

# Arsenic mobility from arsenopyrite-rich gold mine waste, Snow Lake, Manitoba, Canada

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**ABSTRACT:** High concentrations of arsenic occur in one groundwater monitoring well (MW17) at the gold mine site in Snow Lake Manitoba. The likely source of As is an Arsenopyrite Residue Stockpile (ARS) containing arsenopyrite concentrate, which was capped in 2000. Another possible source is the emergency discharge area for Nor Acme tailings, through which MW 17 is drilled.

Pore water in the unoxidized zone of the ARS contains up to 100 mg/L total arsenic (<25 mg/L As (III)) possibly remobilized from secondary phases, amorphous iron sulfo-arsenates, scorodite and jarosite formed prior to capping by oxidation of primary sulfide minerals. Hydrological modeling suggests that As is transported into the aquifer from the ARS by advection and diffusion. The concentration of arsenic in other monitoring wells within the aquifer in the vicinity of the ARS and the Nor Acme tailings is <0.1 mg/L, and in the pore water of the tailings <5 mg/L. This indicates that the tailings are unlikely to be the source of the contamination. Attenuation of As in surface waters appears to be adsorption of As(V) on Fe-oxyhydroxides such as ferrihydrite, but in the aquifer, the majority of the As is the more soluble As(III). Snow Lake, the source of drinking water for the town of Snow Lake has very low concentrations of As.

## 1. INTRODUCTION

Mining and beneficiation of ore deposits, where gold is associated with arsenopyrite produces arsenic-rich mine wastes. Oxidation of sulfides can result in the mobilization and migration of arsenic from these wastes into the environment (Roussel et al., 1998; Langmuir et al., 1999; Shuvaeva et al., 2000).

The objective of this project was to find the source and pathways of the As contamination in the Snow Lake region. The project was initiated because As concentrations average 17 mg/L in one groundwater monitoring well (MW17, Fig. 1). One potential source of this As is the 50 year old Arsenopyrite Residue Stockpile (ARS) containing arsenopyrite concentrate stored in an open waste rock impoundment. In 2000, the ARS was capped with layers of waste rock, clay and silt. Another potential source is the Nor Acme tailings area (NATA), through which MW 17 is drilled.

## 2. SITE DESCRIPTION

The Nor-Acme Gold Mine operated in Snow Lake, Manitoba (Canada), 1948-1959. The mine is in the Paleoproterozoic Flin Flon-Snow Lake greenstone belt (Richardson and Ostry, 1996). The ore assemblage of quartz-carbonate veins contains free gold overgrowing and refractory gold inside arsenopyrite, pyrrhotite, pyrite, and chalcopyrite (Fulton, 1999).

Accessible gold was dissolved by cyanidation of sulfide concentrate from a flotation circuit. Sulfide waste still contained 0.28 oz/ton of refractory gold. From 1948-1959, 250,000 ton of sulfide residue was piped into an uncapped waste rock impoundment.

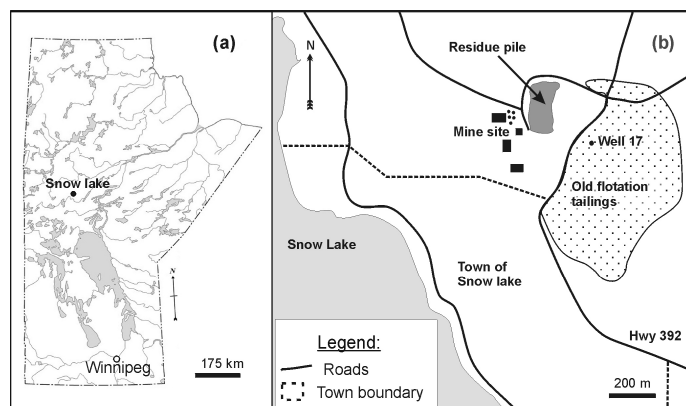


Figure 1: (a) map of Manitoba showing the location of Snow Lake (b) diagram of the mine site showing the ARS, MW17 and the emergency tailings.

