# Selen-IX™ Applied to Coal Ash Pond Clean-up

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ABSTRACT
Coal combustion residues often contain trace metals and selenium that report to the aqueous phase in ash ponds and may require removal prior to discharge of water from these ponds into the environment. WesTech Engineering and BQE Water have created a partnership to treat the water discharged from these ponds in a 2-stage process. WesTech is providing the first stage including a physical-chemical treatment. The second stage, provided by BQE Water, uses ion-exchange for selenium capture.

WesTech is utilizing chemical precipitation methods to remove trace metals. This treatment uses chemical mixing followed by precipitation. The treated water is further polished using a filtration step to remove the metals to discharge levels. The filtration also serves as pretreatment to the Selen-IX™ system. The solids generated in these steps are collected and dewatered for disposal in an offsite landfill.

Selen-IX™ is a treatment technology combining ion exchange with electro-reduction for selenium control. While the technology was originally developed for the mining industry, the typical project settings and requirements associated with ash pond clean-up make Selen-IX™ suitable for selenium control in this sector. This paper reviews the first application of Selen-IX™ in the remediation of coal ash pond water, from the criteria that led to selecting Selen-IX™ as the process option to the engineering design and overall implementation strategy. The latest progress updates of this first Selen-IX™ project for coal ash pond clean-up will also be included.

## INTRODUCTION

The safe treatment and disposal of ash pond water and residual ash is a primary concern for power facilities. Wastewater processes for coal fired power plants need to comply with US Environmental Protection Agency (US EPA) regulations such as the updates to the Coal Combustion Residuals Rule and the Effluent Limitation Guidelines. Included in these changes is a national selenium criterion that is protective of chronic effects, accounts for short-term and long-term exposure, and includes limits for selenium content in fish tissue and water-column[1].

Selenium is a naturally occurring element that is an essential micronutrient. When consumed in excess selenium is known to produce environmental impacts for aquatic life through chronic toxicity caused by bioaccumulation. The ability of selenium to bioaccumulate increases these risks by providing a pathway for selenium to remain in the ecosystem and impose multi-generational impacts long after water-column concentrations have returned to normal.

One source of naturally occurring selenium is coal, particularly coal seams in the eastern United States. Although selenium speciation can vary based on coal type and source, it is typically found in its oxidized states including selenite ($SeO_3$) and selenate ($SeO_4$). Selenite removal via ferric coprecipitation is a well-established process with proven performance at large scale. Selenate removal is more difficult to achieve at scale, with treatment options historically limited to some form of biological system.

Biological systems can effectively reduce both selenite and selenate to elemental selenium, however, several concerns render biological systems difficult to operate. Microorganisms responsible for selenium reduction are highly sensitive to operating conditions including temperature, total dissolved solids, flow and selenium mass load. Abrupt changes in any of these parameters can affect performance. Consequently, biological systems are not suited for operations that require intermittent treatment with rapid start-up and shutdown. Additional risk factors associated with biological systems include reliance on dilution to meet water quality requirements in the receiving environment, release of nutrients into the receiving environment leading to potential algae blooms, production of organo-selenium compounds that bioaccumulate in aquatic organisms at a much quicker rate, and concerns about the long-term stability of selenium in treatment residues.

To mitigate the inherent issues and shortcomings of biological systems, non-biological technologies have seen increased research and development over the last decade. One such process is Selen-IX™, the first non-biological selenate removal system applied on a large scale with three facilities designed and commissioned between 2020 and 2022. While the technology was originally developed for the mining industry, typical project settings and requirements associated with ash pond clean-up makes Selen-IX™ suitable for selenium control in this sector.

