A TIME Network Project

Literature Review of Environmental Toxicity of Mercury, Cadmium, Selenium and Antimony in Metal Mining Effluents

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LITERATURE REVIEW OF ENVIRONMENTAL TOXICITY OF MERCURY, CADMIUM, SELENIUM AND ANTIMONY IN METAL MINING EFFLUENTS

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Lisa Sumi	Environmental Mining Council of BC

DISCLAIMER

The primary purpose in producing this report is to provide a review of mercury, cadmium, selenium and antimony as it relates to metal mining effluents. The objective was to examine the chemical behaviour of the metals under different process and environmental conditions; treatment technologies and mine effluent toxicity. The information provided is based on the opinions of the authors and should not be construed as endorsement in whole or in part by the various reviewers or the partners in TIME (The Government of Canada, Provincial Governments, the Mining Association of Canada, contributing mining companies and participating non-governmental organizations).

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Literature Review of Chemistry and Toxicity of Mercury, Cadmium, Selenium and Antimony in Metal Mining Effluents

Abstract

CANMET, the Mining Association of Canada (MAC) and Environment Canada funded a review of minor elemental constituents that may be of environmental concern in the context of metal mining effluents. The objective of this work was to conduct a critical review of the literature for mercury, cadmium, selenium and antimony with respect to their chemical behaviour under different process and environmental conditions, their potential contribution to mine effluent toxicity, and applicable treatment technologies to reduce or eliminate toxicity due to these four metals. The mineral associations of each metal, and the mine types likely to release them, were discussed. Typical concentrations in mine effluents were compared to acutely toxic levels, with emphasis on levels toxic to *Daphnia magna* and rainbow trout. Based on this review, and considering the usual chemical characteristics of mine effluents, the likely need for treatment was discussed for each metal. Factors that may influence treatment success were discussed, and typical removal efficiencies were given, for the different treatment technologies that could be used to reduce the effluent concentrations of these metals.

Analyse de la documentation sur la chimie et la toxicité du mercure, du cadmium, du sélénium et de l'antimoine dans les effluents des mines de métaux

Résumé

CANMET, l'Association minière du Canada (AMC) et Environnement Canada ont finance l'analyze d'éléments mineurs dans les effluents des mines de métaux qui peuvent être preoccupants pour l'environnement. Il s'agissait d'effectuer une analyze critique de la documentation relative au mercure, au cadmium, au sélénium et à l'antimoine, sous les aspects suivants: leur comportement chimique lorsqu'ils sont soumis à différents procédés et à différentes conditions d'environnement, leur contribution possible à la toxicité de l'effluent et les technologies de traitement pour réduire ou éliminer la toxicité amenée par ces quatre métaux. L'auteur aborde les associations minerals de chaque metal, ainsi que les types de mines susceptibles de les libérer. Les concentrations types des effluents des mines sont comparés aux concentrations toxiques à effets aigus, particulièrement chez

Daphnia magna et chez la truite arc-en-ciel. D'après l'analyse et compte tenu des caractéristiques chimiques habituelles des effluents des mines, l'auteur envisage le besoin probable de traitement dans le cas de chaque métal. Il examine les facteurs qui peuvent influer sur la réussite du traitement et donne les rendements d'élimination habituels des diverses techniques de traitement qui pourraient être utilisées pour réduire les concentrations des métaux visés dans les effluents.

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NPDES	-	National Pollutant Discharge Elimination System
CFS	-	Cubic Feet per Second
NALMET	-	Non-Acutely Lethal Mining Effluent Technologies
TSS	-	Total Suspended Solids
TDS	-	Total Dissolved Solids
ICP	-	Inductively Coupled Plasma-emission (spectrometry)
ILL	-	Incipient Lethal Level
Degussa’s TMT	-	Proprietary Name for Reagent used in Hg Removal
HDS	-	High Density Sludge
HW-FIX	-	Proprietary Name for an Ion Exchange Medium
CIP	-	Carbon in Pulp
SS	-	Suspended Solids

1.0 INTRODUCTION

1.1 Purpose and Scope of Review

In 1977, the Metal Mining Liquid Effluent Regulations (MMLER) were promulgated under *The Fisheries Act* (EPS, 1977). In 1990, the government of Canada announced its intention to update and strengthen these regulations. In 1993, an Assessment of the Aquatic Effects of Mining in Canada (AQUAMIN) was initiated to review the effectiveness of the existing regulations and to develop recommendations for the new regulations. Based on these recommendations (AQUAMIN, 1996a), those of the Aquatic Effects Technology Evaluation (AETE) program, and stakeholder consultations, draft Metal Mining Effluent Regulations (MMER) were proposed in 1999 and gazetted in 2001.

The MMER (2001) would apply to all metal mining and milling facilities that are used to produce a metal concentrate or an ore from which a metal or metal concentrate may be produced and all associated smelters, pelletizing plants, sintering plants, refineries, acid plants, and any similar operation where any effluent from such an operation is combined with the effluents from mining and milling.

As indicated above, the new MMER will set Authorized Levels for the discharge of certain metals of environmental concern, specifically arsenic, copper, cyanide, lead, nickel, zinc and radium-226. No limits were established for a number of metals that are also of environmental concern. However, the new MMER will require that all metal mines in Canada produce effluent that is non-acutely lethal to rainbow trout when tested in accordance with the Environment Canada (1990a, 1996) Reference Method “EPS 1/RM/13”. Mine operators will also be required to monitor the acute lethality of effluent to *Daphnia magna* in accordance with the Environment Canada (1990b) Reference Method “EPS 1/RM/14”. It is anticipated that under the new MMER, the effects from potentially deleterious metals without established Authorized Levels should be captured under the requirement for non-acutely lethal effluents.

The Toxicological Investigations of Mining Effluents (TIME) Network was formed in 1999 to address toxicological issues related to the proposed amendments to the MMER. The TIME Network includes representatives from industry, federal and provincial governments, academia, consulting firms, environmental non-government organizations and non-government organizations.

A key objective of the TIME Network is to foster research aimed at broadening the knowledge base with respect to causes of and solutions to effluent toxicity and to disseminate the information. As part of this objective, CANMET, the Mining Association of Canada (MAC) and Environment Canada funded a review of minor elements that may be of environmental concern in the context of metal mining effluents, including mercury, cadmium, selenium and antimony. A better understanding of the chemical behaviour, toxicity and treatability of these minor elements will assist industry in consistently producing non-acutely lethal effluents.

The overall objective of this review is to provide Natural Resources Canada (NRCan), the lead agency for the study, with comprehensive, up-to-date information on the environmental chemistry and toxicity of mercury, cadmium, selenium and antimony, and to identify and evaluate appropriate treatment technologies to assist the metal mining industry in meeting the MMER effluent quality requirement for non-acutely lethal effluents. The specific study objective is to conduct a critical review of the literature for mercury, cadmium, selenium and antimony with respect to their chemical behaviour under different processes and environmental conditions, their contribution to mine effluent toxicity and applicable treatment technologies to reduce or eliminate toxicity due to these four metals. Based on an improved understanding of metal behaviour and associated toxicity, the best process and treatment practices can be identified and evaluated to achieve metal mine industry compliance with the new MMER.

Since this review is focused on mercury, cadmium, selenium and antimony in the context of metal mining effluents, Section 1.2 outlines the mineral associations of these metals and the mine types most likely to release them. Section 1.3 addresses the levels of these metals in mine effluents, and the chemistry of mine effluents in general. This chemical context is important to the subsequent discussion of environmental chemistry (Section 2), aquatic toxicity (Section 3) and treatment technologies (Section 4) for the four metals of interest. Section 5 presents conclusions and recommendations arising from this review.

1.2 Mineralogy and Mine Types Relevant to the Metals of Interest

The four constituents of concern in this study may have elevated concentrations in ores relative to typical crustal abundances and both mining and milling ore can expose these constituents to biogeochemical conditions that can cause leaching from the solids. The result can be elevated concentrations of these constituents in mine and mill effluents.

Mercury was historically used for gold extraction, however, this practice has since been abandoned for more efficient methods. It is likely that no current mine operations use mercury in their processes. Mercury is often present in both gold and zinc ores, although it may be difficult to detect in mine effluent. Because of its toxic nature and known ability to bioaccumulate, low mercury loadings can pose a risk to receiving environments.

Cadmium minerals are not common, however, cadmium can substitute for other heavy metals in sulphide ores. For example, cadmium has been reported to substitute for zinc, lead and copper in their respective sulphide ores. Typically, this substitution occurs by isomorphic replacement (replacement of a particular metal within the crystal lattice), however, small inclusions of cadmium sulphide minerals (e.g., Greenockite – CdS) can also occur in ores of other base metals.

Selenium resembles sulphur in many of its properties and often occurs together with sulphide minerals that are milled at base metal mine operations. Typical selenium minerals include Klockmannite (CuSe), Stilleite (ZnSe) and Penroseite (Ni_2Se). Whereas these minerals are not abundant, they can occur together with copper, zinc and nickel ores and selenium can be dissolved during processing at the respective refining operations.

Antimony occurs in over one hundred known minerals, however, the most common is the mineral Stibnite (Sb_2S_3). Antimony is also a chalcophile, occurring with sulphur and heavy metals such as copper, lead and silver. It is therefore common that anthropogenic sources of antimony include gold mining, lead and copper smelting operations. Gold inclusions are commonly found in minerals of antimony and gold effluents from these antimony-bearing gold refineries can have elevated concentrations of this constituent.

1.3 Representative Chemistry of Relevant Mine Effluents

The major metals of concern to this study originate as trace elements or as secondary minerals in the ore. Subsequent milling and processing activities mobilize the elements from the ore minerals into a solution phase.

The four metal/metalloids considered here are released from gold mills and base-metal mills, generally in trace quantities. The following associations with type of mining operation have been noted:

- mercury – historically used in gold recovery, and often present in both gold and zinc ores;
- cadmium – in zinc, lead and copper mines;
- selenium – in copper, zinc and nickel mines; and
- antimony – in gold and base metal mines.

A summary of mine effluent chemistry with respect to these four metals is provided in Table 1.1, based on a U.S. EPA survey of mine sites (U.S. EPA, 1999) and a review of gold mine effluent chemistry by Smith and Mudder (1991). The effluents described in Table 1.1 have not been subjected to treatment.

Table 1.2 provides representative concentrations of these four metals at individual operating mines in Canada and the U.S., based on data from BEAK (2000), AQUAMIN (1996b) and Smith and Mudder (1991). Most of the effluents described in Table 1.2 have had some degree of treatment.

Table 1.3 provides a summary of the metal and other chemical characteristics of mine effluents, based on data from Natural Resources Canada (NRCan, 1996, 1998). Again, most of these effluents have received some degree of treatment. Effluent chemistry data for the 23 individual mines represented in Table 1.3 are listed in Appendix 1. These data provide a water quality context in which to consider the environmental fate, toxicity and approaches to removal of mercury, cadmium, selenium and antimony.

Trace element data for mine effluents, particularly mercury data, is often reported as "less than" detection limit. Mine effluent characterization for trace elements may require use of improved sampling and/or analytical techniques. Hall *et al.* (2001) and Brown *et al.* (1979) define appropriate sampling and analytical techniques for mercury.

TABLE 1.1: CONCENTRATIONS OF SELECTED METALS IN VARIOUS UNTREATED MINE EFFLUENTS – SUMMARY DATA (values in mg/L)

Mine Source	Mercury	Cadmium	Selenium	Antimony
Average Concentrations in Process Solutions from 26 Heap Leaching Facilities in Nevada (U.S. EPA, 1999)	1.194 ± 2.90[1]	0.1 ± 0.245	1.6 ± 5.05	0.105 ± 0.768
Meteoric Water Mobility Tests on Waste Rock from 24 Heap Leaching Facilities in Nevada (U.S. EPA, 1999)	0.004 ± 0.036	0.013 ± 0.178	0.016 ± 0.078	0.037 ± 0.244
Copper Mine Tailings Ponds in Arizona (U.S. EPA, 1999)	DL	0.407 ± 0.875	DL	0.014 ± 0.036
Range of Concentrations in Barren, Decant and Seepage for Gold Mines (Smith and Mudder, 1991)	<0.0001 – 0.05	<0.005 – 0.02	<0.02 – 6.0	-
Effluent Limitation for Gold Mines – NPDES U.S. EPA – CFS 40 Part 440.13 Subpart 1, 01 July 1987				
(a) Maximum 24h	0.002	-	-	-
(b) 30 Day Average	0.001	-	-	-

DL = detection limit (not stated).

[1] Value was reported as shown here, but was likely µg/L.

TABLE 1.2: CONCENTRATIONS OF SELECTED METALS IN VARIOUS FINAL MINE EFFLUENTS – INDIVIDUAL MINES (values in mg/L)

Mine Source	Mercury	Cadmium	Selenium	Antimony
Mine A – Gold Mine NALMET Toxicity Study (BEAK, 2000)				
(a) Dec. 16/99 – Total	-	0.0017	0.0056	0.001 - 0.002
(b) Dec. 16/99 – Filtered	-	0.0029	0.0039	0.0009
(c) Feb. 10/00	-	0.0029	0.0071	0.0013
Mine B – Nickel-Cobalt Mine NALMET Study (BEAK, 2000)				
(a) Jan. 24/00 – Total	0.000096	0.0038	0.00491	0.0363
(b) Jan. 24/00 – Filtered	-	<0.0005	0.00467	0.0329
Gold Mine Tailings Pond Discharge (Confidential Data)			-	
a) Mean ± SD	0.000052 ± 0.000006			0.0103 ± 0.0095
b) Min-Max	0.00002 - 0.00008			0.003 - 0.06
Gold Mine – Williams Lake 1993 (AQUAMIN, 1996)				
(a) Mean ± SD	-	-		0.363 ± 0.137
(b) Min-Max	-	-		0.137 - 0.59
Gold Mine - Hemlo 1985 (AQUAMIN, 1996)				
(a) Range	0.0005	-	-	1.0 – 5.1
(b) Limit	0.0005	-		0.001
Hemlo Final Treatment Plant Effluent 1987	0.0012 – 0.006	-	-	1.0 – 3.7
Hemlo Final Treatment Plant Effluent 1988	<0.0005	-	-	0.2 – 0.6
Hemlo Final Treatment Plant Effluent 1989	<0.0005	-	-	0.3 – 0.5
Hemlo Final Treatment Plant Effluent 1990	<0.0005	-	-	0.15 – 0.6
Hemlo Final Treatment Plant Effluent 1991				
a) Mean	<0.0005	-	-	0.279
b) Min-Max.				0.101 - 0.534
Hemlo Final Treatment Plant Effluent 1992				
a) Mean ± SD	<0.0001	-		0.249 ± 0.201
Hemlo Final Effluent				
1993	<0.0001	-		0.074 – 0.709
1994	<0.0001	-	-	0.064 – 0.57
Zn-Cu Mine (Lac Matagami Area) (AQUAMIN, 1996)				
a) Ruisseau Lalanne Stn ll	-	0.0047	-	-
b) Ruisseau Verant Stn 15		0.0005		

TABLE 1.2: CONCENTRATIONS OF SELECTED METALS IN VARIOUS FINAL MINE EFFLUENTS – INDIVIDUAL MINES (values in mg/L)

Mine Source	Mercury	Cadmium	Selenium	Antimony
East Kemptville Tin Mine (1986) Final Effluent (AQUAMIN, 1996)				
a) Mean ± SD		0.006 ± 0.004		
b) Min-Max		0.002 – 0.027		
Homestake Gold Mine RBC (Smith and Mudder, 1991)				
- Pilot Scale Influent	0.0023	-	-	-
- Effluent	<0.0001	-	-	-
Homestake Gold Mill (Smith and Mudder, 1991)			-	-
- Pilot Scale Influent	0.014	-		
- Activated Carbon Treated Effluent	<0.005	-	-	-

[1] Data are derived from effluents that have received some treatment.

TABLE 1.3: FINAL EFFLUENT CHARACTERISTICS FOR 23 CANADIAN MINES (below-detection-limit values were set to one-half of the detection limit for calculating the mean)[1]

Parameters	Units	Mean	Standard Deviation	Median	Range	n
pH		8.38	1.22	8.11	7.25-10.9	23
Conductivity	mMho/cm	1959	957	1836	549-3614	21
Ammonia	mg/L	4.3	5.5	1.85	<0.1-18.5	21
Alkalinity	mg/L	139	206	50	6-900	23
Total Hardness	mg/L	825	637	529	49-1980	23
TSS	mg/L	6.26	5.7	5	<1-16	21
TDS	mg/L	2344	2174	1660	500-9110	23
Chloride	mg/L	897	110	897	819-974	2
Sulphate	mg/L	3058	2207	4020	533-4620	3
Total Metals:						
Antimony[2]	µg/L	115	180	10.3	1.3-710	7
Calcium	mg/L	318602	226413	308200	13000-745300	23
Cadmium	µg/L	11.8	15.1	5	<10-59	21
Magnesium	mg/L	30797	33839	10190	3350-101100	23
Mercury[3]	µg/L	2.2	2.4	<5	0.05-7	9
Selenium[4]	µg/L	49	52	40	4.9-110	4
Sulphur	mg/L	1490	170	1490	1370-1610	2
Sodium	mg/L	365462	804875	77000	8690-3090000	21
Dissolved Metals:						
Antimony	mg/L	129.3	127.2	96	<50-435	21
Calcium	mg/L	344661	213988	314400	8673-676000	21
Cadmium	µg/L	5.43	1.96	5	<10-14	21
Magnesium	mg/L	31980	34685	10330	3000-97460	21
Mercury	µg/L	1	-	<2	<2	4
Sodium	mg/L	166956	283148	63100	120-1178000	21

Main Source: NRCan, 1996, 1998.

[1] Data are derived from effluents that have received some treatment.
[2] Includes n=2 mines from NRCan, plus n=5 mines from Table 1.2.
[3] Includes n=4 mines from NRCan, plus n=5 mines from Table 1.2.
[4] Includes n=2 mines from NRCan, plus n=2 mines from Table 1.2.

2.0 CHEMICAL FATE

2.1 Mercury (Hg)

Mercury is generally found at very low concentrations and is very reactive in the environment. Total mercury levels are generally less than 10 ng/g in crustal materials such as granites, feldspars and clays (Davis *et al*., 1997), and in the range of 40 to 200 ng/g in soils and sediments that are not directly impacted by anthropogenic discharges. Generally, the majority of mercury in aquatic systems is in organic forms (about 95 to 99%) and is found in sediments rather than the dissolved phase.

There are both natural and anthropogenic sources of mercury to the environment. For example, mercury is a trace component of many minerals and economic ore deposits for mercury occur as native mercury and Cinnabar (HgS). Various industrial discharges, coal combustion and medical waste incineration are important anthropogenic sources. Abandoned mines, where mercury was used for extraction purposes, are also important sources.

2.1.1 General Fate Information

Inorganic mercury exists in three known oxidation states: as elemental mercury (Hg°), as mercurous ion (Hg^+) and as mercuric ion (Hg^{2+}). The oxidation state of mercury in an aqueous environment is dependent upon the redox potential, the pH, and the nature of the anions and other chemical forms present with which mercury may form stable complexes (Reimers *et al.*, 1974). Mercurous compounds (Hg^+) are not common as they are rapidly oxidized to mercuric forms (Hg^{2+}) by hydrolysis (Booer, 1944).

Figure 2.1 summarizes the key processes that may affect mobility of mercury and methylation of mercury in receiving environments. The presence of organic matter in the sediments can either enhance mercury mobility, by forming soluble organic complexes, or retard mobility, by creating an environment conducive to precipitation of mercuric sulphides. The presence of iron oxyhydroxides (precipitated from the seepage waters) at the sediment surface may also scavenge mercury by sorption onto the hydrated oxyhydroxide surface. In general, the sediment water interface tends to accumulate inorganic mercury, and both porewater and the water column are possible sites for mercury methylation.

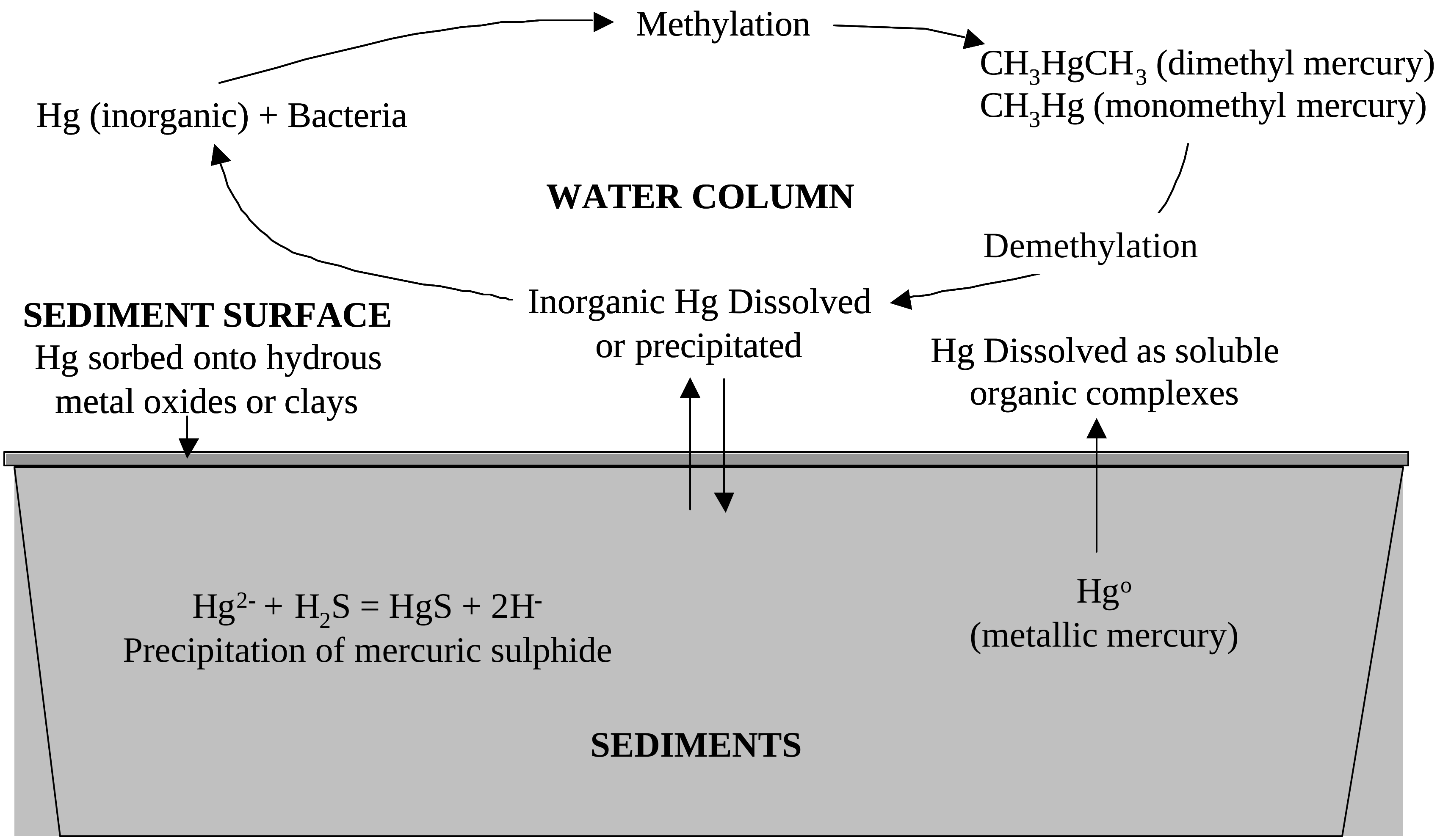

FIGURE 2.1: KEY PROCESSES THAT AFFECT THE SPECIATION AND MOBILITY OF MERCURY IN AQUATIC SYSTEMS.

An important characteristic of mercury is its low solubility as a result of its high probability to coagulate, i.e., to be removed from the soluble aqueous phase. This can occur by a number of physicochemical processes, e.g., precipitation as mercuric sulphide, co-precipitation with hydrated iron and manganese oxides, complexation with organic matter. The solubilization/coagulation of mercury depends on the forms of mercury present, on the amounts and nature of the organic and inorganic matter present, as well as on the environmental conditions, e.g., pH, chloride levels. Balogh *et al.* (1998) showed that total mercury levels in water are strongly correlated with total suspended solids concentrations, suggesting that mercury can remain suspended in the water column attached to colloidal and particulate matter.

In aquatic systems, dissolved mercury can be partitioned between inorganic and organic forms and this is largely controlled by rates of methylation and demethylation by microorganisms (Pak and Bartha, 1998). Organic mercury can occur as an organomercuric salt (RHgX), e.g., methylmercuric chloride, or as an organomercuric compound (R_2Hg), e.g., dimethylmercury. While the majority of mercury in aquatic ecosystems is in the inorganic form (about 95 to 99 %) (Krabbenhoft, 1996), organic mercury complexes remain important influences on the mobility and bioavailability of mercury. Evidence suggests that, when dissolved mercury in natural water systems exists mostly in organic forms, a high level of mercury in fish tissues is observed (Gill and Bruland, 1990). Mercury methylation is a biologically mediated process between dissolved inorganic mercury and, primarily, sulphate reducing bacteria (Driscoll *et al*., 1994). The factors that influence the amount of methyl mercury present in an aquatic system include the amount of dissolved inorganic mercury and physicochemical characteristics of the aquatic system such as pH, organic matter, dissolved sulphate and sediment sulphide (Pak and Bartha, 1998). For example, mercury methylation activity in sediments was found to be positively correlated with the level of organic matter (Driscoll *et al*., 1994). Thus, anaerobic zones such as the basins of small lakes, flooded forest soils and wetlands provide ideal conditions for mercury methylation. However, the science of mercury methylation and dimethylation is not fully understood, and rates of methylmercury formation are not readily predictable. The relative abundance of methylated mercury species is of particular concern since these compounds are highly toxic, they are the major form of mercury that accumulates in fish tissues, and they can enter the food chain by direct uptake from solution (Driscoll *et al*., 1994). Two aspects of chemical structure confer the unique toxic properties of methyl mercury. The bond between mercury and the methyl group is stable, with the methyl group providing a lipophilic character to the compound, while Hg(II) has a tendency to bind with sulfhydryl (or selenol) groups (Craig, 1986; Carty and Malone, 1979). Consequently, methyl mercury is both membrane permeable and thiol reactive, properties which contribute to the toxicity, the long biological half-time, and the tendency toward bioaccumulation of mercury in aquatic organisms.

The organomercuric salts exhibit properties and reactions similar to those of inorganic mercuric salts, and thus do not bioaccumulate as well as methylmercury. The organomercuric compounds other than methyl mercury species are generally subject to abiotic environmental degradation, being volatile, thermally unstable and light sensitive, e.g., decomposition by ultraviolet radiation to elemental mercury and free radicals.

2.1.2 Considerations for Mine Effluents and Receiving Waters

Mine effluent likely contains dissolved inorganic species of mercury. The behaviour of inorganic mercury species is well known and thermodynamic data are available. Figure 2.2 illustrates the dominant inorganic mercury species that occur under aerobic conditions (expected in mine effluent) as a function of pH. Two mercury compounds are predominant: hydrated mercuric oxide ($HgO{\bullet}H_2O$) at high pH and mercuric chloride ($HgCl_2$) at low pH. However, at high concentrations of chlorides (and low pH), the very stable and water-soluble mercuric tetrachloride complex ($HgCl_4$) will form.

