Using Hydrogeochemical Data to Improve Remediation of Historical Gold Mine Tailings in Nova Scotia

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Abstract Between the 1860s and 1940s historical gold mining operations generated over 3,000,000 tonnes of tailings at 64 districts throughout mainland Nova Scotia. This study focuses on hydrogeochemical processes controlling the mobility and attenuation of arsenic (As) and lead (Pb) at the Montague and Goldenville districts. Results from a previous sampling program at Montague investigating the role of hardpans on As cycling show precipitation and dissolution of scorodite ($FeAsO_4 \cdot 2H_2O$) and amorphous iron (Fe) arsenate dominantly control vadose zone water chemistry. The present study investigates stability of As- and Pb-bearing phases, from the tailings surface to a depth of approximately 2 m.

Key Words arsenic, hardpan, scorodite, Montague, Goldenville, remediation

Introduction

The varied and complex nature of mine wastes results in a need for detailed geoscience information when developing remediation strategies. Informed remediation efforts require an understanding of the solid-phase speciation of metal(loid)s and the composition of co-existing aqueous phases. As open systems, abandoned mine sites are subject to weathering effects such as the oxidation of primary ore materials, which is well known for releasing potentially toxic elements along with sulphate and acidity to pore waters, generating acid mine drainage (e.g. Blowes et al. 2003). However, neutral mine drainage can also be associated with negative environmental impacts (Heikkinen et al. 2009) as some metal(loid)s, including As, are more soluble with increasing pH (e.g. Cheng et al. 2009).

Following weathering, dissolved constituents may become transported by ground waters or surface waters. In general, the mobility of trace elements is limited by sorption reactions and pre-

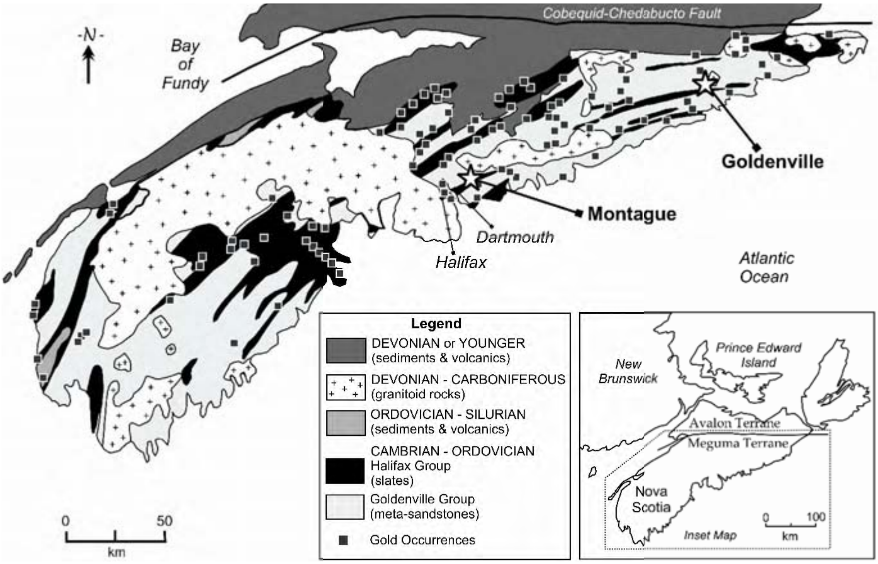

Figure 1 *Map of southern Nova Scotia showing study locations. Modified from Ryan & Smith (1998)*

cipitation of secondary phases. Differing geochemical conditions and secondary mineral assemblages with depth in mine tailings deposits may necessitate diverse remediation approaches. Tailings at Nova Scotia gold mine sites are characterized as As-rich and mineralogically complex with variable pH and redox conditions. Surface waters and ground waters are pH-neutral but where remnant arsenopyrite (FeAsS) has been left from mining operations pore waters are acidic and hardpan has developed (DeSisto 2008). Sulphide oxidation has altered arsenopyrite to various As-hosting secondary phases. These include Fe arsenates (e.g.scorodite, amorphous Fe arsenate), which are stable at low pH and calcium Fe arsenates (e.g. yukonite), which are stable at high pH (Walker et al. 2009).