Project requirements that inhibit biological systems from being an appropriate choice for coal ash pond remediation that allows non-biological processes to be suitable include:

1. Operate intermittently with rapid startup/shutdown
2. Continuously achieve discharge limits <1 µg/L at end of pipe
3. Maintain performance during large fluctuations in water temperature, flow and mass loading
4. Reduce future liabilities by removing selenium as a stable residue suitable for disposal offsite in a regular non-hazardous landfill
5. Direct discharge to the receiving environment with no dilution
6. Selected process must also:
    a. Avoid effluent toxicity through transformation of selenium into organo-selenium and their associated increased chronic toxicity effects
    b. Avoid effluent increase in nutrients, COD/BOD, which can cause toxicity issues in the receiving environment

## PROJECT BACKGROUND

Coal ash generated from a coal fired power plant is being stored in a pond where water quality indicates elevated levels of heavy metals and the selenate form of selenium. The pond is undergoing remediation involving dewatering and relocation of coal ash to an engineered facility. Water from the pond is treated for heavy metals and selenium prior to discharge to the environment. Key process design criteria for the water treatment plant includes:

- Intermittent operation Mon-Fri, 10 hours per day
- Variable plant feed flow rate up to 450 $m^3$/hr (2,000 gpm)
- Variable feed selenium concentration, up to 150 µg/L
- Selenium discharge limit of less than 6.5 µg/L

Ultimately, the need to run the treatment system intermittently was pivotal in the selection of a non-biological system for selenate removal.

## PROJECT TEAM

WesTech Engineering responded to a request for proposal from the owner of the coal ash pond. With their experience in treating wastewater in the mining and power industries, they had the expertise to design an advanced metals removal circuit employing sulphide and ferric precipitation but not one that could remove selenate. Owing to the project criteria of intermittent operation, the incumbent biological technology was dismissed and WesTech reached out to BQE Water about their non-biological Selen-IX™ process. The team of WesTech and BQE Water won the bid for the project and worked together to design, procure, construct, commission and operate the coal ash pond water treatment facility.

## TREATMENT PROCESS DESCRIPTION

The illustration in Figure 1 provides an overview of the process deployed to treat coal ash pond water before discharge to environment. Chemical precipitation and Selen-IX™ are applied for selenite and selenate removal, respectively.

