Removal of selenium by biological reduction and surface complexation: Removal efficiencies and speciation results

Myriam De Ladurantaye-Noël[1], Marc Laliberté[2]

[1]*Veolia Water Technologies Canada, Montréal, Québec, Canada, myriam.deladurantaye@veolia.com*

[2]*Veolia Water Technologies Canada, Montréal, Québec, Canada, marc.laliberte.ext@veolia.com*

Abstract

Due to its chronic toxicity, selenium is a growing concern in many mining activities. One of the main issues with selenium-contaminated waters is the bioaccumulation of selenium in living organisms in the receiving body. This bioaccumulation is highly dependent on the selenium speciation, because organoselenium species are prone to higher bioaccumulation.

Veolia has developed a new treatment method for selenium removal, which is based on biological reduction of selenium to selenite, its subsequent removal using surface complexation on ferric oxyhydroxide and removal of the solid, followed by further biological oxidation of the treated water. This paper reports on the findings of continuing lab investigations of this new process.

First, it was demonstrated that under standard biological denitrification conditions there is a reduction in selenium valence, with the majority of selenium being reduced to various Se^{+4} and Se^{-2} species. Detailed speciation results are presented. It was also found that when the denitrified water is sent to a biological aerobic reactor, most of the remaining reduced selenium species are oxidized back to Se^{+6} (selenate).

Finally, it was confirmed that after denitrification selenium can be removed by solid separation combined with surface complexation, with varying efficiency depending on the ion considered.

Results from the laboratory tests have shown, in over a year of operation, a substantial and constant decrease in concentration of selenium to below 5 µg/L, with Se^{-2} species concentrations below 0.25 µg/L.

Introduction

Selenium is a metalloid known to be toxic to living organisms when present in sufficient concentration. Its most common form in water, the selenate ion (SeO_4^{-2}) is similar to the sulfate ion (SO_{4-}^{2}) and, to a lesser extent, the nitrate ion (NO_3-), ions which are both common in water. Finding a removal technique specific to selenium is a challenge (Golder 2020).

One of the mechanisms that contributes to the toxicity of selenium is the bioaccumulation of selenium in living organisms (Besser 1993, Hamilton 2004). It is generally understood that the selenium tendency to bioaccumulate depends on its form, with "organoselenium" much more likely to bioaccumulate than selenite (SeO_3^{-2}), and selenite more likely than selenate.

However, "organoselenium" is not a defined chemical species. Few studies looking at the toxicity of selenium have done a speciation study to understand which form selenium is present in the environment. When selenium speciation studies have been conducted, they have mostly looked at selenate and selenite, and when "organoselenium" species have been analyzed for, it was mostly selenomethionine and selenocysteine.

Our working hypothesis is that while decreasing the total selenium concentration is important, it is also important to try to lower the potential for bioaccumulation of the residual selenium after treatment. This is understood to mean reducing the "organoselenium" concentration in the treated water. However, very little is known about the speciation of selenium after biological

treatment. This paper will therefore try to answer four questions, more specifically for the process of interest:

- What selenium species are present in water after going through a biological reduction process?
- How much of these different species can be removed by solid removal and surface complexation?
- If the water is afterward treated in a biological oxidation step, can some of the reduced species be oxidized back?
- What is the total selenium concentration that can be expected in water treated by this process?

Previous Work

Veolia is developing a process for removing selenium from wastewater using biological reduction and surface complexation. This process was presented elsewhere (Laliberté 2022, De Ladurantaye-Noël 2023).

This process, which we call the "Tracer Se process" combines biological reduction of selenates to selenites, removal of selenites and biomass under reducing conditions, and reoxygenation of the water. A process schematic is shown in Fig. 1.

Conventional biological processes aiming at decreasing the concentration of selenium usually produce elemental selenium Se^0, with some Se^{+4} and Se^{-2} species by-products. The Tracer Se process was designed not to let the oxidation-reduction potential (ORP) go as low, targeting the production of Se^{+4} species instead of Se^0. The kinetics of reducing Se^{+6} to Se^{+4} being much faster than reducing Se^{+6} to Se^0, this has the advantage of considerably reducing the footprint of the treatment chain.

First, water is directed to a biological reduction reactor containing biomass and operated under denitrifying (anaerobic) conditions, typically using a Moving Bed Biofilm Reactor (MBBR). In this biological reduction reactor, further referred to as biological reduction, selenates are biologically reduced by the biomass to selenites or absorbed on the biomass. The ORP in the biological reduction is controlled to minimize further reduction of Se^{+4} species to Se^0 and Se^{-2} species.

