# Mining-Related Selenium Contamination in Alaska, and the State of Current Knowledge

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**Abstract:** Selenium pollution has been a topic of extensive research dating back further than the last decade and has attracted significant attention from several environmental and regulatory agencies in order to monitor and control its discharge from myriad industrial sources. The mining industry is a prime contributor of hazardous selenium release in the aquatic systems and is responsible for both acute and chronic impacts on living organisms. Herein we provide an overview of selenium contamination issues, with a specific focus on selenium release from mining industries, including a discussion of various technologies commonly employed to treat selenium-impacted waters from mining discharge. Different cases pertaining to selenium release from Alaskan mines (during years 2000–2015) are also presented, along with measures taken to mitigate high concentration releases. For continued resource exploration and economic development activities, as well as environmental preservation, it is important to fundamentally understand such emerging and pressing issues as selenium contamination and investigate efficient technological approaches to counter these challenges.

**Keywords:** selenium; waste; mine; treatment; removal

## 1. Introduction

Selenium release and pollution is a worldwide phenomenon that results from a wide variety of anthropogenic activities, such as agriculture, mining, and other process industries. Selenium is a potentially toxic element, and mining-related selenium release was a major concern during the last decade as high concentrations were reported at some mine sites in the US [1,2]. Selenium contamination is vast, affecting both aquatic and terrestrial ecosystems, and has therefore attracted the attention of natural resource and water quality regulators around the world. Consequently, monitoring and pollution control efforts for selenium have been widely expanded.

Selenium is a naturally occurring semi-metal belonging to the chalcogen group and typically does not occur in pure elemental form. It is a trace element in natural deposits of ores containing other minerals, such as sulfides of heavy metals, but there are no specific geologic deposits in which selenium is a major constituent. The major sources of selenium are black shale, phosphate rocks, coal, and limestone. Selenium can also be found in rare minerals, such as Eucairite (CuAgSe), Crooksite (CuThSe), and Clausthalite (PbSe). Selenium is commonly produced as a by-product of other base metals and is widely used in metallurgy and in the manufacturing of glass, chemicals

and pigments, electronics, fertilizers, etc. Although only present in trace amounts, mining operations expose selenium-bearing elements to air and water. This mobilizes selenium into aquatic systems where it bioaccumulates in the food chain, thereby escalating its hazardous effects. However, the levels of selenium released can be minimized by controlling and treating the effluents from mining operations.

This article provides a brief introduction to selenium chemistry and toxicity, presents a detailed review of currently available techniques for removing selenium from industrial/mining wastewater, and discusses mining-related selenium contamination from Alaskan mines.

*Chemistry, Environmental Fate, and Effects of Selenium*

Selenium exists in the environment in organic and inorganic forms. The speciation of selenium determines its available form and is governed by physical, chemical and biological processes. This discussion will be focused on the inorganic forms, which are of prime concern to the mining industry. Inorganic selenium exists in multiple oxidation states, the most common being $-2$, 0, +4 and +6, which show different chemical and toxicological properties. These characteristics of selenium are affected by the redox conditions and pH, which also plays a crucial role in designing any selenium treatment processes. Figure 1 shows a Pourbaix diagram representing different oxidation states of selenium in an aqueous phase at different pH and reduction potential ($E_h$) conditions. From the figure, it can be seen that in the pH range of 4 to 9, which is the approximate range under which most natural systems (e.g., soil, water) exist, the selenate ($SeO_4^{2-}$) species is found to be more dominant under strongly oxidizing conditions (pe > 8). As we move down along the y-axis to a more reducing environment, the selenate is reduced to selenite ($SeO_3^{2-}$) for alkaline pH and to hydrogen selenite for acidic and neutral pH. Finally, in reducing conditions it exists in the $-2$ oxidation state as selenide ($Se^{2-}$) [3]. The occurrence of selenium in different oxidation states is also affected by the type of surrounding elements and ions.
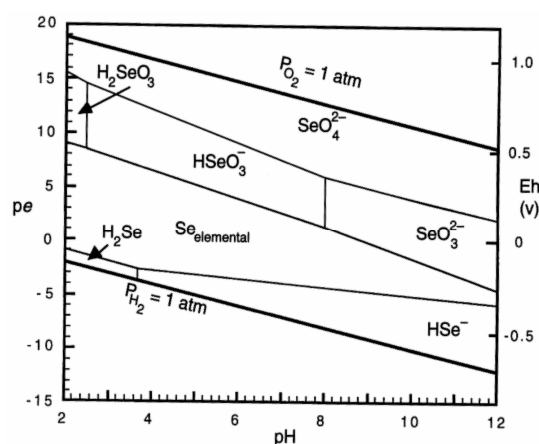


**Figure 1.** $E_h$-pH diagram for the Se–O–H system [4].

However, the speciation standalone does not describe the toxic effect of selenium; instead, factors such as bioavailability, bioaccumulation, and biotransformation should be considered while evaluating its toxic effect.

