Selenium in Mine Waters: A Review

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Abstract Selenium (Se) has a role as both a nutrient and a toxic substance. Diverse in its compounds and oxidations states, Se research spans fields including, but not limited to: geology, chemistry, biology, and toxicology. Many of these fields of research are important from a mining perspective. From information about the origin of Se at a mine site, reactions which may release it to the environment, reactions and interaction with organisms, beneficial or toxic effects on those organisms, transfer through the food chain, and how this relates to treatment and legal requirements, Se research is a diverse field. This paper serves as a review of selenium research relevant to the mining industry, from the perspective of mine waters. The review focuses on the areas of Se geochemistry, biology, toxicity, treatment and advances in analytical methods.

Keywords bioavailability, toxicity, speciation, treatment

Introduction

Selenium is a naturally occurring metalloid element, essential to human and animal health in trace amounts but harmful in excess. Selenium's role in human physiology has been found to include the prevention of atherosclerosis, some cancers, arthritis, diseases of accelerated aging, central nervous system pathologies, male infertility, and altered immunological function (Lyn Patrick 2004). Of all the elements, Se has one of the narrowest ranges between dietary deficiency and toxic levels (Fordyce 2006).

Selenium exists in four oxidation states: 2^-, 0, 4^+, and 6^+. In aqueous environments Se is most often found as oxygenated anions, selenite (SeO_3^{2+}) and selenate (SeO_4^{2+}).In reducing environments selenium exists as selenites and elemental selenium Se^0, both insoluble. Selenium is also incorporated into various organic Se compounds (Fordyce 2006). Knowledge of the different chemical forms and their environmental and biomedical distribution is important because of the dependence of bioavailability and toxicity on speciation (Dauchy *et al.* 1994).

Lemly (2004) suggests one of the primary human activities responsible for the mobilization of Se in the environment is the mining, processing, and combustion of coal for electric power generation. Lemly (2004) further stated that on a total mass basis, the Sudbury ore deposits in Canada are one of the largest source of Se in North America. Although this statement was based upon old data, it illustrates the importance of Se in various settings. Selenium is found in all types of natural materials on earth including rocks, soil, waters, air, and plant and animal tissues. In general Se concentrations in rocks are low; magmatic rocks average 10–50 ppb. Sedimentary rocks are highest in Se. Shales are generally between 500 and 28,000 ppb, though some black shales are over 600,000 ppb. Some phosphatic deposits contain as much as 300,000 ppb. Coal and other organic rich deposits typically contain 1,000–20,000 ppb. The worldwide average in soils is 400 ppb. Some high Se soils from the Great Plains in the U.S. have 6,000–28,000 ppb and have led to a toxic response in several domestic animals (Fordyce 2006, Burau 1985).

Bioavailability and the food chain

Although much focus is currently on Se toxicity and increased concentrations due to human activity, Se deficiency in animals is very common around the globe and many western countries adopt Se supplementation programs (Fordyce 2006). It is therefore important to understand both concentration and bioavailability. A general characteristic of Se that can be used to predict bioavailability is its oxidation state; Se^{4+} and Se^{6+} are more soluble, mobile and bioavailable than Se^0 and Se^{2-} (Ryser *et al.* 2006). Other bioavailability determining factors include the pH, redox conditions, soil texture, mineralogy, organic matter content and the presence of competitive ions (Fordyce 2006). Uptake of Se into the food chain is also dependent on local flora. Some plants are Se accumulators and can absorb more than 1000 mg kg^{-1}, whereas non-accumulators usually contain < 50 mg kg^{-1} (Fordyce 2006). The balance is further complicated by biological processes that can release Se into the atmosphere in a volatile form; a potentially important source for the atmospheric enrichment of Se is natural biomethylation (Dauchy *et al.* 1994). Production of a variety of volatile methyl selenides have been confirmed in rats, fungus, and a variety of plants (Dauchy *et al.* 1994). Along with the complexities of how Se travels through an ecosystem is the complexity of how uptake and concentration of Se in an organism actually affects that organism's health. In 1996, bioaccumulation at levels exceeding published toxic thresholds was found in fish from the Elk Valley with apparently no ill effects (McDonald and Strosher 2000).

There have been many advances to our understanding of processes related to Se in the environment in recent years. A study of select reclaimed coal mine soils (Sharmasarkar and Vance 2002) found that selenite sorption was always greater than selenate sorption. Linear correlations of the adsorption parameters with different soil characteristics can be utilized to determine Se retention behavior in mine environments (Sharmasarkar and Vance 2002). Using our growing knowledge of the physical, chemical and biological interactions of Se, some biological processes are coming to light. For instance, knowing how much Se microorganisms take up based upon environmental levels and how Se travels through the aquatic food chain, it has been shown that using local food chain data modeling can predict Se concentrations in tissue of trout (Orr *et al.* 2012). This modeling can explain why differences in the food chain, such as a different diet of the same species of fish in different areas, can lead to different fish tissue Se levels in water with equal Se concentrations.

