DISTRIBUTION OF AS, NI AND CO IN TAILINGS AND SURFACE WATERS IN THE COBALT AREA, ONTARIO

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Abstract: From 1904 until the mid 1930’s and intermittently until 1989, over 450 million troy ounces of silver was mined from the Cobalt area, Ontario. Currently there is no active mining of silver, but the area has seen recent exploration activities for other commodities such as diamonds. Cobalt, however, has not only a renowned mining history, but also an environmental legacy. The area is characterized by remnant historic mine workings and numerous waste rock piles and tailings ponds. Several elements of concern including arsenic, nickel and cobalt continually enter the local watershed from the tailings and waste rock piles. These elements are transported through surface waters to the wetlands in the Farr Creek drainage basin and ultimately enter Lake Timiskaming.

Tailings samples are composed of abundant plagioclase with subordinate quartz, chlorite, calcite and dolomite. Less common are K-feldspar, amphibole and mica as well as trace minerals such as erythrite, scorodite and pharmocolite. When efflorescent mineral crusts form on tailings surfaces they are dominated by either gypsum or thenardite. The tailings may contain up to 3.5 wt % Co and 2.2 wt% Ni. Lake sediment and tailings cores show concentrations up to 1.8 wt% As, 0.62 wt% Co and 0.27 wt% Ni in the solids, and 160 mg/L As, 74 mg/L Co and 42 mg/L Ni in the pore waters. One core collected from the infilled Hebert Pond situated within the Nipissing Low Grade Mill tailings impoundment show pore water concentrations in excess of 1,500 mg/L As associated with an organic-rich layer. The concentrations of these elements sustain significant aqueous transport through the drainage basin as tailings are continually weathered, eroded or leached. Surface waters contain up to 20 mg/L dissolved As which decreases downstream through the wetlands with a mean annual discharge of over 10,000 kg to Lake Timiskaming.

Key Words: arsenic, attenuation, wetlands, secondary minerals, efflorescence, erythrite, scorodite, thenardite

Introduction

In 1903 the discovery of silver by Fred LaRose led to the beginning of the “silver rush” in the Cobalt area of Ontario. Silver was continuously mined from 1904 to the mid 1930s and then intermittently until 1989. According to Petruk et al. (1971) more than 450 million troy ounces (12.8 x 10^6 kg) of silver were mined from the Cobalt area deposits by 1971. Today, the historic town located in the heart of the District of Timiskaming (Fig.1) is known for its Heritage Silver Trail and Mining Museum. In addition, SMC (Canada) Ltd., a subsidiary of Sabin Metal Corporation of East Hampton, NY (Meyer et al., 2003)

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recovers precious metals from recyclable materials such as waste electronic and microelectronic equipment, jewellery, photographic and X-ray film, slag, crucibles and refractory brick at the McAlpine mill. Current exploration in the region is focused on diamonds and base metals.

Historically, silver was recovered by flotation separation, cyanide dissolution and Hg pan amalgamation in the 18 mills operating in the area. Surface and sub-aqueous tailings disposal was unplanned and generally proximal to the mills. In 1910, Sasaginaga Lake was established as the town reservoir to provide clean drinking water following an outbreak of typhoid (Angus and Griffin, 1996). Today, numerous tailings deposits, waste rock dumps and mine workings are testimony to the extent of the early mining activity in the region (Fig. 1). Mitigation efforts have been limited to fencing obvious mine hazards (shafts, pits and some mill foundations), reprocessing tailings from some of the tailings deposits, and revegetation efforts on at least two major tailings deposits: the Nipissing Low Grade Mill Tailings (NLGM) and Cart Lake.

The purpose of this paper is to summarize the results of water and tailings geochemistry from the different sampling campaigns carried out during the 1990s. It shows how As is mobilized and transported in the surficial environment from the various tailings sites through wetlands of the Farr Creek drainage basin which drains into Lake Timiskaming. Dumaresq (1993) estimated about 18,000 kg of As are discharged to the lake annually. Detailed mineralogy will also show how metals and metalloids are distributed within the tailings sites in the Cobalt area.
**General Geology**

The Cobalt area consists of Archean volcanic and sedimentary rocks unconformably overlain by Proterozoic sediments of the Cobalt Group. The Cobalt Group consists of the Gowganda and Lorrain Formations. The oldest unit, the Coleman Member of the Gowganda Formation, is composed of conglomerate, greywacke, quartzite and arkose. The Coleman Member is overlain by argillite of the Firstbrook Member and both are overlain by arkose and quartzite of the Lorrain Formation. All units are cut by early Proterozoic Nipissing diabase (Boyle, 1968; Jambor, 1971), with which the Ag-Co-Ni-As deposits are spatially associated.

