

**Review of Water Quality Issues in
Neutral pH Drainage: Examples
and Emerging Priorities for the
Mining Industry in Canada**

MEND Report 10.1

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Stantec

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EXECUTIVE SUMMARY

Environmental management at Canadian mines has primarily focused, to date, on the issue of acid drainage related to tailings and mine rock. The large potential liability to the industry represented by acid drainage has, to some degree, overshadowed other water quality issues related to mine waste. There are, however, other chemical elements of interest (EOIs) related to non-acid generating mine waste that can result in unacceptably elevated concentrations in drainage that can enter the environment. Several chemicals do not require acidic conditions to maintain elevated concentrations above environmental guideline levels and can therefore be important in neutral pH drainage, including:

- antimony,
- arsenic,
- cadmium,
- chromium,
- cobalt,
- copper,
- iron,
- manganese,
- mercury,
- molybdenum,
- nickel,
- selenium,
- sulphate,
- uranium, and
- zinc.

There were 57 operating metal mines in Canada in 2003 with a contribution to the GDP in excess of \$9 billion. By value, the top metals mined in Canada include gold, nickel, copper, iron and zinc. Coal and diamonds are among the top ten “minerals” if sand, gravel and stone are not considered. With few exceptions, the elements of interest for the potential contamination of water and air also represent economic products from mines across Canada. The 2002 annual production rates (tonnes) were 140 for antimony, 900 for cadmium, 2,000 for cobalt, 7,500 for molybdenum, 180,000 for nickel, 226 for selenium and 890,000 for zinc. Arsenic and mercury are no longer produced as economic commodities in Canada, but are associated with deposits that have been exploited for other purposes.

In general, these chemicals are a concern because there is some environmental or regulatory driver (or potential environmental impact) associated with each, they are not removed from solution at neutral pH and for many there are specific challenges for cost-effective removal from effluent and waste-waters.

Most of the regulatory drivers for these chemicals are related to the protection of aquatic organisms. Exceptions to this include antimony and chromium with low drinking water standards, manganese that has aesthetic issues and can form unwanted precipitates in the receiving water, and sulphate that can be toxic to some forms of moss that inhabit streams.

The sources of these chemicals vary and many can originate from different types of mining, including base metal, gold and uranium mines.

There are, however, other considerations for potential toxicity for at least two of these chemicals that should also be considered. Both molybdenum and selenium can also play a role in toxicity to terrestrial animals at relatively low concentrations. Molybdenum can be toxic to mammals, and a great deal of attention has been focused on the assessment of the effects on ruminants such as deer and moose around mines with elevated molybdenum in British Columbia and Saskatchewan. Selenium can bioaccumulate in waterfowl, as well as exhibit toxic effects in other wildlife such as ungulates and is therefore also a concern to more than aquatic organisms.

Waste and mine water are commonly treated at mines to remove chemical constituents and to comply with regulatory requirements for discharged effluent. Although no reliable values exist, it is likely that the present value of water and effluent treatment (capital plus operating) at Canadian mines exceeds \$1 billion. The estimate of the incremental cost for upgrades and additions to treatment plants outside of Ontario to comply with the 2002 MMER amendments exceeded \$600M alone to address nine parameters (arsenic, copper, lead, nickel, zinc, radium-226, total cyanide, total suspended solids and pH). One of the difficulties for treatment of EOs in neutral drainage is that several require special or non-traditional treatment systems. For example, arsenic and molybdenum are generally treated with ferric sulphate, but may require more than one pH adjustment step. Although promising technologies have been identified for several EOs, these will generally depend on site-specific conditions. In addition, even metals like nickel that can be treated by lime addition may require other approaches with neutral drainage at some mines where removal efficiency is poor or where traditional treatment (addition of lime) creates other concerns such as elevated dissolved solids concentrations.

The costs of non-lime treatment (or pH control) systems can only be gestimated at this time. However, it may be fair to assume that an arsenic, molybdenum or selenium circuit or stand-alone treatment plant would have a similar capital cost to a lime treatment system. Operating costs may also be similar because, while the reagent use may be lower per unit volume of effluent, the unit cost of chemicals (i.e., ferric sulphate) will be higher than that for lime. There may be some uncertainty associated with long-term sludge stability and management. This has been recognized for arsenic treatment for which long-term stability of sludge remains an open question.

If it is assumed that non-traditional treatment systems represent only one-half of the existing treatment systems for operating mines, the net present value for treating neutral drainage may represent a collective liability to the Canadian mining industry of more than \$500M.

The priority EOs identified in this review include arsenic, molybdenum and selenium. The main drivers for priority assessment are the low regulatory limits and potential terrestrial effects (for Mo and Se) that are outside of the classical scope of environmental effects monitoring (EEM) programs that focus on the aquatic environment only. In addition, the issue of elevated sulphate may represent a significant liability to the mining industry if the

British Columbia guideline of 100 mg/L is applied nation-wide. This issue should be examined carefully by the mining industry.

The following recommendations are proposed:

- Develop technology-transfer and collaborative initiatives and events (e.g., workshops) to focus on selected EOIs, including arsenic, molybdenum and selenium.
- Develop or expand guidelines for the assessment of metal leaching at neutral pH for environment-specific disposal strategies such as flooding, in-pit, etc.
- Evaluate the long-term stability of sludge produced by the addition of ferric sulphate in the treatment of antimony, arsenic, molybdenum and selenium.
- Review terrestrial toxicity related to molybdenum and selenium, and evaluate potential liabilities for application of toxicity benchmarks or regulatory limits.
- Assess the implications of the British Columbia sulphate guideline to protect aquatic mosses.

RÉSUMÉ

La gestion environnementale aux mines canadiennes a mis l'accent jusqu'à maintenant sur le drainage acide produit par les résidus et la roche stérile. L'importance de la responsabilité financière que le drainage acide peut potentiellement représenter pour l'industrie a, dans une certaine mesure, éclipsé les autres enjeux liés aux rejets miniers dans le domaine de la qualité de l'eau. Pourtant, des éléments chimiques présents dans les rejets miniers non producteurs d'acide peuvent se retrouver en des concentrations inacceptables dans les eaux de drainage et entrer dans l'environnement. Plusieurs éléments chimiques n'ont pas besoin d'un milieu acide pour se maintenir en des concentrations supérieures aux concentrations maximales prescrites dans les lignes directrices concernant l'environnement et peuvent, de ce fait, être importants dans le drainage à pH neutre. C'est le cas des éléments mentionnés ci-après.

- antimoine
- arsenic
- cadmium
- chrome
- cobalt
- cuivre
- fer
- manganèse
- mercure
- molybdène
- nickel
- sélénium
- sulfate
- uranium
- zinc

En 2003, 57 mines de métaux étaient en exploitation au Canada. Elles ont contribué plus de 9 milliards de dollars au PIB. En termes de valeur, les principaux métaux extraits au Canada sont l'or, le nickel, le cuivre, le fer et le zinc. Le charbon et le diamant comptent parmi les dix « minéraux » en tête de liste si l'on fait exception du sable, du gravier et de la pierre. À quelques exceptions près, les éléments susceptibles de contaminer l'air et l'eau sont des produits économiques issus de mines réparties dans tout le Canada. Les taux de production annuels (tonnes) ont été les suivants en 2002 : 140 pour l'antimoine, 900 pour le cadmium, 2 000 pour le cobalt, 7 500 pour le molybdène, 180 000 pour le nickel, 226 pour le sélénium et 890 000 pour le zinc. Au Canada, l'arsenic et le mercure ne sont plus produits à titre de matières premières économiques mais comme sous-produits de l'extraction d'autres métaux.

En général, ces éléments chimiques suscitent des inquiétudes parce qu'un vecteur environnemental ou réglementaire (ou un impact potentiel sur l'environnement) est rattaché à chacun d'eux, parce qu'ils ne sont pas retirés de la solution à pH neutre et parce que,

dans le cas de bon nombre d'entre eux, l'élimination efficace des effluents et des eaux usées présente des défis particuliers.

La majeure partie des facteurs réglementaires touchant ces éléments chimiques sont liés à la protection des organismes aquatiques. Font exception l'antimoine et le chrome, pour lesquels les normes pour l'eau potable sont peu sévères; le manganèse, auquel sont rattachées des questions d'esthétisme et qui peut former un précipité dans le milieu récepteur; et le sulfate, qui peut être toxique pour certaines formes de mousses qui vivent dans les cours d'eau. Les sources de ces éléments chimiques varient et bon nombre de ces éléments proviennent de divers types de mines, par exemple, des mines de métaux communs, d'or et d'uranium.

Toutefois, pour ce qui est de la toxicité potentielle, d'autres facteurs entrent en jeu dans le cas d'au moins deux de ces éléments chimiques. Le molybdène et le sélénium peuvent en effet constituer une source de toxicité pour les animaux terrestres, et ce, à des concentrations relativement peu élevées. Le molybdène peut être toxique pour les mammifères, et beaucoup d'attention a été consacrée à l'évaluation de ses effets sur le cerf, l'orignal et d'autres ruminants, aux environs de mines de la Colombie-Britannique et de la Saskatchewan présentant une teneur élevée en molybdène. Le sélénium s'accumule dans la sauvagine et il est toxique pour d'autres animaux sauvages, par exemple les ongulés. Il ne touche donc pas que les organismes aquatiques.

En général, les mines traitent leurs rejets d'exploitation et leurs eaux d'exhaure afin d'en retirer les éléments chimiques et de se conformer aux règlements sur les effluents. Aucun chiffre fiable n'est disponible en ce qui concerne la valeur actuelle du traitement de l'eau et des effluents (les dépenses en capital plus les dépenses d'exploitation) aux mines canadiennes, mais il est probable que ce chiffre dépasse le milliard de dollars. Le coût des modernisations et des ajouts effectués aux usines de traitement situées à l'extérieur de l'Ontario afin que ces usines soient conformes aux modifications du REMM de 2002 dépasse, estime-t-on, les 600 millions de dollars pour neuf paramètres (arsenic, cuivre, plomb, nickel, zinc, radium 226, cyanure total, total des solides en suspension et pH). Plusieurs paramètres chimiques d'intérêt dans le drainage neutre nécessitent des systèmes de traitement spéciaux ou non traditionnels. Par exemple, l'arsenic et le molybdène sont généralement traités avec du sulfate de fer, mais ils peuvent nécessiter plus d'un ajustement de pH. Nous disposons maintenant de technologies prometteuses pour traiter plusieurs des éléments chimiques qui retiennent notre attention, mais ces technologies sont généralement tributaires des conditions propres au site. De plus, même les métaux comme le nickel qui peuvent être traités par ajout de chaux peuvent nécessiter d'autres approches dans le contexte du drainage neutre, à certaines mines où l'efficacité de traitement est peu élevée, ou encore, où le traitement traditionnel (ajout de chaux) crée d'autres problèmes, par exemple, des concentrations élevées de matières dissoutes.

Les coûts des systèmes de traitement sans chaux (autrement dit, les systèmes de régulation du pH) demeurent pour le moment estimatifs. On peut cependant raisonnablement assumer qu'un circuit de traitement de l'arsenic, du molybdène ou du sélénium ou une usine de traitement autonome ont un coût en capital semblable à celui

d'un système de traitement à la chaux. Les coûts d'exploitation pourraient, eux aussi, être semblables parce que, même si moins de réactif est utilisé par unité de volume d'effluent, le coût unitaire des produits chimiques (p. ex., le sulfate de fer) dépasse celui de la chaux. La stabilité et la gestion à long terme des boues sont encore entourées d'une certaine imprévisibilité. C'est un fait que, dans le cadre du traitement de l'arsenic, la stabilité à long terme des boues demeure une question ouverte.

Si l'on assume que les systèmes de traitement non traditionnels ne représentent que la moitié des systèmes de traitement utilisés par les mines en exploitation, la valeur actualisée nette du traitement du drainage neutre pourrait représenter une responsabilité financière collective de plus de 500 millions de dollars pour l'industrie minière canadienne.

L'arsenic, le molybdène et le sélénium comptent parmi les éléments prioritaires retenus aux fins du présent examen. Les principaux facteurs de l'évaluation des éléments prioritaires sont les limites réglementaires peu élevées et les répercussions terrestres potentielles (dans le cas du molybdène et du sélénium) qui échappent à la portée classique des programmes de surveillance des effets sur l'environnement ne visant que le milieu aquatique. De plus, la question des concentrations élevées de sulfate pourrait représenter une responsabilité financière importante pour l'industrie minière si la ligne directrice de 100 mg/l de la Colombie-Britannique est appliquée partout au pays. L'industrie minière devrait examiner cette question en détail.

Les recommandations sont les suivantes :

- élaborer des initiatives et des événements de transfert de la technologie et de coopération (p. ex., des ateliers) afin de mettre l'accent sur les éléments chimiques retenus, notamment l'arsenic, le molybdène et le sélénium;
- élaborer ou augmenter les lignes directrices s'appliquant à l'évaluation de la lixiviation des métaux à pH neutre, à des fins de stratégies d'élimination particulières au milieu, par exemple, en cas d'inondation et dans des fosses à ciel ouvert;
- évaluer la stabilité à long terme des boues produites par l'ajout de sulfate de fer dans le cadre du traitement de l'antimoine, de l'arsenic, du molybdène et du sélénium;
- examiner la toxicité terrestre liée au molybdène et au sélénium, et évaluer les responsabilités financières qui pourraient potentiellement découler de l'application de valeurs de toxicité repères ou de limites de toxicité réglementaires;
- évaluer les retombées de la ligne directrice émise par la Colombie-Britannique à l'égard du sulfate, afin de protéger les mousses aquatiques.

