Arsenic Mobility under a Neutral Mine Drainage Environment in a Gold-Mine Tailings Dam

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ABSTRACT

A geochemical assessment of a lined tailings deposit from an operating gold mine located in a semiarid climate was performed for this study. A total of 58 samples were collected, including surface and deep tailings as well as fresh tailings from the carbon-in-leach circuit. Several analyses were performed on these samples, including the modified acid-base accounting, NAG test, chemical and mineralogical characterization. Kinetic tests were also performed on two samples of fresh tailings. Both mineralogical characterization and the acid-base accounting showed that the neutralization potential in the tailings is at least two times higher than the acidification potential, confirming the current, slightly alkaline conditions of the reservoir, with pH value always higher than 7. The alkalinity trends monitored and gypsum detected in the mineralogical composition (1.3%) of the tailings collected in the reservoir suggest that acid neutralization and precipitation of sulphate salts are occurring. In the oxidizing environment within the tailings, the arsenic concentrations varied from below detection limit to 0.081 mg/L, always with a slightly alkaline pH. This concentration range can be related with the dissolution of amorphous ferric arsenate. The arsenic concentrations monitored in a slightly reducing environment (Eh=-12V) are much higher than the concentrations identified in the oxidizing environment. The Eh, pH, and dissolved iron concentrations (average 3 mg/L) suggest that the arsenic is being released by the reduction of Fe³⁺ to Fe²⁺. Based on the results from this work, it was possible to establish a conceptual model of arsenic behavior in oxidizing and slightly reducing environments within the tailings, as well as recommend actions for a stable closure of the tailings dam to prevent the arsenic release in the long term to the environment.

Keywords: Arsenic, Neutral Drainage, Tailings Dam, Gold Mine
INTRODUCTION

In the semiarid climate of Brazil, a gold mine is operating since 1984. In 1988 the underground mining of sulphide ores started and since then, the tailings generated from processing this material (CIP circuit) are being deposited in a tailings dam.

The deposit has two of the ore occurrence of situations. The first one consists of sulfide ore bodies and the second one is consisting of quartz veins containing free gold, basically embedded in the levels of CAX (carbonate - actinolite - shale) of the intermediate package and corner sequence, northeast of Weber range. In the surface ten bodies of sulfide ore emerges of which eight are located in the first layer (thicker) and the two others in the second layer. The sulfide ore bodies are formed by a set of venules and veins, ranging from a few centimeters up to two meters thick. In the veins there are the occurrence of quartz, pyrite and arsenopyrite in different proportions. When the veins are in agreement with the foliation of the rock, the boundaries of the affected zone are regular and parallel to the edges of the veins.

Alteration zones bordering discordant veins are irregular and thicker, with a tendency to the appearance of jagged edges that penetrate laterally in the foliation planes of rock. In the affected zone there has been a decrease in the volume of chlorite, followed by an increase of albite and carbonates towards the vein. Magnetite is replaced by the sulfides and a small increase in biotite is observed. Carbonate and pyrite occur filling all the faults and fractures existing system in the mine, showing late barren hydrothermal event in gold, presented in many places cavities where well-formed crystals of carbonate and pyrite have been developed. The distribution of gold is very erratic, especially in quartz ore, where it is even possible to find visible particles, due to the gold on this type having a particle size larger than the one found in the sulfide ore.

A preliminary mineralogical characterization of the tailings was performed by X-ray diffraction indicating a significant presence of sulphides and carbonates. The monitoring results along the years indicated that the tailings dam pond presents alkaline conditions and an increase of As and SO₄ concentrations with depth inside the dam. The arsenic concentrations in the lake are in the order of 10 mg/L while in the toe drain these concentrations are as high as 200 mg/L. All the effluent from the toe drains in recycled back to the reservoir resulting in no discharge to the environment. It is also possible to observe a variation in the Eh. The Eh conditions in the toe drain is -12 mV. This value is significantly lower than the ones monitored in the lake (265 mV). These conditions are expected since that in the toe drain, the water is not in contact with oxygen until it reaches the drain.

