



1057 Roberts Creek Road, Unit 21  
PO Box 193  
Roberts Creek, B.C. V0N 2W0  
604 885-0568 phone  
604 885-0598 fax

# Microbial Technologies, Inc.



## Treatment Options for Selenium at Northern Mines

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Contact: Dr André Sobolewski  
[andre@microbialtech.com](mailto:andre@microbialtech.com)

## **Abstract**

The mitigation of selenium in mine water is a recent concerns arising for metal mines in Northern Canada and Alaska. In this presentation, technologies developed to treat selenium-contaminated mine water are reviewed. These include physically-based technologies, chemically-based and biologically-based technologies. These technologies are evaluated on the basis of treatment performance for selenate and selenite, operational constraints (including performance in cold climates), and cost-effectiveness.

The technologies varied considerably with regards to their ability to remove selenate from solution cost-effectively. Treatment costs ranged from USD\$1/1,000 gallons for in-situ treatment to over \$10/1,000 gallons for reverse osmosis and iron precipitation. Some technologies are straightforward with simple process flowsheets (e.g., in-situ treatment or constructed wetlands), whereas others are more complex (e.g., iron precipitation). A few technologies require that residues from treatment be managed, such as brines or wash solutions for membrane filtration, or sludges from iron precipitation.

In-situ treatment and biological treatment plants stand out from the others as being best suited for treatment in cold climates. Four other technologies might possibly be appropriate if favoured by some site-specific factors: reverse osmosis, nanofiltration, the Biopass/passive treatment systems and treatment wetlands. The other technologies are deemed too underdeveloped or inappropriate for application in cold climates.

## Introduction

Concerns about selenium (Se) toxicity were galvanized by its ecotoxicological effects observed in the Kesterson Reservoir in California. Field studies documented dramatic losses in migratory bird populations and specifically attributed to Se the decline in reproduction of waterfowl, shorebirds and other aquatic birds (Ohlendorf, 1989). One other case of Se ecotoxicity had already been documented earlier at Belews Lake, and more reservoirs exhibiting impacts from Se were identified later on, indicating that the Kesterson Reservoir incident was not isolated.

Selenium ecotoxicity is observed from very low input concentrations. Consequently, very stringent discharge criteria have been set for effluents containing Se. In Canada, the guidelines recommended by the Canadian Council for the Ministers of the Environment (CCME Guidelines) for the protection of freshwater aquatic life have been set at 1 µg/L. The proposed (Draft) US EPA criteria (US EPA, 2004) are more complex, but equally stringent:

1. Concentration of selenium in whole-body fish tissue not to exceed 7.91 µg/g dw (dry weight)
2. The 24-hour average concentration of total recoverable (dissolved and particulate) selenium in freshwater is to seldom exceed (e.g., not more than once in three years)  
 $\exp(0.5812[\ln(\text{sulfate})]+3.357)$  for selenate

These criteria have spurred the development of treatment technologies producing effluents that can meet these low discharge limits.

In the North, elevated Se has been found in effluent of the Brewery Creek Mine (and possibly Red Dog), and is associated with the gold deposit at the Wolverine project. Typically, mine effluents also contain other contaminants, such as ammonium, arsenic, or cyanide. The choice of a treatment technology may be governed by these other contaminants as much as by Se.

Se removal from solution is largely determined by its chemistry. To that end, the chemistry of Se will first be briefly reviewed. Different technologies available for treatment will next be reviewed. Although several promising technologies are currently being developed, the review focusses on technologies that are tested or at advanced stages of development. These are divided into physical, chemical, and biologically-based treatment technologies.

Case studies will be presented throughout these sections, and they will provide a basis for evaluating the different technologies. They will be compared using several criteria, among others:

- Achievable discharge concentrations,
- Cost-effectiveness,
- Operational constraints,
- Operational experience, reliability of the technology,
- Post-treatment management of residues.

These most promising candidates for use in the North will then be identified.

## Se Chemistry

Se speciation is largely determined by reduction/oxidation (redox) chemistry. This is especially important because Se oxyanions (selenite: Se(IV) and selenate: Se(VI)) are soluble, while the reduced forms (elemental selenium: Se<sup>0</sup> and selenide: Se(II-)) are insoluble. It is the solubility of the oxidized forms that allows for their mobility in the environment and their biological uptake. Speciation in soil solution is governed by various physico-chemical factors expressed in terms of pH, dissociation constants, solubility products, and oxidation-reduction potentials (Geering *et al.*, 1968).