The water containing the selenium and any biomass lost or released from the biological reactor is then directed to a precipitation reactor. While maintaining reducing conditions, a coagulant such as a ferric or aluminum salt is mixed with the water. By controlling the pH and using sludge recirculation to age the sludge, solids having adsorption sites are formed. Selenites and other selenium species are adsorbed onto these sites. The solids with adsorbed selenium in addition to the biomass are separated from the water, typically using a ballasted flocculation settler such as Veolia's Actiflo®.

The water is further treated in a second biological reactor under aerobic conditions where the water is subjected to reoxygenation (this step is called hereafter the "reox" step). In this stage, reduced selenium species present in the water are oxidized.

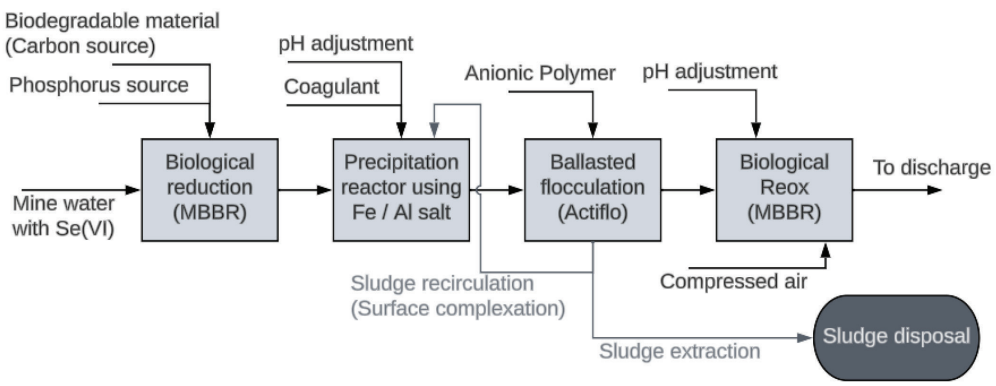

Figure 1 Tracer Se Schematic Diagram

Methodology

The laboratory set-up is illustrated in Fig. 2. It is composed of the following equipment:

- Double-walled glass reactors for biological reduction (5 L) and reox (5 L);
- 1 mechanical stirrer for the biological redox reactor;
- 1 air pump with accessories for reduction reactor;
- Seeded MBBR carriers (K5, Anox Kaldnes) from previous tests;
- Equipment for ballasted flocculation separation.

The water to test was received in a 1000 L container and was kept refrigerated. Once or twice a week a small volume was transferred to a drum and was used to feed the system. The biological reduction reactor was fed on a continuous basis at a flow varying between 2 L/d and 10 L/d. The water coming from the biological reduction reactor was collected in a second drum. Once or twice a week it underwent a batch metal precipitation and ballasted flocculation and was then stored in a third drum. From this third drum, the clarified water was then continuously fed to the reox. Previously we reported results from tests where the reox reactor was not fed on a continuous basis (Laliberté 2022) and it was observed that the selenium mass balance did not close. The objective for continuous feed to the reox was to help on that respect. It should be noted that in a full scale plant, all process steps would be continuous. This is not possible at laboratory scale due to ballasted flocculation, as a minimum of a few hundreds m^3/d would be required.

The water to test was collected at a coal mine site in British Columbia. It contained 520 mg/L of total dissolved solids, mostly calcium and magnesium sulfate, with low concentrations of sodium, chloride and nitrate. The water contained 0.068 mg/L of total selenium. The selenium was mostly present as selenate, with less than 5% as selenite and less than 1% for all other species combined.

The biological reduction reactor, also acting as a denitrification reactor, is designed to reduce approximately 1 g N/d of nitrate ion to nitrogen gas. The low concentration of nitrate in the water was not sufficient to run the test for the time necessary to stabilize the system. The water was therefore spiked with sodium nitrate (210 mg N/L) before testing, allowing to feed the system at 5 L/d on average, and enabling us to run the test for 200 days before running out of water.

The tests were run in late 2022 and early 2023. For the first four months the feed water was fed to the system as previously

