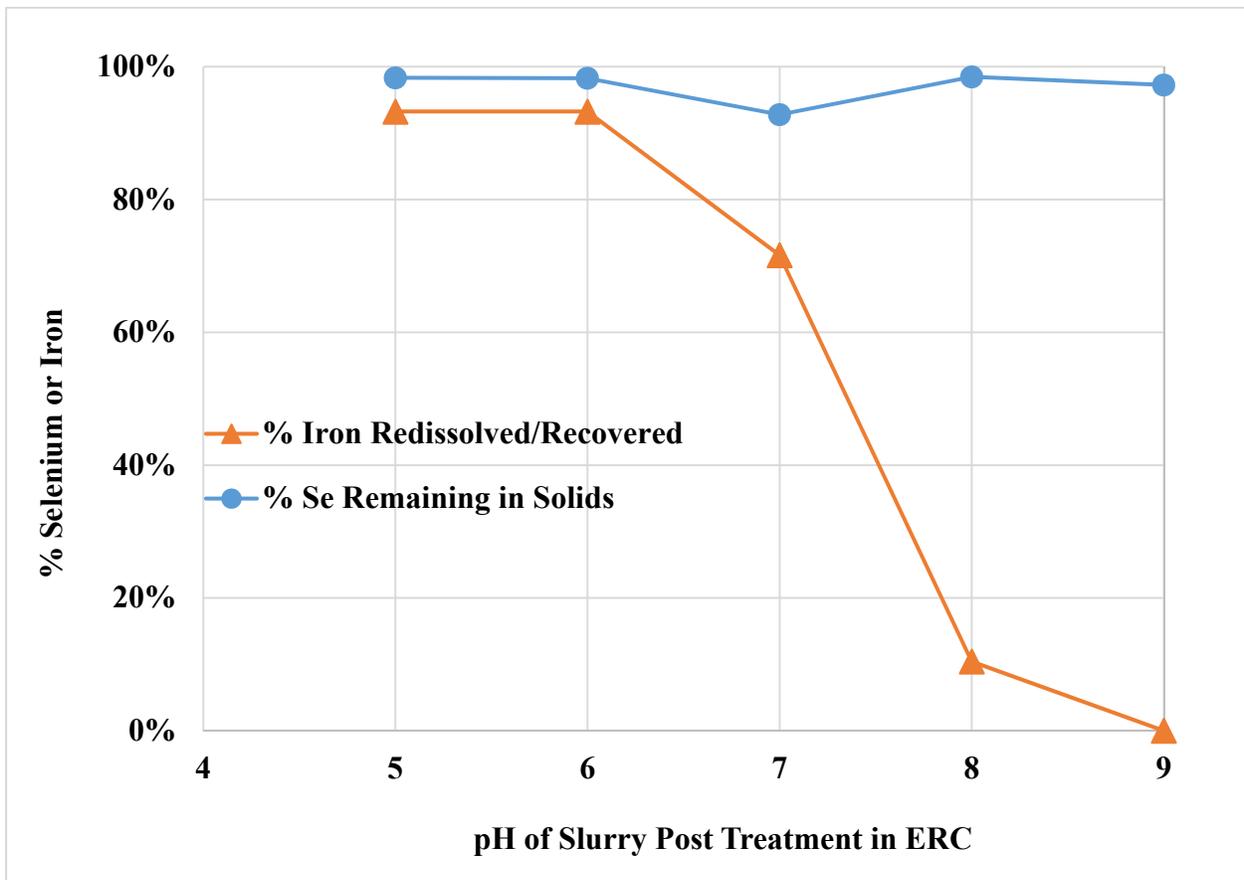

Figure 9. Selenium remobilization and iron recovery due to acidification of residue downstream of ERC

If residue is subjected to iron recovery in this way, the amount of residue requiring disposal drops significantly. In the present case, the mass of dry residue requiring disposal drops from 0.14 kg/m^3 to only 0.01 kg/m^3. This translates into 95% reduction in wet mass of the residue which is commensurate with the 93% iron recovery. Based on the results obtained during this pilot, incorporating the iron recovery process step into the overall flowsheet seems reasonable since not only it reduces the volume of the solids that require disposal, but also provides an opportunity to re-use the iron reagent elsewhere. However, despite the advantages of recovering iron, the economics of this process should be evaluated in detail and were beyond the scope of this pilot campaign.

