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TECHNOLOGIES AND POTENTIAL TECHNOLOGIES FOR REMOVING SELENIUM FROM PROCESS AND MINE WASTEWATER

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Abstract

An extensive review of the literature has been performed to identify appropriate technologies for the removal of selenium from a variety of wastewater. The identified treatments include technologies now being utilized and technologies that show good potential for being implemented in the near future. The technologies are briefly discussed in this paper. A more detailed discussion is available to the reader in a noted reference. The emphasis of this presentation is removal of selenium from mine waters.

Several technologies appear to hold promise for application to mine waters for removing selenium to the low $\mu\text{g/L}$ range, e.g., $<10 \mu\text{g/L}$. Success for achieving effective selenium removal will depend on the site-specific characteristics of the individual wastewater to be treated. Those technologies that are presently being used and those technologies that appear to hold promise for effective selenium removal include: ferrihydrite adsorption, HWFIX, emulsion liquid membranes, nanofiltration, tailored ion exchange, reductive cementation, and biological reduction.

Introduction

An extensive review of the literature has been performed to determine what technologies are presently being utilized, and what technologies may potentially be applicable, for the removal of selenium from industrial mine wastewater. The information presented in this paper emphasizes possible mine water treatment technologies. Detailed presentations of the review results are presented elsewhere¹. A summary of the review is presented in this paper.

Summary of Selenium Removal Technologies

A summary of treatment technologies that are applicable or may be applicable for selenium removal from wastewater is presented in Table 1. Because of the large number of publications on selenium only a very brief summary for each technology will be discussed in this presentation. Literature sources and detailed discussions for other technologies are available to the reader in the reference Issues Identification and Technology Prioritization Report-Selenium¹.

Table 1. Summary of Treatment Technologies for Removing Selenium from Solutions

Technology and Comments
<p>PRECIPITATION</p> <p><u>Selenate, Selenite</u>-Precipitation of selenates and selenites as a mine water treatment technology is ineffective because of their relatively high solubility as a function of pH.</p> <p><u>Selenide, Elemental Selenium</u>-The reduction of selenate and selenite species with the subsequent precipitation of metal selenides or elemental selenium appears to hold promise as a mine water treatment option.</p> <p>ADSORPTION</p> <p><u>Ferrihydrite</u>-Ferrihydrite precipitation has been extensively investigated. Selenium (IV) is effectively removed at pH<~8. This technology is not effective for Se(VI). Reduction of Se(VI) prior to adsorption is required. The presence of other aqueous species in the solution may influence the removal of Se(IV), i.e, the order of adsorption (at pH 7) has been shown to be phosphate>silicate=As(V)≡bicarbonate,carbonate≡citrate=Se(IV)≡molybdate≡oxalate>fluoride=Se(VI)≡sulfate.</p> <p>This is U.S. EPA=s BDAT for treating selenium bearing wastewaters. Long-term solids aging studies are recommended.</p> <p><u>Alumina</u>-Selenium (IV) adsorption is nearly complete at pH levels between 3-8. Aqueous silica adsorbs in preference to Se(IV) at pH 7 but is no problem at pH 4. Selenium (VI) adsorption by alumina is poor. Selenium (VI) adsorption drops off rapidly with increasing pH and is less than 50% at pH 7. Sulfate and carbonate adsorption significantly interferes with Se(VI) adsorption.</p> <p>Application of selenium adsorption by alumina may be a problem in gold heap leach effluents because of the presence of dissolved silica and, in some cases, the presence of cyanide. Alumina may be a viable adsorbent for some mine waters.</p> <p><u>Ferric Oxyhydroxide/Peat/Resins</u>-HW-FIX is a USBM development that shows good promise for Se(IV) removal. The adsorption is not as effective for Se(VI). This technology shows promise for application to mine waters.</p> <p><u>Activated Carbon</u>-Activated carbon adsorption is widely used in treatment of groundwater and as point-of-use treatment of drinking waters for organic adsorption. Activated carbon is ineffective for adsorbing selenium from mine waters.</p> <p>ION EXCHANGE AND MEMBRANE PROCESSES</p> <p><u>Ion Exchange</u>-IX is used for treatment of drinking waters and groundwaters for metals, arsenic and selenium removal. Selenium removal is accomplished by using a strong base anion ion exchange resin. Selenium (VI) is extracted much more effectively than Se(IV). The extraction of Se(VI) is decreased by sulfate.</p> <p>Tailored resins show good selectivity for selenium in the presence of sulfate but only laboratory studies have been performed. Further laboratory studies (on mine waters) are required.</p> <p>Liquid IX has been investigated on a pilot scale for treating gold heap leach solution effluents. The results were encouraging but the technology has been documented at only one site. Further laboratory and pilot test work should be conducted.</p>

