Mine water treatment options for meeting stringent selenium regulatory limits

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Abstract Selenium can be a constituent of concern in mine waters and is often present in neutral waters. Selenium is typically leached from waste rock piles as the selenate ion and mines can be faced with multiple, high-flow contaminated discharges. In recent years, biological treatment has emerged as an effective and relatively inexpensive method compared to physical and chemical methods. With some waters, biological treatment alone is sufficient to achieve stringent regulatory limits; however, in other cases, additional unit processes are required. Three treatment cases studies are included for treating moderate levels of influent selenium (50 – 500 µg/L).

Keywords selenium, biological, water treatment

Introduction

Biological selenium treatment is well-established with dozens of pilot studies and multiple full-scale plants. However, biological treatment is not always capable of meeting stringent regulatory limits (*i.e.* 5 µg/L) currently being promulgated in North America. For mines with influent selenium concentrations in the range of 50 µg/L – 500 µg/L, additional unit processes may be necessary. This concentration range is termed moderate as other industries (*i.e.* oil and gas, power, agriculture) can generate higher concentrations. Selenium is typically present as the oxidized inorganic selenate species in mine waters. A block flow schematic is provided in Fig. 1 for compliance with stringent limits.

Biological treatment relies on the microbial oxidation of organic carbon to reduce selenium and is subject to the preferential reduction of competing electron acceptors including oxygen and nitrate. During anaerobic biological treatment, selenium is reduced to particulate, elemental selenium and organic carbon is oxidized to carbon dioxide, as shown in Equation 1.

$$SeO_4^{2-} + 2\,CH_2O \rightarrow 2\,CO_2 + 2\,H_2O \qquad (1)$$

The process requires an electron donor, or substrate, which can be a variety of organic materials, including molasses, ethanol, or proprietary vendor products. The majority of the elemental selenium is retained within the microbial matrix and some can be released in the

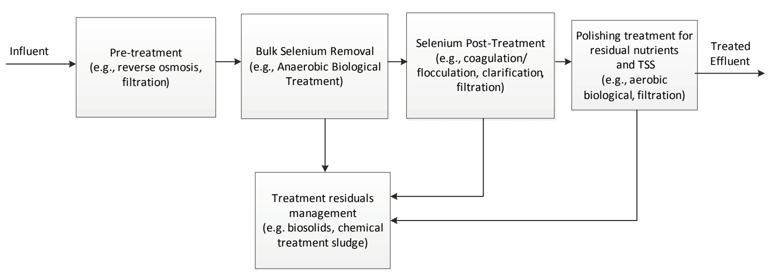

Fig. 1 *Block flow schematic for selenium treatment*

bioreactor effluent. Bulk removal of selenium has been demonstrated with passive and active treatment. Active treatment technologies include packed bed reactors and fluidized bed reactors. Regardless of the bioreactor configuration, the underlying microbial reactions and removal mechanism is the same. After biological treatment, care must be taken to prevent re-oxidation and mobilization of particulate selenium. Depending on project considerations, a solids separation polishing step may be necessary to remove particulate selenium which is not retained within the bioreactor.

Currently, it is believed selenium reduction is carried out by a group of organisms, called denitrifiers, which also reduce nitrate. Denitrifiers will not reduce selenium if oxygen and nitrate are present. Presence of alternative electron acceptors, such as oxygen and nitrate, can increase demand for the substrate. Sulfate reducing bacteria (SRB) can also compete for substrate during biological treatment. Sulfate is a less favorable electron acceptor than selenium, and generally will not be reduced until selenium is treated; however, if excess substrate is present, sulfate reduction can proceed. Sulfate reduction can result in the production of hydrogen sulfide gas, which is a health and safety concern. Thus, substrate addition must be balanced to promote selenium reduction, which may include oxygen and nitrate reduction, while limiting sulfate reduction. The biological treatment process produces biomass which must be periodically removed and disposed of. The solids production for a bioreactor can be expressed as a ratio of the amount of biomass produced to the amount of substrate, or chemical oxygen demand (COD), consumed. In a recent fluidized bed reactor pilot study, the observed yield was 20 g TSS/100 g of COD (Munirathinam 2011). Advantages of biological treatment for mining applications include the ability to function with high influent total dissolved solids concentrations (TDS), relatively small chemical requirement, and low sludge production as compared to chemical treatment. Disadvantages of biological treatment are pH and temperature dependence, a long start-up period (*i.e.* systems can also take several weeks to start-up and achieve full treatment capacity and cannot be shut down for extended periods without repeating the lengthy start-up process), and an aeration requirement to add dissolved oxygen prior to discharge.

