Industrial Scale Non-Biological Selenate Removal – Examples of Plants & Criteria behind Process Selection

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Abstract

Environmental impacts of selenium are complex and highly dependent on the type of receiving environment. Modern regulations stipulate not only water quality limits but also fish tissue criteria to measure success. Every mineral deposit is different and methods of extraction, tailings management and wasterock handling varies from project to project. Moreover, the reliance on dilution to meet environmental compliance is often no longer socially acceptable. It follows then that selenium management is not conducive to a "one-size-fits-all" approach. Until recently, all large-scale selenium treatment systems in mining used some form of biological removal, with several hard lessons learned along the way. These include: constant reliance on dilution to meet water quality requirements in the receiving environment, the production of fast accumulating organo-selenium compounds by bacteria, concerns about the long-term stability of selenium in biological treatment residues, and poor treatment performance in situations with variable flow and water quality.

Following a decade of testing and development, non-biological selenate removal is now being applied on a large industrial scale to avoid the shortcomings of biological systems. The first three industrial scale non-biological systems using electro-reduction of selenium combined with either ion exchange or membrane filtration have been commissioned between 2020 and 2022. As these systems are very new, the operations experience is still limited. However, performance to date matches design expectations and the experience from these projects can help establish criteria for selecting non-biological over biological treatment options.

Introduction

Selenium released from mining operations is known to produce environmental impacts through chronic toxicity caused by bioaccumulation. Consequently, modern regulations (EPA 2016, BC WQG 2017, Alberta 2018) stipulate not only water quality limits but have also established fish tissue criteria to measure success with selenium management in the long term. At the same time, the mining industry has been under ever-increasing scrutiny by both the public and government regulators for using dilution as part of the management and/or storing of selenium-laden residues onsite in perpetuity. Until recently, all selenate removal systems applied in mining were biological, and the experience collected from these revealed multiple weaknesses and shortcomings including:

- Constant reliance on dilution to meet water quality objectives in the receiving environment (NAMC SWG 2013, NAMC SWG 2020)
- Production of organo-selenium compounds that worsen the impact of selenium due to much faster uptake by aquatic organisms which accelerates trophic transfer to fish tissue (LeBlanc & Wallschläger, 2016, Sandy 2016, Phibbs et al. 2011)
- Risk of release of plumes of nutrients leading to low dissolved oxygen in the receiving environment (Teck Coal Limited 2015)
- Lack of proof of long-term stability of selenium captured from water fixed in biological residue
- Poor adaptability to variable water flow and quality

Between 2012 and 2015, BQE Water was approached by several mining companies who recognized that one or more of these shortcomings may prevent them from successfully developing and operating their projects. This provided the impetus for developing a non-biological treatment approach to manage selenate. The effort involved started with proof-of-concept lab testing followed by six years of pilot demonstrations on waters with a wide range of quality and an industrial scale demonstration (Littlejohn et al. 2017, Mohammadi et al. 2016). The effort culminated in the design and construction of three industrial scale plants. And the non-biological selenate removal technology has now been recognized by Environment and Climate Change Canada as a treatment technology for selenium (Environment and Climate Change Canada 2022). All three plants were successfully commissioned and entered operations between 2020 and 2022. Experience from developing and implementing non-biological selenate removal helped us establish criteria that can be used by industry to determine whether non-biological treatment presents a good technical fit for individual projects.

Kemess Selenium Treatment Plant in Canada

Project Requirements

At this site, surface runoff, wasterock seepage and underground mine water are collected in the existing open pit that will serve as the new Tailings Storage Facility (TSF) once the new underground mine is developed. When in production, the mine is expected to discharge excess water from the TSF into the environment.

During permitting, representatives of indigenous groups stipulated that mine discharge must report to a specific creek and that the project cannot rely on dilution to achieve the water quality limit of 2 ppb for selenium. This meant that one of the key requirements for the treatment system was the ability to meet the receiving environment objectives at the end-of-pipe. Speciation completed on selenium contained in the open pit confirmed that more than 90% of total selenium was selenate with the remainder being selenite. The second main requirement was that the solid residue produced by treatment must be stable and suitable for co-disposal with tailings in the TSF. Although the treatment system needs to remove selenium and different heavy metals, this paper will focus only on the removal of selenium. Water quality parameters salient to the design of the selenium removal system are shown in Table 1.