Technology and Comments

Reverse Osmosis-RO is extensively used for removing inorganic contaminants from drinking and groundwater. Publications on industrial application to mine waters were not found. RO may require extensive pretreatment of mine waters to remove solids and to lower the concentration of total dissolved solids.

Emulsion Liquid Membranes-Pilot studies have shown that Se(VI) is extracted rapidly even in the presence of sulfate at all pH values >2. Selenium (IV) extraction is influenced by the presence of sulfate, i.e., the rate of extraction is decreased. Sulfate is extracted in preference to Se(IV) unless the pH is >9.5. This technology shows good potential for application to mine waters but requires further test work to answer questions concerning the stability of the emulsion in acidic, multicomponent solutions.

Nanofiltration-Nanofiltration appears to hold potential for treating some low metal containing selenium bearing mine waters. Nanofiltration has been used commercially for sulfate removal from a variety of waters. Documentation or application to mine waters were not found in the published literature. Nanofiltration technology shows good potential for application to mine waters but requires further test work to answer questions concerning the presence of high total dissolved solids loads, and the stability of the membranes in acidic multicomponent solutions.

REDUCTION PROCESSES

Ferrous Hydroxide-The U.S. Bureau of Reclamation has developed a process for treating selenium surface and agricultural waters. However, the generation of large volumes of iron sludge and the relatively high cost of reagents makes its application to mine waters questionable.

Iron-The successful use of iron as a reductant is based on the reduction of aqueous selenium species in the presence of copper ions. The elemental iron reduces both selenium and copper to produce a copper selenide on the iron surface.

Further test work is required to determine the applicable pH range.

Biological Reduction-Bacterial reduction of selenium aqueous species to elemental selenium has been shown to be a potential candidate for treating mine waters. The bacteria that appears to offer great promise is *P. Stutzeri* which can reduce both Se(IV) and Se(VI) species.

Test work was conducted on mine waters using two different bioprocessing approaches. *Pseudomonas* bacteria were grown on carbon surfaces by pretreating the surfaces with nutrients and biopolymers, i.e., a biofilm was formed on the carbon surfaces. A second approach was to extract enzymes from the *Pseudomonas* bacteria which was then coated onto carbon surfaces or impregnated in gel beads. A mine water containing 620 µg Se(VI)/L was treated in a single-stage aerobic bioreactor. The live biofilms produced effluent waters containing <10 µg Se/L for about nine months without breakthrough. The enzyme preparations also produced effluents containing < 10 µg Se/L with breakthrough occurring after four months of continuous operation.

Further test work was conducted to investigate the possibility of simultaneously removing cyanide and selenium from mine waters. The results showed that simultaneous destruction of cyanide (102 mg/L) and reduction of selenium (from 31.1 mg/L to <10µg/L) could be successfully accomplished.

CONVENTION WATER TREATMENT

Lime Softening/Ferric Coagulation/Filtration-The Best Available Technologies (BAT) for treating selenium bearing drinking and groundwaters are listed by EPA to include ferric coagulation-filtration. Application of these unit operations to mine waters was not found in the literature. The achievement of selenium removal to regulated discharge concentrations by these technologies is doubtful.

Adsorption Processes

A large number of investigations have focused on surface adsorption as a means of removing metals, arsenic, and selenium from aqueous phase solutions, e.g., adsorption by ferric hydroxides, aluminum hydroxides, alumina, activated carbon, clays, etc. Adsorption phenomena on ferric surfaces has been the emphasis of most of the investigations.