Native Ag occurs in veins associated with arsenides, sulfarsenides and sulfides such as nickeline (niccolite), cobaltite, safflorite, löllingite, rammelsbergite, gersdorfitite, skutterudite, arsenopyrite, tetrahedrite, chalcopyrite, bornite, galena, sphalerite, pyrite and marcasite (Petruck, 1971a,b). Gangue minerals include calcite, dolomite, quartz and chlorite. Oxidation of the primary ore minerals produces secondary minerals, in particular, erythrite, annabergite and scorodite. Sulphates (e.g., gypsum and thenardite), Fe and Mn oxides and oxyhydroxides also occur as well as clay minerals (Boyle and Dass, 1971; Percival et al., 2004).

**Sample Sites and Methods of Analyses**

Tailings and water samples were collected from the Farr Creek drainage basin over several sampling campaigns. Tailings samples were collected as grab samples and by hand-coring (Percival et al., 2004). Samples collected were homogenized and ball milled to about -200 mesh prior to their analysis. Major and trace elements were determined by a combination of methods including X-ray fluorescence (XRF), and inductively-coupled atomic emission spectroscopy (ICP-AES) and inductively-coupled mass spectrometry (ICP-MS) following total dissolution (HF-HCl-HNO₃-HClO₄). Subsamples were further processed for X-ray diffraction (XRD) analysis.

Semi-quantitative mineralogy of bulk tailings and clay-size separates were determined using a Philips PW1710 automated powder diffractometer equipped with a graphite monochromater and Co Kα radiation set at 40 kV and 30 mA; See Percival et al. (2001) for analytical details. A Leica Cambridge Stereoscan S360 scanning electron microscope (SEM) was used to examine polished thin sections and grain mounts of the tailings. The SEM was operated at an accelerating voltage of 20kV.

Surface water samples were collected in June to October 1991, May 1992, July and September 1994, May 1995 and September, 1997 with follow-up surveys near the confluence of the Farr and Mill creeks by Kwong et al. (2007) in May 2002 and 2003. Sample stations are shown in Figure 2 for the 1990s samples and numbered consecutively from SW to the NE in the direction of drainage. The physical properties of the 1990s samples were detailed in Percival et al. (1996, 2004) and those of the 2002-03 samples in Kwong et al. (2007). Multiple water samples from each site were filtered in the field through a 0.45 µm Millipore filter paper (type HAWP). One sample was acidified to 0.4% with HNO₃ (Seastar double sub-boiling distilled) for cation determinations, one to 0.4% with HCl (Merck Suprapur) for As speciation study, and one untreated for anion determinations. Major and trace elements were determined on the HNO₃-treated sample by ICP-AES and ICP-MS (note that for water analysis "total" in this paper implies total "dissolved"; i.e., through 0.45 µm filter). Anions were determined using a Dionex ion chromatograph. Porewaters from lake sediments were extracted using high-speed centrifugation and aliquots analysed as indicated above. All analyses were carried out at the Geological Survey of Canada.
Results & Discussion

Tailings and Lake Sediments

Tailings samples were collected from the Nipissing Low Grade (NLGM) and High Grade (NHGM) Mill sites, Cart Lake, Crosswise Lake, Peterson Lake, Mill Creek, Farr Creek and the Bucke Park campground (Fig. 2). The NLGM site was sampled prior to revegetation efforts (Fig. 3); the tailings cover about 60,000 m² and fully enclose the marshy area known as Hebert Pond (Dumaresq, 1993). Samples were collected above and below the main cribwork (central area of Fig. 3A) and include samples from two small hand dug pits (< 60 cm deep). Surface salt crusts were collected above the cribwork.
In a related study, 4.5 m-long cores were collected from the site of the former Hebert Pond for detailed mineralogical and chemical characterisation (Andrews, 1996; Stoddart, 1996). For complete results see Percival et al. (2004). The mineralogy of the tailings samples from all sites is similar. Bulk samples contain abundant plagioclase with subordinate quartz, chlorite, calcite and dolomite. Less common are K-feldspar, amphibole and illite/mica. Secondary arsenates such as erythrite ($\text{Co}_3(\text{AsO}_4)_2\cdot8\text{H}_2\text{O}$) and annabergite ($\text{Ni}_3(\text{AsO}_4)_2\cdot8\text{H}_2\text{O}$) occur as well as trace amounts of mixed-layer clay minerals. In the clay size fraction, chlorite is abundant and quartz, plagioclase and illite/mica generally occur in minor amounts.

