WATER TREATMENT TECHNOLOGIES FOR ULTRA-LOW DISCHARGE REQUIREMENTS

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Ion exchange, wastewater treatment, sulphide precipitation, metal recovery, ultra-low discharge, heavy metals, acid mine drainage.

ABSTRACT

Regulations around the world are tightening for substances present in mine impacted waters. In Canada a review of the Metal Mining Effluent Regulations (MMER) is being undertaken to make more stringent effluent limits and the addition of harmful and potentially toxic substances such as selenium. Alkali precipitation of dissolved metals has been used to meet mine water effluent limits, but it is unclear if this process can reliably meet the changes being proposed. Sulphide precipitation and ion exchange technologies have been applied successfully at mine sites to remove dissolved metal concentrations to ppb and sub ppb levels to meet ultra-low discharge requirements. Additionally, these technologies generate revenues by recovering the dissolved metals as a saleable product and reduce/eliminate waste sludge and the associated long-term costs. This paper profiles these technologies, providing case studies of commercial application for metals removal and pilot testing results for Se removal in mine affected waters.

INTRODUCTION

Recent mining discharge permits and a discussion paper by Environment Canada proposing stricter Metal Mining Effluent Regulations (MMER) requiring mining companies to meet ultra-low discharge limits are fast becoming pressing issues. Site specific discharge criteria for various mining projects in Canada have required even tighter limits than those being proposed by the MMER review. The MMER proposal also includes the addition of new targets to the list of deleterious substances being regulated.

Discharge limits for substances from countries such as the US, Chile and South Africa have been found in many cases to be stricter than the MMER limits. Table 1 presents a comparison of commonly regulated substances including the current and proposed MMER discharge requirements, as well as the most stringent international and Canadian limits [1].

Table 1: Discharge Limits for Cu, Ni and Se

Deleterious Substance	Current MMER Limit	Most Stringent Int'l Limit	Most Stringent Canadian Limit	Proposed New MMER Limit
Cadmium (mg/L)	None	0.001 (Ecuador)	0.00012 (CCME)	No Change
Copper (mg/L)	0.3	0.02 (South Africa)	0.05 (BC)	0.05
Nickel (mg/L)	0.5	0.1 (US)	0.2 (BC)	0.25
Selenium (mg/L)	None	0.0045 (US)	0.001 (CCME)	Tbd

In addition to the new stricter MMER discharge limits, the proposed MMER changes include new additions to the list of deleterious substances such as selenium, although there is no proposed limit at this time [1]. Selenium (Se) is a naturally occurring mineral essential for all life in trace amounts but can be harmful in elevated concentrations. Its presence in mine impacted waters from coal and base metal projects stems from waste rock run-off, pit dewatering and tailings ponds. Feed streams containing Se typically have low concentration levels below 1 ppm and are often associated with high concentrations of other constituents such as SO_4 or NO_3. These streams often have multiple points of both natural flow paths and discharge points, making it difficult and costly to collect and direct the high flows to a central treatment facility. An additional challenge for Se treatment is that the majority of Se in mine waters is present as selenate or Se (VI) as opposed to selenite or Se (IV). Due to the differences in oxidation states, they behave differently with Se (IV) responding well to conventional treatment methods while Se (VI) does not.

To meet the tightening regulatory environment, mining companies need to look to new wastewater treatment technologies such as sulphide precipitation and ion exchange (IX). Mining effluent containing high concentrations of dissolved metals can be effectively treated with sulphide precipitation to reduce metal loadings down to ppb and sub-ppb levels. The low solubility of metal sulphide solids supports the removal of dissolved metals to lower concentrations than can be achieved with alkali precipitation. While sulphide precipitation can be equally effective in treating streams with very low metal concentrations, doing so could increase the size and cost of the plant. High flows of waste streams with very low concentrations of substances targeted for removal can be more cost-effectively treated with IX. In the case of Se (VI) and Se (IV), IX also provides a potential solution to overcome the limitations of current conventional Se treatment options.