Selenium is also an essential element for various animals and fish. Studies relating to deficiency of selenium have reported it as one of the major cause of reduced growth, muscular dystrophy, and increased mortality in fish and aquatic birds [5,6]. Similarly, elevated selenium concentrations have short-term (acute) and long-term (chronic) effects depending upon the exposure concentration and duration. Because of the tendency for selenium to bioaccumulate in different species, it has been difficult for the United States Environmental Protection Agency (EPA) to quantify permissible selenium content in water. Also, the uptake of selenium by biota can be via two different pathways: from the water or through the diet. 1999 EPA selenium criterion for water was based on dissolved concentration

values. However, updated 2016 EPA criteria include the upper limits in terms of tissue residue for different fish organs [7]. The tissue based criteria are then used to derive the water column criteria which are summarized in Table 1. The advantage of tissue residue based criterion is that it allows a measure of assessment of toxicological hazard which is more species and site specific.

**Table 1.** US Environmental Protection Agency (EPA) 2016 Aquatic life criteria for selenium.

| Criteria Version | Egg-Ovary (mg/kg dw [a]) | Whole Body (mg/kg dw [a]) | Muscle (mg/kg dw [a]) | Water Lentic (μg/L) | Water Lotic (μg/L) |
|---|---|---|---|---|---|
| 2016 | 15.1 | 8.5 | 11.3 | 1.5 (30 day) | 3.1 (30 day) |

[a] dw: "dry weight" basis.

## 2. Historical Relevance of Selenium in Mining Industry

The mining industry is one of the prime contributors of selenium release into the environment. The mining of coal, precious metals (gold and silver), and metallic sulfides are key contributors of selenium from mining operations [1]. According to an annual coal report presented by the US Energy Information Administration, the annual coal production for 2015 was about 896 million short tons, which was used for electric power generation [8]. The burning of coal produces ash enriched in selenium, which is then concentrated at the disposal sites of different power plants [9]. Subsequently, selenium can be leached out by rainwater, thereby contaminating groundwater and nearby aquatic systems [10].

Mining and processing of metallic ore deposits release selenium into the environment through waste rock disposal and tailings produced at the mine site. In metallic ore deposits, selenium is associated with sulfur-containing ores, such as pyrite, sphalerite, chalcopyrite, and other sulfides. These sulfide-containing ores are prevalent in the mining of metals, such as copper, silver, lead, zinc, and uranium. Ore processing involves methods such as froth flotation and leaching, which involves chemical treatment of slurry (solids in water) that results in dissolution of selenium in water. This dissolved selenium, when discharged through tailings or wastewater streams, increases the risk of bioaccumulation in aquatic life. Proper measures, such as controlling oxidation of selenium and continuous monitoring of selenium content in various discharge streams, should be taken by waste management systems to ensure minimal discharge of selenium to the ecosystem.

The appropriate way to reduce the potential for selenium contamination from mining activities is to minimize surface disposal of wastewater and tailings. Waters containing high selenium concentrations can be treated prior to discharge through various chemical and biological techniques, including water recycling, in situ leaching processes and backfilling of solids. Table 2 shows the concentration of selenium in various environmental matrices from oil and mineral industry sources, and Figure 2 shows selenium transport in the environment from mining operations.

**Table 2.** Concentration of selenium in different materials.

| Material or Waste | Se Concentration | References |
|---|---|---|
| Surface waters | 0.2 μg/L | [1] |
| Agricultural drainage water | 140–1400 μg/L | [11] |
| Copper ore | 20–82 μg/g | [12] |
| Mining wastewater | 3–12 μg/L | [13] |
| Coal | 0.4–24 μg/g | [12] |
| Coal mining pond water | 8.8–389 μg/L | [14] |
| Gold mine wastewater | 0.2–33 μg/L | [15] |
| Uranium mine wastewater | 1600 μg/L | [15] |
| Oil shale | 1.3–5.2 μg/g | [1] |
| Crude shale oils | 92–540 μg/L | [1] |
| Crude oil | 500–2200 μg/L | [1] |
| Refined oils | 5–258 μg/L | [1] |
| Oil refinery wastewater | 15–75 μg/L | [1] |
| Phosphate ore | 2–20 μg/g | [16] |

