

**Source, Attenuation, and Potential Mobility of Arsenic at New
Britannia Mine, Snow Lake, MB**

By

Stephanie J. Simpson

A Thesis submitted to the Faculty of Graduate Studies of
The University of Manitoba
in partial fulfilment of the requirements of the degree of

MASTER OF SCIENCE



Department of Geological Sciences

University of Manitoba

Winnipeg

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ABSTRACT

Concentrations of arsenic, averaging 17 ppm, are present in groundwater below a tailings disposal area, down gradient from an arsenopyrite residue stockpile (ARS) containing pore water concentrations of 100 ppm arsenic at New Britannia Mine (NBM), Snow Lake, Manitoba. Hydrogeological modeling illustrates arsenic contaminated groundwater will continue to percolate through the base of the ARS and into the local aquifer so long as there is a source concentration. Geochemical distribution of arsenic in surface and pore water (< 8.7 and 9.0 ppm), solids (< 17800 ppm), and plants (< 13600 ppm) along a flow path from the mine to Snow Lake are above Canadian guidelines. Safe levels of arsenic were measured in Snow Lake. Mineralogical investigations of solids by SEM, EMPA, and μ -XRD show arsenic bound to secondary hydrous ferric oxides. Both dissolved and solid phase arsenic are mobile. Arsenic reducing bacteria thrive, thereby enhancing the conversion of arsenic to its more mobile and toxic form. Future monitoring and remediation recommendations for NBM are provided.

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Chapter 1

INTRODUCTION

1.1 Introduction

Elevated concentrations of arsenic are present in the ground water at New Britannia Gold Mine (NBM), Snow Lake, Manitoba, Canada. Between 1995 and 2005, ground water samples from a monitoring well show anomalously high arsenic concentrations, with an average of 17 ppm (mg/L). This monitoring well 17 (MW17) is installed into an aquifer below a low-lying former emergency tailings disposal area. MW17 is also 100 m down gradient from an arsenopyrite residue stockpile (ARS) that contains pore water concentrations of < 100 ppm arsenic (Salzsauler, 2005). Between 1949 and 1958, the Nor-Acme Gold Mine piped 227 000 tonnes of cyanide-treated, refractory gold-bearing sulphide concentrate, (with a grade of 9.60 g / tonne gold) into a rock-walled impoundment. The hope was to eventually acquire a safe and economical means of extracting the precious metal from the mine waste. The ARS remained uncovered for 50 years, during which time, surface runoff containing concentrated arsenic drained north into a low-lying area. In the late 1990's, a cover was placed on the ARS to inhibit sulphide oxidation and prevent further surface runoff. Arsenic is now suspected to be leaching through the base of the ARS into the local underlying aquifer.

The maximum acceptable concentration (MAC) of arsenic in drinking water, according to Health Canada's Canadian Drinking Water Quality Guideline, is 0.025 mg/L (Health Canada, 2004) and according to the World Health Organization is 0.001 mg/L. Arsenic

is toxic and mobile under typical surface and ground water conditions (pH 5-9). Snow Lake is approximately 500 m from the mine and provides drinking water as well as a recreation site for the population of the town of Snow Lake.

1.1.1 Objectives

1. To determine the potential for contamination of Snow Lake and the local environment;
2. To identify the source of arsenic in the ground water at MW17
3. To measure the distribution of arsenic in surface and pore water, sediments and soil, and plants along the flow path from the mine towards Snow Lake.
4. To identify the mechanisms by which arsenic is attenuated in the environment at NBM.
5. To identify the potential mechanisms for mobility of arsenic from the mine site.

1.2 Arsenic

1.2.1 Toxicity

Arsenic poisons living organisms by inducing cell transformation and altering the regulation of cell replication (Cervantes et al., 1994). It is carcinogenic, mutagenic, and teratogenic (affecting embryo or fetus) (Plant et al. 2004). It enters the body mainly through ingestion and inhalation, but can also be absorbed through the skin (Le, 2002). It is readily absorbed through the gastrointestinal tract and carried by the bloodstream to the organs. Arsenic combines with thiol groups and substitutes for phosphorous, thereby interfering with mitochondrial oxidative phosphorylation and consequently adenosine triphosphate synthesis (Stolz and Oremland, 1999, Ehrlich, 2002). Essentially, arsenic

breaks down the fundamental functioning cells in the organs (Roy and Saha, 2002). Ingestion of a large dose of arsenic can be fatal, but even slow accumulation of repeated small doses of arsenic over a long period of time can lead to diabetes, cardiovascular and neurological disorders, cancers of the organs and skin, and eventually death.