TREATMENT TECHNOLOGIES

Non-Selective Technologies

Alkali Precipitation. A conventional treatment method for metal laden mine waters is alkali precipitation, which is a proven technology that uses a neutralization agent such as lime/limestone to remove all metals in the water as a combined metal hydroxide sludge [2]. The relatively high solubility value of certain metal hydroxides prevents the achievement of the proposed MMER limits over a wide range of pH. Given that pH is the only degree of freedom available and different metals reach their minimum solubility at different pH, alkali precipitation is not effective to meet the stricter discharge requirements in cases where several metals have to meet ultra-low discharge limits at the same time. Another disadvantage is the generation of large quantities of waste sludge requiring long-term management to ensure the metals do not remobilize and enter the environment.

Although alkali precipitation can be very effective for treating feed water with large loads of Fe and Al, another limitation of the process is that it cannot effectively deal with oxo-anions such as Se (VI), As (V) or Mo (VI). Although As and Mo can be removed by ferric co-precipitation, excess reagents are often required to reach low discharge limits which results in an increase in the amount of waste sludge produced. In the case of Se (VI), the anions simply pass through the system. Alkali precipitation has been found to remove less than 40% of Se (VI) [3].

Biological Reduction. Using Biological Reduction to treat Se waters is effective but it is not cost effective for large flows of cold water in remote locations. Microbial activity is sensitive to temperatures and these large flows of cold water would need to be heated for treatment to be effective. Heating this volume of water could pose logistical challenges and ultimately, prove uneconomic. Biological Reduction also increases Biological Oxidation Demand (BOD) in the treated water to the extent that BOD limits will be exceeded, necessitating further treatment before the treated water can be discharged into the receiving environment. The by-product of this process is a large volume of biomass requiring disposal. This biomass is made up of mostly water and is therefore difficult to dewater but more concerning is that the biomass is unstable and is not suited for long-term storage. Industry also has its hesitations surrounding this system as a fail proof method of treatment.

Membranes. Membrane diffusion has its merits and can meet strict discharge regulations, but it is not selective for Se or any substances. The process also generates large volumes of liquid brine waste requiring disposal. If no storage is available for the brine, an evaporator crystallizer system would be necessary. And depending on the water chemistry, the presence of certain species such as iron, aluminum, barium and silica would require pre-treatment to mitigate membrane scaling and fouling. Membranes are best suited to treat water containing multiple substances at very dilute concentrations. For acid mine drainage, membranes are best used as a final polishing step in combination with other treatment technologies.

Selective Technologies

Sulphide Precipitation. New technologies are available and have demonstrated success for removing substances from wastewater to comply with both the MMER limits and even stricter site specific discharge requirements. ChemSulphide® and BioSulphide® are commercial technologies that use a sulphide source to selectively precipitate dissolved metals as metal sulphides. The low solubility of metal sulphide solids allows sulphide precipitation technology to reach lower discharge limits than alkali treatment [4].

Figure 1 illustrates the sulphide and hydroxide solubility curves for selected metals against pH. The data was generated by PHREEQC and is based on the solubility of metal sulphides and hydroxides as pure precipitates in pure water at 25°C and pH adjusted by either H_2SO_4 or NaOH. As can be seen on the graph, sulphide precipitation provides a much lower discharge result than hydroxide precipitation. Additionally, the sulphide solubility values demonstrate a greater pH range whereby the discharge limit can be met.