The receiving environment has a variety of biogeochemical conditions that may influence the behaviour of mercury. The Eh-pH diagram provided in Figure 2.3 illustrates how mercury will respond to both aerobic and anaerobic conditions. The formation and dissolution of inorganic Hg-solids is controlled by redox and pH conditions and redox conditions in particular occur over a wide range in surface water environments. Under aerobic conditions, at lower pH, mercuric chloride is the dominant solid, and at higher pH hydrated mercuric oxide is found. Waters in equilibrium with these solids would have very high concentrations of mercury. For example, water in equilibrium with mercury hydroxide $Hg(OH)_2$ has mercury concentrations that range from approximately 350 mg/L at pH 6 to approximately 75 mg/L at pH 8 to 11. Because mercury is not found in effluents at concentrations near these levels, it is unlikely that solids precipitation will affect mercury concentrations in mill effluent.

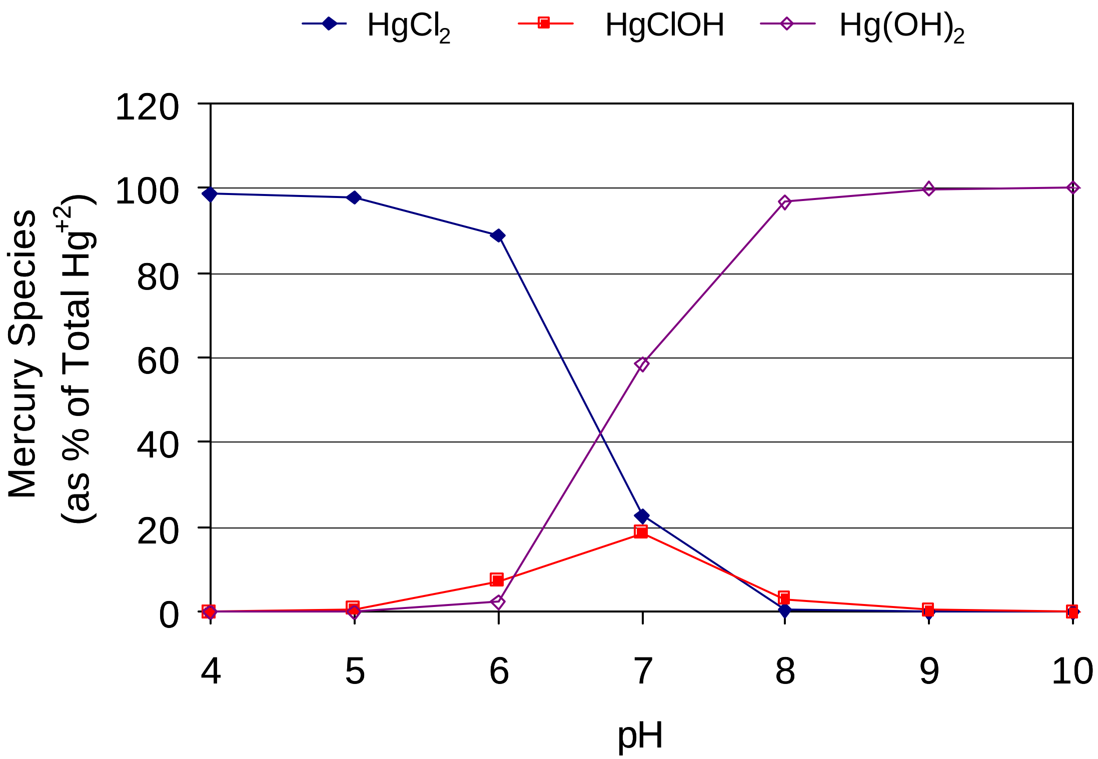

FIGURE 2.2: MAJOR INORGANIC SPECIES OF MERCURY AS A FUNCTION OF pH.

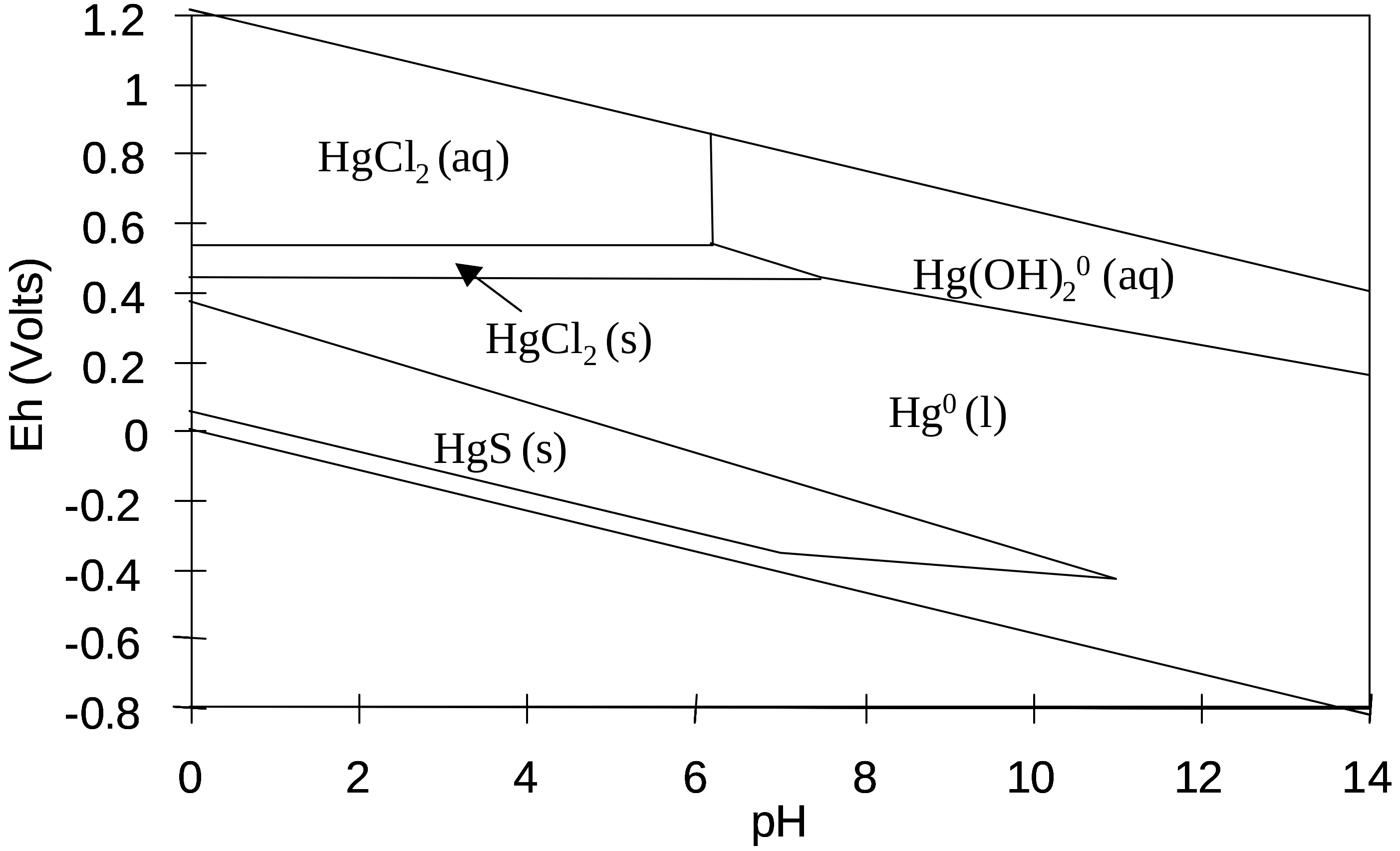

FIGURE 2.3: Eh-pH DIAGRAM FOR THE MERCURY SYSTEM. DIAGRAM ADAPTED FROM DAVIS *et al*. (1997).

Under anaerobic conditions, mercury is stable in two forms: elemental mercury and mercuric sulphide. Mercury exhibits a very high affinity for sulphide in mildly reducing environments such as stream and lake sediments, forming the relatively insoluble mercury sulphide (HgS (s)) (Davis *et al*., 1997; Wang and Driscoll, 1995). Typical pore water concentrations range from approximately 2 ng/L at pH 6 to several mg/L at pH values greater than 8.5. In highly anaerobic systems, the mercuric sulphide may be reduced to elemental mercury and sulphide, whereas under alkaline conditions with high levels of sulphides the more soluble mercuric disulphide complex (HgS_2^{2-}) may exist.

2.1.3 Interactions with Other Metals, including Adsorption

Dissolved mercury sorbs strongly to sediment and suspended solids including organic material and Fe- or Mn-oxyhydroxides (Balogh *et al*., 1998). Gagnon and Fisher (1997) demonstrated that the binding strength of mercury to sediments is very high at near neutral pH values and that very little desorption (less than 10%) occurs at lower or acidic pH values (pH <5). Therefore, the increase in iron oxyhydroxides present on the sediment surface (resulting from precipitation of iron and manganese from seepage waters) may be accompanied by a decrease in mercury mobility, due to the tendency of inorganic mercury and mercury bound organic complexes to adsorb onto these iron oxyhydroxide surfaces (Schutler, 1997).

There is a large body of literature demonstrating the antagonism of selenium towards mercury toxicity in animals (Rudd *et al.*, 1980). In spite of several demonstrations that selenium interacts with Hg in surface waters (Rudd *et al.*, 1980; Rudd *et al.*, 1983; Bjornberg *et al.*, 1988; Paulsson and Lundberg, 1989), the mechanism(s) responsible for the interactions remain unknown (Pelletier, 1985). Selenium may bind with mercury, mercury and selenium may become bound as insoluble mercuric selenide in sediments, making mercury unavailable for methylation, or selenium may cause indirect effects (as a toxicant) inhibiting bacterially mediated mercury methylation. One specific hypothesis relates to this possibility; the methylation of sedimentary selenium to dimethyl selenide may be stimulated by elevated selenium concentrations, which may in turn inhibit mercury methylation. Because of the relative infancy of the research field, there is little information available in the literature with which to judge the relative merits of these potential mechanisms.

2.2 Cadmium (Cd)

Cadmium is a very rare element in the Earth's crust (0.00002%) and occurs mainly as the sulphide or carbonate in zinc ores. The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 µg/g, but much higher and much lower values have also been reported depending on a large number of factors. Igneous and metamorphic rocks tend to show lower values, from 0.02 to 0.2 µg/g, whereas sedimentary rocks have much higher values, from 0.1 to 25 µg/g (Cook and Morrow, 1995). Zinc, lead and copper ores, which are mainly sulphides and oxides, contain even higher levels; 200 to 14,000 µg/g for zinc ores and around 500 µg/g for typical lead and copper ores (Cook and Morrow, 1995).

Cadmium is a natural, usually minor constituent of surface and groundwater. It may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids (Sauve *et al*., 1999). Large variations were reported for the average cadmium contents of rainwater, fresh waters, and surface waters in urban and industrialized areas. Levels from 10 ng/L to 4000 ng/L have been reported in the literature depending on the specific location and whether or not total cadmium or dissolved cadmium is measured (Elinder, 1985; WHO, 1992).

Compounds of cadmium, in contrast to those of zinc, appear to have little or no biological role. Cadmium ions tend to accumulate up the trophic levels because very few living organisms have evolved methods for regulating these ions.

2.2.1 General Fate Information

Cadmium may enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition or direct discharge from industrial operations. Much of the cadmium entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment (WHO, 1992). Once cadmium enters sediments, it can react with sulphur and form relatively insoluble cadmium sulphide. Partitioning of cadmium between the adsorbed-in-sediment state and dissolved-in-water state is, therefore, an important factor in whether cadmium emitted to waters is bioavailable. Soft water environments are of particular concern since bioavailability and aquatic toxicity are enhanced in soft water.

2.2.2 Considerations for Mine Effluents and Receiving Waters

Solution pH is the main factor that controls cadmium solubility in aerated waters, such as mill effluent or surface waters, and the total level of cadmium in the solids associated with this water is important also. Figure 2.4a provides the main dissolved cadmium species in aerated water as a function of pH. All have a $^{+}2$ oxidation state. The main dissolved species are Cd^{2+} at pH values below 8 and cadmium carbonate ($CdCO_3$) at pH values above 8. Cadmium sulphate ($CdSO_4$) is a minor species at pH values less than 9. The dissolved species cadmium disulphide ($Cd(HS)_2$) is dominant only in solutions with a low redox potential and where dissolved sulphide is the dominant sulphur ion (Figure 2.4b). Neither soluble nor total organic matter has much effect on soluble cadmium, so the levels of cadmium in the pore water or surface waters can be predicted from a relatively simple model based on only pH and total content of cadmium in the sediment.

The pH and redox conditions also influence potential solids formation and this is shown in the Eh-pH diagram provided in Figure 2.5. Cadmium hydroxide ($Cd(OH)_2$) solids tend to form at relatively high pH values (pH > 10) and cadmium carbonate ($CdCO_3$) solids can form in the pH range of 8 to 11. Both solids exhibit amphoteric characteristics (i.e., $CdCO_3$ is stable in the pH range 8 to 11, and $Cd(OH)_2$ is stable in the pH range 11 to 13). The $Cd(OH)_2$ solid is relatively soluble and is not expected to control cadmium concentrations in the receiving environment. By contrast, the $CdCO_3$ solid can control cadmium concentrations to 10 to 20 mg/L at pH 6 and as low as 0.01 mg/L at pH 8.5.

Cadmium sulphides (CdS) are highly insoluble and can precipitate from solutions that have dissolved sulphide (e.g., sediment pore water). Typical cadmium concentrations in water that is in equilibrium with cadmium sulphide solids are near 0.1 µg/L at pH 6 to less than 1 ng/L at pH 8.5 or greater. These sulphides can form over a large pH range and precipitation is generally limited to availability of dissolved sulphide sulphur. Dissolution of sulphide solids requires oxidation and this is unlikely after burial in sediments.

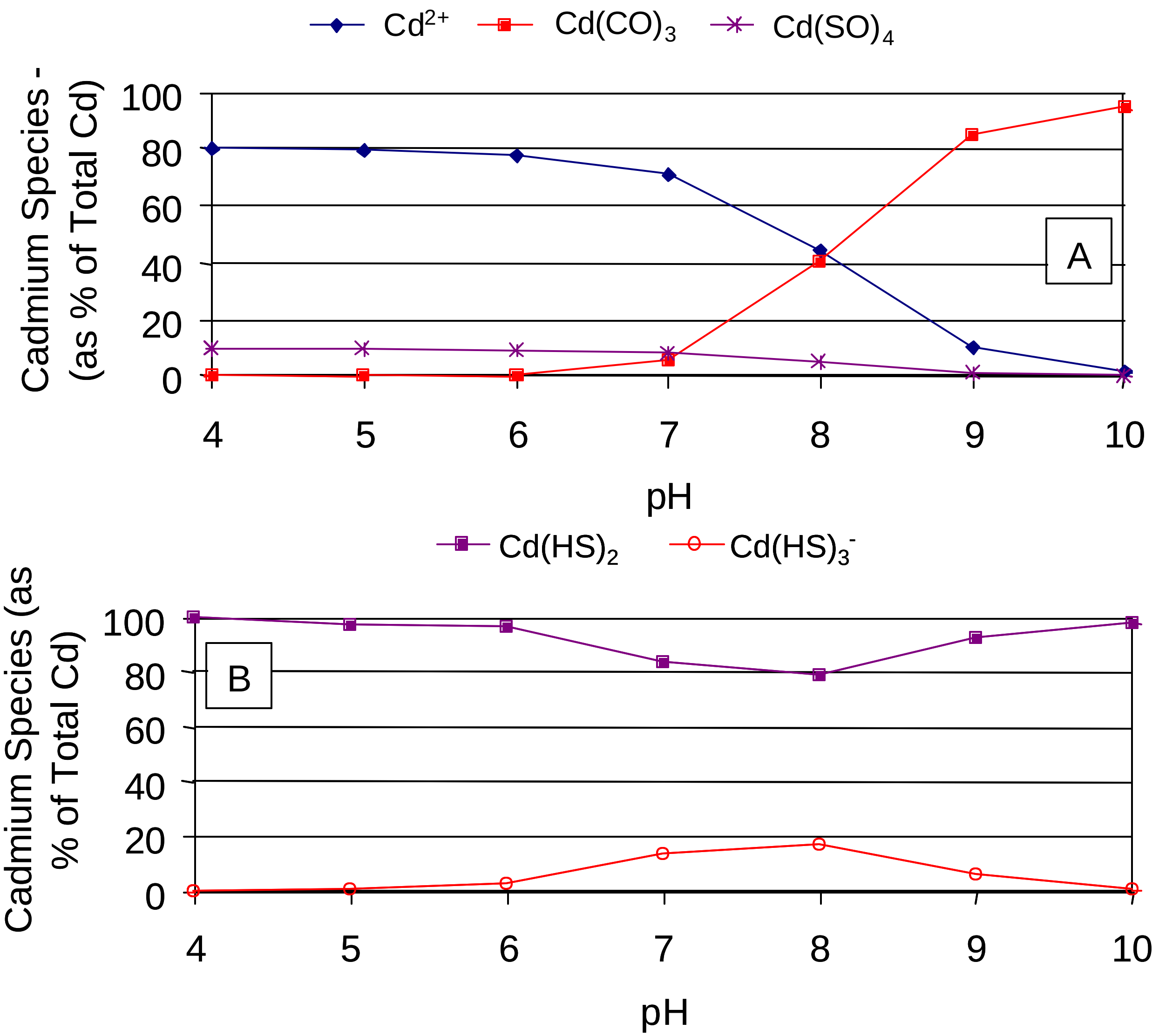

FIGURE 2.4: MAJOR INORGANIC SPECIES OF CADMIUM AS A FUNCTION OF pH UNDER AERATED CONDITIONS (A) AND ANOXIC CONDITIONS (B).

2.2.3 Interactions with Other Metals, including Adsorption

Isomorphous replacement of Cd in calcite ($CaCO_3$) lattice is an important factor that controls Cd levels in natural waters and is particularly important in mine waters that are subject to treatment with lime. Typically, dissolved calcium present from lime addition scavenges dissolved CO_2(g) and reacts to form calcium carbonate ($CaCO_3$). Precipitation of $CaCO_3$ in treated mine waters likely causes co-precipitation of cadmium carbonate or isomorphous replacement of cadmium according to:

$$CaCO_3(s) + Cd^{2+} \Leftrightarrow CdCO_3 + Ca^{2+}$$

The solubility of $CdCO_3$(s) as a minor constituent in the solid solution is reduced in comparison to the solubility of pure $CdCO_3$(s). If one considered the solubility of $CdCO_3$(s) alone, one might infer by neglecting the solid solution that the solution is undersaturated with respect to $CdCO_3$. Although the solubility of $CaCO_3$(s) is not affected by Cd substitution, the solubility of $CdCO_3$ is greatly reduced.

Adsorption and desorption processes are major factors that can control the concentration of cadmium in natural waters. Leyva-Ramos *et al*. (1997) studied the adsorption isotherm of cadmium on activated carbon using a batch adsorber. The effects of temperature and solution pH on the adsorption isotherm were investigated by determining the adsorption isotherm at temperatures of 10, 25, and 40^{o}C and at initial pH values from 2 to 8. It was reported that the amount of Cd^{2+} adsorbed was reduced about three times by increasing the temperature from 10 to 40^{o}C. It was also found that Cd^{2+} was not adsorbed on activated carbon at pH 2 or lower and that Cd^{2+} was precipitated out as cadmium hydroxide ($Cd(OH)_2$) at pH values above 9. Maximum adsorption capacity was observed at pH 8 and the adsorption capacity was decreased about 12 times by reducing the initial pH from 8 to 3. According to the cadmium speciation diagram (Figure 2.5) the predominant species below pH 8 is Cd^{2+}. Thus, cadmium was adsorbed on the activated carbon surface primarily as Cd^{2+}.

Pickering (1980) summarized the sorption behaviour of cadmium ions onto surfaces of metal oxides and clays. His work demonstrated that cadmium is efficiently sorbed onto hydrous metal oxides of iron, manganese and aluminum. The sorption was reversible and a function of pH whereby the amount sorbed increases with pH (Pickering, 1980). Similarly, the amount of cadmium sorbed to clay materials increases with pH. Maximum sorption on clay surfaces occurs at pH values near 8 (Pickering, 1980).

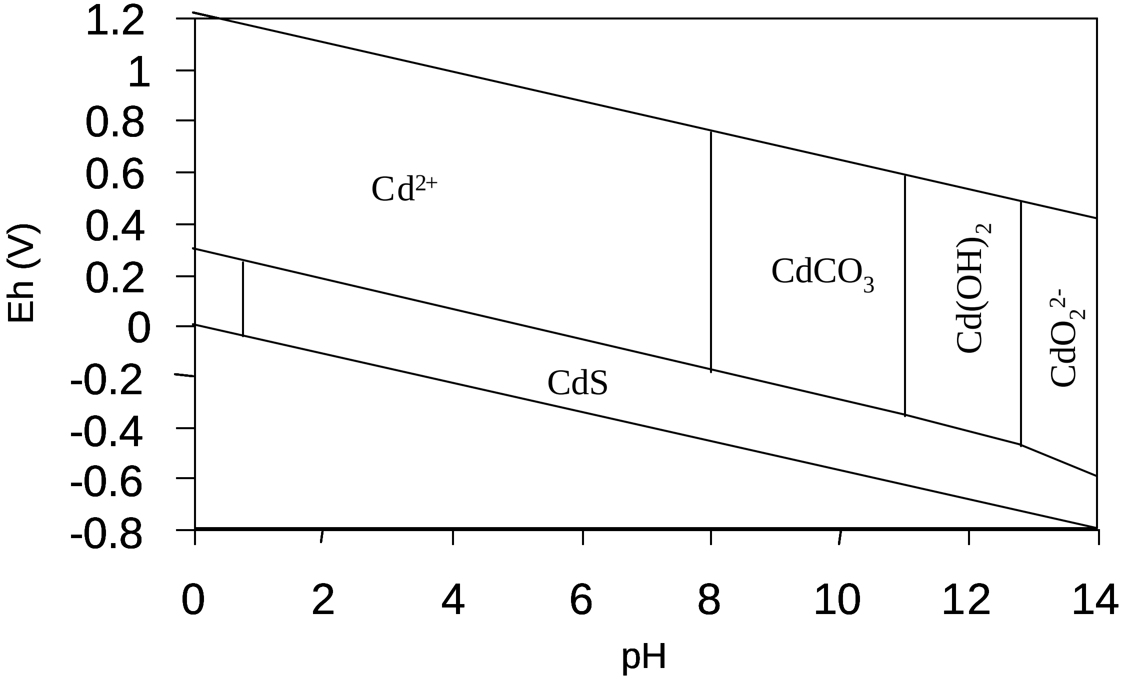

FIGURE 2.5: Eh-pH DIAGRAM FOR THE Cd-C-S-O-H SYSTEM. TOTAL Cd 10^{-6}, C 10^{-3}, S 10^{-3}. ADAPTED FROM BROOKINS (1988).

2.3 Selenium (Se)

Total selenium concentrations in natural waters have been reported to be in the range of 0.1 to 1.5 µg/L (Demayo *et al.,* 1979). Natural selenium concentrations in solids range from 0.05 µg/g in ultramafic to felsic igneous rocks, up to 0.08 µg/g in limestones and as high as 0.6 µg/g in shales (Faure, 1991). Selenium resembles sulphur in many of its properties and often occurs together with or substituted for sulphur in soils and rocks. For example, selenide can substitute for sulphide in pyrite and is known to accumulate to 300 µg/g in sedimentary pyrite. Selenate can also substitute for sulphate in very hydrous sulphate salts such as jarosite, but does not substitute for sulphate in less hydrous sulphate salts such as gypsum.

Anthropogenic sources of selenium include copper, lead and nickel refining and sulphuric acid manufacturing. Selenium is an essential element, with a recommended daily intake of 1.7 µg/kg body weight for infants, and 0.9 µg/kg body weight for adults. Most of the natural human intake arises from food (approximately 75%) with the remainder coming mainly from drinking water (WHO, 1996).

2.3.1 General Fate Information

Selenium exists in four oxidation states in the natural environment - selenide (Se^{2-}), elemental selenium (Se^{o}), selenite (Se^{4+}) and selenate (Se^{6+}). Selenium is often subject to non-equilibrium inorganic redox processes and biogeochemical cycling (White and Dubrovsky, 1994). Biogeochemical processes tend to control selenium cycling and organic forms of selenium are common in surface waters. Organic forms of selenium include seleno amino acids, methyl selenides, methyl seleninic esters, methyl selenones, and methylselenonium ions (Cooke and Bruland, 1987). These organic compounds occur as products of bio-methylation and are more volatile than inorganic forms of selenium (Atkinson *et al.,* 1990). Bacterial selenium methylation occurs in temperate lake sediments (Chau *et al.,* 1976) and is stimulated by organic carbon and temperature (Chau *et al*., 1976; Doran, 1982; Thompson-Eagle and Frankenberger, 1990a, 1990b). In general, selenium methylation is a detoxification process in all biota, and microbial methylation is an important pathway of the biogeochemical selenium cycle (Doran, 1982).

The greatest proportion of total selenium in lakes and streams can normally be found in the sediments, reflecting a net removal of selenium from the water column (Cutter, 1989; Lemly and

Smith, 1987). Both abiotic and biotic factors determine sedimentation rates. The abiotic sedimentation of selenium is a function of pH, metal concentrations (Mn, Fe, and heavy metals), and the prevalence of anion-scavenging sediments (Rudd *et al.,* 1980; Lemly and Smith, 1987; Cutter, 1989; Besser *et al.,* 1989), while biotic sedimentation relates to trophic dynamics and the associated incorporation of selenium into biota, such as phytoplankton.

Cutter (1985, 1989) has examined sedimentary selenium by sequential extraction of sediments. The selenide (Se^{2-}) plus elemental selenium (Se^0) fraction (calculated as the difference between 'total' selenium and (selenite plus selenate) accounted for more than 93% of sedimentary selenium in five lakes. Sequential extraction has also shown that more than 90% of the sedimentary selenium was associated with organic matter and was identified as Se^{-2} plus Se^0, while less than 10% of the sedimentary selenium was associated with iron and manganese oxides (Cutter, 1989). Rudd *et al*. (1980) studied selenium scavenging by sediments and demonstrated that selenium sedimentation was effectively halted by sealing off the bottom of an experimental mesocosm from the sediments. These results suggest further that selenium can be effectively scavenged by natural sediments and that sediments are an important sink for selenium loadings from mining.

2.3.2 Considerations for Mine Effluents and Receiving Waters

It is expected that dissolved inorganic selenium will be prevalent in mine effluents and will likely occur in both selenite (Se^{4+}) and selenate (Se^{6+}) oxidation states. In general, inorganic selenium speciation is controlled by redox conditions, pH, complexation with metals and interactions with solids such as sorption processes. The inorganic species of selenium are shown in the Eh-pH diagram provided in Figure 2.6 which illustrates the approximate stability fields for selenate, selenite, elemental Se and selenide. Selenate (SeO_4^{2-}), predominates under alkaline, oxidizing conditions and this is shown in the upper area of the selenium Eh-pH diagram (Faust and Aly, 1981; Robberecht and Van Grieken, 1982).