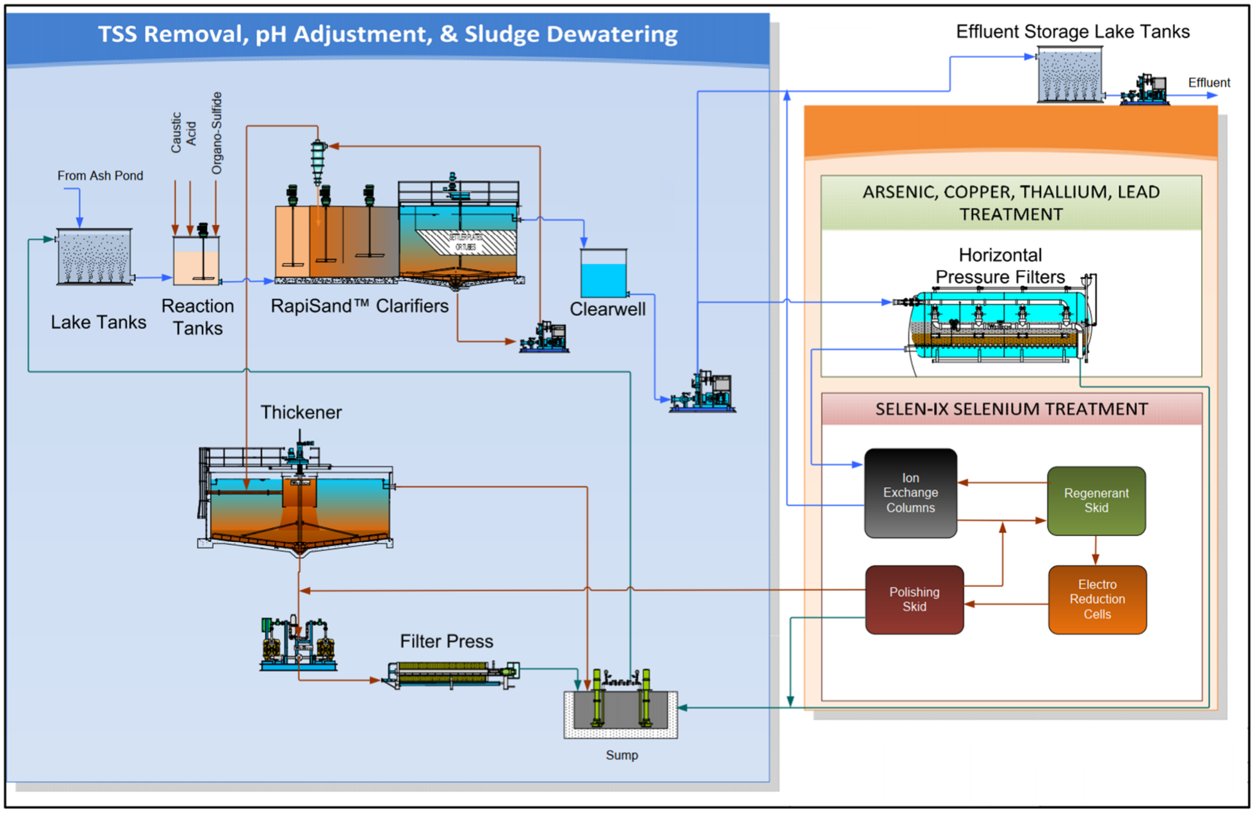


Figure 1: Treatment Process Overview

## Feed & Discharge System

Five 1 million gallon aerated lake tanks are used in the system, with one designated for feed, three for discharge and one swing tank that can be used for either feed or discharge. With an average treatment rate of 340 $m^3/h$ (1,500 gpm), 3,800 $m^3$ (1 million gallons) of effluent is produced within each 10-hour operating day. Inclusion of the lake tanks enables: 1) flow equalization to maintain steady state operation and 2) precise monitoring of composite feed and discharge water qualities to ensure all parameters meet effluent concentration limits prior to discharge into the local watershed.

## Reaction Tanks

The first step in the treatment process is pH adjustment and chemical precipitation. Organo-sulphide and ferric chloride are dosed to target heavy metals and oxyanions (arsenic and selenite) respectively.

## Rapisand™ Clarifiers

Total suspended solids from ash pond water and chemical precipitation are removed in the Rapisand™ clarifiers. Coagulant, flocculant and microsand are mixed in a series of tanks to remove suspended solids and form dense ballasted flocs. The microsand has a specific gravity of 2.6 which allows the ballasted flocs to settle at rates much faster than conventional clarification processes. A mixture of settled solids and microsand are pumped from the bottom of the clarifier to a hydrocyclone where microsand is recovered and recycled in the process; solids overflowing from the hydrocyclone are thickened and dewatered in a filter press.

Horizontal Pressure Filter
Fine suspended solids in the clarifier supernatant are captured in horizontal pressure filters and backwashed to the sump before its subsequent transfer into the feed tank. This allows the solids to be iteratively cycled in the plant; eventually, solids land in the clarifier underflow stream and are directed to the thickener and filter press for dewatering. Filtrate from the horizontal pressure filters reports to the Selen-IX™ circuit.

Selen-IX™ Process
Figure 2 presents a high-level block flow diagram of the Selen-IX™ process. The process consists of two treatment circuits: ion exchange and electroreduction.