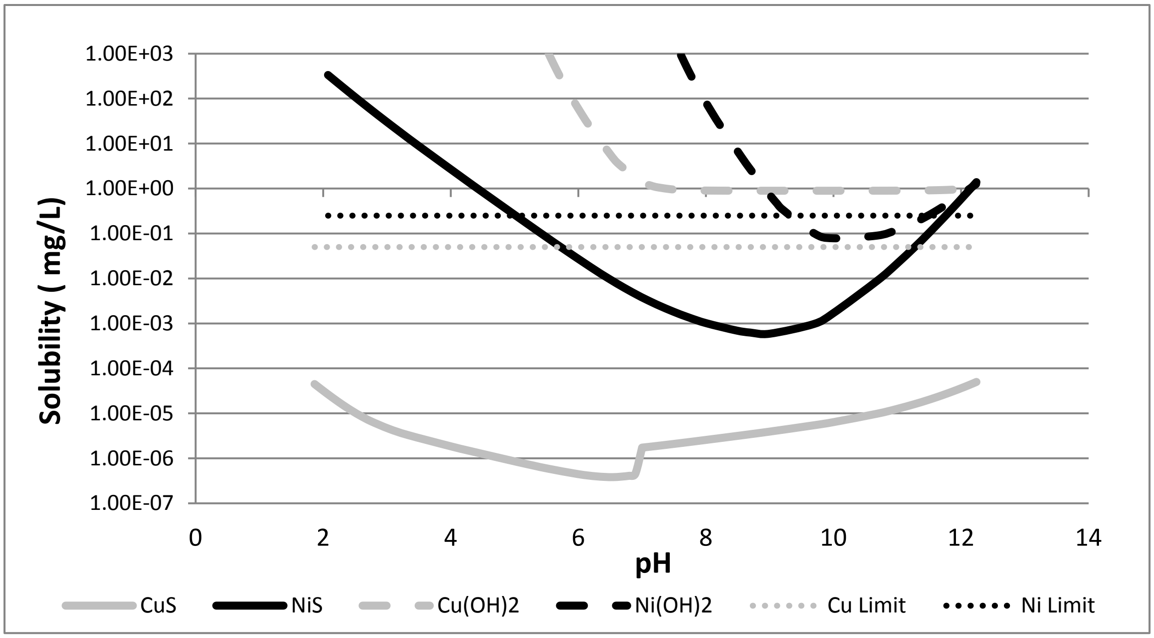

Figure 1. Sulphide and Hydroxide Solubility Curves for Cu and Ni

In addition to meeting the required discharge limits, sulphide precipitation technologies reduce or eliminate the production of waste sludge and any associated liabilities with long-term management. Another benefit is the ability to selectively recover the metals in a form that can be sold to generate revenues that can offset treatment costs.

<u>Ion Exchange</u>. Another commercially available technology suitable for addressing ultra-low discharge requirements is Met-IX™ which uses resins to selectively load the targeted substances. When the resins are fully exhausted, the target substances are stripped off with a reagent, often using low-cost reagents, into a small volume, highly concentrated stream that can be directed to sulphide precipitation to produce a valuable product. With its ability to integrate with sulphide precipitation and existing system infrastructure, Met-IX™ can also be deployed as a mobile and fixed facility option to increase the hydraulic treatment capacity of existing fixed facilities.

Specific for selenium removal and Se (VI), Selen-IX™ has been developed. The technology removes selenium using IX to meet ultra-low discharge requirements. When the resin is at capacity for selenium uptake, the selenium is removed from the resin by washing with a regenerant solution that is free of selenium to produce a selenite rich regenerant stream. The spent regenerant is further treated by physico-chemical reduction of selenate and is then recycled to the IX process, allowing for a significant reduction in operating costs and eliminates liquid waste. The Selen-IX™ process is robust as neither sulphate presence in the feed or the water chemistry itself has any notable impact on the treatment results. Finally, IX technology for selenium removes Se from both hard rock and coal impacted mine waters.

<u>Technology Comparison</u>

Comparisons of the technologies outlined are presented in Table 2. Sulphide precipitation and ion exchange provide several benefits such as complying with ultra-low effluent discharge limits, revenue generation, and reducing or eliminating waste sludge over non-selective technologies. The benefit of alkali precipitation is its effectiveness with large loads of Fe, Al and MN. Biological reduction is not effective with cold feed water while membrane technology is not selective for specific ions and creates large waste streams requiring further processing.

