Commissioning and Long-Term Operation of Large Scale Non-Biological Selenate Removal Systems

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Abstract

Due to its ubiquitous occurrence across mineral deposits, the risk of long-term environmental impacts, and advancing regulations, effective management of selenium from early mine permitting stages to post-closure is important for the industry moving forward. Therefore, it is not surprising that treatment for selenium is one of the fastest evolving areas of mine water treatment. Selenate is the most prevalent selenium species in most mine waters. Broadly speaking, there are two groups of selenate removal approaches: biological and non-biological. On the biological treatment side, Saturated Rock Fills (SRFs) have been scaled up to treat large volumes of water in the coal mines in Southeastern BC. On the non-biological side, the electro-reduction of selenium combined with either selective ion exchange or nanofiltration (NF) has been implemented at several projects in Canada and the US. The selection of the treatment approach is driven by site and/or project-specific factors, and the completion of Best Available Technology (BAT) studies is often required by regulatory agencies. Access to data and information about operation and maintenance is important to ensure that BAT studies are comprehensive and truly holistic. This presentation focuses on the start-up and ongoing operation of non-biological systems removing selenate to the end-of-pipe limits ranging from 1.5 to 10 ppb. The plant performance data are presented, operational challenges and successes are discussed, and maintenance requirements are reviewed.

Introduction

Selenium introduced into the environment from mining and other industrial operations produces deleterious effects on biota in the receiving environment (Brandt et al., 2019; Wilkin et al., 2018) due to chronic toxicity caused by bioaccumulation and biomagnification. Because of selenium's impacts, regulations (EPA 2016, BC WQG 2017, Alberta 2018) have been updated to stipulate not only more stringent water quality limits but also to establish fish tissue criteria for measuring success in selenium management over the long term. Before the four industrial-scale non-biological selenium treatment plants described in this paper were implemented, all selenate removal systems applied in mining and other industries relied on biological selenium reduction, and the data and experience gathered from these biological treatment facilities revealed multiple weaknesses and shortcomings. One shortcoming of biological selenium treatment is the reliance on dilution to meet water quality objectives in the receiving environment, as biological treatment processes often cannot achieve sufficiently low end-of-pipe selenium concentrations (NAMC SWG, 2013; NAMC SWG, 2020). Another weakness of biological treatment is the formation of highly bioavailable organoselenium compounds that enhance the uptake of selenium by aquatic organisms and worsen its impact, accelerating trophic transfer to fish tissue (LeBlanc & Wallschläger, 2016; Sandy, 2016; Phibbs et al., 2011). Other issues with biological selenium treatment include the risk of nutrient plume releases leading to low dissolved oxygen levels in the receiving environment (Teck Coal Limited, 2015) and the lack of proof of long-term stability of selenium captured from water that becomes sequestered in biological residue. Additional potential issues that impact operators of biological selenium removal plants are the relatively poor adaptability of biological treatment processes to variable water flow rates and rapid fluctuations in water quality and temperatures.

Due to the reasons mentioned above, several mining companies recognized that one or more of these shortcomings might impede their ability to successfully develop and operate their projects. This sparked their interest in approaching us to create a non-biological treatment method for managing selenate. The effort began with proof-of-concept lab testing, followed by six years of pilot demonstrations on waters of varying quality and an industrial-scale demonstration (Littlejohn et al., 2017; Mohammadi et al., 2016). These efforts culminated in the design and construction of four industrial-scale plants to date, with a fifth currently in final design, scheduled for construction in late 2024 and set to begin operations in 2025. The non-biological selenate removal technology has now been acknowledged by Environment and Climate Change Canada as a treatment technology for selenium (Environment and Climate Change Canada 2022). All four plants were successfully commissioned and began operations between 2020 and 2023. This paper will provide the project background for the four plants and discuss their commissioning, operations, and lessons learned.