In 1995, the Nor-Acme mine reopened as the New Britannia Mine. In 2000, a multilayer cap of waste rock and silt was placed on the pile to prevent water infiltration and contaminated runoff. However, groundwater in a monitoring well south of the ARS still has concentrations of arsenic <40 times greater than the Canadian Mining Metal Effluent Regulation for As release from active mine sites: 0.5 mg/L.

## 3. METHODOLOGY

Solid cores, 6.25 cm in diameter, were extracted from depths of 8.6 to 14.6 m at the ARS using a sonic drill and immediately frozen (Fig.2).

Core samples were also collected from the Nor-Acme tailings and adjacent wetland using 5 cm diameter PVC tubes, with 3m deep samples collected with an auger. Solid material was obtained from the aquifer beneath the Nor Acme Tailings Area (NATA) by filtering water samples from MW17 and collecting the

sediments. In the laboratory, the cores were split while still frozen. Polished thin sections were made in the absence of water to prevent dissolution of soluble phases. Mineral composition was determined using a combination of powder X-ray diffraction (XRD),  $\mu$ XRD, electron microprobe analysis, and scanning electron microscopy with energy dispersive X-ray spectrometry.

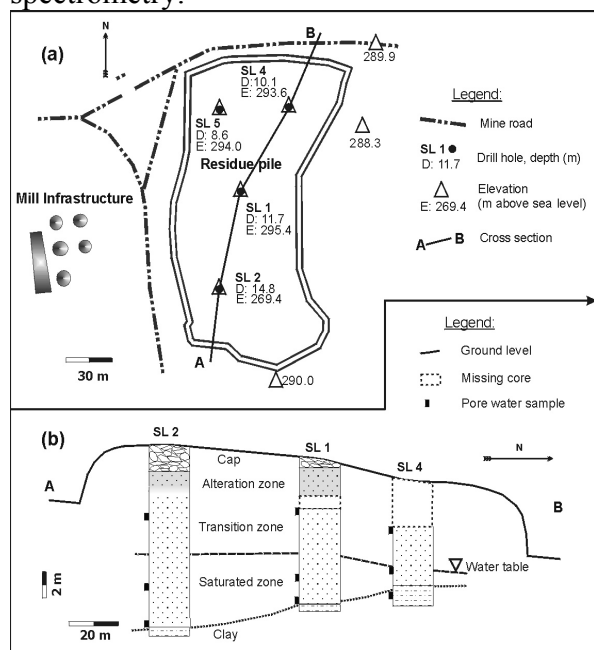


Figure 2: (a) Elevation and location of drill holes in the ARS. (B) Cross section of the ARS from S (drill hole SL2) to N (SL4)

Pore water was extracted from cores by squeezing in a hydraulic press. Ground, surface and lake water samples were filtered (0.2  $\mu$ m filter) in the field and aliquots acidified to preserve cations. Arsenic species were separated on site by passing filtrate through SAX cartridges (Le et al., 2000).

Solid and solution samples were analyzed using a combination of induced neutron activation analysis, infrared spectroscopy and inductively coupled plasma, optical emission and mass spectroscopy.

Phases controlling water composition were assessed with the geochemical modeling program WATEQ4F (Ball and Nordstrom, 1991).

In August of 2004, four 5 cm diameter well pipes with permeable screen units were installed into the NATA to determine static water table elevations and hydraulic conductivity of the tailings. The hydrology of the site was modeled using Geostudio SEEPW.

Live and dead shoots and roots of the common cattail (*Typha latifolia*) and water sedge (*Carex aquatilis*) were collected and analyzed to examine the passage of As into the plants and the food chain.

## 4. RESULTS

### 4.1 ARS

The surface of the ARS drains to the NW but the base of the pile dips south (Fig. 2). The pile is under-

lain by red-brown clayey soil which overlies a sand-gravel aquifer.

