

## Selenium Removal from Effluents in Industrial Mineral Processes

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**Abstract** Selenium is a trace mineral that can lead to contamination in mine related aqueous waste streams. Although selenium is essential for life and necessary for cellular function in many organisms, at elevated concentrations, the elemental forms and aqueous oxyanions of selenium are considered toxic. The most common forms of selenium released during mining processes are the aqueous forms, selenite and selenate. An innovative chemical technology that can successfully reduce selenium to a level below the permitted discharge criterion of 5 µg/L was developed. An evaluation of dosage and process limitations, such as temperature, filtration methods, and treatment dosage were explored on water obtained from a mine site in North America that processes industrial minerals.

**Keywords** selenium removal, effluents, water treatment

### Introduction

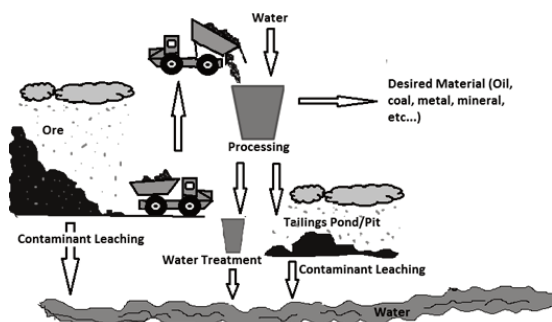
Selenium is a naturally occurring metalloid that is applied in global industries including electronics, vitamin and mineral supplements, plastics, fertilizers, anti-dandruff shampoos and many others. In small doses (0.1–0.5 mg/L), selenium is a micronutrient that is a part of everyday life for humans and animals, but it becomes toxic at higher levels (>3 mg/L dry weight). The National Primary Drinking Water Standard is 50 µg/L for selenium and the National Fresh Water Quality Standard is 5 µg/L for total selenium (EPA 2001; EPA 2011). In some regions, the selenium standards for discharge are even lower. In the US, there are several research groups and committees, who have presented evidence that the level should be as low as 2 µg/L. Examples of these groups include the California Environmental Protection Agency (CEPA), the State Water Resources Control Board Committee (SWRCBC), and the University of California Committee (UCC; Hamilton *et al.* 1999).

Selenium enters local ecosystems through a number of different methods. For instance, the release of selenium to aquatic systems is generally a result of weathering and anthropogenic activities, such as oil refining, coal

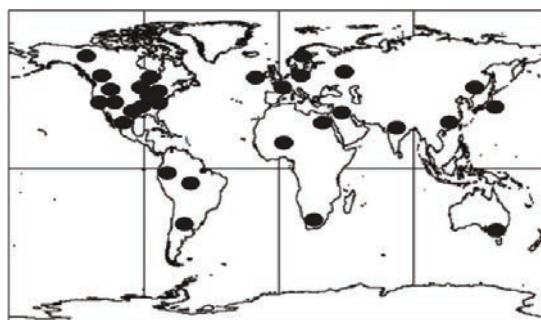
power production, and various mine-related activities (Presser and Luoma 2006). After weathering and oxidation occurs, soluble forms of selenium (selenite and selenate) are generated, thus can potentially contaminate the local water and soil sources. These mobile forms of selenium can bioaccumulate in some plants and animals causing various negative side effects such as selenosis, which is chronic selenium poisoning (Buck *et al.* 2002).

For that reason, selenium is a widespread problem in many wastewaters and a common contaminant in certain regions globally (US EPA 2012). Selenium is commonly found in mining effluents at concentrations that can reach 12,000 µg/L, in extreme cases (Leonard 2001). Because selenium chemically behaves very similarly to sulfur, mining operations where selenium contamination is prevalent are generally comprised of sulfide rich ores. These include copper, nickel, and uranium, as well as sphalerite and chalcopyrite, among others. Fig. 1 shows an example of a mining process demonstrating the potential sources where selenium can enter into aquatic systems.