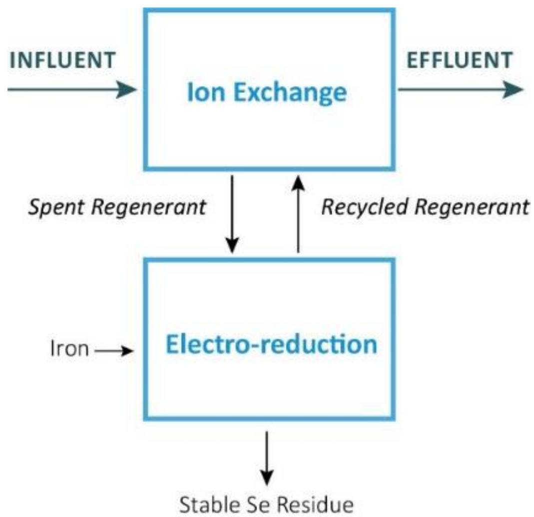


Figure 1: Selen-IX™ Block Flow Diagram

Ion Exchange
Selenate is selectively removed from influent and loaded onto ion exchange resins, continuously producing effluent with residual selenium content of less than 2 µg/L. The resins are periodically regenerated with a small volume of sodium sulphate brine solution to elute selenate from the resin and restore exchange capacity. The selenium laden brine solution undergoes additional treatment in the electroreduction circuit.

Electroreduction
The selenium laden brine is recirculated through an electrocell system to reduce selenate and fix it into a stable iron-selenium residue. Solids are separated from the brine solution by conventional clarification and filter press. After solid-liquid separation, the brine solution is again available to the ion exchange circuit for the next regeneration cycle, leading to a zero liquid discharge process. Analysis of the iron-selenium solids by x-ray diffraction (XRD) and toxicity characteristic leaching procedure (TCLP) have verified the solids to be highly stable.

Due to the high variability of selenium concentrations in the feed solution, Selen-IX™ is brought online only when selenate treatment is required and can be running at full capacity within minutes of an elevated selenate measurement in the feed water. The ion exchange system applies a lead-lag-standby configuration arranged in two independent trains (columns train A & B); the lead and lag vessels operate and actively remove selenate from water whereas the standby column undergoes regeneration and remains offline until the load cycle ends. When the load cycle ends, the lead columns come offline for regeneration, the lag columns move into the lead position and the standby columns move into the lag position. Each vessel is outfitted with automatic valves to enable complete automation of the load and regeneration sequences with minimal operator intervention. Continuous treatment rates are maintained as vessels change positions seamlessly within their sequence.

Each regeneration sequence produces a volume of spent regenerant that needs to be treated in the electroreduction circuit. The electroreduction system treats the spent regenerant volume in several smaller batches. Like ion exchange, electroreduction is completely automated and batches run perpetually with minimal operator intervention. Over the duration of treatment, the spent regenerant tank is depleted and the recycled regenerant tank is replenished. Sodium sulphate is added to the recycled regenerant to make up for any salt losses during processing.

## OPERATING DATA

Selen-IX™ operating results since the plant start-up is summarized in Figures 3 to 6. Figure 3 shows influent and effluent selenate concentrations during a single load cycle, ie loading with feed solution, but not having undergone any regenerations.