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1.0 INTRODUCTION

In 2002, there were 57 operating metal mines in Canada contributing in excess of \$9 billion (CND) to the Gross Domestic Product (GDP) directly from primary mineral production. The total contribution of the mineral and metals industry, including smelting, refining and fabrication, was estimated to be in excess of \$36 billion (in 1997 dollars, Mining Association of Canada, 2002). By value, the top metals mined in Canada include gold, nickel, copper, iron and zinc. Coal and diamonds are among the top ten “minerals” if construction or industrial materials are not considered. All of these valued products are also commonly associated with some chemical elements that can affect water quality, and appropriate water and waste management practices are often required to prevent adverse environmental impacts as a result of mining activities. Examples of 2002 production rates and releases to water are presented in Table 1.1.

Acid drainage associated with existing tailings and mine rock from metal mines in Canada has been identified as a multi-billion dollar liability, and has been the focus of environmental management over the previous two decades. The large potential liability to the mining industry has, to some degree, overshadowed other water quality issues related to mine waste management. However, it is evident that acid or low pH conditions are not necessary to cause impaired water quality, and many chemicals that are not necessarily related to acid generation can represent environmental risks when leached from mine waste. This process has been termed “metal leaching” and may involve non-metals as well. When issues arise from metal leaching in the absence of acid drainage, the term neutral drainage has been applied.

It is likely that acid drainage associated with tailings or mine rock will result in unacceptable impacts to near-field water quality. That is one reason why so much emphasis has been placed on the determination of whether or not specific materials are potentially acid-generating. However, the assessment of water quality impairment from interactions with waste is actually the issue of concern, because many chemical constituents not associated with acid conditions can cause impairment to water quality. Although many protocols have been developed and applied for the assessment of potentially acid-generating materials, there are few equivalent protocols to determine the risk of metal leaching in neutral pH drainage.

1.1 What is Neutral pH Drainage?

It is well known that acid drainage results from the weathering of iron sulphide minerals, generally pyrite and pyrrhotite, when mined materials are exposed to oxygen and water. The acid-generating reactions are related to the presence of sulphide in minerals that were previously stable when they were undisturbed, but are unstable and reactive when exposed to the atmosphere. There are many other minerals that are also unstable in the atmosphere after being disturbed, but do not contain sulphur and therefore do not generate acid during weathering. However, there is no doubt that weathering of many materials disturbed during mining is accelerated as a result of exposure to air and water at the earth's surface. In many cases, the weathering reactions have little or no noticeable effects

TABLE 1.1: SUMMARY OF ANNUAL ECONOMIC PRODUCTION (TONNES) AND RELEASES TO THE ENVIRONMENT (WATER) FOR SELECTED METALS AND OTHER ELEMENTS OF INTEREST (MAC, 2002)

Metal	Production (tonnes/yr)	Release to Water (tonnes/yr) ¹
Antimony	143	ND
Arsenic	ND ²	3.0
Cadmium	896	0.54
Chromium	ND	0.43
Cobalt	2,027	2.43
Mercury	ND	0.054
Molybdenum	7,521	ND
Nickel	178,2338	54.4
Selenium	226	ND
Zinc	891,924	51.4

¹ Excluding non-point source discharges such as seepage.

² No data available.

because the minerals release common major ions in water such as calcium and magnesium, for example, that are not toxic or a threat to the environment. In addition, many weathering reactions result in the formation of other secondary solids, such as clays, and other weathering products that prevent the dissolution of excess concentrations of many chemicals.

There are two general categories of waters that exhibit neutral pH conditions and yet may have elevated concentrations of elements of interest. The first category results from the natural or *in situ* neutralization of acidic waters produced during the oxidative weathering of sulphide-bearing rock or tailings. In this case, there is an excess of neutralization potential (NP) in rock or tailings that reacts with and consumes acid in the waters that have contacted the sulphides. The neutralization may occur *in situ* such that no acidic conditions are observed. An example of this is provided by Jambor and Blowes (1991) who studied the oxidation profile in a pyretic gold mine tailings containing excess carbonate minerals such as calcite and dolomite. In that case, the porewater pH was controlled at neutral values by reactions with the carbonate minerals. In other cases, acidic waters may be generated in sulphide rock or tailings, and the drainage is neutralized “downstream” as the acidic waters are transported through materials containing adequate NP. An early example of this condition was reported by Morin *et al.* (1988) who studied the neutralization of acidic tailings drainage as it migrated with groundwater through a sandy glacial deposit containing carbonate minerals. In both cases, these types of neutral drainage waters are readily identified by their chemical characteristics that generally include sulphate concentrations in the thousands of mg/L, high dissolved hardness ($\text{Ca}^{2+} + \text{Mg}^{2+}$) levels and high alkalinity levels.

There are also many minerals that may occur in minor to trace quantities and also contain chemicals that may represent risks to environmental quality involving chemical reactions in the absence of acid generation. Rapid or accelerated weathering can release these chemicals at rates that can affect water quality without affecting pH. These are the types of neutral pH waters that are the focus of this report, rather than acidic waters that have been neutralized after the fact. The water that is affected by interaction with mine waste but is not acidified is referred to as neutral drainage and would typically be in the pH range of 6.5 to 8.5. It is perhaps not appropriate to label all neutral pH waters from mine sites as “neutral drainage”, as that may imply that all waters that are not acidic are also impacted by elevated concentrations of deleterious substances. This would be far from the truth and very misleading. The use of the term “neutral drainage” here simply implies that non-acidic drainage may also represent waters requiring management or treatment to prevent impacts in the receiving environment.

1.2 Objectives and Scope

The primary objectives of this report are to highlight the key issues related to neutral drainage associated with mine wastes, provide guidance for future research priorities related to neutral drainage, and to provide an overview of the Canadian experience with water quality impairment in the absence of acid conditions. This report is not intended to represent a comprehensive assessment of neutral drainage issues. Rather, it is intended to

be a starting point for discussion and awareness of an environmental issue that has had less attention to date than acid drainage, and one that may become important at operations without acid drainage issues or where acid drainage has been mitigated.

This report was completed through a review of the literature and knowledge of case histories of mines in Canada. The report is also based on project experience with the mining industry in Canada and discussions with individuals in regulatory positions, as well as practitioners that are or have been responsible for environmental compliance at mining operations.

2.0 THE NATURE OF THE PROBLEM

The generation of acid drainage associated with sulphide-bearing tailings or waste rock is generally accompanied by elevated levels of a variety of metals, that may include aluminum, cobalt, copper, iron, manganese, nickel and zinc, among others. Most metals are very soluble in acidic waters and pH adjustment is commonly used to treat metal-contaminated water. However, some metals require not just neutral pH but very alkaline conditions to become insoluble and to be removed from solution. For example, nickel treatment may require a pH value of 8.5 or greater and zinc may require a pH of 9.5 or higher for effective removal from effluent. The high pH values are commonly induced by the addition of lime (quick lime is CaO or hydrated lime is Ca(OH)₂) that has a pH of about 12 in slurry form. In nature, the most common minerals that control pH near neutral levels are carbonates (e.g., calcite = CaCO₃, dolomite = CaMg(CO₃)₂) and the highest pH values are generally less than 8. Therefore, it is common to observe metals like nickel and zinc in neutral pH drainage associated with mine wastes.

There are also chemicals that are related to metals but do not have the same relationship between pH and solubility as do most metals of environmental interest. Arsenic, molybdenum and selenium are examples of elements that are generally more soluble at alkaline and very low pH values, and less soluble under mildly acidic conditions (pH from 4 to 6). Although this is a generalization and the chemistry of these elements is complex, it is clear that raising the pH with lime is not used to treat elevated concentrations of these types of chemicals and, in some cases, raising pH to control concentrations of some metals can exacerbate the concentrations of other metalloids.

Water quality issues related to mining properties with neutral pH drainage have been the subject of research for some time. Although there are several examples provided in the literature, these have not been given the same attention as those related to acidic drainage at mine sites.

2.1 What are the Key Elements of Interest (EOIs) in Neutral Drainage?

There are several characteristics that determine whether chemicals are a concern in neutral drainage. These include:

1. **Regulatory Thresholds:** In general, the concentrations in effluent or mine drainage must be able to exceed some threshold or benchmark value in the environment in neutral pH waters.
2. **Availability:** The chemical would likely be at above-average concentrations in the solids (tailings or mine rock), either as specific mineral forms or as trace elements within other common minerals.

3. **Accelerated Weathering:** The chemical would likely need to be associated with solids that will be unstable under weathering conditions in the mine waste deposit.

The chemicals that can fall into these categories at a variety of mining operations are listed in Table 2.1. The table also lists example effluent concentrations for each of the EOs along with the commonly associated mining operations. Table 2.2 lists several regulatory thresholds or benchmarks for the EOs, including those in sediment that can also be affected by concentrations in water. It is evident that some of these chemicals are more of a concern than others in neutral pH drainage; however, a more complete list is presented at this stage to provide a broader perspective.

Table 2.2 illustrates the very low concentration guidelines for water and lake sediment for selected EOs in various Canadian jurisdictions. Five of the water values have guidelines at or below the microgram per litre (0.001 mg/L) level. Sediment guidelines are also low for many of these EOs. Sediment generally accumulates EOs that are elevated in drainage and, if the transfer coefficients (or sediment K_d values) are large, then the sediment may act as a sink for specific EOs. In general, sediment concentrations will increase with time if the concentration of EO in a water body exceeds background concentrations. As concentrations decrease, possibly as a result of mitigation or rehabilitation, the sediment can represent a source of EOs as release occurs to the water column. Elevated concentrations in sediments downstream from mining operations were clearly identified in the review of environmental data from mines reported by AQUAMIN (1996). The sediment concentrations can also be an important pathway for EOs in food webs that are considered in an ecological risk assessment.

Most of the focus to date on mine and mill effluent has been on the aquatic environment. This was highlighted in the development of the Environmental Effects Monitoring (EEM) program that is a requirement of the Metal Mine Effluent Regulations (MMERs) under the *Fisheries Act* in Canada enacted in 2002. The MMER defines regulated “deleterious” substances that include arsenic, copper, cyanide, lead, nickel, zinc, radium-226 and pH. Nine other parameters are required for effluent characterization, while 18 additional parameters are listed as site-specific and therefore optional for monitoring. Of the list of EOs in Table 2.2, however, several, including antimony, chromium and cobalt, are not on any of the MMER lists. There have been reviews of other chemicals with respect to protection of aquatic life and these have focused on antimony, cadmium, mercury and selenium (BEAK, 2002). Although the aquatic environment is the most direct link to mine effluents and drainage, it is also evident that there can be other potential effects outside of the aquatic environment, as exemplified by concern for selenium toxicity in waterfowl (Brix *et al.*, 2000) and molybdenum toxicity in mammals (particularly in ruminants).

To be consistent with the AQUAMIN recommendations, the protection to the environment should be ecosystem-based and not restricted to any one environmental component (i.e., water, sediment, fish, etc.). This means that discharges should be consistent with the protection of terrestrial as well as aquatic concerns. This infers that toxicity benchmarks should be considered in planning (and assessment) that can be applied to ecological risk

TABLE 2.1: SUMMARY OF EOI CONCENTRATIONS OBSERVED IN PRE-TREATED MINE WATERS AND MILL EFFLUENT FROM SELECTED MINE OPERATIONS

Chemical	Concentration (mg/L)	Mine Type
Antimony	0.001 to 0.7	Gold
Arsenic	2 to 4	Gold/uranium
Cadmium	<0.01 to 0.06	Several
Chromium	NA	Several
Cobalt	0.001 to 1	Nickel/copper
Copper	-	Copper/nickel
Lead	-	Several
Manganese	0.5 to 2	Several
Mercury	0.00005 to 0.007	Gold/silver
Molybdenum	1 to 10	Uranium/molybdenum/copper
Nickel	0.5 to 3	Nickel/uranium
Radium-226	0.001 to 2	Uranium/phosphate
Selenium	0.005 to 0.11	Gold/uranium/coal/copper
Sulphate	533 to 4,620	Several
Uranium	0.001 to 2	Uranium/phosphate
Zinc	0.5 to 5	Zinc/silver/gold

TABLE 2.2: SUMMARY OF EOIs AND EXAMPLES OF REGULATORY GUIDELINES FOR WATER AND SEDIMENT

Chemical	Water		Sediment	
	MMER (mg/L)	Most Restrictive Guideline (mg/L)	ISGQ ¹ (mg/kg)	PEL ² (mg/kg)
Antimony	-	0.006 ³	-	-
Arsenic	0.5	0.005 ⁴	5.9	17
Cadmium	-	0.000017 ⁴	0.6	3.5
Chromium	-	0.05 ³	37.3	90
Cobalt	-	0.0009 ⁵	-	-
Copper	0.3	0.002 ⁴	37.5	197
Lead	0.2	0.001	35	91.3
Manganese	-	0.05 ⁶	460 ⁷	-
Mercury	-	0.0001 ⁴	0.17	0.486
Molybdenum	-	0.073 ⁴	-	-
Nickel	0.5	0.025 ⁴	16 ⁷	-
Radium-226	0.37 (Bq/L)	0.11 (Bq/L) ⁸	5 ⁹	-
Selenium	-	0.001 ⁴	-	-
Sulphate	-	100 ¹⁰	-	-
Uranium	-	0.005 ⁵	-	104
Zinc	0.5	0.03 ⁴	123	315

¹ Canadian Interim Sediment Quality Guideline

² Canadian Probable Effects Level

³ CCME IMAC Drinking Water

⁴ CCME Protection of Aquatic Life

⁵ Ontario Surface Water Quality Objective

⁶ CCME Aesthetic Objective

⁷ Ontario Sediment Quality Guideline (Lowest Effects Level; OMEE, 1993)

⁸ Saskatchewan Surface Water Quality Objective

⁹ B.C. Criterion

¹⁰ B.C. Ambient Water Quality Guideline for the Protection of Freshwater Aquatic Life

assessments. These benchmarks are given as chemical uptake rates, typically in mg/kg-body-weight/day, and pathways analysis calculations are required for comparison to estimated uptake rates. In general, a pathways analysis is more challenging and costly than a simple screening assessment of anticipated water and sediment concentrations.