CASE 3: REMOVAL OF SELENIUM FROM LOW TDS SCRUBBER WATER

Background

A petrochemical refinery was evaluating the need for selenium removal from waste water resulting from sour gas scrubbing. This water is significantly reduced in terms of ORP and is currently treated using dissolved air flotation to remove free oil followed by bio-treatment for BOD/COD. The effluent of the bio-treater passes through sand filters prior to being used as cooling tower makeup water. The system is pictured schematically in Figure 10.
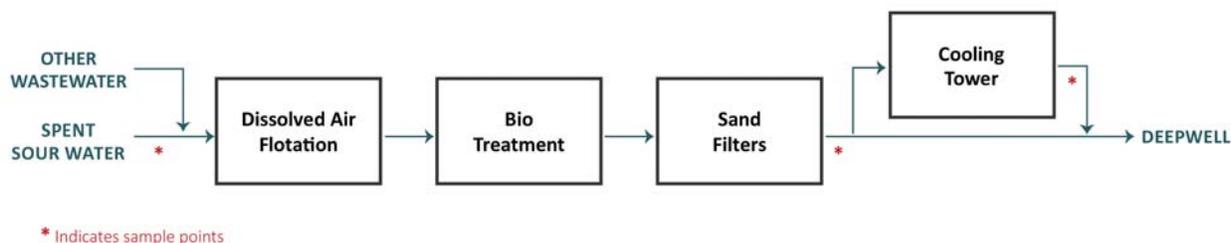

Figure 10. Existing waste water treatment system at petroleum refinery

To better understand the deportment of selenium at site, the site owner undertook a sampling campaign around the existing water treatment system to evaluate the speciation of selenium across the circuit and to identify the best candidate stream for treatment to remove selenium. The sampling program included the spent sour water feed, the discharge of the existing water treatment system, and cooling tower blow down. The character of the spent sour water and treated waste water are show in Table 10.

Table 10. Water chemistry and speciation of selenium in relevant process streams

Analyte	Unit	Spent Sour Water	Treated Waste Water
Total Selenium	mg/L	1.34	0.705
Selenium +4	mg/L	0.0519	0.0096
Selenium +6	mg/L	<0.003	0.687
Selenocyanate (SeCN⁻)	mg/L	0.811	<0.0025
Selenomethionine	mg/L	<0.0015	<0.0015
Unknown Se Species	mg/L	0.099	<0.004
pH	S.U.	6.5	7.8
Sulphate	mg/L	1.9	47

As can be seen, the speciation of selenium in the stream has changed radically across the existing treatment circuit. The total selenium in the system was reduced by removal of solid elemental selenium by dissolved air flotation and filtration, and the dominant species has changed from reduced selenium in selenocyanate to oxidized selenate. While Table 10 shows a concentration of <0.004 mg/L of unknown selenium species in the Treated Waste Water, later assays with lower detection limit would reveal that there was approximately 0.002 mg/L of unknown selenium species in this stream. Sulphate concentrations increase between the two streams because of the conversion of sulphite to sulphate.

Recognizing that the selenium chemistry in the treated waste water would be more amenable to removal, BQE Water focused on this stream in the laboratory program. Figure 11 shows a schematic flowsheet of the processes tested in the program. The objective of this program was to demonstrate removal of selenium to below 0.001 mg/L total selenium.
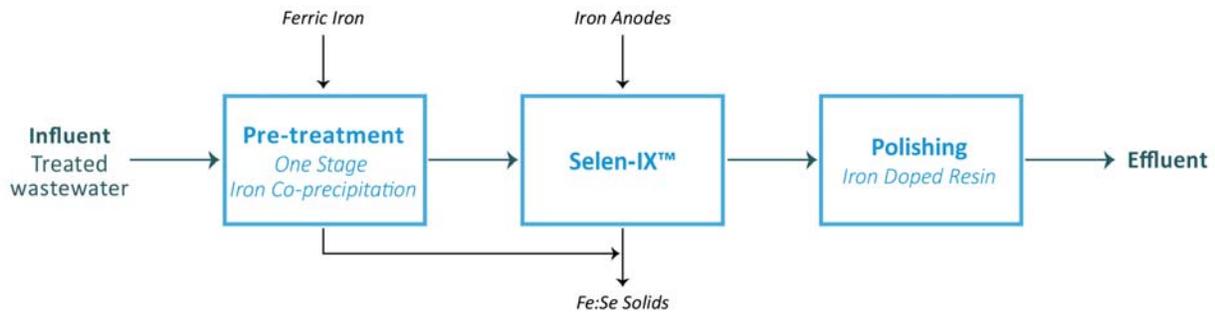