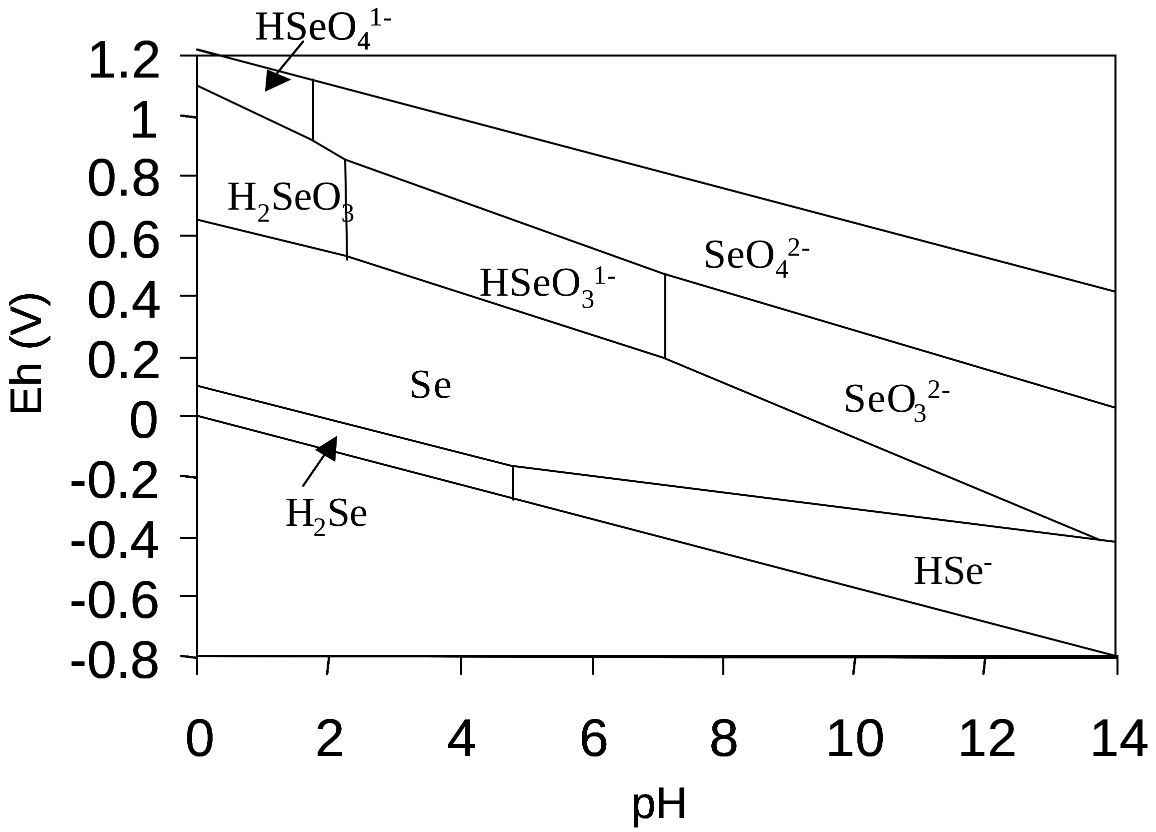

FIGURE 2.6: Eh-pH DIAGRAM FOR THE Se-O-H SYSTEM. TOTAL Se 10^{-6}. ADAPTED FROM BROOKINS (1988).

Under moderately oxidizing conditions, the selenious acid species selenite (SeO_3^{2-}) and biselenite ($HSeO_3^-$) predominate, the proportions of which vary with pH. Metal selenite solids can precipitate under these conditions. For example, a ferric-selenite solid ($Fe_2(SeO_3)_3 \bullet 2H_2O$) can precipitate and dissolved selenium concentrations are in the range of 0.1 mg/L (pH 6) to 10 mg/L (pH 8.5) in water that is in equilibrium with these solids.

The largest stability field is for elemental selenium, which covers a wide range of natural waters. Elemental selenium (Se^0) is relatively stable at all pH values in waters that are free of oxidizing and reducing agents (Faust and Aly, 1981). Selenide, primarily as hydrogen selenide (HSe^-) can form in environments with a large reservoir of free electrons, such as organic rich sediments, that are characterized by low Eh values.

2.3.3 Interactions with Other Metals, including Adsorption

An important process regulating the dissolved concentration and mobility of inorganic selenium is adsorption onto solid surfaces (Balistrieri and Chao, 1990). Selenite (Se^{4+}) efficiently adsorbs onto both iron and manganese oxides. Sorption tends to decrease with increasing pH and is further inhibited by the presence of dissolved phosphate, silicate, and molybdate (Balistrieri and Chao, 1990). By contrast, selenate (Se^{6+}) sorbs weakly to clays and Fe-oxyhydroxides and does not adsorb to manganese oxides. Moreover, selenate sorption is further limited by competitive effects with sulphate at neutral pH. Therefore, sorption reactions can reduce concentrations of dissolved selenite but do not significantly influence selenate concentrations, particularly in sulphate rich waters.

At low redox potentials, which may occur below the sediment-water interface, selenium can be reduced to hydrogen selenide (H_2Se). However, if dissolved heavy metals are present under these conditions, quite insoluble metal selenides can precipitate. Sillen and Martell (1971) reported the solubility for several metal selenides and their data suggest that, in general, metal selenides are very insoluble. Therefore, selenium concentrations would be expected to be less than 0.01 mg/L in water that is in equilibrium with these solids.

2.4 Antimony (Sb)

Total antimony concentrations in natural waters have been reported to be in the range of 0.01 to 1.1 µg/L (Takayanagi and Cossa, 1997; U.S. EPA, 1980a). Natural antimony concentrations in solids are in the range of 0.2 µg/g (Anderson, 2000) to 0.7 µg/g (Pilarski *et al*., 1995). Antimony is a chalcophile, occurring with sulphur and heavy metals such as copper, lead, silver and gold, and has been reported to be associated with arsenic minerals at some gold mines. There are more than 100 naturally occurring minerals of antimony; industrially, stibnite (Sb_2S_3) is the predominant ore of interest. Anthropogenic sources of antimony include gold mining, lead and copper smelting as well as other smelting operations. The crustal abundance has been reported to be greatly exceeded near such operations, e.g., up to 10 mg Sb/g was found near a copper smelter and values of 5 to 260 µg/g were found near lead smelting operations (Pilarski *et al*., 1995).

2.4.1 General Fate Information

Antimony can exist in several oxidation states in natural environments and is normally found in aqueous solutions as the trivalent (Sb^{3+}) and pentavalent (Sb^{5+}) forms. In this way, antimony is superficially similar to arsenic, but its higher atomic number makes it slightly more metallic than arsenic and this characteristic distinguishes its geochemical behaviour from arsenic.

The Sb-H_2O system is not completely understood because of a lack of reliable free energy data for both Sb^{3+} and Sb^{5+} species. It is likely that sorption reactions dominate the mobility of antimony in surface waters and that dissolved antimony is partitioned between surface waters and lake and stream sediments. Mobilization of antimony from sediments is more likely to occur in sediments with low iron and manganese oxide content (Mok and Wai, 1990) and is more likely to occur at relatively low or high (not moderate) pH values. Long term stability of antimony in mine waste is favoured at near neutral pH values (Mok and Wai, 1990).

2.4.2 Considerations for Mine Effluents and Receiving Waters

The inorganic species of antimony are shown in the Eh-pH diagram provided in Figure 2.7 and the approximate stability fields are indicated for Sb^{3+} (i.e., species SbO^+, $Sb(OH)_3$, SbO_2^- Sb_2S_3, $HSb_2S_4^-$ and $Sb_2S_4^{2-}$) and Sb^{5+} (i.e., species Sb_2O_5). The Sb^{+4} oxidation state does not exist and the compound shown as Sb_2O_4 is a mixed oxide of the formula $Sb^VSb^{III}O_4$. The major inorganic antimony species in rivers studied by Mok and Wai (1990) was the pentavalent species Sb_2O_5 (can dissociate to SbO_3^-) and this species represents the predominant species expected in mine effluents and surface water. In solutions of pH from 1 to 10, Sb_2O_3 is a stable Sb^{3+} species. More alkaline solutions dissolve the oxide as SbO_2^-. In neutral and alkaline solutions, Sb^{5+} species exist as SbO_3^- (Nishimura *et al*., 2000). Antimony trioxide solids ($Sb(OH)_3$) can precipitate. Aqueous antimony concentrations in equilibrium with this solid are expected to be approximately 200 mg/L in the pH range of natural waters (pH 6.5 to 8.5). This solid has an amphoteric nature and dissolves as SbO^+ in extremely acid solutions (pH <1).

Antimony tends to complex with sulphur species rather than Cl^-, NH_4^+ or HCO_3^- and Sb-complexes with these species are only important in solutions with very low sulphur concentrations (Brookins, 1972). Dissolved Sb-S species include antimony trisulphide (Sb_2S_3), $HSb_2S_4^-$ and $Sb_2S_4^{2-}$ and these species can occur under highly reducing conditions such as organic rich sediment pore water (Figure 2.7).

2.4.3 Interactions with Other Metals, including Adsorption

Iron and manganese oxyhydroxides have been reported to cause a major effect on concentrations of heavy metals in natural waters. Typically, the interaction between these oxides and heavy metals is attributed to adsorption, ion-exchange and/or co-precipitation (Inoue and Munemori, 1980). Lintschinger *et al*. (1998) performed sequential extractions on sediments and found that Sb was bound to relatively immobile Fe and Al oxides. Substantial amounts were also bound to organic solids. Addition of Fe(III) and Al(III) salts has also been reported to cause sorption/co-precipitation of Sb, and Meima and Comans (1998) report that leaching of Sb is controlled by sorption to amorphous Fe/Al oxyhydroxides at neutral pH values. Humic acid was found to adsorb Sb(III) from solutions of $Sb(OH)_3$ in accordance with Langmuir type isotherms (Pilarski *et al*., 1995) and hydrous oxides of Fe/Mn and Al can sorb Sb(III) in solutions with pH values <6 (Thanabalasingam and Pickering, 1990). These results suggest that antimony is largely affected by sorption reactions with oxides of aluminum, iron and manganese, as well as sorption reactions with organic matter such as humic acid.

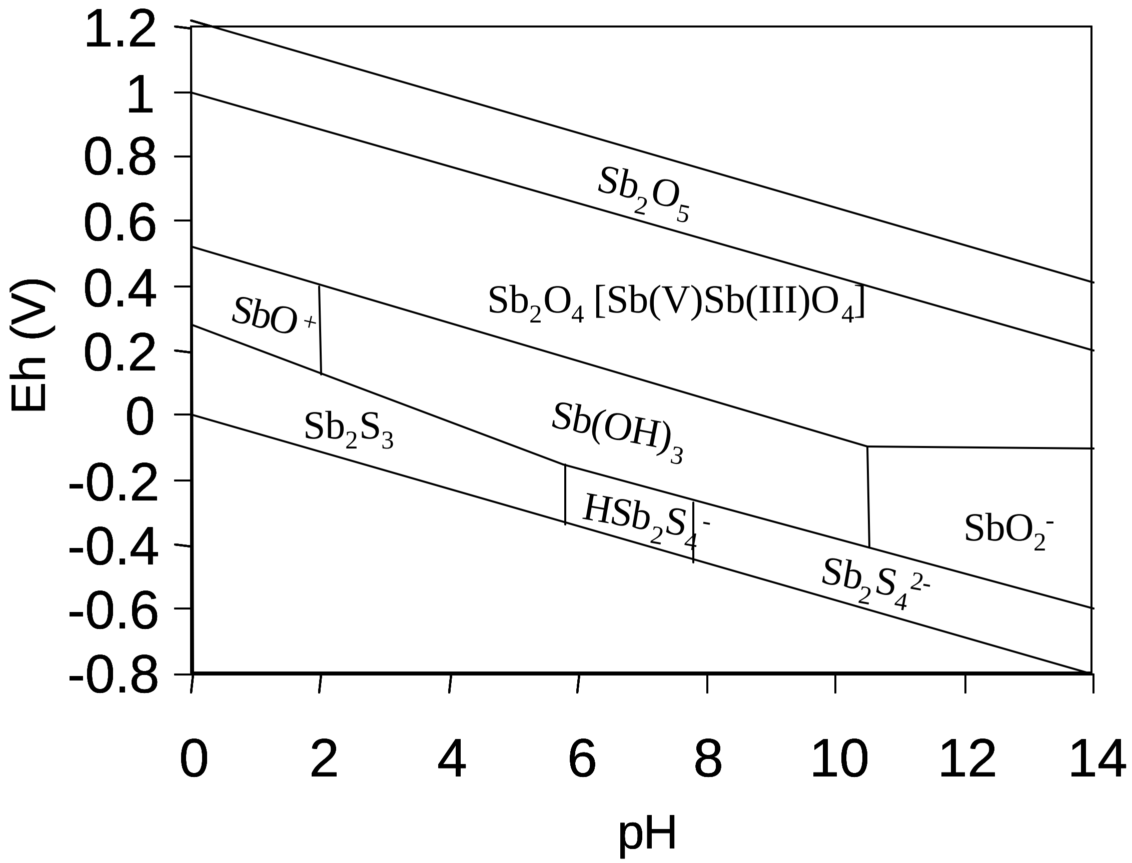

FIGURE 2.7: Eh-pH DIAGRAM FOR THE Sb-S-H_2O SYSTEM. DIAGRAM ADAPTED FROM BROOKINS (1986).

3.0 TOXICITY

The composition of industrial effluents is typically complex, and the resultant toxicity of such effluents is similarly complicated. This generality holds for mine effluents, the composition of which is a function of source ores, the methods involved in ore processing, and pollution control methods applied before release of effluent. The contribution of individual metallic constituents to the overall toxicity of effluents may be reduced or enhanced in relation to these factors.

In total, the toxicity of individual metal constituents of mine effluents could be influenced by speciation, by non-metal constituents of the effluent (suspended and dissolved solids, ammonia, anions, cations), and by interactions with other metals. Of course, if the individual metals in effluents are present below toxic threshold levels, the presence of these other constituents (e.g. calcium) at elevated levels would indicate a large margin of safety for toxicity in the effluents.

The toxicity of mine effluents is of interest in relation to regulatory requirements for acute non-lethality and in relation to the potential for chronic toxicity in the receiving environment. Regardless of acute toxicity, there could be implications for the receiving waters, if metals accumulate substantially in the near- or far-field environments.

Under conditions of acute exposure, the various metal salts tend to involve similar toxicity mechanisms, resulting in a broad spectrum of physical effects such as mucous proliferation at gill surfaces (and the resultant asphyxiation due to impaired gas exchange across gill lamellae) (Dalzell and MacFarlane, 1999). In contrast, the unique toxic characteristics of metals are often only revealed during chronic exposure. This review primarily considers acute toxicity issues regarding mercury, cadmium, selenium, and antimony in mine effluents. The primary focus is on two standard freshwater toxicity testing organisms, rainbow trout (*Oncorhynchus mykiss*) and *Daphnia magna*, although other fish and invertebrate species have been considered to some extent.

The U.S. EPA (1986) water quality criteria documents provide a good database of acute (and chronic) toxicity data. The acute freshwater data for fish and invertebrates are included in Appendix 2. These data have been supplemented by similar data from literature cited in the Cambridge Abstracts and AQUIRE databases, searched as far back as 1980. Only literature that reported acute LC50 values based on a demonstrated dose response were included in this update.

3.1 Mercury

3.1.1 General Toxicity Considerations for Mercury

Mercury is unique among the elements in its volatility. This makes it quite mobile in the environment. This mobility is further enhanced because it can be methylated biologically (primarily by aquatic bacteria). Methylated Hg (MeHg) has unique chemical characteristics (due to the methyl group) that make it prone to bioaccumulate in animals and plants; in contrast, inorganic Hg does not bioaccumulate. Therefore, inputs of inorganic Hg from air into water, either from direct deposition or via transport through watersheds, can lead to increases in the concentrations of methylated (organic) Hg in local ecosystems.

Inorganic mercury compounds are expected to be the primary species in mine effluents. The bioavailability and toxicity of inorganic ionic mercury to aquatic life can be influenced by hardness parameters similar to cadmium, as both metals are “soft” metal ions with a tendency to seek sulfhydryl binding sites in biota (Williams *et al.*, 1985). However, hardness is not normally a consideration with mercury in the aquatic environment because of the relatively low concentrations of mercury typically observed in natural waters. In normal circumstances, methyl mercury is of more relevance to toxicity. Inorganic mercury is not well absorbed relative to the short-chain alkyl mercurials such as methyl mercury (Kaiser and Tolg, 1980; Carty and Malone, 1979), and accumulates primarily in the liver and kidney. Targets of inorganic mercury toxicity include proteins, which bind mercuric ions to sulfhydryl groups resulting in structural and catalytic protein impairment. Inorganic mercury is a central nervous system and renal toxicant. In contrast, methyl mercury is well-absorbed across membranes and is efficiently accumulated by biota. The primary target of methyl mercury toxicity is the central nervous system (Kaiser and Tolg, 1980; Craig, 1986). Methyl mercury accumulates in muscle tissue where it binds to sulfhydryl groups of muscle proteins.

The acute toxicity thresholds for inorganic mercury (typically as $HgCl_2$) in freshwater organisms vary from approximately 5-230 µg/L in crustaceans, to 60-800 µg/L in fish (Ramamoorthy and Baddaloo, 1995). The no-observed-effect-levels (NOELs) for chronic toxicity of inorganic mercury to freshwater invertebrates vary around 1 µg/L (Ramamoorthy and Baddaloo, 1995). Total Hg concentrations in fresh surface waters of North America are typically in the order of 2 ng/L (Wiener *et al*., 1990; Hurley *et al*., 1991), although in mercury-polluted lakes, concentrations can reach 25 ng/L (Bloom and Effler, 1990). Thus, mercury concentrations are generally well below the acute threshold concentrations, and it is clear that mercury does not typically represent an acute toxicity hazard for aquatic organisms.

Mercury toxicity can be alleviated by selenium compounds in some circumstances. This antagonism of selenium towards mercury toxicity in animals has been well documented in the toxicological literature (Rudd *et al*., 1980; Ebyl *et al*., 1969; Frost and Lish, 1976; Ohi *et al*., 1976; Magos and Webb, 1980). The potential for mercury-selenium antagonism could be of importance in mine effluents.

3.1.2 Review of the Acute Toxicity Literature for Mercury

Characteristic toxicity estimates from the early literature have been summarized by Armstrong (1979) in terms of concentrations of mercuric chloride that kill or injure fish. An acute (4-day) value of 200 µg/L was provided for sticklebacks. It is not clear whether this value was for lethality or injury (Armstrong, 1979). Appendix 2 presents a complete listing of freshwater acute toxicity values.

A range of acute values for inorganic mercury toxicity to freshwater fish, including more recent literature, is provided in Table 3.1. 96-h LC50 estimates vary from approximately 17 µg/L to almost 700 µg/L. This 47-fold variation in toxicity likely reflects species differences in susceptibility and differences in specific test conditions. The somewhat higher value (1,500 µg/L) for the 48-h LC50 for one species of fish likely reflects the general toxicological principle that toxicity is a function of both exposure time and concentration or dose. For rainbow trout, the LC50 values range from 155-420 µg/L.

Representative acute toxicity values for inorganic mercury to *Daphnia magna* and other invertebrates are summarized in Table 3.2. For daphnid species, toxicity values are in the range of 1-15 µg/L. With respect to regulatory acute toxicity testing, it appears that *Daphnia* is 10-100 times more sensitive to mercury than rainbow trout.

TABLE 3.1: ACUTE TOXICITY VALUES FOR MERCURY IN FISH

Species	Endpoint	Value	Comments	Ref.
Rainbow Trout	96-h LC_{50}	155.1 µg/L	• Juveniles (mercuric chloride)	1
Rainbow Trout	96-h LC_{50}	280 µg/L	• Juveniles (mercuric chloride)	2
Rainbow Trout	96-h LC_{50}	220 µg/L	• Juveniles (mercuric chloride)	2
Rainbow Trout	96-h LC_{50}	420 µg/L	• Juveniles (mercuric chloride)	3
Rainbow Trout	96-h LC_{50}	275 µg/L	• Juveniles (mercuric chloride)	4
Colorado squawfish, bonytail, razorback sucker	96-h LC_{50}	57-168 µg/L	• Larval and juvenile stages	5
Common carp	96-h LC_{50}	160-770 µg/L	• Juvenile fish (3.5-6 g)	6
Mosquitofish, golden shiner	96-hr LC_{50}	52.62 µg Hg/L 16.75 µg Hg/L		7
Anabas testudineus	96-hr LC_{50}	640 µg Hg/L	• Mercuric chloride	8
Freshwater Catfish	96-hr LC_{50}	300 µg/L	• Mercuric chloride	9
Etroplus maculates	96-hr LC_{50}	670 µg/L	• Mercuric chloride	10
Common Guppy	96-hr LC_{50}	260 µg/L		11
Sarotherodon mossambicus	48-hr LC_{50}	1,500 µg/L	• Mercuric chloride	12
Channa marulius	96-hr LC_{50}	314 µg/L		13

1. Matida *et al*. (1971), 2. MacLeod and Pessah (1973), 3. Daoust (1981), 4. Lock and van Overbeeke (1981), 5. Buhl (1997), 6. Alam and Maughan (1995), 7. McCrary and Heagler (1997), 8. Sinha and Kumar (1992), 9. Rajan and Banerjee (1991), 10. Gaikwad (1989), 11. Khangarot and Ray (1987), 12. Naidu *et al*. (1984), 13. Khangarot (1981).

TABLE 3.2: ACUTE TOXICITY VALUES FOR MERCURY IN INVERTEBRATES

Species	Endpoint	Value (µg/L)	Comments	Ref.
Daphnia magna	48-hr LC_{50}	5		1
Daphnia magna	48-hr LC_{50}	3.2		2
Daphnia magna	48-hr LC_{50}	1.5		2
Daphnia magna	48-hr LC_{50}	2.2		2
Daphnia magna	48-hr LC_{50}	4.4	• < 6 h old	3
Daphnia magna	48-hr LC_{50}	4.4	• <24 h old	3
Daphnia magna	48-hr LC_{50}	5.2-14.8	• 1-9 d old	3
Daphnia pulex	48-hr LC_{50}	2.2		2
Macrobrachium lammarrei	24-hr LC_{50} 96-hr LC_{50}	167 95	• Freshwater prawn	4

1. Biesinger and Christensen (1972), 2. Canton and Adema (1978), 3. Barera and Adams (1983),
4. Murti and Shukla (1984).

Methylmercury is considerably more toxic to fish, with acute values for rainbow trout as low as 24 µg/L (Wobeser, 1973). No data are available regarding acute toxicity of methylmercury in daphnids. Methylmercury is unlikely to be an important constituent of mine effluents.

For comparison, chronic toxicity values for inorganic mercury range from <0.23 to 1.3 µg/L, with fish showing the lower values (U.S. EPA, 1985a). Chronic values for methylmercury range from <0.04 µg/L to 0.67 µg/L for daphnids (Biesinger *et al.*, 1982) and a brook trout value of 0.52 µg/L (McKim *et al.*, 1976) is in the same range.

Recent findings indicate that the whole body "critical body residue" (CBR) for chronic toxicity of methylmercury to fish is in the range of 1 to 5 mg/kg (Niimi and Kissoon, 1994). If this estimate is correct, it would mean that approximately one-half of Ontario lakes have fish populations that may be chronically mercury-stressed. This is based on the findings of the Sportfish Contaminant Monitoring Program (OME, 1993) that 706 of 1,357 sampling sites have mercury levels in fish muscle exceeding 1 mg/kg. Residue guidelines for protection of wildlife consuming fish (CCME, 1999) are approximately 30 times lower than the tissue levels that may be harmful to the fish themselves. The biomagnification of methylmercury through the riparian food chain is often of particular concern in mercury-contaminated environments. A vast literature exists on this topic, which is outside the scope of this review.

3.1.3 Scale of Potential Toxicity Concern around End-of-Pipe

The effluent composition data in Table 1.3 includes only four mercury concentrations. These were determined by ICP, with relatively high detection limits. The average concentration in Table 1.3 is 4.4 µg/L (total), but the true average concentration is likely much lower since three of the four measured values were non-detects (mercury was assumed to be present at one-half the detection limit). On the basis of this limited information, the mercury concentration could be near the threshold for acute toxicity for *Daphnia magna*. It would be approximately 50 to 100 times lower than that of rainbow trout.

Suspended solids are in the range of 5 mg/L. Since the suspended solids in mine effluents can serve as adsorptive surfaces for metals such as mercury (Section 2.1.3), the solids could act to reduce effluent toxicity. The importance of this effect will depend upon the adsorptive properties of the solids present in the effluent.

The effluents are hard, with elevated calcium concentrations. This hardness would be expected to act to minimize the bioavailability and toxicity of inorganic mercury ions. This could be relevant for *Daphnia* toxicity (Brkovic-Popovic, 1990).

Although mercury concentrations in effluent are not likely to be toxic to effluent test organisms or to biota in the receiving environment, depending on the mass release rate and the nature of the receiving environment, mercury in the low µg/L range could produce a significant loading of mercury, which would ultimately add to the mercury pool of downstream systems. This mercury would be expected to add to the methylation capacity of these systems. Higher levels of methyl mercury in fish could ultimately result.

3.2 Cadmium

3.2.1 General Toxicity Considerations for Cadmium

Cadmium is a rare element, with an average crustal concentration of 0.1-0.2 mg/kg (0.89-1.78 µmol/kg), 1/350 as common as zinc (Nriagu, 1980a). Cadmium and zinc are closely related chemically, and cadmium is typically found in zinc ores. Thus, cadmium and zinc frequently undergo geochemical processes together. Smelting has released cadmium to the atmosphere for thousands of years (Elinder, 1985). However, it is only within this century that atmospheric emissions of cadmium have dramatically increased (Elinder, 1985), so that anthropogenic sources of atmospheric cadmium may now exceed natural sources by approximately nine times (Nriagu, 1980a). Even in remote regions, cadmium concentrations have increased between 15- and 60-fold in the last century (Nriagu, 1980b). In North American freshwaters, cadmium concentrations have increased over the past two decades (Smith *et al*., 1987), indicating that cadmium pollution is not uncommon on this continent.

Non-ferrous metal smelting contributes approximately 76% of the anthropogenic cadmium emissions, while fossil fuel combustion accounts for the remaining 24% (Nriagu, 1980b). Point source emissions of cadmium are of obvious importance near smelters (Franzin *et al*., 1979; Franzin, 1984; Harrison and Klaverkamp, 1990), but elevated cadmium concentrations in the water and sediments of remote lakes in eastern North America indicate that long-range atmospheric transport of cadmium is also significant (Johnston, 1987; Smith *et al*., 1987). In either case, the anthropogenic emissions of cadmium are usually associated with the release of nitrogen and sulfur oxides, and the subsequent acidification of poorly buffered receiving waters of the Precambrian Shield. Because the cadmium concentration in freshwater is typically inversely related to pH (Breder, 1988; Stephenson and Mackie, 1988), cadmium may be retained for longer periods in the water column of acidified lakes relative to non-acidified lakes, in which cadmium is normally partitioned to the particulate phase and rapidly deposited to sediments (Breder, 1988).

The bioaccumulation of cadmium in terrestrial and aquatic biota is well-documented, with accumulation half-lives in the order of years to decades (Eisler, 1985; Norberg *et al*., 1985; WHO, 1992) indicating that cadmium is excreted very slowly. Cadmium bioaccumulates primarily in the kidney and liver (Nordberg *et al.*, 1985), with the kidney being the target organ of chronic toxicity (Kjellstrom, 1985; Foulkes, 1986), although in fish the gill is the target organ of toxicity under conditions of acute waterborne exposure. Cadmium continues to increase in the aquatic environment (Smith *et al.*, 1987), is a priority pollutant in the United States, Canada, and Europe, and is a significant contaminant in Canadian lakes and aquatic biota (Yan *et al*., 1990; Bendell-Young *et al.*, 1986).

The toxicity and bioaccumulation of cadmium is a function of free ion activity (Sprague, 1985) and is therefore affected by interactions with other inorganic elements particularly calcium, magnesium, zinc, copper, and iron (Spivey-Fox, 1988), and humic substances. The classic example of these interactions is the inverse relationship between cadmium toxicity and water hardness (Markich and Jeffree, 1994; Hollis *et al*., 2000). Calcium is the primary ion responsible for the protective effect of hardness, particularly with respect to acute exposure. The interactions between calcium and metals such as cadmium and lead have long been known (Moriuchi, 1982), and the toxicity of these metals ultimately involves the disruption of calcium metabolism. The interactions of cadmium with iron and zinc are secondary interactions, and since these are essential metals themselves, cadmium toxicity can include impairment of the metabolism of these metals, including anemia (Schafer and Forth, 1985; Spivey Fox, 1988).