2.2 How Does Neutral Drainage Occur?

Neutral drainage can result from different processes, but there are three general causes for this phenomenon. The first process is related to sulphide mineral oxidation and acid generation in which metals are released and initially soluble. After acid generation, the low pH drainage containing elevated levels of many metals contacts solids with sufficient neutralization potential (NP) to consume the acid and re-establish neutral pH conditions. During the neutralization process, some, but not all, metals are removed from solution. Those metals and related EOs that are not affected by neutralization can remain at elevated levels in solution. Scharer *et al.* (2000) provide examples of this type of drainage and examples are provided in Table 2.3.

Metal leaching can also occur in the absence of acid generation. Oxidation of arsenic minerals in gold-mine wastes is an example of this process. The sulphide content is either insufficient to produce acid or the waste contains sufficient NP to prevent acid formation. The arsenic is released during oxidation and remains mobile in the drainage from the waste. Arsenic release from waste rock at neutral pH is well documented (CRI and CLMC, 2001). Kwong (1995) and Kwong *et al.* (2003) also presented an example of metal leaching as a result of oxidation and galvanic interaction in the absence of acidic conditions. Neutral drainage at other mine sites have been described by Kwong *et al.* (1997) in the Keno Hill district of the Yukon and by Percival *et al.* (2004) near Cobalt, Ontario.

A third mechanism for metal leaching is related to potentially acid-generating mine wastes that are mitigated to prevent oxidation. Flooded tailings and waste rock will remain neutral but can, in specific cases, release metals such as nickel and zinc that are soluble at neutral pH. Examples of zinc leaching from submerged tailings have been reported by Arnesen *et al.* (1997) for impoundments in Norway where underwater disposal began in the late 1960s. Doepker and Drake (1991) also observed leaching of metals in submerged tailings in the laboratory. In general, metal leaching from subaqueous waste occurs if the waste has previously been subject to weathering and release of oxidation products.

It is also evident that leaching can occur as a result of basic pH conditions. High pH values in effluent can preferentially dissolve some elements that occur as anions, such as antimony, arsenic, molybdenum and selenium.

2.3 Treatment Issues

Treatment of many metals to achieve compliance with regulatory objectives is effectively accomplished by pH adjustment, generally with lime, so that metals are removed from solution and are allowed to settle as particles, forming a sludge that can be contained and managed. Many EOs that are associated with neutral drainage are not amenable to

TABLE 2.3: EXAMPLES OF “NEUTRAL MINE DRAINAGE” ADAPTED FROM SCHARER *et al.* (2000)

	Waste Rock Uranium, Ronneburg, Germany	Waste Rock Uranium, Aue, Germany	Waste Rock Gold, Kyrgyzstan	Waste Rock Gold, Kyrgyzstan	Large Coal Discard Dump, South Africa	Small Coal Slurry and Discard Dump, South Africa
	Dump Seepage (median) (1989-95)	Dump Seepage (median) (1993-96)	Seep Grab Sample (July 1997)	Intermittent Seepage (Jul-Aug 1998)	Collection Ditches (1997)	Collection Ditches (1998)
pH	7.53	7.75	7.3	7.3 to 8.0	7.9 to 8.6	7.1 to 8.4
Sulphate	26,208	3,174	5,836	2,510 to 3,581	146 to 7,720	4,510 to 6,140
Iron	0.56	0.69	1.32	0.19 to 4.74	0.1 to 2.5	0.12 to 39.8
Calcium	377	321	360	124 to 314	51 to 474	332 to 490
Magnesium	6,947	634	1,320	140 to 752	20 to 471	243 to 362
Arsenic	0.007	0.14	0.03	0.04	0.005	0.1
Nickel	0.74	0.04	0.92	0.07 to 0.31	0.05	0.01
Manganese	15.95	0.06	12.15	1.14 to 4.02	0.05 to 0.64	0.36 to 13.9
Molybdenum	-	0.03	0.007	0.006 to 0.017	-	-
Selenium	-	0.07	0.08	0.04	-	-
Uranium	4.08	6.5	-	-	-	-
Zinc	0.23	0.06	0.10	0.001 to 0.008	0.04	0.01 to 0.04

Note: All values are reported in mg/L except pH.

treatment with lime or other alkaline chemicals. The treatment of several EOs in neutral drainage is not standard practice, and require methods specific to the individual EO.

Several EOs associated with neutral drainage have a common characteristic; they occur as neutral or negatively charged ions for oxidizing conditions rather than positively charged as most metals exist. This is the case for arsenic (H_2AsO_4^-), antimony (SbO_3^-), molybdenum (HMoO_4^-) and selenium (SeO_4^{2-}). Although no one standard method for treatment exists for these chemicals, a common approach to treatment involves ferric iron. In principle, ferric iron forms a precipitate that has positively charged surfaces and causes the negatively charged ions to adsorb to the precipitate and then settles out of solution. Different chemicals are treated at different pH values to ensure efficient removal. However, it has been noted that selenium treatment can be more challenging, especially with the CCME guideline of 0.001 mg/L in the receiving environment.

3.0 EXAMPLES OF NEUTRAL DRAINAGE ISSUES

The majority of operating or inactive mines in Canada either have had environmental assessments applying historic standards that were less stringent than those applied today, while many historic mines may not have been subjected to environmental assessments to gain approval to operate. More recent mining operations have undergone environmental assessments under the *Canadian Environmental Assessment Act* (CEAA) that was enacted in 1992. The more recent assessments have highlighted environmental issues in the aquatic environment that go beyond acid drainage as the sole concern for mine waste management. For example, environmental assessments of uranium mines in northern Saskatchewan in the 1980s and 1990s focused on the potential for acid generation in mine rock. Proposed mitigation at the mines included underwater disposal of “special waste” that was anticipated to generate acid if disposed on-land. In the late 1990s and into this decade, the focus of environmental assessment of mine waste has moved to other potential elements of interest, including arsenic, molybdenum and selenium.

In an assessment for a uranium mine in Saskatchewan in 2003, molybdenum toxicity in mammals (including ruminants) was an issue requiring significant review and site specific considerations as well as provision for treatment, if required, to proceed through the CEAA process. The detailed assessment was driven by toxicity concerns by regulatory authorities. However, the science behind the toxicity benchmarks to apply in an assessment are not irrefutable, and the literature commonly contains contradictory evidence describing the lowest levels that exhibit toxic effects. The results of assessments based on restrictively low benchmarks or concentrations can result in the requirement to treat water to remove those substances if the project is to avoid causing “significant adverse impacts”. This required mitigation measure, based on uncertain science, has important economic implications for the mining industry. The example of molybdenum toxicity in terrestrial animals is therefore discussed in further detail in a later section of this chapter to highlight the linkage between uncertain science and financial liability if treatment is a prerequisite for similar operations.

In a recent assessment of the proposed Voisey’s Bay nickel mine in Labrador, the proponent proposed underwater disposal of tailings and mine rock in order to mitigate the potential for acid drainage. Laboratory testing confirmed that underwater disposal prevented acid generation, but also showed that some leaching of nickel from the waste may be expected. Allowance was therefore made to add a layer of sand as a diffusion barrier on the surface of the underwater mine waste to mitigate nickel leaching into the overlying water column. So, while the main issue of concern, acid drainage, is likely to be mitigated by underwater disposal, there may be some circumstances in which additional control for neutral pH metal leaching may be required.

This section of the report presents examples of three EOIs that have become water quality issues associated with disposal of neutral pH mine waste or mine effluent during operation. Arsenic, molybdenum and nickel were selected as examples, because more detailed data were readily available, and this is not intended to be a comprehensive list. Selenium and sulphate are also briefly discussed in the context of uncertain implications in the long term.

3.1 Arsenic

Of the operating metal mines in Canada in 2002, 29 (or 51%) were gold (or silver) operations, two-thirds of which are located in Ontario and Quebec. The arsenic association with almost all gold deposits suggests that this EOI will represent a wide-ranging environmental issue well into the future in Canadian mining.

Interest in arsenic as a EOI has increased as a result of changes to the Canadian Water Quality Guidelines (CWQGs) that set a limit of 0.005 mg/L in the environment for the protection of aquatic life (CCME, 2002). This value established for the protection of aquatic life is based on a 20% decrease in growth rate for a species of green algae at a concentration of 0.05 mg/L that is assumed to be the lowest observable adverse effects level (LOAEL) for arsenic. A factor of safety of ten was applied to arrive at a no observable adverse effects level (NOAEL) of 0.005 mg/L. The previous guideline was ten times higher or 0.05 mg/L. By comparison, the MMER average monthly value for mine effluent discharge for arsenic is 0.5 mg/L or 100 times the CWQG value. This means that, at mines that comply with the MMER value, dilution or attenuation of 100 times is required in the mixing zone to prevent exceedance of the CWQG value in the downstream environment.

It is also probable that the new guideline value will be exceeded at many mine operations where arsenic occurs naturally, or may be elevated as a result of accelerated weathering of mine rock and tailings. In any case, it is clear that arsenic related to mining has become a focus of attention as exemplified by an Arsenic Technical Workshop, sponsored by MAC and NRCAN in November 2002 in Winnipeg. Mining industry representatives at that workshop identified historic "roaster" tailings and precipitated residues of arsenic as significant issues related to arsenic in water. Proceedings from the workshop are available from the MEND Secretariat.

3.1.1 Sources

Arsenic is ubiquitous in some types of gold deposits in Canada but is also associated with uranium and copper-nickel deposits. Table 3.1 contains a list of minerals that represent potential sources of arsenic in ore and mine rock. One of the most common arsenic-bearing minerals associated with mineral deposits is arsenopyrite (FeAsS). This arsenic sulphide is not stable in oxidizing environments, and will oxidize and release arsenic when exposed to water and oxygen in the atmosphere. Less common but important sources of arsenic in uranium deposits in Saskatchewan include nickel arsenides such as gersdorffite (Watkinson *et al.*, 1975) that appear to oxidize very rapidly when disturbed during mining. For example, arsenopyrite oxidation rates are similar to those for pyrite oxidation (Rimstidt *et al.*, 1994; Walker, 2004), and can result in arsenic concentrations in drainage that may be as high as a few milligrams per litre. Oxidation of arsenopyrite can be mitigated by deposition underwater, thereby preventing or significantly restricting arsenic leaching from fresh material. In contrast, mine rock containing nickel arsenides can exhibit arsenic concentrations of tens of milligrams per litre when placed underwater soon after being removed or disturbed from the original geologic setting as shown in Cogema (1999). This behaviour can represent a significant challenge for mine rock management.

TABLE 3.1: SUMMARY OF MINERALS REPRESENTING POTENTIAL SOURCES OF SELECTED EOIs IN ORES AND MINE ROCK

Element	Mineral Name	Chemical Formula	Comment
Arsenic	Arsenopyrite	FeAsS	Primary
	Cobaltite	(Co,Fe)AsS	Primary
	Orpiment	As ₂ S ₃	Primary
	Realgar	AsS	Primary
	Gersdorffite	NiAsS	Primary
	Nickeline	NiAs	Primary
	Annabergite	Ni ₃ (AsO ₄) ₂ •8H ₂ O	Secondary
	Skutterdite	(Co,Ni)As ₃	Primary
	Scorodite	FeAsO ₄ •2H ₂ O	Secondary
	Arsenian Pyrite	(Fe,As)S ₂	Primary
Molybdenum	Molybdenite	MoS ₂	Primary
	Molybdite	MoO ₃	Secondary
	Powellite	CaMoO ₄	Secondary
	Wulfenite	PbMoO ₄	Secondary
	Ferrimolybdite	Fe ₂ (MoO ₄) ₃ •8H ₂ O	Secondary
Nickel	Pentlandite	(Ni,Fe) ₉ S ₈	Primary
	Millerite	NiS	Primary

Arsenic can also be released from the primary minerals during milling. Historic processing of gold ores may have involved autoclaving (high temperature processing) that resulted in the oxidation and release of the majority of arsenic from the original mineral form. In some cases, the arsenic was collected as arsenic trioxide, the material that is the focus of long-term management initiatives at the former Giant gold mine in Yellowknife, NWT. Arsenic residues have also been disposed with tailings, and these historic deposits may have arsenic concentrations in porewater that can be in the tens to hundreds of milligrams per litre.

Gold extraction with cyanide is more common at modern mills. Arsenic minerals are subject to mild oxidation in cyanide milling so that arsenic concentrations in tailings mill effluent may be in the milligrams per litre range. In addition, traditional tailings disposal with beaches and ponds can result in long-term oxidation of arsenic minerals in exposed tailings with ongoing release of arsenic into local drainage. Tailings effluent is commonly treated with ferric sulphate to reduce arsenic concentrations to levels below the maximum discharge limit (0.5 mg/L) set in the MMER as part of the *Fisheries Act*.

3.1.2 Issues

Goldcorp was the industry supporter of the Arsenic Technical Workshop (2002) in Winnipeg. Goldcorp's experience at the Red Lake mine was presented, and several important issues were presented and discussed. Placer Dome's Campbell mine also operates facilities adjacent to Balmer Lake. It would be fair to assume that other gold mine operations in Canada share some or all of the key issues related to arsenic. The following sections provide a brief summary of the arsenic issues related to environmental management at Goldcorp's Red Lake mine.