As with sulphur compounds, selenite is much more reactive than selenate and is more easily reduced to elemental Se. Most selenite salts are less soluble than the corresponding selenates. The extremely low solubility of ferric selenite Fe<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub> ( $K_s = 2.0 \pm 1.7 \times 10^{-31}$ ), and of the basic ferric selenite Fe<sub>2</sub>(OH)<sub>4</sub>SeO<sub>3</sub> ( $K_s = 10^{-61.7}$ ), is important to the environmental cycling of selenium, as well as providing a basis for treatment (Clifford *et al.* 1986). Selenite adsorbs to surfaces far more than selenate. Sorption can be onto detritus, clays, Fe- and Mn-oxyhydroxides, or onto soils, and each is pH-dependent (Masschelyn and Patrick, 1993). It forms stable ferric oxide complexes with even lower solubilities than the ferric selenites. Under certain conditions, selenite (in contrast to selenate) seems to be completely adsorbed in high amounts by ferric hydroxide and, to a lesser extent, by aluminum hydroxide (Faust and Aly, 1981).

The transformation of selenate to selenite occurs slowly in the environment because the activation energy for this reaction is very high. **The feasibility and/or economics of different treatment systems often revolves around this fact.** Typically, chemically-based treatment processes require an initial reduction of selenate (stable) to selenite (reactive) using strong reductants (e.g., zinc powder). In contrast, microbes catalyze this reduction at ambient conditions, a strength of biologically-based processes.

As redox conditions change, reduced compounds can become sources of soluble selenium. Oxidation of elemental selenium and Se-containing pyrite was credited as a source of increased soluble Se concentrations in Kesterson Reservoir sediment suspensions (Masschelyn *et al.*, 1990). Similarly, the continued release of selenium in the British Columbia and Wyoming coal fields, and in the Idaho phosphate region, has been shown to arise from the oxidation of Se-containing pyrite (Bond, 2000; Lussier, 2002). This suggests that selenium release may persist for decades, as long as the sulphide minerals are exposed to the atmosphere and allowed to weather.

Selenium also exists in organic and volatile forms, the latter providing a means for removing Se from the environment. Dimethyl selenide (DMSe, (CH<sub>3</sub>)<sub>2</sub>Se) and dimethyl diselenide (DMDS, (CH<sub>3</sub>)<sub>2</sub>Se<sub>2</sub>) are two volatile species of Se. In natural waters, the production of DMSe involves biological and non-biological processes. Se volatilization in plants appears to be a detoxification mechanism and is correlated with tissue Se concentration. Volatilization rates of Se from soils and plants are affected by temperature, moisture, time, season, concentration of soluble Se, and microbiological activity.

Other species can also be found, including hydrogen selenite, cyano-selenium species, etc. The latter can be problematic in resisting treatment. However, they are only found in special circumstances and are not routinely analyzed.

The toxicity of selenium arises because of its chemical similarity to sulphur. Se will substitute for sulphur in the amino acids cysteine and methionine, and these seleno-amino acids can be incorporated into proteins. However, difference in chemistry between the seleno-amino acids and the normal amino acids will produce abnormal or non-functional proteins, resulting in toxicological effects.

## Se Treatment

Many different processes have been examined for the removal of selenium from contaminated surface waters, but few engineered solutions have been successful on a commercial scale. The most widely used approach in the past involved chemical co-precipitation with iron salts. However, this is only effective with selenite and it will not consistently decrease Se concentrations to low concentrations. Recent advances in membrane technology and biological processes have brought a new generation of treatment systems. These various systems, divided into physical, chemical, and biological processes (Table 1), are reviewed below.

**Table 1. Types of treatment systems available for selenium.**

Physical	Chemical	Biological
Reverse Osmosis	Zinc or iron reduction	Volatilization
Nanofiltration	Iron precipitation	Biological treatment plant
Deep Injection/ Evaporation		“Passive system”, e.g., Biopass, “In-situ” treatment
		Treatment wetland

### Physical

Physical methods used for selenium removal include membrane filtration and ion exchange (electrostatic interactions) methods. However, ion exchange is only effective on selenite and rarely produces compliant water. In contrast, membrane filtration does not discriminate between selenate and selenite and can produce compliant water.

Adsorption onto activated carbon has not proven effective for selenium removal, at least in achieving low concentrations (<10 µg/L).

### Membrane Filtration

Reverse osmosis (RO) and nanofiltration are two membrane filtration methods for treating contaminated water. RO is a widely used and tested technology, whereas nanofiltration is relatively new. Both technologies use a membrane that is semi-permeable, allowing the fluid that is being purified to pass through it, while rejecting the contaminants that remain. The membrane for nanofiltration is different from that used in RO, in being charged and having a hydrophobic reject layer, selectively rejecting divalent salts while retaining monovalent salts.

Membrane filtration requires a driving force to push the fluid through the membrane, and the most common force is pressure from a pump. The higher the pressure, the larger the driving force. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases. The pressure can reach 1,000 psi, and this requirement constitutes a high proportion of the operating cost. One advantage of nanofiltration is that it operates at lower pressures, thereby reducing operating costs.

Their ability to meet acceptable discharge criteria depends on the characteristics of the water to be treated. It is generally agreed that complex or hard water cannot be treated to below 10 ppb. Such waters require water softening as pre-treatment, for treatment effectiveness and to prevent excessive membrane fouling.

