Geochemical and Mineralogical Characterization of Gold mine tailings for the potential of acid mine drainage in the Sabie-Pilgrim’s Rest Goldfields, South Africa

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Abstract
The environmental hazards arising from active and abandoned mine tailings are a cause for concern. We report on the presence of mineral-related environmental hazards in both Glynn Lydenburg and Nestor mine tailings, approximately 6 km apart and located in the Mpumalanga Province of South Africa. Based on XRD, shows a wide range of minerals: pyritic sulphide, quartz and mica. The XRF results showed that quartz was the dominant oxide in both the mine tailings; followed by Fe2O3 and Al2O3. Furthermore, trace elements, such as As, Cr, Cu, Pb, V and Zn, were also found which are hazardous to the environment.

Key words
Acid Mine Drainage, Mine Residues Deposits, environmental hazards

Introduction
Mining is one of the most important economic activities in South Africa. The country receives huge economic benefits from the mining industry. However, different kinds of mine residue deposits (herein referred to as mine tailings) associated with the extraction and processing of metals which have accumulated stand out as sources of potential environmental pollution in specific mining areas and the country at large (McCarthy 2011). For coal and gold mining operations, these mine tailings are a continuous source of acid mine drainage (AMD) generation (Kleinman et al. 1981; Oberholster et al. 2013) and an environmental hazards (Rosner et al. 1998; Nelushi et al. 2013).

The Sabie-Pilgrim’s Rest goldfield, Mpumalanga is one such area where gold mining activities occurred in the past. The area has various mine tailings of different ages and sizes. What is key here is that a few or no environmental studies had been carried out on mine tailings; hence this study focused on the Nestor and Glynn Lydenburg Gold mine tailings. The main objective of this study was to determine the mineralogy and the geochemistry of mine tailings.

Methods

Location of the study area
The Nestor (NS) and Glynn Lydenburg (GL) mine tailings, are located in the Sabie area of the Mpumalanga Province of South Africa (Fig. 1).
Sampling

Thirty tailings profile samples and five grab samples were collected at mine tailings from 20 to 23 February 2015. A truck-mounted and a hand auger were used at GL (drilling to 10 m) and NS (drilling to 3 m) respectfully. The collected samples were sent to the Council for Geoscience’s laboratory in Pretoria, South Africa, for analysis.

Sample preparation and quality control

The samples were then ground using milling pots made of carbon steel to minimize the level of contamination on a single swing mill (TM-SPR003) method which involved air drying, crushing and milling of samples to a size reduction of <75 µm. In between milling, the equipment was washed using distilled water and wiped with the disposable paper towels wetted with ethanol and then allowed to dry to avoid the contamination of samples.

Geochemical and mineralogical analysis

The samples were analysed by X-ray florescence spectrometry (XRF) and X-ray diffraction spectrometry (XRD) according to procedures of USEPA (1986). The glass disks and wax pallets were analyzed using a PANalytical wavelength dispersive AXIOS X-ray fluorescence spectrometer that was equipped with a 4kW Rh tube. Both major and minor elements have been determined and reported as oxides and trace elements. Quality control/Quality assurance (QC/QA) was done using the in-house amphibolite reference material (sample 12/76). Furthermore, one in every ten samples was duplicated during sample preparation. The X-ray diffraction (XRD) technique employed scanning from 2 to 70° 2θ Cu radiation at a speed of 0.02° 2θ steps size/0.5 sec, with a LYNXEYE detector and generator settings of 40 kV and 40mA. Semi-quantitative approximations of the minerals present were based on the relative peak heights to area proportion according to Brime (1985).
ICP MS analysis

The milled samples were weighed and transferred to a 100 ml glass beaker, where acids HCl and HNO₃ (mixture) were then added and heated on hotplate in fume hood. The mixture was cooled and then was transferred to a 100 ml volumetric flask and then this was topped to the mark with deionised water. The acid digests samples were analysed using the ICP-MS (Perkin Elmer Elan 9000, Weltham, USA) in triplicates.