Additional examples of mining activities where selenium contamination is an issue in-



**Fig. 1** Example of a mine site and possible routes for contamination.



**Fig. 2** Map providing various sites that reported high levels of selenium contamination (2004).

clude that of phosphate and coal. Fig. 2 shows a map of areas that have experienced issues related to increased selenium contamination. Industries depicted include coal mining/combustion, oil refining, phosphate mining, gold mining, silver mining, nickel mining, metal smelting, and landfill leachate (Moore *et al.* 2011). Selenium is often found in phosphate ore mining in overburden and mine runoff and oxidized forms of selenium are easily mobilized in runoff or infiltration water (Desborough *et al.* 1999). Globally, 158 million metric tons of phosphate rock was mined in 2009 and 17.2 % of that was mined in the United States (RMG 2012). In coal processing, effluents generated from leaching of coal combustion residues (CCRs) have high toxic element concentrations, including selenium. In the US, approximately six hundred power plants generate 130 million tons of CCRs annually, of which 56 % is stored in surface impoundments and landfills (Ruhl *et al.* 2012).

The common treatment technologies for removal of selenium from mine effluents to date can be summed up in three major categories: media filtration, chemical treatment, and biomediated removal. These methods often involve high capital and operational expenses that may also be limited by variables such as total dissolved solids, presence of other ions, and ability to maintain microbial health. The EPA listed selenium in at least 508 of the 1,636 sites reported on the National Pri-

orities List (ATSDR 2011). The focus of this work was to introduce a novel chemical treatment for reducing selenium concentrations to the National Fresh Water Quality Standard recommended by the US EPA.

### Results and Discussion

A 55 gal (208 L) drum of water was obtained from an industrial minerals processing site in North America. The water, which was contaminated with selenium due to naturally occurring mineral dissolution into a small stream that runs through the mine site, was shipped to and stored in a cooler at 1 °C prior to use. Water analysis was carried out as it is important to understand the other ions present in the water, as they can act as either competing ions (*e.g.* sulfate, nitrate) for the treatment or provide an alternative coordination possibility for the contaminant itself. The raw water (untreated effluent) comes from a naturally occurring spring and as such only exceeds the discharge permit with selenium. This water contained sulfate levels of 43.1 mg/L, calcium levels of 37 mg/L and a total dissolved solids (TDS) concentration at 410 mg/L, as shown in Table 1. This water also contained 69 µg/L of selenium which needed to be reduced to 5 µg/L or less.

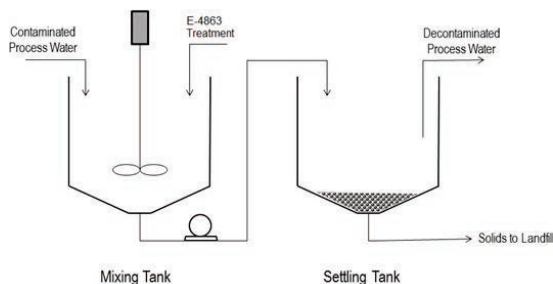
A novel proprietary technology, E-4863 was evaluated in the above mentioned contaminated effluent to remove selenium to below the desired <5 µg/L discharge criterion.

| IC Analysis                       | Concentration | ICP Analysis                   | Concentration |
|-----------------------------------|---------------|--------------------------------|---------------|
| Fluoride (mg/L)                   | 3.8           | Copper ( $\mu\text{g/L}$ )     | 7.2           |
| Chloride (mg/L)                   | 8.7           | Arsenic ( $\mu\text{g/L}$ )    | < 1.0         |
| Sulfate (mg/L)                    | 43.1          | Selenium ( $\mu\text{g/L}$ )   | 69            |
| Bromide (mg/L)                    | ND            | Cadmium ( $\mu\text{g/L}$ )    | < 1.0         |
| Nitrate (mg/L)                    | ND            | Sodium (mg/L)                  | 4.7           |
| Phosphate (mg/L)                  | ND            | Magnesium (mg/L)               | 21            |
| <b>Conditions</b>                 |               | Aluminum ( $\mu\text{g/L}$ )   | < 1.0         |
| pH (-)                            | 7.9           | Calcium (mg/L)                 | 37            |
| Turbidity (NTU)                   | 0.31          | Manganese ( $\mu\text{g/L}$ )  | < 1.0         |
| Total dissolved solids (mg/L)     | 410           | Iron ( $\mu\text{g/L}$ )       | 27            |
| Hardness (as $\text{CaCO}_3$ )    | 114           | Nickel ( $\mu\text{g/L}$ )     | 16            |
| Conductivity ( $\mu\text{S/cm}$ ) | 438           | Molybdenum ( $\mu\text{g/L}$ ) | < 1.0         |
| Total suspended solids (mg/L)     | 47            | Barium ( $\mu\text{g/L}$ )     | 48            |