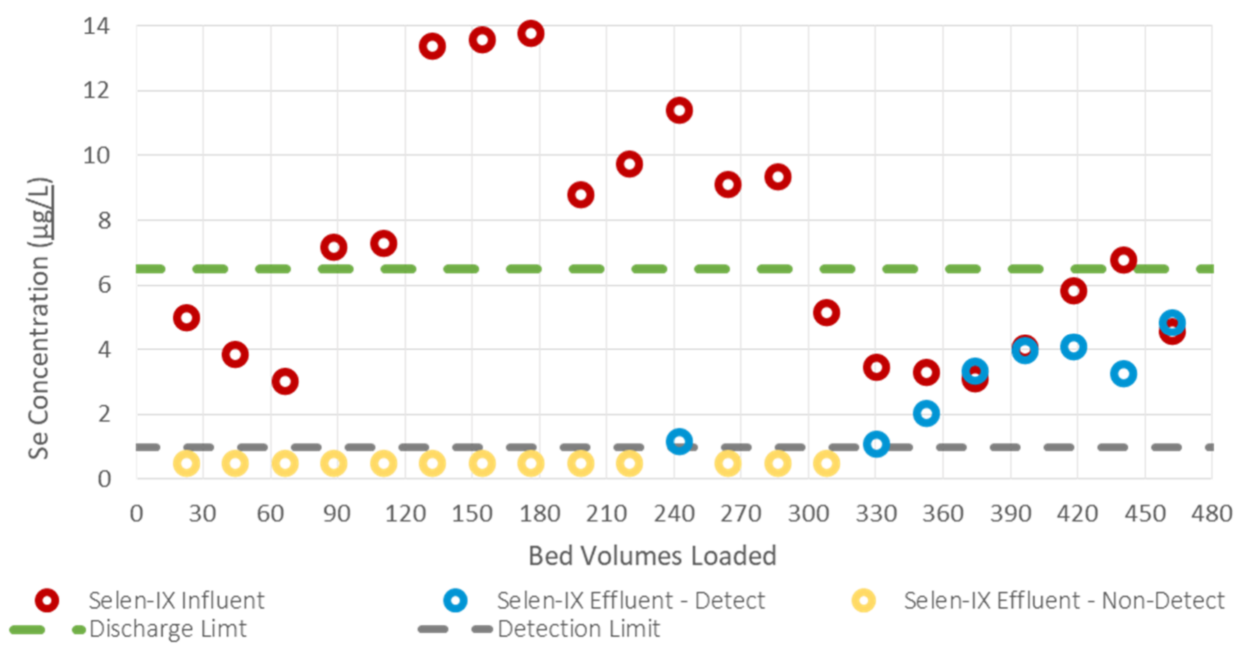


Figure 3: Selen-IX™ Load Performance

The data points are from two months of intermittent operation, where the maximum operating time on any given day was less than 10 hours. The data illustrates that the system can consistently achieve effluent selenate concentrations below the detection limit value of 1 µg/L despite fluctuations in influent selenate levels. After 300 bed volumes, the resin approaches saturation as indicated by the convergence of influent and effluent selenate. When this occurs, the vessels switch positions (lead to regeneration; lag to lead; standby to lag) to begin a new load cycle and the new standby columns undergo regeneration.

Figures 4 and 5 show the selenate elution curve during the regeneration of two ion exchange vessels (A2 and B2). Both curves are similar in terms of peak selenate concentration and total number of regenerant bed volumes required to restore ion exchange capacity.