There are problems inherently associated with these technologies. Fundamentally, treatment is extended until constituents of concern (e.g., Se) reach the desired final concentrations. As solutes are being concentrated, some salts initially present at high concentrations may crystallize, thereby impairing function or damaging membranes. This is particularly true for hard waters containing high calcium and magnesium

concentrations. In general, membrane life is expected to be 2-3 years, depending on the Total Dissolved Solids (TDS) of the water being treated. In addition, the concentrated brine containing the rejected contaminant(s) must be dealt with safely and cost-effectively.

Treatment costs are high, which has limited application of this technology at mines. Depending on necessary pre- and post-treatment requirements, operating costs can range from USD\$4.7-71/1,000 gallon, with a median around USD\$10-15/1,000 gallon. Capital costs can exceed USD\$1 million for the RO unit alone, depending on volumes being treated.

At Lac Mineral's (now Barrick) Richmond Hill Mine, reverse osmosis was selected to treat mine water that is incompletely treated by iron precipitation (see below). The latter decreases Se concentrations from over 100 ppb to 12-22 ppb, whereas RO decreases it further to approximately 2 ppb. The RO unit is operated at 250 psi and up, which contributes substantially to the operating cost. Flows of 200 gpm are fed to the RO unit, and it produces a permeate at 100 gpm and a reject stream at 100 gpm. This brine, which is a Se concentrate, is cycled back to the iron treatment circuit. Selenium is produced from 52 acres (21 hectares) of leach pads, and water treatment is expected to be required for at least 50 years.

A filtration pre-treatment is necessary to remove TSS. In addition, the operator is currently evaluating the need to remove calcium in a softening plant. Calcium concentrations in the feed have gradually increased to the present 450 ppm, causing gypsum to be deposited on membranes as salts become concentrated. The cost of this additional softening plant is compared against that of the shortened membrane life, which is presently replaced every 1-2 years at USD\$30,000, instead of the normal 3 years.

During winter operation, water is heated to 15 °C to prevent the cold-induced salt crystallization. The heating cost is approximately USD\$5,500/week, and depends on the weather and propane costs.

The capital costs include purchase of a used RO unit at USD\$750,000 (a new unit with the same capacity is approximately \$1.2 million) and a multimedia pre-filtration unit at \$200,000. Overall monthly operating costs are \$50,000, or \$10/1,000 gallon when the RO unit operates without trouble. The above issues are presently increasing treatment costs to \$18/1,000 gallon. Some of these problems stem from changing water chemistry, some are caused by algal growth.

Nanofiltration is potentially less expensive than RO, due to its more selective nature and the lower pressures under which it operates. There are no examples of mines currently using this technology, although it is being evaluated at some sites.

The same issues of membrane fouling must be considered: pre-treatment for high TDS, addition of anti-scalants, anti-bacterial agents and Total Suspended Solids (TSS) removal may be necessary. These can add 10-20% to the operating cost of treatment.

Capital costs for a single-stage filtration unit are quoted at USD\$2,000/gpm feed: a plant treating 500 gpm would cost \$1 million<sup>1</sup>. Additional pre-treatment may be 50% of the treatment plant cost, ranging from \$300 - 1,000/gpm feed. Operating costs are quoted at approximately \$0.50-0.60/1,000 gallons for a nanofiltration unit, with an additional \$0.10-0.15/1,000 gallons for additional pre-treatment. Additional maintenance costs include changing membranes every 2-3 years. Thus, nanofiltration promises to be less expensive than RO, but these predicted costs remain to be confirmed by experience.

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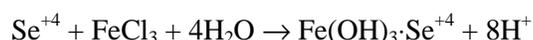
<sup>1</sup> J. Lombardi. Harrisson-Western, Denver, CO. Personal communication.

## Chemical

Several chemically-based treatment processes have been investigated, but only iron co-precipitation has met with success on a commercial scale. Precipitation with activated alumina has not met with success, though it has been tested extensively. Precipitation on lanthanum oxides looks promising, but has not yet been tried beyond the laboratory.

## Iron Precipitation

Ferrihydrite precipitation with concurrent adsorption of selenium onto the ferrihydrite surface is an USEPA-approved technology for treating selenium-bearing waters. For the coprecipitation to occur, ferric ion ( $\text{Fe}^{+3}$ ) must be present in the water. The chemical reaction for ferrihydrite precipitation of selenium is:



Adsorption on ferrihydrite has been investigated by several researchers. Se(IV) is effectively removed at  $\text{pH} < 8$ . This technology is not very effective for Se(VI) except at high Fe/Se weight ratios and relatively low pH levels. Reduction of Se(VI) prior to adsorption is required for effective removal. The presence of other aqueous species may have a detrimental influence on the removal of Se(IV) and Se(VI).