Ferrihydrite/Selenium-Ferrihydrite adsorption of selenium has been selected as the Best Demonstrated Available Technology (BDAT) for selenium removal from wastewater solutions by the U.S. EPA².

Many investigators have considered the adsorption of selenium on ferrihydrite surfaces³⁻²¹. The commonality between these studies is that:

- X Se(IV) is adsorbed much more effectively than Se(VI);
- X Se(IV) adsorption is a function of type of oxyhydroxide present (amorphous ferrihydrite is best, crystalline FeOOH is considerably less effective);
- X The initial concentration of Se(IV) in solution is very important (the higher the Se(IV) concentration the more effective the adsorption);
- X The best pH for effective Se(IV) adsorption is 4-6 (85-90% removal), adsorption decreases slowly until about 7 (80-85% removal), then decreases drastically to about (20-40% removal);
- X Se(VI) adsorption is poor (<10% removal) at all pH levels;
- X Se(VI) adsorption may be strongly effected by the presence of sulfate, bicarbonate, and aqueous silica species.

Merrill, et al¹⁵ and EPRI^{8,22} found that the optimum pH for Se(IV) removal was 6.5 and optimum iron dosage was 14 mg/L for a water initially containing 40-60 µg Se/L. The effluent selenium concentration resulting from the treatment of 33 gallons/min in a continuous pilot facility was < 10 µg/L. WSPA¹⁸ found fairly similar results for the treatment of a petroleum biotreater effluent (similar to gold heap leach effluent solutions, i.e., they contain cyanide as well as selenium and sulfate), e.g., after solution oxidation to destroy any selenocyanate species the optimal pH was 5-7; optimal ferric chloride dosage was 40-80 mg/L. The process treatment created 2.1-3.1 kg sludge/kg iron added.

Merrill, et al¹⁵ estimated the cost of processing 26 million gallons/day (for arsenic, heavy metals and selenium removal) would be 35¢/1000 gallons. The estimate is based on a flowsheet consisting of ferric chloride addition to form ferrihydrite, rapid mixing, polymer addition for agglomeration, clarification, sludge thickening and dewatering, and disposal of dewatered sludge in a municipal landfill. They suggest that the estimated processing cost is within ±30%. Updating this cost figure using the M&S index ratio gives a present day processing cost of 50¢±15¢/1000 gallons.

Parida, et al²³ investigated the adsorption of Se(IV) onto various ferric oxyhydroxide surfaces. They found that amorphous ferrihydrite adsorbed significantly more Se(IV) than the other phases. The order of adsorption was ferrihydrite (225 m²/g)>δ-FeOOH (117 m²/g)>γ-FeOOH (61.1 m²/g)>β-FeOOH (77.8 m²/g)>α-FeOOH (70.8 m²/g), e.g., at 20 mg Se(IV)/L, ferrihydrite was loaded to 48 mg Se(IV)/g; α-FeOOH was loaded to 10 mg Se(IV)/g. Essentially complete removal of Se(IV) from a 20 mg Se(IV)/L solution was attained by using 1.2 g ferrihydrite/L at a pH of 3. Whereas, α-FeOOH removed only about 25% of the Se(IV) under the same conditions. Adsorption was a relatively strong function of solution pH, i.e., adsorption fell rapidly as the pH was increased from 3.5 to 9.5. There was essentially no adsorption at pH 9.5.

Balistreri and Chao³ investigated the role of the presence of other anions on the adsorption of selenium. Their results are in agreement with the conclusions stated above. However, they found that if other anions are present they may preferentially adsorb to the ferric oxyhydroxide surface. The order of adsorption at pH 7 was found to be phosphate>silicate=As(V)>bicarbonate/carbonate>citrate=Se(IV)>molybdate>oxalate>fluoride=Se(VI)>sulfate.

Hayes, et al⁹ studied the adsorption of selenium oxyanions on α-FeOOH surfaces. Their conclusion was that Se(IV) adsorbs in a bidentate manner (inner-sphere adsorption which is much stronger than outer-sphere adsorption). Selenium (VI) adsorbs as an outer-sphere hydrated complex which is why it can be easily replaced by other solution anions such as sulfate. This conclusion has also been confirmed by others^{4,9,24}.