The nature of interactions between cadmium and other elements has led several researchers to propose that toxicity correlates better with tissue cadmium concentrations than with waterborne cadmium levels (Borgmann *et al.*, 1991; Davies, 1978; Connolly, 1985). If toxicity is related to the action of cadmium at the cellular level, then toxicity will occur once tissue concentrations reach a certain critical threshold level, although water quality parameters (e.g., hardness) will affect uptake kinetics. Obviously, in hard waters the toxicity threshold may never be reached, but in soft water lakes with significant cadmium loadings, chronic toxicity may occur.

Considering the speciation of cadmium in effluent, the primary species of cadmium responsible for toxicity is the free Cd^{2+} ion (Sprague, 1985). Any conditions promoting the removal of cadmium ions from solution will reduce toxicity. Consequently, suspended and dissolved solids are potentially important factors in mine effluent toxicity.

3.2.2 Review of the Acute Toxicity Literature for Cadmium

A range of acute values for cadmium toxicity to freshwater fish and invertebrates is provided in Tables 3.3 and 3.4. 96-h LC_{50} estimates vary from approximately 1 µg/L to 8,000 µg/L for rainbow trout depending on hardness and life stage. The range for daphnids is 1 to almost 500 µg/L. The hardness conditions of each test are noted wherever these conditions were reported. Appendix 2 presents a complete listing of freshwater acute toxicity values.

The U.S. EPA (1986) has described the influence of hardness on acute toxicity criterion values for aquatic life. Specifically, the suggested criterion (C) is given in µg/L as:

$$C = e^{1.128 \ln(H) - 3.828}$$

where H = hardness as mg/L $CaCO_3$. This relationship can be used to derive criteria at any two hardness values. The ratio between these criteria provides an appropriate factor by which to adjust the acute toxicity value for a particular fish or daphnid species, in order to estimate what the toxicity value might be at a different hardness.

For comparison, chronic toxicity values for cadmium range from 0.2 to 5 µg/L for daphnids and from 1.5 to 156 µg/L for salmonid fishes (U.S. EPA, 1985). Chronic toxicity also displays a predictable hardness dependence, although the relationship takes a slightly different form than that shown above for acute toxicity.

Campbell (1995) discusses the free-ion activity model of metal toxicity in detail.

TABLE 3.3: TOXICITY VALUES FOR CADMIUM IN FRESHWATER FISH

Species	Endpoint	Value	Comments	Ref.
Colorado squawfish, bonytail, razorback sucker	96-h LC_{50}	78-168 µg/L	• Larval and juvenile stages	1
Rainbow Trout	Incipient lethal level (ILL)	6 µg/L at 187 hrs 122 µg/L at 266 hrs	• Non acclimated adult fish • Acclimated to 10.2 µg/L for 21 d	2
Rainbow Trout	96-hr LC_{50}	3.02 µg/L 6.12 µg/L 5.70 µg/L	• 50 mg/L hardness (Mg) • 200 mg/L hardness • 400 mg/L hardness	3
Rainbow Trout	48-hr LC_{50}	5.0 µg/L	• Embryo-larval toxicity	4
Rainbow Trout	48-hr LC_{50}	91-677 µg/L 358 µg/L 3,698 µg/L	• 20 mg/L hardness (Ca) • 80 mg/L hardness • 320 mg/L hardness	5
Rainbow Trout	96-hr LC_{50}	6-7 µg/L		6
Rainbow Trout	96-hr LOEC	1.5-2.4 µg/L	• Lowest effect concentration	7
Rainbow Trout	96-hr LC_{50}	10-20 ug/L and 4,700-8,000 µg/L	• Early life stages	8
Rainbow Trout	1 mo. LOEC 2 mo. LOEC 19 mo. LOEC	1.5 µg/L 26 µg/L 7.1 µg/L		7
Rainbow Trout	1 mo. NOEC 2 mo. NOEC 19 mo. NOEC	0.7 µg/L 14.8 µg/L 3.4 µg/L		7
Fathead Minnow	96-hr LC_{50}	60 µg/L	• 290 mg/L hardness	9
Fathead Minnow	96-hr LC_{50}	4.8 µg/L	• 20 mg/L hardness	10

1. Buhl (1997), 2. Stubblefield *et al*. (1999), 3. Davies *et al*. (1993), 4. Dave *et al*. (1981), 5. Calamari *et al*. (1980), 6. Kumada *et al*. (1973), 7. Goettl *et al*. (1976), 8. Van Leeuwen *et al*. (1985), 9. Schubauer-Berigan *et al*. (1993), 10. Suedel *et al*. (1997).

TABLE 3.4: TOXICITY VALUES FOR CADMIUM IN INVERTEBRATES

Species	Endpoint	Value	Comments	Ref.
Anodonta imbecilis	48-hr LC_{50}	57 µg/L	• Juvenile mussels	1
Daphnia pulex	48-hr LC_{50}	78 µg/L		2
Daphnia carinata	48-hr LC_{50} 96-hr LC_{50}	265-350 µg/L 110-480 µg/L	• Varying food levels • 50 mg/L hardness	3
Echinisca triserialis	48-hr LC_{50} 96-hr LC_{50}	345-460 µg/L 58-340 µg/L		
Hydropsyche angustipennis	96-hr LC_{50}	520 mg/L	• Whole range of invertebrate organisms in between this range	4
Gammarus pulex	96-hr LC_{50}	20 µg/L		
Daphnia magna	48-hr LC_{50}	24-40 µg/L 18-31 µg/L	• Without sediment	5
Hyalella azteca	96–hr LC_{50} 10-d LC_{50}	8 µg/L <2.8 and <6.0 µg/L		
	96–hr LC_{50} 10-d LC_{50}	74 µg/L 80 µg/L	• With sediment	
Daphnia magna	48-hr EC_{50}	23-164 µg/L	• Varying ages	6
Daphnia magna	48-hr LC_{50}	39 µg/L 91 µg/L	• Tested in water • Tested in a water-sediment slurry	7
Daphnia magna	48-hr LC_{50}	69 µg/L		8
Daphnia magna	48-hr LC_{50}	38 µg/L @ 20°C 0.009 mg/L @ 26°C		9
Daphnia pulex	48-hr LC_{50}	0.042 mg/L @ 20°C 0.006 mg/L @26°C		
Macrobrachium lammarrei	24-hr LC_{50} 96-hr LC_{50}	374 µg $CdCl_2$/L 195 µg/L	• Freshwater prawn	10
Daphnia magna	28-d EC_{50}	0.002 mg/L	• Growth inhibition (Chronic)	11
Daphnia magna	48-hr LC_{50}	65 µg/L	• 45 mg/L hardness (Ca)	12
Daphnia magna	96-hr LC_{50}	12.7 µg/L	• 78 mg/L hardness	13
Daphnia magna	48-hr LC_{50}	120 µg/L	• 170 mg/L hardness	14

TABLE 3.4: TOXICITY VALUES FOR CADMIUM IN INVERTEBRATES

Species	Endpoint	Value	Comments	Ref.
Daphnia magna	48-hr LC_{50}	360 µg/L	• 10 mg/L hardness	15
Ceriodaphnia dubia	48-hr LC_{50}	350 µg/L	• 290 mg/L hardness	16
Ceriodaphnia dubia	48-hr LC_{50} 96-hr LC_{50}	63.1 µg/L 16.9 µg/L	• 20 mg/L hardness	13
Ceriodaphnia dubia	48-hr LC_{50}	78.2 µg/L	• 81 mg/L hardness	17
Hyalella azteca	96-hr LC_{50}	190 µg/L	• 50 mg/L hardness	18
Hyalella azteca	96-hr LC_{50}	2.8 µg/L	• 20 mg/L hardness	13

1. Keller and Zam (1991), 2. Roux *et al*. (1993), 3. Chandin (1988), 4. Williams *et al*. (1985),
5. Nebeker *et al*. (1986a), 6. Nebeker *et al*. (1986b), 7. Schuytema *et al*. (1984), 8. Dave *et al*. (1981),
9. Lewis and Horning (1991), 10. Murti and Shukla (1984), 11. Enserink *et al*. (1991),
12. Biesinger and Christensen (1972), 13. Suedel *et al*. (1997), 14. Taylor *et al*. (1998), 15. Fargasova (1994),
16. Schubauer-Berigan *et al*. (1993), 17. Nelson and Roline (1998), 18. Schlekat *et al*. (1992).

3.2.3 Scale of Potential Toxicity Concern around End-of-Pipe

Cadmium toxicity is inversely related to both water hardness and calcium concentrations. Therefore, pH control using lime would be expected to reduce cadmium toxicity. Alternatively, the toxicity of aqueous cadmium can be enhanced by ammonia (Gargiulo *et al*., 1996). Therefore, since ammonia can be a relatively important contributor to mine effluent toxicity, such interactions could enhance toxicity under certain specific conditions.

Based on the effluent composition from Table 1.3, the average cadmium concentration in a typical mine effluent is 11.8 µg/L (total) or 5.43 µg/L (dissolved). This average includes below-detection limit data and could be a high estimate of cadmium concentrations in such effluents. Nonetheless, if compared with the toxicity values of Tables 3.3 and 3.4, this value is in the range of the acute toxicity thresholds of both rainbow trout and *Daphnia magna* in soft water. However, the effluents are hard, with an average hardness of 825 mg/L. This hardness would be expected to act to minimize the bioavailability and toxicity of cadmium ions. Considered as a component of a whole effluent, the cadmium concentrations at the indicated levels would be toxic in soft water, but not in a typical mine effluent. Furthermore, the cadmium released in an effluent, after dilution in a soft receiving water, is not likely to become acutely toxic, because the cadmium concentration is reduced as the hardness is reduced.

Suspended solids are in the range of 5 mg/L. Since the suspended solids in mine effluents can serve as adsorptive surfaces for metals such as cadmium (Section 2.2.3), the solids could act to reduce effluent toxicity. The limited data in Table 1.3 and Appendix 1 indicate that cadmium could be approximately 50% particulate-bound in the effluents. The suspended solids would supplement the toxicity reduction due to hardness.

3.3 Selenium

3.3.1 General Toxicity Considerations for Selenium

Selenium is a metalloid element, classified in Group VIA of the chemical periodic table, in the period below the non-metal sulfur (S) and above the metal tellurium (Te). As a consequence of its position between these two related elements, selenium shares several chemical properties with them, especially with sulfur. The shared properties mean that selenium and sulfur can be chemically interchangeable in many circumstances. This interaction between sulfur and selenium is thematic, and is critical to understanding the toxicity of selenium in effluents and freshwaters.

Inorganic selenium speciation is controlled by redox conditions, pH, solubility, sorption processes, and complexation with metals. Selenate (SeO_4^{2-}) is the predominant inorganic selenium species under alkaline, oxidizing conditions (Faust and Aly, 1981; Robberecht and Van Grieken, 1982). Under moderately oxidizing conditions, the selenious acid species selenite (SeO_3^{2-}) and biselenite ($HSeO_3^-$) predominate (the proportions varying with pH).

For comparison with the redox reactions of selenium, sulfur behaves differently from selenium in several ways. Most importantly, sulfite is not thermodynamically likely. As a result, the sulphate stability field is large, and encompasses ranges of pH and Eh over which selenium exists as both selenate and selenite. Therefore, the potential competitive interactions between inorganic sulfur and selenium are limited to those between sulphate and selenate. No such interaction exists for selenite. However, an additional process that is capable of regulating the toxicity of inorganic selenium is adsorption on solid surfaces, with selenite adsorbing on both iron and manganese oxides, while selenate is only weakly adsorbed on iron oxides and does not adsorb at all on manganese oxides (Balistrieri and Chao, 1990). Taken together, these processes demonstrate that selenium toxicity in effluents could vary considerably according to both the speciation of selenium and the presence of other factors (solids and sulphate) that could further influence bioavailability and toxicity. Selenium and mercury are antagonistic with respect to toxicity (Sec.3.1.1).

Considering the whole effluent, potential toxic interactions of selenium could be influenced by: (1) basic bioavailability issues (related to speciation); (2) competition between sulfur and selenium analogues; and (3) binding of metals (cadmium and mercury) to selenium to form complexes that remove both metal and selenium from solution.

3.3.2 Review of the Acute Toxicity Literature for Selenium

Some acute toxicity values for fish exposed to selenium are presented in Table 3.5. Selenate is found to be generally less toxic than selenite. The role of aqueous sulphate concentrations in the differential toxicity of these selenium species has not been adequately researched. Acute values for rainbow trout range from 4.2 to 32.3 mg/L, however acute values as low as 1 mg/L are reported for fathead minnows (Halter *et al.*, 1980) and other values as high as 88 mg/L have been reported.

TABLE 3.5: ACUTE TOXICITY VALUES FOR SELENIUM IN FRESHWATER FISH (values in mg/L)

Species	Endpoint	Value	Comments	Ref.
Etroplus maculates	96-hr LC_{50}	10.7	• Selenium oxide	1
Arctic Grayling	96-hr LC_{50}	34.3 100	• Sodium selenite (juvenile) • Sodium selenate (alevin)	2
Rainbow Trout	96-hr LC_{50}	9 32.3	• Sodium selenite (juvenile) • Sodium selenate (juvenile)	2
Rainbow Trout	96-hr LC_{50}	4.2 4.5	• Selenite • Selenite	8
Rainbow Trout	96-hr LC_{50}	12.5	• Selenite	9
Rainbow Trout	Chronic lethality	7.2 8.2 8.8	• Selenite • Selenite • Selinite	10
Coho Salmon	96-hr LC_{50}	7.8 74	• Sodium selenite (juvenile) • Sodium selenate (juvenile)	2
Coho Salmon	96-hr LC_{50}	7.8 32.5	• Sodium selenite (juvenile) • Sodium selenate (juvenile)	3
Chinook Salmon	96-hr LC_{50}	13.8 115	• Sodium selenite (fry) • Sodium selenate (fry)	3
Colorado Squawfish	96-hr LC_{50}	14 66	• Sodium selenite (fry) • Sodium selenate (fry)	4
Colorado Squawfish	96-hr LC_{50}	20.7 88	• Sodium selenite (fry) • Sodium selenate (fry)	5
Colorado Squawfish	96-hr LC_{50}	12.8 24.6	• Sodium selenite (larva) • Sodium selenate (larva)	6
Bonytail Chub	96-hr LC_{50}	19 55	• Sodium selenite (fry) • Sodium selenate (fry)	4
Razorback Sucker	96-hr LC_{50}	15 48	• Sodium selenite (fry) • Sodium selenate (fry)	4

TABLE 3.5: ACUTE TOXICITY VALUES FOR SELENIUM IN FRESHWATER FISH (values in mg/L)

Species	Endpoint	Value	Comments	Ref.
Razorback Sucker	96-hr LC_{50}	13.7 13.8	• Sodium selenite (juvenile) • Sodium selenate (juvenile)	6
Razorback Sucker	96-hr LC_{50}	11.3 15.9	• Sodium selenite (fry) • Sodium selenate (fry)	4
Flannelmouth Sucker	96-hr LC_{50}	19.1 26.9	• Sodium selenite (fry) • Sodium selenate (fry)	7
Fathead Minnow	96-h LC_{50}	1.0		11
Bluegill	96-h LC_{50}	28.5		12

1. Gaikwad (1989), 2. Buhl and Hamilton (1991), 3. Hamilton and Buhl (1990), 4. Hamilton (1995),
5. Hamilton and Buhl (1997a), 6. Buhl and Hamilton (1996), 7. Hamilton and Buhl (1997b),
8. Adams (1976), 9. Goettl and Davies (1976), 10. Hodson *et al*. (1980), 11. Halter *et al*. (1980),
12. Cardwell *et al*. (1976).

A range of acute toxicity values for invertebrates exposed to selenium is presented in Table 3.6. The values for daphnids range from 0.43 to 5.3 mg/L. Halter *et al.* (1980) reported acute toxicity to the amphipod *Hyalella azteca* at selenium concentrations as low as 0.34 mg/L. Appendix 2 presents a complete listing of freshwater acute toxicity values.

For comparison, chronic toxicity tests involving long-term exposure to selenite have shown increased mortality and deformities in rainbow trout at concentrations as low as 0.13 mg/L (Goettl *et al.*, 1976). Some field studies have suggested developmental effects on fish at even lower levels of selenium, in association with a phytoplankton food chain (Cumbie and Van Horne, 1978). Multigeneration experimental stream studies with fish (Hermanutz *et al.*, 1992) and experimental pond studies with invertebrates (Crane *et al.*, 1992) seem to confirm such effects at selenium concentrations in the order of 0.01 mg/L.

3.3.3 Scale of Potential Toxicity Concern around End-of-Pipe

Toxicity of selenium in the immediate receiving environment and in regulatory testing would be influenced by a number of factors. Typical interactions for selenium in the aquatic environment involve pH (Brix *et al*., 2001a) and sulphate, at least with respect to selenate toxicity (Brix *et al*., 2001b). These are common considerations for ambient freshwaters as well as effluent. In addition, there is a potential for metal-Se interactions in mine effluent, although a quantitative estimate of the degree of interaction is not possible from the limited data available in the literature at this time.

Based on the effluent composition from Table 1.3, the average selenium concentration is 92 μg/L (0.092 mg/L) (total). In comparison with the toxicity values of Tables 3.5 and 3.6, this value is in the order of 50- and 5-fold below the acute toxicity thresholds of rainbow trout and *Daphnia magna* (respectively). Therefore, selenium is not expected to make an important contribution to acute toxicity in these tests.

Suspended solids are in the range of 5 mg/L. Since the suspended solids in mine effluents can serve as adsorptive surfaces for selenite (Section 2.3.3), the solids could act to reduce effluent toxicity. The importance of this effect will depend upon the adsorptive properties of the solids present in the effluent.

TABLE 3.6: ACUTE TOXICITY VALUES FOR SELENIUM IN INVERTEBRATES (values in mg/L)

Species	Endpoint	Value	Comments	Ref.
Daphnia magna	48-hr LC_{50} 72-hr LC_{50}	0.68 selenite 0.75 selenate 0.55 selenate 1.4 selenate	• Adults • Juveniles • Eggs and embryos	1
Daphnia magna	48-hr LC_{50}	0.430		2
Daphnia magna	48-hr LC_{50}	0.710		3
Daphnia magna	48-hr LC_{50}	5.3 1.45	• Selenate • Species mean value	4
Daphnia magna	48-hr LC_{50}	1.01	• Selenate	5
Hyalella azteca	48-hr LC_{50}	0.34	• Sodium selenite	7
Daphnia magna	48-hr LC_{50}	1.2	• Selenous acid	8
Daphnia magna	48-hr LC_{50}	0.43	• Selenous acid	9
Ceriodaphnia dubia	48-hr LC_{50}	1.92	• Selenate	6

1. Johnston (1987), 2. LeBlanc (1980), 3. Halter *et al*. (1980), 4. Dunbar *et al*. (1983), 5. Brooke *et al*. (1985), 6. Brix *et al*. (2001a), 7. Halter *et al*. (1980), 8. Kimball (unpubl.), 9. U.S. EPA (1980b).

3.4 Antimony

3.4.1 General Toxicity Considerations for Antimony

Antimony is a metalloid in Group VB of the chemical periodic table. It is one period below arsenic, and as is the case with selenium and sulfur, antimony and arsenic have chemical similarities. For instance, both elements are known to be biomethylated in the environment and appear to act competitively with respect to toxicity (Andrewes *et al*., 2000). Relatively little information is available regarding antimony toxicity to freshwater organisms, although the limited toxicological information that exists for mammals likely has general relevance for aquatic biota (Gebel, 1997). It is possible that the most important characteristic of antimony in the context of mine effluents is its potential to competitively inhibit arsenic toxicity due to the similarity of these two elements.

3.4.2 Review of the Acute Toxicity Literature for Antimony

Few data exist for antimony toxicity. The available data indicate that antimony is not a particularly potent toxicant to fish (Table 3.7). The 96-h LC_{50} estimate varies from 21.9 to 35.5 mg/L, based on two tests involving fish. Chronic data for rainbow trout exposed over a 28-day period indicate the median lethal concentration may be as low as 600 µg/L (0.6 mg/L), while similar data for fathead minnows indicate a somewhat higher value.

For *Daphnia magna*, acute toxicity occurs in the range of 9-20 mg/L antimony, with a high estimate of 530 mg/L in one study (Table 3.8). Chronic test data for *Daphnia magna* (28-day life cycle exposure) indicate measurable toxic effects at 5.4 mg/L antimony.

3.4.3 Scale of Potential Toxicity Concern around End-of-Pipe

Based on the effluent composition from Table 1.3, the average dissolved antimony concentration is 129 µg/L (0.129 mg/L). In comparison with the toxicity values of Tables 3.7 and 3.8, this value is in the order of 50- to 100-fold below the acute toxicity thresholds of both rainbow trout and *Daphnia magna*. Therefore, antimony is not expected to make an important contribution to acute toxicity in these tests. Where arsenic is a concern, interactions of antimony to reduce arsenic toxicity could be relevant.

TABLE 3.7: TOXICITY VALUES FOR ANTIMONY IN FRESHWATER FISH (values in mg/L)

Species	Endpoint	Value	Comments	Ref.
Oreochromis mossambicus	96-hr LC_{50}	35.5	• 3-day-old larvae	1
Rainbow Trout	28-d LC_{50}	0.580		2
Rainbow Trout	28-d LC_{50}	0.660		3
Fathead Minnow	96-hr LC_{50}	21.9	• embryo larval test	4
Fathead Minnow	28-d CV	1.6	• embryo larval test	4

1. Lin and Hwang (1998), 2. Birge (1978), 3. Birge *et al*. (1980), 4. Kimball (unpublished).

TABLE 3.8: TOXICITY VALUES FOR ANTIMONY IN INVERTEBRATES (values in mg/L)

Species	Endpoint	Value	Comments	Ref.
Daphnia magna	48-hr LC_{50}	530		1
Daphnia magna	64-hr LC_{50}	19.8	• Antimony trichloride	2
Daphnia magna	48-hr LC_{50}	9	• Antimony potassium tartarate	3
Daphnia magna	48-hr LC_{50}	18.8 12.1	• Unfed • Fed	4
Daphnia magna	28-d CV	5.4	• Life cycle test	4

1. LeBlanc (1980), 2. Anderson (2000), 3. Bringman and Kuhn (1959), 4. Kimball (unpubl.).

Suspended solids are in the range of 5 mg/L. Since the suspended solids in mine effluents can serve as absorptive surfaces for elements such as antimony (Section 2.4.3), the solids could act to reduce effluent toxicity. The importance of this effect will depend upon the adsorptive properties of the solids present in the effluent.

4.0 TREATMENT TECHNOLOGIES

4.1 Introduction

4.1.1 Potential Technologies Available

As part of the revised MMLER studies, SENES (1999) recently completed an evaluation of Best Available Technologies (BAT) for application to mine sites in Canada, including BAT for the control of mercury and cadmium. More recently, BEAK undertook a review of mine effluent treatment options based on Toxicity Identification Evaluation/Toxicity Treatment Evaluation (TIE/TTE) investigations of effluents from two mines as part of the Non-Acutely Lethal Mining Effluent Technologies (NALMET) Program for Environment Canada (BEAK, 2000).

Alternative treatment technologies for the removal or reduction of mercury, cadmium, selenium and/or antimony include:

- precipitation, e.g., oxidation, reduction, sulphide co-precipitation, coagulation/settling;
- adsorption, e.g., ferrihydrite, activated alumina, ferric oxyhydroxide, peat, resin, activated carbon, lanthanum oxide, zeolite, silica gel;
- ion exchange, e.g., resins, proprietary reagents;
- membrane processes, e.g., reverse osmosis, emulsion liquid membranes, nanofiltration;
- reduction processes, e.g., ferrous salts, iron reduction;
- conventional water treatment, e.g., lime softening/ferric coagulation/filtration;
- biological processes, e.g., *Pseudomonas stutzeri* bacteria/immobilized alginate enzymes, bacterial inoculum, *Clostridium* bacteria, biological anaerobic reactors; and
- passive treatment, e.g., utilizing the iron (co-precipitation/adsorption) and sulphide (metal species transformation by sulphate-reducing bacteria) present in acid rock drainage (ARD).

The evaluation of an appropriate treatment technology is founded on the knowledge of the chemical behaviour of the metal and the efficacy of the treatment to reduce the metal concentration and/or transform it to a less toxic form.

The key to efficient metals removal is to convert the metals, if bound, to a form amenable to conventional treatment, or take advantage of the unique characteristics of a specific metal complex. In gold mine effluents, nearly all heavy metals are present in cyanidation wastewaters in varying concentrations (Smith and Mudder, 1991). As a result of those concentrations and the effluent discharge strategy, treatment may or may not be required.

In addition to knowledge of the metal behaviour and species occurrence, treatment success will depend on the site-specific characteristics of the individual wastewater to be treated. Treatment optimization will also usually require site-specific treatability testing.

4.1.2 Rule of Thumb Concerning Treatment Technologies

The removal of all four metals from a single effluent presents some difficulties. Based on current technology, mercury is removed by sulphide or calomel (H_2Cl_2) precipitation under reducing conditions. Selenium is also generally removed under reducing conditions. Cadmium is removed by co-precipitation with zinc/iron, although it could also probably be removed by sulphide precipitation. However, antimony is removed by precipitation of ferric antimonite along with ferric hydroxide (and ferric arsenate) under oxidizing conditions. There are other technologies that may be applicable to all four metals, e.g., ion exchange. However, these technologies may have limitations, such as high concentrations of iron and/or magnesium in the effluent.

4.1.3 Screening Level Information Summarized in the 1980s

Smith and Mudder (1991) provided a summary of the various treatment processes and removal efficiencies for the various metals. These are presented in Tables 4.1 to 4.5 and were taken from a U.S. EPA publication (Denit *et al.*, 1984).

In addition, Table 4.6, from Smith and Mudder (1991), presents a summary of actual effluent data from five mines treating moderate to high strength acid mine drainage (AMD) originating from various base metal recovery processes. The results indicate that very good removal is achievable using lime precipitation when the metals are present in their free forms.