In a review of this technology, Tidwell and co-workers (2000) indicated that:

- Se(IV) adsorption is a function of type of oxyhydroxide present (amorphous ferrihydrite is best, crystalline FeOOH is considerably less effective);
- The initial concentration of Se(IV) in solution is very important (the higher the Se(IV) concentration the more effective the adsorption);
- 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)

In early studies on selenium treatment, Merrill and co-workers (1986) reported 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  $\mu\text{g}$  Se/L. The effluent selenium concentration resulting from the treatment of 33 gpm in a continuous pilot facility was  $< 10 \mu\text{g/L}$ . The process treatment created 2.1-3.1 kg sludge/kg iron added. The estimated cost of processing 26 million gallons/day (for arsenic, heavy metals and selenium removal) would be USD\$ 0.50/1000 gallons. This estimate, which seems very optimistic, 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.

Certain anions preferentially adsorb onto ferric oxyhydroxide, affecting the adsorption of selenium. The order of adsorption at pH 7 was found to be phosphate  $>$  silicate = As(V)  $>$  bicarbonate/carbonate  $>$  Se(IV)  $>$  oxalate  $>$  fluoride = Se(VI)  $>$  sulphate. The order of adsorption at the lower pH used in treatment plants may be different.

The long term aging stability of adsorbed/co-precipitated selenium remains to be demonstrated. Adsorbed Se may be released when amorphous iron oxide crystallizes to the more thermodynamically stable phases of goethite ( $\text{FeOOH}$ ) or hematite ( $\text{Fe}_2\text{O}_3$ ).

At Lac Mineral's Richmond Hill Mine, a selenium treatment system was developed in 1994, based on a process using elemental iron to reduce selenate to selenite, followed by ferric sulphate precipitation at pH 4.5, with a copper sulphate catalyst. The resulting slurry is sent to a thickener to produce a peanut-butter-like sludge that is stored in a sludge pond.

The treatment process needed three years to be optimized. Even so, the best that could be achieved is

effluent Se concentrations of 12-22 ppb, which is unacceptable for direct discharge to the environment. The treatment system is now used in conjunction with an RO treatment, described above.

A treatment plant was developed at FMC's (now Meridian) Dry Valley Mine for selenium removal. The process used zinc powder as a reductant, converting all the selenium to selenite, followed by iron salt precipitation at acidic pH. A similar plant was designed at a Homestake mine, where (elemental) iron powder and ferrous sulphate were used as reductants and ferric chloride was used to form ferric hydroxide, which co-precipitates selenite. Again, the reaction was carried out at ~pH 4.5 and requires tight pH control (+/- 0.2 pH units). Unfortunately, capital and operating costs are not available for both operations.

## **Biological**

Treatment by biologically-based processes primarily relies on the activity of a small group of bacteria that reduce selenate to selenite, then to elemental selenium. Another process for Se removal is volatilization. Both processes are described below.

### **Se volatilization**

Microalgae and submerged aquatic plants can volatilize significant quantities of selenium from the water column. This ability has been exploited in California to remove Se from contaminated agricultural drainage. Drainage entering the Hacienda Evaporation Basin of the Tulare Lake Drainage District, Corcoran, CA, shows a progressive decrease in Se concentrations despite becoming more concentrated due to water evaporation. Rates of volatilization from planktonic algae can reach 220 ng/hour when conditions in the pond are favorable (Fan and Higashi, 1997). These include slightly alkaline pH, clear water, non-limiting nutrient (i.e., nitrogen and phosphorus) concentrations, etc. A retention time of approximately 80 days is required to remove Se completely from the above agricultural drainage.

Unfortunately, these evaporation basins have caused reproductive impacts to avocets feeding and nesting. The operators of these basins have modified the design and management of the basins to discourage shorebird use and nesting (Gordus *et al.*, 1998). Modified designs include: greater water depths, steep banks with 3:1 slopes, no islands or windbreaks, level bottoms, and plastic lined or "stacked" rip-rap banks for erosion control. Management strategies include rapid filling and drawdowns of the ponds, intensive hazing during the pre-breeding and breeding seasons, vegetation control on the banks and ponds, and clean, smooth, scraped dikes and banks. Hazing efforts include: propane cannons, cracker shells, bird bombs, mylar flagging, airboat, and vehicles. Other management strategies include modifying sites adjacent to the basin that attracted birds to the basin area or providing a freshwater mitigation wetland adjacent to the evaporation basin. These mitigation efforts have succeeded in reducing bird use and, consequently, Se-induced reproductive failures.