First Commercial Non-Biological Selenium Treatment Plant—Kemess Treatment Plant in Northern British Columbia, Canada

Project Background

Waste rock seepage, underground mine water, and surface runoff are collected in the existing open pit, which 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. Therefore, one of the key requirements for the treatment system is to meet the receiving environment objective of 2 ppb selenium at the end of the pipe. Speciation completed on selenium contained in the open pit confirmed that more than 90% of the total selenium was selenate, with the remainder being selenite. Another project requirement is 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 relevant 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)
Selenium	0 to 0.120	< 0.002
Sulfate	350 to 2,100	None
Nitrate	0 to 25 as N	None

Table 1 shows that no end-of-pipe targets were established for sulfate and nitrate. This was due to the fact that, unlike with selenium, no objection was raised to using dilution for nitrate and sulfate 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 was 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 diagram of the treatment system that includes metals removal upstream of the Selen-IX™ process for removing selenate. The Selen-IX™ process consists of an ion exchange (IX) and an electro-reduction (ERC) circuit. The design flow rate of the treatment system is 6,500 m^3/d. The purpose of the IX circuit is two-fold: 1) to use strong base anion (SBA) 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 regenerant brine solution for processing in the ERC circuit. The regenerant brine, consisting mostly of Na_2SO_4 and selenate, is processed through the ERC circuit. The purpose of the ERC is also two-fold: first, to remove selenate from the regenerant brine and fix it in a stable residue and to generate brine that is sufficiently depleted of selenate to allow for its re-use in resin regeneration in IX.

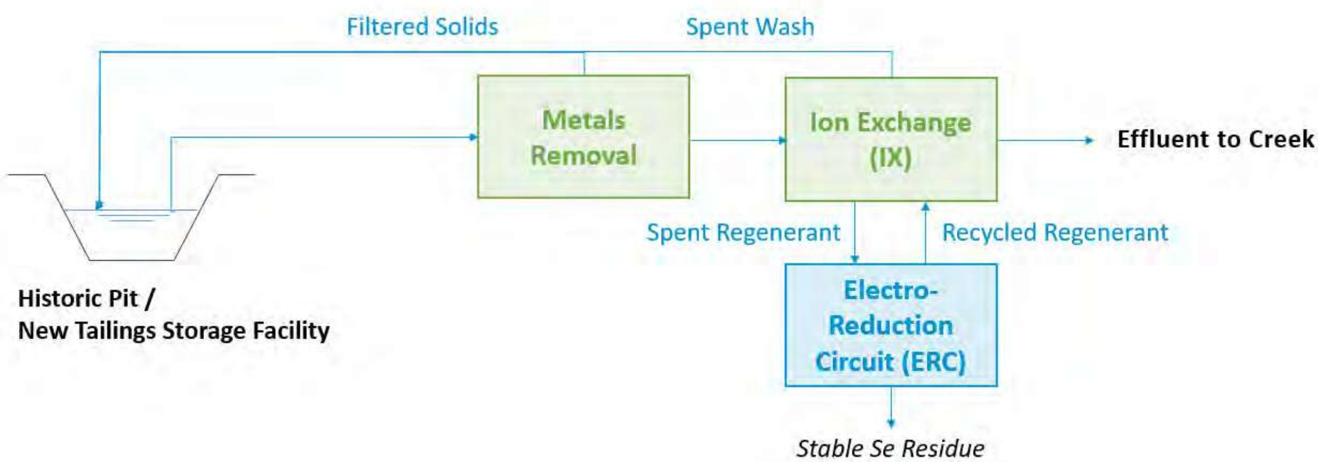

Figure 1: Diagram of Treatment Processes Including Selen-IX™

Selenite 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: Kemess Selen-IX™ Plant with IX and ERC Circuits

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

Commissioning, Startup, Performance Testing, and Operations

The timeline and major milestones for this project are summarized below, including the commissioning during the worldwide COVID-19 pandemic, which introduced additional challenges to the project:

- Construction was completed in September 2019.
- Dry commissioning occurred from September to December 2019.
- Returned in May 2020 for wet commissioning, initiating IX resin conditioning and the process startup of the upstream metals removal circuit.
- IX and ERC started in July 2020 but were paused at the beginning of August due to issues with rectifiers.
- Restarted at the end of August 2020, with commissioning completed on September 12, 2020, following the successful completion of a 14-day performance test.
- The operations phase commenced on September 13, 2020, and continued until October 2020, when the plant was taken down for the winter.