Another major source of selenium in the environment is atmospheric release through pyrometallurgical treatment of metallic ores to recover metals, such as copper, nickel, lead, and zinc. This involves the process of smelting in which the volatile inorganic forms of selenium (Se (0), $SeO_2$, $H_2Se$) are vaporized, emitted into the atmosphere, and deposited back to nearby land. There are various theories describing the mechanisms of inorganic selenium transformation and deposition, but further research is needed [17].
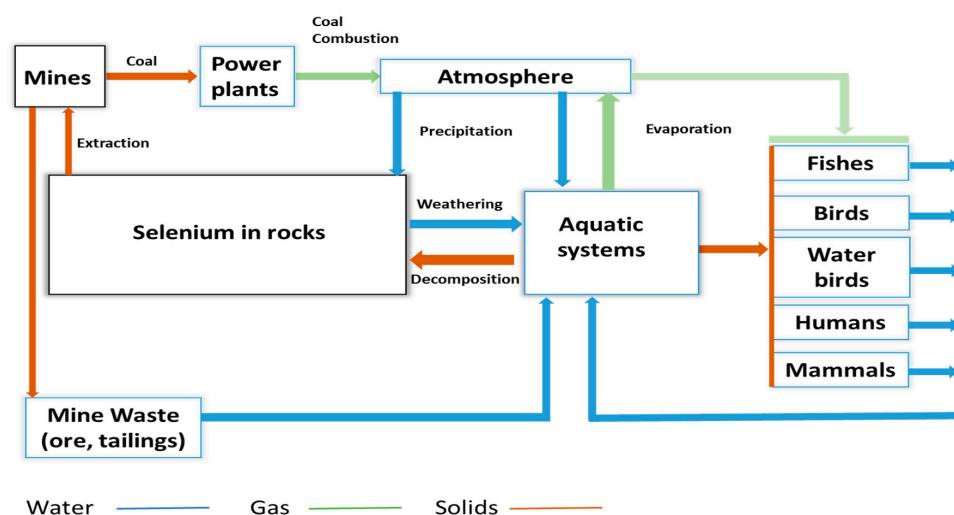


**Figure 2.** Schematic showing selenium cycling in the environment from mining.

## 3. Selenium Treatment Technologies

Tailings discharge from mining operations contains selenium in aqueous form as selenate and selenites. Various tailings discharge treatment methods are employed by the mining industry to prevent, control and remove selenium content at the source. These methods can be classified into three major categories that are discussed below: (a) physical treatment, (b) chemical treatment, and (c) biological treatment.

### 3.1. Physical Treatment

Physical treatment methods that are widely used on an industrial scale for selenium removal include membrane filtration, media filtration, and ion exchange. They are the conventional methods employed for industrial wastewater treatment and are relatively simple in operation compared to other treatment methods. Membrane filtration utilizes a semi-permeable membrane to which a pressure gradient is applied, resulting in the contaminants being retained on the membrane (retentate) and clean water being forced through it (permeate). Membrane filtration technologies are further classified as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (RO), depending on the filtration size. Additionally, these processes differ in the type of membranes used and the operating pressure range for separation. The advantage of using membrane technology is its capability to produce very high-quality permeate. It is most often used for water reuse, boiler feed water, and drinking water applications [2]. However, membrane filtration is an expensive method and poses operational challenges, such as fouling and scaling of the membrane, disposal, and the requirement for pretreatment such as filtration to remove organics. Also, these methods are sensitive to other ions, such as nitrates, sulfates, and chlorides, which renders selenates inactive, causing them to respond poorly to separation processes. Of the four methods, RO has been successfully implemented for mine wastewater treatment. For example, a permanent RO facility was successfully established at Barrick's Richmond Hill Mines (Lead, SD, USA) as a post step after using iron reduction and precipitation for the treatment of mine water [18].
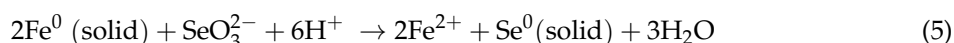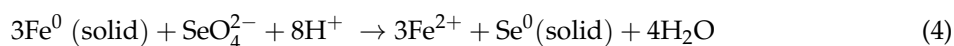
Another physical method is ion exchange, which is widely used for wastewater treatment. Ion exchange works by adsorbing undesirable ions on a solid or gel surface present in water and reversibly releasing other appropriate ions into the solution. The solid surface can be a resin or synthetic zeolite, known as a polystyrene resin. The process can be used for the preferential treatment of ions as well, however, its application for selenium treatment has not been successful because selenium in the form of selenates has similar chemical properties to that of sulfate. The sulfate, usually present in high concentration, hinders adsorption of selenates and decreases the rate of reaction, thereby making the process ineffective for selenium removal. An alternate solution is the application of a pretreatment stage for sulfate ion treatment followed by ion exchange, but this is rarely preferred because it increases the cost of treatment. Overall, physical treatment has found limited application for selenium removal, but physical treatment technologies are still being tested in the laboratory and pilot scale.