Toxicity

Debate and research around the topic of Se toxicity continues. There is inherent variability in Se toxicity that can be attributed to its interaction with other trace elements, different bioaccumulation potential in lotic and lentic ecosystems, and differences in sensitivity among species (Wayland and Crosley 2006). Elevated Se levels are no guarantee of a harmful reaction. Bujdos *et al.* (2005) found that plants in a contaminated study area were higher in Se concentration than outside the contaminated area, but were not hazardous and therefore posed no poisonous risk to other organisms. The results of individual studies that form the basis for many guidelines have also been called into question. Brix *et al.* (2000) claims the U.S. Fish and Wildlife Service (USFWS) thresholds for fish tissue appear overly conservative and do not appear to be adequately supported by the scientific literature. It is likely that the matter will not be resolved without further independent studies. Brix *et al.* (2000) further states "in several cases, the USFWS interpretation of the studies on which the thresholds are based are contrary to our interpretation, that of the U.S. EPA, and the authors that published the study."

The interaction of Se with other elements makes the toxicity issue a complicated one. Other elements can reduce the toxic effect of Se and if other toxic elements are present, concentrations of Se that would otherwise be toxic may be beneficial. The protective effect of Se against mercury toxicity and vice versa has been observed in a number of different organisms(Cuvin-Aralar and Furness 1991). Although the benefits of Se in an equal molar ratio with mercury have been established, Ouedraogo and Amyot (2013) note that selenium to mercury molar ratio is not yet a widely accepted tool in mercury risk assessment. It has also been shown that Se toxicity may be alleviated by other trace elements (Wayland and Crosley 2006). The ecotoxicological complexities of this element dictate that thorough, well-designed assessments of effects, or lack thereof, are required in each instance of Se contamination before decisions can be made regarding remediation and management (McDonald and Strosher 2000).

Treatment

The key to successful treatment of selenium contaminated water is to reduce selenite to selenite (Sheoran and Sheoran 2006). Millimolar levels of selenite can be removed from waters quickly and efficiently by sodium sulfide (Pettine *et al.* 2012).

In cases where conditions permit, a more passive treatment system is often preferred. In pilot wetlands testing, cattails and saltmarsh bulrush have been shown to be efficient at removing Se from the water column (Huang *et al.* 2012).

Work by Knotek-Smith *et al.* (2006) supports an approach for remediation of Se-impacted soils using accelerated microbial reduction via nutrient amendment in concert with an iron amendment to enhance more stable mineralization. From association with pyrite, to adsorption characteristics on iron compounds, the geochemistry of Se is largely controlled by that of iron, with which Se is closely affiliated (Howard 1977). Iron-selenide and iron-selenite compounds are resistant to leaching by infiltration waters; thus coupling organic amendment and iron metal may be a preferred treatment technology for longer term stabilization of Se in contaminated soil environments, especially those not exposed to surface weathering (Knotek-Smith *et al.* 2006).

Analytical methods

As it is important to know both concentration and speciation of Se even when it exists in miniscule quantities, research has worked to lower detection limits and improve speciation techniques. “The fact that the lower limit of detectablility of our analytical method is not sufficient to indicate exactly the content of many of the Se-poor ores, precludes the drawing of any firm conclusions with respect to them.” (Hawley and Nichol 1959). Though detection limits have improved many orders of magnitude since Hawley and Nichol (1959) had a stated lower detectability limit of 15 ppm, improvements are still needed and being made. Hydride generation atomic adsorption spectrometry using multi commutated flow analysis for the hydride generation has been shown to achieve a detection limit of 0.08 ppb, while providing low reagent and sample consumption (Piston *et al.* 2012).

Another recent method of Se speciation involving magnetic nanoparticle adsorption coupled with ICP-MS is rapid and sensitive (Huang *et al.* 2012).Selenite is adsorbed to the nanoparticles and can then be removed from the solution using a magnetic field.

Ryser *et al.* (2006) used micro-X-ray absorption near-edge structure spectroscopy for Se speciation. This method is able to determine speciation in solid samples on micron scale areas of a sample or map an area for speciation by location in the sample. Atomic adsorption spectroscopy with hydride generation (AAS-HG) and ion chromatography (IC) are both used for selenite/selenate speciation (Sharmasarkar *et al.* 1998).

Interest in increasingly lower concentrations of Se has kept pace with developments in modern analytical instruments, such that extraction and preconcentration processes are needed for the determination and speciation of Se in many cases (Najafi *et al.* 2012). Some thermodynamic data on Se compounds and species is available for modeling purposes; however, in reviewing thermodynamic data Seby *et al.* (2001) states that several values for selenide and selenate are reported but they are not always in agreement. More data is needed to predict what species may be present under given conditions.

Recent developments

The state of Kentucky recently changed regulations governing Se concentrations. The new regulations increased the limits on acute levels from 20 to 258 µg/d and changed the way the chronic standard is to be measured. Chronic level regulation uses a threshold Se concentration, which, if exceeded mandates fish tissue sampling is conducted (Payne 2013).

Similarly the state of West Virginia passed a bill requiring a Se concentration threshold be set and fish tissue monitoring conducted if that threshold is exceeded. The West Virginia bill also mandates a monitoring plan to include selenium chemical speciation (Phillips *et al.* 2013).

Conclusions

Many advances have been made to our understanding of Se. Detection limits are now lower than 1 ppb and speciation is becoming faster and more accurate (Piston *et al.* 2012). Understanding of important biological processes including how Se travels through the food chain and differences in toxicity among organisms continue to improve (Orr *et al.* 2012). Another area of toxicity which is being further explored is the interaction of Se with other elements. Some treatment methods which may be preferred, including passive wetlands based systems, have shown good initial results (Huang *et al.* 2012). Regulations continue to adapt and change, showing what seems to be balance protecting the environment while trying to set realistic expectations of companies and protecting economic interests (Payne 2013).

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