TABLE 4.1: WASTEWATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - MERCURY II REMOVAL

Treatment Technology	pH	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
Sulphide	-	0.3 – 50.0	0.01 – 0.12	-
Sulphide	10.0	10.0	1.8	96.4
Sulphide/Filter	5.5	16.0	0.04	99
Sulphide/Filter	4.0	36.0	0.06	99.8
Sulphide/Filter	5.8 – 8.0	0.3 – 6.0	0.01 – 0.125	87 – 99.2
Ferrite Coprecipitation/Filter	-	6.0 – 7.4	0.001 – 0.005	99.9
Activated Carbon	-	0.01 – 0.05	<0.0005	-
Activated Carbon/Alum	-	0.02 – 0.03	0.009	-
Activated Carbon	-	0.06 – 0.09	0.006	-

TABLE 4.2: WASTEWATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - BERYLLIUM AND CADMIUM REMOVAL

Treatment Technology	pH	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
Beryllium				-
Lime/Filter	11.5	0.1	0.006	99.4
Cadmium				-
Lime (260 mg/L)/Filter	10.0	5.0	0.25	95
Lime (600 mg/L)/Filter	11.5	5.0	0.10	98
Lime Softening	5 – 6.5	0.44 – 1.0	0.008	92 – 98
Lime/Sulphide	8.5 – 11.3	0.3 – 10	0.006	98+
Ferrous Sulphide (Sulphex)	8.5 – 9.0	4.0	<0.01	99+
Ferrite Coprecipitation/Filter	Neutral	240	0.08	99+

TABLE 4.3: WASTEWATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - SELENIUM AND THALLIUM REMOVAL

Treatment Technology	pH	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
Selenium				-
Ferric Chloride/Filter	6.2	0.1	0.03	75
Ferric Chloride/Filter	6.2	0.05	0.01	80
Alum/Filter	6.4	0.5	0.26	48
Ferric Sulphate	5.5	0.10	0.02	82
Ferric Sulphate	7.0	0.10	0.03	75
Lime/Filter	11.5	0.5	0.3	35
Lime/Filter	11.5	0.06	0.04	38
Thallium				-
Lime/Filter	11.5	0.5	0.2	60
Ferric Chloride/Filter	6.2	0.6	0.4	30
Alum/Filter	6.4	0.6	0.4	31

TABLE 4.4: WASTEWATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - ANTIMONY AND ARSENIC REMOVAL

Treatment Technology	pH	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
Antimony				-
Lime/Filter	11.5	0.6	0.4	28
Ferric Chloride/Filter	6.2	0.5	0.2	65
Alum/Filter	6.4	0.6	0.2	62
Arsenic				-
Lime Softening	-	0.2	0.03	85
Sulphide/Filter	6 – 7	-	0.05	-
Lime (260 mg/L)/Filter	10.0	5.0	1.0	80
Lime (600 mg/L)/Filter	11.5	5.0	1.4	72
Ferric Sulphate	5 – 7.5	0.05	0.005	90
Ferric Sulphate	6.0	5.0	0.5	90
Lime/Ferric Chloride/Filter	10.3	3.0	0.05	98
Activated Alumina (2 mg/L)	6.8	0.4 – 10	<0.4	96 – 99+
Activated Carbon (3 mg/L)	3.1 – 3.6	0.4 – 10	<4.0	63 – 97
Ferric Chloride	-	0.3	0.05	98
Ferric Chloride	-	0.6 – 0.9	<0.13	-

TABLE 4.5: ACHIEVABLE LONG-TERM AVERAGE EFFLUENT CONCENTRATIONS FOR SELECTED TECHNOLOGIES (values in mg/L)

	Lime + Settling	Lime + Filter	Sulphide + Filter	Ferrite Coprecipitation + Filter	Soda Ash + Settling	Soda Ash + Filter	Alum
Antimony, Sb	0.8 – 1.5	0.4 – 0.8					
Arsenic V, As^{+5}	0.5 – 1.0	0.5 – 1.0	0.05 – 0.1				
Beryllium, Be	0.1 – 0.5	0.01 – 0.1					
Cadmium, Cd	0.1 – 0.5	0.05 – 0.1	0.01 – 0.1	<0.05			
Copper, Cu	0.5 – 1.0	0.4 – 0.7	0.05 – 0.5	<0.05			
Chromium III, Cr^{+3}	0.1 – 0.5	0.05 – 0.5		0.01			
Lead, Pb	0.3 – 1.6	0.05 – 0.6	0.05 – 0.4				
Mercury II, Hg			0.01 – 0.05	0.20	0.4 – 0.8	0.1 – 0.6	
Nickel, Ni	0.2 – 1.5	0.1 – 0.5	0.05 – 0.5	<0.01			
Silver, Ag	0.4 – 0.8	0.2 – 0.4	0.05 – 0.2				
Selenium, Se	0.2 – 1.0	0.1 – 0.5					
Thallium, Tl	0.2 – 1.0	0.1 – 0.5					0.2 – 0.5
Zinc, Zn	0.5 – 1.5	0.4 – 1.2	0.02 – 1.2	0.02 – 0.5			

	Ferric Chloride	Activated Carbon	Bisulphite Reduction	Lime/$FeCl_2$ + Filter
Arsenic V, As^{+5}	0.05 – 0.5	0.3		0.02 – 0.1
Chromium VI, Cr^{+6}		0.1	0.05 – 0.5	
Mercury II, Hg		0.01		
Silver, Ag	0.05 – 0.1			
Selenium, Se	0.05 – 0.1			
Thallium, Tl	0.7			

TABLE 4.6: SUMMARY OF PERFORMANCE OF SOME AMD TREATMENT SYSTEMS USING LIME PRECIPITATION[1]

	50th Percentile Effluent Concentrations[1]						90th Percentile Effluent Concentrations[1]				
Chemical Parameter[2]	Mine A	Mine B	Mine C	Mine D	Mine E	Chemical Parameter[2]	Mine A	Mine B	Mine C	Mine D	Mine E
SS	16.2	18.4	-	-	-	SS	34	112	-	-	-
pH	9.1	9.3	10.8	9.4	9.8	pH	9.3	112	11.4	11.2	10.2
SO_4	-	1,890	-	-	-	SO_4	-	2,250	-	-	-
D.As	0.001	0.0025	-	-	-	D.As	0.250	0.0055	-	-	-
T.As	0.001	0.0072	-	-	-	T.As	0.250	0.050	-	-	-
D.Cu	0.024	0.0090	0.004	-	-	D.Cu	0.092	0.120	0.012	-	-
T.Cu	0.059	0.063	0.015	0.045	0.04	T.Cu	0.20	0.32	0.040	0.27	0.08
D.Fe	0.050	0.030	-	-	-	D.Fe	0.110	0.080	-	-	-
T.Fe	1.62	0.426	-	-	0.22	T.Fe	3.63	3.48	-	-	1.49
D.Zn	0.016	0.005	0.010	-	-	D.Zn	0.060	0.120	0.050	-	-
T.Zn	0.20	0.048	0.17	0.68	0.31	T.Zn	0.36	0.680	0.50	16.7	1.21
D.Al	0.87	0.430	-	-	-	D.Al	14.1	3.31	-	-	-
T.Al	1.05	1.14	-	-	-	T.Al	1.22	4.33	-	-	-
D.Cd	0.010	0.0005	-	-	-	D.Cd	0.010	0.0023	-	-	-
T.Cd	0.015	0.0005	-	-	-	T.Cd	0.040	0.0050	-	-	-
D.Cr	0.010	-	-	-	-	D.Cr	0.025	-	-	-	-
T.Cr	0.025	-	-	-	-	T.Cr	0.070	-	-	-	-
D.Pb	0.025	-	-	-	-	D.Pb	0.082	-	-	-	-
T.Pb	0.082	-	-	0.12	0.24	T.Pb	0.170	-	-	0.161	0.43

[1] All units are mg/L except pH.
[2] D indicates dissolved and T indicates total metals.

4.2 Mercury

4.2.1 Overview of Technologies for Mercury

Based on knowledge of its chemical behaviour, mercury can be removed from aqueous media by precipitation as the sulphide, by use of ion exchange resins, by reduction and separation as metallic mercury, and by sorption on proteins (organic matter). Numerous studies have investigated the use of various scavenging materials for the removal of mercury from water, e.g., polyamine-carbohydrates (Masri and Friedman, 1972), walnut expeller meal or peanut skins (Friedman and Waiss, 1972), hydrous manganese oxides (Lockwood and Chen, 1973), starch xanthate-cationic polymer complex (Swanson *et al.*, 1973), peat moss (Coupal and Lalancette, 1976), cellulose derivatives (Gasparrini *et al.*, 1976), raw and aged bark (Henderson *et al.*, 1977), iron sulphide minerals (Brown *et al.*, 1979) and polysulphides (Findlay and McLean, 1981).

4.2.2 Treatment of Mercury in Gold Mill Effluents

Very low effluent limits are normally applied for mercury. Mercury is bound in a relatively weak complex with cyanide and has a great affinity for sulphide and activated carbon, both of which form the basis of primary removal processes (Smith and Mudder, 1991). Effluent levels of <0.005 mg/L are achievable in the case of activated carbon. With regards to sulphide treatment, one approach is to utilize a commercially available reagent (i.e., Degussa’s TMT), which reduces effluent mercury levels into the range of <0.001-0.002 mg/L, while eliminating the problems associated with handling and feeding of sodium sulphide. The Degussa reagent has been shown to be effective in removing mercury from cyanidation wastewaters, but only after cyanide destruction.

4.2.3 Treatment of Mercury in Other Mine Effluents

Mercury is commonly found in zinc ores as mercury commonly replaces zinc in the sphalerite structure. Acid mine drainage from such mines rarely if ever contains mercury, and it appears that mercury may not mobilize even when the sphalerite with which it is associated decomposes. If mercury is in solution, as it is in some acidic industrial effluents, it is generally removed with the sludge from a lime neutralization plant; however, the effluent may require secondary treatment with sulphide to precipitate any residual mercury. Ion exchange resin has also been proposed for this polishing step.

Of more significance is the mercury associated with the zinc metal concentrates and their processing to refined metal (which may be a mine site activity). The bulk of the mercury will end up in acidic effluents from roasting. The removal of mercury as calomel (Hg_2Cl_2) is the standard technology for these gas streams. Weak acid bleed streams can be treated for mercury removal with sulphide precipitation or ion exchange resin absorption.

It is interesting to note that, in the hydrometallurgical treatment of zinc concentrates containing mercury in autoclaves, the mercury ends up in the solid residue while the zinc dissolves, suggesting that mercury does not readily mobilize in sulphuric acid despite the significant solubility of all mercury sulphates. Mercury appears to form jarosites which may be the reason for this lack of solubility.

4.2.4 Summary of Performance for Mercury

Table 4.1 indicates that sulphide precipitation generally achieves 95% to 99% removal of mercury when the initial concentration is in the 10's of mg/L range. Filtration is effective ensuring continuous effective removal in the 99 to 99.9% range when coupled with sulphide precipitation.

Activated carbon has a special niche when applied to relatively low levels of mercury (0.01–0.09 mg/L) in the influent to an activated carbon unit. Activated carbon alone or in combination with alum is able to achieve an approximate 90% removal, delivering effluent concentrations in the order of <0.0005 to 0.01 mg/L.

4.3 Cadmium

4.3.1 Overview of Technologies for Cadmium

Various treatment technologies have been shown to be effective in the removal of cadmium from mine effluent, including chemical precipitation, adsorption, ion exchange and ultra-filtration.

4.3.2 Treatment of Cadmium in Gold Mine Effluents

Cadmium is very important from an aquatic life and toxicity viewpoint and very low cadmium limits may be imposed on a treated discharge.

With regards to treatment, cadmium is considered in the free form in solution, since the cadmium cyanide is virtually non-existent (Smith and Mudder, 1991). As a result, conventional treatment processes (i.e., lime precipitation and addition of ferric salts and sulphides) will remove cadmium effectively, yielding effluent levels in the range of 0.01-0.10 mg/L. The upper end of this range could be toxic in typical effluents, while even the lower end could be toxic in soft water. Generally, effluent hardness will provide sufficient protection against acute cadmium toxicity, but this should be verified during pilot studies. While hardness may be reduced in a softwater receiving environment, the cadmium concentration is also reduced, by the same dilution that lowers the hardness.

4.3.3 Treatment of Cadmium in Other Mine Effluents

Cadmium is almost invariably found in zinc ores, and therefore in effluents from zinc mines. Zinc is removed by one of the lime neutralization processes such as HDS where zinc may be co-precipitated with gypsum and iron and other metal hydroxides. Cadmium is generally co-precipitated. Some clarification of the treated effluents, i.e., removal of finely suspended solids, may be required to meet discharge standards. Soluble cadmium associated with runoff from zinc concentrate storage facilities (where total metal loadings have been modest) has been treated by ion exchange resin.

4.3.4 Summary of Performance for Cadmium

The performance data summarized from the early 1980s (Table 4.2) concentrate on three processes: lime precipitation, lime precipitation with sulphide precipitates, and iron hydroxide co-precipitation.

Lime precipitation has a varying level of performance achieving a range of 0.01 to 0.25 mg/L cadmium in the effluent when the influent concentration ranges from 1 to 10 mg/L Cd. Careful control of pH, along with filtration clarification of the treated effluent to remove finely suspended solids, or polishing ponds, may be required to guarantee performance at the lower end of the range.

Sulphide precipitation or lime in combination with sulphide achieves effluent concentrations in the range of 0.006 mg/L.

Iron co-precipitation in combination with filtration achieved greater than 99% removal and an effluent concentration of the order of 0.01 mg/L when the influent concentration was four orders of magnitude larger.

4.4 Selenium

4.4.1 Overview of Technologies for Selenium

Knowledge of the species of selenium present in the effluent is critical for identifying the appropriate treatment method. Selenate, Se^{6+}, is the predominant species in oxygenated waters and ARD but is not readily removed regardless of the treatment technology employed. The key to successful treatment is to reduce selenate to selenite, Se^{4+}, by chemical or biological processes. Selenite is then amenable to removal by sorption processes.

MSE and Montana Tech (1999) and Twidwell *et al.* (2000) recently undertook an extensive review of the literature to identify potential technologies for the removal of selenium from a variety of wastewaters, including mine effluents. A number of technologies were identified as having promise for application to mine wastewaters for the removal of selenium to the low µg/L range, e.g., less than 10 µg/L. Some of these technologies have been demonstrated at full scale, while others have yet to be proven.

4.4.2 Treatment of Selenium in Gold Mill Effluents

Selenium may appear in cyanidation wastewaters in levels ranging from about 0.02-5.0 mg/L. It may be present as a cyanate salt similar to thiocyanate.

There are two primary forms of selenium including selenite and selenate (Smith and Mudder, 1991). Although selenite is readily removed through conventional precipitation and ferric salt addition, selenate is very difficult to remove. In order to promote selenate removal it must first be reduced to the selenite form. There are several processes available including reduction with sulphur dioxide, reduction with metallic zinc and iron, or ferrous salts, and microbial reduction. The use of biological systems has been studied intensively by the U.S. Bureau of Mines and others, and has been shown to be effective in removal of selenium. In addition, some promise has been demonstrated in the removal of selenium (including selenate) using ion exchange resins and silica gel systems, but further studies are required. The importance of selenium from a water quality standpoint, and the approach to selenium removal, requires a detailed and thorough investigation on a site-specific basis.

4.4.3 Comparative Evaluation of Innovative Technologies

Recent interest in lowering the U.S. drinking water objective for selenium (from 0.05 to 0.01 mg/L) has sparked a parallel interest in developing innovative technologies for better removal of selenium from wastewaters. Conventional technologies, such as precipitation with ferric salts, can generally achieve ≤0.1 mg/L in mine effluents (Table 4.3). A variety of newer technologies was evaluated by MSE and Montana Tech (1999) in terms of their ability to consistently achieve a <0.01 mg/L objective. Relative costs were also evaluated and compared to those of conventional technologies.

Appendix 3 provides a detailed synopsis of this evaluation. The overall conclusion was that technologies do not yet exist that can be rated as generally achieving the more stringent objective. However, a number of technologies were found to show promise of possibly meeting this objective (Table 4.7). Those that have been demonstrated at full scale include bacterial reduction to elemental selenium, or reduction to selenide, with subsequent precipitation, reduction using elemental iron, adsorption to ferric oxyhydroxide and peat resin, adsorption to ferrihydrite, and nanofiltration. Other technologies, such as tailored ion exchange and solvent extraction/liquid membrane methods, show promise but have not been demonstrated at full scale.

Operating and capital costs of these technologies were evaluated on a relative scale, since operating costs are highly dependent on production rates and other variables (Table 4.8). All were considered by MSE and Montana Tech (1999) to be cost-competitive with conventional technologies. The values shown in Table 4.8 are unitless and represent a relative comparison of cost.

TABLE 4.7: SOLUTION TREATMENT TECHNOLOGIES POTENTIALLY APPLICABLE TO MINING INDUSTRY WASTEWATERS[1]

Technology for Solution Treatment	**Studies**			**Comments**
	Lab	**Pilot**	**Industry**	
OXIDATION	x	x		Oxidation of Se (IV) to Se (VI) is important for some of the subsequent removal technologies. Effective oxidation has been demonstrated; however, the oxidizing reagents are expensive. Efforts to find low-cost treatment technologies and lower cost oxidizing reagents (for use at ambient temperatures) need to be continued.
REDUCTION	x	x	x	Reduction of Se (VI) to Se (IV) (for adsorption technologies) or to selenide (for metal selenide compound formation) is important for some of the subsequent removal technologies. Conditions for successful reduction are known and are well characterized in the literature. Bacteria, ferrous hydroxide, ferrous sulphate, iron, aluminum, zinc, sulphur dioxide and hydrazine have been used as reductants.
PRECIPITATION				
Selenate	x	x		The precipitation of selenates as a treatment technology is ineffective because of the relatively high solubility of metal selenates.
Selenite	x	x		The precipitation of metal selenites as a mine water treatment technology is not appropriate because the solubility of metal selenites is not low enough to achieve the very low Se discharge requirements.
Selenide	x	x	x	The reduction of selenate and selenite species with the subsequent precipitation of metal selenides is promising as a mine water treatment option.
Se^0	x	x	x	The reduction of Se (VI) and se (IV) species to Se^0 by bacterial processes is promising as a mine water treatment option.
ADSORPTION				
Ferrihydrite	x	x	x	Amorphous ferric hydroxide precipitation has been extensively investigated. Selenium (IV) is effectively removed at pH <~8. This technology is not effective for Se (VI). Therefore, reduction of the Se (VI) prior to adsorption is often required. The presence of other aqueous species in the solution to be treated may influence the removal of Se (IV).

TABLE 4.7: SOLUTION TREATMENT TECHNOLOGIES POTENTIALLY APPLICABLE TO MINING INDUSTRY WASTEWATERS[1]

Technology for Solution Treatment	**Studies**			**Comments**
	Lab	**Pilot**	**Industry**	
Alumina	x	x		Selenium (IV) is adsorbed effectively by alumina. Selenium (IV) adsorption is nearly complete (for concentrations up to 4 ppm Se using 3.3 g/L Al_2O_3) at pH levels between 3-8. Selenium (VI) adsorption by alumina is poor. Selenium (VI) adsorption drops off rapidly with increasing pH and is less than 50% at pH 7. Sulphate and carbonate adsorption significantly interferes with Se (VI) adsorption. Application of Se 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.
Ferric Oxyhydroxide//Peat/ Resins	x	x	x	HW-FIX is a USBM development that shows promise for Se (IV) removal. The adsorption is not as effective for Se (VI). This technology shows promise for application to mine waters.
Activated Carbon	x	x		Activated carbon adsorption is widely used in treatment of groundwater and as point-of-use treatment of drinking waters for organic adsorption. It is not very effective for adsorbing Se.
ION EXCHANGE (IX)	x	x		Ion exchange is used for treatment of drinking water and groundwater for metals, As and Se removal. Selenium removal is accomplished by using a strong base anion IX resin. Selenium (VI) is extracted much more effectively than Se (IV). The extraction of Se (VI) is a function of sulphate concentration. Tailored resins show good selectivity for Se in the presence of sulphate; however, only laboratory studies have been performed, and further laboratory studies (on mine waters) are recommended.
SOLVENT EXTRACTION (SX)	x	x		Solvent extraction has been investigated on a pilot scale for treating gold heap leach solution effluents. The results were encouraging; however, the technology has been applied at only one site. Further laboratory test work should be conducted.

TABLE 4.7: SOLUTION TREATMENT TECHNOLOGIES POTENTIALLY APPLICABLE TO MINING INDUSTRY WASTEWATERS[1]

Technology for Solution Treatment	**Studies**			**Comments**
	Lab	**Pilot**	**Industry**	
REVERSE OSMOSIS (RO)	x	x		Reverse osmosis is extensively used for removing inorganic contaminants from drinking water and groundwater. It has not been applied industrially to mine waters. Reverse osmosis may require extensive pre-treatment of mine waters to remove solids and to lower the concentration of TDS. Otherwise, extensive membrane fouling may occur. It is doubtful that RO will ever be applied to mine waters.
EMULSION LIQUID MEMBRANES	x	x		Pilot studies have shown that Se (VI) is extracted rapidly even in the presence of sulphate at all pH values >2. Selenium (IV) extraction is influenced by the presence of sulphate (i.e., the rate of extraction is decreased). This technology shows much potential for application to mine waters; however, it requires further test work to answer questions concerning the presence of multiple anionic species, presence of suspended solids, etc.
NANOFILTRATION	x	x	x (for sulphate)	Nanofiltration appears to be a potential technology for treating some low metal-containing Se-bearing mine waters. Nanofiltration technology shows good potential for application to mine waters; however, it requires further test work to answer questions concerning the presence of multiple anionic species, presence of suspended solids, etc.
REDUCTION PROCESSES				
Ferrous Hydroxide	x	x		The Bureau of Reclamation has developed a process for treating Se surface and agricultural waters. This technology does not appear to be applicable (at a reasonable cost) to mine waters.
Fe	x	x	x	The successful use of Fe as a reductant is based on the reduction of Se in the presence of Cu ions. Further test work is required to determine the final Cu content achievable in the treated effluent water and to delineate the applicable pH range. This technology shows promise for application to mine waters.

TABLE 4.7: SOLUTION TREATMENT TECHNOLOGIES POTENTIALLY APPLICABLE TO MINING INDUSTRY WASTEWATERS[1]

Technology for Solution Treatment	Studies			Comments
	Lab	Pilot	Industry	
BIOLOGICAL REDUCTION	x	x		Bacterial reduction of Se aqueous species to Se^0 has been shown to be a potential candidate for treating mine waters. Bench scale work has been successful in reducing 620 ppb Se (VI) to <10 ppb Se for nine months of operation.
CONVENTION WATER TREATMENT				
Lime Softening/Ferric Coagulation/Filtration	x	x		The BAT for treating Se-bearing drinking and groundwaters are 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)]. However, the application of these unit operations to mine waters has not been made. Achieving Se removal to regulated discharge concentrations by these technologies is not likely unless the Se concentrations are already near the required discharge requirements.

[1] Adapted from MSE (1999).

TABLE 4.8: COMPARATIVE COSTS OF ALTERNATIVE TECHNOLOGY FOR SELENIUM REMOVAL[1]

Technology Name	Reliability	Technical Feasibility	Technical Innovation	Operating Costs	Capital Costs
Biological Reduction	4	3	4	4	3
Elemental Selenium Precipitation	3	3	4	3	4
Elemental Iron Reduction	4	4	4	3	3
Selenide Precipitation	3	3	3	3	3
Reduction	3	3	2	3	3
Ferric Oxyhydroxide/Peat/Resins	4	4	3	2	3
Nanofiltration	3	3	3	3	3
Ferrihydrite Adsorption	3	3	2	2	3
Ion Exchange	4	3	2	2	2
Solvent Extraction	3	3	2	2	2
Reverse Osmosis	4	2	2	2	2
Alumina Adsorption	3	2	2	2	2
Lime Softening/Ferric Coagulation/Filtration	3	3	2	2	2
Oxidation	2	3	2	1	3
Ferrous Hydroxide Reduction	2	3	3	1	2
Activated Carbon	2	2	2	2	3
Selenite Precipitation	1	1	1	3	3
Selenate Precipitation	1	1	1	3	3

[1] Adapted from MSE (1999).

Note: Refer to Appendix 3 for description of factors

4.5 Antimony

4.5.1 Overview of Technologies for Antimony

Gannon and Wilson (1986) have undertaken an extensive review of the treatment technologies applicable to the removal of antimony from aqueous solutions.

4.5.2 Treatment of Antimony in Gold Mill Effluents

The discussion in this section is extracted from Smith and Mudder (1991).

Arsenic and antimony are classified as metalloids and tend to exhibit similar chemical properties (Smith and Mudder, 1991). They can occur in gold ores as the free elements, as the simple sulphides (orpiment, As_2S_3; realgar, As_2S_2; stibnite, Sb_2S_3), and as arsenides or sulpharsenides of silver, cobalt, nickel, copper, lead and iron. The principal minerals of concern in cyanidation are the simple sulphides and the sulpharsenide of iron, arsenopyrite (FeAsS).

Orpiment, realgar and stibnite dissolve in alkaline solution to form thioarsenite and thioantimonite initially, which convert to the arsenite and antimonite with time (Smith and Mudder, 1991). Arsenopyrite itself is almost completely insoluble in alkali cyanide leach solutions, but where the ore has been roasted the arsenic is converted to the highly soluble arsenious oxide and converts to arsenite ion on dissolution. Neither arsenite nor antimonite undergo oxidation in leaching and hence these are the principal dissolved forms present in the barren bleed or CIP leach slurry.

None of the forms resulting from reactions between arsenite ion and metallic ions are sufficiently insoluble for use in meeting environmental criteria for mining effluents. Attempts have been made to control arsenic in effluents by additions of large excesses of lime, but this practice may not be suitable, due both to the high solubility of calcium arsenite and, in the case of calcium arsenate, the potential for increased solubility as pH decreases in solution (Robins and Tozawa, 1982). The use of excess lime (5:1 over stoichiometric) and calcination have enabled calcium arsenate precipitates to meet leach test requirements.

Arsenate compounds provide more suitable precipitates, those formed with copper, lead, nickel and zinc being particularly insoluble. Stoichiometric ferric arsenate is relatively soluble but the solubility decreases as the iron to arsenic ratio is increased. It has been shown that basic ferric arsenates with molar ratios of 4 or more (weight ratios of 3 or more) give 100 to 1,000 times lower solubilities of arsenic over the pH range 3 to 7, and provide environmentally stable forms (Krause and Ettel, 1985). The current practice is to treat for cyanide removal, followed by addition of ferric ion for removal of arsenic. In conjunction with aeration, ferrous ion can be used for arsenic removal.

Much less is known about antimony removal than arsenic removal, and at present there is too little information on the actual species present in antimony solutions. Antimony chemistry resembles that of bismuth more than that of arsenic. Solutions of both +3 and +5 antimony readily hydrolyse when diluted or partly neutralized, and precipitate either as the oxides or basic salts. The salts of both metals, with the exception of their sodium salts, are only sparingly soluble. Parker *et al.* (1979) reported that lime precipitation will not remove antimony levels below 1.0 mg/L. If this level is achieved, it is likely sufficient to eliminate acute toxicity from antimony. As in the case of arsenic, precipitation appears to be more effective in the presence of ferric hydroxide. It is not known whether iron antimonite or antimonate compounds are formed or whether the iron hydroxide precipitate simply adsorbs the hydrolysed antimony compounds.

Current practice at gold mills in Canada is to employ the same precipitation/co-precipitation reaction with iron hydroxides as is used in the case of arsenic. The iron is added as ferric sulphate or as pickling liquor and pH is controlled between 7.5 and 8.5. An antimony mine in New Brunswick substitutes ferric chloride and a pH of 4.5, to remove lead, arsenic and antimony from its tailings pond overflow. After settling, the pH is readjusted to 7.0 (St. Pierre, 1977).

An alternative technology for dealing with arsenic and antimony is pretreatment of the mill feed. Examples of this practice are the process employed at the Sunshine Mine in Idaho (Jackson, 1980) and also once used at Equity Silver Mines in British Columbia (Dayton, 1982). Arsenic and antimony were preleached at these operations with sodium sulphide and sodium hydroxide solutions. Through precipitation, arsenic at levels of 5-10 mg/L can be reduced to <0.20 mg/L.

4.5.3 Treatment of Antimony in Base Metal Mine Effluent

The solubility of antimony (and arsenic) is not directly related to cyanide (unlike mercury and some other metals) and thus the treatment of base metal effluents is essentially the same as for gold mill effluents. Very often AMD solutions will contain antimonites and arsenites (along with the more oxidized species), as well as ferrous and ferric iron and other base metals. Treatment by liming for metal precipitation and aeration for oxidation of ferrous iron to ferric and antimonites/arsenites to antimonates/arsenates will usually result in very significant removal. Depending on the metal species and ratios, it may be possible to essentially remove all arsenic and antimony, as in most instances sufficient iron will be present in the effluent to exceed the minimum ratios (4:1). Ion exchange or secondary precipitation with iron can be used to complete the arsenic/antimony removal if necessary.

4.5.4 Summary of Performance for Antimony in the Early 1980s

Performance data summarized for the early 1980s provide only a fair level of performance for antimony (removal efficiencies in the range of 30-60%) but these data are based on relatively low influent concentrations (0.5-0.6 mg/L). The applicable treatment processes (Table 4.4) are all precipitation based.