In higher organisms, arsenic is methylated to less toxic derivatives in the liver and excreted via urine. In the recent studies of arsenic contaminated aquifers around the world (e.g. Bangladesh), one main concern is that symptoms from chronic exposure to low doses are delayed at least five years (Roy and Saha, 2002).

1.2.2 Speciation

Arsenic is toxic to life forms in very low doses and is soluble under a wide range of pH and Eh conditions rendering it mobile in nearly every natural environment. Arsenic can exist in several different oxidation states, including 3-, 1-, 0, 3+, and 5+, and forms both organic and inorganic compounds (Plant et al., 2002). Arsenic speciation depends on the pH and Eh (redox potential) of its environment. Native arsenic (As^0) is rare in nature since it is only stable under strongly reducing conditions. As(-I) forms common minerals such as arsenopyrite (FeAsS). Trivalent arsenite (As(III)) and pentavalent arsenate (As(V)) are the most common inorganic arsenic oxidation states in natural waters and soils. They are generally found together over a range of pH conditions and are easily interconverted (Francesconi and Kuehnelt, 2002).

Arsenate is the dominant inorganic form under oxidizing conditions and under all but strongly reducing conditions, therefore, this is the major arsenical found in freshwater environments, aquifers, soils, and sediments. Arsenite is the dominant stable inorganic form under reducing conditions (O'Day, 2006). It is much more soluble and mobile, and

50 to 100 times more toxic than arsenate (Plant et al., 2004). From pH 7 – 12 arsenate will occur as HAsO_4^{2-} , while under more acidic conditions (pH 2 – 7) arsenate occurs as H_2AsO_4^- and at pH < 2 as H_3AsO_4 (Inskeep et al., 2002) (Figure 1.1). Less oxidized environments can also contain arsenite as H_3AsO_3 , which is stable at pH < 9.3. When pH drops below 4 and the system is sufficiently reduced, arsenite will convert to arsine gas (H_3As^3-) (Bentley and Chasteen, 2002).

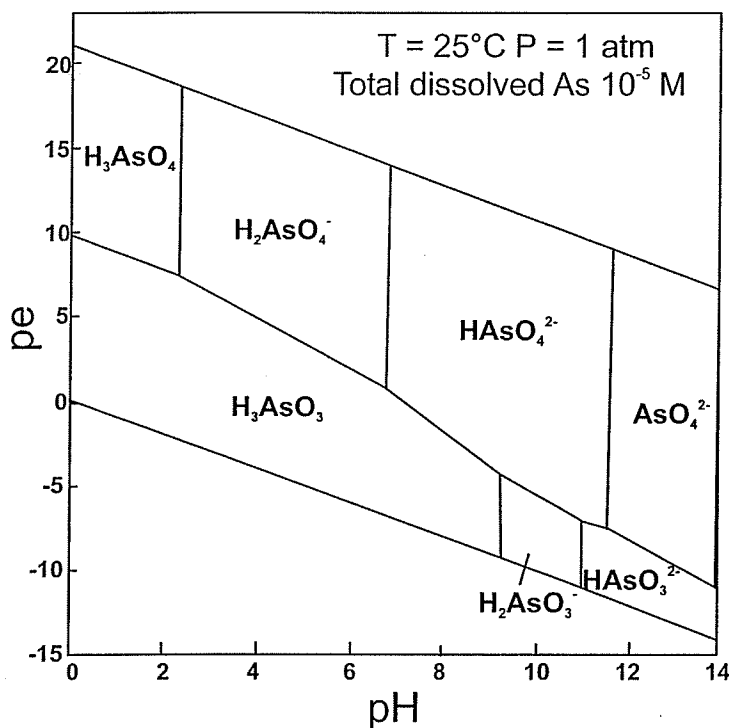


Figure 1.1 Eh – pH diagram for arsenic (after Cherry et al., 1979)