Results and discussion

Geochemistry of mine tailings

The three dominant oxides in both tailings materials are SiO₂, Fe₂O₃ and Al₂O₃. CaO (average ≈5.4%) is the fourth abundant oxide in Glynn Lydenburg tailings whereas TiO₂ and K₂O are the fourth abundant oxides in the Nestor tailings materials (Fig. 2A). It is important to note herein that the concentration of CaO in most samples of the Nestor tailings is <0.05 % with a few samples showing higher concentration ranging from 0.3 to as high as 3.2% which brings the overall average concentration of CaO in the Nestor tailings to 0.45% which still is significantly lower than that of the Glynn Lydenburg tailings which contains an average concentration of 5.4 % CaO. MgO is also high in Glynn Lydenburg tailings with an average concentration of 3.6% compared to that which is in Nestor tailings (average ≈0.33%). The chemical composition therefore shows that the Glynn Lydenburg mine tailings material shows high acid neutralizing capacity due to its high calcite percentage compared to the Nestor mine tailings material (Figure 2B).

Figure 2 Distribution of (A) dominant oxides (B) dominant neutralizing oxides and acid-forming oxide in Nestor (NS) and Glynn Lydenburg (GL) mine tailings

The concentration of aluminum oxide (Al₂O₃) and ferric oxide (Fe₂O₃) increases with depth indicating the progressive decrease of oxidation with depth which in turn indicates the decrease in availability of oxygen with depth.

Trace metals such as Cu, As, Cr, Ni, Pb, V and Zn occur within the mine tailings (Tab. 1) in excess of South African guidelines soil screening levels, National Norms and Standards for
Remediation of Contaminated Land and Soil Quality in the Republic of South Africa (DEA, 2013).

**Table 1** The distribution of metals and As at the mine tailings (range, ppm), average values are shown in brackets

<table>
<thead>
<tr>
<th>Metal</th>
<th>Nestor</th>
<th>Glynn Lydenburg</th>
<th>All land uses, protective of water sources</th>
<th>Informal residential</th>
<th>Standard residential</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>137-1599 (599)</td>
<td>807-2502 (1471)</td>
<td>5.8</td>
<td>23</td>
<td>48</td>
</tr>
<tr>
<td>Cu</td>
<td>34-571 (154)</td>
<td>10-104 (30)</td>
<td>16</td>
<td>1100</td>
<td>2300</td>
</tr>
<tr>
<td>Cr</td>
<td>43-273 (172)</td>
<td>117-238 (140)</td>
<td>6.5</td>
<td>6.5</td>
<td>13</td>
</tr>
<tr>
<td>Pb</td>
<td>12-276 (54)</td>
<td>13-63 (37)</td>
<td>20</td>
<td>110</td>
<td>230</td>
</tr>
<tr>
<td>Ni</td>
<td>16-157 (53)</td>
<td>45-132 (66)</td>
<td>91</td>
<td>620</td>
<td>1200</td>
</tr>
<tr>
<td>V</td>
<td>29-255 (140)</td>
<td>56-235 (82)</td>
<td>150</td>
<td>150</td>
<td>320</td>
</tr>
<tr>
<td>Zn</td>
<td>7-485 (73)</td>
<td>90-240 (150)</td>
<td>240</td>
<td>920</td>
<td>19000</td>
</tr>
</tbody>
</table>

This is likely to result in As poisoning through water pollution, dust inhalation and contamination of the food chain as especially evident in the Nestor tailings storage facility, which is highly weathered and exposed to erosion yet lying adjacent to Sabie River. According to Harkada (1996), a concentration of 100 mg/kg As in soil can reduce crop yield by 90% and lead to As poisoning, which results in diseases such as skin and lung cancer. Other possible effects associated with As poisoning are cardiovascular disease and diabetes (Centeno and Finkelman 2007). Copper provides essential micronutrients to plants, animals and humans. Nevertheless a Cu concentration in water over 30 ppm may result in liver, kidney and blood cell damage (DWAF 1996), hence the likely environmental disaster. The total Cr levels including Cr⁶⁺ were high and may have a negative impact on the environment. Cr⁶⁺ is more toxic than Cr³⁺, with a Cr⁶⁺ concentration of more than 0.5 g/mL being considered as having a negative effect (Alloway and Ayres 1998). In addition the excessive ingestion of Cr⁶⁺ is carcinogenic. The concentration of Cr was in the range of 10-19 mg/kg which is in suitable range for plant growth (Alloway and Ayres 1998). The Zn levels may have a negative impact on the aquatic environment. The Pb levels though lower in Glynn Lydenburg mine tailings than Nestor are still able to contaminate the aquatic environment (Ngole-Jeme et al. 2017). The high V levels are likely to impact negatively on the environment (Luo et. al. 2017). Generally, a Zn content of over 15 ppm of water is considered toxic and can result in renal damage. Furthermore, a deposition of Zn salts into fish gills can lead to their death (USEPA, 2009).