4.6 Relative Treatment Cost

SENES (1999) evaluated technologies available for treating liquid effluents. This study included a summary of BAT ratings and cost for specific technologies. The BAT ratings were based on:

- a comprehensive study of BAT applicable to the mining sector for the Ontario Municipal/Industrial Strategy for Abatement (MISA) (Kilborn, 1991);
- the liquid effluent guidelines that were established by the Ontario MOE (Ontario Regulation 560/94);
- work completed by AQUAMIN (1996); and
- new data collected SENES (1999).

Treatment costs are dependent on several factors, including the untreated constituent concentration and the level to which a constituent must be treated to in the effluent. The available information on treatment costs are based on successful treatment to “sub-mg/L”, but not necessarily to sub-0.1

mg/L levels. Additional research is required to validate treatment ratings at sub–mg/L levels that may, for example, be required for some constituents such as mercury.

SENES (1999) defined anticipated technological performance in terms of treatment efficiency and costs of the technologies for three basic categories:

- low cost (e.g., simple technologies such as lime addition/sedimentation),
- moderate cost (e.g., granular media filtration), and
- high cost (e.g., advanced technologies such as ion exchange).

Capital and operating costs for available technologies are provided in Table 4.9. This information is based on low, moderate and high cost technologies to provide a relative comparison of costs. The costs are highly variable. In addition, other factors not accounted for in Table 4.9 may have an even larger influence on treatment costs (SENES, 1999). For example, water management costs (e.g., storage to modulate highly variable flows, outside water sources such as mine water or lagoon water requiring treatment) may have a significant impact on capital and operating costs. The results show that both capital and operating costs for advanced technologies are approximately three to four times higher than capital and operating costs for simple technologies.

SENES (1999) also provided costs estimates for "add-on" technologies that are potentially capable of developing a non-toxic effluent where specific toxicants are known (see Table 4.10). The technologies were selected to treat the following constituents:

- pH adjustment – toxicity caused by a low pH;
- ammonia removal – a pilot scale investigation was used for the basis of costing, the technology stream uses a zeolite adsorption unit followed by a biological nitrification/ de-nitrification set of units;
- improved lime treatment involving coagulation as a key technology, to achieve further metals reduction (the metals are presumed to be Cu, Pb, Zn, Ni – metals evaluated by SENES in the BAT review);
- activated carbon for removal of toxicity of metals; and
- polishing pond to reduce toxicity from cyanide and associated metals in Gold Mill effluents such as Cu, Cd and Zn.

TABLE 4.9: CAPITAL AND OPERATING COSTS OF REPRESENTATIVE ADD-ON TECHNOLOGIES FOR 1999 TIMEFRAME[1]

Flow Rate (m^3/d)	Capital Cost ($)	Operating Cost ($/a)	Total Cost($/$m^3$ of effluent)	
			10 a / 10%[2]	30 a / 10 %[3]
Low Cost:				
1,000	586,000	81,000	0.48	0.39
5,000	1,310,000	288,000	0.27	0.23
25,000	2,929,000	1,144,000	0.16	0.16
Moderate Cost:				
1,000	1,162,000	116,000	0.84	0.66
5,000	2,678,000	334,000	0.42	0.34
25,000	7,020,000	1,194,000	0.26	0.21
High Cost:				
1,000	960,000	192,000	0.95	0.81
5,000	2,962,000	796,000	0.70	0.61
25,000	9,138,000	3,674,000	0.57	0.51

[1] Adapted from SENES (1999).
[2] 10 a / 10% - assumes 10 year operating life, 10% financing.
[3] 30 a / 10% - assumes 30 year operating life, 10% financing.

TABLE 4.10: CAPITAL AND OPERATING COSTS FOR REPRESENTATIVE ADD-ON TECHNOLOGIES TO REDUCE TOXICITY FOR A PLANT TREATING 10,000 m^3/d WITH A DESIGN FLOW OF 25,000 m^3/d[1]

Technology	Capital costs ($)	Operating Costs ($/a)	Reference
pH adjustment	100,000 (approx.)	100,000 (approx)	Estimated (SENES, 1999)
Ammonia removal	4,400,000 (approx.)	1,880,000 (approx)	CANMET (1995)
Improved lime treatment	2,930,000	500,000 (approx.)	MISA (1991)
Activated carbon adsorption	12,300,000	630,000	MISA (1991)
Polishing pond (six month retention time)	4,500,000	73,000	Estimated (SENES, 1999)

[1] Adapted from SENES (1999).

These results show that capital costs and operating costs for add-on technologies are highly variable and dependent on the particular parameter that requires treatment. Very little data exists to provide BAT ratings for constituents of interest in this study (e.g., Hg, Cd, Se, Sb). In addition, significant research and development and/or full scale operating data are required to provide a basis for defining a BAT rating for innovative treatment technologies, if ultra low effluent levels (<0.01 mg/L, or 0.01 to 0.1 mg/L) are required to ensure that the effluent is non-toxic with respect to Cd, Hg, Se and Sb.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Table 5.1 summarizes the information from preceding sections regarding typical mine/mill effluent concentrations of mercury, cadmium, selenium and antimony, in relation to background concentrations and acutely toxic concentrations. Table 5.2 summarizes the information from Section 4.0 regarding the effluent concentrations that are generally achievable for these constituents using different treatment technologies. The conclusions are outlined below for each constituent.

5.1.1 Mercury

Mercury is often associated with gold and zinc ores, and has been used historically as a reagent in gold recovery operations. It has been found in final mine/mill effluents at concentrations ranging from 0.05 to 7 µg/L (total). When found in effluents, it is likely present as a mercuric hydroxide complex (at high pH) or as a mercuric chloride complex (at low pH). Dissolved concentrations are low, either due to the absence of Hg in the ore and mill leaching solutions, or due to the strong tendency of mercury to coagulate, e.g., by co-precipitation with hydrated Fe/Mn oxides if this treatment process is utilized. There is a need for better data on mercury concentrations in mine/mill effluents.

Acutely toxic concentrations for inorganic mercury are in the range of 155 to 420 µg/L for rainbow trout, and 1 to 15 µg/L for daphnids. Mercury and selenium are antagonistic with respect to toxicity. The higher concentrations of mercury in mine effluents may be in the range associated with acute toxicity to daphnids. However, dissolved concentrations are unlikely to reach toxic levels. The mercury concentrations in mine effluents are not within the range associated with acute toxicity to rainbow trout.

Mercury is generally removed from mine effluents by sulphide precipitation under reducing conditions. This is often followed by filtration. The combined approach can generally achieve <0.1 mg/L mercury concentrations in effluent. Ferrite co-precipitation followed by filtration has also been used with success. Activated carbon can be used when influent concentrations of mercury are below 0.1 mg/L, and can generally achieve order of magnitude mercury reductions.

TABLE 5.1: MILL EFFLUENT CONCENTRATIONS COMPARED TO TOXICITY THRESHOLDS

	Mercury	Cadmium	Selenium	Antimony
Background Concentrations (fresh water)	2-25 ng/L	10-4,000 ng/L	0.1-1.5 µg/L	0.01-1.1 µg/L
Mine/Mill Effluent Concentrations (see Table 1.3)	0.05-7 µg/L Total (n = 9) <2 µg/L Dissolved (n = 4)	<10-59 µg/L Total (n = 21) <10-14 µg/L Dissolved (n = 21)	0.005-0.11 mg/L Total (n = 4)	0.001-0.71 mg/L Total (n = 7) <0.05-0.44 mg/L Dissolved (n = 21)
Acute Toxicity Threshold - daphnids	1-15 µg/L inorganic mercury	1-500 µg/L hardness-dependent	0.43-5.3 mg/L	9-20 mg/L
Conclusion – daphnids	Within Threshold Range	Within Threshold Range	Below Threshold Range	Below Threshold Range
Acute Toxicity Threshold - rainbow trout	155-420 µg/L inorganic mercury	1-8,000 µg/L hardness-dependent	4.2-32.3 mg/L	21.9-35.5 mg/L
Conclusion – rainbow trout	Below Threshold Range	Within Threshold Range	Well Below Threshold Range	Well Below Threshold Range
Adequacy of Canadian Mine Data to Characterize the Effluents	Inadequate	Adequate, as a First Approximation	Inadequate	Adequate, as a First Approximation

TABLE 5.2: RATING OF DIFFERENT TREATMENT TECHNOLOGIES
(based on data from Table 4.5)

	Achievable Mine Effluent Concentrations for Constituents[1]			
Technology	Mercury (Hg)	Cadmium (Cd)	Selenium (Se)	Antimony (Sb)
Lime + settling		Sub mg/L	mg/L	mg/L
Lime + filter		0.1 mg/L	mg/L	mg/L
Sulphide + filter	Sub 0.1 mg/L	Sub 0.1 mg/L		
Ferric co-precipitation + filter	Sub mg/L	Sub 0.1 mg/L		
Soda ash + settling	mg/L			
Soda ash + filter	Sub mg/L			
Alum				
Ferric Chloride			0.1 mg/L	
Activated Carbon	0.01 mg/L			
Bisulphite reduction				
Lime/$FeCl_2$ + filter				

[1] Technologies without a rating had insufficient data to define generally achievable effluent concentrations for these constituents.

5.1.2 Cadmium

Cadmium is associated with sulphide ores of base metals such as copper, zinc and lead. It has been found in final mine/mill effluents at concentrations ranging from <0.01 to 0.06 mg/L. When found in effluents, it is mainly present as a cadmium carbonate complex (at pH above 8) or as free ion (at pH below 8). Dissolved concentrations are reduced by adsorption on Fe/Mn oxides or Al oxides.

Acutely toxic concentrations for cadmium are highly dependent on hardness, ranging from 1 to 8,000 µg/L for rainbow trout (various life stages) and from 1 to almost 500 µg/L for daphnids. Other invertebrates display higher values. The free ion (Cd^{2+}) is mainly responsible for aquatic toxicity. The lowest acute values in the literature are associated with soft water test systems, and the highest acute values are associated with hard water test systems. Based on fish and invertebrate test results, the U.S. EPA criterion to prevent acute toxicity is 1.8 µg/L cadmium at a hardness of 50 mg/L (as $CaCO_3$) and 42 µg/L cadmium at a hardness of 825 mg/L (the average hardness of mine effluent). The average concentration of cadmium in effluent is 5.4 µg/L (dissolved) or 11.8 µg/L (total). Therefore, in most effluents, cadmium is unlikely to make an important contribution to effluent acute toxicity. Nor is cadmium released in effluents likely to be acutely toxic in soft receiving waters after dilution to ambient hardness, because the same dilution reduces the cadmium concentration.

Cadmium is generally removed from mine effluents by using lime to promote precipitation, followed by filtration, or sulphide precipitation. Ferrite co-precipitation followed by filtration has also been used with success, as has ferrous sulphide precipitation with or without filtration. These technologies are generally able to achieve ≤0.1 mg/L cadmium concentrations in effluent.

5.1.3 Selenium

Selenium is associated with sulphide ores of base metals such as copper, zinc and nickel. It has been found in final mine/mill effluents at concentrations ranging from 0.07 to 0.11 mg/L. When found in effluents, it is mainly present as selenite (at low pH) or selenate (at high pH). Dissolved concentrations are reduced at low pH by adsorption of selenite on Fe/Mn oxides. On the other hand, selenate is not appreciably adsorbed.

Acutely toxic concentrations of selenium are in the range of 4.2 to 32.3 mg/L for rainbow trout, although values as low as 1 mg/L have been reported for fathead minnows. Acute values for daphnids range from 0.43 to 5.3 mg/L. All these values are above the typical range of selenium concentrations in mine effluents. Therefore, selenium is unlikely to contribute appreciably to effluent acute toxicity. Selenium and mercury are antagonistic with respect to toxicity.

Selenium can be removed from mine effluents by using lime to promote precipitation, followed by filtration, or by precipitation with ferric salts (sulphate or chloride), which also may be followed by filtration. The ferric salt methods can generally achieve ≤0.1 mg/L selenium concentrations in effluent. All conventional treatments will mainly remove selenite. Most of the selenate in the effluent will remain. Thus, selenium removal efficiencies are typically low (35 to 80%) using these conventional methods. A number of technologies under development, e.g., nanofiltration, ion exchange resins and emulsion liquid membranes, show promise for removal of selenate, but are as yet unproven.

5.1.4 Antimony

Antimony is often found in gold ores, and also in sulphide ores of base metals, such as copper and lead. It has been found in final mine/mill effluents at concentrations ranging from <0.05 to 0.435 mg/L (dissolved) or as high as 0.71 mg/L (total). Concentrations above 1 mg/L have been historically associated with some gold mining operations. When found in effluents, it is likely to be mainly in the pentavalent form (Sb_2O_5 or SbO_3^-). Dissolved concentrations are reduced by adsorption on Fe/Mn oxides or Al oxides.

Acutely toxic concentrations of antimony are in the range of 22 to 36 mg/L for fish, and 9 to 20 mg/L for daphnids, although the toxicity database is small. All these concentrations are above the typical range of concentrations in mine effluents. Therefore, antimony is unlikely to contribute appreciably to effluent acute toxicity.

Antimony removal from mine effluents has not been widely studied. There is a need for basic information on the species present and their prevalence under different effluent conditions. In theory, the same precipitation/co-precipitation methods that are used for arsenic removal should be effective for antimony. Alum precipitation followed by filtration, and ferric chloride treatment followed by filtration, have been moderately successful in removing antimony to levels of 0.2 mg/L.

With removal efficiencies of 60 to 65%, there is considerable room for improvement; however, a target of 1 mg/L is likely sufficient to avoid acute toxicity due to antimony.

5.2 Recommendations

A number of data limitations have been identified where additional research would help to improve the current state of knowledge with respect to the minor metals that were the subject of this review. These data limitations and research areas are briefly outlined below.

- The aquatic toxicity database for antimony is limited. While there have been several studies involving *Daphnia magna* and rainbow trout, it would be useful to explore the sensitivities of other invertebrates, and other fish species and life stages, and to confirm that the antimony species tested are the same as those found in mine effluents. Speciation in mine effluents is not well characterized, as noted below.

- The knowledge of antimony species in mine effluents is limited and generally based on inference. Empirical studies on speciation in mine effluents would be useful, and would help to inform the development of optimal treatment technologies.

- The conventional mine effluent treatment technologies have been only moderately successful for antimony and selenium. In the case of selenium, this is due to the difficulty of removing selenate. Research focused on improved treatment technologies for these two elements would be useful, particularly in situations where environmental issues relevant to these elements have been identified.

- There is a need to develop a more comprehensive database of trace element concentrations in mine effluents, particularly for mercury and selenium. Effluent toxicity data should be included in this database to facilitate exploration of chemistry-toxicity relationships.

- Improved sampling and analytical techniques may be needed to adequately characterize effluent concentrations of mercury. Much of the available data are censored at a level above the lowest acute toxicity threshold values.

- Efforts to reduce or eliminate effluent toxicity at particular mine/mill sites should be focused on the constituents or classes of constituents most likely to contribute to the problem, as determined by TIE/TTE studies.

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APPENDIX 1

Detailed Effluent Chemistry Data for 23 Mine/Mill Operations
(NRCan, 1996, 1998)

TABLE A1.1: DETAILED EFFLUENT CHEMISTRY DATA FOR 23 MINE/MILL OPERATIONS

Parameters:	Units:	1	2	3	4	5	6	7	8	9	10	11	12
pH		8.9	9.1	7.95	10.9	9.62	9.29	10.23	8.47	7.31	8.11	8.96	7.46
Conductivity	µMho/cm			1911	1565	2824	1100	1076	846	1038	1424	1836	1714
Ammonia	mg/L			1.85	1.45	8.48	3.79	<0.1	0.4	0.1	1.3	3.06	3.91
Alkalinity	mg/L	350	456	900	81	50	44	41	44	62	329	30	56
Total Hardness	mg/L	114	60	90	724	1429	405	507	417	469	517	356	726
TSS	mg/L			2	15	16	<1	11	7	3	2	11	<1
TDS	mg/L	7880	9110	1300	1380	2668	784	896	660	804	908	1660	1361
Chloride	mg/L	974	819										
Sulphate	mg/L	4020	4620					533					
Total Metals:													
Antimony	µg/L	2.5	<5										
Calcium	µg/L	19500	13000	25900	330900	489600	147700	237900	177800	187100	155800	338700	308200
Cadmium	µg/L			59	<10	<10	<10	<10	<10	33	<10	<10	<10
Magnesium	µg/L	15900	6800	8080	4895	101100	9330	4520	3350	15850	46300	94820	3680
Mercury	µg/L		<7		<7		7						
Selenium	µg/L	74	110										
Sulphur	µg/L	1370000	1610000										
Sodium	µg/L	2470000	3090000	448000	77000	168800	46900	23200	8690	20200	112500	16550	93170
Dissolved Metals:													
Antimony	µg/L			<50	<50	109	<50	253	<50	205	76	96	<50
Calcium	µg/L			24600	284000	487900	145000	237200	162000	199200	151300	338000	314400
Cadmium	µg/L			<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Magnesium	µg/L			7600	3280	97460	8440	4286	3000	16000	44560	90200	3688
Mercury	µg/L		<2		<2		<2						
Sodium	µg/L			460000	63100	162600	45600	18950	7090	22100	106900	16200	91440

TABLE A1.1: DETAILED EFFLUENT CHEMISTRY DATA FOR 23 MINE/MILL OPERATIONS

Parameters:	Units:	13	14	15	16	17	18	19	20	21	22	23
pH		8.07	6.61	8.06	7.51	6.91	6.26	8.91	9.88	9.65	7.25	7.33
Conductivity	μMho/cm	1054	2514	3160	2240	2590	3614	3091	549	3330	723	2951
Ammonia	mg/L	0.96	0.1	4.69	2.94	15.3	<0.1	10.1	<0.1	12.8	0.32	18.5
Alkalinity	mg/L	83	90	47	56	45	15	44	283	50	6	36
Total Hardness	mg/L	529	1293	1980	1204	1102	1211	2151	49	1850	352	1449
TSS	mg/L	<1	<1	<1	<1	8	14	5	11	14	<1.0	9
TDS	mg/L	844	2424	2928	2160	2484	3468	3148	500	3280	540	2728
Chloride												
Sulphate												
Total Metals:												
Antimony	μg/L											
Calcium	μg/L	226600	572600	745300	491100	500600	414800	663000	13320	592900	97930	577600
Cadmium	μg/L	<10	34	<10	<10	<10	<10	<10	<10	<10	36	<10
Magnesium	μg/L	10190	7075	73560	27100	6290	73800	67110	6916	88480	25600	7595
Mercury	μg/L	<7										
Selenium	μg/L											
Sulphur	μg/L											
Sodium	μg/L	19090	91540	59200	31740	20430	67400	95580	1162000	154700	13240	115700
Dissolved Metals:												
Antimony	μg/L	<50	187	163	<50	385	321	135	435	<50	125	<50
Calcium	μg/L	225300	599000	676000	443000	519000	456000	672300	8673	621000	105700	568300
Cadmium	μg/L	<10	<10	<10	<10	<10	<10	<10	14	<10	<10	<10
Magnesium	μg/L	10330	6281	65100	23200	5733	77700	69160	6754	94030	27720	7058
Mercury	μg/L	<2										
Sodium	μg/L	18450	86320	56300	32100	201000	668000	87610	1178000	172200	12000	120

Site 1: Untreated Effluent, Cobalt/Nickel and Precious Metal Refinery
Site 2: Untreated Effluent, Cobalt/Nickel and Precious Metal Refinery
Site 3: Bit Mine
Site 4: Lead/Zinc Mine
Site 5: Nickel/Copper Mine
Site 6: Nickel/Copper Mine
Site 7: Nickel/Copper Mine
Site 8: Tin Mine
Site 9: Copper/Zinc Mine
Site 10: Gold Mine
Site 11: Lead/Zinc Mine
Site 12: Nickel/Copper Mine
Site 13: Zinc Mine
Site 14: Copper/Zinc Mine
Site 15: Gold Mine
Site 16: Uranium Mine
Site 17: Gold Mine
Site 18: Lead/Zinc Mine
Site 19: Copper Mine
Site 20: Nickel/Copper Mine
Site 21: Gold Mine
Site 22: Uranium Mine
Site 23: Gold Mine

APPENDIX 2

Detailed Acute Toxicity Data for Freshwater Fish And Invertebrates

TABLE A2.1: ACUTE TOXICITY OF MERCURY TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Amphipod, *Gammarus* sp.	S, M	Mercuric nitrate		10	Rehwoldt *et al*., 1973
Bluegill (juvenile), *Lepomis macrochirus*	S, U	Mercuric chloride		160	Holcombe *et al*., 1983
Bonytail chub, *Gila elegans*	S	Mercuric chloride	96	61	Buhl, 1997
Brook trout (juvenile), *Salvelinus fontinalis*	FT, M	Methylmercuric chloride		84	McKim *et al*., 1976
Brook trout (yearling), *Salvelinus fontinalis*	FT, M	Methylmercuric chloride		65	McKim *et al*., 1976
Caddisfly, (unidentified)	S, M	Mercuric nitrate		1,200	Rehwoldt *et al*., 1973
Caddisfly, *Hydropsyche betteni*	S, U	Mercuric chloride		2,000	Warnick and Bell, 1969
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Ethylmercuric p-toluene sufonanilide		51	Clemens and Sneed, 1959
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Ethylmercuric phosphate		49	Clemens and Sneed, 1959
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Phenylmercuric acetate		1,966	Clemens and Sneed, 1959
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Phenylmercuric acetate		28	Clemens and Sneed, 1958a, 1959
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Pyridylmercuric acetate		<176	Clemens and Sneed, 1958b
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Pyridylmercuric acetate		224	Clemens and Sneed, 1958b
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Pyridylmercuric acetate		<153	Clemens and Sneed, 1958b
Cladoceran, (<24 hr old), *Daphnia magna*	S, U	Mercuric chloride		4.4	Barera and Adams, 1983
Cladoceran, (<6 hr old), *Daphnia magna*	S, U	Mercuric chloride		4.4	Barera and Adams, 1983
Cladoceran, (1-9 day old), *Daphnia magna*	S, U	Mercuric chloride		5.2-14-8	Barera and Adams, 1983
Cladoceran, *Daphnia magna*	S	Mercuric chloride	1	20	Janssen and Persoone, 1993
Cladoceran, *Daphnia magna*	S	Mercuric chloride	24	30	Janssen and Persoone, 1993
Cladoceran, *Daphnia magna*	S	Mercuric chloride	48	10	Janssen and Persoone, 1993
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride		<4.4	Anderson, 1948
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride		5	Biesinger and Christensen, 1972
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride		3.177	Canton and Adema, 1978
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride		1.478	Canton and Adema, 1978
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride		2.180	Canton and Adema, 1978
Cladoceran, *Daphnia pulex*	S, U	Mercuric chloride		2.217	Canton and Adema, 1978
Climbing perch, *Anabus testudineus*	S	Mercuric chloride	96	640	Sinha and Kumar, 1992
Coho salmon (juvenile), *Oncorhynchus kisutch*	R, M	Mercuric chloride		240	Lorz *et al*., 1978
Colorado squawfish, *Ptychocheilus lucius*	S	Mercuric chloride	96	57	Buhl, 1997

TABLE A2.1: ACUTE TOXICITY OF MERCURY TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Common carp, *Cyprinus carpio*	R	Mercury	96	160	Alam and Maughan, 1995
Common carp, *Cyprinus carpio*	R, U	2-Methoxy ethyl mercuric chloride		139	Das and Misra, 1982
Common guppy, *Poecilia reticulata*			96	260	Khangarot and Ray, 1987
Crayfish (male, mixed ages), *Faxonella clypeatus*	R, M	Mercuric chloride		20	Heit and Fingerman, 1977; Heit, 1981
Crayfish, *Orconectes limosus*	S, M	Mercuric chloride		50	Boutet and Chaisemartin, 1973
Damselfly, (unidentified)	S, M	Mercuric nitrate		1,200	Rehwoldt *et al*., 1973
Fathead minnow, *Pimephales promelas*	FT, M	Mercuric chloride		168	Snarski and Olson, 1982
Fathead minnow, *Pimephales promelas*	FT, M	Mercuric chloride		150	Call *et al*., 1983
Fathead minnow, *Pimephales promelas*	S, M	Mercuric acetate		40	Curtis *et al*., 1979; Curtis and Ward, 1981
Fathead minnow, *Pimephales promelas*	S, M	Mercuric thiocyanate		115	Curtis *et al*., 1979; Curtis and Ward, 1981
Golden shiner, *Notemigonus crysoleucas*			96	16.75	McCrary and Heagler, 1997
Goldfish, *Carassius auratus*	S, U	Phenylmercuric lactate		82	Ellis, 1947
Guppy (116-157 mg), *Poecilla reticulata*	R, U	Mercuric chloride		30	Deshmukh and Marathe, 1980
Guppy (362-621 mg), *Poecilla reticulata*	R, U	Mercuric chloride		53.5	Deshmukh and Marathe, 1980
Indian catfish, *Heteropneustes follilis*	R	Mercuric chloride	96	300	Rajan and Banerjee, 1991
Mayfly, *Ephermerella subvaria*	S, U	Mercuric chloride		2,000	Warnick and Bell, 1969
Midge, *Chironomus* sp.	S, M	Mercuric nitrate		20	Rehwoldt *et al*., 1973
Mosquitofish (female), *Gambusia affinis*	S, U	Mercuric chloride		180	Joshi and Rege, 1980
Mosquitofish (female), *Gambusia affinis*	S, U	Methoxy ethyl mercuric chloride		910	Joshi and Rege, 1980
Mosquitofish (female), *Gambusia affinis*	S, U	Phenylmercuric acetate		37	Joshi and Rege, 1980
Mosquitofish (female), *Gambusia affinis*	S, U	Phenylmercuric acetate (Ceresan)		44	Joshi and Rege, 1980
Mozambique tilapia, *Tilapia mossambica*	S, U	Mercuric chloride		1,000	Qureshi and Saksena, 1980
Pearlspot, *Etroplus maculates*	S	Mercuric chloride	96	670	Gaikwad, 1989
Rainbow trout (2 mos), *Salmo gairdneri*	FT, M	Mercurous nitrate		33.0	Hale, 1977
Rainbow trout (juvenile), *Salmo gairdneri*	R, U	Mercuric chloride		155.1	Matida *et al*., 1971
Rainbow trout (juvenile), *Salmo gairdneri*	FT, U	Mercuric chloride		280	MacLeod and Pessah, 1973
Rainbow trout (juvenile), *Salmo gairdneri*	FT, U	Mercuric chloride		220	MacLeod and Pessah, 1973
Rainbow trout (juvenile), *Salmo gairdneri*	FT, M	Mercuric chloride		275	Lock and van Overbeeke, 1981
Rainbow trout (juvenile), *Salmo gairdneri*	R, U	Methylmercuric chloride		25	Matida *et al*., 1971

TABLE A2.1: ACUTE TOXICITY OF MERCURY TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Rainbow trout (juvenile), *Salmo gairdneri*	R, U	Methylmercuric chloride		42	Wobeser, 1973
Rainbow trout (juvenile), *Salmo gairdneri*	FT, M	Methylmercuric chloride		24	Lock and van Overbeeke, 1981; Lock *et al*., 1981
Rainbow trout (juvenile), *Salmo gairdneri*	R, U	Phenylmercuric acetate		5	Matida *et al*., 1971
Rainbow trout (larva), *Salmo gairdneri*	R, U	Methylmercuric chloride		24	Wobeser, 1973
Rainbow trout, *Salmo gairdneri*	FT, U	Mercuric chloride		420	Daoust, 1981
Razorback sucker, *Xyrauchen texanus*	S	Mercuric chloride	96	90	Buhl, 1997
Sarotherodon mossambicus		Mercuric chloride	48	1500	Naidu *et al*., 1984
Shrimp, *Macrobrachium lammarrei*	R	Mercuric chloride	24	167	Murti and Shukla, 1984
Shrimp, *Macrobrachium lammarrei*	R	Mercuric chloride	96	95	Murti and Shukla, 1984
Snail (adult), *Amnicola* sp.	S, M	Mercuric chloride		80	Rehwoldt *et al*., 1973
Snail (embryo), *Amnicola* sp.	S, M	Mercuric nitrate		2,100	Rehwoldt *et al*., 1973
Snail, *Aplea hypnorum*	S, U	Mercuric chloride		370	Holcombe *et al*., 1983
Snake-head catfish, *Channa marulius*	R	Mercuric chloride	96	314	Khangarot, 1981
Stonefly, *Acroneuria lycorias*	S, U	Mercuric chloride		2,000	Warnick and Bell, 1969
Tubicid worm, *Stylodrilus heringianus*	R, U	Mercuric chloride		140	Chapman *et al*., 1982a
Tubificid worm, *Branchiura sowerbyl*	R, U	Mercuric chloride		80	Chapman *et al*., 1982a
Tubificid worm, *Limnodrilus hoffmeisteri*	R, U	Mercuric chloride		180	Chapman *et al*., 1982a, b
Tubificid worm, *Quistadrilus multisetosus*	R, U	Mercuric chloride		250	Chapman *et al*., 1982a
Tubificid worm, *Rhyacodrilus Montana*	R, U	Mercuric chloride		240	Chapman *et al*., 1982a
Tubificid worm, *Spirosperma ferox*	R, U	Mercuric chloride		330	Chapman *et al*., 1982a
Tubificid worm, *Spirosperma nikolskyl*	R, U	Mercuric chloride		500	Chapman *et al*., 1982a
Tubificid worm, *Tubifex tubifex*	R, U	Mercuric chloride		140	Chapman *et al*., 1982a, b
Tubificid worm, *Varichaeta pacifica*	R, U	Mercuric chloride		100	Chapman *et al*., 1982a
Western mosquitofish, *Gambusia affinis*			96	52.62	McCrary and Heagler, 1997
Worm, *Nais* sp.	S, M	Mercuric nitrate		1,000	Rehwoldt *et al*., 1973

* S = static, R = renewal, FT = flow-through, M = measured, U = unmeasured.
** Results are expressed as mercury, not as the chemical.