Selenium post-treatment is required when biological removal is insufficient to achieve stringent regulatory limits. The goal of post-treatment is to reduce total selenium concentrations with conventional treatment processes that can remove particulate selenium that is not retained in the bioreactor. The following processes can be applied for selenium post-treatment:

- Coagulation/Flocculation – Coagulation is the process of inducing contacts between a chemical and colloidal particle to encourage a reaction to form microfloc particles. Flocculation is the process of encouraging contact between coagulated particles to form larger particles referred to as floc particles which settle more effectively.
- Clarification – Coagulation/flocculation can be followed by clarification to settle and collect precipitated solids.
- Filtration – Filtration can be employed, if necessary, to treat clarifier effluent for total selenium and TSS removal. Multimedia or media filtration, rather than membrane filtration, is preferred for cost purposes. Filtration testing is recommended for evaluation during pilot testing by testing with multiple pore size filters.

The processes may be combined depending on testing results. Proprietary sorption media may be an alternative to these conventional processes. Consideration of selenium oxidation and mobilization is important when designing post-treatment and polishing processes. If selenium post-treatment and nutrient/TSS polishing processes are both required, the post-treatment process will remove total selenium prior to aerobic treatment and mobilization of selenium should not be a concern. If bulk removal is sufficient to meet the selenium treatment goals and nutrient/TSS polishing is necessary, then the possibility of selenium mobilization in the aerobic treatment process should be considered. Three case studies are presented below for treatment of moderate selenium levels to stringent regulatory limits.

Golder Case Study 1 – Reverse Osmosis with Immobilized Cell Bioreactor Treatment

Golder designed and constructed an active treatment system that includes biological treatment to remove selenium at a closed mine site in South Dakota, U.S. The biological technology is the Immobilized Cell Bioreactor (ICB). The treatment system is designed to treat pH-neutral, waste rock leachate characterized by high TDS (approximately 5,000 to 15,000 mg/L), high hardness, and high sulfate concentrations. The average influent selenium concentrations are approximately 70 µg/L, the discharge limit is 4.6 µg/L, and the maximum design flow is 160 cubic meters per hour (m^3/h). Influent selenium is present as selenate. The process flow includes the following processes.

- Reverse Osmosis (RO) for TDS management and volume management during peak flows. The RO system includes influent water heating (including a boiler and heat exchanger), anti-scalant addition, and membrane cleaning; and,
- Active biological treatment to remove selenium from the RO reject stream. Treated biological effluent is recombined with RO permeate to meet the regulatory limit for TDS. Any excess bio-treated brine is discharged to the local municipal wastewater treatment system.

The biological treatment system achieves removal of selenium to residuals less than 10 µg/L and the regulatory limit is achieved by blending with the RO permeate prior to stream discharge. The combination of RO and a microbial reduction treatment system is beneficial because it meets stringent regulatory limit while allowing the installation of a treatment system with a large range of treatment capacity in a 0.4 ha treatment facility.