Figure 3 shows selenium data from startup through operations in 2020.

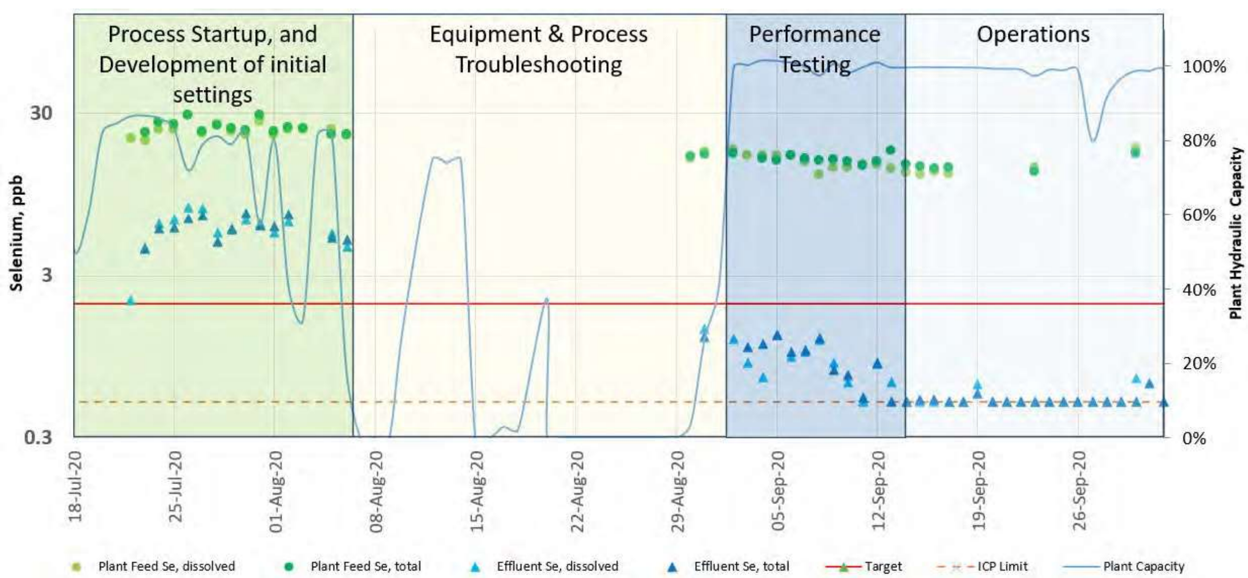

Figure 3: Kemess Selen-IX™ Plant Startup, Process Troubleshooting, Performance Testing, and Operations Data

Figures 4 and 5 summarize more detailed operating data. Figure 4 shows the influent and effluent selenium concentrations, and Figure 5 shows the concentrations of selenium in the IX regenerant entering and exiting the ERC circuit.