The relationship between metal(loid) release and attenuation forms the basis for this work. Montague Gold Mines and Goldenville, two former gold mines located along the eastern seaboard of mainland Nova Scotia (Figure 1), provide an opportunity to study geochemical variations in surface and ground waters, in hardpan, and in historical tailings. Characterization of these materials from the surface to the base of the tailings is focused on identifying current As- and Pb-bearing phases and therefore, sources or sinks influencing the mobility of these contaminants. This information is essential for defining what materials will eventually be remediated and determining how remediation-induced geochemical changes may influence these metal(loid)-bearing phases.

Methods

Field parameters (temperature, pH, Eh, specific conductivity) were measured for all water samples. Vadose zone waters were collected with suction lysimeters and drive-point piezometers were used to collect saturated zone waters. All waters were acidified and kept chilled until analysis. Cores were collected by hand driving 6 cm diameter aluminum tubes into the tailings to obtain material from surface to approximately 1.8 m depth. All sections of core were sealed and frozen until being split for sub-sampling.

Water samples were analyzed for 31 elements by ICP-OES and for anions by ion chromatography. Doubly polished thin sections were prepared from epoxy plugs of selected tailings samples. Micro-X-ray diffraction, electron microprobe and environmental scanning electron microscopy – energy dispersive spectrometry (ESEM-EDS) analyses were performed.

Results

Solid Phases

Tailings from both sites show distinct visual characteristics that have been used to group the tailings into several end members. Within the vadose zone, hardpan occurs as thin, dispersed layers (< 2 cm) to thicker (>30 cm), more indurated layers. Cements within these hardpan layers show compositions ranging from scorodite to mixtures of scorodite and amorphous iron arsenate (Figure 2). Qualitative analyses using ESEM-EDS have also identified Pb-bearing phases within the Montague hardpans.

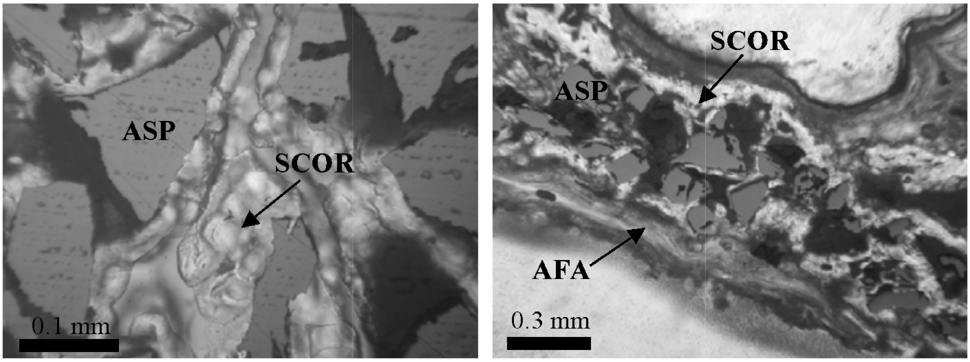

Figure 2 *Left: Scorodite (SCOR) cements surrounding arsenopyrite (ASP) grains. Right: Scorodite and amorphous iron arsenate (AFA) cements around arsenopyrite grains*

Materials from the vadose and saturated zones identified as high Ca/As tailings are grey and clay-sized. Bulk chemistry remains to be determined so grouping these tailings as having high Ca/As ratios is based on previous reconnaissance work and pore water chemistry (Tables 1, 2). The third end member type is original tailings that have remained permanently saturated due to their deposition in wetland areas of the sites. All other tailings that do not contain hardpan, are not distinctly finer grained or that have not remained permanently saturated are, for now, referred to as typical tailings.