Table 2. Technology Comparison

	Alkali Precipitation	Biological Reduction**	Membranes	Sulphide Precipitation	Ion Exchange
Compliance with effluent discharge limits	Limited	✓**	✓	✓	✓
Selectivity for target substances	No	No	No	✓	✓
Revenue generation*	No	No	No	✓	✓
Reduce/eliminate waste sludge/brine	No	✓	No	✓	✓
Transportable option	No	No	✓	✓	✓
Integrate with existing systems	No	No	✓	✓	✓
Effective with large loads of Fe/Al/MN	✓	No	No	No	No
Capacity to deal with oxo-anions (Se, Mo, As)	Limited	Limited	✓	Limited	Selective

*Applies to substances targeted for recovery due to their potential market value.
**Applies to select ions.

In some cases a combination of these technologies may be required to meet the discharge targets. With the capacity to meet ultra-low discharge requirements and be integrated into existing process flows, sulphide precipitation and IX technologies have the potential to play a bigger role in the future as regulators tighten discharge limits around the world. Tightening regulations will force mining companies to seek out innovative and cost-effective tools, especially when faced with new regulations where conventional treatment technologies are ineffective.

CASE STUDIES

Case Study 1: Copper Discharge

This Yukon based open pit copper mine has strict site specific copper discharge requirements that must be complied with for their water use license. Pit water containing dissolved copper is the targeted substance for removal to meet ultra-low discharge requirements. ChemSulphide® technology was selected and in 2010 a full-scale treatment facility designed to treat 4,000 m^3/day was built and commissioned, in combination with conventional water treatment processes, to reduce copper concentration levels. Target requirements and average parameters for feed and treatment results are provided in Table 3.

Table 3. Copper Mine Feed, Target and Results

Parameter	Feed	Effluent Target	Actual Results
pH	8.0	6.5 to 9.0	7
Copper	0.05 to 0.25 mg/L	< 10 ppb	< 10 ppb

The plant is comprised of three stages as shown in Figure 3. First, the sulphide source is injected into the feed line where it is mixed and precipitates the copper which settles in a lamella clarifier. Second, the overflow reports to a polishing stage before undergoing the third for pH adjustment prior to the final discharge to the environment.

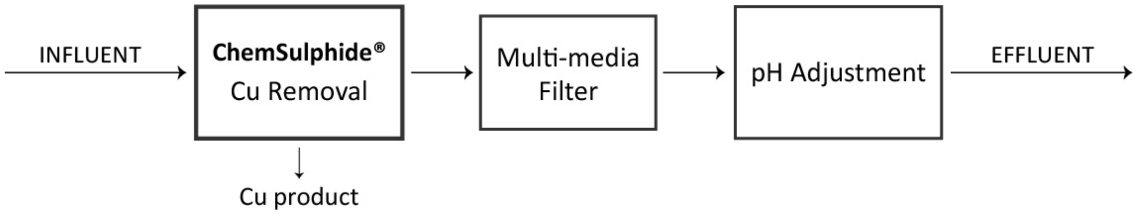

Figure 2. Water Treatment Process Flow

The plant is consistently able to meet discharge requirements despite the variations in the copper concentrations in the feed. Figure 2 illustrates the fluctuations in copper levels in the feed and treated water.