**Table 1** Raw water analysis

Fig. 3 shows the process of water treatment using E-4863. This treatment could either be continuously fed or applied via a batch process. This single stage treatment takes place in a mixing tank containing the contaminated process water, followed by transfer to a gravity settling tank. Once the solids have settled, they may be discharged to a landfill and the decontaminated process water may be discharged or undergo further treatment, if necessary. Faster solids/liquid separation was accomplished by the addition of common organic flocculants.

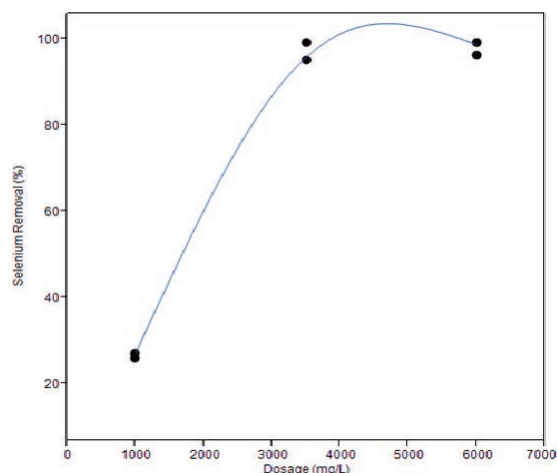
A DOE (design of experiment) was developed for the purpose of evaluating effects of dosage, temperature, and filtration techniques on selenium removal. Dosage was examined at 1000, 3500, and 6000 mg/L treatment, shown in Fig. 4. At a dosage of 3500 mg/L E-4863 treatment, selenium removal reached 99 % removal.



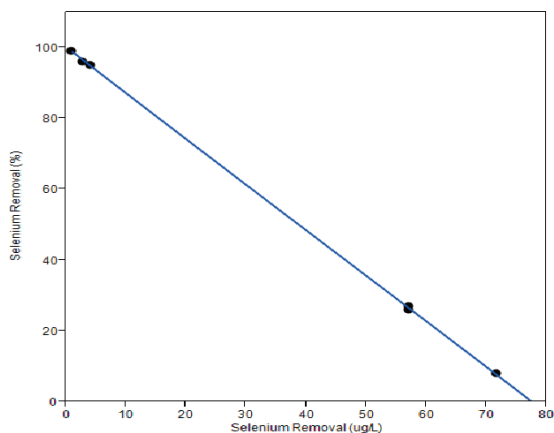
**Fig. 3** Schematic representation of water treatment in this work

Fig. 5 shows selenium removal (%) as a function of the amount of selenium remaining in solution. At 99 % removal, the remaining selenium in solution was less than  $1 \mu\text{g/L}$ , which was the detectable limit of the instrument. At 1000 mg/L E-4863, selenium levels were only reduced by approximately 28 % (to  $56 \mu\text{g/L}$  remaining selenium). Therefore, no experiments were conducted at concentrations below this dosage level.

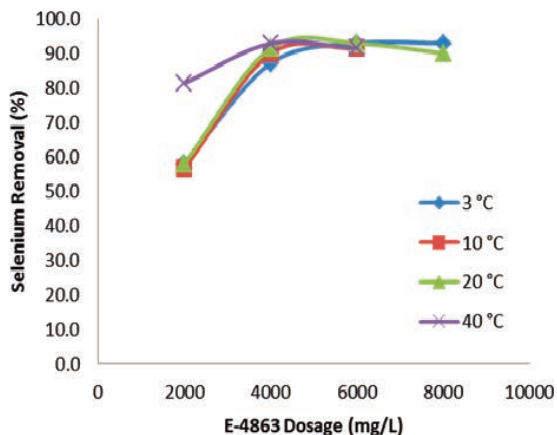
Many of the North American mines that have selenium discharge restrictions are in regions that have broad temperature ranges as a function of season. Therefore, the effect of temperature on selenium removal was also