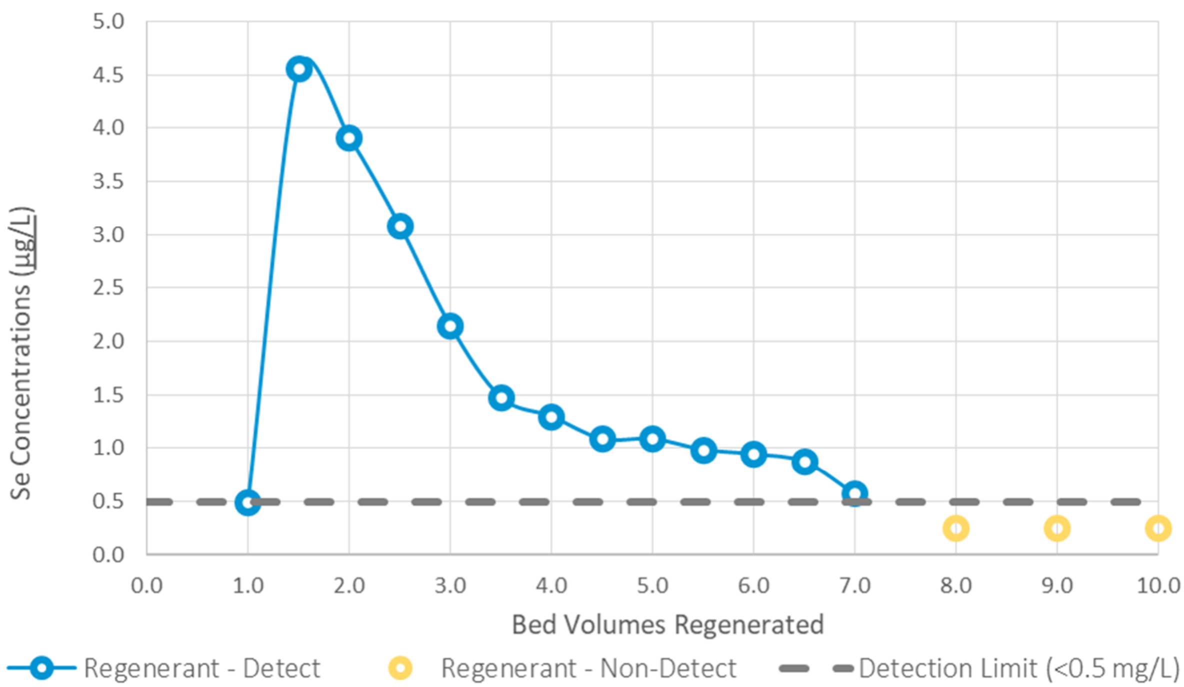


Figure 4: Selen-IX™ Regeneration Performance – Column A2

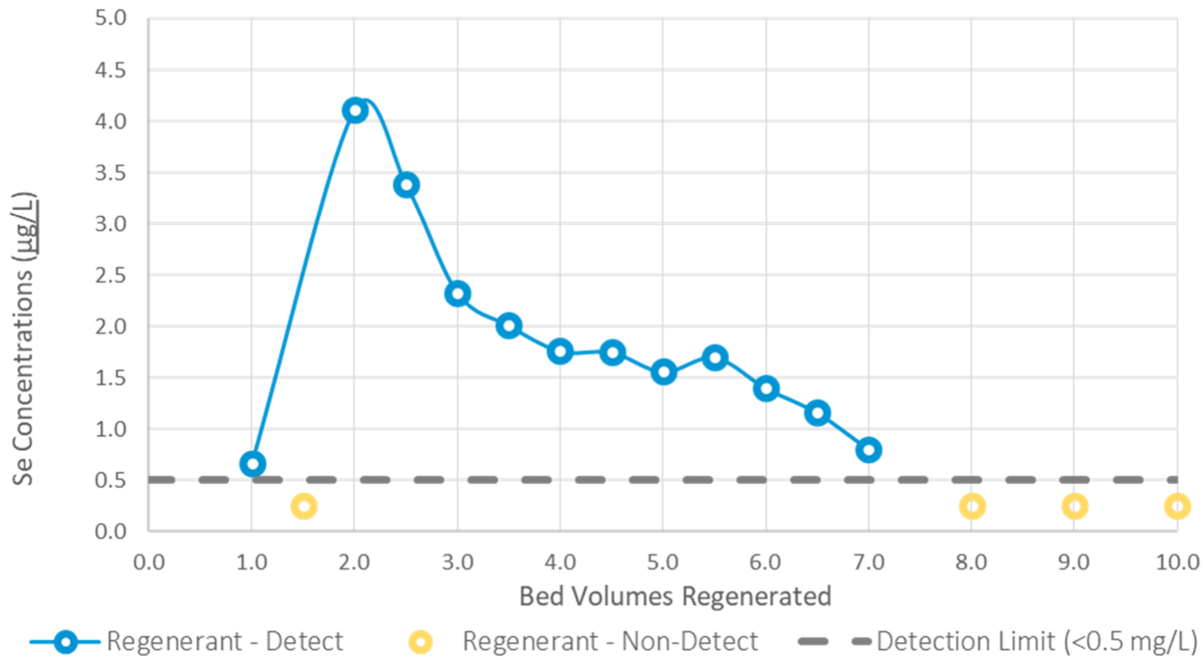


Figure 5: Selen-IX™ Regeneration Performance – Column B2

The first bed volume of regeneration displaces the residual water within the column with regenerant and is sent to the sump – no selenate is eluted in this first bed volume, as the solution exiting the column is simply displaced effluent. Selenate begins to elute once the regenerant phase passes through the resin bed. Elution is complete when the selenium concentration reaches a plateau. The last three bed volumes represent the wash step, where residual regenerant in the vessel is displaced with wash water. The initial bed volume of wash is regained within the regenerant system, while the remainder is sent to the sump. As with the first bed volume, little to no selenate is eluted during the last three bed volumes. Regardless of the wash water quality, the bed volumes sent to the sump are returned to the feed tank to be retreated in the Selen-IX™ process, indicating a high system water recovery rate of ~99%.