Golder Case Study #2 – Biological Treatment with Selenium Post-Treatment

Bench testing was conducted for a mine water with high levels of nitrate and selenium over the course of four months with the ICB technology in continuous flow reactors. Influent and effluent selenium and nitrate concentrations are provided in Table 1. The average total and dissolved selenium concentrations for influent were 179 and 177 µg/L, respectively. Influent selenium was present as selenate. The average total and dissolved effluent selenium concentrations were 41 µg/L and 24 µg/L, respectively. The lowest observed effluent concentrations were 19 µg/L total selenium and 16 µg/L dissolved selenium. A graph of selenium concentrations and a bench test photo are provided in Attachment 1. Effluent concen-

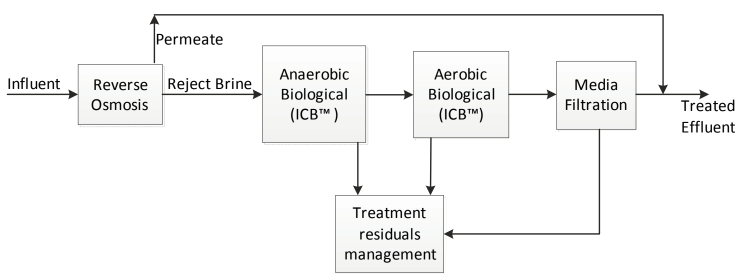

***Fig. 2** Block flow schematic for Case Study #1*

Description	Influent Se_{tot} (µg/L)	Biological Effluent Se_{tot} (µg/L)	Biological Treatment, Percent Removal	Influent $Se_{filtered}$ (µg/L)	Biological Effluent $Se_{filtered}$ (µg/L)	Biological Treatment, Percent Removal
Average	179	41.0	77%	177	24.5	86%
Minimum	NA	19.1	56%	NA	16.7	91%
Maximum	NA	78.6	89%	NA	36.1	80%

Table 1 *Bench testing results for biological treatment*

Iron Dose (mg/L)	Se_{tot}(µg/L)	$Se_{filtred}$ (µg/L)	% Removal
0	13.6	13.5	20.9
5	13.2	13.0	23.3
10	10.4	11.5	39.5
20	7.08	7.82	58.8
40	4.53	4.03	73.7
50	4.42	3.70	74.3

Table 2 *Bench testing results for iron co-precipitation*

trations for total selenium were consistently higher than dissolved concentrations, likely due to the presence of volatile and particulate selenium. Selenate was effectively reduced to less than 1.0 µg/L, but low levels of selenite and selenocyanate remained in the treated effluent. An average influent nitrate concentration of 168 mg/L as N was reduced to an average of 1.0 mg/L in the effluent. Iron co-precipitation was also tested as potential polishing treatment (Table 2). Iron co-precipitation results indicated a dose of 40 mg/L iron was able to reduce dissolved selenium to less than 5 µg/L in the effluent.

Note: Only average values are shown for influent concentrations since testing was conducted on one bulk sample and influent values did not vary. All values are dissolved values. Effluent total selenium was somewhat higher than effluent dissolved values.

Based on the bench testing outcome, the recommended block flow schematic to achieve an effluent concentration of 5 µg/L is provide in Fig. 3.

Golder Case Study #3 – Passive Biological Treatment

Passive biological treatment of selenium typically consists of a gravity flow reactor containing solid organic media. The organic media slowly degrades and provides a carbon source to sustain the microbial reduction of selenate to elemental selenium. Examples of successfully-implemented organic media include hay, wood chips, sawdust, rice straw (Pahler 2007; Zhang 2008). The media can also contain an alkalinity buffer such as limestone. This is a passive technology as it operates without electricity or continuous chemical inputs and does not generate continuous treatment residuals. BCR effluent can contain elevated levels of biochemical oxygen demand and may require a polishing step in order to comply with regulatory standards. BCRs are typically used to treat