Gold mining and processing began at Red Lake in 1948. Roasting of a concentrate was practiced until 1980 after which a combination of gravity separation and cyanide leach was implemented for gold recovery. From 1948 to 1960, two independent mining operations deposited tailings on-land adjacent to Balmer Lake into which tailings effluent drained. Elevated arsenic levels in the lake have been consistently observed. In 1983, the two mines received Certificates-of-Approval (C-of-A) by the Ontario Ministry of the Environment to discharge a maximum arsenic concentration of 0.5 mg/L from Balmer Lake. Since 1992, the discharge from Balmer Lake has been managed to conform to the C-of-A limits. More recently, Goldcorp has been encouraged to move the discharge compliance point upstream to a location that discharges to Balmer Lake. This would imply that the MMER limit (0.5 mg/L) would apply at the compliance point prior to discharge into Balmer Lake, with no mixing zone available.

There were two major challenges identified by the mine to comply with the discharge limits. First, the mill process water consistently exhibits arsenic concentrations in excess of the limit. Efforts have been made to accomplish in-mill treatment of arsenic using ferric sulphate. Second, the historic tailings that have roaster residues incorporated continue to release (seepage, etc.) waters with arsenic in excess of the prescribed limit. Several investigations were being conducted to address the historic tailings issues.

In addition to ongoing effluent issues, the water in Balmer Lake continues to be influenced by the accumulated arsenic inventory in the sediment as a result of elevated arsenic concentrations in effluent in the past. Arsenic is stored in sediments, likely adsorbed to or co-precipitated with ferric hydroxide solids and other solids.

Arsenic can be remobilized, however, if redox conditions in Balmer Lake sediment changes to more reducing levels and the iron hydroxides are dissolved. This can occur if oxygen is limited and there is sufficient organic material to drive chemical reduction reactions. This arsenic cycling appears to be occurring on a seasonal basis in the lake and it is a complex cycle likely involving the trophic status of the lake, organics in the sediment and ice cover in winter, among others. Data from Balmer Lake suggest that some number of years will be required before the sediment becomes an insignificant source of arsenic to the overlying water column.

The conditions in Balmer Lake are not likely to be unique. The elevated loadings of EOs can result in accumulation in downstream lake sediments. Concentrations of several EOs, including arsenic, selenium and zinc, were observed to exceed sediment quality guidelines and to be elevated above baseline values downstream of several mines in Canada (ESG, 1999). In many cases, analysis shows that the accumulation in lake sediments can have mitigative effects on water quality. However, sediment that is loaded by EOs during operations can become an interim source of EOs when the primary source, such as effluent, is shut off because the stored constituents in the sediment can slowly “bleed” back into the water column over time. It is likely that historical mining operations that released water with elevated arsenic concentrations will have residual arsenic issues related to lake sediment even if arsenic levels in effluent or drainage are lowered or eliminated in the future.

Despite the elevated arsenic concentrations in Balmer Lake, there has been a phenomenal biological recovery over the last ten years since the mid-1990s (Wepruk, pers. comm., 2004). As biological recovery progresses, the redox conditions in the sediments have contributed to the elevated arsenic levels in the water column.

Goldcorp and Placer Dome have jointly undertaken a project to develop a site-specific water quality objective (SSWQO) for Balmer Lake. This approach is consistent with considerations outlined by both federal and provincial governments. Given that Balmer Lake was historically (and still is provincially) designated as a repository for gold mill tailings, and given the magnitude of degradation from historic practices, there is strong argument to suggest that “reasonable and preventative” measures will not result in achieving compliance with PWQO or CCME guidelines for arsenic (0.005 mg/L) at the time of proposed mine closure.

Arsenic minerals are also associated with uranium mines in northern Saskatchewan. Since the mid-1990s, there has been an intensive effort to characterize the leaching of arsenic from the ore during milling, from tailings after deposition and from mine rock. There are two significant issues. The first is the significant fraction of arsenic that is leached in the sulphuric acid milling process. The mill water is treated before discharge of tailings to reduce dissolved arsenic concentrations. More recent milling has used mined-out open pits

for tailings deposition. Even with deposition of tailings in open pits to provide secure containment, extensive assessments were completed to confirm that the receiving environments were not at risk of contamination by arsenic.

The second issue involves the unusual leaching behaviour of mine rock. The mine rock exhibits elevated arsenic with typical levels in the hundreds of mg/kg. It has been observed in some types of mine rock that 1 to 3% of the total arsenic can dissolve immediately when the rock is added to water, and between 10 and 30% of the arsenic can leach into the first few pore volumes of water after the rock is inundated. Because some of the mine rock has sufficient sulphide levels to be potentially acid-generating, the preferred method of "special" waste rock management is backfilling of pits where the rock would eventually be flooded by the natural groundwater levels. Leaching of arsenic from the rock is predicted to result in concentrations in the porewater in the tens of mg/L range (CRI and CLMC, 2001). The leakage of porewater to groundwater from the pit is relatively small and, although groundwater represents a pathway to regional surface waterbodies, the loadings from the backfilled pits will remain low enough to prevent impacts in surface water.

Disposal of tailings and waste rock with drainage or porewater exhibiting mg/L levels of arsenic would not likely be acceptable above grade, but is reasonably protective when open pits are used for isolation of the waste. Open pits are available in the mill areas because of the types of uranium deposits and the mining plans that are used in northern Saskatchewan. It is fortunate that in-pit disposal is practical in the uranium mining district. However, if similar arsenic leaching occurred at more traditional mining operations where open pits are not usually available for tailings disposal, management of the arsenic may be more challenging and possibly more costly. Open pits may be available for waste rock disposal at non-uranium mines, but use of the pits would require double handling of rock, a practice that may be common at uranium mines but is considered undesirable.

3.2 Molybdenum

Molybdenum has a Canadian Water Quality Guideline value of 0.073 mg/L for the protection of aquatic life. The threat to fish species is not high because most fish species are not sensitive to molybdenum, and exhibit LC50 values in the tens to hundreds of mg/L levels (McConnell, 1977). However, some benthic organisms such as daphnids (or water fleas) are more sensitive to molybdenum. In addition, molybdenum has become a concern for terrestrial animals, especially ruminants (or hoofed animals) that have been identified as especially sensitive to molybdenosis by uptake through water and the food chain, mainly aquatic and wetland plants. Other terrestrial animals such as muskrats that depend on aquatic plants may also be at risk of molybdenosis if toxicity benchmarks based on laboratory mice are considered in the assessment.

3.2.1 Sources

Elevated molybdenum concentrations in water are associated with molybdenum deposits (mainly in British Columbia) but have also been observed at copper and uranium deposits. The primary form of molybdenum is the sulphide mineral, molybdenite (Table 3.1). There

are also secondary forms of molybdenum, including an oxide and several metal-molybdates as shown in Table 3.1. In general, however, the solubility of secondary molybdenum minerals is relatively high and dissolved molybdenum concentration can easily exceed 20 mg/L if leached from mine rock or released in the mill to the tailings effluent. Ranges of dissolved molybdenum concentrations observed in effluents at different mine types is shown in Table 3.2. The CCME guideline for molybdenum is also shown in the table for comparison.

3.2.2 Issues

The CWQG value for molybdenum (0.073 mg/L) was established to protect aquatic organisms. The CCME guideline for molybdenum is based on a toxicity test on rainbow trout that was dramatically different than all other tests reported in the literature. Birge *et al.* (1979) and Birge (1978) report 28-day LC50 results of 0.79 and 0.73 mg/L, respectively. Those values were factors of 20 and 1,000 times lower than no observable effects levels and the lowest 96-hour LC50 test results (800 mg/L) reported for rainbow trout, respectively (McConnell, 1977). The CCME guideline was taken as one-tenth of the 0.73 mg/L 28-day LC50 value. Without additional evidence to the contrary, the CCME guideline represents an application of the precautionary principle. If additional information is not developed, this approach may lead to the requirement to be excessively cautious and to treat all water causing receiving water concentrations to exceed the guideline.

The other concern for molybdenum is related to toxicity to terrestrial animals in the downstream environment. Assessment of terrestrial toxicity is not a simple matter of defining a concentration limit and in general, must be considered on a site-specific basis (Chapman *et al.*, 2003). A pathway analysis for molybdenum at a typical northern mine setting in Canada, however, can show that there can be a predicted risk to mammals such as muskrat and beaver at values that are close to the water-based CCME guideline. The reason for the prediction of unacceptable risk is related to two main pathways for ingestion, aquatic plants and water. Aquatic plants have a tendency to bioconcentrate molybdenum from the water in which they grow. Although the bioconcentration factors are generally species specific, the values for molybdenum may be in the range of 100 to 300 L/kg(dry weight), meaning that if the water has a concentration of 1 mg/L then the aquatic plants will have molybdenum contents ranging between 100 and 300 mg/Kg (dry weight). With typical intake rates, aquatic plants can be a significant source of molybdenum ingestion or intake when the water has elevated concentrations.

The other aspect of the risk assessment equation is the benchmark value that determines a level above which an organism would be at risk of toxicity if more than the benchmark value was ingested. Like most guidelines, toxicity benchmarks are generally based on testing an effect and often include safety factors to be protective of organisms. Toxicity benchmarks are commonly reported as intake rates that are in units of mg (EOI) per kg (organism) per day (or mg/kg/d).

Toxicity benchmarks are intended to be conservative values that are protective of the most sensitive organisms in the environment. A pathways analysis is conducted to estimate the intake rates for specific EOIs and compare the predicted intake rates to EOI-specific toxicity

TABLE 3.2: EXAMPLE OF MOLYBDENUM CONCENTRATIONS IN EFFLUENTS AND DRAINAGES AT MINE DEPOSITS IN CANADA

Type of Mine	Dissolved Molybdenum (mg/L)	Comment
Molybdenum	10 to 50	Pit waters, waste rock drainage
Copper	1 to 30	Tailings porewater, drainage
Uranium	1 to 5	Mine water
CCME Guideline	0.073	

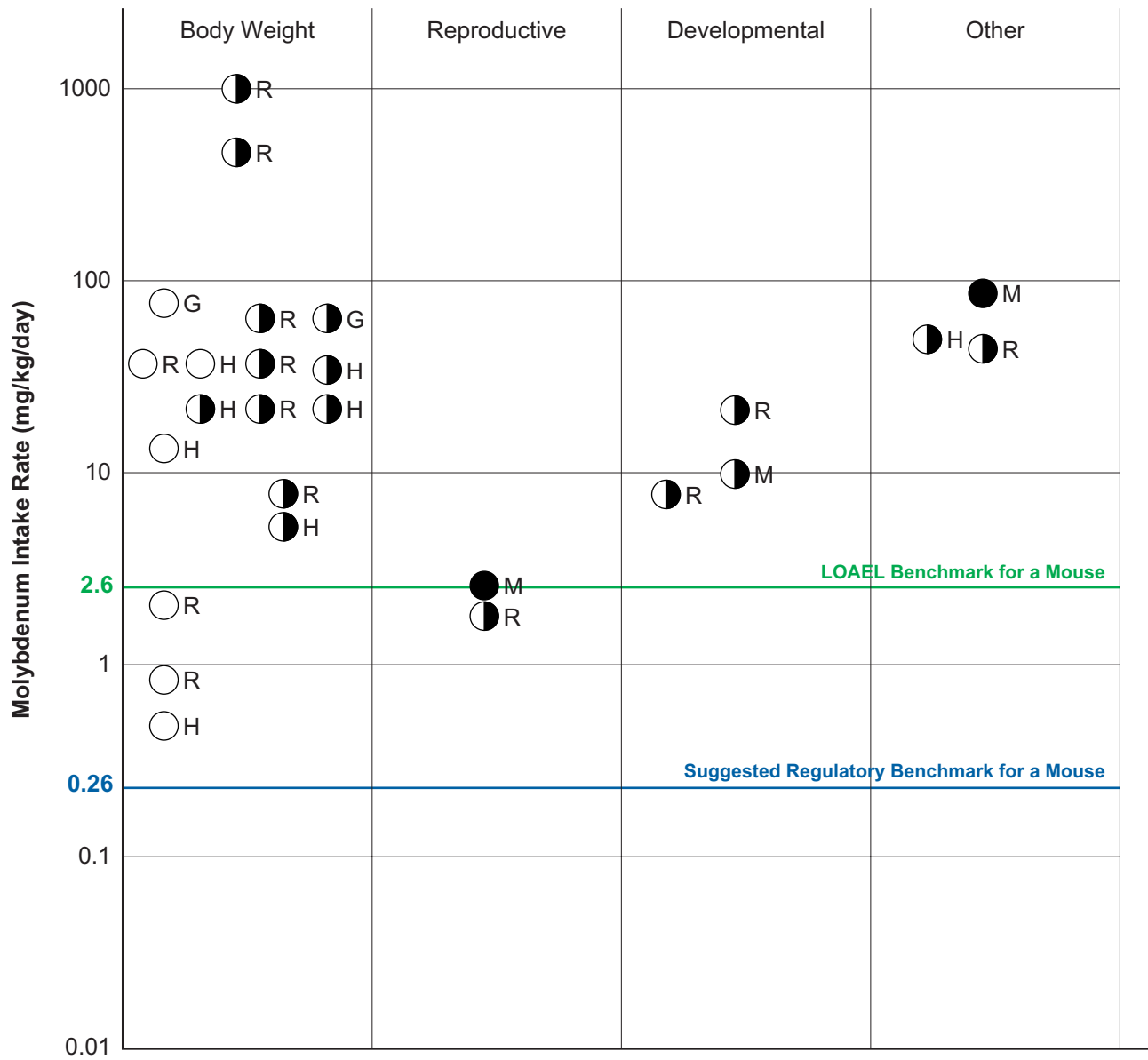
benchmarks. There are reasonably dependable methods of estimating transfer rates in a pathways assessment and, where available, site specific data can be applied in place of more generic, conservative data. However, the selection of the toxicity benchmark values of specific EOs can be an area of controversy. While benchmark values are intended to be protective, it is possible to select values that may be considered overly conservative and therefore overly restrictive for release limits to the environment. For example, molybdenum toxicity in mammals is known to be more prevalent when there is a copper deficiency in the diet and, conversely, toxicity is rarely noted if copper is adequate in dietary intake (Riordan, 2003).