Differently from some other trace elements, As can be mobile under neutral to alkaline conditions, depending on the redox of the system (Craw et al., 2003). Since the operation is reaching its closure phase, it is important to evaluate the Acid Rock Drainage potential in the long term and understand the factors that are affecting the As mobility. This evaluation is important in order to establish mitigation actions for closure and post-closure and to immobilize and stabilize As concentrations.

A store and release cover system was designed based on field experiments that ran for 15 months. The objective of the designed cover is to avoid water to get in contact with the tailings. Since the
field experiments presented very good results, it is expected that once this cover is installed above the tailings in the closure stages, that the amount of water seeping at the toe drain decreases and eventually discontinue along the years, which would prevent elevated concentrations of arsenic from the anaerobic environment. This paper, documenting the site conditions and the ARD and As evaluations, is based on a Master of Science thesis presented in 2014 (Bissacot, 2014).

METHODOLOGY

Tailings Sampling
Tailings samples were selected for geochemical characterization beyond that of the standard protocols of the operation. The definition of the tailings sampling locations was carried out with the support of the mine’s geology department. Twenty-one equidistant points on 150 meter centers were distributed along the tailings area and sampled at different depths (Figure 1). Two fresh CIL tailings samples and one composite sample of precipitated salts were also collected. For the deposited tailings, a cylindrical soil auger with 4.5 meters inches diameter and 39 cm length was used. The maximum depth achieved is 6 meters. A total of 55 samples of tailings were collected at different depths in the 21 points, totalizing 58 samples sent to the laboratory for further analyzes.

Figure 1 Sample Locations

Tailings Characterization
Several analyzes were performed for understanding the short and long term behave of these tailings and especially the arsenic mobility. The modified acid-base accounting (MABA) was performed in order to understand the potential of these samples for generating acidy. The Lawrence method (MEND, 1991) was selected for this analyzes. The Net Acid Generating test (NAG) was performed as an additional test according the procedure described by Stewart et al. in order to confirm the MABA results. The chemical composition of each sample was conducted by
digesting 0.500 g in aqua regia at 95°C for one hour. The extract was then diluted to 10.0 mL and analyzed for metals by combination of OES and MS using Optima 7300DV for ICP-OES and Elan 9000 for ICP-MS. These results were complemented by mineralogical analyzes by X-ray diffraction with Rietveld refinement and kinetic tests in leach columns according to the AMIRA (2002) procedure.

RESULTS AND DISCUSSION

Acid Rock Drainage Evaluation

The results of the MABA tests in the deposited tailings indicated an average sulfur concentration of 1.36% while the average sulfide sulfur was 1.09%, according to the figure 2 below.

![Figure 2](image)

**Figure 2** Comparison between S-total and S-sulfide

This can be related to the partial sulfur content that was oxidized into sulfates. In contrast, the fresh tailings collected after the CIL circuit presented an average concentration of 1.54% total sulfur and 1.48% sulfide sulfur. The composite sample collected of the precipitates presented 0.5% of total sulphur on its composition and 0.01% of sulfide sulfur. The average concentration of sulfur can be considered reasonably high, but the average neutralization potential (NP) was also elevated, with an average of 106 kgCaCO₃eq/ton. In addition to these results, the NAG tests also indicated an elevated NAGpH for all the tailings tested. According to the NAG test procedure, a sample with a NAGpH greater than 4.5 can be considered as non-acid forming. The test results are summarized in Figure 2.
Figure 2 combines the results of the MABA and NAG tests. The X-axis represents the MABA results as the difference of AP and NP. [Note that this is the Net Acid Producing Potential, the inverse of the Net Neutralization Potential typically used in North America. In the NAPP system values less than zero imply an excess of NP over AP.] The Y-axis represents the NAGpH. It is possible to observe that all samples were classified in the non-acid forming area of the diagram. In yellow it is possible to observe the fresh tailings and the circles represent the deposited tailings. Both deposited and fresh tailings presented similar characteristics in terms of ARD generation. The results indicated that acid rock drainage should not occur in the short and long term.