Arsenic participates in covalent bonding as it has an excess of electrons in its outer *p* orbital (O’Day, 2006). It bonds to a variety of ligands, which in turn strongly influences its chemical behaviour. Arsenic binds most commonly to oxygen in nature to form oxyanions. Arsenite ($\text{As}^{\text{III}}(\text{OH})_3$) forms a tetrahedron that consists of three simple (monodentate) oxygen ligands and a lone electron pair in the fourth arm. Spectroscopic

analysis shows that this pyramidal structure is retained in solution (Figure 1.2). Arsenate ($\text{H}_3\text{As}^{\text{V}}\text{O}_4$) and its more common form $[\text{As}^{\text{V}}\text{O}_4^{3-}]$, form tetrahedral comprising three monodentate oxygen ligands and a fourth bidentate oxygen ligand.

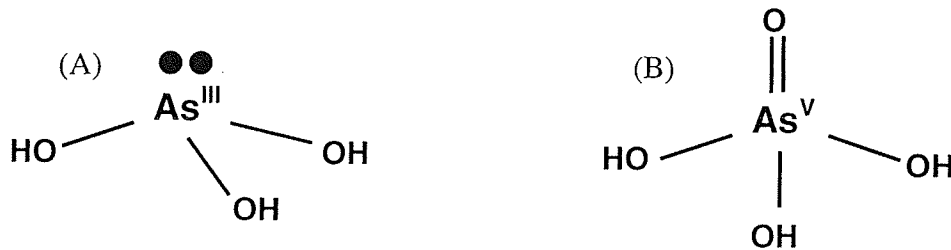


Figure 1.2 (A) Arsenite and (B) arsenate oxyanions

1.3 Sources and Distribution of Arsenic

The exploitation of gold deposits associated with complex sulphide mining and the attendant oxidation of arsenic-bearing ore minerals has been identified as a cause of contamination of surface drainage and ground water in several countries (Thornton 1994; Williams and Smith 1994; Williams et al, 1996; Smidley and Kinniburgh, 2001).

Three major factors controlling the concentration of arsenic in the environments are (1) the source of arsenic, (2) its solubility and attenuation, and (3) its subsequent transportation and distribution (Smedley and Kinniburgh, 2002). Natural sources of arsenic, for example the geothermally produced arsenic contamination of Mono Lake, California, are commonly more widespread than anthropogenic sources, such as mining, where arsenic tends to be more localized around the contaminant source.

1.3.1 Arsenic in the Environment

The greatest range and highest concentrations of arsenic are found in ground water, soil solutions and sediment pore water because these environments have high solid / solution ratios. Arsenic also occurs as adsorbed species on secondary minerals, notably Fe, Al, and Mn oxides (Smedley and Kinniburgh, 2002). Concentration of arsenic in most ground water is <10 µg/L. Variations in redox conditions can produce large disparities in As(III)/As(V) ratios (Plant et al., 2004, Smedley and Kinniburgh, 2002). Ground water contamination is largely affected by aquifer recharge rates. In closed basins, where aquifers are confined, or under low hydraulic gradients, ground water flow is relatively slow with minimal recharge, resulting in the accumulation of contaminants. Where there is a greater ground water flow, arsenic released into solution can be transported into a different environment.

Concentration of arsenic in lakes and river water is generally relatively low, with baseline values of <1 µg/L in Canada (Smedley and Kinniburgh, 2002). Arsenic levels in stratified lakes may increase with depth reaching a maximum at the sediment-water interface due to changes in redox conditions through the water column. While surface waters are oxygenated, dissolved oxygen content decreases with depth and lake bottom water is more reduced. When arsenic enters a water body, it either cycles through the surface water or binds to particles, particularly FeO(OH), and sinks through the water column to accumulate in the sediments (Newman et al., 1998).

In some parts of Canada, such as Yellowknife, NWT, where mineral deposits are rich in arsenic, naturally occurring levels of arsenic in soils can reach 1500 ppm (Health Canada, 2004). Mine-tailings areas can reach concentrations well above this level. The most

common arsenic oxidation state in soils, including mine tailings, is As(V). Increased soil pH by the addition of lime (a common practice applied to mine tailings to inhibit the production of acid mine drainage) minimizes the mobility of heavy metals such as Cu, Zn, Cd, and Pb. However, high pH levels have an opposite effect on arsenic (Inskeep et al., 2002). For example, a soil pH above 8 increases the mobility of As(V) from the soil.