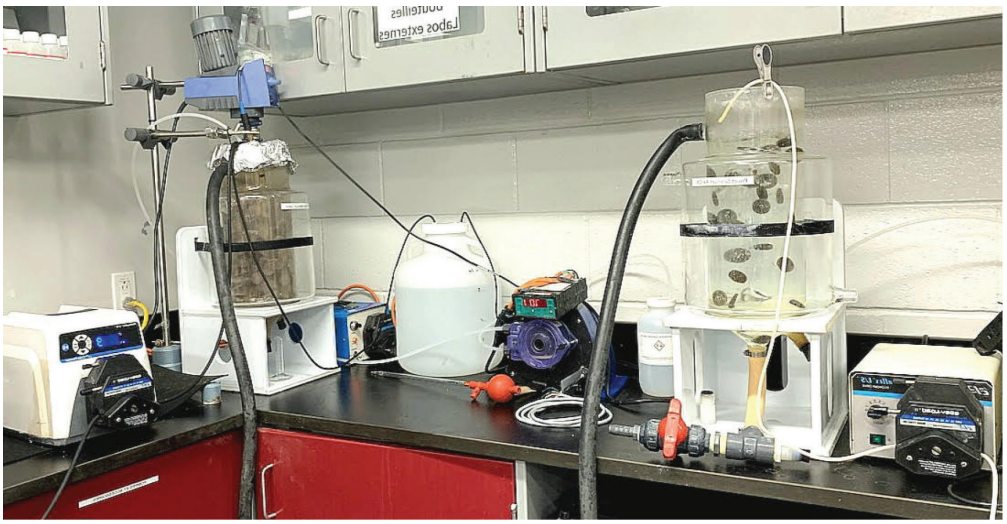

Figure 2 Laboratory set-up showing the biological reduction reactor followed by the reox reactor

described. For the last two months the water was additionally spiked with sodium selenate to obtain a final concentration of 325 µg/L of selenium. Three samples were taken for detailed speciation analysis during each phase of the tests. The last two samples for the spiked water were found to be invalid, with the total of ionic species being substantially greater than the dissolved and the total selenium. These last two samples are therefore excluded from further discussion.

Analytical methods

Selenium speciation analysis is difficult. A specialized laboratory has been used through our studies (Brooks Applied Lab, Seattle, WA). Their analytical methods can be summarized as follows:

- For total recoverable and dissolved Se, each sample was digested in a closed vessel with nitric and hydrochloric acids. The resulting digests were analyzed for Se content via inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS). Particulate selenium was calculated by difference. The sample analyzed for dissolved selenium was filtered on a 0.45 µm filter.
- For the selenium speciation, each filtered sample (dissolved fraction) was analyzed using ion chromatography inductively coupled plasma collision reaction cell mass spectrometry (IC-ICP-CRC-MS). In this process, selenium species are chromatographically separated on an ion exchange column and then quantified using ICP-CRC-MS.
- Most of elemental selenium present in the water will pass through a 0.45 µm filter due to the small size of its particles. Therefore, the measured "dissolved" selenium will include most of the elemental selenium present. However, elemental selenium being electrically neutral, it is not measured in the speciation analysis. It can therefore be inferred as the difference between measured dissolved concentration and calculated dissolved concentration from the speciation results.

In this paper the speciated selenium species are selenate, selenite, dimethylselenoxide, methyl seleninic acid, selenocyanate, selenomethionine and selenosulfate. In addition, an estimate of the elemental selenium concentration is calculated. The concentration of unknown ionic selenium species detected by ion chromatography is reported as well.

Results and Discussion

The test results are presented in Table 1. As stated above, for the first test the average of three samples is reported while for the second test only one sample is available.

The concentration of total selenium should be roughly equal in the influent water and in the biological reduction, as well as in the clarified water and the reox. The fact that the selenium concentration is higher between those steps indicates that the reactors were not quite at equilibrium. It's a bit closer to equilibrium in the first test that ran for four months than in the second test that ran for only two. That gives an indication that the time required to achieve equilibrium is probably from six to eight months. It should also be noted that the reox reactor lags behind the biological reduction.

The ionic chromatography systematically shows that there are some unknown ionic selenium species present in the water. Given that these unknowns are more concentrated in the biological reduction reactor, these have been tentatively identified as some other Se^{-2} species.

Considering the ionic selenium species, selenium is efficiently oxidized in the reox reactor. For example, the total concentration of Se^{-2} species (selenocyanate, selenomethionine, selenosulfate and unknown ionic species) in Test 1 goes from 0.69 µg Se/L in the clarified water to 0.10 µg Se/L after reox, while in Test 2 the concentration goes from 3.64 µg Se/L to 0.17 µg Se/L. The performance of the reox reactor is expected to improve with time, and it can be seen that while there is a much lower concentration of Se^{-2} species in the reox there is still some residual Se^{0}.

Table 1 Selenium speciation evolution through the process chain for the two laboratory bench tests

All concentrations are expressed as µg Se/L	Test # 1				Test # 2			
	Influent water	Biological reduction	Clarified water	Reox	Influent water	Biological reduction	Clarified water	Reox
Macro Parameters								
Se total	57.9	53.9	4.13	2.53	326	310	18.5	7.02
Se particulate (calculated)	4.01	48.8	2.85	0.94	17.4	302	13.5	1.54
Se dissolved	58.8	9.15	3.32	2.19	322	11.8	12.0	6.57
Sum of dissolved ionic species (calculated)	56.9	5.07	1.28	1.59	309	8.20	4.99	5.48
Se^{+6} species								
Selenate	54.3	0.97	0.10	0.11	306	0.75	0.03	0.26
Se^{+4} species								
Dimethyl selenoxide	0.07	0.04	0.06	0.03	0.04	< 0.01	0.18	0.03
Methyl seleninic acid	0.03	0.16	< 0.01	< 0.01	0.02	0.24	0.23	0.04
Selenite	2.45	2.06	0.40	1.30	2.52	3.57	0.49	4.98
Se^{0} species								
Se0 (calculated)	1.97	4.08	2.04	0.60	13.4	3.61	7.01	1.09
Se^{-2} species								
Selenocyanate	< 0.01	0.77	0.59	0.10	< 0.01	2.66	2.74	0.11
Selenomethionine	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01
Selenosulfate	< 0.01	0.22	0.04	< 0.01	< 0.01	0.40	0.06	0.02
Unknown ionic Se species	< 0.01	0.85	0.06	< 0.01	0.02	0.55	1.25	0.04