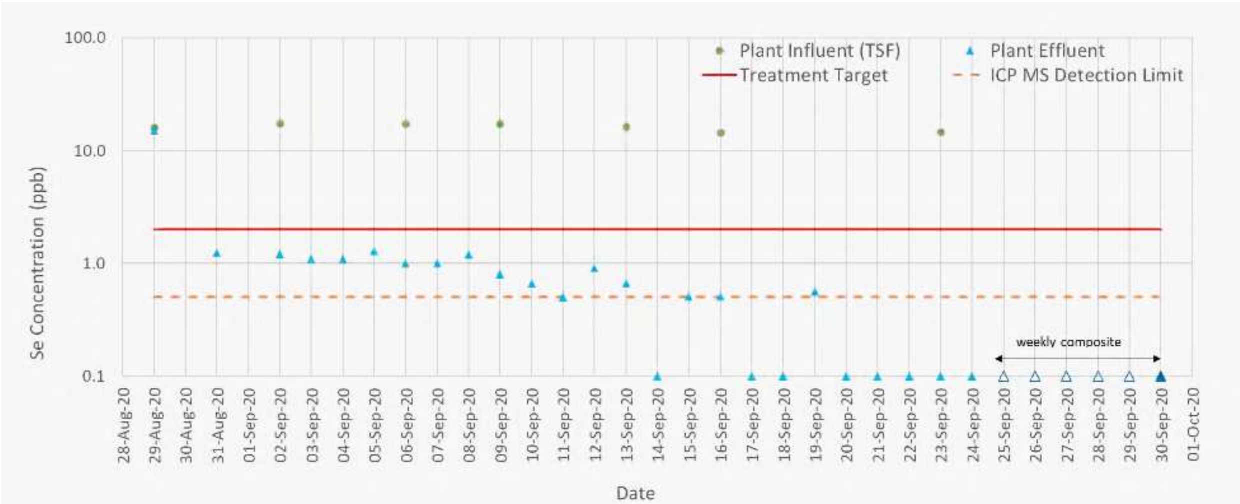

Figure 4: Selenium Concentrations in Plant Feed and End-of-Pipe Discharge

From Figure 4, 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.

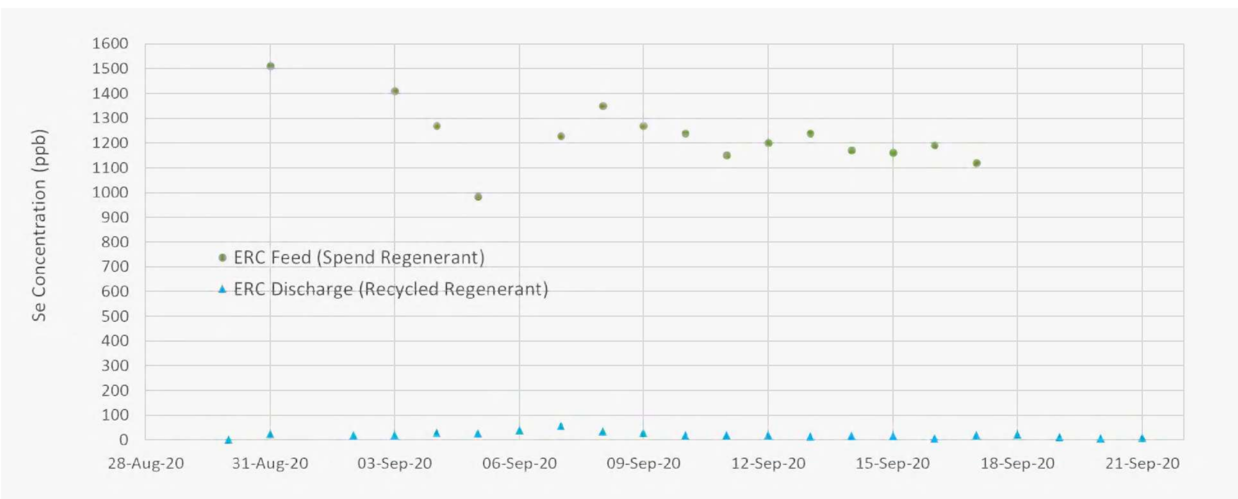

Figure 5: Selenium Concentrations in IX Regenerating Entering and Exiting ERC

Figure 5 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 approximately 1,200 to 1,600 ppb shown in Figure 5 provides a direct indication that the IX circuit pre-concentrates selenium by a factor of ~100× compared to selenium contained in the feed. Figure 6 shows a picture of the ERC solids cake that is 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 6: Dewatered ERC Solids for Co-disposal in 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.

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 operates only during mine construction and operation. During care and maintenance, waste rock seepage water containing selenium is collected and stored in the existing open pit. 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.