Figure 11. Conceptual flowsheet tested in laboratory campaign

The flowsheet tested included pretreatment with ferric iron for removal of selenite, Selen-IX™ for removal of selenate, and polishing of organoselenium species using Lewatit FO 36 iron doped IX resin.

Pretreatment via ferric co-precipitation

The objectives of pretreatment were to remove selenite as well as phosphate from the influent using iron co-precipitation. Phosphate was present in solution as residue from the upstream biotreater in the existing water treatment system. Figure 12 shows the removal of selenium as well as phosphate from the influent as a function of amount of ferric dosed.
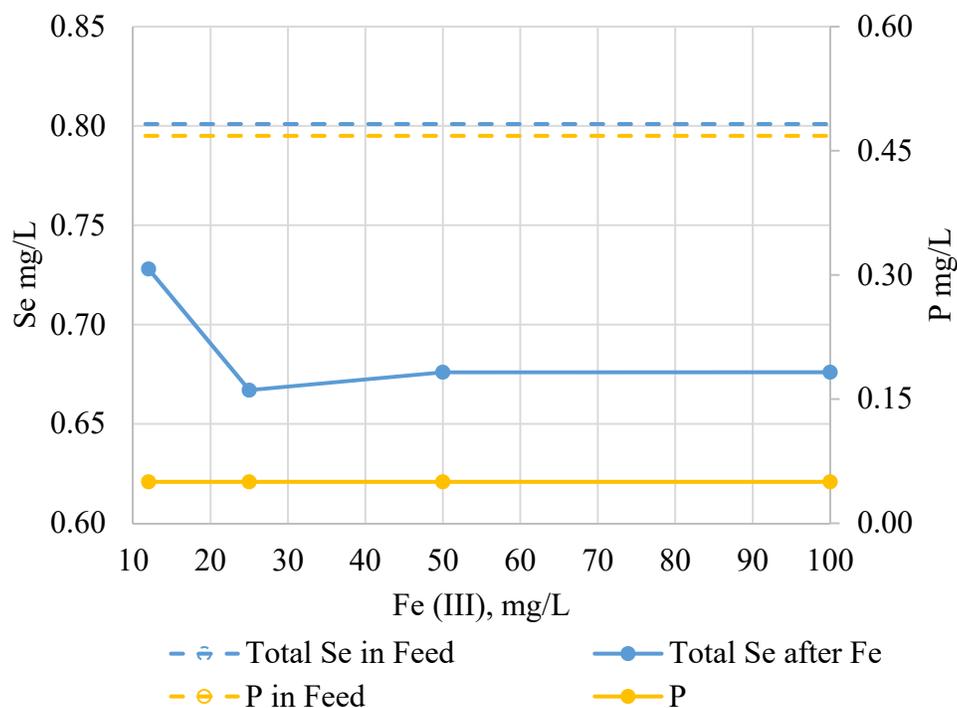
Figure 12. Selenium removal with different ferric dosages at pH 4.5

As can be seen in Figure 12, the ferric dosage from 25 mg/L to 100 mg/L had similar Se removal rate. A dose of 50 mg/L of iron was used in further work. Only 0.009 mg/L of the selenium in this sample was selenite and so the remainder of the selenium removed is selenate. The removal of ~0.125 mg/L of selenium corresponds to 10-20% removal of selenate using ferric. The amount of selenate removal shown in this work is higher than that shown in previous cases because of the high influent level of selenate.

