Evaluation of Pore Water Chemistry to Simulate Dry Covers for the Remediation of Arsenic-bearing Gold Mine Tailings using Laboratory Columns

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Abstract
Historical small-scale gold mining operations in Nova Scotia have resulted in many high arsenic tailings areas across the province. Many of these tailings areas are easily accessible by local residents and are used as recreational areas for ATVs and dirt bikes. One of these sites, Montague, contains up to 31 wt. % arsenic (As) in surficial hardpan tailings. Arsenic-bearing phases in hardpan tailings include primary arsenopyrite (FeAsS) and its oxidation products scorodite ($FeAsO_4 \bullet 2H_2O$) and hydrous ferric arsenate (HFA). The overall objective of this project was to investigate the geochemical effects of using physical barriers (i.e. dry covers) to reduce human exposure to As-bearing tailings and limit potential future degradation of groundwater quality. A laboratory column study was used to investigate arsenic mobility from tailings under three scenarios: unremediated tailings exposed to acid rain; tailings remediated with a crushed limestone cover; and tailings remediated with a vegetative cover. Despite the range in input solution pH (from 4.6 to 10), column leachate reported similar pH values and similar concentrations of sulphate, and dissolved Fe and As, indicating that mineralogy is a primary control over leachate chemistry.

Key words: column studies, hardpan

Introduction
Arsenopyrite is naturally associated with orogenic gold mineralization in Nova Scotia. Historical mining operations have resulted in several high As tailings areas (up to 30 wt% As), many of which are located near towns and new housing developments. These sites are easily accessible and are frequently used as recreational areas, which poses a risk of ingestion and/or inhalation of dust and fine particles. It has been suggested that a physical barrier such as a layer of crushed limestone or vegetation may effectively isolate the tailings from human activities and mitigate future inhalation/ingestion risks.

As a result of decades of weathering, multiple As-bearing phases including primary arsenopyrite and its oxidation products scorodite and HFA are present at the surface of the Nova Scotia tailings (Walker *et al.* 2009; Corriveau *et al.* 2011). Scorodite is hypothesized to control aqueous arsenate concentrations in low pH drainage from oxidizing arsenic-rich ores that contains high concentrations of aqueous Fe^{3+} and As^{5+} (Zhu and Merkel 2001). Scorodite is metastable in most environments and tends to dissolve incongruently into iron hydroxides and mobilized arsenic between approximately pH 2 and pH 6 (DeSisto *et al*. 2011; Zhu and Merkel 2001; Dove and Rimstidt 1985). Less commonly, scorodite may dissolve congruently at lower pH values.

Amorphous and poorly crystalline ferric arsenate minerals, usually referred to as HFA, amorphous ferric arsenate (AFA) or pitticite, are also closely associated with scorodite in low pH mine drainage (Walker *et al*. 2009; Drahota and Filippi 2009; Salzsauler *et al*. 2005). HFA is reported to be more soluble than scorodite (Paktunc and Bruggeman 2010; Drahota and Filippi 2009; Krause and Ettel 1989).

A laboratory column study was used to investigate As mobility from scorodite- and HFA-bearing hardpan tailings under three different scenarios:

1. Unremediated tailings, in which a synthetic acid rain solution was used to simulate percolation of natural precipitation into unremediated tailings;

2. Tailings remediated with a crushed limestone cover, in which a synthetic acid rain solution was equilibrated with calcium carbonate to simulate percolation of rainwater through a crushed limestone cover and into underlying tailings; and
3. Tailings remediated with a vegetative cover, in which an organic acid solution was used to simulate the plant root environment in revegetated tailings.

Materials and Methods

Laboratory columns were constructed out of 10 cm diameter Plexiglas tubing cut into 30 cm lengths. Each column was fitted with a square base that was lined with a non-reactive geomembrane and a basal sampling port. Sample leachate was collected via food-grade nylon tubing attached with a PVC elbow joint to the basal drains. Each tube was equipped with a watertight hose clamp to prevent leakage and to minimize oxygen ingress through the bottom of the column.