Molybdenum is an example of a EOI with a range of possible benchmark values. Toxicity benchmarks for mammals are often based on toxicity tests on small laboratory animals such as mice, rats, guinea pigs and rabbits. The animals are “fed” known quantities of the EOI and observations on health indicators are made over time. These indicators could include weight (gain or loss), hair loss, activity and reproduction, for example. Selection of a toxicity benchmark can be taken as a lowest observable adverse effects level (LOAEL). This represents a level that shows a measurable effect below which no effects have been observed. Multiple studies are generally reviewed for this selection. Figure 3.1 illustrates the results of a number of toxicity studies for molybdenum. This figure shows the intake rate (mg/kg/d) in the test and the type of effect observed in the study. Most studies resulted in observed toxicity at intake rates exceeding 10 mg/kg/d. One study on mice reported an effect at an intake rate of about 2.6 mg/kg/d (Schroeder and Mitchener, 1971). The reported toxicity effect was a reduced reproduction capability in the third generation of laboratory mice with a continuous intake of molybdenum in spiked feed. Although numerous other studies suggest that larger animals such as rats and guinea pigs exhibit LOAEL values that are orders of magnitude higher than that in the mouse study, the low value has been selected as the Critical Toxicity Value (CTV) for molybdenum by some regulators in Canada. In addition, the approach taken by Environment Canada applies a factor of 10 to the CTV to derive the toxicity benchmark resulting in a value of 0.26 mg/kg/d for mice. By convention and through the use of allometric equations, the benchmark is adjusted to even lower values for larger animals (U.S. EPA, 1993). A summary of toxicity benchmarks for molybdenum in selected mammals is presented in Table 3.3.

While it can be argued that application of a safety factor to a LOAEL value provides a conservative level of protection to the species of interest, it is also likely that wildlife are more tolerant and adaptable to exposure of many toxicants than laboratory test animals. There have been efforts to assess toxicity of molybdenum in mammals in the field as reported in the proceedings of symposia sponsored by the British Columbia Technical and Research Committee on Reclamation (September 2003). However, it appears that there is a need to provide a continuing weight-of-evidence assessment of a realistic molybdenum toxicity benchmark for mammals if restrictively low discharge limits are to be avoided in the future.

The case for toxicity in wildlife exposed to elevated molybdenum has been driven mainly by two observations. First is the observation that domestic cattle do not gain as much weight when grazing on forage with elevated molybdenum (10 mg/kg dry weight is the

Systemic Toxicity Effect



LEGEND

- LOAEL, More Serious - Animals
- ◐ LOAEL, Less Serious - Animals
- NOAEL - Animals (No Effects)
- R Rat
- M Mouse
- H Rabbit
- G Guinea Pig

Note: The data are summarized from various sources, including Fairhall *et al.* (1945), Neilands *et al.* (1948), Arrington and Davies (1953), Ostrom *et al.* (1961), Gray and Daniel (1964), Schroeder and Mitchener (1971), Wide (1984), Fungwe *et al.* (1990) and Vyskocil and Viau (1999).


MEND Initiative			
Levels of Significant Exposure to Molybdenum - Oral			
	Project No. 63122996	May 2004	Figure 3.1

TABLE 3.3: SUMMARY OF MOLYBDENUM TOXICITY BENCHMARKS FOR SELECTED MAMMALS

Animal	LOAEL ¹ (mg/kg/d)	ENEV ² (mg/kg/d)
Mouse ³	2.6	0.26
Muskrat ⁴	0.99	0.10
Moose ⁴	0.24	0.02
Moose ⁵	0.17	-

¹ Lowest Observable Adverse Effect Level.

² Estimated No Effect Value.

³ LOAEL from study reported by Schroeder and Mitchener (1971).

⁴ Calculated from mouse LOAEL, weight corrected.

⁵ Calculated from lactating dairy cow value and weight corrected.

recommended maximum content in forage). And second, a moose-wasting disease was identified in Sweden in the 1990s and was attributed, but not clearly shown, to be linked to elevated molybdenum in watersheds that were amended with lime to raise the pH of soils and waters affected by acid rain. Wildlife observations in the vicinities of the Brenda mine (a former copper mine near Kelowna, B.C.) where molybdenum is naturally elevated in bedrock and in waters related to mining have not exhibited any signs of molybdenosis (Taylor and McKee, 2003). Studies of small mammals (Mathieu, 1996) and larger wildlife species (Riordon, 2003) on and near the Endako molybdenum mine (near Smithers, BC) also found no evidence of molybdenosis even though the vegetation is also naturally high in molybdenum in addition to soils and waters.

If it is not clearly demonstrated that the risk of molybdenosis is low in wildlife, it is likely that treatment of molybdenum will be a condition for final approval for operating where concentrations are elevated. Molybdenum treatment could represent a significant cost issue at many mines where the flow rates during operation are high. After closure, treatment costs at molybdenum-affected mines may be similar to those where water is treated with lime for acid drainage. Molybdenum toxicity in wildlife is one issue that would benefit from a concerted effort to develop reasonable risk levels by the sub-set of Canadian mines (molybdenum, copper, uranium) that have elevated molybdenum in mine waters and drainage from mine waste.

While the “easy” answer to concerns about molybdenum levels is to treat effluent to reduce levels released to the environment, it is not clear whether or not such treatment is justified. Treatment of molybdenum at mines to levels below the CWQG value of 0.073 mg/L is achieved at the closed Brenda mine near Peachland, BC. However, there is a community immediately downstream of the mine, and the water affected by drainage from the mine is used for irrigation of fruit and other produce intended for human consumption. While treatment may be justified in this case, the rationale for treatment at other mines is not at all clear.

3.3 Nickel

Nickel is generally associated with base metal mining and classic acid drainage issues. However, nickel is very soluble and can reach levels of tens of mg/L at pH values near 7, far exceeding the CCME guideline for the protection of aquatic life (0.025 mg/L). It has been shown that nickel drainage from waste rock can exhibit concentrations of several milligrams per litre at pH values below 8, as shown in laboratory test studies on rock from the Voisey’s Bay deposit (Nicholson and Rinker, 2000). Nickel is also a good example of behaviour for other metals such as cobalt and zinc that are also not solubility-controlled near neutral pH.

3.3.1 Sources

Nickel generally occurs as sulphides or arsenides in mineral deposits. Potential source minerals for nickel are listed in Table 3.1 under nickel- and arsenic-bearing minerals. The mechanism for nickel release through oxidation of mine wastes appears to be consistent

with other common sulphides. However, oxidation of nickel sulphide and arsenide minerals does not cause acidification, and therefore nickel can leach from waste in the absence of acid drainage. Once nickel is mobilized in drainage, the pH must be raised above a value of 8.5 to 9 to remove it to levels that are consistent with MMER discharge values.

3.3.2 Issues

Acute nickel toxicity for fish in the salmonid family occurs at values near 30 mg/L for rainbow trout (CCREM, 1987). However, nickel is more toxic to benthic organisms, and that is the main driver for the guideline for protection of aquatic life (0.025 mg/L). Because nickel can leach from rock in the absence of acidic drainage, some assessments to determine the potential for acid generation of tailings and waste rock may not identify the risk of nickel leaching and resulting loadings that may impact the receiving environment. Special precautions and protocols may be needed to evaluate the leaching potential of metals (nickel, cobalt and zinc) that are soluble near neutral pH and to mitigate environmental impacts. An example of a modified humidity cell test incorporating a weak acetic acid leach solution was presented by Rinker *et al.* (2003) to prevent the delayed release of nickel in tests completed in less than 20 weeks.

There are several examples where nickel leaching and concentrations in the receiving environment are, or are potentially, the main drivers for mine waste management and closure controls. These include nickel leaching from mine rock in a permafrost environment, nickel leaching from tailings and mine rock in underwater repositories, and nickel leaching from low sulphur nickel-copper tailings.

Nickel Leaching from Mine Rock

The Raglan mine on the Ungava Peninsula in northern Quebec (approx. 62°N lat., 75°W long.) is a nickel-copper-cobalt operation. Several ore deposits occur within the Raglan formation that extends over tens of kilometres. The initial assessment of mine rock and tailings in the mid-1990s identified that all of the tailings and some mine rock would have the potential to generate acid. It was found that much of the mine rock had sufficient neutralization potential to consume acid that would likely be produced by oxidation of the sulphide minerals, predominantly pentlandite, within the mine rock. Reclamation plans were therefore developed in the late 1990s to manage the potentially acid-generating materials by backfilling pits that would eventually flood to prevent acid generation from the mine rock. The assessment considered all of the known issues of the day and provided a management approach that considered long-term environmental protection.

Updates and refinement of the mine rock management plan in 2001 included additional assessment of metal leaching that was not recognized in the original assessment. The metal leaching assessment concluded that a greater portion of the mine rock would contribute to nickel loadings than was considered to contribute to acidic drainage. The assessment showed that, while much of the rock that was planned for excavation from open pit operations would remain neutral, nickel leaching may result in unacceptable loadings from the majority of mine rock if deposited on land. The loading rates from mine rock did not need to be extreme to adversely affect water quality (i.e., exceed about

0.025 mg/L) in the pristine soft water environment in the permafrost setting of this sub-arctic location.

As a result of the identification of a metal leaching issue and the greater proportion of mine rock that would require special management, the mine plan was altered to develop more underground operations and less open pit mining. This approach reduced mine rock production and therefore limited the amount of rock that would require special management, such as backfilling into pits after closure of each mine. The new mine plan has reduced the amount of mine rock by about 10M tonnes. The mine is now closely monitoring nickel loadings from the various mines and planned mining locations. Progressive reclamation of approximately eight proposed mini-pits is planned in order to control nickel loadings and protect the larger watershed from excessive nickel loadings. It appears that Raglan is the first known operation where neutral drainage and metal leaching was a driver for environmental management and mitigation that involved major operational changes.

Metal Leaching Underwater

The Voisey's Bay project is developing a mine in a nickel-copper deposit in northern Labrador. The main ore body consists of a high-grade sulphide zone, and it is evident that tailings will be acid-generating if deposited in a traditional land-based impoundment. The main ore body will be mined with open pit methods and some mine rock could also generate acid if deposited in on-land stockpiles. Recognition of the potential for acid generation in tailings and waste rock led to early planning for underwater management of tailings and the potentially acid-generating mine rock. As part of the environmental assessment conducted in the late 1990s, laboratory studies were completed to verify acid prevention when tailings and waste rock are stored in underwater repositories (BEAK, 1998).

The laboratory test programs on tailings and waste rock clearly demonstrated that underwater deposition was successful at preventing acid conditions. The results also showed that small amounts of nickel continued to leach into the water column, as a diffusion-controlled release process from the surface of the underwater waste. The resulting concentration of nickel in the water column therefore effectively depends on the flow rate of water moving through the water column reservoir or the retention time of the water cover. When this process was recognized, it was apparent that a contingency plan may be required to mitigate the nickel concentrations in the water column of the reservoir that results from leaching from the underwater waste. Because the leaching process is diffusion-controlled, a diffusion barrier was proposed and tested in the laboratory. No special chemical properties were required for the diffusion barrier. Sand, which is in plentiful supply in the area, was found to mitigate the nickel leaching, and could be applied, if required. Proposals for construction of such a layer have included hydraulic placement or traditional placement after temporarily lowering the water level in the reservoir. Such a diffusion barrier was constructed in a flooded tailings impoundment in Elliot Lake, Ontario, in 2003.

Nickel Leaching from Low-Sulphur Tailings

Dry or soil covers have been proposed to mitigate acid generation in sulphide tailings. One variation on the theme for such covers is to desulphurize run-of-mill tailings for construction as a final protective cover to limit entry of oxygen and/or water to the underlying tailings. Inevitably, it is not practical to remove all of the sulphide, and therefore it is important to assess the effects of the residual sulphide in the desulphurized tailings cover. A laboratory investigation of desulphurized nickel-sulphide tailings was conducted to assess the water quality associated with low-sulphur tailings (MEND, 1998).

One of the significant findings of the laboratory investigation was the relative amount of nickel leaching as a function of sulphur content in the tailings. Normally, production rates of acid and metals are somewhat proportional to the sulphide content in oxidizing tailings. The results of the investigation showed that the low-sulphur tailings (0.2% S) exhibited higher concentrations of nickel in the tailings porewater than tailings with a higher sulphur content (2% S). In this case, it appeared that the nickel released to porewater was related to the amount of iron released from the sulphides during oxidation. Tailings with a higher sulphur content resulted in large loadings of iron that precipitates as ferric hydroxide, a solid that scavenges (or co-precipitates) nickel from porewater. Less iron is released from the low-sulphur tailings during oxidation and consequently less ferric hydroxide forms in the tailings. The smaller loading of iron appeared to result in less scavenging of nickel and higher nickel concentrations in the tailings porewater.