The question is always whether the wasteform product will be stable when stored outdoors in storage ponds exposed to air. It appears that there is, at least, a good possibility that such storage is appropriate. Long term aging stability, however, needs to be experimentally demonstrated. The question that still remains as to what happens when the amorphous wasteform crystallizes to the more thermodynamically stable phases of goethite (FeOOH) or hematite (Fe₂O₃). Large decreases in surface area will result.

Aluminum Hydroxide/Alumina-Activated alumina has been studied for selenium adsorption by several investigators²⁵⁻²⁹. Trusell, et al²⁵ investigated the adsorption of Se(IV) and Se(VI) on activated alumina. Selenium (IV) was effectively adsorbed over the pH range 3-7 (for concentrations of 100-200 µg Se/L, one hour contact time. The loading capacity was 90 mg Se/L of alumina. Selenium (VI) adsorption was much less effective (loading capacity was 7 mg Se/L of alumina). They demonstrated that the order of selectivity for anions was $\text{OH}^{-1} > \text{H}_2\text{PO}_4^{-1} > \text{F}^{-1} > \text{H}_2\text{AsO}_4^{-1} > \text{Se(IV)}$ (from batch studies) and that the order of other less adsorbed anions was $\text{SO}_4^{-2} > \text{Se(VI)} > \text{HCO}_3^{-1} > \text{Cl}^{-1} > \text{NO}_3^{-1} > \text{H}_3\text{AsO}_3^0$ (from column tests). Sulfate and bicarbonate had no effect on Se(IV) but greatly affected Se(VI) adsorption.

Trusell³⁰ demonstrated alumina regeneration using 0.5% NaOH. A cost estimate was presented for treating 1 MGD containing 100 µg Se/L. The cost estimate was 23¢/1000 gallons for Se(IV) and 78¢/1000 gallons for Se(VI). This estimated cost when updated (by using the current 1999 M&S index) is 26¢/1000 gallons for Se(IV); 88¢/1000 gallons for Se(VI). Yaun²⁶ is in agreement with the Trusell results. He, however, demonstrated successful Se(VI) removal by reducing the pH of the solution to four or less. He also demonstrated that alumina could be regenerated repeatedly without loss of adsorptive power; that regeneration was effective using 0.25% NaOH.

The above studies were conducted on groundwaters not on mine waters. Investigators^{27,28,31} have applied alumina adsorption to an actual gold mine effluent (FMC Gold=s Paradise Peak Mine in Nevada). They demonstrated that selenium recovery is not very effective if aqueous silicon species are present. Mine waters that have appreciable silica present cannot be effectively treated by alumina adsorption. The alumina adsorption capacities for selenium and silica were determined to be 5.6 mg Se/ft³ alumina, 103 mg Si/ft³ alumina, respectively. In the absence of silica the alumina adsorption capacity for selenium was 24.4 mg/ft³ alumina.

Activated Carbon-Activated carbon adsorption is the most universally used technique to remove organic contamination from drinking water point-of-use supplies³². It is widely used in treatment of point-of-use waters for metals recovery. Activated carbon adsorption of selenium, either Se(IV) or Se(VI), is completely ineffective, e.g., Se(IV) or Se(VI) at concentrations from 30-100 µg/L showed < 4% removal using dosages of activated carbon up to 100 mg/L³³.

Other Absorbents-The USBM has performed studies utilizing peat impregnated with ferric oxyhydroxide³⁴⁻³⁶. Ferric oxyhydroxide/peat mixtures were formed into beads of polysulfone resin (designated HW-FIX). Loadings of 1,700 mg Se/L of resin were demonstrated on synthetic solutions containing 4800 µg Se(IV)/L, 4500 µg Se(VI)/L. The treated effluent contained from 10-20 µg/L Se(IV), and approximately 1000 µg/L Se(VI). The beads were stripped with 10 g/L NaOH. The strip solution was treated with iron to precipitate elemental selenium, thereby producing only a small amount of disposable selenium bearing waste.