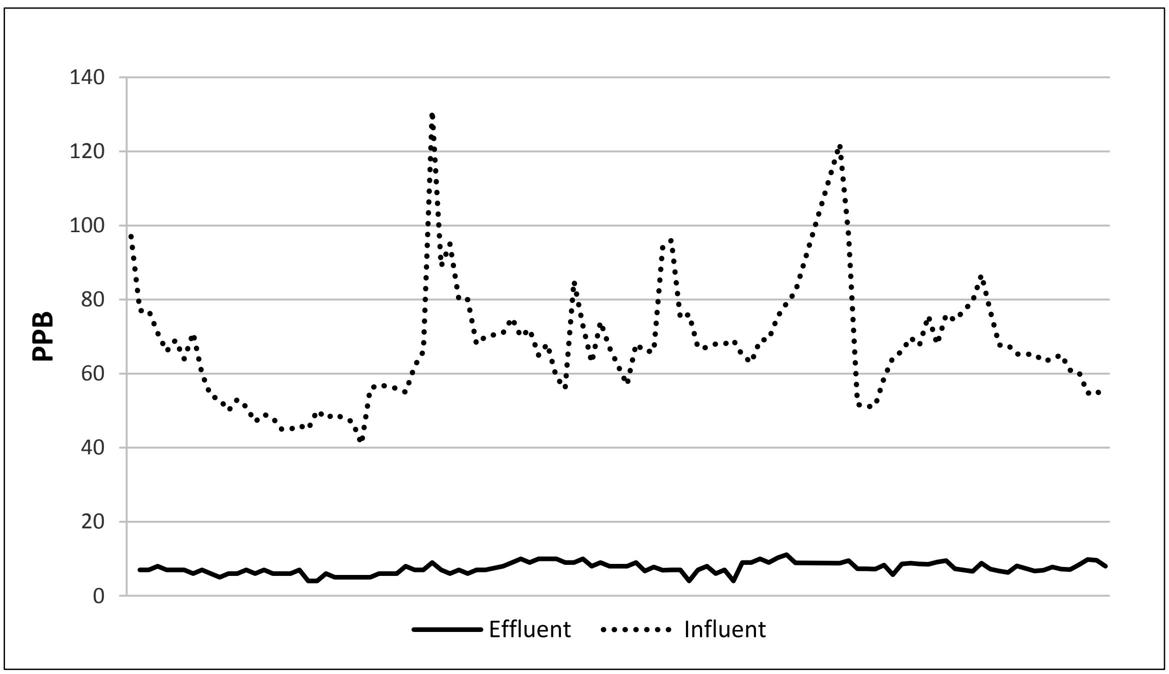

Figure 3. Influent and Effluent Copper Concentrations

Case Study 2: Nickel Discharge

This mine in Northern Quebec, Canada is an active nickel mine with seasonal water treatment needs. The plant feed source comes from surface water drainage and the treated water is discharged to the pristine northern environment. The project objective is to comply with strict water quality regulations for pH, nickel and TSS. Target requirements and average parameters are displayed in Table 4. It is also worthwhile to note that the ChemSulphide® process eliminated waste sludge and disposal requirements.

Table 4. Nickel Mine Feed, Target and Results

Parameter	Feed	Effluent Targets	Actual Results
pH	6.4 to 8.0	6.0 to 9.5	7 to 8
Nickel	13 to 30 mg/L	0.50 mg/L	<0.25 mg/L
TSS	Variable	15 mg/L	< 1 mg/L

ChemSulphide® technology was selected in 2003 to replace an existing low density sludge (LDS) lime plant due to treatment challenges posed by the technology and the short treatment season. Unlike alkali precipitation, sulphide precipitation can operate in cold environments which extends the available treatment season. Additionally, the plant availability and treatment capacity increased with the ChemSulphide® plant because it eliminated the need to stop operation to allow for settling, which was a significant issue with the alkali plant.

A Met-IX™ unit was added several years after the construction of the ChemSulphide® plant as a means to increase the site's treatment capacity without requiring the deployment of a new full-scale plant which is costly on remote sites. Rather, the Met-IX™ mobile plant is housed in a standard 53 foot trailer and was shipped to site. As shown in Figure 4, both plants run in parallel and can discharge to the environment independent of one another. However, the IX plant is integrated with the ChemSulphide® plant because once the IX resin is loaded, the small amount of regenerant containing a high concentration of nickel is directed to the ChemSulphide® plant to process and recover the dissolved nickel. The ChemSulphide® and Met-IX™ plants are designed to treat 6,500 m^3 and 4,000 m^3 of wastewater per day respectively.