The nickel leaching that was related to the low-sulphur tailings does not negate the use of the material for tailings covers. Fortunately, as the tailings porewater infiltrates into the tailings, nickel is further sorbed and retained in the solids. This removal mechanism represents a natural attenuation of nickel in the tailings. Nonetheless, it is important to recognize the issue of nickel leaching in the desulphurized tailings so that it can be managed in the initial period of oxidation before the residual sulphide content of the tailings is depleted.

3.4 A Brief Overview of Other Substances

3.4.1 Selenium

Selenium is an essential trace element for animal metabolism that is associated with sulphur in geologic materials. Arsenic is about 20 times more abundant in the earth's crust than selenium. Although a rare element with no major deposits known, about 300 tonnes of selenium are produced in Canada, usually as a by-product of electrolytic copper refining. Of the estimated 10,000 to 70,000 tonnes of selenium released to water worldwide each year, between 3,000 and 20,000 tonnes are thought to originate from mining, smelting and refining activities (Nriagu and Pacyna, 1988). Even at these release rates, the average concentration of selenium in fresh water is estimated to be less than 0.001 mg/L (Anderson *et al.*, 1994; Hem, 1989).

One issue that contributes to the concern for selenium in higher organisms is the propensity to bioaccumulate and biomagnify from lower to higher trophic forms. A wide range of toxic

concentrations have been reported for freshwater aquatic organisms with LC50 fish values from 0.6 up to about 100 mg/L (U.S. EPA, 1980). As expected, chronic toxicity to selenium exhibited a lower range of values with lower limits close to 0.01 mg/L for effects in larvae (Hermanutz *et al.*, 1992). The CCME has established a guideline value of 0.001 mg/L for selenium to protect aquatic organisms. Acute and chronic toxicity levels in aquatic invertebrates are also variable and in the ranges reported for fish. Selenium toxicity has also been observed in terrestrial animals, including waterfowl. Based on bioaccumulation effects and expected feed intake rates, the British Columbia Ministry of Water, Land and Air Protection have established a recommended maximum water concentration of 0.004 mg/L for the protection of wildlife.

The guideline level for selenium may result in a need for treatment of large volumes of water at sites where the drainage or effluent is expected to cause exceedance in the receiving environment downstream of the site-specific mixing zone. Rosengrant and Fargo (1990) suggest that treatment of selenium down to 0.01 mg/L is possible with available technology such as ferric sulphate treatment. The challenge may be to effectively treat large volumes that may be produced at some operating or closed mines. This could have important cost implications for several mines and the industry overall.

As is the case for molybdenum, the science upon which the environmental guidelines are based is not without controversy and there are several issues that could use further scrutiny to define protective limits without overly conservative constraints. As is also the case for molybdenum, there are likely to be site-specific conditions that would allow much higher concentrations than the CCME guideline and still remain protective of the environment. It would clearly be beneficial to the mining industry to explore the main issues and environmental conditions that have led to the selection of the current guideline value of 0.001 mg/L for selenium and conversely to define those conditions where less restrictive yet protective values could be justified.

3.4.2 Sulphate

Sulphate has been viewed as a relatively innocuous substance in water. It occurs naturally in surface water and groundwater at levels that are commonly in the mg/L to tens of mg/L. Sulphate is one of the main products of sulphide oxidation and can occur at levels of hundreds to a few thousand mg/L after neutralization occurs, either as a result of natural processes or during water treatment of acidic waters with lime, for example. Most jurisdictions in Canada have set drinking water standards for sulphate at 500 mg/L as an aesthetic objective. There is also some concern about the laxative effect in humans when water with elevated sulphate concentrations is initially consumed, but a tolerance to high levels is usually developed by regular consumers (OMOE, 2000).

A guideline for sulphate was introduced by British Columbia of 100 mg/L for the protection of aquatic life. The most protective level is related to observed toxicity effects in one study on aquatic moss (*Fontinalis antipyretica*) that is known to be widely distributed throughout the province (BCMWLAP, 2000). As part of the guideline application, it is also recommended that "the health of aquatic moss populations should be checked on an

occasional basis” if sulphate values from anthropogenic sources raise sulphate levels above 50 mg/L.

It was recognized that increased water hardness may ameliorate the effects of sulphate toxicity and that may allow for the development of site-specific objectives that can be less stringent than the recommended guideline value. Nonetheless, a limit of 100 mg/L sulphate may be readily exceeded at many operating or closed mines where sulphide oxidation has occurred even when the drainage or effluent is near neutral. Although this guideline for sulphate appears to be relatively specific to flora in British Columbia, experience would suggest that the lowest or most protective guidelines tend to be adopted by other jurisdictions within Canada. The mining industry should be aware of the implications of the BC guideline for sulphate at many mining operations, those with and without acid drainage issues.

4.0 ASSESSMENT OF LEACHING NEAR NEUTRAL pH

There are protocols and methods to evaluate the potential for acid generation in and the production of acid drainage from tailings and mine rock (Price, 1997). The assessment of metal leaching in the absence of acid drainage has not, however, been discussed or demonstrated at nearly the same level of detail. While there are screening tests such as acid base accounting (ABA) procedures to address the potential for a material such as mine rock to generate acidic drainage, there are no equivalent screening tests to indicate a potential or probability for leaching of a specific EOI. Some screening procedures attempt to address metal leaching with short-term leach tests such as the special waste extraction procedure (SWEP; BC, 1992) or the toxicity characteristic leaching protocol (TCLP; U.S. EPA, 1996) generally involves a high water to solids ratio (20:1). A modification of the SWEP test with a lower water to solids ratio (3:1) has been proposed by Price (1997). These tests were originally designed to be a mild acetic acid solution to enhance the solubility of "metals". Modifications to these tests have been proposed for purposes of characterizing mine waste materials to include leaching with distilled water and other solutions containing weak acids. These tests may only give an indication of leachability if the sample has already been subjected to oxidation or weathering prior to the test during which time the weathering products have accumulated in the sample. In addition, these tests fail to consider the EOIs that are more soluble or leachable at neutral to alkaline pH values than in acidic conditions, including arsenic, molybdenum and selenium.

Protocols for assessing acidic drainage also include longer-term weathering tests such as humidity cell tests (Price, 1997). This involves the exposure of a moist sample to oxidizing conditions for a selected period of time (usually one week) followed by a rinse of water to remove all soluble weathering products accumulated during the exposure period. This procedure is repeated and the release or loading rates for EOIs are measured over time by analyzing the chemical composition of the rinse solution. In general terms, this protocol is also useful to assess leachability of EOIs and is applicable for leaching in stockpiles in the absence of acid conditions. The results are subject to similar challenges of scale-up to field conditions for the interpretation of loading rates and prediction of water quality in drainage associated with the waste. Other methods or protocols, however, need to be considered for metal leaching in the absence of acid drainage or oxidative weathering.

4.1 Screening Tests

Short-term leach tests such as the SWEP protocol or modifications of this protocol can provide useful information on potential candidates for leaching. However, the results may be biased to those EOIs that have enhanced solubility at low pH or by complexing with acetic acid. There are alternative procedures that may help define leachability of other EOIs that may have enhanced solubility at neutral to alkaline pH values.

Tessier *et al.* (1979) proposed a procedure that sequentially extracted EOIs from lake sediment in an attempt to define what forms of solids contained the inventories of EOIs. The procedure starts with an extraction step to remove the water-soluble fraction and progresses to extraction of ion-exchangeable (sorbed cations) EOIs, to inventories

associated with carbonate minerals, iron and manganese oxides and other more resistant solid phases. The protocol suggested by Tessier was intended for use on lake sediments and is not directly applicable to the assessment of mine rock and tailings, but the concept has merit for helping to define the operational forms of EOIs in mine waste. The extraction procedures are based on the concept of chemical reactions of EOIs associated with the various chemical or solid forms expected in the sample. Using these concepts, leaching procedures can be defined for specific EOIs, such as arsenic or molybdenum, that are expected to behave differently from most of the true metals, such as copper, nickel or zinc, for example.

An example of a leaching protocol, developed specifically for arsenic, was described by Cogema (2001). The mine rock in that case was considered to be potentially acid-generating, was designated for underwater disposal in a mined-out pit. Arsenic remained as a potential concern because it was observed to leach from the solids even for flooded conditions. It was therefore important to determine what concentrations may be expected in porewater within the flooded rock and what inventory of leachable arsenic could be expected over the long term. Both the leached concentration and the leachable inventories are necessary to provide an assessment of the potential impacts on the receiving environment.

The concentrations of arsenic and other EOIs in porewater were determined through a series of column tests that simulated flooded conditions with long residence times. The inventories of arsenic that could leach under flooded conditions were evaluated through sequential leach tests with high water to solids ratios (20:1).

The forms of arsenic in the solids appeared to consist of primary nickel arsenides and soluble secondary solids containing arsenic. An investigation was designed to assess the quantity of arsenic that could be leached from the solids and what solution chemistries would accomplish the extraction. The results showed that a de-ionized water rinse was able to extract a significant portion of the "soluble" arsenic, up to one-half of the soluble inventory was extracted by either an alkaline (pH = 10) solution or one with elevated phosphate concentrations. Phosphate is chemically analogous to the oxidized form of arsenic (arsenate) and can replace arsenic in the solids if it is held by sorption. The final protocol that was selected to quantify soluble arsenic included two sequential steps involving de-ionized water followed by two steps involving a phosphate solution (200 to 400 mg/L). This protocol was used to characterize rock samples with a range of arsenic contents (total). The results were quite consistent and showed that about 10% of the total arsenic was water soluble, and that an additional 10% could be extracted with the phosphate solutions. For conservative assessments, a total of 20% of the total arsenic inventory was assumed to be soluble. The remaining arsenic inventory likely consists of primary (chemically reduced) arsenides that will remain relatively stable when flooded and leaching of that fraction is not expected to be significant. Incidentally, the protocol for arsenic was also very effective at extracting soluble molybdenum in the same samples.

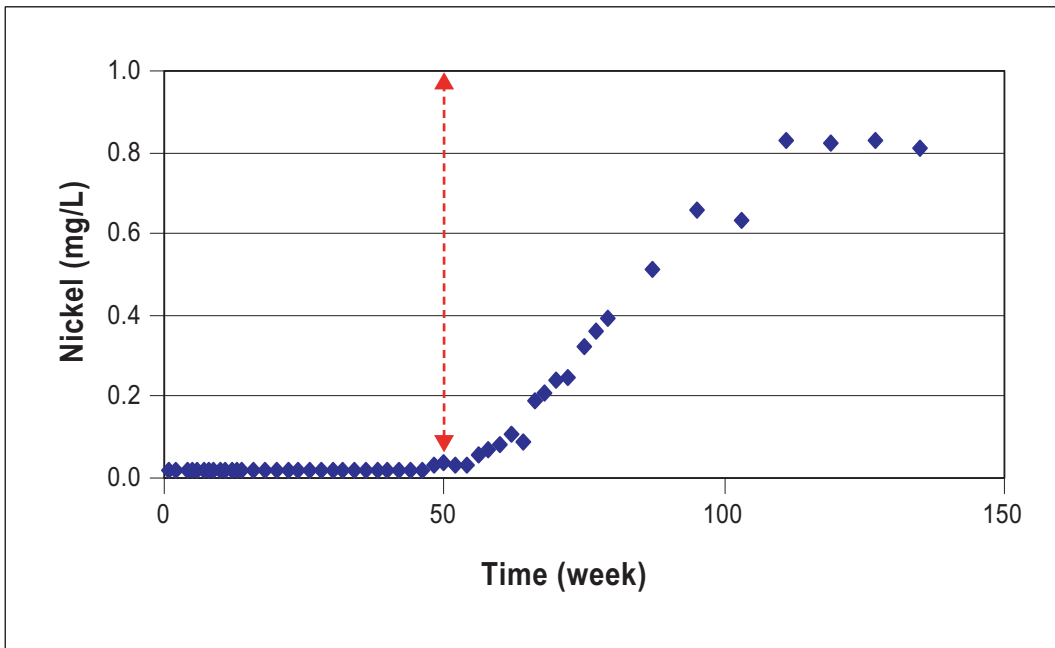
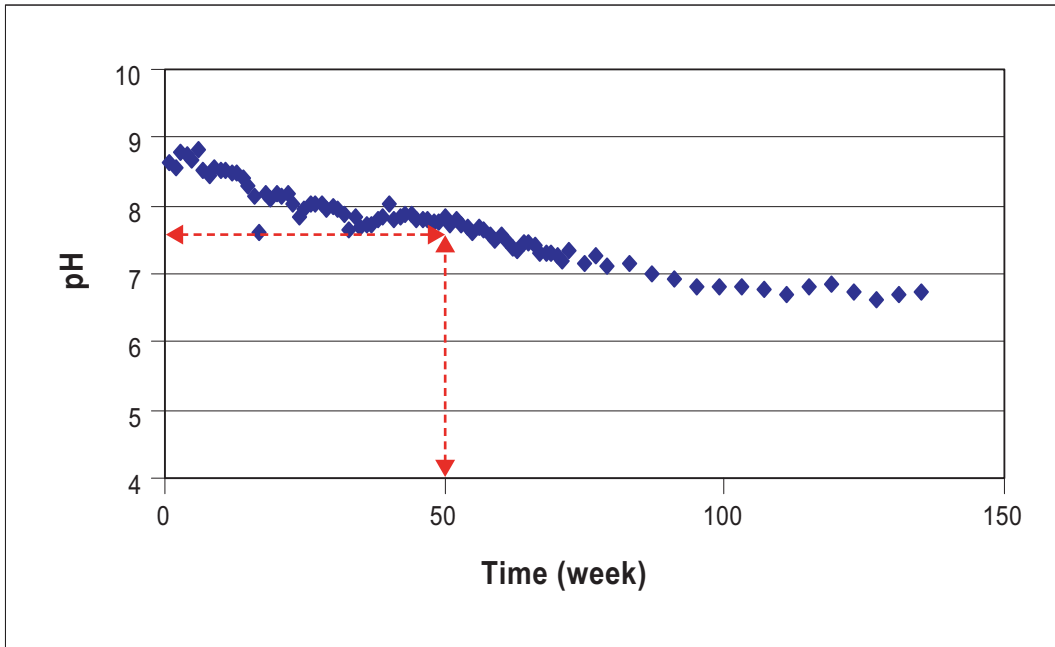
The column studies showed that not all of the water-leachable arsenic dissolves in one pore volume of water. Because the column conditions simulated more natural water to solid

ratios (0.3:1 for water in a porous matrix of rock), a solubility limit appeared to control the maximum arsenic concentrations with only 1 to 2 % of the arsenic dissolved in any pore volume of water. This means that the arsenic could continue to leach into about 10 pore volumes of water before depleting the leachable arsenic from the solids.