**Fig. 4** Effect of dosage on selenium removal using E4863 Treatment.



**Fig. 5** Percent selenium removal as a function of selenium remaining in solution.



**Fig. 6** Effect of dosage and temperature on selenium removal.

studied, as shown in Fig. 6. As temperature was decreased, there did not appear to be a significant effect on the removal. However, an increase in temperature could allow for a lower treatment dosage. Removal of 80 % selenium, or 12 µg/L remaining selenium, was observed at 2000 mg/L E-4863 dosage.

Another evaluation addressed how treatment, along with filtration methods, affected TDS of the processed water. As mentioned in Table 1, the TDS for the raw water was 410 mg/L. Once treated with 3500 mg/L of E-4863, three filtration methods were applied to study the effect of treatment and filtration on TDS. The standard method of filtration for treated water samples involves using a 0.45 µm filtration membrane. Using 3500 mg/L treatment followed by filtration through a 0.45 µm membrane resulted in an increase from 410 mg/L to 2250 mg/L. Similarly, a smaller membrane, 0.22 µm did not improve the removal of TDS, yielding 2210 mg/L TDS. The least effective filtration method studied was filtration through sand, which yielded 3260 mg/L TDS post-treatment. Therefore, if TDS is a concern, other filtration or TDS removal methods may need to be evaluated in the future. When the three filtration methods were compared for selenium removal after treatment with 3500 mg/L E-4863, the result-

ing selenium levels were < 1 µg/L after filtration through the three methods evaluated.

## Experimental

### Materials

The treatment used, E-4863, is an experimental proprietary product. Superfloc A130HMW is a flocculant manufactured and sold by Kemira, Inc. The flocculant is sold as a solid material and was prepared by dissolution in DI Water to 0.25 % solids in solution before adding to selenium containing mine water.

### Procedure

A sample of 500 mL of supplied mine water was added to a 600 mL beaker equipped with magnetic stirring. The pH was adjusted to the desired range using diluted nitric acid or 10 % sodium hydroxide. Once the experiment desired pH and temperature was reached and controlled, the E-4863 was added using a 100–1000 µL precision pipette equipped with disposable pipette tips. At the end of the two minutes agitation, flocculant (Superfloc A130 HMW) was added and allowed to agitate at the same speed for 5 minutes. The precipitate was allowed to settle for 10 minutes prior to filtering through a 0.45 µm Millipore filter, unless otherwise stated. The filtrate was then submitted for ICP to obtain selenium analysis.

### Instrumentation

In this study, an Agilent ICP-MS 7700x system equipped with a helium collision cell was used for determination of the selenium in water samples. All samples were digested according to EPA 200.8 protocol adapted for Environmental Express digesters. The samples were then diluted 10 times with 5 % nitric acid and analyzed on ICP-MS. An SRM (NIST 1643e) was used to check the accuracy of the instrument. The samples were compared to Ge for precision and results were obtained by comparing samples against a 4-point calibration curve for each element and low detection limits (1 µg/L for selenium) were achieved. The instrument was calibrated with PE Pure Plus Instrument Calibration Standard 1, 10, 100, and 1000 µg/L.

### Conclusions

Selenium was successfully removed from water obtained from a mineral mine to levels below the detectable limit of the instrument (<1 µg/L) with 3500 mg/L of E-4863. The optimal dosage may need to be better determined by tightening the range between 1000 mg/L and 3500 mg/L E-4863. To examine seasonal sensitivities, the treatment was evaluated toward the effect of temperature on selenium removal. Results suggested that over a range of temperatures between 3 and 40 °C, selenium removal was not negatively affected. Filtration methods were also examined and results yielded no significant difference between samples filtered through 0.22 µm and 0.45 µm membranes. However, a decrease in efficiency of filtration removal of approximately 1000 mg/L of TDS was seen using sand filtration. Work continues to optimize the flocculation package in efforts to improve the solids liquid separation.

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