Second Commercial Non-Biological Selenium Treatment Plant—Coal Ash Pond Dewatering Facility in the Eastern USA

Project Background

This project involves the remediation of an ash pond at a coal-fired power plant. Ash residue from coal combustion has been stored in a pond where the ash has leached metals and selenium into the water. The project involves the treatment of water that has come into contact with ash, the discharge of treated water into the environment, and the 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 Friday.
- 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 System

The treatment process for selenate removal for this coal ash pond is similar to that applied at Kemess, described in the previous section. Similar to Kemess, selenite and metals are removed upstream of the selenate removal process (Figure 7).

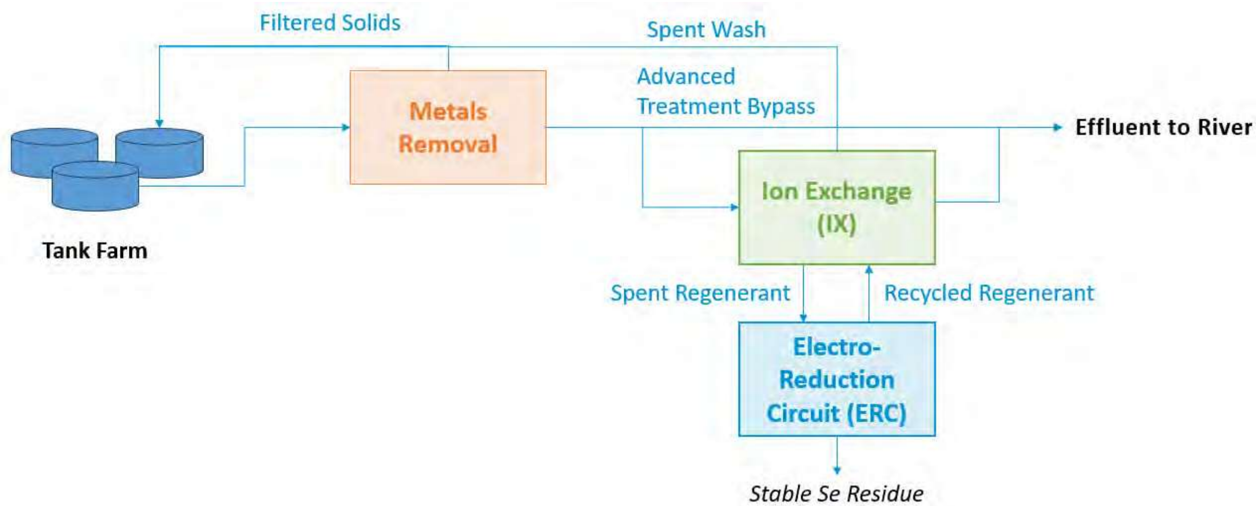

Figure 7: Diagram of Treatment Processes Including Selen-IX™

A Major Lesson from Operations

This plant was commissioned in Q4 of 2021 and is now operational. A major lesson from its operations is how to gauge when the anodes require replacement/changeout. When operating, the voltage was monitored to gauge anode consumption and ultimately trigger an anode replacement when the voltage exceeded the maximum allowed levels. After the anode changeout, the mass of iron consumed and energy consumed, based on Coulombs per litre, were evaluated. Key learnings are:

- Good predictability using voltage and Coulombs/L
- Anode wear was uniform across all cells.
- The calculated anode consumptions were within 10% of the theoretical, predicted values.
- Anode changeout required two 10-hour days at this site; this insight allows for reliably coordinating IX loading with an expected ~20 hours of ERC downtime.

Figure 8 shows pictures from anode changeout at this Selen-IX™ facility. Other key learnings from this facility include the fact that the sodium sulfate (Na_2SO_4) reagent that were initially used for regeneration contained considerable selenium content. We learned based on this experience to be on the lookout and avoid high selenium content Na_2SO_4 to use for regenerating the IX resins.

