Potential of Alkaline Gold Mine Tailings to Treat and Prevent AMD Formation: A Case of an Acidic Gold Mine of Sabie-Pilgrim’s Rest Goldfields in South Africa

Naythan van Wyk¹, Elvis Fosso-Kankeu² and Andrew Eloka-Eboka ³

Abstract—Acid mine drainage (AMD) pollutes vast quantities of surface water and underground water supplies. AMD is considered to be the second-largest threat to sustainable life after global warming.

South Africa is a water-scarce country in a water-scarce continent (Africa). It is of utmost importance to prevent and treat AMD to preserve water resources and protect all forms of life, primarily aquatic life.

The South African government has recently postponed its R10 billion long-term AMD treatment plan, which involves treating AMD polluted water in order to produce potable water or industrial water using desalination.

Tailing or waste rock piles usually consist of low ore grades. However, most tailing deposits still contain elevated concentrations of sulphide minerals such as Pyrite (FeS₂) and Pyrrhotite (Fe₁₋ₓS (x = 0 - 0.2)) [2 - 3]. These sulphide minerals generate large quantities of acids referred to as acid mine drainage (AMD) when oxidised by oxygen and water supplied by the surrounding environment [2],[4 - 5].

Pyrite (FeS₂) generated 4 mol of protons when oxidised by oxygen (1). However, at low pH conditions (pH < 4), 16 moles of protons are generated per mol of pyrite when oxidised by ferric iron (Fe³⁺) (3). Sulphide minerals such as Sphalerite (ZnS), which are generally considered to be non-acid generating minerals (2), become acid generating minerals when oxidised by Ferric Iron (4) [6].

It is important to maintain the pH above 4 in order to minimise the quantity of acids generated.

The pH decreases within the tailings, enhancing conditions for acid generation and the dissolution of metals [7]. It is essential to maintain the pH of the tailings or waste rock above a pH of 4 to minimise the quantity of acid generated.

The acid-neutralising or pH-buffering reactions that contribute the most to acid neutralisation are the dissolution of carbonate minerals, aluminosilicates minerals and ferric iron hydroxides [7].

<table>
<thead>
<tr>
<th>Sulphide mineral</th>
<th>Reaction Equation</th>
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</thead>
<tbody>
<tr>
<td>Pyrite (FeS₂)</td>
<td>FeS₂ + 3.75O₂ + 3.5H₂O = Fe(OH)₃ + 2O₂ + 4H⁺</td>
</tr>
<tr>
<td>Sphalerite (ZnS)</td>
<td>ZnS + 2O₂ = Zn²⁺ + SO₄²⁻</td>
</tr>
<tr>
<td>Pyrite (FeS₂)</td>
<td>FeS₂ + 14Fe³⁺ + 8H₂O = 15Fe²⁺ + 2SO₄²⁻ + 16H⁺</td>
</tr>
<tr>
<td>Sphalerite (ZnS)</td>
<td>ZnS + 8Fe³⁺ + 4H₂O = Zn²⁺ + 8Fe²⁺ + SO₄²⁻ + 8H⁺</td>
</tr>
</tbody>
</table>

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It is imperative to assess the acid-generating capabilities of mine tailings or waste rock for the development of a suitable AMD treatment or prevention strategy. The acid-generating capabilities can either be evaluated using static tests such as ABA or NAG test or kinetic tests such as leach columns tests. The ABA and NAG tests are the most frequently used screening tools in the evaluation of the acid-generating capabilities of tailings and waste rock [5],[8 - 9].

The ABA results are usually used in conjunction with the NAG results to classify the tailings or waste rock as Potential acid-forming (PAF), non-acid-forming (NAF) or uncertain (UC). ABA and NAG are used in conjunction to compensate for some of the shortfalls encountered in both ABA and NAG test procedures [5],[8 - 9].

Table II summarises the classification criteria used to classify the acid-generating capabilities of mine tailings of water Rock as PAF, NAF or UC [5],[9].