For this study, a 20 kg sample of broken up hardpan was collected from the former Montague Mine in Nova Scotia. The sample of collected hardpan tailings consisted of 1 cm to 5 cm angular fragments of cemented hardpan that were broken from the surface of the Montague Tailings using a rake. This sample was selected because it was visually and texturally distinct from the majority of the tailings at the site (green-yellow and cemented). Each of three columns was loaded with a representative 4 kg subsample of hardpan fragments. Samples were tamped into each column, but due to the large grain size of hardpan fragments, the loaded columns were visibly porous.

Prior to kinetic testing, the hardpan sample was characterized using acid base accounting (ABA), elemental composition (using aqua regia digestion and ICP-MS), quantitative mineralogy by Rietveld XRD, and leachability testing using shake flask extraction (SFE) tests. Results of sample characterization are summarized in Tables 1 to 3 below.

Table 1. Summary of acid base accounting (ABA) and elemental composition results

		08-MGJK-01 Hardpan
Acid Base Accounting Results		
Paste pH	-	2.76
Total Inorganic Carbon (TIC)	%	<0.01
Acid Potential (AP)	kg $CaCO_3$/t	80.3
Neutralization Potential (NP)	kg $CaCO_3$/t	-12.3
NPR (NP/AP)	-	-
Elemental Composition		
As	%	12.4
Ca	%	0.02
Fe	%	14.3
Hg	ppb	9062
Pb	ppm	577
S	%	2.47

Table 2. Rietveld X-Ray diffraction results (%)

		08-MGJK-01 Hardpan
Mineral	**Ideal formula**	
Quartz	SiO_2	31.7
Muscovite	$KAl_2AlSi_3O_{10}(OH)_2$	15.9
Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	2.4
Clinochlore	$(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	1.7
Plagioclase	$NaAlSi_3O_8 – CaAl_2Si_2O_8$	5.3
Scorodite	$FeAsO_4 \cdot 2H_2O$	35.6
Arsenopyrite	FeAsS	6.4
Sulfur, elemental	S	1.1
Total		100.1

Table 3. Summary of selected shake flask extraction results

		08-MGJK-01 Hardpan
pH		2.6
Dissolved Metals		
As	mg/L	5.5
Ca	mg/L	2.3
Cu	mg/L	0.15
Fe	mg/L	21
Hg	ug/L	0.23
Mg	mg/L	1.3
Pb	mg/L	0.033
Sb	mg/L	0.0056

Kinetic laboratory column test procedures

Three columns containing 4 kg each of hardpan tailings fragments were leached weekly with one of three input solutions:

1. Synthetic acid rainwater to simulate unremediated tailings exposed to natural acid rain;
2. Synthetic acid rainwater equilibrated with calcium carbonate to simulate rainwater percolation through a crushed limestone cover; and,
3. Weak organic acid solution designed to simulate the environment surrounding plant roots under a vegetative cover.

The pH values for the three input solutions were 4.6, 10 and 5, respectively.

Each week, the input solutions were added to the top of each column and allowed to percolate through the column. Due to the high porosity of the loaded columns, the leaching procedure was completed within

minutes, and unsaturated conditions were maintained. Outgoing leachate volume was measured and tested for pH, then filtered to 0.45 µm and tested for alkalinity using a HACH digital titration kit. Specific conductance and oxidation-reduction potential (ORP) were determined using a YSI multimeter that was calibrated weekly. Dissolved metals and dissolved ions were analysed using ICP-MS and Ion Chromatography (IC), respectively. The duration of kinetic testing was 29 weeks.

Results and Discussion

The hardpan columns all reported acidic leachate pH values of approximately 2 for the duration of kinetic testing (Figure 1), despite the range in input solution pH values from 4.6 to 10. Similarly, the concentrations of sulphate, dissolved Fe (Figure 2) and dissolved As (Figure 3) were similar in all of the columns regardless of input solution. These results indicate that inflowing pore water chemistry had a negligible impact on As leaching from high As tailings. This trend was also observed for other tailings types investigated in this study, which found that mineralogy is the primary control on leachate quality regardless of solution type (Kavalench 2010).