*3.2. Chemical Treatment*

In chemical treatment methods, the physical and chemical properties of dissolved selenium are altered by chemicals, such that it develops a tendency to agglomerate either as a precipitate or a floc. The agglomerated particles are then removed by filtration, flotation, or gravity settling methods. Three principal chemical methods that are favored by the industries for selenium treatment include precipitation, adsorption, and reduction. In the precipitation method, the sulfide ion is used as the most common precipitating agent for selenium removal. Compounds such as sodium dithionite and sodium sulfide are used as a source of sulfide ions in the industry [19]. The typical reaction of selenite by sulfide is given by

$$H_2S + SeO_2 \rightarrow SeS_2 + 2H_2O \tag{1}$$

Ferrihydrite adsorption is another prevalent technique in which the contaminants containing selenium are coagulated using ferrous and ferric salts. The ferrous and ferric ions work by altering surface properties, such as the surface charge of the contaminants, resulting in agglomeration of selenium particles to flocs. Both methods are effective for selenite treatment, but they tend to fail for selenates because of their low reactivity. A combination of both methods with reduction can remove the majority of selenate contamination. However, a major disadvantage of most chemical methods when compared to physical methods is the huge amount of chemical usage, and handling of solid waste produced during the operation. A popular reduction method widely tested on a pilot scale is the use of "zero valent iron" (ZVI) for selenate and selenite reduction [20]. ZVI provides a source of ferrous and ferric iron that stays in the system as hydroxides of iron (ferrous and ferric hydroxides) and directly or indirectly reduces selenate and selenite oxyanions to elemental selenium. The iron dissolution and selenium reduction by ferrous ions are represented by the following reactions:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{2}$$

$$4Fe^{4+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \tag{3}$$

$$3Fe^0 \text{ (solid)} + SeO_4^{2-} + 8H^+ \rightarrow 3Fe^{2+} + Se^0 \text{(solid)} + 4H_2O \tag{4}$$

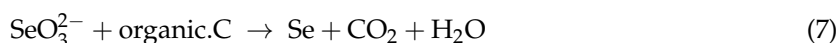$$2Fe^0 \text{ (solid)} + SeO_3^{2-} + 6H^+ \rightarrow 2Fe^{2+} + Se^0 \text{(solid)} + 3H_2O \tag{5}$$

The reduced elemental form of selenium is insoluble and gets cemented onto the solid iron matrix. Zinc is often used as a reducing agent, as a substitute to iron. Other chemical methods, such as electrocoagulation, photoreduction, and catalyzed cementation, have also been tested on a pilot scale, but have not been implemented on an industrial scale. Table 3 provides a list of available techniques, reported in the literature, that have been employed for treatment of wastewater containing selenium contamination.

**Table 3.** Overview of selenium removal technologies reported in the literature.

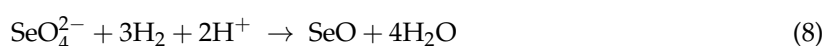| Category | Treatment Technology | Test Scale | Treatment Performance | Location of Test | References |
|---|---|---|---|---|---|
| Physical | Reverse osmosis | Full scale | Effective levels below 5 µg/L; Reduced concentration from 12–22 µg/L to 2 µg/L | Barrick's Richmond Hill Mine, SD, USA | [21] |
| | Activated Alumina Adsorption | Lab Scale | Selenium was adsorbed over pH range 3–7 for concentrations of 100–200 µg/L | Municipal Environmental Research Lab, OH, USA | [22] |
| | Nanofiltration | Lab and field scale | Up to 95% selenium removal from highly contaminated agricultural drainage (up to 1000 µg/L) | Los Banos, California, USA (Lab scale), Kennecott South, UT, USA (Field Scale) | [23] |
| | Ferrihydrite adsorption | Full scale | Reduction from 1950 µg/L to 90 µg/L | KUCC Garfield Wetlands-Kessler Springs, UT, USA | [24] |
| | Ion-exchange (physicochemical) | Lab scale | Reduction from 1 g/L to 0.1 mg/L | Kennecott Mining Company, Boyle Engineering Corp, USA | [18] |
| Chemical | Precipitation | Full scale | Reduction from 0.213 mg/L to 0.014 mg/L | Cameco's Key Lake Operation, Canada | [25] |
| | Cupric co-precipitation | Lab scale | Precipitation of Selenocyanate from petroleum refinery process | University of Grenoble, France and Unocal Corporation, CA, USA | [26] |
| | Electrocoagulation | Lab scale | Reduction from 2.32 mg/L to 0.03 mg/L | University of Mining and Geology, Bulgaria and Saarland University, Germany | [27] |
| | Zero- valent iron | Full scale | Reduction of influent selenium drop from 19 to 4.7 µg/L | West Virginia coal mines, Phosphate mine in Idaho, USA | [28] |
| | Fixed bed adsorption | Pilot scale and full scale | Reduction from 0.07–0.86 mg/L to 1–11 µg/L | Cameco Resources Smith Ranch-Highland operation, WY, USA | [29] |
| | Cementation | Lab scale | Reduction from 1950 µg/L to below 5 µg/L | University of Montana, MT, USA | [24] |
| Biological | Algal-bacterial | Lab scale | Reduction from 300–500 ppb to 0–100 ppb | University of California, Berkeley, USA | [30] |
| | Algal volatilization | Lab scale | Approximately reduction by 23% | University of California, Riverside, USA | [30] |
| | Microbial reduction | Full scale | Reduction from 70 µg/L to 4.6 µg/L | Golder, Closed mine in South Dakota, USA | [31] |
| | Fluidized bed reactor treatment | Pilot scale | Achieved less than 4.7 µg/L in effluent | West Virginia, USA | [32] |
| | ABMet | Pilot scale and full scale | Reduction from 20–300 µg/L (influent Selenium) to 0.7–2.0 µg/L (effluent Selenium) | British Columbia, Canada (pilot scale), West Virginia, USA (full scale) | [28] |
| | Biochemical reactor | Full scale | Inlet concentrations of 180 µg/L decreased to effluent concentrations from 3 to 33 µg/L | Alberta, Canada | [18] |