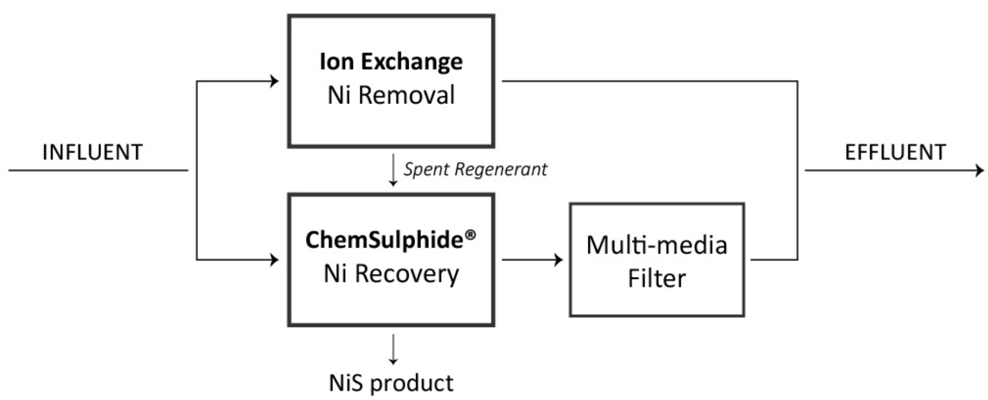

Figure 4. Water Treatment Process Flow

Figure 5 shows the actual results from the 2012 treatment season for both plants. The ChemSulphide® and Met-IX™ plants consistently discharged water containing less than 0.25 ppm nickel, half of the site discharge requirements. They achieved these results regardless of the feed concentration or water temperature which can reach as low as 0.3 °C.