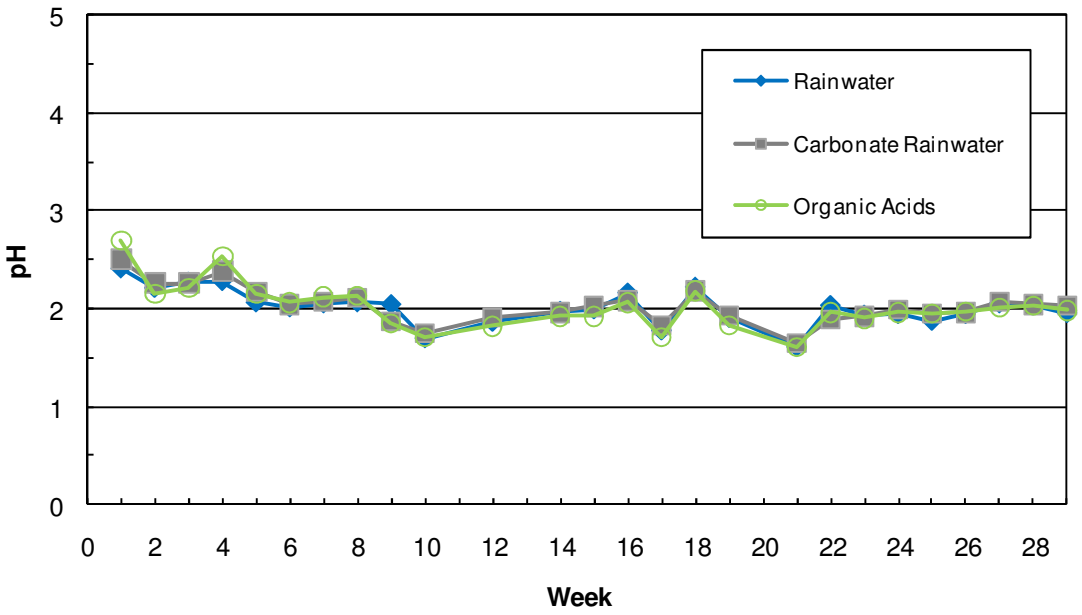

Figure 1. Weekly leachate pH values for hardpan columns.

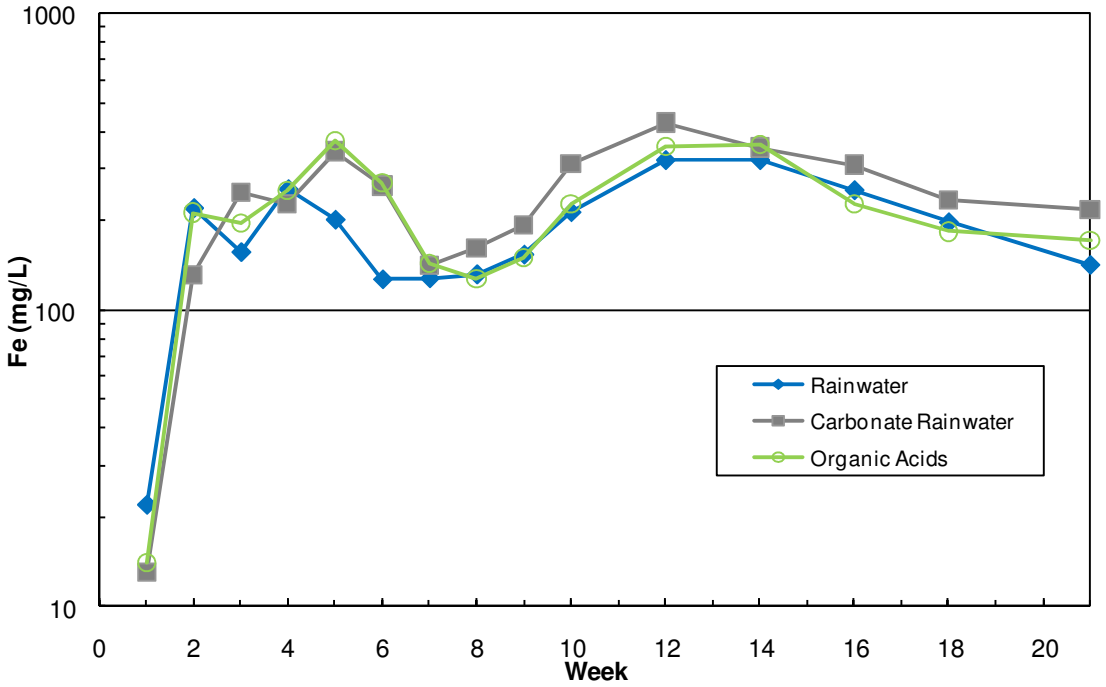

Figure 2. Dissolved Fe concentrations in hardpan column leachate.