Surface crusts collected from the NLGM tailings surface ranged in colour from white to yellow, although Andrews (1996) reported the presence of grey to brown crusts as well. The crusts often contain gypsum ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$) or thenardite ($\text{Na}_2\text{SO}_4$) and are formed by efflorescence during dry seasons. Dumaresq (1993) reported that these salt crusts tended to be enriched in Ni, Co and As contents relative to the tailings. Furthermore, they readily dissolve during rainy periods and redistribute through surface runoff, or can be subjected to wind transport. Current revegetation efforts will mitigate this chronic problem.

In an area to the east of the present-day lookout tower on the Heritage Silver Trail, adjacent to the NHGM site, a small waste material pile was observed and contained primary sulphide minerals including pyrite as well as gypsum and jarosite. Kwong et al. (2000) reported that minor amounts of chalcopyrite ($\text{CuFeS}_2$), bornite ($\text{Cu}_9\text{FeS}_8$), galena ($\text{PbS}$), sphalerite ($\text{ZnS}$) and pyrite ($\text{FeS}_2$) occur in tailings. They also noted that erythrite with minor annabergite was observed only in unsaturated tailings and scorodite ($\text{FeAsO}_4\cdot2\text{H}_2\text{O}$) in both saturated and unsaturated tailings.

A pile of material of unknown origin, possibly concentrate, ore or furnace residue, was found adjacent to the lookout tower on Nipissing Hill (Fig. 4A). This material was well weathered and is referred here as “furnace residue”. The material contains pink and white efflorescent blooms, similar to the efflorescent crusts formed on the tailings surface. The pink bloom contains erythrite, a secondary arsenate formed by the alteration of cobaltite ($\text{CoAsS}$). The minerals present in the white bloom include gypsum, pharmacolite ($\text{CaHAsO}_4\cdot2\text{H}_2\text{O}$) and weilite ($\text{CaHAsO}_4$) based on Debye-Sherrer powder diffraction and SEM analyses, as well as brassite ($\text{MgHAsO}_4\cdot4\text{H}_2\text{O}$) (Fig. 4B) based on XRD and SEM analyses. This is the first known occurrence of brassite in Canada.
Figure 4: A) Furnace residue (?) pile found near lookout tower at NHGM site showing efflorescence (white (brassite) and pink (erythrite) blooms); B) SEM photomicrograph of brassite.

The chemical composition of the tailings reflects their bulk mineralogy. Samples contain, on average, 57% silica, 15% alumina and 8% total iron by weight. The concentrations of Ca, Mg, Na and K reflect the presence of calcite, dolomite, plagioclase feldspar and mica. The mean total S content is 0.15 wt%. The trace elements Co, Cu and Ni dominate the tailings (note As determinations were not made on these tailings samples) with mean concentrations of 1170, 425 and 645 ppm, respectively (Table 1). Dumaresq (1993) reported mean As concentrations in the NLGM tailings as 4200 ppm. Silver can be found in concentrations up to 220 ppm with a mean value of 77 ppm. Concentrations of Ag, Co and Ni in the sulphide pile and furnace residue, however, range from 600 to 1500 ppm, 500 to 35,000 ppm and 400 to 22,000 ppm, respectively, providing strong evidence that these accumulations comprise ore concentrates.

The lake sediment cores taken from Cobalt Lake, Mill Creek and Farr Creek have mineralogy and major element chemistry similar to that of the tailings. They also have similar physical characteristics, except they are covered by a thin veneer of organic matter. The trace element chemistry differs between Cobalt Lake and the creek samples (Table 1). Concentrations in the Cobalt Lake cores are variable for Ag (24-170 ppm), As (306-8380 ppm), Co (240-4,100 ppm), Cu (240-1,200 ppm) and Ni (170-2,200 ppm). Cores from the Mill and Farr Creeks generally contain lower concentrations of trace elements except for Ag such that mean concentrations are 108 ppm Ag, 1,212 ppm As, 378 ppm Co, 423 ppm Cu and 1,185 ppm Ni, respectively. Cores collected from the NHGM drainage area (close to Cobalt Lake) contain up to 2 ppm Ag, 18,400 ppm As, 7,400 ppm Co, 2,500 ppm Cu and 3,800 ppm Ni. The lake core samples collected near the outlet of this “high grade” drainage contain minor amounts of erythrite; this mineral was not detected in the other lake cores.

**Pore Waters**

Arsenic, Co and Ni concentrations in the lake sediment porewaters are greater than those of the overlying water, suggesting a potential efflux of the trace elements from the submerged tailings to the overlying water by diffusion under a chemical gradient (there may also be a groundwater component). Thus, the tailings in the lake may act as a source of these elements to the overlying water column. With few exceptions, As concentrations are greater than those of dissolved Co and Ni by an order of magnitude, especially in lake water. There also appears to be a concentration maximum for all of these elements in porewaters close to the water-sediment (tailings) interface (Percival et al., 2004).
Table 1: Mean concentrations of selected trace elements in solid samples from the Cobalt area (after Percival et al., 2004). Tailings samples include surface samples collected from the NHGM site. All values given in ppm (ICP-MS results).