Adutwum³⁷ investigated a process for adsorbing selenium onto a lanthanum oxide or lanthanum oxide/alumina substrates. The adsorption is effective for both Se(IV) and Se(VI). The loading capacity of the lanthanum oxide is 30-40 mg Se/g of oxide. Residence times are in the range 5-30 minutes. Sulfate is an interfering ion. If it is present in a concentration >1000 mg/L then the sulfate should be removed prior to exposure to the lanthanum oxide. The applicable pH range is 3-10. Cost estimates have were not presented.

Conventional Water Treatment

Ferric sulfate and alum coagulation-pilot scale studies (using EPA=s 2 gallon/min plant) for treating waters containing 30-100 µg Se/L) have been conducted³⁸. The conclusions of the study were: ferric sulfate and alum coagulation (at 25 mg/L) can achieve EPA=s selenium maximum concentration levels (MCL) when the Se(IV) concentration is only slightly above the MCL and the pH of the water is 7 or less. However, the Best Available Technologies (BAT) for treating selenium bearing waters are still listed by EPA to include ferric coagulation-filtration (removals=40-80% for Se(IV); <40% for Se(VI)) and lime softening (removals=40-80% for Se(IV); <40% for Se(VI)). Alumina adsorption (removals>80%), reverse osmosis (removals>80%) and ion exchange (removals>80%) perform better and are also listed as BATs^{39,40}.

Conventional water treatment technologies of ferric sulfate and alum coagulation are not viewed by the authors of this review as viable processes from treating mine waters that contain dissolved selenium. However, Patterson⁴¹ summarized full scale selenium removal from coal mining, coal preparation, metallic ore mining and milling by conventional sedimentation processing. The predominate form of selenium in these waters is particulate. Sedimentation removals have been shown to be greater than 90% for selenium concentrations >20 µg/L.

Ion Exchange (IX)

IX is used widely for treating drinking waters, dilute metal bearing solutions, wastewaters, and groundwaters. However, its application for removing selenium has some successes and some failures^{42,43}. Please see reference 1 for detailed discussions.

The Western States Petroleum Association¹⁸ investigated the use of IX (strong base anion resins) for treating refinery wastewaters (sourwater and biotreater effluent, containing 11-4,870 µgSe/L). Their conclusions included:

- X IX is very inefficient for selenium because other anionic species may load in preference to the selenium, especially sulfate. Selenium loaded well but after 200-600 bed volumes sulfate displaced the selenium. High sulfur and high total dissolved solids reduce the effectiveness of selenium extraction. Bed volumes to breakthrough of selenium ranged from 50 to 750.
- X IX is not able to routinely produce effluents with <50 µg/L total selenium.
- X Efforts to identify selective resins were unsuccessful.

Tailored chelating polymer resins have been investigated⁴⁴ for extracting selenium in the presence of high concentrations of sulfate. The resins investigated included Dow 2N (loaded with copper, 1.7 meq/g) and IRA-900 (no copper loading). The resins were evaluated for extraction in a solution containing 250 mg sulfate/L. The selectivity sequence at pH 9.5 was $\text{SeO}_4^{2-} > \text{SO}_4^{2-} > \text{SeO}_3^{2-} > \text{NO}_3^{-1} > \text{Cl}^{-1}$. Resin loading capacities and cost evaluations were not presented by the authors.

Virnig and Weerts⁴⁵ considered the use of liquid ion exchange as a way to treat spent gold heap leach effluent. The ion exchange reagent was CyanoMet R, a proprietary reagent. The reagent extracted anion complexes including gold, silver, nickel, copper, zinc, and selenium. Laboratory studies were conducted. The extracting reagent contained 30 weight percent CyanoMet R. There were three stages of extraction followed by two stages of strip (4 volume percent NaOH). The selenium removal from the influent feed (11 mg Se/L) was very good, e.g., the final raffinate solution contained 70 µg Se/L. Pilot studies were conducted at a Nevada gold mine. The feed rate was 1 gallon/minute, the reagent consisted of 15 % CyanoMet R in kerosene. The selenium removal from the influent feed (1.7 mg Se/L) was very good, e.g., the final raffinate solution contained 300 µg Se/L for the first pass; 36 µg Se/L for the final second pass.