<table>
<thead>
<tr>
<th>TABLE II: CLASSIFICATION CRITERIA</th>
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<tbody>
<tr>
<td>Criteria</td>
</tr>
<tr>
<td>NAPP ≤ 0 and NAGpH ≥ 4.4</td>
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<tr>
<td>NAPP &gt; 0 and NAGpH &lt; 4.4</td>
</tr>
<tr>
<td>(NAPP ≤ 0 and NAGpH &lt; 4.5) or if</td>
</tr>
<tr>
<td>(NAPP &gt; 0 and NAGpH ≥ 4.5)</td>
</tr>
</tbody>
</table>

Many AMD treatment and prevention techniques can be utilised to prevent and treat AMD generated by acid-generating waste rock or tailings. Many of these techniques have their advantages and disadvantages. Depletion of natural resources, high implementation costs, design inaccuracies, poor performance, and the generation of additional waste are the significant disadvantages associated with implementing traditional/conventional AMD treatment and prevention techniques [10].

II. METHOD

A. Sample collection

Two sets of samples were collected from two gold mine tailing piles in the Sabie-Pilgrim’s rest Goldfields, South Africa.

The first set of samples were collected from a gold mine tailings pile that was considered to be acid generating (AGS). The second set of samples were collected from gold mine tailings considered to be alkaline (ALK).

The AGS and ALK were mixed at a ratio of 3:1 and 1:1 to produce MIX1 and MIX2, respectively. AGS, MIX1, MIX2, and ALK were subjected to the static test as described below.

B. Acid-Base Accounting (ABA)

1) Paste pH

25 g of sample was mixed with 50 mL deionised water. The pH of the paste-like mixture was measured and recorded after two hours.

2) Acid Neutralising Capacity (ANC)

The ANC of the samples were determined using the modified ANC test procedure found in [5],[8].

Two grams of sample (M_{ANC}) were digested using hydrochloric acid (HCl), heated at 80 - 90 °C for two hours and then allowed to cool down to room temperature. A blank was prepared for each sample.

The digested sample solutions and blanks were titrated to a pH of 8.3 using sodium hydroxide (NaOH), of which the volumes (V_{NaOH}) and (V_{NaOH,Blank}) were recorded. Two drops of hydrogen peroxide (H_{2}O_{2}) were added at a pH of 5 during the titration procedure to promote precipitation of Fe(OH)_{3} and the oxidation of Fe^{2+}.

Equation (5) was used to calculate the ANC using volume sodium hydroxide (V_{NaOH}), sample weight (W), volume (V_{HCl}) and concentration (M_{HCl}) hydrochloric acid, and ANC constant C_{ANC} with a value of 49 as input variables.

\[
ANC = \left( V_{HCl} - \frac{V_{NaOH} \times V_{HCl,Blank}}{V_{NaOH,Blank}} \right) \times \frac{M_{HCl}}{W} \times C_{ANC} \tag{5}
\]

The ANC was reported in kilograms sulphuric acid per tonne of material (kg H_{2}SO_{4}/t).

3) Maximum Potential Acidity (MPA)

The MPA was calculated by multiplying the total sulphur content with a factor of 30.6 (6) to determine the quantity of acid that could theoretically be generated based on the sulphur content [5],[8]. The MPA is reported kg H_{2}SO_{4}/t.

\[
MPA = (S\%) \times 30.6 \tag{6}
\]

The NAPP and R_{ANC/MPA} were calculated using equations (7) and (8), respectively.

\[
NAPP = MPA - ANC \tag{7}
\]

\[
R_{ANC/MPA} = \frac{ANC}{MPA} \tag{8}
\]

C. Net Acid Generation (NAG)

A single addition NAG test was conducted in accordance with the test procedure stipulated in [5],[8].

Two and a half grams (M_{NAGO}) of each sample were added to a pH corrected, 250 mL, 15% H_{2}O_{2} solution and allowed to react overnight. The pH of the 15% H_{2}O_{2} solution was adjusted to a pH of 4.5 using NaOH as per procedure to prevent the misclassification of the acid-generating capabilities [5],[8].