### 3.3. Biological Treatment

Biological treatment methods primarily employ sulfate-reducing bacteria (SRB) species (*Desulfomicrobium* sp.) to treat wastewater containing oxyanions of heavy metals, such as chromium, selenium, and arsenic. The method involves fixing or culturing SRB on an activated carbon bed, which acts as a substrate for their growth (thus forming SRB biofilms), and passing the wastewater through these activated carbon beds laden with SRB biofilms. The SRB, under anaerobic conditions, reduces dissolved selenite and selenate ions to insoluble selenium, thereby precipitating them from the wastewater stream [25,26]. The underlying biochemical conversion is represented by the reactions below [33]:

$$SeO_4^{2-} + organic.C \rightarrow SeO_3^{2-} + CO_2 \tag{6}$$

$$SeO_3^{2-} + organic.C \rightarrow Se + CO_2 + H_2O \tag{7}$$

One of the major factors that affect the process is the surrounding environment, which should be devoid of oxygen (SRB are anaerobic species) and maintained within a fixed temperature range to support bacterial growth. The environment is also affected by other dissolved contaminants in the wastewater, and their specific oxidation-reduction potential (ORP). For example, the presence of nitrates is detrimental to selenate and selenite reduction because the reduction of nitrates occurs at a higher ORP than selenates, thereby causing bacteria to preferentially utilize nitrates. Therefore, a pretreatment stage for nitrates is generally added to the treatment plant to allow effective selenite/selenate reduction.

Biological treatment has been found more effective in treating these oxyanions than other chemical and physical methods. Common variations to this method can be found for agricultural wastewater treatment such as the use of immobilized alginate enzymes, bacterial inoculum treatment, and nitrate-bearing solution treatment. However, the huge amount of sludge generated and its safe disposal are major disadvantages of biological treatment.

Another variation of the biological method is the membrane biofilm reactor, in which hydrogen in its gaseous form is passed through a thin biofilm grown on a permeable membrane (rather than the activated carbon bed). This hydrogen acts as a substrate for bacterial growth and reduction. Autotrophic bacteria are used for the biofilm instead of heterotrophs, which offers an advantage of less sludge production over the previously mentioned method [19]. The underlying chemical reaction is represented below:

$$SeO_4^{2-} + 3H_2 + 2H^+ \rightarrow SeO + 4H_2O \tag{8}$$

This process has also been referred to as the Advanced Biological Metals Removal (ABMet) Process and Hydrogen-based Fluidized Bed Reactor (FBR) system.

Passive biological treatment is another commercially-applied biotreatment technique. Oxidized forms of selenium (selenite and selenate) can be reduced to selenite, elemental selenium, and selenides through microbial reduction, followed by impounding in soil and sediments. Passive biological treatment is designed for vertical and horizontal subsurface flow of water through a reducing organic substrate to achieve microbial and chemical reduction of selenium with shorter residence times and smaller areas than constructed wetlands. Passive treatments offer advantages of low capital, operating, and maintenance costs without external energy inputs or use of chemicals. However, there are some limitations to their application, such as the requirement of a large land area and meeting the acceptable limits for selenium concentrations [2].