Membrane Separations

Reverse Osmosis-RO is listed by EPA as one of the BATs for selenium removal^{39,40}, i.e., the removal effectiveness is quoted as being >80% irregardless of valence state. Reverse osmosis/membrane ultrafiltration processes require that the solutions to be treated contain very dilute concentration of solids. Therefore, pretreatments are normally required in order not to foul the separating membrane. Whereas, reverse osmosis is readily applicable to drinking waters it is doubtful that these separation techniques are applicable to acid mine waters except as a final polishing step after rather extensive pretreatment.

Emulsion Liquid Membranes- ELM technology is presently being developed by TDA Research for selenium removal⁴⁶. This technology is based on the transfer of selenium from the aqueous phase to a liquid extractant phase contained inside droplets of organic. The exchange process is similar to that which occurs during conventional solvent extraction except an aqueous strip phase (0.1-5 µm diam) is present as an emulsion within organic droplets (0.1-2 mm diam). The organic droplets are, in turn, dispersed throughout the bulk aqueous phase. Selenium is transferred from the bulk wastewater to the organic phase. Internal within the organic phase the selenium is transferred to the aqueous strip solution. The organic emulsion is subsequently recovered from the bulk wastewater

phase and the loaded aqueous strip solution is separated from the organic. Laboratory studies have shown that Se(VI) is extracted rapidly even in the presence of sulfate at all pH values >2. Pilot studies at pH 10.5 have shown that Se(VI) (at 1 mg/L) can be reduced to below 1 µg/L in 2 min.; that Se(IV) can be reduced to below 1 µg/L in 5 min.. Sulfate is extracted in preference to Se(IV) unless the pH is >9.5. In spite of this, extraction of Se(IV) in the presence of up to 1 mg sulfate/L at pH 10.5 was very effective. The concentration of selenium in the strip phase shows an enrichment factor of ~40.

Nanofiltration-Nanofiltration appears to be a technology on the horizon for treating some low metal-containing selenium bearing mine waters. Nanofiltration has been used commercially for sulfate removal from seawater prior to injection into oil field reservoirs, for sulfate removal from concentrated brines, for organic compound removal from paper plant effluents, and for organic compound removal from groundwater. Publications demonstrating the application of nanofiltration to mine waters were not found but the technology has been applied to agricultural drainage water high in Se(VI), sulfate and total dissolved solids taken from San Joaquin Valley

Nanofiltration is based the use of membranes constructed of a porous inert layer of polysulfone and a negatively charged hydrophobic rejection layer (generally polyamide). These membranes reject multivalence anions, including sulfate. The technology is similar to reverse osmosis but the nanofiltration system is operated at pressures that are about one-third of that required for reverse osmosis. Kharaka⁴⁷ demonstrated >95% removal of selenium for waters (pH 6.3-8.5) containing 24-308 µg Se(VI)/L; 2,080-26,100 µg sulfate/L; and 780-38,800 µg TDS/L. Similar recoveries were demonstrated for Se(VI) concentrations up to ~1000 µg/L.

Reduction Processes

Various reductants can be used to produce elemental selenium or metal selenides. Reductants such as ferrous hydroxide, iron, zinc, aluminum have been proposed.

Ferrous Hydroxide-Murphy⁵² patented a process for the Bureau of Reclamation (BOF) for treating selenium bearing waters. The process consisted of reducing selenium species to elemental selenium by using ferrous hydroxide as the reducing agent. The reduction is accomplished at a pH of 8.8-9.2 under reducing conditions. Magnetite and/or maghemite formed. Interferences in the process are nitrate, dissolved oxygen (DO), and bicarbonate. Costs were estimated⁵³ at 31¢/1000 gallons for low nitrate, DO, and bicarbonate. For high nitrate, DO, bicarbonate the costs were estimated to be 58¢/1000 gallons. These costs when updated using the M&S index ratio to 1999 are 37¢/1000 gallons (for the low nitrate, DO, and bicarbonate treatment) and 68¢/1000 gallons (for the high nitrate, DO, and bicarbonate treatment).

Lien, et al⁵⁴ applied the BOR recipe to a silver tailing mine water (4 mg Se(VI)/L, pH 9). They used ferrous sulfate as the source of iron. They found that in order to attain a selenium effluence concentration of less than 100 µg/L, 25 g/L ferrous sulfate was required. The cost for the reagent alone would be about \$5-\$15/1000 gallons of water treated. Also, large quantities of iron bearing sludge would have to be handled and treated for disposal.