Figure 8: Anode Changeout at Selen-IX™ Plant

Third Commercial Non-Biological Selenium Treatment Plant—Selenium And Sulfate Removal Plant in Southwestern USA

Project Background

This site involves active treatment of tailings seepage and underground mine water. In addition to heavy metals, the constituents of concern include sulfate 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)
Selenium	0 to 0.010	< 0.0016
Sulfate	1,850 to 2,550	720 to 950

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 passes WET tests with daphnids.
- 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 a selenium electro-reduction circuit, and its design flow rate is 800 m^3/d. The purpose of nanofiltration is two-fold: 1) to produce clean permeate suitable for discharge and 2) to concentrate both sulfate and selenium in the retentate prior to further processing. A diagram of the treatment system is shown in Figure 9.

The plant operates at 65-70% water recovery, which equates to sulfate and selenium concentrations in the retentate approximately 3× greater than in the plant feed due to excellent rejection of these ions by the NF membranes. 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 sulfate at gypsum saturation levels of approximately 1,600 ppm. From there, the retentate passes through the ERC, where selenium is removed from the solution and fixed into a stable and solid residue. The gypsum solids are blended with the ERC solids before disposal in the tailings facility.

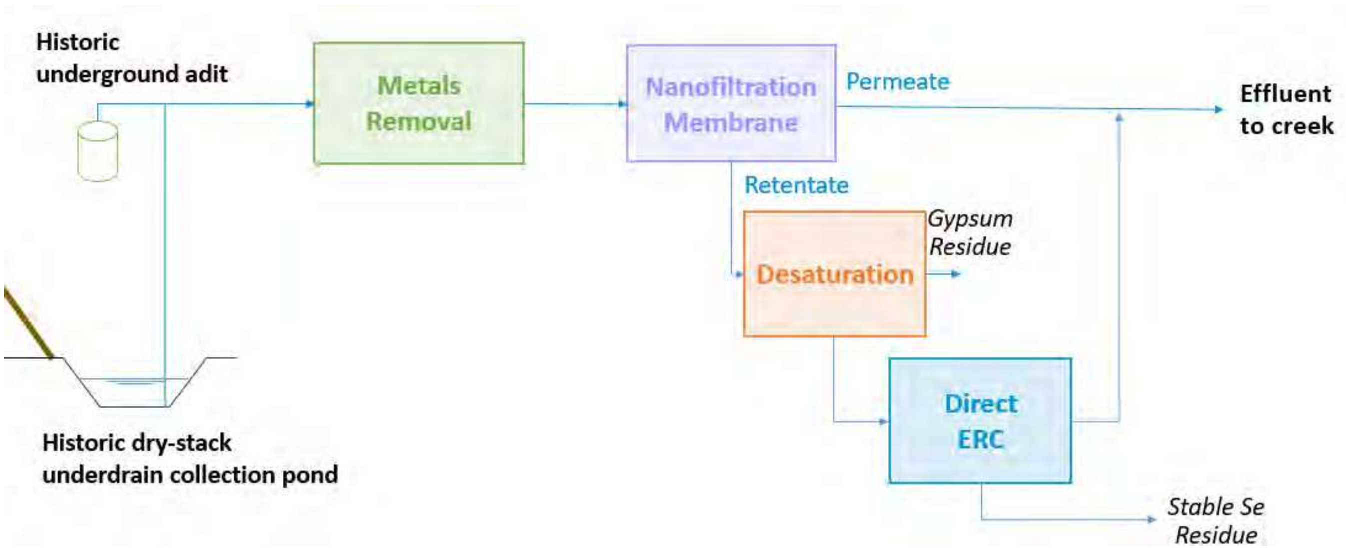

Figure 9: Diagram of the Treatment System for Simultaneous Sulfate and Selenium Removal

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's 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 electro-cells—as the anode is consumed, the gap is automatically adjusted continuously. Figure 10 shows the ERC with the constant-gap cells.