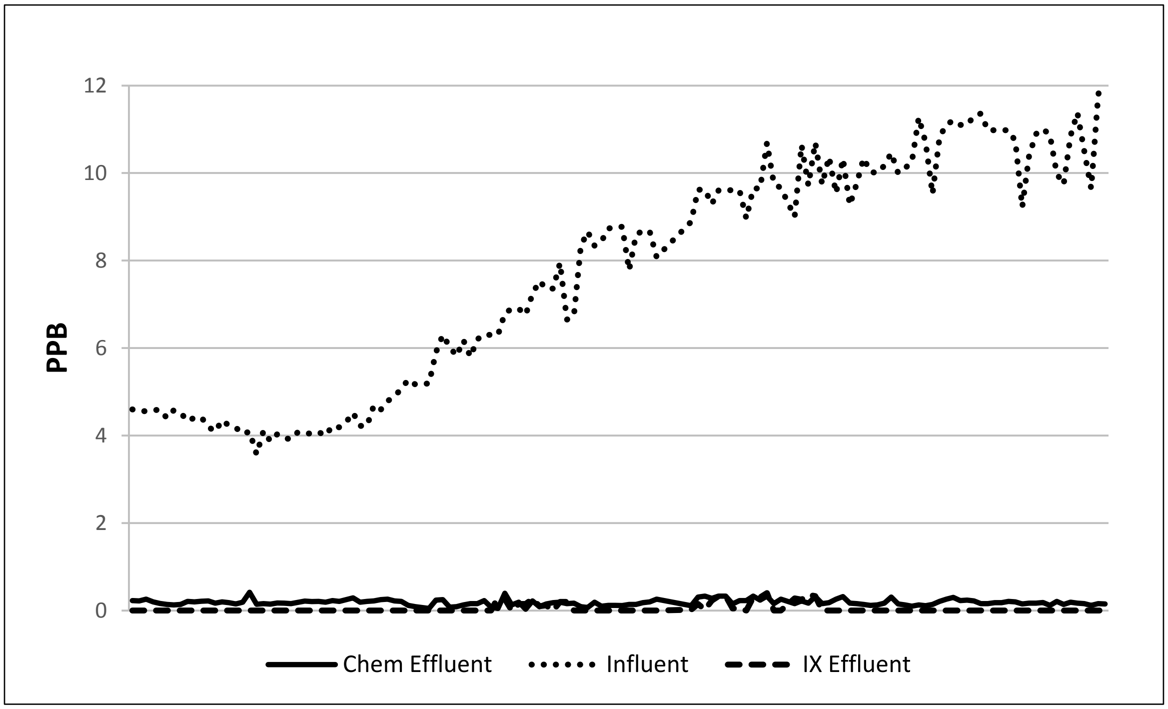

Figure 5. Influent and Effluent Nickel Concentrations

Case Study 3: Selenium Discharge

This BC based coal mine is investigating technologies for strict selenium discharge. The Selen-IX™ process for selenium removal was selected for on-site field testing after successful laboratory work demonstrated the capacity of Selen-IX™ to remove selenium and confirmed the potential for low operating costs.

The process employs a novel physico-chemical step which reduced virtually all selenate from the regenerant stream, converting selenate to elemental Se and selenite, which can be precipitated downstream. The process recycles all of the regenerant effectively eliminating liquid waste. The only product from the Selen-IX™ process is a small quantity of stable Se solid product.

Table 5. Selenium Average Lab Results

Parameter	Feed	Effluent Target	Average Actual Results
Selenium (VI)	>0.500 mg/L	0.005 mg/L	< 0.005 mg/L

The proposed process for the pilot is shown in Figure 6. It includes selenate removal using IX then reduction of the Se (VI) to elemental Se using a physic-chemical step.

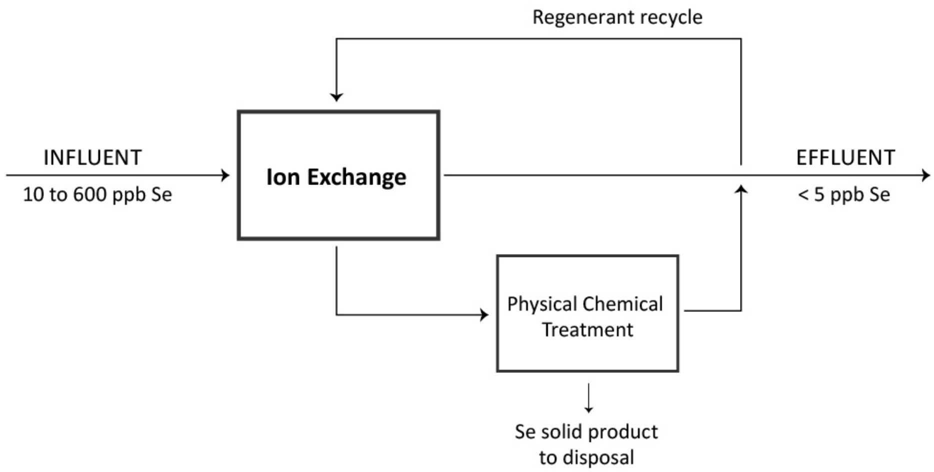

Figure 6. Selen-IX™ Process Schematic

The process selectively removes selenium regardless of water chemistry, meaning other constituents such as sulphate pass through the process without consuming power or reagents. IX is a non-biological approach that addresses industry concern with Biological Reduction as a Best Available Technology (BAT) solution.

CONCLUSION

New regulations for metals and other deleterious substances are tightening around the world. In some instances, site specific limits might be even more stringent than broad guidelines in order to protect local receiving environments. As concerns cloud the existing technologies commonly used to treat mine waters, sulphide precipitation and IX technologies are proven and innovative solutions that will play more important roles going forward to effectively and consistently meet ultra-low discharge requirements. These selective technologies can address metals, non-metals and oxo-anions while providing other benefits that include generating revenues from the recovery of dissolved metals as a saleable product, reducing or eliminating waste sludge and its associated long-term costs, plus lowering the life cycle costs for water treatment.

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