TABLE A2.2: ACUTE TOXICITY OF CADMIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Hardness (mg/L as $CaCO_3$)	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Amphipod, *Echinogammarus tibaldi*			240	96	1100	Pantani *et al*. 1997
Amphipod, *Gammarus italicus*			240	96	9100	Pantani *et al*. 1997
American eel, *Anguilla rostrata*	S, M		55		820	Rehwoldt *et al*., 1972
Amphipod, *Gammarus pseudolimnaeus*	S, M	Cadmium chloride	55-79		54.4	Spehar and Carlson, 1984a, b
Amphipod, *Gammarus pseudolimnaeus*	S, M	Cadmium chloride	39-48		68.3	Spehar and Carlson, 1984a, b
Amphipod, *Gammarus pulex*	FT	Cadmium		96	20	Williams *et al*., 1985
Amphipod, *Gammarus sp.*	S, U		50		70	Rehwoldt *et al*., 1973
Amphipod, *Hyalella azteca*			50	96	190	Schlekat *et al*., 1992
Amphipod, *Hyalella azteca*	S	Cadmium chloride	20	48	5.6	Suedel *et al*., 1997
Amphipod, *Hyalella azteca*	S	Cadmium chloride	20	96	2.8	Suedel *et al*., 1997
Amphipod, *Hyalella azteca*				96	8	Nebeker *et al*., 1986a
Amphipod, *Hyalella azteca*				96	74	Nebeker *et al*., 1986a
Amphipod, *Hyalella azteca*	S, M	Cadmium chloride	55-79		285	Spehar and Carlson, 1984a, b
Banded killifish, *Fundulus diaphanus*	S, M		55		110	Rehwoldt *et al*., 1972
Bluegill, *Lepomis macrochirus*	S, U	Cadmium chloride	20		1,940	Pickering and Henderson, 1966
Bluegill, *Lepomis macrochirus*	FT, M	Cadmium chloride	207		21,100	Eaton, 1980
Bluegill, *Lepomis macrochirus*	S, M	Cadmium chloride	18		3,860	Bishop and McIntosh, 1981
Bluegill, *Lepomis macrochirus*	S, M	Cadmium chloride	18		2,800	Bishop and McIntosh, 1981
Bluegill, *Lepomis macrochirus*	S, M	Cadmium chloride	18		2,260	Bishop and McIntosh, 1981
Bluegill, *Lepomis macrochirus*	S, M	Cadmium chloride	55-79		8,810	Spehar and Carlson, 1984a, b
Bonytail chub, *Gila elegans*	S	Cadmium chloride	199	96	148	Buhl, 1997
Brook trout, *Salvelinus fontinalis*	FT, M	Cadmium chloride	47.4		5,080	Holcombe *et al*., 1983
Brook trout, *Salvelinus fontinalis*	S, M	Cadmium sulphate	42		<1.5	Carroll, *et al*., 1979
Brown trout, *Salmo trutta*	S, M	Cadmium chloride	55-79		15.1	Spehar and Carlson, 1984a, b
Brown trout, *Salmo trutta*	S, M	Cadmium chloride	39-48		1.4	Spehar and Carlson, 1984a, b
Bryozoan, *Lophopodella carteri*	S, U		190-220		150	Pardue and Wood, 1980

TABLE A2.2: ACUTE TOXICITY OF CADMIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Hardness (mg/L as $CaCO_3$)	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Bryozoan, *Pectinatella magnifica*	S, U		190-220		700	Pardue and Wood, 1980
Bryozoan, *Plumatella emarginata*	S, U		190-220		1,090	Pardue and Wood, 1980
Caddisfly, (unidentified)	S, U		50		5,400	Rehwoldt *et al*., 1973
Caddisfly, *Hydropsyche angustipennis*	FT	Cadmium		96	520000	Williams *et al*., 1985
Channel catfish, *Ictalurus punctatus*	S, M	Cadmium chloride	55-79		7,940	Spehar and Carlson, 1984a, b
Chinook salmon (alevin), *Oncorhynchus tshawytscha*	FT, M	Cadmium chloride	23		>26	Chapman, 1975, 1978
Chinook salmon (juvenile), *Oncorhynchus tshawytscha*	FT, M	Cadmium chloride	25		1.41	Chapman, 1982
Chinook salmon (juvenile), *Oncorhynchus tshawytscha*	FT, M	Cadmium sulphate	20-22		1.1	Finlayson and Verrue, 1982
Chinook salmon (parr), *Oncorhynchus tshawytscha*	FT, M	Cadmium chloride	23		3.5	Chapman, 1975, 1978
Chinook salmon (smolt), *Oncorhynchus tshawytscha*	FT, M	Cadmium chloride	23		>2.9	Chapman, 1975, 1978
Chinook salmon (swim-up), *Oncorhynchus tshawytscha*	FT, M	Cadmium chloride	23		1.8	Chapman, 1975, 1978
Cladoceran, *Ceriodaphnia dubia*			290	48	350	Schubauer-Berigan *et al*., 1993
Cladoceran, *Ceriodaphnia dubia*	S	Cadmium chloride	20	48	63.1	Suedel *et al*., 1997
Cladoceran, *Ceriodaphnia dubia*	S	Cadmium chloride	20	96	16.9	Suedel *et al*., 1997
Cladoceran, *Ceriodaphnia dubia*	S	cadmium nitrate	81	24	132	Nelson and Roline, 1998
Cladoceran, *Ceriodaphnia dubia*	S	cadmium nitrate	81	48	78.2	Nelson and Roline, 1998
Cladoceran, *Ceriodaphnia reticulata*	S, U		45		66	Mount and Norberg, 1984
Cladoceran, *Ceriodaphnia reticulata*	S, M	Cadmium chloride	55-79		129	Spehar and Carlson, 1984a, b
Cladoceran, *Daphnia carinata*	R	Cadmium chloride	50	48	265	Chandin, 1988
Cladoceran, *Daphnia carinata*	R	Cadmium chloride	50	96	110	Chandin, 1988
Cladoceran, *Daphnia magna*	S	Cadmium chloride	170	48	3.6	Baird *et al*., 1991
Cladoceran, *Daphnia magna*	S	Cadmium chloride	78	48	26.4	Suedel *et al*., 1997
Cladoceran, *Daphnia magna*	S	Cadmium chloride	78	96	12.7	Suedel *et al*., 1997
Cladoceran, *Daphnia magna*	S	Cadmium chloride	250	1	410	Janssen and Persoone, 1993
Cladoceran, *Daphnia magna*	S	Cadmium chloride	250	24	1900	Janssen and Persoone, 1993

TABLE A2.2: ACUTE TOXICITY OF CADMIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Hardness (mg/L as $CaCO_3$)	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Cladoceran, *Daphnia magna*	S	Cadmium chloride	250	48	970	Janssen and Persoone, 1993
Cladoceran, *Daphnia magna*	S	Cadmium chloride	170	48	120	Taylor *et al*., 1998
Cladoceran, *Daphnia magna*	S	Cadmium chloride	170	48	125	Taylor *et al*., 1998
Cladoceran, *Daphnia magna*	S	Cadmium chloride	170	48	131	Taylor *et al*., 1998
Cladoceran, *Daphnia magna*	S	Cadmium chloride	170	48	134	Taylor *et al*., 1998
Cladoceran, *Daphnia magna*			10	48	360	Fargasova 1994
Cladoceran, *Daphnia magna*	S	Cadmium sulphate	240	48	1880	Khangarot and Ray, 1989a
Cladoceran, *Daphnia magna*	S	Cadmium chloride	74	48	18	Nebeker *et al*., 1986a
Cladoceran, *Daphnia magna*	S	Cadmium chloride	74	48	23	Nebeker *et al*., 1986b
Cladoceran, *Daphnia magna*	S	Cadmium		48	39	Schuytema *et al*., 1984
Cladoceran, *Daphnia magna*	S	Cadmium		48	91	Schuytema *et al*., 1984
Cladoceran, *Daphnia magna*	S	Cadmium sulphate		48	69	Dave *et al*., 1981
Cladoceran, *Daphnia magna*	S	Cadmium chloride		48	38	Lewis and Horning, 1991
Cladoceran, *Daphnia magna*	S, U	Cadmium chloride			<1.6	Anderson, 1948
Cladoceran, *Daphnia magna*	S, U	Cadmium chloride	45		65	Biesinger and Christensen, 1972
Cladoceran, *Daphnia magna*	FT, M	Cadmium chloride	130		58	Attar and Maly, 1982
Cladoceran, *Daphnia magna*	S, M	Cadmium chloride	51		9.9	Chapman *et al*., Manuscript
Cladoceran, *Daphnia magna*	S, M	Cadmium chloride	104		33	Chapman *et al*., Manuscript
Cladoceran, *Daphnia magna*	S, M	Cadmium chloride	105		34	Chapman *et al*., Manuscript
Cladoceran, *Daphnia magna*	S, M	Cadmium chloride	197		63	Chapman *et al*., Manuscript
Cladoceran, *Daphnia magna*	S, M	Cadmium chloride	209		49	Chapman *et al*., Manuscript
Cladoceran, *Daphnia magna*	R, M	Cadmium chloride	100		30	Canton and Slooff, 1982
Cladoceran, *Daphnia magna*	S, M	Cadmium chloride	55-79		166	Spehar and Carlson, 1984a, b
Cladoceran, *Daphnia magna*	S, U	Cadmium nitrate			27	Canton and Adema, 1978

TABLE A2.2: ACUTE TOXICITY OF CADMIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Hardness (mg/L as $CaCO_3$)	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Cladoceran, *Daphnia magna*	S, U	Cadmium nitrate			28	Canton and Adema, 1978
Cladoceran, *Daphnia magna*	S, U	Cadmium nitrate			35	Canton and Adema, 1978
Cladoceran, *Daphnia magna*	S, U		45		118	Mount and Norberg, 1984
Cladoceran, *Daphnia pulex*	S	Cadmium chloride		48	78	Roux *et al*., 1993
Cladoceran, *Daphnia pulex*	S	Cadmium chloride		48	42	Lewis and Horning, 1991
Cladoceran, *Daphnia pulex*	S, U	Cadmium nitrate			93.45	Canton and Adema, 1978
Cladoceran, *Daphnia pulex*	S, U		45		68	Mount and Norberg, 1984
Cladoceran, *Daphnia pulex*	S, U	Cadmium chloride	57		47	Bertram and Hart, 1979
Cladoceran, *Echinsca triseralis*	R	Cadmium chloride	50	48	345	Chandin, 1988
Cladoceran, *Echinsca triseralis*	R	Cadmium chloride	50	96	58	Chandin, 1988
Cladoceran, *Moina irrasa*	S	Cadmium chloride	5	96	9.57	Zou and Bu, 1994
Cladoceran, *Moina irrasa*	S	Cadmium chloride	5	96	2.52	Zou and Bu, 1994
Cladoceran, *Moina macrocopa*	S, U	Cadmium chloride	80-84		71.25	Hatakeyama and Yasuno, 1981
Cladoceran, *Simocephalus serrulatus*	S, M	Cadmium chloride	11.1		7.0	Giesy *et al*., 1977
Cladoceran, *Simocephalus serrulatus*	S, M	Cadmium chloride	55-79		123	Spehar and Carlson, 1984a, b
Cladoceran, *Simocephalus serrulatus*	S, M	Cadmium chloride	39-48		24.5	Spehar and Carlson, 1984a, b
Cladoceran, *Simocephalus vetulus*	S, U		45		24	Mount and Norberg, 1984
Cladoceran, *Simocephalus vetulus*	S, M	Cadmium chloride	55-79		89.3	Spehar and Carlson, 1984a, b
Coho salmon (1 year), *Oncorhynchus kisutch*	S, U	Cadmium chloride	90		10.4	Lorz *et al*., 1978
Coho salmon (adult), *Oncorhynchus kisutch*	FT, M	Cadmium chloride	23		17.5	Chapman, 1975
Coho salmon (parr), *Oncorhynchus kisutch*	FT, M	Cadmium chloride	23		2.7	Chapman, 1975
Colorado squawfish, *Ptychocheilus lucius*	S	Cadmium chloride	199	96	78	Buhl, 1997
Common carp, *Cyprinus carpio*	R	Cadmium	100	96	4260	Suresh *et al*., 1993
Common carp, *Cyprinus carpio*	S, M		55		240	Rehwoldt *et al*., 1972
Crayfish, *Orconectes Iimosus*	S, M	Cadmium chloride			400	Boutet and Chalsemartin, 1973

TABLE A2.2: ACUTE TOXICITY OF CADMIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Hardness (mg/L as $CaCO_3$)	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Damselfly, (unidentified)	S, U		50		8,100	Rehwoldt *et al*., 1973
Fathead minnow (adult), *Pimephales promelas*	S, M	Cadmium chloride	103		3,060	Birge *et al*., 1983
Fathead minnow (adult), *Pimephales promelas*	S, M	Cadmium chloride	103		2,900	Birge *et al*., 1983
Fathead minnow (adult), *Pimephales promelas*	S, M	Cadmium chloride	103		3,100	Birge *et al*., 1983
Fathead minnow (adult), *Pimephales promelas*	S, M	Cadmium chloride	254-271		7,160	Birge *et al*., 1983
Fathead minnow (fry), *Pimephales promelas*	S, M	Cadmium chloride	40		21.5	Spehar, 1982
Fathead minnow (fry), *Pimephales promelas*	S, M	Cadmium chloride	48		11.7	Spehar, 1982
Fathead minnow (fry), *Pimephales promelas*	S, M	Cadmium chloride	39		19.3	Spehar, 1982
Fathead minnow (fry), *Pimephales promelas*	S, M	Cadmium chloride	45		42.4	Spehar, 1982
Fathead minnow (fry), *Pimephales promelas*	S, M	Cadmium chloride	47		54.2	Spehar, 1982
Fathead minnow (fry), *Pimephales promelas*	S, M	Cadmium chloride	44		29.0	Spehar, 1982
Fathead minnow, *Pimephales promelas*			290	96	60	Schubauer-Berigan *et al*., 1993
Fathead minnow, *Pimephales promelas*	S	Cadmium chloride	20	48	8.9	Suedel *et al*., 1997
Fathead minnow, *Pimephales promelas*	S	Cadmium chloride	20	96	4.8	Suedel *et al*., 1997
Fathead minnow, *Pimephales promelas*	S, U	Cadmium chloride	20		1,050	Pickering and Henderson, 1966
Fathead minnow, *Pimephales promelas*	S, U	Cadmium chloride	20		630	Pickering and Henderson, 1966
Fathead minnow, *Pimephales promelas*	S, U	Cadmium chloride	360		72,600	Pickering and Henderson, 1966
Fathead minnow, *Pimephales promelas*	S, U	Cadmium chloride	360		73,500	Pickering and Henderson, 1966
Fathead minnow, *Pimephales promelas*	FT, M	Cadmium sulphate	201		11,200	Pickering and Gast, 1972
Fathead minnow, *Pimephales promelas*	FT, M	Cadmium sulphate	201		12,000	Pickering and Gast, 1972
Fathead minnow, *Pimephales promelas*	FT, M	Cadmium sulphate	201		6,400	Pickering and Gast, 1972
Fathead minnow, *Pimephales promelas*	FT, M	Cadmium sulphate	201		2,000	Pickering and Gast, 1972
Fathead minnow, *Pimephales promelas*	FT, M	Cadmium sulphate	201		4,500	Pickering and Gast, 1972
Fathead minnow, *Pimephales promelas*	S, M	Cadmium chloride	55-79		3,390	Spehar and Carlson, 1984a, b
Fathead minnow, *Pimephales promelas*	S, M	Cadmium chloride	39-48		1,280	Spehar and Carlson, 1984a, b
Fathead minnow, *Pimephales promelas*	FT, M	Cadmium chloride	55-79		1,830	Spehar and Carlson, 1984a, b
Flagfish, *Jordanella floridae*	FT, M	Cadmium chloride	44		2,500	Spehar, 1976a, b
Goldfish, *Carassius auratus*	S, U	Cadmium chloride	20		2,340	Pickering and Henderson, 1966

TABLE A2.2: ACUTE TOXICITY OF CADMIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Hardness (mg/L as $CaCO_3$)	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Goldfish, *Carassius auratus*	S, M	Cadmium chloride	20		2,130	McCarty *et al*., 1978
Goldfish, *Carassius auratus*	S, M	Cadmium chloride	140		46,800	McCarty *et al*., 1978
Green sunfish, *Leopmis cyanellus*	S, U	Cadmium chloride	20		2,840	Pickering and Henderson, 1966
Green sunfish, *Leopmis cyanellus*	S, U	Cadmium chloride	360		66,000	Pickering and Henderson, 1966
Green sunfish, *Leopmis cyanellus*	FT, M	Cadmium chloride	335		20,500	Jude, 1973
Guppy, *Poecilla reticulata*	S, U	Cadmium chloride	20		1,270	Pickering and Henderson, 1966
Isopod, *Asellus bicrenata*	FT, M	Cadmium chloride	220		2,130	Bosnak and Morgan, 1981
Isopod, *Lirceus alabamae*	FT, M	Cadmium chloride	152		150	Bosnak and Morgan, 1981
Leech, *Nephelopsis obscura*	S	cadmium chloride	50	96	23	Wicklum *et al*., 1997
Mayfly, *Ephermerella grandis*	FT, M	Cadmium chloride			28,000	Clubb *et al*., 1975
Mayfly, *Ephermerella grandis*	S, U	Cadmium sulphate	44		2,000	Warnick and Bell, 1969
Mayfly, *Paraleptophlebia praepedita*	S, M	Cadmium chloride	55-79		449	Spehar and Carlson, 1984a, b
Midge, *Chironomus* sp.	S, U		50		1,200	Rehwoldt *et al*., 1973
Midge, *Chironomus tentans*	S	Cadmium chloride	240	24	23250	Khangarot and Ray, 1989b
Midge, *Chironomus tentans*	S	Cadmium chloride	240	48	8050	Khangarot and Ray, 1989b
Midge, *Chironomus tentans*	S	Cadmium chloride	20	48	29560	Suedel *et al*., 1997
Midge, *Chironomus tentans*	S	Cadmium chloride	20	96	8000	Suedel *et al*., 1997
Mosquitofish, *Gambusia affinis*	FT, M	Cadmium chloride	11.1		900	Giesy *et al*., 1977
Mosquitofish, *Gambusia affinis*	FT, M	Cadmium chloride	11.1		2,200	Giesy *et al*., 1977
Mussel, *Anodonta imbecilis*				48	57	Keller and Zam, 1991
Northern squawfish, *Ptychocheilus oregonensis*	FT, M	Cadmium chloride	20-30		1,092	Andros and Garton, 1980
Northern squawfish, *Ptychocheilus oregonensis*	FT, M	Cadmium chloride	20-30		1,104	Andros and Garton, 1980
Pumpkinsee, *Leopmis gibbosus*	S, M		55		1,500	Rehwoldt *et al*., 1972
Rainbow trout (2-mos), *Salmo gairdneri*	FT, M	Cadmium nitrate			6.6	Hale, 1977
Rainbow trout (alevin), *Salmo gairdneri*	FT, M	Cadmium chloride	23		>27	Chapman, 1975, 1978
Rainbow trout (parr), *Salmo gairdneri*	FT, M	Cadmium chloride	23		1.0	Chapman, 1978
Rainbow trout (smolt), *Salmo gairdneri*	FT, M	Cadmium chloride	23		4.1	Chapman, 1975
Rainbow trout (smolt), *Salmo gairdneri*	FT, M	Cadmium chloride	23		>29	Chapman, 1978

TABLE A2.2: ACUTE TOXICITY OF CADMIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Hardness (mg/L as $CaCO_3$)	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Rainbow trout (swim-up), *Salmo gairdneri*	FT, M	Cadmium chloride	23		1.3	Chapman, 1975, 1978
Rainbow trout, *Oncorhynchus mykiss*	FT	Cadmium chloride	50	96	3.02	Davies *et al*., 1993
Rainbow trout, *Oncorhynchus mykiss*	FT	Cadmium chloride	200	96	6.12	Davies *et al*., 1993
Rainbow trout, *Oncorhynchus mykiss*	FT	Cadmium chloride	400	96	5.7	Davies *et al*., 1993
Rainbow trout, *Oncorhynchus mykiss*				48	5	Dave *et al*., 1981
Rainbow trout, *Oncorhynchus mykiss*	S	Cadmium chloride	20	48	91	Calamari *et al*., 1980
Rainbow trout, *Oncorhynchus mykiss*	S	Cadmium chloride	80	48	358	Calamari *et al*., 1980
Rainbow trout, *Oncorhynchus mykiss*	S	Cadmium chloride	320	48	3698	Calamari *et al*., 1980
Rainbow trout, *Oncorhynchus mykiss*	R	Cadmium chloride		96	10	Van Leeuwen *et al*., 1985
Rainbow trout, *Salmo gairdneri*	FT, M	Cadmium sulphate	31		1.75	Davies, 1976
Rainbow trout, *Salmo gairdneri*	S, U				6	Kumada *et al*., 1973
Rainbow trout, *Salmo gairdneri*	S, U				7	Kumada *et al*., 1973
Rainbow trout, *Salmo gairdneri*	S, U	Cadmium chloride			6.0	Kumada *et al*., 1980
Rainbow trout, *Salmo gairdneri*	S, M	Cadmium chloride	55-79		10.2	Spehar and Carlson, 1984a, b
Rainbow trout, *Salmo gairdneri*	S, M	Cadmium chloride	39-48		2.3	Spehar and Carlson, 1984a, b
Razorback sucker, *Xyrauchen texanus*	S	Cadmium chloride	199	96	139	Buhl, 1997
Rotifer, *Brachionus calyciflorus*	S	Cadmium nitrate	81	24	1116	Nelson and Roline, 1998
Rotifer, *Brachionus calyciflorus*			51	24	1300	Juchelka and Snell, 1994
Shrimp, *Macrobrachium lammarrei*	R	Cadmium chloride		24	374	Murti and Shukla, 1984
Shrimp, *Macrobrachium lammarrei*	R	Cadmium choride		96	195	Murti and Shukla, 1984
Snail (adult), *Amnicola* sp.	S, U		50		8,400	Rehwoldt *et al*., 1973
Snail (adult), *Physa gyrina*	S, M		200		1,370	Wier and Walter, 1976
Snail (embryo), *Amnicola* sp.	S, U		50		3,800	Rehwoldt *et al*., 1973
Snail (immature), *Physa gyrina*	S, M		200		410	Wier and Walter, 1976
Snail, *Aplexa hypnorum*	FT, M	Cadmium chloride	45.3		93	Holcombe *et al*., 1983
Stonefly, *Pteronarcella badla*	FT, M	Cadmium chloride			18,000	Clubb *et al*., 1975
Striped bass (fingerling), *Morone saxatilis*	S, U	Cadmium chloride	34.5		2	Hughes, 1973
Striped bass (larva), *Morone saxatilis*	S, U	Cadmium chloride	34.5		1	Hughes, 1973

TABLE A2.2: ACUTE TOXICITY OF CADMIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Hardness (mg/L as $CaCO_3$)	Duration (hr)	LC50/EC50 (µg/L)**	Reference
Striped bass, *Morone saxatilis*	S, M		558		1,100	Rehwoldt *et al*., 1972
Threespine stickleback, *Gasterosteus aculeatus*	S, U	Cadmium chloride	115		6,500	Pascoe and Cram, 1977
Threespine stickleback, *Gasterosteus aculeatus*	R, M	Cadmium chloride	103-111		23,000	Pascoe and Mattey, 1977
Tubificid worm, *Branchiura sowerbyl*	S, M	Cadmium sulphate	5.3		240	Chapman *et al*., 1982a
Tubificid worm, *Limnodrilus hoffmelsteri*	S, M	Cadmium sulphate	5.3		170	Chapman *et al*., 1982a, b
Tubificid worm, *Quistadrilus multisetosus*	S, M	Cadmium sulphate	5.3		320	Chapman *et al*., 1982a
Tubificid worm, *Rhyacodrilus Montana*	S, M	Cadmium sulphate	5.3		630	Chapman *et al*., 1982a
Tubificid worm, *Spirosperma ferox*	S, M	Cadmium sulphate	5.3		350	Chapman *et al*., 1982a
Tubificid worm, *Spirosperma nikolskyl*	S, M	Cadmium sulphate	5.3		450	Chapman *et al*., 1982a
Tubificid worm, *Stylodrilus heringlanus*	S, M	Cadmium sulphate	5.3		550	Chapman *et al*., 1982a
Tubificid worm, *Tubifex tubifex*			10	96	1032	Fargasova 1994
Tubificid worm, *Tubifex tubifex*	S, M	Cadmium sulphate	5.3		320	Chapman *et al*., 1982a, b
Tubificid worm, *Varichaeta pacifica*	S, M	Cadmium sulphate	5.3		380	Chapman *et al*., 1982a
White perch, *Morone Americana*	S, M		55		8,400	Rehwoldt *et al*., 1972
White sucker, *Catostomus commersoni*	FT, M	Cadmium chloride	18		1,110	Duncan and Klaverkamp, 1983
Worm, *Lumbriculus variegatus*			290	96	780	Schubauer-Berigan *et al*., 1993
Worm, *Nais* sp.	S, U		50		1,700	Rehwoldt *et al*., 1973
Zebra mussel, *Dreissena polymorpha*	R	Cadmium chloride	150	48	388	Kraak *et al*., 1994

* S = static, R = renewal, FT = flow-through, M = measured, U = unmeasured.