Table 1: Feed Water Quality for Kemess Selen-IX™ Plant

Constituent of Concern	Feed Concentration [ppm]	End-of-Pipe Target [ppm]
Sulphate	350 to 2100	None
Selenium	0 to 0.120	< 0.002
Nitrate	0 to 25	None

Table 1 shows that no end-of-pipe targets were established for sulphate and nitrate. This was due to the fact that, unlike with selenium, no objection was raised to using dilution for nitrate and sulphate in the creek. This highlights the unique role selenium has as the constituent of concern for local communities who understand the outsized risk of the long-term consequences of selenium – that once released, it could persist in the environment and create multi-generational impacts through bioaccumulation. The Selen-IX™ non-biological process for selenium removal was successfully pilot tested during permitting, and the stability of the solids evaluated using humidity cells containing blends of tailings with solids simulating conditions in the TSF.

Since the 2 ppb limit has never been achieved by any industrial scale selenium removal plant, the decision was made to first build the water treatment plant to demonstrate the ability to manage selenium already present in the site water before developing the new deposit that would release additional selenium.

Description of Treatment System

Figure 1 presents a block diagram of the Selen-IX™ process which consists of two circuits: Ion Exchange (IX) and Electro-reduction (ERC). The purpose of IX is two-fold: 1) use resins to selectively remove selenate from feed water and produce effluent containing less than 2 ppb of residual selenium for discharge to the environment and 2) to concentrate the selenate into a small volume of brine solution. The brine, mostly Na_2SO_4, is processed through the ERC circuit. The purpose of the ERC is also two-fold, first to remove selenate from the brine and fix it in a stable residue, and to produce brine sufficiently depleted of selenate to allow for its re-use in resin regeneration in IX.

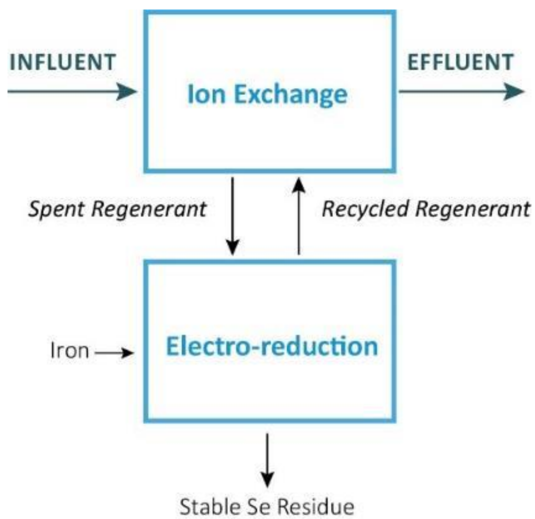

Figure 1: Block Diagram of Selen-IX™ Process

Any selenite that may be present in the plant feed is removed via ferric iron co-precipitation upstream of Selen-IX™. While this co-precipitation process is part of the treatment plant at Kemess, the focus of this paper is on the removal of selenate, as selenite co-precipitation is a well-established conventional process.

Figure 2: IX and ERC Circuits – Kemess Selen-IX™ Plant

Figure 2 shows the IX vessels and electrocells installed in the IX and ERC circuits at Kemess used for the selective removal of selenate.

Operating Results

The operating results are best summarized by Figures 3 and 4. Figure 3 shows the influent and effluent selenium concentrations. Figure 4 shows the concentrations of selenium in the IX regenerant entering and exiting the ERC circuit.