Pore Waters

Pore waters are characterized by variable element concentrations and pH (Tables 1, 2). In the vadose zone, hardpan-bearing tailings show the highest dissolved As, Fe and sulphate and lowest calcium (Ca) concentrations. Hardpan-bearing tailings also contain low pH pore waters, whereas all other pore waters are near neutral to alkaline. The highest dissolved Ca concentrations occur within pore waters from the finer grained high Ca/As tailings.

From the saturated zone, the highest dissolved As concentrations are associated with tailings occurring below the hardpan layers. The highest dissolved Ca and sulphate are from tailings below the wetland and highest Fe is from the high Ca/As tailings.

Discussion

Detailed characterization of vadose zone waters and solids demonstrates that the main controls on pore water chemistry are oxidation of arsenopyrite, and precipitation and dissolution of crystalline scorodite and amorphous Fe arsenate. Previous work (Walker et al. 2009) has also identified Ca-bearing arsenates in near-surface gold mine tailings from Nova Scotia; however, identification of metal(loid)-bearing phases with depth in this study is on-going. The heterogeneity in tailings composition, which includes Fe arsenates, Ca-Fe arsenates as well as remnant sulphide concentrate (DeSisto et al. 2008) and Pb phases, means any form of remediation could de-stabilize at least some of these materials.

A common practice in tailings remediation involves installation of a cover material. The intent of using a cover is to reduce oxygen infiltration, limiting further sulphide oxidation and subsequent AMD formation. While this method can be successful both alone (e.g. Romano et al. 2003, Demers et al. 2009) and in combination with raising the water table (e.g. Ouangrawa et al. 2009), changes in geochemical conditions may also lead to element desorption or mineral dissolution (e.g. Holmström et al. 2001).

Scorodite solubility is strongly pH-dependent yet in many tailings areas it is the least soluble As-bearing phase. Ideal conditions for crystalline scorodite precipitation and stability are acidic, oxidizing environments. As conditions become more alkaline or reducing, scorodite will dissolve incongruently producing Fe oxyhydroxides (e.g. Harvey et al. 2006). Current geochemical conditions at Montague and Goldenville indicate scorodite and amorphous Fe arsenate are likely stable. Applying a cover could create reducing conditions that would de-stabilize these phases, releasing

Table 1 *Average pore water element concentrations from vadose zone tailings types*

End members (mg/L)	As	Ca	Fe	SO_4^{2-}	pH
Typical tailings	5.25	18.4	1.19	68.1	5.42
Hardpan-bearing tailings	24.8	16.1	45.1	515	2.40
High Ca/As tailings	15.2	197	12.9	465	6.79

Table 2 *Average pore water element concentrations from saturated zone tailings types*

End members (mg/L)	As	Ca	Fe	SO_4^{2-}	pH
Typical tailings	1.19	29.6	0.71	35.2	8.05
Below hardpan tailings	24.4	48	20.5	204	6.70
High Ca/As tailings	2.00	92.7	63.4	341	6.85
Below wetland tailings	1.21	118	43.3	402	6.83

a flush of As to local surface and ground waters. Conversely, if phases with depth are stable in reducing environments, exposure to atmospheric conditions, as would occur if tailings were excavated and removed from site, could lead to their dissolution. The ideal remediation method has the challenge of simultaneously stabilizing such diverse mineralogy.

Conclusions

Release of As from gold mine wastes can result in negative impacts on water quality. Secondary phases such as scorodite and amorphous Fe arsenates can provide a temporary form of natural attenuation; however, these phases may dissolve under certain types of tailings covers. Preliminary results from pore water chemistry and petrography indicate that Ca and Pb phases are also present in tailings from Nova Scotia. Detailed characterization of the hydrogeology of these abandoned mine tailings and further analyses of solid and aqueous phases are underway to provide science-based guidelines to help guide future remediation decisions.

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