## 4. Overview of Selenium in Alaskan Mines

Alaska has a rich history in mining and is known for its precious metal deposits. Currently, there are six major operating mines in Alaska that produce gold, silver, lead, zinc, and coal with a combined annual production of up to 36 million tons per year [34]. Figure 3 shows the mines that are in production, along with the types of deposits.
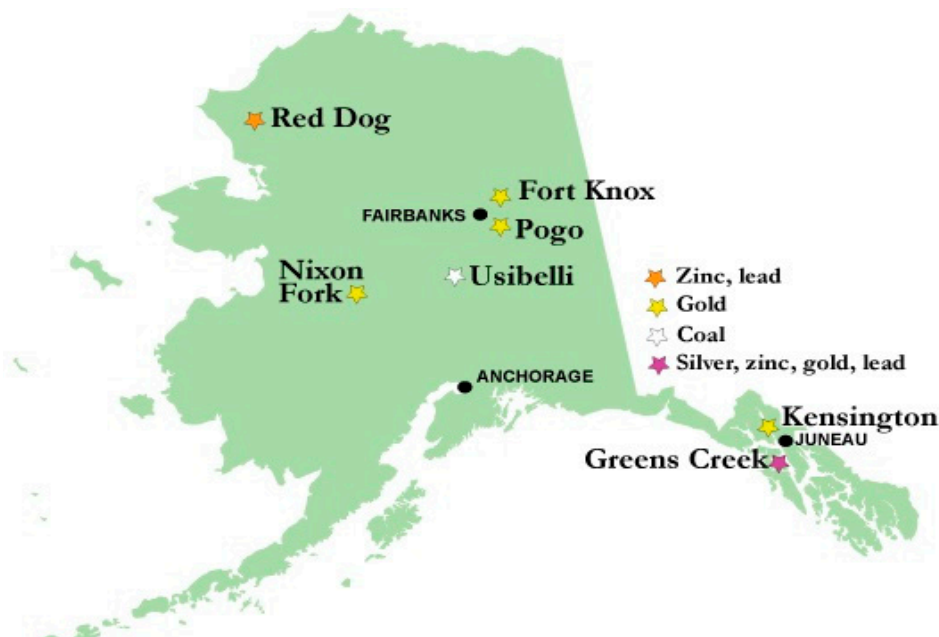
**Figure 3.** Map showing the location of different mine sites in Alaska and the respective deposits [34].

The Alaska Department of Environmental Conservation (ADEC) and Alaska Department of Natural Resources (ADNR) are responsible for implementing regulations and monitoring waste discharge from these mines to nearby water streams and to the groundwater. The Alaska Water Quality Standards chronic and acute criteria for selenium are 5 µg/L and 20 µg/L, respectively [35]. As per the report of ADNR and ADEC [36–38], most of the operating mines were able to maintain selenium levels within the acceptable limit in their discharge, though minor deviations were observed for Kinross Fort Knox, Teck Red Dog Mine, and Sumitomo Pogo Mine. Each of the mines is summarized below.

Kinross Fort Knox: Located 25 miles northeast of Fairbanks is a mine operated by Kinross Gold Corp. (Toronto, ON, Canada) that consists of two open-pit gold mine complexes—Fort Knox and True North. The Fort Knox orebody is a low-grade gold deposit with an average grade of 0.68 g/ton, hosted in and along the margins of quartz veins, shears, fractures, and pegmatites within a granite intrusion [39]. Gold is associated with anomalously high bismuth and is low in sulfide content. The mined ore is processed on site in a milling facility where the gold is recovered using carbon-in-pulp, heap leach, and gravity separation processes, thereby producing 400,000 ounces of gold annually. The tailings produced during processing are discharged in a Tailings Storage Facility (TSF), which consists of deposited tailings, a decant pond, dam, seepage interception system, and a seepage monitoring system.

Fort Knox monitors the concentration of selenium in the tailings decant and the seepage reclaim. Selenium concentrations were low when ore was mined from the Fort Knox pit, but significantly higher values were measured when True North ore was mined from 2001 to 2004 [39]: concentrations of selenium ranged from 10 to 65 µg/L. After True North production was discontinued in 2004, the concentration showed a downward trend (Figure 4) to a constant mean value of 1 to 2 µg/L.