High concentrations of selenocyanate and selenosulfate were observed in the biological reduction, while neither of the species are present in the influent water[1]. They are both Se^{-2} species, but no information is available in the literature on whether they are more or less susceptible to bioaccumulation in living organisms than selenite or selenate, and thus on their potential toxicity.

No relevant concentration of selenomethionine was detected. Thus the fact that Besser (1993) reported that selenomethionine is highly susceptible to bioaccumulation might not be of much practical significance for this process. It is however possible that if the ORP in the biological reduction was lower, selenomethionine might have been formed. As stated above, the ORP would be lower if the target of the biological reduction was the formation of elemental selenium.

The main mechanism for selenium removal in this process is the capture of selenium by the biomass in the biological reduction. This accounts for 80–90% of the selenium removed. The remainder is removed by surface complexation using metal oxides such as ferric oxy hydroxide. The results show that some species (mainly selenate, selenite and selenosulfate and to a lesser extent methyl seleninic acid) are well removed by this process (> 80% removal), while other species (dimethyl selenoxide and selenocyanate) are not as susceptible to removal by this process (< 20% removal). The high removal of selenate is unexpected as this ion is generally not considered to be captured by this mechanism. However, this was observed in every sample.

Finally, the results show that total selenium below 5 µg/L can be reached in the laboratory while producing treated water that

[1]Cyanate is a relevent but often overlooked part of the nitrogen cycle (Mooshammer 2021), and the same might be true of selenocyanate in the selenium cycle. Alternatively, selenocyanate might be a by-product of cyanate metabolism where selenium replaces oxygen. Selenosulfate and selenocyanate have also been reported together in other biological reduction processes (Yan 2021).

contains mostly selenite and selenate, the forms of selenium which are understood to be less susceptible to bioaccumulation.

The results shown above, the speciation results in the biological reduction and our experience with surface complexation processes suggest that total selenium concentration below 10 µg/L could be achieved in a full scale plant, 5 µg/L would be possible with a good process control and 2 µg/L is probably the best that can be achieved without modification to the presented process.

Conclusions

We have shown that, in addition to selenite, biological reduction process where selenium is present produce water that contains a number of reduced species, including dimethyl selenoxide, methyl seleninic acid, selenocyanate and selenosulfate. Selenomethionine was not detected in relevant concentration. Other ionic selenium species of unknown nature, presumably some Se^{-2} species, are also present.

Selenate, selenite, selenosulfate and to a lesser extent methyl seleninic acid present in the water can be removed by surface complexation. Dimethyl selenoxide and selenocyanate are poorly removed by surface complexation. The high removal of selenate is unexpected.

Finally, the results show that the reox reactor is highly efficient in oxidizing reduced selenium species, and the overall treatment chain can achieve a global selenium removal down to 5 µg/L with low organoselenium concentrations.

References

Besser, J. M. (1993) et al. Bioaccumulation of organic and inorganic selenium in a laboratory food chain. Environmental Toxicology and Chemistry: An International Journal, 12, no 1, 57–72.

De Ladurantaye-Noël, M. (2023) et al. Removal of selenium by reduction to selenite and surface complexation. Proceedings of SME Annual Conference, Feb. 26–Mar. 01, 2023, Denver, CO

Golder, A. (2020). State-of-Knowledge on Selenium Treatment Technology. North American Metals Council – Selenium Working Group: Vancouver, BC, Canada.

Hamilton, S. J. (2004). Review of selenium toxicity in the aquatic food chain. Science of the total environment, 326(1–3), 1–31.

Laliberté, M. (2022) et al. Removal of selenium by reduction to selenite and surface complexation. Proceedings of Mine Water Solutions 2022, June 14–16, 2022, Vancouver, Canada

Mooshammer, M. (2021) et al. Cyanate is a low abundance but actively cycled nitrogen compound in soil. Communications Earth & Environment, 2(1), 161.

Yan, S. (2021) et al. Optimization of nitrate and selenate reduction in an ethanol-fed fluidized bed reactor via redox potential feedback control. Journal of Hazardous Materials, 402, 123770.