The NAG solutions were gently heated at 30°C for an hour and then allowed to cool down to room temperature. The pH of the NAG solutions (NAGpH) was then measured and recorded. The NAG solutions were titrated to a pH of 4.5 and 7 using a 0.1 M NaOH solution. The volume (V_{NaOH}) and concentration (M_{NaOH}) Sodium hydroxide used during the titration as well as sample weight (W) were used to calculate the NAG (9) and reported in kg H_{2}SO_{4}/t.
\[ NAG = (49 \times V_{NaOH} \times M_{NaOH})/W \]  

(9)

III. RESULTS

AGS has a NAPP of 13 kg H$_2$SO$_4$/t of material and a NAGpH of 2.7, as seen in Table III. The acid-generating capabilities of AGS were classified as PAF using the classification criteria summarised in Table II.

The paste pH of AGS is extremely low, with a value of 2.5. The low paste pH indicated that the tailing from which the sample has collected has become acidic and is most likely generating an acidic effluent.

Furthermore, it was found that AGS has no acid neutralising capabilities and, based on the sulphur content of 0.43, will generate up to 13 kg H$_2$SO$_4$/t of material. A substantial portion of the MPA will most likely be in the form of stored acidity, which will be released instantaneously when in contact with water due to the low pH conditions (paste pH) [11].

The acid-generating capabilities of M1, M2 and ALK are considered to be NAF as M1, M2, and M3 have negative NAPP values and NAGpH values above 4.4. The negative NAPP value indicates that the acid neutralising capabilities are more pronounced than the acid-generating capabilities. In other words, any acid generated by the sample will be neutralised by the acid neutralising minerals such as calcite or dolomite contained in the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Paste pH (g H$_2$SO$_4$/kg)</th>
<th>ANC (kg H$_2$SO$_4$/t)</th>
<th>Total Sulphur (% of material)</th>
<th>MPA (kg H$_2$SO$_4$/t)</th>
<th>R$_{NAG\text{MPA}}$</th>
<th>NAPP (kg H$_2$SO$_4$/t)</th>
<th>NAGpH</th>
<th>NAG (kg H$_2$SO$_4$/t)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGS</td>
<td>2.5</td>
<td>0</td>
<td>0.43</td>
<td>13</td>
<td>0</td>
<td>13</td>
<td>2.7</td>
<td>6.9</td>
<td>PAF</td>
</tr>
<tr>
<td>MIX1</td>
<td>5.2</td>
<td>56</td>
<td>0.34</td>
<td>10</td>
<td>5</td>
<td>-46</td>
<td>4.9</td>
<td>0</td>
<td>NAF</td>
</tr>
<tr>
<td>MIX2</td>
<td>6.1</td>
<td>96</td>
<td>0.25</td>
<td>8</td>
<td>13</td>
<td>-89</td>
<td>5</td>
<td>0</td>
<td>NAF</td>
</tr>
<tr>
<td>ALK</td>
<td>7.7</td>
<td>184</td>
<td>0.07</td>
<td>2</td>
<td>86</td>
<td>-182</td>
<td>5.9</td>
<td>0</td>
<td>NAF</td>
</tr>
</tbody>
</table>

The ALK sample seems to contain a relatively high acid ANC and a high paste pH, indicating that a substantial portion of the ANC is present as readily available acid neutralising carbonates. The ANC of the ALK sample seems to provide sufficient ANC to the MIX1 and MIX2 samples to neutralise acid generated by the AGS portion of the mixtures.

IV. CONCLUSION

Using the ABA and NAG results of AGS, MIX1, MIX2 and ALK, it was concluded that ALK tailings have high acid neutralising capabilities and that the AGS tailings have become acidic and are most likely generating an acidic effluent leading to AMD.

The preliminary static test indicates that ALK tailings could either be mixed into AGS tailings or used as a cover to neutralise any acid generated by the AGS tailings in order to treat and prevent any further AMD generated by AGS.

Using the ALK as a pH neutralising cover could be an environmentally sustainable option. Thus, leach column tests have been conducted to study the feasibility of using ALK as a pH neutralising cover.

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