In addition to the above, micro-organisms can also volatilize Se from sediments. Frankenberger and Karlson (1989) attempted the remediation of sediments from both the Peck and the Kesterson ponds in the West San Joaquin Valley in California using this approach. The sediments were amended to stimulate bacterial volatilization of selenium. The Peck pond was bioremediated from a mean of 11.4 mg Se/kg sediment to the goal of 4 mg in 2.6 years. In contrast, the Kesterson pond was not remediated to the 4 mg goal from 47.8 mg Se/kg after 8 years, using the same techniques. The results can be explained by the distribution of selenium species in these sediments. For Peck, the Se distribution was 6.6% Se(VI), 67.6% Se(IV), 18.4% Se(0), 7.3% Se(II-). For Kesterson, it was 5.2% Se(VI), 9.1% Se(IV), 58.0% Se(0), 27.7% Se(II-). Thus, the difference in Se(0) and Se(II-) distributions (25.7% vs. 86%) indicates that most of the Se in Kesterson sediments was unavailable to microbial volatilization.

### **Biological treatment plant**

Biological treatment plants are of two different types: active systems, essentially conventional treatment

plants in which operational parameters (pH, oxygen concentration, retention time, etc) are tightly controlled, and passive systems in which operator intervention is minimal. Both types of treatment systems have been designed for Se removal. Both use Se-reducing bacteria that are naturally found in anaerobic sediments. Many factors affect their activity, including dissolved oxygen and nitrate concentrations (both are antagonists), temperature, pH, etc. Although it may be beneficial to identify the bacterial species used in a treatment process, this is not always necessary, since it is usually sufficient to identify the conditions that favour their activity.

## Active Systems

Many efforts were made in the early 1990's to develop bioreactors for treatment of Se in agricultural drainage. These reactors were mostly small laboratory-scale systems based on anaerobic bacteria that reduce Se oxyanions to elemental Se via the reactions:



The reactors utilized either acetate or methanol as carbon sources (methanol being cheaper), and ammonium sulfate as a supplementary nitrogen source. Most of this organic carbon was consumed by bacteria respiring on nitrate (abundant in agricultural drainage), outcompeting selenium-reducing bacteria.

Different reactor configurations were tested, including upflow anaerobic sludge blanket reactors (UASBR), fluidized bed reactors, sequential batch reactors, packed-bed reactors, and slow sand filters (SSF). The latter were necessary under most configurations because they retained elemental selenium released by treatment bioreactors. Removal to 15-30 µg/L was achieved with retention times of 10-30 hours.

A common problem identified in most reactors was the formation of calcium carbonate and the potential for plugging. This results directly from the high calcium concentrations present in agricultural drainage and the production of bicarbonate during anaerobic bacteria respiration on nitrate or selenate. Although this makes these treatment systems inherently problematic, it was anticipated that these problems would be addressed during planned pilot tests.

These studies eventually resulted in the development of treatment systems. A number of treatment plants have been constructed and operated at mine sites in the past five years. At Goldcorp's former Wharf Resources Mine, in Leads, SD, a biological treatment plant has been operated for three years. Mine water containing approximately 30 ppm nitrate, 15 ppb Se (as Se(VI)), and 70 ppb arsenic is collected in a French drain underlying barren rock. Flows are seasonal, ranging from 40-300 gallons per minute (gpm). All these contaminants are removed during treatment, with nitrate decreasing to <1 ppm, Se to < 5 ppb, and As to < 1 ppb. Overall, this treatment plant functions very well, though contaminant loadings are fairly light.

The plant is operated year-round, with no water heating (except to keep pipes from freezing). Water temperatures range from 1.5-4.0 °C during the winter, to 15 °C during the summer. The rate of bacterial activity decreases during winter operation, which is compensated with the addition of more nutrient. Problems develop when excessive nutrients are added, as the oxidation-reduction potential decreases to very low levels, causing nitrate to be reduced to ammonia. Otherwise, the system requires little maintenance, and has no scaling or odour (from hydrogen sulphide) problems, though it is checked regularly for sliming or other potential issues.

The overall capital cost for the treatment plant was under USD\$1 million, and annual operating costs are USD\$40-60,000. The plant made use of tanks existing on the property, as well as constructing new tanks. The biggest capital cost item was the purchase of activated carbon as support matrix for the bacteria. A total of 800,000 lbs (362 metric tons) of activated carbon was purchased at USD\$0.37/lb.

The system was first tested in the laboratory on a bench-scale, followed by a pilot campaign (Summer 2001) that lasted one month. Design, procurement and construction followed through Fall and Winter

2001/2002. The plant was operational in March 2002. The bacterial inoculum was grown in 3-4 weeks, and does not constitute a significant time constraint.

At the former Zortman-Landusky gold mine, in Montana, acidic water collected from leach pads is treated biologically before discharge by land application. The neutralized influent to the treatment plant contains approximately 200 ppm NO<sub>3</sub><sup>-</sup>, 500-700 ppb Se (as Se(VI)), and 300-400 ppb T-CN. The effluent contains <10 ppm NO<sub>3</sub><sup>-</sup>, 100 ppb Se, and 200 T-CN. While this water does not meet state discharge criteria, it is sufficiently treated to allow for its disposal by land application.