1.4 Solubility and Attenuation

Solubility, attenuation and mobilization of arsenic, is influenced by interrelated geochemical conditions including Eh, pH, competing organic and inorganic species in solution, and the nature of available surface substrates. Microbial activity additionally induces and enhances these properties and associated reactions.

There are several ways in which arsenic can be taken out of solution and be immobilized. Arsenic can precipitate or co-precipitate with secondary arsenate salts, although these are generally too soluble to control the activity of As(V) in soils and natural waters (Inskeep et al., 2002). The activity of arsenate is more commonly controlled by surface complexation reactions on inorganic surfaces such as Mn, Al, and Fe(III) oxides and hydroxides, clays, or on organic matter including live roots and decomposed plant litter. Arsenite is more selective having a strong preference for Fe oxides and hydrous ferric oxides (HFO) such as ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) and goethite (FeOOH). HFO are forms of Fe oxide with high surface areas that often form in response to rapid changes in pH. Both arsenite and arsenate have a strong adsorption capacity for HFO over a wide range of pH. Both inorganic oxidation state also have their greatest adsorption potential on HFO at neutral pH (6-8) (Figure 1.3). However, arsenite has a strong adsorption potential under more alkaline pH conditions, whereas the adsorption potential of arsenate increases

continually with decreasing pH. Other oxyanions, such as phosphate (PO_4) can compete with, and displace, adsorbed arsenate oxyanions and minor amounts of arsenite.

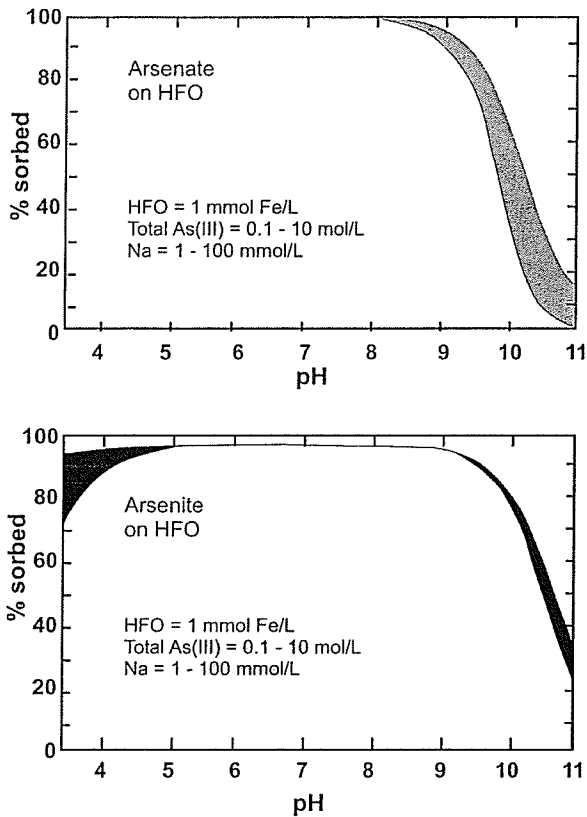


Figure 1.3 Sorption curves for arsenate and arsenite showing sorption potential on hydrous ferric oxides (HFO) depending on pH (modified from Inskeep et al., 2002).

The localized pollution at mine sites is not surprising since it takes very little dissolved arsenic to cause contamination of an aqueous body. Unlike metal cations, oxyanions, such as arsenate, tend to desorb from Fe, Al, and Mn oxides when the pH of the system increases (Figure 3.1). A change from oxidizing to more reducing conditions can also lead to arsenic desorption, generally in direct response to changes in the oxidation state of the arsenic (Figure 1.1), but also indirectly by changes in the structural components, surface properties and the partial dissolution of oxide minerals on which arsenic is sorbed (Smedley and Kinniburgh, 2002). For example, under reducing conditions and in the

presence of excess hydrous ferric oxides, dissimilatory reduction of Fe(III) to its more soluble form, Fe(II), can result in the dissolution of iron arsenates such as scorodite (FeAsO₄·2H₂O) or ferric iron oxides containing arsenic, subsequently releasing As(V) into solution (Cumming et al., 1999). This process is an important source of arsenic contamination in natural waters (Inskeep et al., 2002).