Pogo Gold Mine: Located 38 miles northeast of Delta Junction in the Goodpaster River Valley is an underground gold mine owned by Sumitomo Metal Mining Co. (Tokyo, Japan). The Pogo deposit is a gold sulfide ore body hosted in a large quartz vein system, with low-grade gold present in quartz stockworks and an average grade of 10 to 12 g/ton. Ore is produced at a rate of up to 2500 tons per day and is processed in a milling facility using flotation, leaching, and gravity separation processes, thereby producing around 400,000 ounces of gold annually.
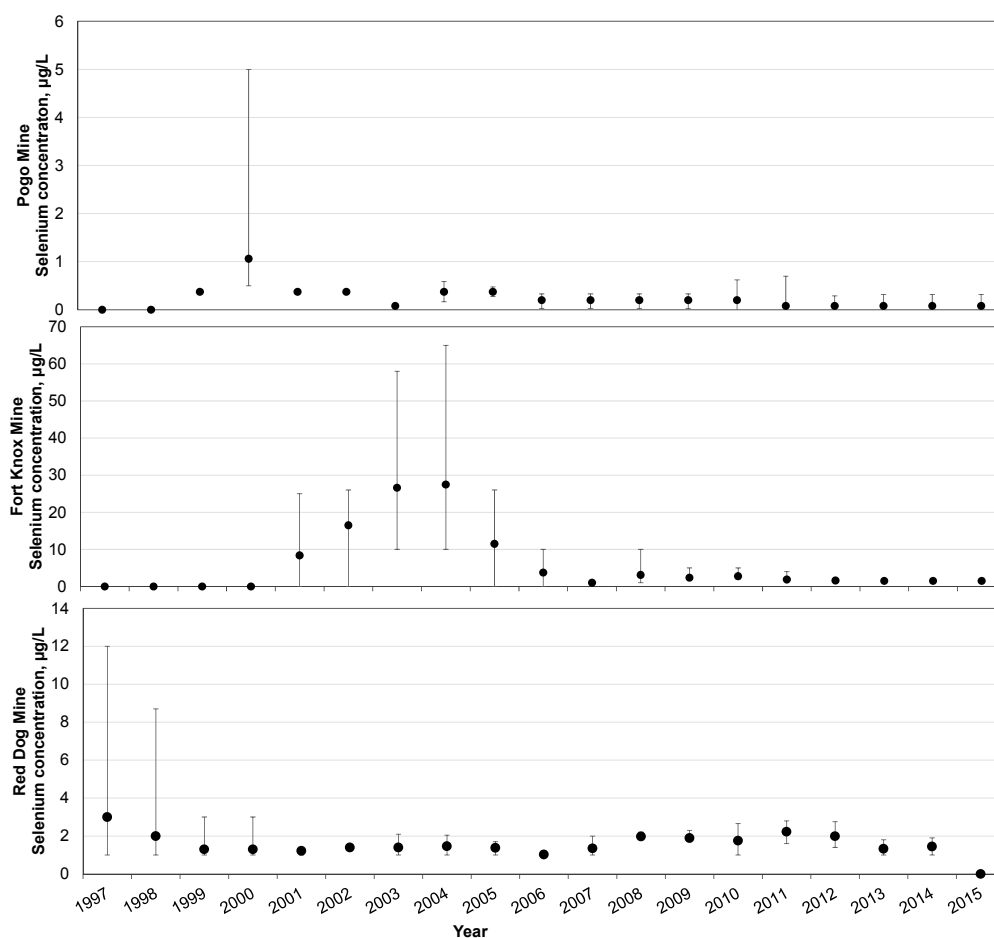
**Figure 4.** Mean selenium concentrations at Alaskan mines (Pogo Mine, Fort Knox, and Red Dog Mine) from 1998 to 2015. Error bars represent the concentration ranges. Fort Knox mine data from 2001–2004 includes two pits—Fort Knox pit and True North pit.

Tailings produced from the mine are from two sources, flotation and cyanide leaching. The tailings are treated separately; the one free of cyanide is used for dry stacking, while the other is detoxified and used as backfill in the underground mine. Pogo Mine monitors the groundwater, surface water, and effluent discharge for contaminants. The high concentration of selenium in 2000–2001 was due to specific groundwater chemistry that had high concentrations of different toxic elements including selenium. Hence, selenium limits were not exceeded. According to the Pogo Mine annual activity and monitoring report submitted to ADEC [38], high concentrations of selenium were reported from flotation tailings in the year 2013–2014. Typical selenium concentrations for other years were below 3 µg/L. The elevated concentration was because of the trial of using a copper sulfate reagent with high selenium concentration. The selenium concentration returned to acceptable limits after the company transitioned to another reagent [38]. Since the transition to the new reagent was swift and immediate, the temporary exceedances in 2013–2014 did not impact monthly and yearly data and hence are not reflected in Figure 4.

Red Dog Mine: Located 82 miles north of Kotzebue is the world's largest zinc mine, owned by Teck Resources Ltd. (Vancouver, BC, Canada). The deposit consists of sulfides of zinc, lead, and iron-bearing minerals in a Mississippian formation. Ore mineralogy primarily consists of chalcopyrite, galena, marcasite, pyrite, sphalerite, and quartz, with an average grade of 17% zinc, 4.8% lead and 80 g/t silver [37]. Ore is produced at a rate of up to 9000 tons per day and processed in a milling facility using flotation, thereby producing about 580,000 tons of zinc concentrate annually.