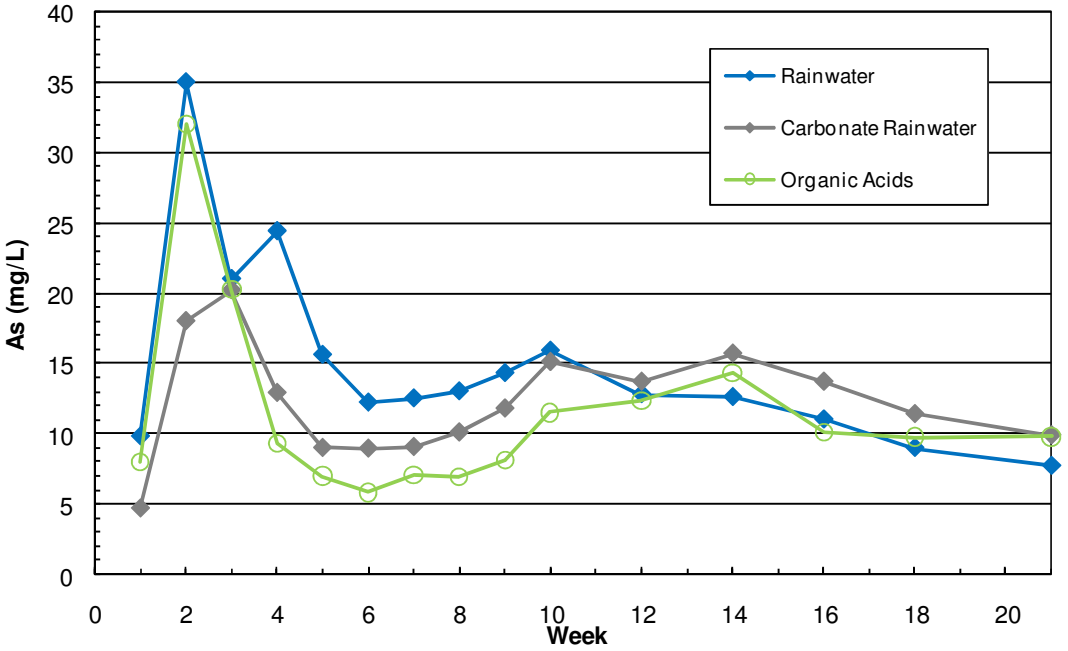

Figure 3. Dissolved As concentrations in hardpan column leachate.

Scorodite is the dominant As mineral in hardpan (Table 2) and accounts for 36% of the total normalized percentage of crystalline phases as identified by Rietveld-XRD. High As leachate chemistries from the three columns suggests that infiltration of columns with input solutions having pH values greater than 2 may cause the incongruent dissolution of scorodite and accompanying release of acidity according to equation 1 (Drahota and Filippi 2009):

$$FeAsO_4 \cdot 2H_2O + H_2O \rightarrow H_2AsO_4^- + Fe(OH)_{3(s)} + H^+ \quad (1)$$

However, geochemical modelling using the PHREEQC computer code (Parkhurst and Appelo 1999) indicates that dissolution of scorodite in rainwater would result in equilibrium As and Fe concentrations of 18.6 mg/L and 13.8 mg/L, respectively. In the rainwater column, the concentrations of As and Fe are approximately 10 mg/L and 100 mg/L, respectively, indicating that As and Fe concentrations are likely controlled by a combination of factors, which may include:

- Dissolution of other As phases;
- Precipitation reactions;
- As sorption processes;
- Oxidation of arsenopyrite; and/or
- An additional Fe source.

These factors are described briefly in the following sections.