1.5 Geochemistry of Snow Lake Gold Mine Waste

The geochemistry of mine waste is complex as there are simultaneous reactions generating acid, consuming acid, and forming simple and complex stable and unstable secondary phases, all of which are dependent on several conditional parameters.

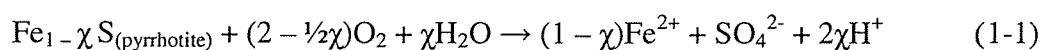
1.5.1 Dissolution of Primary Minerals

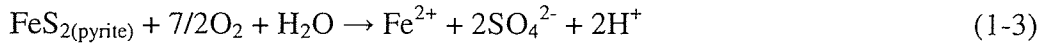
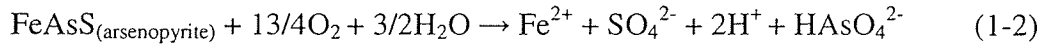
The gold mineralization at Snow Lake is associated with arsenopyrite, pyrite, and pyrrhotite, all of which are susceptible to oxidation and consequent release of H⁺ and arsenic into solution. The weathering rate of sulphides depends on the pH, Eh, grain size (related to exposed surface area), temperature, dominant oxidant in the system (O₂ and/or Fe(III)) and microbial activity (Blowes and Ptacek, 2005). The relative rate of abiotic sulphide weathering for these tailings (in order of decreasing reactivity) is:

pyrrhotite > arsenopyrite and pyrite (Jambor, 1994)

The environment of tailings waste following beneficiation tends to be favourable for sulphide dissociation due to the fine grain size and wet oxidizing conditions.

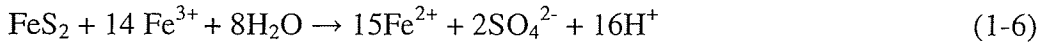
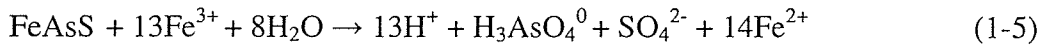
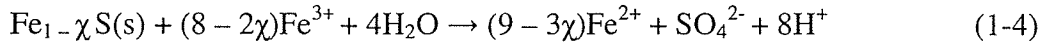
The dissolution of pyrrhotite, arsenopyrite and pyrite, respectively, under neutral conditions when oxygen is the main oxidant are:





(Blowes et al., 2003)

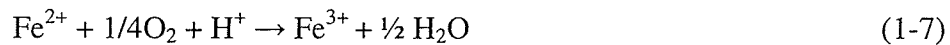
The dissolution of the same sulphides when ferric iron is the dominant oxidant are:



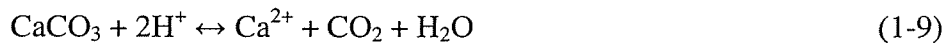
(Blowes et al., 2003)

The oxidation and dissociation of pyrite produces 2 moles of H^+ for every mole of pyrite oxidized when O_2 is the oxidant and 16 moles H^+ when Fe(III) is the oxidant. The predominant oxidant depends on the pH of the system as well as the availability of oxygen and ferric iron.

Following the dissociation of sulphides, Fe(II) can oxidize to Fe(III) and subsequently precipitate various, pH dependent, forms of iron oxyhydroxide on the pyrite surface (Blowes and Ptacek, 2003) according to:



As sulphides weather and the pH of the system drops, dissolution of carbonates consumes H^+ thus maintaining a neutral pH pore water. Under low pH, dissolution of 1 mole of calcite will consume 2 moles of H^+ according to the reaction (Blowes and Ptacek, 2005):



Under more neutral conditions (pH 6.5 – 7.5), the reaction follows the path:



At NBM much of the gold is found in carbonate-bearing veins so that the carbonate content of the tailings is greater than the sulphide concentration. Therefore, dissolution of carbonates neutralizes acid generated.