Selenate removal via Selen-IX™

The purpose of the IX loading stage is to remove selenium, specifically selenate, from the influent water. In this part of the program the objective was to determine the length of the IX loading cycle and the concentration factor of selenium across the IX. Figure 13 shows an IX breakthrough curve showing the removal of selenate following pretreatment with iron co-precipitation. The figure shows the concentration of selenium in water exiting the IX column as a function of bed volumes, or volume of water treated.
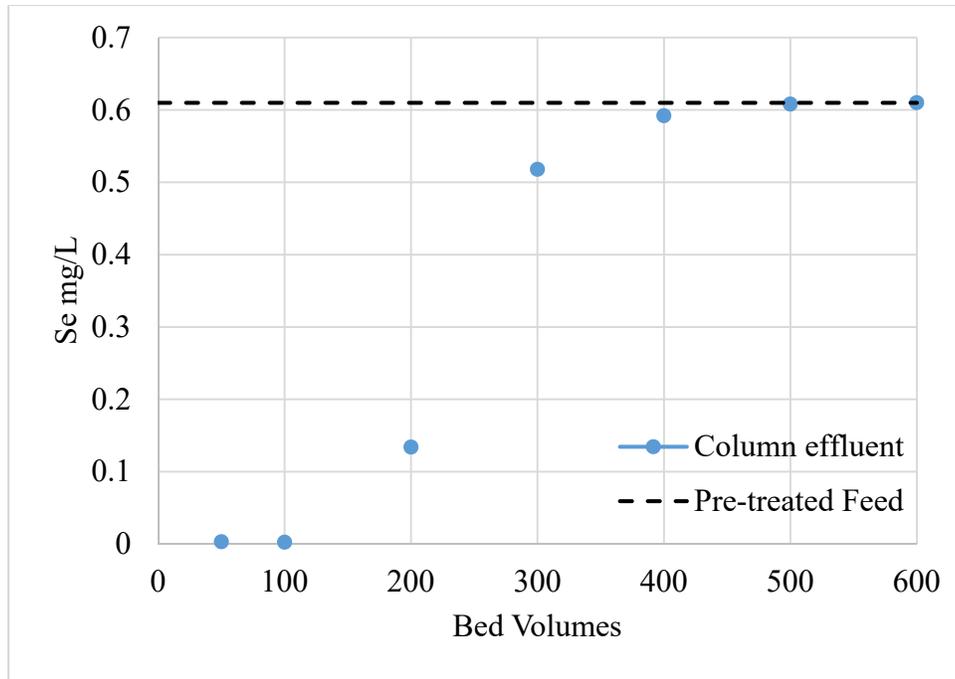
Figure 13. Breakthrough curve of IX for selenate removal

When analyzing breakthrough curves two features are important. First is the load duration before breakthrough, the time when a significant portion of the selenium passing through the column is not being removed. This indicates the point when the IX resin is close to saturated in selenium. This factor is important as it dictates how frequently resin must be regenerated when in service full time. Figure 13 shows that in this case the column breakthrough occurs at a value greater than 100 bed volumes (BV) which indicates that the frequency of regeneration will be relatively low, reducing operating costs due to reagent consumption. The high load duration in this case lead to a selenium concentration of 48 mg/L of selenium in the regenerant brine, or a concentration factor of approximately 70. This significantly reduces the hydraulic capacity of the electroreduction circuit.

The second important feature of a breakthrough curve is the "floor" selenium concentration which is the lowest concentration of selenium achieved in the effluent when the column is still far from breakthrough. The floor selenium concentration represents the best case scenario for the circuit. In the present case, the discharge target of the system is 0.001 mg/L and so the objective is to achieve a floor selenium level lower than that. The two samples pictured in Figure 13 that were taken at 50 and 100 BV both measure ~0.003 mg/L of selenium, thus 0.003 mg/L is the approximate floor selenium concentration. While this represents a removal of greater than 99% of the influent selenium, these levels are still above the 0.001 mg/L selenium discharge target for the project. This result contrasts with BQE's experience from previous projects where selenium levels below < 0.001 mg/L were readily achievable when all selenium present in the IX feed was Se(VI). Consequently, speciation of IX discharge was conducted and revealed that the selenium in the IX discharge was unknown species rather than inorganic selenium. This is shown in Table 11.