The treatment plant consists of 3 x 250,000 gallon insulated (outdoor) tanks filled with activated carbon. It has treated flows of 75-300 gpm year-round for the past three years. Water temperatures vary seasonally, from approximately 1-15 °C, without affecting treatment performance. The capital cost for the treatment plant was USD\$3 million, for which the highest cost item is the activated carbon. Operating costs are somewhat less than USD\$250,000/year, and are broken down as follows (Table 2).

**Table 2. Operating costs for Zortman-Landusky treatment plant.**

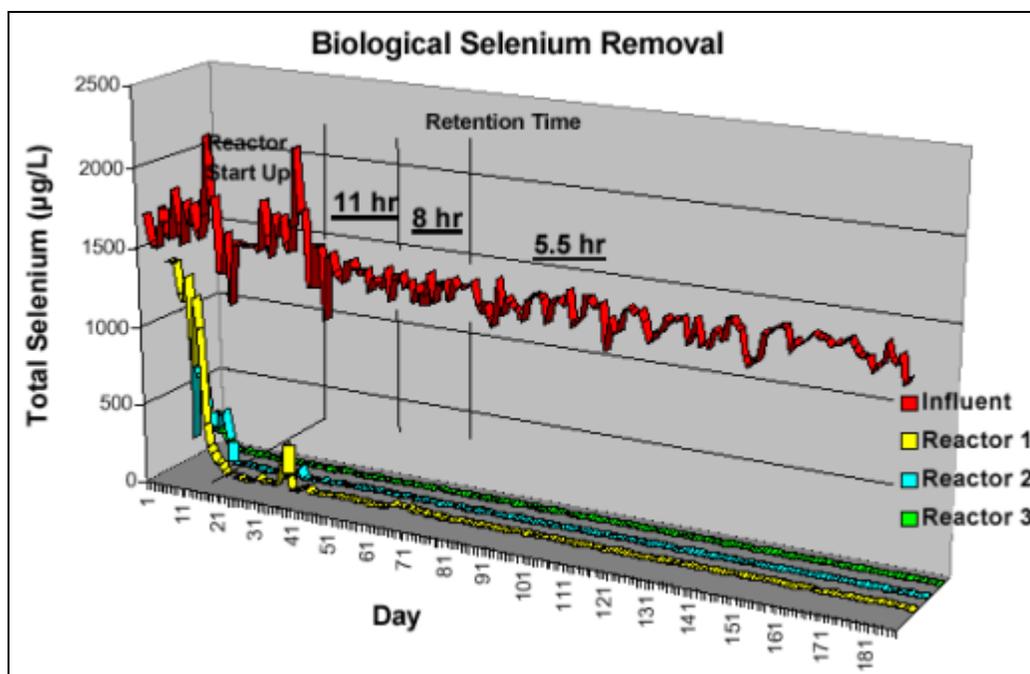
Item	Annual Cost
Bacterial nutrients	\$100,000
Labour	\$43,000
Reagent (lime, etc)	\$35,000
Maintenance	\$25,000
Power	\$15,000
Laboratory analysis	\$14,000
Filtration	\$10,000
Total	\$240,000

A biological treatment system, comparable to the above systems, was tested at Kennecott Utah Copper Corporation's (KUCC) Garfield Wetlands-Kessler Springs site. The site provides water with uniformly high selenium concentrations of 1,600 ppb Se, mostly as Se(VI).

The treatment system comprises a series of tanks (total 500 gallon) that contain activated carbon seeded with selected bacteria. The tanks are fed groundwater (temperature = 13 °C) at a rate of 1 gpm and a nutrient solution. The discharge flows through a slow sand filter to remove elemental selenium produced in the tanks. Treatment performance was excellent at all times (Table 3 and Figure 1). Selenium removal was complete, even with a 5.5 hours retention time.

**Table 3. Mean effluent Se concentrations from biological treatment pilot plant.**

Residence Time	Mean Selenium Effluent Concentration (µg/L) ±Standard Deviation	Minimum Selenium Effluent Concentration (µg/L)
12 hrs (Series 1)	8.8 µg/L ±10.2	<2 µg/L
11 hr (Series 2)	4.9 µg/ L ±4.9	<2 µg/L
8 hr (Series 3)	<2 µg/L ±2.6	<2 µg/L
5.5 hr (Series 2)	<2 µg/L ±2.1	<2 µg/L



**Figure 1. Treatment performance of the biological treatment process at Kennecott.**

An economic analysis for a full-scale treatment plant receiving 300 gpm of the above groundwater indicated that the capital costs, utilizing some tanks available on site, would be \$603,999. Annual operating costs are calculated to be \$135,029. The treatment cost, amortized over ten years, is calculated to be USD\$1.32/1,000 gallons, comparable with the costs for the above biological treatment plants.

## Passive System

Bioreactors designed as passive treatment systems are cavities or vessels filled with a medium that supports bacteria. The bacteria remove contaminants as water flows through this medium. Operating parameters (e.g., pH, ORP, temperature, etc) are set by the system design, so that an operator is unnecessary. These systems have been developed in the past 5-10 years to treat flows of 5-15 L/s (80-250 gpm).