<table>
<thead>
<tr>
<th>Element</th>
<th>Tailings (n=29)</th>
<th>Lake Cores (n=27)</th>
<th>Creek Cores (n=15)</th>
<th>NLGM cores (n=7)</th>
<th>NHGM cores (n=10)</th>
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<td>108</td>
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<td>2200</td>
<td>360</td>
<td>1460</td>
<td>3810</td>
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</table>

* na= not analysed

Porewater in cores collected from the NLGM tailings at the former Hebert Pond contains dissolved As ranging from 63 to 1,570 mg/L, Co ranging from 1 to 44 mg/L and Ni ranging from 0.13 to 85 mg/L (Andrews, 1996). These values are intermediate between those of the low-grade tailings upstream of the lower dam and submerged tailings in Cobalt Lake and the Mill-Farr Creek wetland area. In contrast to profiles observed in submerged (i.e., lake sediment) tailings, however, porewater concentrations of As, Co and Ni increase with depth in the Hebert pond tailings.

**Surface Waters**

All surface waters are alkaline with an average pH of 7.7, and are oxygenated (Eh from +200 to +444 mV) with dissolved oxygen levels at or near saturation (average 8.7 mg/L at about 23 °C). Conductivity is relatively high (average 308 µS/cm) with peak values in drainage from exposed tailings. Groundwaters are also alkaline (mean pH 7.4) but with higher conductivities (mean 457 µS/cm) and lower Eh (+138 to +154 mV) than surface waters (Percival et al., 1996). These results are similar to those reported by Boyle and Dass (1971).

Arsenic concentrations of surface water samples collected during the 1990s from the Cobalt region exceed the Guideline for Canadian Drinking Water Quality of 10 µg/L (Health Canada, 2007) and the Canadian Water Quality Guideline for the Protection of Freshwater Aquatic Life of 5 µg/L (CCME, 1999; Summary Table, updated 2002; www.ccme.ca/assets/pdf/e1_06.pdf). Only 5 samples contain <100 µg/L
total As and the highest concentrations (15,000 – 20,000 µg/L) are associated with drainage from a small area that contains NHGM tailings (Percival et al., 1996).

The trend in As concentration in the Farr Creek drainage system is plotted in Fig. 5 as the mean concentration for data collected during the 1990s campaigns (Dumaresq, 1993; Percival et al., 1996; 2004). Samples are arranged numerically by station number, in a SW to NE (drainage) direction. Low concentrations (e.g., < 300 µg/L As) were observed in Brief Lake and Short Lake, where only waste rock dumps occur. Concentrations increase downstream, especially through Cobalt Lake, and are relatively constant along Mill Creek, and then decrease through the Farr Creek wetland due to uptake by aquatic vegetation (Kelly, 2006; Kelly et al., 2007). Tailings are ubiquitous in the creek beds and throughout the wetlands. Samples collected during 2002-2003 campaign at the Mill-Farr Creek wetland area have similar concentrations with total dissolved As ranging from 210 to 540 µg/L (Kwong et al., 2007). The high concentration of As in Cobalt Lake water (station 6) is attributable to tailings in the lake, as well as run-off from various sources around the lake, including the run-off from the NHGM site where concentrations in runoff are (total dissolved As) up to 20 mg/L. Dumaresq (1993) estimated a mean annual discharge of about 18,000 kg As entering Lake Timiskaming.

Cobalt and Ni concentrations show similar trends to total As (Fig. 5). Concentrations are very low (< 20 µg/L) in the Brief Lake/Short Lake area and high at station 6, located below the NHGM tailings dam. Concentrations gradually decrease due to dilution in Cobalt Lake and increase again due to contributions from the Larose tailings outlet (station 15). The Co and Ni concentrations then decrease through the Mill Creek and Farr Creek wetlands until discharge into Lake Timiskaming.

Figure 5: Concentration of As, Ni and Co in µg/L from stations in the Farr Creek drainage system, trending from SW to NE.
Summary and Conclusions

Tailings and waste rock dumps are widespread in the Cobalt region and are a major source of contaminants to surface waters. Concentrations of As exceed water quality criteria for drinking water (10 µg/L) and aquatic life (5 µg/L), often by 2-3 orders of magnitude. The source of As, Ni and Co is the weathering of primary Co and Ni arsenides and sulpharsenides, as well as secondary minerals such as erythrite and annabergite. Submerged tailings contribute contaminants to surface waters but at a slower rate than exposed tailings. Despite attenuation of As, Ni and Co in wetlands of the Farr Creek drainage system, significant loadings continue to discharge into Lake Timiksaming.

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Literature Cited