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

Fourth Commercial Non-Biological Selenium Treatment Plant—Selenium Removal Plant in Southwestern USA

Project Background

This facility is at the same mine site as the third commercial non-biological selenium treatment plant described in the preceding section and has the same issues with the arid climate that has a receiving environment that is affected by extremes in seasonality. This facility was designed and built to dewater the site to lower the water table to allow for underground mining. The selenium treatment facility here also has an end-of-pipe selenium limit of 1.6 ppb.

Figure 10: ERC with Constant-Gap Electro-Cells Applied to NF Retentate

Description of the Treatment System

Similar to the first and second commercial non-biological selenium treatment facilities described in this paper, this facility also has metals removal upstream of the Selen-IX™ process. There is also a cooling tower upstream of the metals removal process (Figure 11). The design flow rate is 4,000 m^3/d.

Commissioning and Operations

This facility was commissioned in Q4 of 2023 and is operational. Because there is not always sufficient selenate to require treatment, the Selen-IX™ process only operates intermittently as required. As stated in previous sections of this paper, this is a benefit of non-biological vs. biological selenium treatment, which allows for smoother intermittent operations.

A key lesson from commissioning this facility was to ensure that the strong base anion (SBA) resin used is properly conditioned and rinsed; the Selen-IX™ process requires SBA resin in sulfate form to operate properly, and most SBA resins are not commercially available in their sulfate form and need to be converted to sulfate form and conditioned properly prior to use in the Selen-IX™ process using sulfuric acid (H_2SO_4). This process requires sufficient rinsing with clean water afterwards before it can be used.

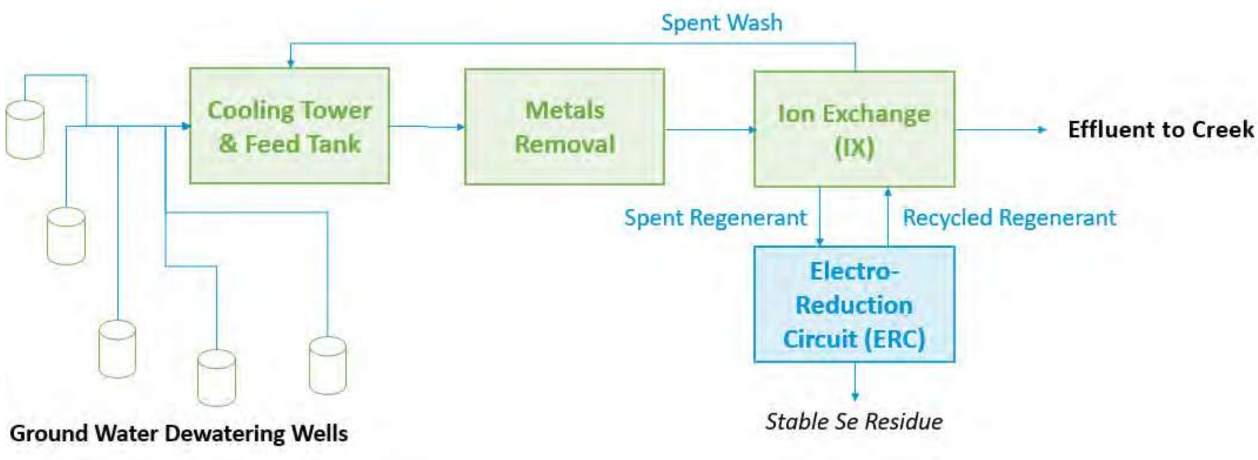

Figure 11: Diagram of the Treatment System

Conclusion

The first four industrial-scale, non-biological systems using either ion exchange or membrane filtration to remove and concentrate selenium for stabilization via electro-reduction were commissioned between 2020 and 2023. As these systems are relatively new, operational experience is still limited. However, performance to date matches design expectations, and the experience gained from commissioning and operating these treatment facilities will help ensure continued improvements in the design and operations of current and future non-biological selenium removal facilities in the mining and other industrial sectors, promoting environmentally and socially responsible mining.

Acknowledgments

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