Dissolution of other As phases

In addition to scorodite, HFA was also detected in hardpan samples. The As/Fe molar ratios of HFA as determined using EMPA are lower than scorodite molar ratios, indicating that dissolution of this phase could result in lower concentrations of dissolved As and higher concentrations of dissolved Fe than that which can be attributed to scorodite dissolution. Reportedly, the solubility of HFA is controlled by the As/Fe molar ratio, where higher ratios (above 0.5) are more soluble than ratios below 0.1 (Drahota and Filippi 2009). EMPA analysis of HFA phases reported As/Fe ratios between 1.5 and 1.1 (Figure 4), suggesting that this phase is soluble and may contribute to aqueous As concentrations.

Precipitation reactions

Lower than expected aqueous As concentrations may be due to As sequestration at a higher rate than Fe. Precipitation of As phases such as scorodite or HFA within the column is supported by visual observations during deconstruction of columns after testing. All three hardpan columns were originally packed with gravel-sized pieces of angular hardpan. By the end of testing, the hardpan had reformed into a cohesive mass. Note that precipitation reactions would also result in a corresponding decrease in aqueous Fe concentrations.

As sorption processes

Aqueous As concentrations that are lower than the theoretical equilibrium concentrations of 18.6 mg/L could also be due to adsorption processes of the As anion $H_2AsO_4^-$ onto clay minerals and iron oxyhydroxides (Bissen and Frimmel 2003; Harvey *et al.* 2006).

Oxidation of arsenopyrite

Arsenopyrite is the original As mineral host prior to weathering. Unstable under oxidizing conditions, arsenopyrite releases Fe, As, SO_4 and acidity during oxidation:

$$FeAsS + 2.5\ H_2O + 2.75\ O_{2(aq)} = Fe^{++} + As(OH)_4^- + H^+ + SO_4^{--} \quad (2)$$

Measured sulphate concentrations in hardpan columns support this mechanism as a factor contributing to aqueous Fe and As concentrations in column leachate (Figure 5).