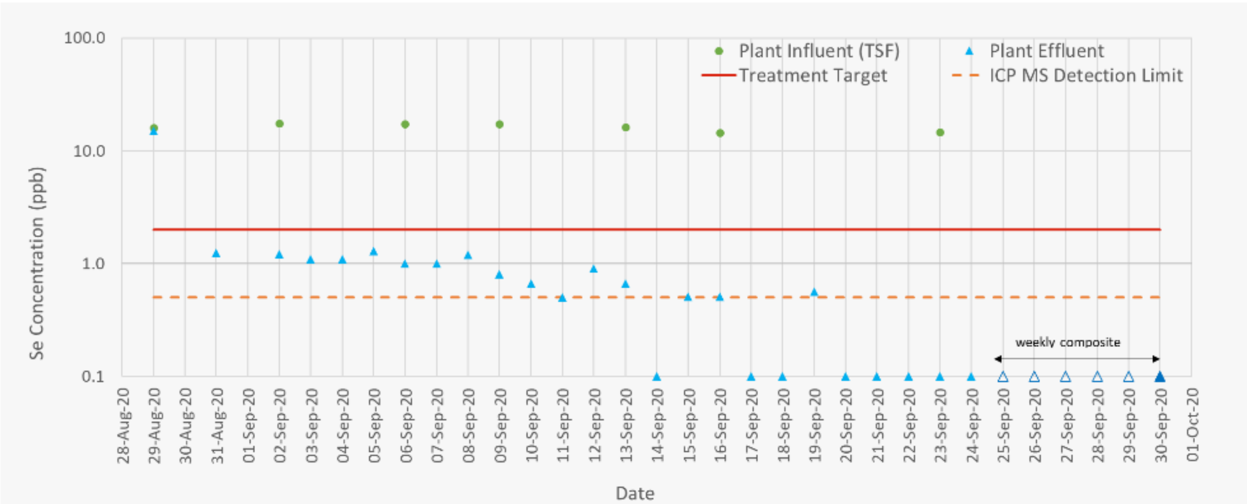

Figure 3: Selenium Concentrations in Plant Feed and End-of-Pipe discharge

From Figure 3, the Selen-IX™ process not only achieved a consistent selenium removal to below the target of 2 ppb but also demonstrated on an industrial scale that selenium levels below the ICP-MS reporting limit of 0.5 ppb are possible.

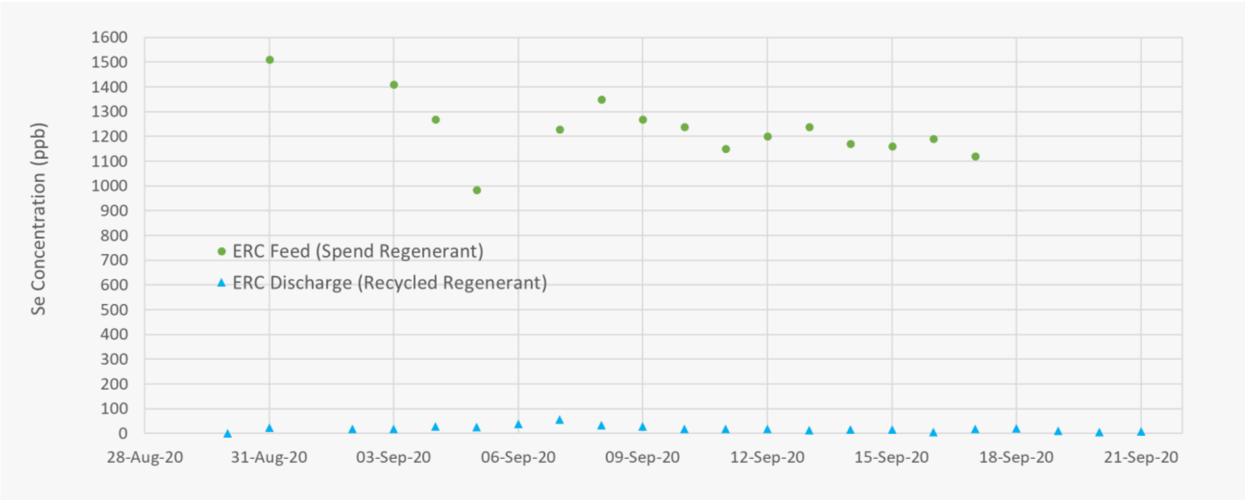

Figure 4: Selenium Concentrations in IX regenerating entering and exiting ERC

Figure 4 provides evidence of high efficiency selenium removal from the IX regenerant into the ERC solids. The concentration in the feed to the ERC circuit of 1.2 to 1.6 ppm shown in Figure 2 provides a direct indication that the IX circuit pre-concentrates selenium by a factor of ~ 100x compared to selenium contained in the feed. Figure 5 shows a picture of the ERC solids cake that are placed in the TSF. The stability of ERC solids was evaluated during project permitting using humidity cells containing blends of tailings with solids mimicking conditions in the TSF.