One example is the Biopass system, developed in the early 1990's to treat water from a reclaimed heap leach facility at the Santa Fe Mine, in Nevada (Cellan *et al.*, 1997). This system relies on the flow of mine water through decaying organic matter to support bacteria and treat weak acid dissociable cyanide (WAD-CN), nitrate ( $\text{NO}_3^-$ ), mercury (Hg), and selenium (Se). Anaerobic bacteria in the substrate layer remove sulfate from the effluent, reduce selenium oxyanions to insoluble elemental selenium and form insoluble mercury sulfides. Other microorganisms biodegrade cyanide and remove nitrate from the water. Results to date indicate that every contaminant of concern is removed sufficiently for the effluent to meet mandated discharge criteria.

The system is constructed in an emptied double geomembrane lined solution pond and consisted of, from the bottom upward: a seepage collection (influent) layer, a substrate layer comprised of spent ore gravel and composted cow manure, an effluent collection layer, a geotextile cushion, a geomembrane liner, and a vegetative soil cover. Treated solution flows by gravity through a buried pipeline from the effluent layer to a leach field where it is aerobically treated. The Biopass system is designed to be sealed and operated passively. As a consequence, living organisms are not exposed to the fixed selenium and metals. However, these contaminants must be prevented from re-oxidizing in the future, or the system must be sealed off to prevent the discharge of re-oxidized contaminants. Unfortunately, no cost information is available on this treatment system.

In general, these are very compact systems, a distinct benefit in certain settings. The majority of designs rely on the organic matter placed in them to feed the bacteria that provide treatment. The decomposition of organic matter in the system produces the anaerobic environment required by nitrate-, sulphate- and selenium-reducing bacteria. Typical materials include alfalfa, compost, manure, wood mulch, mushroom sawdust, straw, etc. However, one drawback of these materials is that they have poor or deteriorating hydraulic properties, due to decomposition, compaction, sliming, accumulating sludge, etc. For that reason, most current designs are best suited for modest flows. Potentially, they represent a “walk-away” scenario, or an inexpensive solution for abandoned mines, specially since some of them have been shown to operate at low temperature.

## In-Situ Remediation

In-situ remediation involves the treatment of selenium in groundwater through stimulation of bacterial activity. In one typical application, aquifer sediments are sampled for the presence of selenium-reducing bacteria and, if present, they are stimulated by addition of nutrient solutions (Nelson *et al.*, 2003). The reduction of selenate and selenite produces elemental selenium, which is retained in the subsurface.

This approach is been carried out in full-scale at Homestake Mining Co.’s Grants New Mexico Reclamation Project. Se present in a groundwater plume at 50-100 µg/L is being decreased through the action of bacteria to <5 µg/L. This process is very cost-effective, at less than USD\$1.00/1,000 gallons, due to low capital costs. However, this approach may not be applicable everywhere, due to different aquifer characteristics. Moreover, the potential remobilization of elemental selenium retained in the subsurface has not been conclusively ruled out.

## Treatment wetland

ChevronTexaco’s (Chevron’s) Richmond, CA refinery, one of the largest on the West Coast, produces a effluent containing selenium that is removed in a restored wetlands (Duda, 1992). Planted near the mouth of San Pablo Bay in Richmond in the late '80s, the restored wetland grows typical California marsh plants including salt marsh bulrush, cattail and rabbitfoot grass. The 3x30-acre cell wetland receives flows of 1,000 gallons per minute (gpm) containing 10-30 ppb (predominantly selenite), a mass loading of  $156 \pm 13$  g/day. Se concentrations are reduced by 60-70% at the outlet on Cell 1 and attain < 5 ppb dissolved Se at the outlet of the wetland complex.

Most of the dissolved Se is retained in the wetland sediments, where it has built up to concentrations of 3-8 mg/dry kg (Hensen *et al.*, 1998). A significant portion of the Se, estimated at 10-30%, is transformed to volatile selenides, which are lost from the system. Rates of volatilization in the wetland vary over two orders of magnitude and are a function of time of year and plant coverage (Table 4).

The wetland has attracted considerable attention because of its abundant bird life. The marsh is home to black-necked stilts, Canada geese, Savannah sparrows, endangered California clapper rails, as well as grey foxes, raccoons, skunks, muskrats, mice and moles. Some of the latter carnivores were actively trapped to increase egg survival, thus enhancing bird populations.

Se is taken up by organisms living in the wetlands. Se concentrations reach 31.0 µg/dry g in midge larvae (*Chironomus* species), 17.3 µg/dry g in water boatmen and 12.8 µg/dry g in snails (Chevron, 1995). The U.S. Fish and Wildlife Service is concerned that Se is accumulating in the wetlands and causing toxic effects. Se concentrations in black-neck stilt eggs average (geometric mean) 20.4 µg/dry g, a concentration predicted to result in non-viability and/or embryonic deformations. These concentrations have increased the rate of deformities in young birds to an estimated 10-30%, whereas the rate of deformities is expected to be less than 1% (Skorupa, 1998).