Other procedures and protocols have been developed to assess leaching rates over the long term for different disposal scenarios. The meteoric water mobility procedure (MWMP; NDEP, 1996) has been proposed as a method to assess weathering of mine rock in a similar manner that is addressed in humidity cell tests but uses water without acid to attempt to simulate solubility controls with a water to solids ratio of 1:1. This sequential leaching mimics, to some extent, the infiltration of water through a rock stockpile. However, it is a short-term test with water contact times of hours and has similar limitations as do other short-term tests if the leaching is time-dependent (or kinetically controlled) on the time scale of the test. The method appears to be intended to address some of the issues related to scale-up from the laboratory to field conditions for previously oxidized or weathered waste. However, it is likely that the resulting concentrations from the leach test cannot be directly compared to concentrations expected in the field for similar reasons that concentrations from standard humidity cell tests should not be used to imply concentrations from a full-scale stockpile. Indeed, the arsenic leaching tests described by CRI and CLMC (2001) showed that when low water to solid ratios are used (as in the column tests, arsenic leaching required more than eight weeks to establish a quasi-equilibrium concentration. It was also recognized that previous test programs involving column experiments with residence times of less than four weeks, underestimated arsenic concentrations in the column porewater by factors of 10 to 20 times (CRI and CLMC, 2001).

Modified humidity cell tests have also been developed to address metal solubility and delayed response of metal leaching. Standard humidity cell tests have shown that nickel leaching in a nickel sulphide mine rock was delayed for more than one year because the pH of rinse water remained above a value of 8 (BEAK, 1998). In this case, nickel was being released from the sulphide minerals during oxidation but was re-precipitating as nickel hydroxide or sorbing onto iron oxides at the high pH values in the leachate. High pH is common when water is added to freshly crushed rock, but tends to decrease to near neutral values when the rock weathers, even in the absence of sulphide minerals in the rock. The delayed release of nickel is illustrated in Figure 4.1. Metal leaching would have been recognized after about 50 weeks of testing in this case. A modified protocol using weak acetic acid for humidity cell rinse solution was applied to similar rock to avoid the long delay of nickel leaching (Nicholson *et al.*, 2003). The pH adjustment to values between 5 and 6 prevents the solubility control of secondary nickel solids above a pH value of 8, and nickel leaching was recognized early in the test rather than after an extended test period.

Several examples have been presented in this report to show that metal leaching can occur for wastes that have been placed underwater to mitigate acid drainage. There are no standard protocols to assess metal leaching from flooded wastes. As found in the Voisey's Bay assessment, underwater leaching may require further mitigation to prevent long-term impacts to surface water. The depositional environment can also play an important role in the mobility and leaching of EOIs from submerged waste. Martin *et al.* (2003) present four



MEND Initiative

Nickel Concentrations in Humidity Cell Leachate over Time are Shown to Increase after pH decreased below a Value of about 8



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Figure 4.1

field examples of underwater waste (or enriched sediment) to illustrate that remobilization of EOs from the solids can negatively affect the overlying water quality. The primary message in the review is the importance of understanding the chemical nature of the mine waste, and the compatibility of the waste with the depositional environment that will occur over the long term.

It is evident that assessment of underwater disposal is necessary for waste management planning. With no standard protocols and with the likely inappropriateness of any one protocol for the range of possible disposal conditions, it is important to carefully document methods and procedures, and to present the rationale for test conditions with the specific wastes destined for disposal. Only by careful testing and documentation will a body of evidence be developed similar to that for the evaluation of acid generation potential in the past. Assessment of acid generation potential has been ongoing since the late 1970's and interpretation of results remains controversial among the experts in many cases. There is a clear need to carefully document testing and assessment methods and outcomes in the field so that systematic methodologies will be available for the evaluation of metal leaching at neutral pH.

5.0 TREATMENT ISSUES AND CHALLENGES

The main issues that are related to the treatment of neutral drainage waters or effluent include:

- the need for methods other than lime addition;
- inefficient removal of metals such as nickel or zinc with lime addition when dissolved iron concentrations are low (common at neutral pH);
- a significant input of dissolved solids in low TDS waters containing metals at neutral pH;
- far less experience with treatment solids or sludge compared to lime treatment sludge over longer time periods; and
- the potential need for multiple-step processes when more than one EOI requires treatment.

Water treatment methods for many of the EOIs that are associated with neutral drainage are quite different from those needed for most pH-sensitive metals. The preferred approach to treat mine effluent containing EOIs, such as antimony, arsenic, molybdenum and selenium, is based on the addition of ferric sulphate that forms a ferric hydroxide solid from mildly acidic conditions to alkaline conditions. The effect of pH on metals (copper, iron, zinc, etc.) is quite different than that on metalloids (arsenic, molybdenum, selenium). While concentrations of metals generally decrease with increasing pH (Figure 5.1A), the concentration of arsenic is low at pH = 4 and increases with increasing pH (Figure 5.1B). Each of the metalloids has an optimal pH for removal by ferric sulphate. For example, molybdenum removal is most efficient if ferric sulphate is added to the effluent at a pH value of about 4.5. After the ferric hydroxide solids form and have been removed from the effluent stream, the pH requires upward adjustment before discharge.

While there is a wealth of experience with lime treatment to remove metals from effluent in mining operations, there is much less experience with treatment of metalloids and other non-metals. Treatment of many potential contaminants is an area of ongoing research in the mining sector. Although methods are available, application to mining applications are often hampered by excessive costs related to the need for treating high flow rates that affect reactor size (or holding times) as well as reagent usage. For lime treatment, the flow rate is directly related to the capital cost as shown in Figure 5.2 that illustrates a range between \$4M and \$14M (R. Schwenger, pers. comm., 2003). The operating costs depend on the acid loadings and lime requirements, and lime cost alone can be in the range from a few hundred thousand to one million or more dollars per year. In addition, an operator is required for the treatment plant and sludge management can represent a significant portion of the operating costs.

The future potential costs of non-lime treatment systems can only be guesstimated at this time. Although no reliable data exist, it is very likely that the present value of water treatment systems at Canadian mines exceeds \$1 billion. It was estimated that the

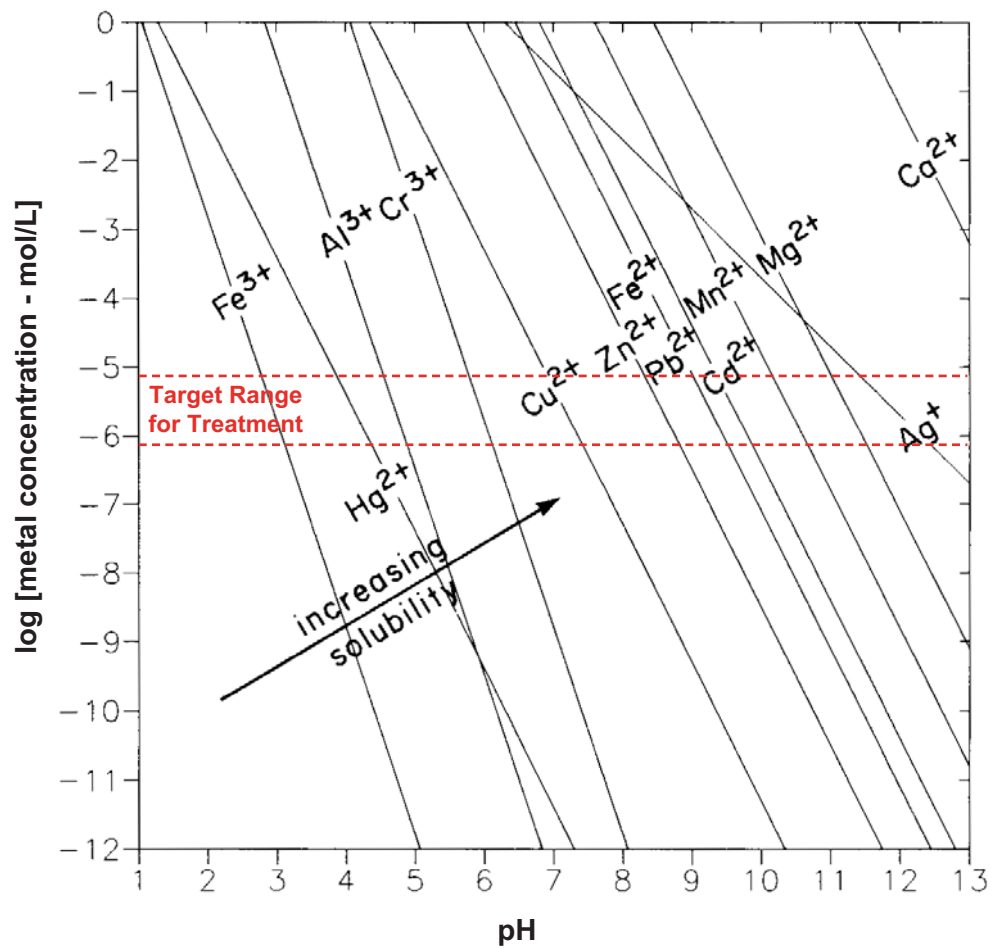


Figure 5.1A) Solubility of various metal ions as controlled by their oxides or hydroxides as a function of pH. (Adapted from Stumm and Morgan (1981).)

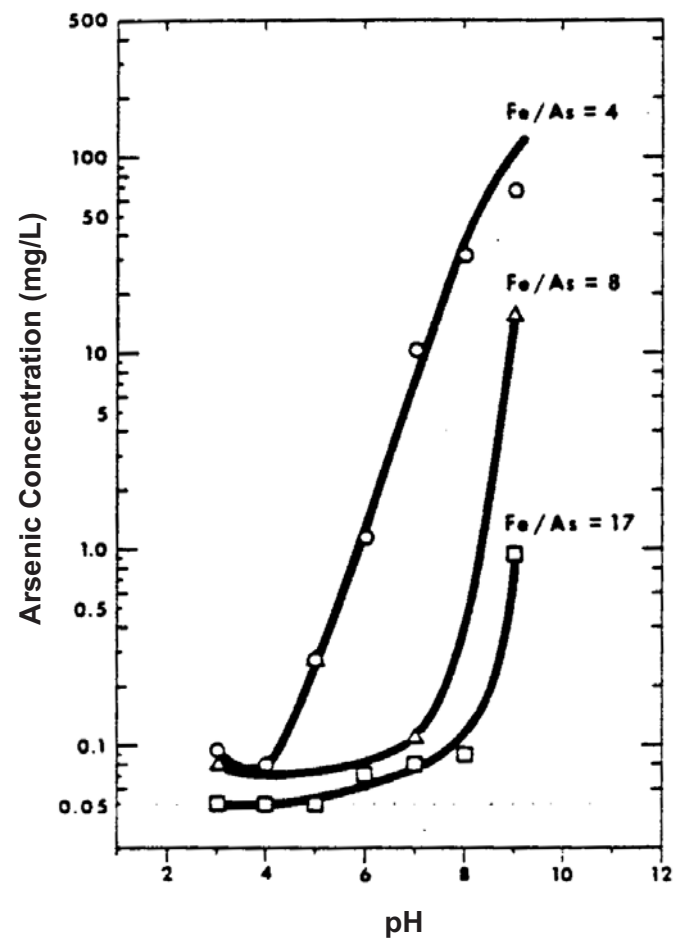


Figure 5.1B) Effect of the pH and Fe/As Ratio on the As Solubility at 25°C (Krause and Ettel, 1985).