Figure 5: De-watered ERC Solids to TSF

Following plant commissioning, the plant operated continuously 24/7 for approximately two months. During this period, the IX resin was regenerated and re-used six times while the entire inventory of regenerant solution was processed and recycled more than 60 times, indicating a steady state was reached. Values for Key Performance Indicators were also validated with all criteria matching design expectations.

Current Project Status

Following commissioning and operation in the summer and fall, the plant was shut down for the winter in Q4 2020. Subsequently, plans for the construction and development of the new underground mine were put on hold and the water treatment plant was placed in care and maintenance. The permit stipulates that the treatment facility operate only during mine construction and operation. During care and maintenance, wasterock seepage water containing selenium is collected and stored in the existing open pit. And while under care and maintenance, activities are carried out semi-annually to maintain the plant's operational readiness and ensure that the life of the IX resin is preserved.

Coal Ash Pond Dewatering Treatment Facility in the US

Project Requirements

This project deals with the remediation of an ash pond at a coal fired power plant. Ash generated residue from coal combustion has been stored in a pond where water quality indicates contamination from heavy metals and selenium. The project involves treatment of water that has come into contact with ash, discharge of treated water into the environment, and simultaneous relocation of dewatered ash into a new properly engineered facility for permanent disposal. Key project requirements can be summarized as follows:

- Meet an end-of-pipe selenium discharge limit of 7 ppb.
- Operate to a schedule of 50 hours per week Monday to Fridays.
- Able to adjust to highly variable feed water flow and quality.

The client selected non-biological treatment as it is the only treatment option that could meet the key requirements related to intermittent operation.

Description of Treatment Process

The treatment process for selenate removal for this coal ash pond is the same as that applied at Kemess described in the previous section. And similar to Kemess, selenite and heavy metals are removed upstream of selenate removal.

Current Project Status

This plant was commissioned in Q4 of 2021 and is now operational.

Simultaneous Selenium and Sulphate Removal Plant in the US

Project Requirements

This site involves active treatment of tailings seepage and underground mine water. In addition to heavy metals, the constituents of concern include sulphate and selenium. One of the main requirements is for the final effluent to pass Whole Effluent Toxicity (WET) tests using *Daphnia magna* and *Ceriodaphnia dubia*. Notably, due to alternating dry and wet seasons, the treatment system is subject to extreme fluctuations in the volume of water reporting to it. This seasonality affects not only the mine site but also the receiving environment which cannot always provide sufficient dilution to ensure that water quality objectives in the downstream environment are achieved. Consequently, another requirement is for selenium concentration at end-of-pipe to remain below a 1.6 ppb limit.

Selenium speciation assays showed that virtually 100% of the selenium dissolved in the mine-influenced water is selenate. Table 2 summarizes the feed range of concentrations and their respective end-of-pipe targets for the constituents of concern.

Table 2: Feed Water Quality and Effluent Targets

Constituent of Concern	Feed Concentration [ppm]	End-of-Pipe Target [ppm]
Sulphate	1,850 to 2,550	720 to 950
Selenium	0 to 0.010	< 0.0016

The overall project requirements can be summarized as follows:

- Treatment must be capable of fast ramp-up and turn-down to respond to seasonal flows.
- Meet an end-of-pipe selenium discharge limit of 1.6 ppb.
- Treated effluent pass WET tests with *daphnia* and *ceriodaphnia*.
- Solid residue produced by treatment must be suitable for co-disposal with tailings.

Description of Treatment System

The system uses nanofiltration in combination with a gypsum desaturation circuit and selenium electro-reduction circuit. The purpose of nanofiltration is two-fold: 1) to produce clean permeate suitable for discharge and 2) to concentrate both sulphate and selenium in the retentate prior to further processing. A block diagram of the treatment system is shown in Figure 6.