Iron Reductant-McGrew, et al⁵⁵ have developed a selenium recovery process using iron powder as the reductant. McGrew notes that mine waters are usually extremely high in sulfate compared to selenium (and compared to drinking waters and groundwaters), e.g., the ratios are often of the order 10⁸ sulfate/selenium. Therefore, a process is required that is not influenced by sulfate. The success of this process compared to other proposed iron reduction processes is that the rate of Se(VI) reduction by iron to selenium is catalyzed by the presence of copper.

McGrew demonstrated their process on a gold mine heap leach effluent (Brewer Pit water, 257 µg Se/L). The water was tested (pH 3-3.5) using 1 to 10 g Fe/L, and copper levels between 10 and 81 mg/L. The optimum conditions resulted in selenium concentrations less than detection limit (<5 µg/L). Residence times of 10-20 minutes were required for a copper content of 10 mg/L at an iron dose of 10 g/L. The consumption of iron was ~3 pounds/1000 gallons. The product could be further treated for selenium recovery. Simple conventional hydrometallurgical equipment would be required, i.e., mix chambers, dewatering settlers, and clarifiers. This process has been applied at the Brewer mine since 1994.

Biological Processes

There are several patents and studies in the literature that propose potential biological processes for removing selenium⁵⁶⁻⁶⁹.

Pseudomonas stutzeri bacteria/immobilized alginate enzymes-Adams, et al⁵⁶ have investigated selenium removal (on a bench scale) from agricultural and mining wastewaters by bacteria and immobilized alginate enzymes. *Pseudomonas stutzeri* isolates have been identified and grown from mining wastes. *Pseudomonas stutzeri* are known to reduce selenium from solutions under aerobic conditions. The authors treated solutions containing up to 1000 mg/L of Se(VI) and 285 mg/L sulfate over a wide range of pH. Selenium was removed from mine waters containing 620 µg/L to <10 µg/L in an 18 hr residence time. Enzymatic bioremediation processes have been used to treat mining solutions containing 600 µg/L to 30,000 µg/L selenium. Continuous selenium removal to <10 µg/L has been demonstrated for up to four month periods.

A *P. stutzeri* isolate that was acclimated to mining process waters was capable of removing 33 mg/L Se(VI) from mining waters containing 285 mg/L sulfate in a bioreactor in residence times as short as six hours. Test work was conducted on mine waters using two different bioprocessing approaches. *Pseudomonas* bacteria were grown on carbon surfaces by pretreating the surfaces with nutrients and biopolymers, i.e., a biofilm was formed on the carbon surfaces. A second approach was to extract enzymes from the *Pseudomonas* bacteria which was then coated onto carbon surfaces or impregnated in gel beads. A mine water containing 620 µg Se(VI)/L was treated in a single-stage aerobic bioreactor for a residence time of 18 hours. The live biofilms produced effluent waters containing <10 µg Se/L for about nine months without breakthrough. The enzyme preparations also produced effluents containing < 10 µg/L with breakthrough occurring after four months of continuous operation. Further test work using enzymes showed simultaneous destruction of cyanide. The above described bioprocessing techniques were also successful in removing nitrate from 53 mg/L to <0.1 mg/L at a rate of >3.3 mg/L/hr.

Koren, et al⁵⁷ also investigated the use of *Pseudomonas stutzeri* for selenium specie reduction to elemental selenium. The authors demonstrated that bacteria could survive and operate effectively in Se(VI) solutions containing over 3500 mg Se/L. The rate of reduction was ~32 mg Se/L/hr. The bacteria could also survive and operate effectively in Se(IV) solutions to approximately 1500 mg/L, then the rate of reduction dropped dramatically. Maximum reduction rates occurred in the pH range 7-9.5; optimal temperature was 25-35°C. The presence of sulfate, nitrate, and nitrite ions had no harmful effect on either Se(VI) or Se(IV) reduction.