Table 11. Speciation of selenium across pretreatment and Selen-IX

Analyte	Unit	Treated Waste Water	Pre-treated IX Feed	IX Discharge
Selenium +4	mg/L	0.0096	<0.0001	<0.0001
Selenium +6	mg/L	0.687	0.618	<0.0001
Selenocyanate	mg/L	<0.0002	<0.0001	<0.0001
Unknown Se Species	mg/L	<0.004	0.00215	0.00216

The fact that a small portion of selenium was present in IX effluent as unknown selenium species led to the use of post-treatment polishing to remove this species.

Organoselenium polishing via iron doped IX resin

Polishing to remove the final trace amounts of selenium was conducted using Lewatit FO 36, an off the shelf iron doped IX resin designed to remove trace amounts of oxyanions from water. BQE Water has used this product in previous projects to remove species such as selenium as well as arsenic, tin and antimony. In the present case, effluent from previous tests was polished with FO 36 and it was determined that this resin was effective at removing selenium to below the 0.001 mg/L selenium discharge target.

In this test program, the iron doped polishing resin was not loaded to breakthrough due to lack of time and solution. In previous projects, the capacity of the polishing resin is on the order of 0.5-1.5 g selenium/L resin when used as a single use product. Considering an influent value of 0.003 mg Se/L in the feed water, this corresponds to a loading duration of approximately 100,000-300,000 bed volumes, or a service life of greater than 1 year. BQE Water has demonstrated regeneration and re-use of this resin for other applications in other projects and so this may be an option for the present application. However, the demonstration of polishing resin re-use was outside the scope of this study. Recognizing the inherent unknowns when studying unknown selenium speciation, there is further work to do in this area.

Project summary

Table 12 shows the removal of selenium across each stage of the circuit achieved in the laboratory campaign.

Table 12. Removal of selenium by stage

Parameter	Unit	Influent	Effluent of Pretreatment	Effluent of Selen-IX	Effluent of Polishing
Species targeted	-	-	Selenite	Selenate	Unknown selenium species
Selenium +4	mg/L	0.0096	<0.0001	<0.0001	<0.0001
Selenium +6	mg/L	0.687	0.618	<0.0001	<0.0001
Unknown organoselenium species	mg/L	<0.004	0.002	0.002	<0.0001
Total Selenium	mg/L	0.697	0.632	0.002	<0.0003
Cumulative level of removal	Percent	-	9.30%	99.80%	99.95%

This program successfully showed how several non-biological process technologies could be integrated to remove selenium from water. The next step in the project is to conduct a pilot demonstration.

CONCLUSIONS

BQE Water has conducted four years of pilot demonstration and laboratory study of Selen-IX™ and have shown that the technology is an effective non-biological method of removing selenium from industrial waste water. The technology has a number of features that led to an overall reduction in risk adjusted lifecycle cost for some projects, including the following:

- Selen-IX™ can remove selenium to levels below 0.001 mg/L at end-of-pipe. This removes the reliance on dilution to achieve water quality objectives in the receiving environment. This simplifies water management by avoiding the need to match water discharge with receiving environment hydrographs and facilitates permitting by avoiding the storage of selenium laden water.
- Selen-IX™ is an entirely physico-chemical process and so the system removes inorganic selenium from feed water without risk of transforming any of it into highly bioaccumulative organoselenium species. Therefore, the risk of non-compliance with fish tissue selenium limits is much lower than with biological treatment systems.
- Selen-IX™ does not introduce any new compounds into the treated effluent that were not present in the feed water. As such, there is no need to include polishing of BOD/COD/nutrients into feed water and no risk of these compounds negatively impacting the receiving environment.
- Selen-IX™ fixes selenium into stable and purely inorganic iron-selenium solids. There are multiple options for cost-effective and environmentally responsible long-term disposal of the solids.

The first commercial installation of the Selen-IX™ process has completed detailed engineering design and is expected to be built in 2018, with operations beginning in 2019.

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