*Unoxidized sulfide residue* extends from about 2 m below the top of the residue to the base. This consists of fine-grained anhedral arsenopyrite, pyrrhotite, pyrite and chalcopyrite with quartz, albite, orthoclase, biotite and actinolite. It contains <23 wt % As, 25 wt % Fe and 18 wt % S. Some disintegration of pyrrhotite, pyrite and arsenopyrite was observed, but no secondary phases found.

*Highly altered material*, taken from the top of the pile prior to cap emplacement, consists of hard, gel-like dark yellowish brown amorphous iron sulfo-arsenates (AISA) coating powdery, yellow AISA and powdery, grayish green iron arsenates. It contains <13 wt % As and Fe, and 7 wt % S. No pyrrhotite or chalcopyrite remains but traces of arsenopyrite and pyrite occur as inclusions in secondary AISA, scorodite, and jarosite. Anhedral equant 5  $\mu$ m grains of scorodite are enclosed in AISA cement.

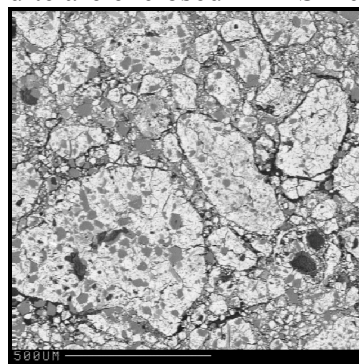


Figure 3: SEM electron backscatter image of AISA "balls" in the alteration zone.

In the *alteration zone* (0-40 cm depth), layers of friable, olive brown and yellow AISA are interbedded with layers of green-grey, slightly altered sulfides. The secondary phases are AISA, scorodite and jarosite, with remnant arsenopyrite, pyrite and chalcopyrite in the green-grey layers. The dominant arsenopyrite alteration products are orange gel-like AISA forming zoned spherules about 500  $\mu$ m in diameter (Fig. 3). A mixture of <60 % primary silicate gangue, and altered sulfide grains cemented by AISA is contained in thick rims (<50  $\mu$ m) of red-brown AISA gel-like material.

The *transition zone* (40 cm to 2 m) is similar to the unoxidized material but mottled with 50 to 300  $\mu$ m, microcrystalline scorodite aggregates, which cement primary silicate and sulfide grains (Fig.4). These have 35 wt % As, 1 wt % S and 25 wt % Fe.

The sequence of precipitation of AISA phases can be inferred by their morphological relationships. The earlier AISA have higher As/S ratios than later.

### 4.2 NATA

The NATA tailings are 97% quartz and 3% sulphides. They contain <1.5 wt% As. Concentrations of As in clay 3 m below NATA is <0.005 ppm but is 0.2ppm in the sediments from the MW17 aquifer.

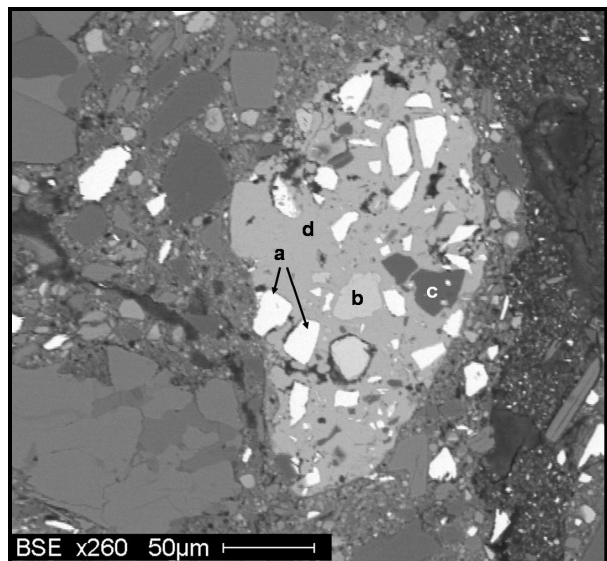


Figure 4: Arsenopyrite (a), pyrite (b), silicate (c) inclusions in a scorodite (d) aggregate in the *transition zone*

### 4.3 Hydrology

The NATA site consists of tailings overlying relatively low permeability clay soil, gravel-sand, and bed-rock units. The water table within the tailings is slightly elevated compared to the aquifer suggesting minimal vertical ground water flow into the aquifer.