Bacterial inoculum-Altringer, et al^{58,59} investigated both chemical and biological treatment of three mine waters, e.g., tailings pond water from a silver mine (4.2 mg Se/L, pH 8.9), barren solution from a gold heap leach operation (30 mg Se/L, pH 8.4), and pregnant solution from a gold heap leach operation (1.7 mg Se/L, pH 8.8). Selenium reducing bacteria were not found in the mine waters so bacteria from the Kesterson reservoir (San Joaquin Valley, CA) were separated and cultured (*Pseudomonadaceas* and *Enterobacteriaceae* families) in mine waters. The waters were first treated by oxidation to destroy cyanide (to <3 mg/L) and to oxidize the selenium to Se(VI). Solution pH levels were adjusted to ~8.5. The bacterial inoculum was added to the waters to produce 10⁹ cells/mL. The tests were run in 2.1 L solutions, 25°C, 350 rpm stirring, 5 g/L peptone nutrient, and 40 cc/min N₂, 10 cc/min air (this gave a solution oxygen content of 2 mg/L). The effluents from the tests contained 160 to 1000 µg Se/L.

Clostridium Bacteria-Kauffman, et al⁶⁰ investigated microbiological treatment of uranium mine waters for selenium removal. Pilot scale column tests were performed for selenium and sulfate removal using *clostridium* and *desulfovibrio* bacteria containing local soils, respectively. Selenium(VI) removal from 1.6 mg/L to less than 50 µg/L was achieved in both laboratory and field test columns. Selenium break through (100-175 L/m²/day) never occurred even after 7-months of continuous operation. Selenium was present in the column material in the elemental form.

Biological Anaerobic Reactors-Ergas, et al⁶¹ demonstrated on a laboratory scale the successful utilization of anaerobic bacterial reactors for selenium removal from agricultural waters. The test work utilized an anaerobic biological bacterial growth reactor. The Se(VI) was reduced to elemental selenium. Owens, et al⁶² followed up this work in a pilot-scale study. Water from agricultural drainage sites (pH 8) in California was used for the study. The anaerobic reactors used

in the study were two parallel 50 gallon tanks, each tank was fed the same water but a different nutrient source (either acetate or methanol). The results showed that Se(VI) was reduced through a two step sequence, i.e., Se(VI) was reduced to Se(IV) then to Se(O) in the anaerobic reactors. Influent selenium concentration was 453 $\mu\text{g Se(VI)/L}$. At the end of a 24-hr cycle the average concentration of selenium (at a pH of 8) was 280 $\mu\text{g/L}$ (for the acetate reactor) and 265 $\mu\text{g/L}$ (for the methanol reactor). Filtering of the product water through 0.22 μm filters resulted in a solution selenium content of 45 $\mu\text{g/L}$ (for the acetate reactor) and 65 $\mu\text{g/L}$ (for the methanol reactor). Nitrate was removed completely by both reactors.

Oremland⁶³⁻⁶⁶ patented a process for treating selenium and nitrate bearing solutions. His process can also handle sulfate solutions. The proposed process includes an aerobic bioreactor (first stage) to remove nitrate. Nitrate has been shown to inhibit the reduction of Se(VI) at concentrations >0.5 millimoles nitrate/L. Nitrate can be removed to below 1 millimole/L by aerobic bioreactor treatment. The nitrate free water can then be treated in a second stage anaerobic reactor (pH 7-10) using selenium respiring microorganisms. The biomass from the first stage can be utilized in the second stage as the nutrient source for the microorganisms. A further development was to treat sulfate bearing waters in a bioreactor containing sulfate reducing bacteria. The product from this reactor was aqueous hydrogen sulfide (1-3 millimoles/L) which can then be fed into the selenium removal stage to further reduce the solution potential so that a better yield of elemental selenium can be obtained. The selenium concentration in the product water should be within the range 1-10 $\mu\text{g/L}$.

Summary

Several technologies appear to hold promise for application to mine waters for removing selenium to the low $\mu\text{g/L}$ range, e.g., <10 $\mu\text{g/L}$. Success for achieving effective selenium removal will depend on the site-specific characteristics of the individual wastewater to be treated. Those technologies that appear to hold promise for effective selenium removal include: ferrihydrite adsorption, HWFIX, emulsion liquid membranes, nanofiltration, iron reduction and biological reduction.

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