**Table 4. Volatilization rates in Chevron's treatment wetlands.**

Site	Volatilization Rate $\mu\text{g Se/m}^2/\text{day}$
Vegetated - Rabbitfoot grass	190 $\pm$ 150
Vegetated - Cattails	180 $\pm$ 100
Vegetated – Saltmarsh bulrush	150 $\pm$ 40
Vegetated – Saltgrass	80 $\pm$ 40
Vegetated – Brass buttons	60 $\pm$ 30
Unvegetated – Inlet channel	170 $\pm$ 30
Unvegetated – Fungal mat	110 $\pm$ 60
Unvegetated – Algal puddle	50 $\pm$ 20
Unvegetated – Uncovered sediments	20 $\pm$ 10

To mitigating impacts of Se toxicity on bird populations, Chevron modified the treatment wetland by densely planting the first two passes and modifying their shoreline, both to deter bird usage. These passes was further altered to remain continually submerged, thereby improving treatment performance and preventing accidental drying out of sediments and release of accumulated selenium. Finally, the last pass was modified to enhance bird usage. The result of these modifications is that treatment efficiency is maintained, while selenium content in bird eggs decreased dramatically<sup>2</sup>.

Unfortunately, no cost information is available for this system. However, such a system would be expected to cost between \$1-3 million to design and construct (depending on topography, soils, flow control structures, etc), and \$50-100,000/year to operate (including monitoring costs) and maintain. Such a system could accept up to 2,000 gpm (454 m<sup>3</sup>/hr), removing 80-95% of input Se, depending on flows. Operation in a Northern climate would be seasonal, with water stored in an impoundment or reservoir during the winter.

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<sup>2</sup> Smart, R. ChevronTexaco, Richmond, CA. Personal communication. The company is unwilling to release figures on Se concentrations in bird eggs, being very sensitive as a consequence of past criticism.

## Comparison of Treatment Options

Any of the technologies reviewed above could be used to treat mine effluents containing selenium, but they may not all operate equally well in the North. To compare their relative suitability, these technologies were assessed on the basis of different criteria, including (in order of importance):

1. Cost-effectiveness
2. Achievable discharge concentrations
3. Operational constraints (i.e., land area or power requirement, temperature-dependence, by-product disposal, etc)
4. Operational experience, reliability of the technology
5. Post-treatment management (Brine disposal, sludge storage/management)
6. Maturity of the technology (bench-, pilot-, or full-scale experience)
7. Volumes of water that can be treated
8. Development time

Using these criteria, two technologies stand out from the others as being most suitable: In-situ treatment and biological treatment plants. Both technologies produce low effluent selenium concentrations and are cost-effective. Unlike filtration methods, treatment wetlands or evaporation ponds, these technologies have been operated in (relatively) cold climates without heating. The fact that biological treatment systems have been favoured in the past five years undoubtedly reflects the above results.

In-situ treatment is the method of choice *if applicable at a site* because it is the most cost-effective. However, its applicability is dependent on favourable subsurface conditions.

Biological treatment plants have proved to be more reliable than expected in treating selenium, as well as a number of other contaminants. Another unexpected characteristic is their apparently good treatment efficiency at cold temperatures (e.g., 2-4 °C). There are now four biological treatment plants that remove selenium in the USA, suggesting that this technology is becoming more mature.

Four other technologies are somewhat less preferred: reverse osmosis, nanofiltration, the Biopass/passive treatment systems and treatment wetlands. However, they might be appropriate to some Northern mines if favoured by site-specific factors, e.g., suitable land available for treatment wetland or inexpensive equipment or other factors that reduce the cost for RO treatment. Passive technologies might be favoured over others if several dispersed small flows require treatment, if they contribute significant loadings of selenium to receiving waters, and if their continued collection after mine closure proves onerous.

Treatment plants using iron precipitation could be suitable for waters containing low selenite concentrations. Otherwise, they are not cost-effective, particularly for waters with selenate. The remaining technologies are too underdeveloped or inappropriate for application in the North.

It should be noted that preventative measures will always be preferred over treatment systems, whenever long-term selenium release is expected. A substantial body of literature describes reclamation techniques that minimize or prevent contaminant release.

In summary, this review concludes that the two best treatment technologies for Se removal are in-situ treatment and biological treatment plant, because they can remove selenium down to acceptable levels cost-effectively, even during cold weather. Four other technologies – reverse osmosis, nanofiltration, the

Biopass/passive treatment systems and treatment wetlands – merit consideration and may be appropriate in certain circumstances. Notwithstanding the advantages or disadvantages of each technology, preventative measures to minimize selenium release should be implemented as an integral component of any management plan.

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