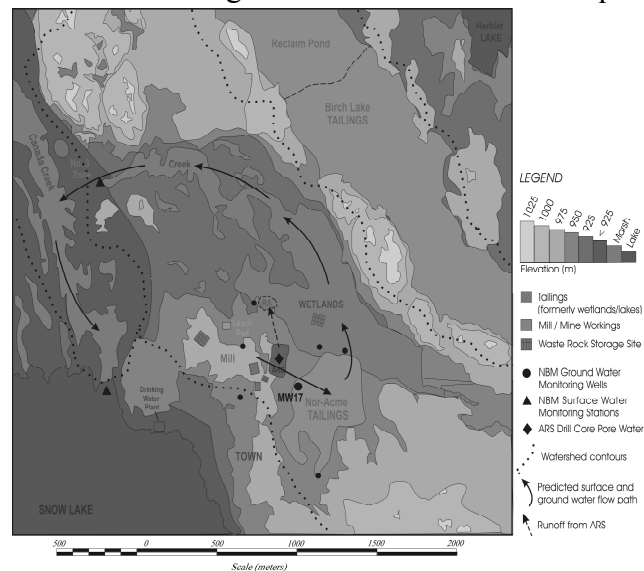


Figure 5: Topographic map of mine showing the drainage path. The water table in the pile is elevated compared the aquifer hydraulic heads which would promote the transport of As from the pile into the aquifer by advection. Given the higher concentration of As in the pile compared to the aquifer, As transport could also occur by diffusion through the clayey soil. Surface and groundwater flow within the Canada Creek watershed is SE from the high level of the mill and ARS to the low lying NATA then north through the wetlands (Fig. 5). This path is based on local topography, core log data, and hydraulic head values for the confined aquifer. Hydraulic heads show groundwater in the Canada Creek watershed flowing in the general direction as surface water.

### 4.4 Aqueous Geochemistry

The NATA groundwater has a neutral pH but the surface water varies from 3 to 8. As concentration at MW17 appears to have decreased from 2004 to 2006 (Fig. 6) New Britannia Mines' (NBM) values are consistently <10 mg/L lower than Salzsauler et al. (2005), Simpson (2007). This may be related to different sampling methods or variation in data incorporated in averages presented per year. As(III) is the predominant species in groundwater at MW17.

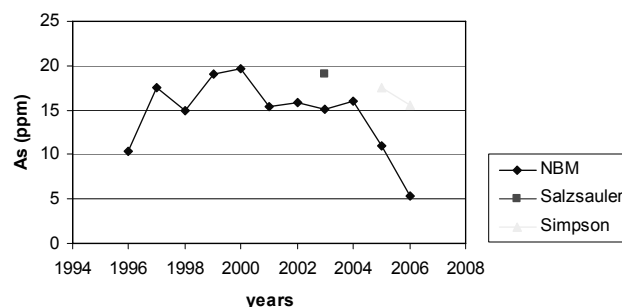


Figure 6: Graph showing total arsenic concentrations in the groundwater at MW17. Data points represent annual averages.

Surface water contains from 1mg/L at the NATA to 11 mg/L As in the region (RA) of the original runoff of the ARS. As concentration in wetlands decreases from NATA towards Snow Lake (Fig. 7), which contains <0.005 mg/L As with 0.016 mg/L at the water sediment interface.

### 4.5 Hydrophytic Plants and Wetland Accumulators

Concentrations of As are significantly greater in the roots of cattails (<1200 mg/L) and sedges (<3000 mg/L) than in shoots probably due to adhering soils and sediments, which contain <6800 mg/L As. Both cattails and sedge plants contain significant As in live (<138 mg/L) and dead (<235 mg/L) shoots. The higher concentration in dead shoots indicates that arsenic is translocated from roots to shoots even after death.