** Results are expressed as cadmium, not as the chemical.

TABLE A2.3: ACUTE TOXICITY OF SELENIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Duration (hrs)	LC50/EC50 (µg/L)**	Reference
Amphipod, *Hyallela azteca*	FT, M	Sodium selenite		340	Halter *et al*., 1980
Amphipod, *Hyallela azteca*	FT, M	Sodium selenate		760	Adams, 1976
Arctic grayling, *Thymallus arcticus*	S	Sodium selenate	96	34300	Buhl and Hamilton, 1991
Arctic grayling, *Thymallus arcticus*	S	Sodium selenate	96	100000	Buhl and Hamilton, 1991
Bluegill, *Lepomis macrochirus*	FT, M	Selenium dioxide		28,500	Cardwell *et al*., 1976
Bonytail chub, *Gila elegans*	S	Sodium selenate	96	19000	Hamilton, 1995
Bonytail chub, *Gila elegans*	S	Sodium selenate	96	55000	Hamilton, 1995
Brook trout, *Salvelinus fontinalis*	FT, M	Selenium dioxide		10,200	Cardwell *et al*., 1976
Channel catfish, *Ictalurus punctatus*	FT, M	Selenium dioxide		13,600	Cardwell *et al*., 1976
Chinook salmon, *Oncorhynchus tshawytscha*	S	Sodium selenite	96	13800	Hamilton and Buhl, 1990
Chinook salmon, *Oncorhynchus tshawytscha*	S	Sodium selenate	96	115000	Hamilton and Buhl, 1990
Cladoceran, *Ceriodaphnia dubia*		Selenate	48	1920	Brix *et al*., 2001a
Cladoceran, *Daphnia magna*	R	Selenite	48	680	Johnston, 1987
Cladoceran, *Daphnia magna*	R	Selenate	48	750	Johnston, 1987
Cladoceran, *Daphnia magna*	R	Selenate	72	1400	Johnston, 1987
Cladoceran, *Daphnia magna*	S	Selenium	48	430	LeBlanc, 1980
Cladoceran, *Daphnia magna*	S	Selenate	48	5300	Dunbar *et al*., 1983
Cladoceran, *Daphnia magna*		Selenate	48	1010	Brooke *et al*., 1985
Cladoceran, *Daphnia magna*	S, U	Sodium selenite		2,500	Bringman and Kuhn, 1959
Cladoceran, *Daphnia magna*	FT, M	Sodium selenite		710	Halter *et al*., 1980
Cladoceran, *Daphnia magna*	S, M	Selenous acid		1,220	Kimball, Manuscript
Cladoceran, *Daphnia magna*	S, M	Selenous acid		1,220	Kimball, Manuscript
Cladoceran, *Daphnia magna*	S, U	Selenous acid		430	U.S. EPA, 1978
Cladoceran, *Daphnia pulex*	S, M	Sodium selenite		3,870	Reading, 1979

TABLE A2.3: ACUTE TOXICITY OF SELENIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Duration (hrs)	LC50/EC50 (µg/L)**	Reference
Coho salmon, *Oncorhynchus kisutch*	S	Sodium selenite	96	7800	Buhl and Hamilton, 1991
Coho salmon, *Oncorhynchus kisutch*	S	Sodium selenate	96	74000	Buhl and Hamilton, 1991
Coho salmon, *Oncorhynchus kisutch*	S	Sodium selenite	96	7800	Hamilton and Buhl, 1990
Coho salmon, *Oncorhynchus kisutch*	S	Sodium selenate	96	32500	Hamilton and Buhl, 1990
Colorado squawfish, *Ptychocheilus lucius*	S	Sodium selenite	96	14000	Hamilton, 1995
Colorado squawfish, *Ptychocheilus lucius*	S	Sodium selenate	96	66000	Hamilton, 1995
Colorado squawfish, *Ptychocheilus lucius*	S	Sodium selenite	96	20700	Hamilton and Buhl, 1997a
Colorado squawfish, *Ptychocheilus lucius*	S	Sodium selenate	96	88000	Hamilton and Buhl, 1997a
Colorado squawfish, *Ptychocheilus lucius*	S	Sodium selenite	96	12800	Buhl and Hamilton, 1996
Colorado squawfish, *Ptychocheilus lucius*	S	Sodium selenate	96	24600	Buhl and Hamilton, 1996
Fathead minnow (fry), *Pimephales promelas*	FT, M	Selenium dioxide		2,100	Cardwell *et al*., 1976
Fathead minnow (juvenile), *Pimephales promelas*	FT, M	Selenium dioxide		5,200	Cardwell *et al*., 1976
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenite		10,500	Adams, 1976
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenite		11,300	Adams, 1976
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenite		6,000	Adams, 1976
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenite		7,400	Adams, 1976
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenite		3,400	Adams, 1976
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenite		2,200	Cardwell *et al*., 1976
Fathead minnow, *Pimephales promelas*	FT, M	Sodium selenite		1,000	Halter *et al*., 1980
Fathead minnow, *Pimephales promelas*	FT, M	Selenous acid		620	Kimball, Manuscript
Fathead minnow, *Pimephales promelas*	FT, M	Selenous acid		970	Kimball, Manuscript
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenate		11,800	Adams, 1976
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenate		11,000	Adams, 1976
Fathead minnow, *Pimephales promelas*	S, U	Sodium selenate		12,500	Adams, 1976

TABLE A2.3: ACUTE TOXICITY OF SELENIUM TO FRESHWATER FISH AND INVERTEBRATES

Species	Method*	Chemical	Duration (hrs)	LC50/EC50 (µg/L)**	Reference
Flagfish, *Jordanella floridae*	FT, M	Selenium dioxide		6,500	Cardwell *et al*., 1976
Flannelmouth sucker, *Catostomus latipinnis*	S	Sodium selenite	96	19100	Hamilton and Buhl, 1997b
Flannelmouth sucker, *Catostomus latipinnis*	S	Sodium selenate	96	26900	Hamilton and Buhl, 1997b
Goldfish, *Carassius auratus*	FT, M	Selenium dioxide		26,100	Cardwell *et al*., 1976
Midge, *Tanytarsus dissimilis*	FT, M	Selenium dioxide		42,400	U.S. EPA, 1978
Mosquitofish, *Gambusia affinis*	S, U	Sodium selenite		12,600	Reading, 1979
Pearlspot, *Etroplus maculates*	S	Selenium oxide	96	10700	Gaidwad, 1989
Rainbow trout, *Oncorhynchus mykiss*	S	Sodium selenite	96	9000	Buhl and Hamilton, 1991
Rainbow trout, *Oncorhynchus mykiss*	S	Sodium selenate	96	32300	Buhl and Hamilton, 1991
Rainbow trout, *Salmo gairdneri*	S, U	Sodium selenite		4,500	Adams, 1976
Rainbow trout, *Salmo gairdneri*	S, U	Sodium selenite		4,200	Adams, 1976
Rainbow trout, *Salmo gairdneri*	FT, M	Sodium selenite		12,500	Goettl and Davies, 1976
Rainbow trout, *Salmo gairdneri*	FT, M	Sodium selenite		7,200	Hodson *et al*., 1980
Rainbow trout, *Salmo gairdneri*	FT, M	Sodium selenite		8,200	Hodson *et al*., 1980
Rainbow trout, *Salmo gairdneri*	FT, M	Sodium selenite		8,800	Hodson *et al*., 1980
Razorback sucker, *Xyrauchen texanus*	S	Sodium selenite	96	15000	Hamilton, 1995
Razorback sucker, *Xyrauchen texanus*	S	Sodium selenate	96	48000	Hamilton, 1995
Razorback sucker, *Xyrauchen texanus*	S	Sodium selenite	96	13700	Buhl and Hamilton, 1996
Razorback sucker, *Xyrauchen texanus*	S	Sodium selenate	96	13800	Buhl and Hamilton, 1996
Snail, *Physa* sp.	S, U	Sodium selenite		24,100	Reading, 1979

* S = static, FT = flow-through, R = Renewal, U = unmeasured, M = measured
** Results are expressed as selenium, not as the compound.

APPENDIX 3

Comparative Evaluation of Innovative Technologies for Selenium Removal

APPENDIX 3: COMPARATIVE EVALUATION OF INNOVATIVE TECHNOLOGIES FOR SELENIUM REMOVAL

A3.1 Introduction

Provincial, state and federal discharge limits for mines and metal plating wastewaters have decreased over the past decades. For example, the state discharge limit for selenium was approximately 3 mg/L in 1977 for one mine in the western USA (MSE and Montana Tech, 1999). The conventional technologies for selenium appear to be capable of achieving this effluent limit. Conventional technologies include use of alum, lime or ferric salts to promote precipitation, often followed by filtration.

Present-day treatment objectives for selenium are much lower than this value. An example of these lower limits is an effluent concentration limit of 0.006 mg/L for selenium (MSE and Montana Tech, 1999) contained in the permit issued to a mine by one State Government.

A desired effluent objective of <0.01 mg/L for Se appears to be underlying the treatment technology assessment for mining wasteforms in the USA in the late 1990s (MSE and Montana, 1999). This is based on groundwater drinking objectives which are presently 0.05 mg/L but which are tending toward 0.01 mg/L in recent water quality standard setting discussions. The U.S. National Primary Drinking Water Standard (NPDWS) Maximum Contaminant Level (MCL) is 50 µg/L selenium and the Maximum Contaminant Level Goal (MCLG) is 10 µg/L.

Current “conventional technologies” are not sufficient for achieving such levels for the following reasons:

- The ferrihydrite treatment technology was classified as the Final Best Demonstrated Available Technology (BDAT) for selenium control, in an investigation for the US Environmental Protection Agency by Rosengrant and Fargo (1990). This “BDAT” treatment technology is rated to achieve <1 mg/L as the effluent objective. This effluent objective was still the rating employed by the US EPA in 1998-99 (MSE and Montana Tech, 1999).

- Available performance data indicate that ferrihydrite sorption can achieve ***sub mg/L*** levels, but ***official re-evaluation*** is needed to change the rating on a BDAT.

- While technologies such as ferrihydrite sorption are recognized as BDAT at the mg/L level, there is also concern about the long term stability of the wasteforms.

Treatment technologies to meet stringent discharge requirements, such as <0.01 mg/L, for “toxic anions and heavy metals” do not exist (MSE and Montana Tech, 1999).

A3.2 Technological and Cost Evaluation of Technologies

MSE and Montana Tech (1999) evaluated technologies which potentially could meet lower discharge limits for selenium in mining wastestreams. A summary of the technologies and their current technological status is provided in Table A3.1 for the following technologies:

- oxidation processes
- precipitation of a selenate, selenite, selenide, or elemental Se
- adsorption onto ferrihydrite, alumina, peat resins, or activated carbon
- ion exchange (IX)
- solvent extraction (SX)
- emulsion liquid membranes
- reverse osmosis
- nanofiltration,
- chemical reduction processes (with ferrous hydroxide or iron), and
- conventional lime softening/ferric coagulation/ filtration

Oxidation processes are used, especially as a precursor to certain technologies, e.g., ion exchange, which selectively remove selenate (SeO_4^-) in preference to selenite (SeO_3^-).

Precipitation processes for selenate, selenite or selenide all involve direct precipitation of a metal with the selenium ion – for example, copper selenide or copper selenate. The precipitation of selenates and selenites are ineffective because the solubility constants are such that the dissolved selenium concentration is too high, relative to an effluent treatment objective of 1 mg/L. The precipitation of selenides or elemental selenium is more effective.

Adsorption processes generally involve sorption onto preformed media through which the solution phase flows. In the detailed description of the ferrihydrite sorption process (MSE and Montana Tech, 1999), soluble iron is introduced into the solution phase, which results in ferrihydrite solid formation. Thus, the precipitation of ferrihydrite should more properly be described as the “ferric coagulation” process, which is listed at he bottom of Table A3.1.

Ion exchange (IX) originated from the water treatment field and uses a specially designed ion exchange media; the current media remove many ions, such that selenium removal is influenced by interfering ions present in the solution matrix. Media specific to selenium have not been used at full scale in the mining industry.

Solvent exchange (SX) uses a solvent in contact with the wastewater to remove contaminants of concern and then the ‘spent solvent’ is regenerated. Emulsion liquid membranes use similar physico-chemical principles to SX , but the “solvent” phase is present in droplets rather than in a separate liquid phase (SX).

TABLE A3.1: SOLUTION TREATMENT TECHNOLOGIES POTENTIALLY APPLICABLE TO MINING INDUSTRY WASTEWATERS FOR SELENIUM REMOVAL[1]

Technology for Solution Treatment	**Studies**			**Comments**
	Lab	**Pilot**	**Industry**	
OXIDATION	x	x		Oxidation of Se (IV) to Se (VI) is important for some of the subsequent removal technologies, e.g., ion exchange. Effective oxidation has been demonstrated; however, the oxidizing reagents are expensive. Efforts to find low-cost treatment technologies and lower cost oxidizing reagents (for use at ambient temperatures) need to be continued.
PRECIPITATION				
Selenate	x	x		The precipitation of selenates as a treatment technology is ineffective because of the relatively high solubility of metal selenates.
Selenite	x	x		The precipitation of metal selenites as a mine water treatment technology is not appropriate because the solubility of metal selenites is not low enough to achieve the very low Se discharge requirements.
Selenide	x	x	x	The reduction of selenate and selenite species with the subsequent precipitation of metal selenides is promising as a mine water treatment option.
Se^0	x	x	x	The reduction of Se (VI) and Se (IV) species to Se^0 by bacterial processes is promising as a mine water treatment option.
ADSORPTION				
Ferrihydrite	x	x	x	Amorphous ferric hydroxide precipitation has been extensively investigated. Selenium (IV) is effectively removed at pH <~8. This technology is not effective for Se (VI). Therefore, reduction of the Se (VI) prior to adsorption is often required. The presence of other aqueous species in the solution to be treated may influence the removal of Se (IV).
Alumina	x	x		Selenium (IV) is adsorbed effectively by alumina. Selenium (IV) adsorption is nearly complete (for concentrations up to 4 ppm Se using 3.3 g/L Al_2O_3) at pH levels between 3-8. Selenium (VI) adsorption by alumina is poor. Selenium (VI) adsorption drops off rapidly with increasing pH and is less than 50% at pH 7. Sulphate and carbonate adsorption significantly interferes with Se (VI) adsorption. Application of Se 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.

TABLE A3.1: SOLUTION TREATMENT TECHNOLOGIES POTENTIALLY APPLICABLE TO MINING INDUSTRY WASTEWATERS FOR SELENIUM REMOVAL[1]

Technology for Solution Treatment	**Studies**			**Comments**
	Lab	**Pilot**	**Industry**	
Ferric Oxyhydroxide//Peat/ Resins	x	x	x	HW-FIX is a USBM development that shows promise for Se (IV) removal. The adsorption is not as effective for Se (VI). This technology shows promise for application to mine waters.
Activated Carbon	x	x		Activated carbon adsorption is widely used in treatment of groundwater and as point-of-use treatment of drinking waters for organic adsorption. It is not very effective for adsorbing Se.
ION EXCHANGE (IX)	x	x		Ion exchange is used for treatment of drinking water and groundwater for metals, As and Se removal. Selenium removal is accomplished by using a strong base anion IX resin. Selenium (VI) is extracted much more effectively than Se (IV). The extraction of Se (VI) is a function of sulphate concentration. Tailored resins show good selectivity for Se in the presence of sulphate; however, only laboratory studies have been performed, and further laboratory studies (on mine waters) are recommended.
SOLVENT EXTRACTION (SX)	x	x		Solvent extraction has been investigated on a pilot scale for treating gold heap leach solution effluents. The results were encouraging; however, the technology has been applied at only one site. Further laboratory test work should be conducted.
EMULSION LIQUID MEMBRANES	x	x		Pilot studies have shown that Se (VI) is extracted rapidly even in the presence of sulphate at all pH values >2. Selenium (IV) extraction is influenced by the presence of sulphate (i.e., the rate of extraction is decreased). This technology shows much potential for application to mine waters; however, it requires further test work to answer questions concerning the presence of multiple anionic species, presence of suspended solids, etc.
REVERSE OSMOSIS (RO)	x	x		Reverse osmosis is extensively used for removing inorganic contaminants from drinking water and groundwater. It has not been applied industrially to mine waters. Reverse osmosis may require extensive pre-treatment of mine waters to remove solids and to lower the concentration of TDS. Otherwise, extensive membrane fouling may occur. It is doubtful that RO will ever be applied to mine waters.

TABLE A3.1: SOLUTION TREATMENT TECHNOLOGIES POTENTIALLY APPLICABLE TO MINING INDUSTRY WASTEWATERS FOR SELENIUM REMOVAL[1]

Technology for Solution Treatment	**Studies**			**Comments**
	Lab	**Pilot**	**Industry**	
NANOFILTRATION	x	x	x (for sulphate)	Nanofiltration appears to be a potential technology for treating some low metal-containing Se-bearing mine waters. Nanofiltration technology shows good potential for application to mine waters; however, it requires further test work to answer questions concerning the presence of multiple anionic species, presence of suspended solids, etc.
CHEMICAL REDUCTION				
Ferrous Hydroxide	x	x		The Bureau of Reclamation has developed a process for treating Se surface and agricultural waters. This technology does not appear to be applicable (at a reasonable cost) to mine waters.
Fe	x	x	x	The successful use of Fe as a reductant is based on the reduction of Se in the presence of Cu ions. Further test work is required to determine the final Cu content achievable in the treated effluent water and to delineate the applicable pH range. This technology shows promise for application to mine waters.
CONVENTION WATER TREATMENT				
Lime Softening/Ferric Coagulation/Filtration	x	x	x	The BAT for treating Se-bearing drinking and groundwaters are 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)]. However, the application of these unit operations to mine waters has not been made. Achieving Se removal to regulated discharge concentrations by these technologies is not likely unless the Se concentrations are already near the required discharge requirements.

[1] Adapted from MSE and Montana Tech (1999).

Reverse osmosis (RO) is a process in which all “soluble metals” are separated simultaneously from purified water. It needs extensive pre-treatment to protect the membrane from suspended solids and chemical precipitation.

Nanofiltration uses similar principles to RO, but its membrane rejects mainly multivalent anions such as sulphate and selenate/selenite, while RO rejects all ions, positive and negative (e.g., Na, K, Ca, Mg, Hg, Cd, sulphate, chloride, carbonate/ bicarbonate, selenate, antimony).

Reduction processes are essential, especially as a precursor (also called pre-treatment), for sorption of Se onto media such as ferrihydrite, because the sorption of the reduced form – selenite (SeO_3^-) - is much more efficient than sorption of the more oxidized form – selenate (SeO_4^-**)**. Since many mills have selenium in their effluents in the selenate form, a reduction process step before a sorption step results in consistently lower Se concentrations in the liquid effluent. Reduction can be accomplished using ferrous hydroxide, elemental Fe, or biological processes.

Conventional processes such as lime softening/ferric coagulation/filtration are widely used. One conventional process, “ferric coagulation”, is listed in the 1980s as EPA’s “Best Available Technology” (BAT; which is different from the “Best Demonstrated Available technology – BDAT – see below), but it is unlikely to achieve effluent limits as low as <0.01 mg/L.

Table A3.1 compares the advantages of the various technologies, and summarizes whether the technical investigations and performance evaluations have been completed at:

- bench scale,
- pilot scale, or
- full scale.

For example, all of the 17 treatment technology categories have been investigated at bench and pilot scale, but only 7 of 17 have full scale performance information.

The study (MSE and Montana Tech, 1999) concludes that only the following technologies have the potential of achieving effective selenium removal to the low ppb range (<10 ppb):

- Ferrihydrite adsorption – this is the EPA’s BDAT, but the cited full scale removal efficiencies of 80 to 90% apply only to Se(IV) and will not achieve the <0.01 mg/L objective if the influent solution concentration of Se is 0.5 to 1 mg/L.
- Ferric oxyhydroxide/peat resins (HW-FIX) – the peat resin enhances the removal achieved by oxyhydroxide - demonstrated at full scale but not for mine effluent.
- Fe reduction – much more bench work and technology development is needed – demonstrated at full scale but not for mine effluent.
- Selenide precipitation – demonstrated at full scale but not for mine effluent.
- Nanofiltration –demonstrated at full scale for sulphate (not selenium).

- Biological reduction to elemental Se - demonstrated at full scale but not for mine effluent.
- Emulsion liquid membranes – demonstrated at pilot scale.
- Tailored ion exchange – demonstrated at pilot scale.

In addition, the special notes for each technology (see summary above, and specific notes in Table A3.1) indicate that substantially more work is needed to evaluate the applicability of any one of these technologies for mining application, before they can be considered for wide spread applicability. Demonstration and evaluation of an appropriate technology for a specific mine site and wasteform was anticipated as the next step by MSE and Montana Tech (1999).

Other technology performance and relative cost information is summarized in Table A3.2. A numerical scale from 1 to 5 was used to assess these factors. A value of 1 emphasizes that the technology has significant challenges, deficiencies, or development work needed relative to the other technologies, while a value of 5 emphasizes that the technology has significant advantages.

The factors listed in Table A3.2 are defined as follows:

- **Treatment Goal** – ability of the technology to reduce volume, toxicity, or mobility of a waste. A value of 1 means the technology is incapable of reducing any of these characteristics, while a value of 5 means that the technology greatly reduces one or more of these characteristics.

- **Reliability** – Both short–term and long–term aspects of the technology, operational reliability and maintenance are assessed. A value of 1 is applied to technologies that are unreliable, or difficult to maintain, or to “conceptual technologies” that appear to be unreliable or difficult to maintain. A value of 5 means that the technology is extremely reliable for the technological treatment objective.

- **Technical Feasibility** - This factor addresses the ease of use and practicality of the technology. A value of 1 means that the technology is extremely difficult to initiate and/or operate, while a value of 5 means that the technology is simple to initiate and to operate. In addition, active technologies (those which require a power source and around the clock operators) were assigned lower values (which means that they are not easy to operate) while passive technologies (those which function for substantive time periods without human supervision/assistance) are assigned higher values.

TABLE A3.2: RELATIVE ADVANTAGES AND COSTS OF ALTERNATIVE TECHNOLOGIES FOR SELENIUM REMOVAL[1]

Technology Name	Treatment Goal	Reliability	Technical Feasibility	Technical Innovation	Operating Costs	Capital Costs	Industrial Acceptability
Selenium Precipitation (Bacterial)	2	3	3	4	3	4	3
Elemental Iron Reduction	3	4	4	4	3	3	3
Selenide Precipitation	3	3	3	3	3	3	3
Ferric Oxyhydroxide/Peat/Resins	3	4	4	3	2	3	3
Nanofiltration	3	3	3	3	3	3	4
Ferrihydrite Adsorption	4	3	3	2	2	3	3
Ion Exchange (Tailored)	3	4	3	2	2	2	3
Solvent Extraction/Liquid Membrane	3	3	3	2	2	2	4
Reverse Osmosis	2	4	2	2	2	2	4
Alumina Adsorption	3	3	2	2	2	2	3
Lime Softening/Ferric Coagulation/ Filtration	3	3	3	2	2	2	4
Oxidation	3	2	3	2	1	3	2
Ferrous Hydroxide Reduction	2	2	3	3	1	2	2
Activated Carbon	2	2	2	2	2	3	2
Selenite Precipitation	3	1	1	1	3	3	1
Selenate Precipitation	4	1	1	1	3	3	1

[1] Adapted from MSE and Montana Tech (1999).

- **Technical Innovation** – This describes use of the technology in a novel, modern, or new manner. A value of 1 means that the technology is not innovative while a value of 5 means that the technology is very innovative. The assigned values are used in this report as an indicator of whether the technology needs a lot of further development before it is ready for industrial use.

- **Operating Cost** – Operating costs include ongoing technology operations and maintenance costs ***minus*** the financial value of any resource recovery. A value of 1 is assigned for high operating costs, defined as 2 X the average of the costs of the other cited technologies. A value of 5 is assigned for low operating costs, defined as costs which are one–quarter (1/4) of the costs of the other cited technologies.

- **Capital Cost** – A value of 1 is assigned for very high capital costs, estimated as costing "millions of dollars". A value of 5 is assigned for low capital costs, usually in the "tens of thousands of dollars".

- **Industrial Acceptability** – The main criteria for this factor is an assessment of the complexity of the technology, because the "resounding thought from industrial contacts is to maintain as non-complex a process as is functional". A value of 1 means the process is unacceptable to industry; a value of 5 means that the technology is in general use in industry, or that it showed promise of sizable cost reduction or increasing reliability over technologies that are in use.

In terms of rating these technologies (see Table A3.2), the following observations can be made:

- Selenite precipitation and selenate precipitation would appear to be unlikely as candidate treatment technologies because they have a numerical rating of 1 for four of the six categories.

- In terms of treatment goal, only 4 technologies are rated as 2 or less (elemental selenium precipitation, RO, ferrous hydroxide reduction, and activated carbon), indicating that these four technologies may not be candidates for achieving effluent quality goals.

- Three technologies have a reliability rating of 2 : oxidation, ferrous hydroxide reduction, and activated carbon, suggesting that their reliability may be somewhat suspect.

- The majority of technologies have a small degree of technological innovation (an assigned rating of 2 or less), indicating that technological development is not a major need for most technologies.

- Several technologies have operating costs that are above average (a rating of 2), and two technologies (oxidation and ferrous hydroxide reduction) have "large" operating costs (i.e., are 2 times the average).

- There are no technologies whose capital costs are "high" (assigned rating of 1) nor "low" (assigned value of 5).

- All technologies have a reasonable degree of industrial acceptability, except for two technologies which have a value of 1; three technologies (oxidation, ferrous hydroxide reduction, activated carbon) have an acceptability value of 2.

An overall summary might be that 2 technologies need no further consideration (selenite precipitation and selenate precipitation) and that three have significant challenges (oxidation, ferrous hydroxide reduction, activated carbon) compared to the others.

A3.3 Generalization Based on Selenium Study

The general conclusions that can be synthesized from the MSE and Montana Tech (1999) study, especially with respect to selenium treatment, are:

- Treatment technologies can be rated based on typical treatment efficiencies (conventional technologies achieve 60 to 80% removal) or based on typically achievable effluent concentrations (1 mg/L for conventional technologies).

- Present technology ratings define BDAT in terms of consistently achieving these benchmarks for conventional treatment technologies.

- Specialized applications and technology innovations carried out at bench, pilot and full scale (e.g., ferrihydrite removal for selenium) cite treatment efficiency values in the 80 to 90% removal range. Some of these studies appear to have been conducted on relatively simple water matrices (i.e., there are few other constituents competing with selenium for "sorption sites"); removal efficiencies may be reduced for more complex water matrices.

- Innovative technologies can often achieve effluent concentrations that are an order of magnitude lower than conventional technologies. For example, it is quite plausible that ferrihydrite together with reduction technologies could achieve 0.1 mg/L Se and be certified as a full scale BDAT for this effluent objective. Since ferrihydrite is also effective for other constituents such as Cd and Hg, and especially antimony, its ability to remove these substances should also be evaluated.

- Another order of magnitude reduction is needed to achieve effluent levels of <0.01 mg/L (<10 µg/L). This level has not been achieved with present technologies in full scale use for selenium control in mining wastewater systems ; this level is not likely achievable with technologies presently in use in their present form (MSE and Montana Tech, 1999). A significant effort involving bench scale, pilot scale, and full scale demonstrations would be needed to achieve such levels.

- Conceptually, each major treatment process stream (treatment unit which removes contaminant from solution) could achieve an order of magnitude reduction, and be certified for an order of magnitude reduction which means that two sets of treatment units would be needed to move from a 1 mg/L effluent limit to a <0.01 mg/L effluent limit.

The above points, based on an evaluation of technologies for Se removal, can likely be generalized by extension to other metal contaminants of concern such as Cd, Hg, and Sb.