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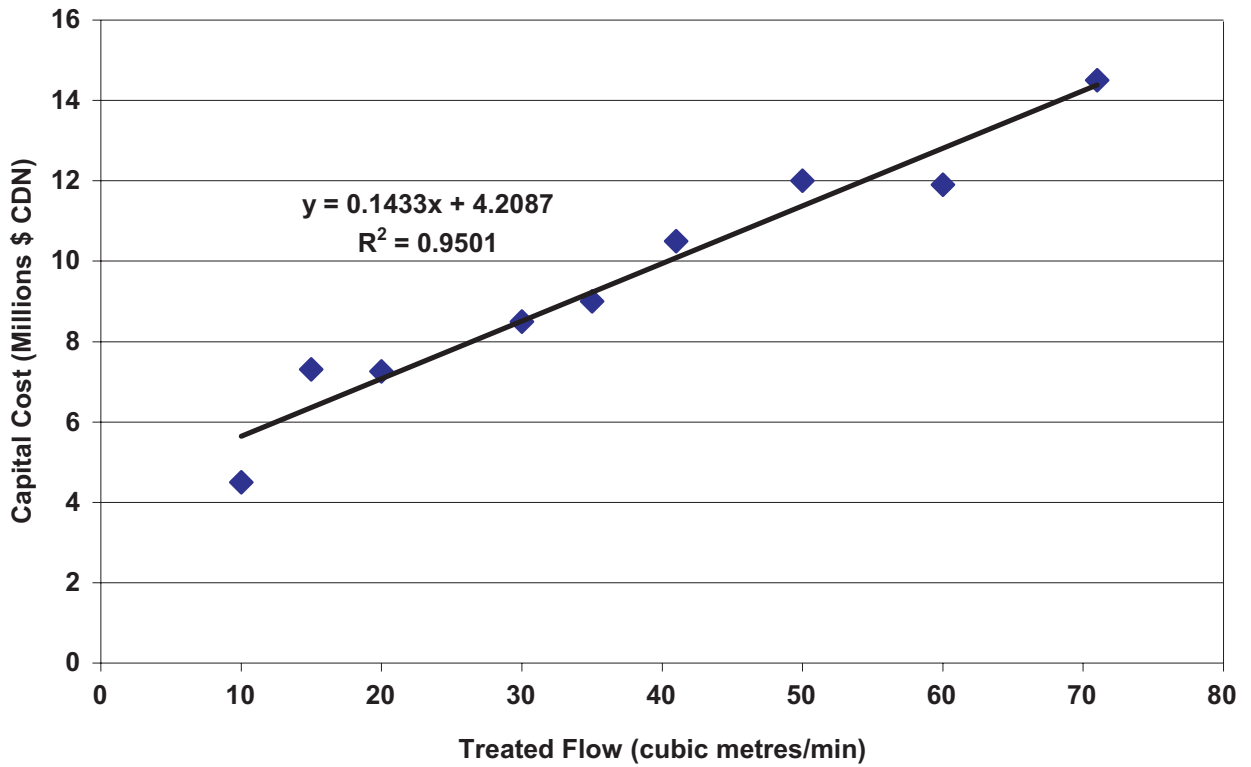
Concentrations of Selected Chemical Constituents as a Function of pH



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Figure 5.1



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Capital Cost of Traditional Lime-based Water Treatment Plants
as a Function of Flow Rate of Effluent



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Figure 5.2

incremental capital and operating costs (NPV) for adding or upgrading treatment systems at operating mines, outside of Ontario, to meet the 2003 MMER limits would exceed \$600M (Senes and Lakefield, 1999). It may be fair to assume that treatment systems for metalloids such as arsenic and molybdenum would have similar capital and operating costs as those for lime-based treatment systems. Although lower reagent usage may be expected for non-lime treatment systems, unit costs for reagents are higher (e.g., ferric sulphate) for these systems. However, there are significant uncertainties with respect to long-term sludge management for non-lime treatment systems. This has been recognized for arsenic treatment by ferric sulphate for which long-term stability of sludge remains as an issue of ongoing debate.

It is recognized that many operating mines that treat for arsenic, and possibly other EOs are doing so without “designed” waste-water treatment plants. Some operations treat effluent by adding ferric sulphate, for example, and sending the treated effluent to a holding pond where the ferric-arsenic sludge accumulates prior to discharge of the treated effluent. In some cases, ponds are batch-treated by adding ferric sulphate, and sludge is allowed to settle before batch release of treated water. These treatment options provide lower cost alternatives to designed treatment plants, but these methods may not be practical for a variety of operating conditions.

Neutral drainage may be characterized by low total dissolved solids (TDS) values but can contain metal concentrations that exceed discharge limits. An example of this water quality issue has been observed at the Raglan mine where runoff from mine rock stockpiles and an open pit area requires treatment. The runoff is characterized by low milligram per litre levels of nickel, with low TDS consisting mainly of sulphate that is typically less than 50 mg/L. There is effectively no dissolved iron in the runoff. The runoff has been treated with lime in the past. Treatment efficiency was not always as good as desired and the resulting treated effluent had very high TDS values compared to the soft receiving waters.

In an attempt to increase nickel treatment efficiency and to reduce the TDS load in the effluent, Raglan is implementing an alternate technology for nickel removal. The proposed treatment method is based on removal of nickel as nickel sulphide solids after addition of sulphide to the effluent. The treatment system was being scaled-up to the design capacity of 140 m³/h during the summer and fall of 2004.

When ferric sulphate is used to treat metalloids, a ferric hydroxide sludge is produced. The treatment method has been applied to arsenic treatment for several decades. However, the chemical characteristics and long-term stability of the ferric-arsenic solids has been a topic of controversy in the scientific literature over much of that period. While lime sludge is known to contain insoluble oxides of treated metals, there is no pure solid phase responsible for the removal of arsenic by ferric sulphate. The formation of amorphous solids in the sludge is not that different than the amorphous solids that form in lime-treatment plants. However, unlike lime treatment systems, the most efficient removal of arsenic appears to occur at pH values between 4 and 5 (Krause and Ettel, 1988) when arsenate (As:V) is present and at pH values between 8 and 9 when arsenite (As:III) dominates (Wang *et al.*, 2000). Arsenic treatment efficiency is also controlled by the ratio of

iron to arsenic concentrations in the treated water. Higher removal efficiencies are observed when the Fe/As (molar) ratios are greater than 3 and the best efficiencies are observed for ratios between 5 and 10. This means that significant quantities of ferric sulphate may be required to treat effluent solutions containing high arsenic concentrations.

At this time, it appears that arsenic is sorbed or co-precipitated with ferric hydroxide. There is some concern that the sorption mechanism may not be effective over the longer term as the sludge ages. This concern is based on theoretical knowledge that as pure amorphous ferric hydroxide solids age, more crystallinity is developed and the density of sorption sites on the solid decreases. However, iron-arsenic treatment sludge is not a pure solid. There is some evidence that ferric hydroxide solids that contain more than about 5 mole % of arsenic are stable in the laboratory, and that ferric hydroxide will not easily "mature" to a more crystalline form such as goethite or hematite (Paige et al., 1997). A large research program was initiated by Cogema Resources Inc. in the late 1990s to demonstrate the treatability of arsenic and nickel in the mill circuit prior to tailings discharge (Cogema, 1998). The principle for arsenic precipitation with ferric iron was demonstrated. In addition, regular monitoring of the tailings, which are being deposited underwater in a mined out pit, is being conducted to demonstrate the longer term stability of arsenic in the tailings. Although the in-mill treatment produces a complex mixture of tailings and treatment sludge, the results to date have been very supportive of the successful arsenic removal process. Nonetheless, additional experience with ferric-arsenic sludge, from more traditional treatment systems, in storage impoundments will be useful to gain confidence in the management and long-term behaviour of these treatment solids.

There are other emerging technologies for treatment that are applicable to neutral pH drainages. One process that has been implemented at a number of site is an Activated Silica Gel Process with excellent success (S. Basra, Pers. Comm., 2004). The method is effective at removing several constituents that can be associated with neutral pH drainage, including arsenic, antimony, cadmium, mercury, nickel, selenium and zinc. The method produces a low volume of highly concentrated sludge that requires long-term storage. There may be a need to further investigate alternate treatment technologies such as this for neutral pH drainages that pose special challenges.

6.0 SUMMARY OF CONCLUSIONS

There were about 60 metal mines operating in Canada in 2003 with a GDP in excess of \$9 billion (CDN). The economic products of mining include antimony, cadmium, cobalt, molybdenum, nickel, selenium and zinc. However, these products also represent elements of interest when released to water. These products plus other elements of interest (arsenic, chromium, manganese and mercury) do enter waterways in regulated mine effluents and in seepage associated with mine waste.

Although much of the focus in the past has been on acid generation in mine waste, many metals and metalloids can be released from waste and are mobile at neutral pH. Neutral pH drainage can have unacceptable concentrations of many EOs. The release of EOs at neutral pH can occur in tailings and mine rock that may have no potential for acid generation because the waste is devoid of sulphide minerals that can produce acid. Alternatively, metal leaching can occur when potentially acid-generating materials are mitigated, for example, when wastes are deposited underwater to prevent oxidation.

While there is a significant body of research and experience with the assessment of acid-generating mine waste, there has been very little experience in the assessment of neutral drainage metal leaching. It is apparent that guidelines are required for the assessment of metal leaching that reflect the conditions of mine waste disposal environment such as flooded or on-land placement.

There are several examples of neutral drainage issues that are likely to be relatively common to many mining operations. Arsenic is known to be associated with gold and uranium mines in Canada. Arsenic can be released from tailings during and after milling, and from waste rock after disposal. Although the arsenic release may be associated with oxidation of arsenic minerals, acid generation is not generally associated with elevated arsenic concentrations in drainage from mine wastes.

There are also examples of metal leaching at neutral pH when acid generation has been mitigated. For example, nickel and zinc leaching can occur when sulphide tailings are deposited underwater to prevent oxidation and acid generation. It is likely that some residual metal leaching will be observed when other mitigation strategies are applied to potentially acid generating wastes.

There are several reasons why a group of EOs are of special concern in neutral pH drainage. First, several EOs have regulatory limits at $\mu\text{g/L}$ levels. For example, arsenic, molybdenum and selenium have guideline values of 0.005, 0.073 and 0.001 mg/L, respectively, for the protection of aquatic life. Second, these substances occur as neutral or negatively charged ions in solution, and are generally more soluble at high pH and less soluble at lower pH values. A third reason that these EOs are of concern is that they require treatment that is significantly different from lime treatment that is standard practice for many metals. In addition, EOs such as molybdenum and selenium may represent risks to terrestrial organisms in addition to those in the aquatic environment. In order to gain

approval for new mines, it may be necessary to consider mitigation of these EOs if risks to the terrestrial ecosystem are significant.

It appears that several EOs will become the focus of more rigorous assessment in mine operations in the near future. These EOs include but are not limited to arsenic, molybdenum and selenium. The drivers for additional scrutiny include a recent ten-fold decrease in the CCME water quality guideline for arsenic, together with $\mu\text{g/L}$ level regulatory limits for molybdenum and selenium in addition to concerns for toxicity to terrestrial organisms. Arsenic, and likely other EOs, has legacy issues associated with high concentrations in historic wastes as well as elevated levels in lake sediments that can redistribute into surface water as effluent concentration decrease as a result of mitigation measures. Molybdenum concentrations in effluent have been observed in the 1 to 10 mg/L range at several mining operations. These concentrations may not represent a risk to many aquatic environments, but may be considered to significantly impact terrestrial organisms, especially small mammals and ruminants. Selenium has a CCME guideline concentration of 0.001 mg/L that may be exceeded in the downstream environment at some mining operations. In addition to the concern for protecting aquatic life, selenium can be toxic to waterfowl at relatively low intake rates that may be affected by bioaccumulation in aquatic plants and other organisms.

The most common method of treatment for antimony, arsenic, molybdenum and selenium is by addition of ferric sulphate, resulting in a ferric hydroxide sludge. Specific treatment circuits may be needed for each of these chemicals because efficient removal requires specific oxidation states (redox) and pH conditions for each of these EOs. The costs for treatment of neutral drainage are not well defined, but will likely be similar to those associated with lime treatment, and may represent a collective liability to Canadian mines of about \$500 million. The stability of the ferric hydroxide sludge over the long term is not known at this time, and sludge management strategies for this type of water treatment by-product have not been well defined.

7.0 RECOMMENDATIONS

This review has led to the following recommendations.

- Develop tech-transfer and collaboration initiatives and events similar to the arsenic workshop on arsenic. The common aspects of several EOs (arsenic, molybdenum and selenium) suggest that there may be significant benefit in addressing these EOs with a common initiative similar to the workshop on environmental aspects of arsenic in Winnipeg in 2002, sponsored by MAC, NRCan and the mining industry. The Annual British Columbia Mine Reclamation Symposiums have featured molybdenum in 2003 and selenium in 2002 and 2004. It would be beneficial to extend these efforts to national initiatives in order to focus on environmental issues and priority needs for molybdenum and selenium.
- Develop more specific guidelines (or description of experience) for the assessment of metal leaching at neutral pH. These guidelines could build upon those developed in British Columbia (Price, 1997).
- The longer-term stability of sludge produced by ferric sulphate addition should be evaluated. The sludge can contain arsenic, antimony, molybdenum and selenium. The geochemical conditions to maintain stability of ferric sulphate sludge is not as well understood, but basic chemical principles suggest that the ideal conditions would be different from those for long-term stability of lime-based sludge, for example. It is therefore recommended that a guidance document be produced for the management of wastewater treatment sludge to avoid inappropriate management scenarios.
- Develop a guidance document for the management of sludge. The stability of water treatment sludge will likely be related to the process that produced the sludge. There have been efforts to assess the stability of sludge from lime treatment processes (Zinck, 2000), and the results may be adapted to select appropriate (and inappropriate) storage or management options.
- Review the non-aquatic toxicity issues and implications for EOs associated with metal leaching at neutral pH. It is evident that terrestrial effects require site-specific assessment for EOs such as molybdenum and selenium. These assessments are founded on risk-based benchmarks that are not as widely accepted as those for concentrations in water and sediment that have been established for the protection of aquatic life. It is therefore recommended that the terrestrial toxicity benchmarks be reviewed and critically evaluated to determine whether or not specific values are appropriate or may be unnecessarily restrictive for mining operations, and to evaluate the implications of those benchmarks for mitigation of elevated concentrations in effluent.
- Assess the implications of the British Columbia guideline for sulphate that is intended to protect aquatic mosses.

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