**Mineralogical analysis of mine tailings**

The mineralogical composition (primary and secondary minerals) based on X-ray diffraction as expressed in weight percent (wt %) of bulk samples show variation among the Nestor and Glynn Lydenburg mine tailings (Fig. 4). The primary minerals for tailings are defined by Jambor (1994) as the ore and gangue minerals processed and deposited in an impoundment without any changes other than reduction in grain size by comminution. Alpers et al.
(1994), define secondary minerals as those minerals formed by processes that lead to precipitation, such as evaporation, oxidation, reduction, dilution, mixing and neutralisation.

Quartz is the dominant mineral here and showed an almost constant trend throughout the mine tailings. This can be attributed to its dominance in the original tailings as well as to its high resistance to physical and chemical weathering and dissolution. The important primary minerals to consider for the purpose of this study (for acid generating potential vs. neutralization potential of the materials) are pyrite, calcite, and dolomite. The Glynn Lydenburg samples show low pyrite (0.73%), high calcite (4.4%) and very high dolomite (19%) compared to the Nestor tailings materials which are composed of high pyrite (4.2%), very low calcite (0.01 %), and 0.96 % of dolomite. The associated secondary minerals are gypsum, Jarosite and goethite all of which are higher in concentration in Nestor tailings materials than that of which are in GL. This mineralogical data shows the high net acid generating capacity of the Nestor tailings compared to the Glynn Lydenburg ones.

Jarosite and Gypsum are the dominant secondary minerals on top layers (first top 5 samples) of the tailings at Nestor Mine. Furthermore, Goethite, a secondary oxide mineral, is absent from the grab samples collected from Nestor tailings but observed in high concentrations in the samples from the deeper part of the auger hole. Gibbsite is also not present in all Nestor mine tailings samples except for the one recorded at un-oxidized part of the tailings at about 2 m depth in one of the auger hole samples. Minerals such as quartz have no potential to neutralize acid due to their physical property (hardness) and their low relative reactivity rate of 0.004 that is twice slower than the relative reactivity rate of kaolinite (Sverdrup 1990; Kwong 1993).

Pyrite \(\text{(FeS}_2\text{)}\) and hematite are the major acid producing minerals. Mica is also common in high concentrations in both samples collected using handheld auger and grab samples. There is irregular trend in handheld auger drilled samples with some showing a decrease with depth which might be due to original mineralogical variation of the tailings deposits. Jarosite is a secondary mineral from oxidation of sulphides and it precipitates during evaporation of acidic, iron, and sulfate-rich water within mine waste material and store acid generated by oxidation process. The dissolution of soluble and less soluble iron sulfate minerals also contribute to the acid mine drainage; however, most of the AMD from sulphide-bearing geological formations are from oxidation of sulphide minerals (Lapakko 2002).

Calcite is very low or absent in the Nestor Mine tailings with dolomite only found in two oxidized grab samples thus indicating that these tailings have high acid generating potential which has the potential to generate acidic discharge which may result in adverse conditions for the growth of plants and grass. The tailings from Glynn Lydenburg are comprised of quartz and dolomite \([\text{CaMg(CO}_3\text{)}]\) as major mineral assemblages (Fig. 4B). Other primary minerals that are acid neutralizing include mica and plagioclase. Gypsum and goethite are also present as secondary and neutralizing minerals, while the absence of jarosite in Glynn Lydenburg mine tailings could be attributed to the high neutralizing capacity of the materials due to the high concentrations of carbonates within the Malmani dolomite host rocks.
Plagioclase is mainly found in truck-mounted auger samples and showed a constant trend of decreasing with depth. Mica being common in all three drilled holes including handheld auger samples also showed a decrease with depth trend.

![Plagioclase vs. Mica Trend](image)

**Figure 4** The mineralogical analysis of (A) Nestor and (B) Glynn Lydenburg mine tailings

**Conclusions**

The study showed that the metal mobility was enhanced by the net acid generating capacity of the Nestor mine tailings. Whereas the alkaline conditions of the Glynn Lydenburg mine tailings lead to a non-acidic discharge. The presence of metals, metal oxides, neutralizing oxides and acid-forming oxides in the mine tailings are likely to have negative impact on the environment.
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References