## 5. DISCUSSION

The source of arsenic in the ARS and NATA is arsenopyrite which is stable in low Eh, high pH conditions of the unoxidized residue. Oxidation would have been initiated during deposition of the residue and continued in the ARS for 50 years prior to the emplacement of the cap. During this time As rich runoff would have flowed into the runoff area (RA) where As was concentrated by plant material.

The earliest secondary As phases in the ARS are preserved in the *transition zone*, where aggregates of scorodite cement altered arsenopyrite grains. The enclosure of arsenopyrite would reduce further oxidation. In the uncapped pile, the reaction of arsenate and ferric ions in the pore water causes the precipitation of scorodite. Acid produced during the oxidation of sul-

fides and precipitation of scorodite was initially buffered by the dissolution of carbonate minerals.

With the advancement of sulfide oxidation and the dissolution of available neutralizing phases in the upper zones of the ARS, the pH of pore water would have been reduced. Prior to the emplacement of the cap, the surface water on the pile had a pH of 3 (UMA, 1987). Under these conditions, scorodite becomes stable. Jarosite-group minerals can precipitate at low pH in the presence of high concentrations of Fe(III) and sulfate (Dutrizac & Jambor, 2000). In the neutral pH of the *transition zone*, jarosite should not precipitate. However, jarosite and AISA forming in veins indicates that they might precipitate from solutions percolating from the upper horizons, where pH could have been lower prior to capping. Jarosite can incorporate  $\text{AsO}_4^{3-}$  by the partial replacement of  $\text{SO}_4^{2-}$  in the unit cell (Paktunc & Dutrizac, 2003). In the ARS, jarosite contains up to 6 wt % As.

The precipitation of low-solubility, crystalline scorodite and jarosite is followed by the formation of disordered, more soluble phases such as AISA from late stage, high arsenic and iron solutions. The final product to form is a dehydrated AISA gel coating aggregates of earlier AISA.

With the addition of the waste rock cap, the source of atmospheric oxygen that fueled the precipitation of secondary arsenic phases has been removed. Existing phases such as jarosite, scorodite and AISA are unstable in the present conditions of the pore water in the ARS. The concentration of As, Fe and sulfate in the pore water of the pile is now controlled by the reductive dissolution of residual arsenopyrite and unstable secondary phases to give 100 mg/L in the pore water at the base of the residue pile. Arsenic released from these phases could be only partially absorbed by iron oxyhydroxides stable in the present conditions of pore waters. A combination of these effects may explain the high level of arsenic in pore water towards the base of the residue, which is up to 20 times higher than in the transition zone. The AS leaches from the base of the ARS, transports through the underlying clayey soil, and into the underlying aquifer producing the high concentration in MW17.

From MW17, the ground water flows initially SE beneath the NATA but due to rock outcrops veers N to combine with surface water in the runoff area, NE of the ARS. The sediment in this area has been polluted with As from the surficial runoff from the ARS as well as earlier mining operations. The As in the surface water is then attenuated by Fe(III) oxyhydroxides so that by the time it reaches Snow Lake it is <0.005 mg/L.

## 6. CONCLUSIONS

The process of capping the arsenopyrite residue pile at Snow Lake prevented further oxidation and run off of As rich surface water. However, secondary As phases are now soluble in the reduced environment producing 100 mg/L As in the pore water at the base of the pile that transports into the aquifer and causes high As in the ground water aquifer at MW17. The NorAcme emergency tailings do not significantly contribute to this contamination although As may be mobilized from the earlier runoff from the ARS. As is absorbed by Fe(III) oxyhydroxides prior to discharge to Snow Lake. Plant material is able to concentrate As making it available to the food chain.

## 7. ACKNOWLEDGEMENTS

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