**Chemical and Mineralogical Composition**

The mineralogical characterization by X-ray diffraction with Rietveld refinement was carried out in all the samples. The advantages of this method are the quantitative nature of the method as well as the lower detection limits (Raudsepp & Pani, 2003). In terms of environmental relevance, the sulfides and carbonates are the most important. The silicates are relatively stable and do not significantly change the pH of the solution under most conditions in relevant time periods. The results presented a significant presence of pyrite (1%), arsenopyrite (0.5%) and pyrrhotite (0.7%). Regarding the carbonates, it was identified even higher concentrations of dolomite (3.7%), calcite (6.1%) and calcite/magnesian (2.9%). This may be explained by the limitations of the Rietveld method to identify arsenopyrite phase under at levels below 1%. The gypsum concentrations were detected in the deposited tailings with an average of 1.3%, while in the fresh tailings it was not detected. These concentrations of gypsum indicate that sulfate salts are being formed in the reservoir most like due to the sulfides oxidation. The presence of silicates represents around 80% of the minerals present in the samples, mostly present in the form of quartz and plagioclases. The mineralogy assessment summary is presented in Table 1:
Table 1 Average mineralogy composition - 58 samples

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Average %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>1.0</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>0.7</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>0.5</td>
</tr>
<tr>
<td>Calcite</td>
<td>6.1</td>
</tr>
<tr>
<td>Ankerite – Dolomite</td>
<td>3.7</td>
</tr>
<tr>
<td>Calcite, magnesian</td>
<td>2.9</td>
</tr>
<tr>
<td>Gypsum</td>
<td>1.3</td>
</tr>
<tr>
<td>Silicates</td>
<td>80.3</td>
</tr>
<tr>
<td>Iron Oxides</td>
<td>3.6</td>
</tr>
</tbody>
</table>

In addition to these results, elevated grades of arsenic, with an average of 3860 mg/kg, were detected in all the 58 samples analyzed by ICP-MS. The average sulfur detected by ICP was 1.3%, confirming the results previously presented in the MABA.

Kinetic Tests

The kinetic tests are being performed in PVC columns according to the AMIRA 2002 procedure. The water addition is performed once a week in an entire cycle of four weeks. An amount of 200 mL of water is added in the first three weeks and in the fourth week, 800 mL is added. The leachate solution is collected and analyzed for pH, conductivity, sulfate and metals. The results of As and Fe are presented in Figure 3.

![Figure 4 arsenic and iron leaching after 17 months](image)

It is possible to observe that after 17 months of water addition, the arsenic leached from below detection limit until concentrations of 0.229 mg L\(^{-1}\). The iron concentrations varied from 0.09 to 2.6 mg/L. The concentrations of arsenic leached in the columns are significantly lower than the concentrations found deep in the lined tailings reservoir. According to the graph, it is possible to observe some correlation of the iron and arsenic concentrations in some of the cycles. Concentrations of iron on this order of magnitude are mainly in Fe\(^{2+}\) form since the Fe\(^{3+}\) would
precipitate quantitatively at pH 7 – 8.5. The low concentrations of As in the column can be related to the As co-precipitation with Fe$^{3+}$ hydroxides that are stable under the pH-Eh conditions of the other months in the columns (Bissacot, 2014). These conditions are likely to be different from those conditions in the tailings pond water, where the redox varies from oxidizing to reducing conditions and concentrations of Fe of 5 mg L$^{-1}$ are found at neutral pH. The results highlight the need to control the redox conditions to prevent arsenic mobilization and have important implications on environmental management in the industrial unit.

CONCLUSION

The mineralogical composition is consistent with both MABA results and current data available for the tailings dam, showing alkaline conditions. Arsenic mobility in the tailings water is mostly related to the presence and oxidation of arsenopyrite combined with the redox conditions variation along the tailings deposit (oxidizing to reducing). It is recommended that similar tailings with potential alkaline conditions and high concentrations of arsenic are disposed under oxidizing conditions and have the redox conditions controlled in order to avoid the long-term arsenic mobility. It is also important to avoid as much as possible seepage areas in the reservoir that creates reducing environments and potential discharges.

The oxidizing environment tested in the laboratory showed concentrations of leached As very low when compared to the ones observed in the anaerobic conditions of the toe drains. Also, as an alternative option, iron can also be added to the system in order to adsorb and decrease the dissolved arsenic concentrations but this action should be performed only when it is possible to maintain controlled redox conditions.

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REFERENCES