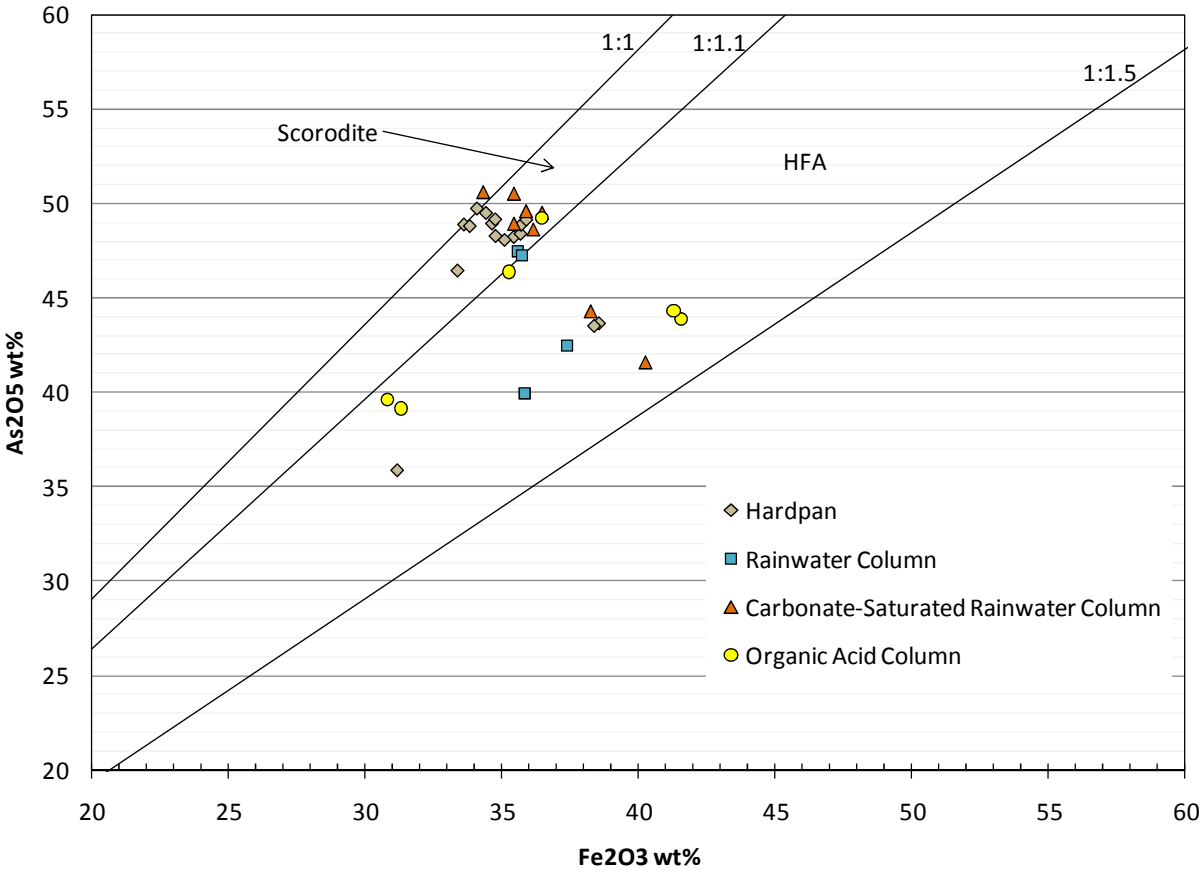

Figure 4. As/Fe molar ratios for hardpan arsenic phases, as determined using EMPA.

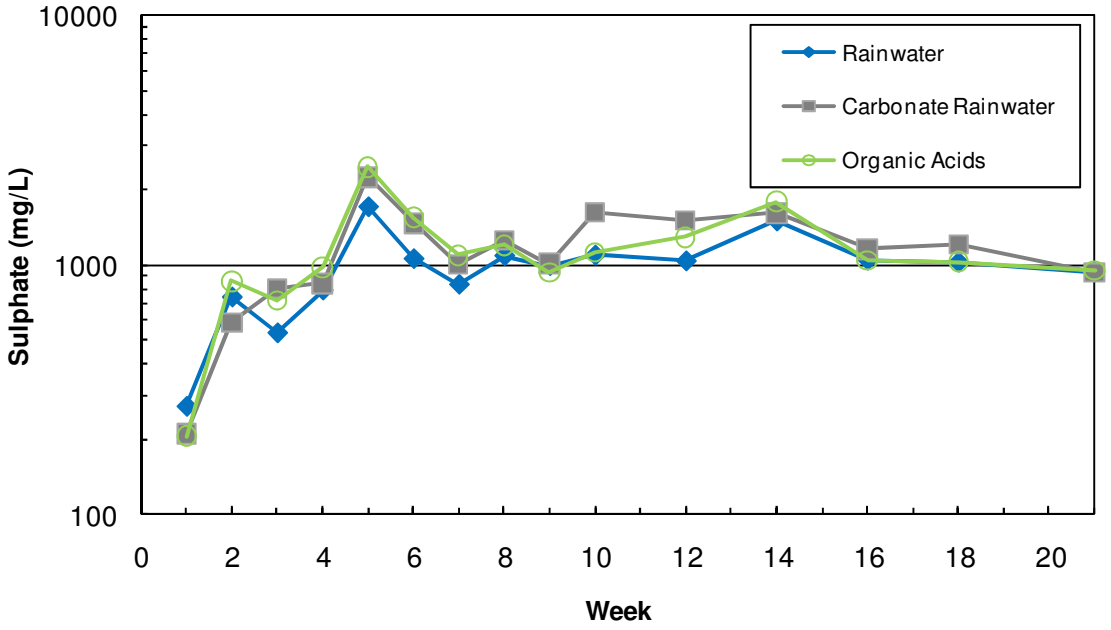

Figure 5. Dissolved sulphate concentrations from hardpan column leachate.

Additional Fe sources

Most likely, high concentrations of dissolved Fe may be attributed to dissolution of non-ore minerals such as biotite and clinochlore.

Conclusions

In general, all three hardpan columns reported similar pH values and similar concentrations of sulphate and dissolved Fe and As regardless of infiltrating pore water chemistry. A combination of several factors including dissolution/precipitation, sorption, and oxidation processes seem to control aqueous As and Fe concentrations in hardpan column leachate, regardless of solution types used in this study. Column test results indicate that the pore water chemistries used to simulate leachate from a crushed limestone cover or vegetative cover may not effectively mitigate As leaching from hardpan tailings due to the complex geochemical reactions that occur when any solution passes through hardpan tailings.

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Acronyms

PVC
ICP-MS
ABA
SFE
XRD
HFA
AFA