Figure 6 shows selenate reduction in the electroreduction circuit and includes data from three consecutive batches. It reveals the kinetics of selenate removal to be consistent and repeatable across all batches.

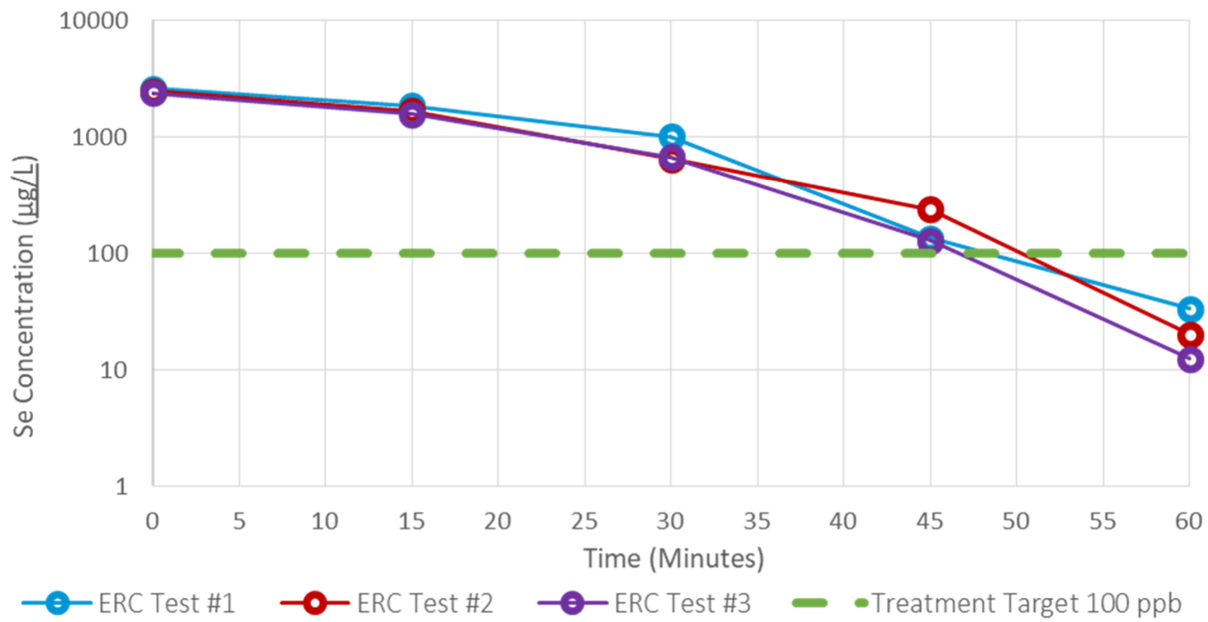


Figure 6: Selen-IX™ Electroreduction Performance

Approximately 50 minutes of operating time is required per batch to achieve the selenate removal target of 100 µg/L. Use of the log y-axis shows that selenate removal follows first order kinetics, where the removal rate is initially fast and then slows down over time. From this, the required operating time per batch can be calculated from the initial selenate concentration.

## CONCLUSIONS

The Selen-IX™ selenate removal system commissioned in 2022 for coal ash pond clean-up is still new with limited operations due to factors beyond the control of the plant, namely the lack of feed water system. However, initial operating data verifies the efficacy of the process to meet design expectations. Additional operating data and experience from this site will help to further establish Selen-IX™ as a viable alternative to biological systems for selenate management.

## REFERENCES

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