Tailings produced from the mine are discharged in a tailings dam, from which the water is recovered and sent to the water treatment plant (WTP). The WTP uses sodium sulfide and oxygen to precipitate heavy metals as insoluble metal sulfides and hydroxides that are flocculated together and separated by allowing them to settle in a settling tank. The treated water is then checked for dissolved metals and contaminants; if they are within acceptable limits, the water is discharged into Red Dog Creek; otherwise it is recirculated to the tailings dam. The selenium concentration at Red Dog Mine had been a prime concern, as in 1997 it reached an approximate value of 12 μg/L (Figure 4), which exceeded the mandated level of 6 μg/L [39]. The milling and the flotation circuits were surveyed and it was found that flotation reagents (predominantly a cyanide reagent) were responsible for unexpected selenium increases in the tailings stream. Survey results showed enrichment of selenium as selenocyanate ($SeCN^-$) at up to 93 μg/L in the lead rougher circuit, which was a point of cyanide addition. However, most of the selenocyanate was oxidized because of the presence of other reagents. The final concentration of selenium reported in the tailings dam and reclaimed water ranged from 4 to 6 μg/L [40]. The unusual decrease in 1998–1999 of selenium concentration in Red Dog Mine was studied by taking samples and conducting simulation studies. It was concluded that the selenium concentration decrease was from precipitation due to the presence of gypsum ($CaSO_4 \cdot H_2O$) and hematite ($Fe_2O_3$) in the tailings impoundment [41]. Another reason was microbial activity (owing to the presence of SRB) at the tailings dam that converted dissolved selenates to selenides.

Several tests for selenium removal were conducted at Red Dog mine: GE advanced metals removal process, electrochemical process (ion-exchange membrane with electrical currents), and RO membrane filtration [39–42]. A promising method that emerged was in-situ pit lake microbial treatment. Using this technology, it is possible to decrease selenium loading by generating an anaerobic environment through the addition of carbon nutrients [40]. Many of these methods are currently in the pilot testing phase, and eventually, field deployment will demonstrate the actual efficacy and benefit of these techniques.

## 5. Future Directions

In the past 10 years, biological treatment has emerged as one of the preferred techniques for selenium treatment. It offers a low-cost alternative to more expensive chemical and physical selenium removal methods. Furthermore, it has the proven ability to reduce selenium concentrations to levels acceptable by different environmental regulatory agencies. Both active and passive biological systems have been developed in the past few years. Biochemical and in-situ microbial reduction appear to be treatment processes suited for cold climatic regions, although work is needed to characterize the efficacy of these biological approaches in colder environments. Also, more fundamental work is needed to understand the role of SRB and biological treatments in reducing selenium levels at the Red Dog Mine.

## 6. Conclusions

This paper discussed the key aspects related to selenium contamination, environmental impacts of selenium release, and an overview of extant technologies used for removal of selenium in industrial and mining settings; both traditional and novel methods were reviewed. The efficiency of selenium removal depends on the characteristics of the source or the waste to be treated. One of the up-and-coming and promising methods for selenium removal is the biological treatment that is both technologically feasible and economically efficient in meeting the mandated selenium levels. However, selection of any treatment process is very context and site-specific, depending on the required reduction from existing levels, as well as resource needs and resource availability at the site.

Additionally, this paper discussed and reviewed selenium issues at Alaskan mines and discharge sites. Some of the mines reported higher selenium in their discharge waters in early years (earlier than 2006), primarily due to the enrichment of selenium during processing of other metals. Red Dog Mine has been considered a significant source of selenium release; however, a potential water management

system using precipitation and flocculation methods to control selenium levels is being evaluated. The unusual decrease in selenium concentrations at Red Dog Mine, owing to the presence of SRB and gypsum in tailings, opens a new area of study to allow selenium treatment methods to be applied and duplicated at a commercial scale. Overall, continued research in selenium removal technologies will provide tools to the industries to successfully develop and expand economic initiatives while also allaying any environmental concerns in a cost-effective manner.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## Abbreviations

The following abbreviations are used in this manuscript:

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| ABMet | The Advanced Biological Metals Removal Process |
| ADEC | Alaska Department of Environmental Conservation |
| ADNR | Alaska Department of Natural Resources |
| EPA | Environmental Protection Agency |
| FBR | Fluidized Bed Reactor |
| MCL | Maximum contaminant level |
| RO | Reverse Osmosis |
| ZVI | Zero-Valent iron |

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