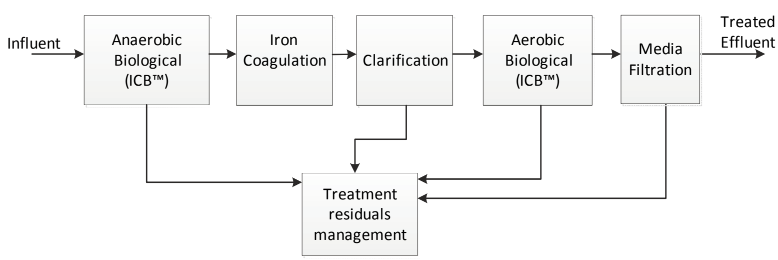

Fig. 3 *Block flow schematic for Case Study #2*

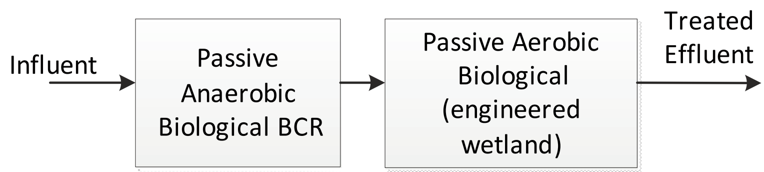

Fig. 4 *Block flow schematic for passive treatment*

Description	Influent Se_{tot} (μg/L)	Biological Effluent Se_{tot} (μg/L)	Biological Treatment, Percent Removal	Influent $Se_{filtered}$ (μg/L)	Biological Effluent $Se_{filtered}$ (μg/L)	Biological Treatment, Percent Removal
Average	22.3	1.0	94%	24.4	2.0	90%
Minimum	5.3	0.5	75%	5.9	0.4	46%
Maximum	41.6	1.5	98%	48.4	14.0	99%

Table 3 *Pilot testing results for passive BCR treatment – Test Condition 1*

Description	Influent Se_{tot} (μg/L)	Biological Effluent Se_{tot} (μg/L)	Biological Treatment, Percent Removal	Influent $Se_{filtered}$ (μg/L)	Biological Effluent $Se_{filtered}$ (μg/L)	Biological Treatment, Percent Removal
Average	68.5	8.5	87%	66.0	7.3	88%
Minimum	61.5	1.1	69%	58.1	1.5	69%
Maximum	79.5	18.9	98%	76.8	18.4	98%

Table 4 *Pilot testing results for passive BCR treatment – Test Condition 2*

contaminants that precipitate or are biologically removed under reducing conditions, such as metals, nitrate, and sulfate. Full-scale BCRs have been constructed in the US, Canada, Europe, and South Africa.

A pilot study was conducted with a single 124 m^3 pilot BCR to treat an average flow of 3 m^3/h. Influent was drawn from a dewatering trench in a gravel pit next to the Colorado River near Grand Junction, Colorado, US. The pilot operated, with varying detention times, over a thirteen-month period from September 2008 until October 2009. Influent selenium was predominantly present as the selenate species. Influent and effluent selenium concentrations are provided in Attachment 2. During the first eight months, influent selenium concentrations were less than 40 μg/L and effluent concentrations were less than 5 μg/L. This period is labeled Test Condition 1 in Attachment 2 and Table 3. During Test Condition 2 (Table 4), the influent source was altered to evaluate removal efficiencies with higher concentration water. With low influent selenium concentrations during Test Condition 1, effluent concentrations of total and dissolved selenium were below 5 μg/L. During Test Condition 2 with moderate influent concentrations, effluent total and dissolved concentrations averaged 8.5 and 7.3 μg/L, respectively. An additional unit process would be necessary under moderate influent concentrations to achieve the regulatory limit of 5 μg/L. The BCR treatment process was effective throughout the winter months with ambient temperatures below freezing and influent water temperatures below 10 degrees Celsius.

Conclusions

Treatment of moderate selenium concentrations in mine waters to meet stringent regulatory limits remains a technical challenge. Biological treatment methods are capable of bulk selenium removal but are not always capable of meetings stringent limits due to residual particulate or reduced selenium species in bioreactor effluent. In these circumstances, pre-treatment with reverse osmosis or selenium post-treatment are necessary. These processes have been demonstrated at full-scale but add significant complexity and cost. Removal efficiencies and effluent concentrations are similar for active and passive biological treatment processes.

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