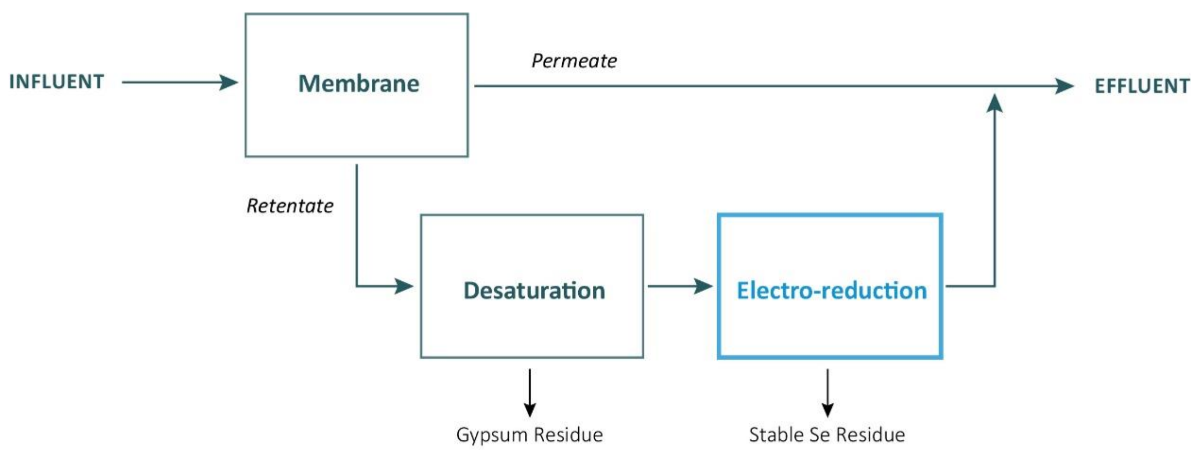

Figure 6: Block Diagram of Treatment System for Simultaneous Sulphate and Selenium Removal

The plant operates at 66% water recovery which equates to sulphate and selenium concentrations in the retentate approximately 3x greater than in the plant feed. The first step in retentate processing is gypsum desaturation to precipitate solid gypsum. The precipitation is spontaneous and catalyzed by seed gypsum.

The discharge from the desaturation stage contains sulphate at gypsum saturation levels of approximately 1,600 ppm. From there the retentate passes through the ERC where selenium is removed from solution and fixed into a stable and solid residue. The gypsum solids are blended with the ERC solids prior to disposal in the tailings facility.

The ERC design at this plant differs from those utilized in the Selen-IX™ plants. This is due to the retentate produced by nanofiltration having relatively low levels of total dissolved solids (TDS), compared to the IX brine, which reduces the solution electric conductivity. Utilizing the same ERC here would significantly increase power consumption. The unique design feature of the ERC applied to the nanofiltration retentate is that it maintains a constant gap between the cathode and anode in the electrocells – as the anode is consumed, the gap is automatically adjusted continuously. Figure 7 shows the ERC with the constant-gap cells.

Figure 7: ERC with Constant-Gap Electrocells Applied to NF Retentate

Current Project Status

The treatment system has been fully commissioned and the plant began operations in April 2022.

Conclusions: Criteria for Assessing the Technical Fit of Non-Biological Selenate Removal Systems

Selenium management in mining projects is heavily influenced by a large number of site and project specific factors. Based on the performance of biological treatment systems and our experience with applying non-biological treatment, the latter represents the "only possible option" when one or more of the following criteria apply:

- No reliance on dilution to meet receiving environment end-of-pipe limits when the selenium target is at or below 3 ppb.

- Requirement for intermittent or seasonal treatment.
- Proof for the long-term stability of residue containing selenium.
- Project owner preference to ship selenium residue for beneficial re-use off-site.

Additionally, a non-biological treatment approach is generally favoured over biological treatment when one or more of the following criteria apply:

- End-of-pipe discharge limit for selenium is below 10 ppb.
- Effluent discharges into a sensitive environment, increasing the risk of impacts caused by constituents introduced into the treated water by biological systems including organo-selenium compounds, nutrients (ammonia and phosphorus), and/or residual BOD and COD.
- Treatment must handle large fluctuations in water flow and quality.

The first three industrial scale non-biological systems using electro-reduction of selenium combined with either ion exchange or membrane filtration have been commissioned between 2020 and 2022. As these systems are very new, the operations experience is still limited. However, performance to date matches design expectations and the experience from these projects can help to establish criteria for selecting non-biological treatment over biological options.

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