Passive neutralization of acid mine drainage using basic oxygen furnace slag as neutralization material: experimental and modelling

John N. Zvimba*a, Njabulo Siyakatshana*b, Matlhodi Mathye*c

bAdvanced Mathematical Modelling, Modelling and Digital Science, CSIR, P.O. Box 395, Pretoria 0001, South Africa.
cSource Directed Scientific Measures, Natural Resources and Environment, CSIR, P.O. Box 395, Pretoria 0001, South Africa.

John N. Zvimba (Johnz@wrc.org.za), Njabulo Siyakatshana (NSiyakatshana@csir.co.za), Matlhodi Mathye (MMaty@csir.co.za)

ABSTRACT

This study investigated the passive neutralization of acid mine drainage (AMD) using basic oxygen furnace (BOF) slag as neutralization agent over 90 days, with monitoring of the AMD quality parameters and assessment of their removal kinetics. The AMD quality was observed to significantly improve over time with most AMD parameters removed from the influent during the first 10 days. In this regard, removal of acidity, Fe(II), Mn, Co, Ni and Zn was characterized by fast kinetics while removal kinetics for Mg and SO$_4^{2-}$ were observed to proceed slowly. The fast removal kinetics of acidity was attributed to fast release of alkalinity from the slag minerals under mild acidic conditions of the AMD utilized resulting in rapid consumption of AMD acidity. The removal of AMD acidity through generation of alkalinity from BOF slag passive treatment system was also observed to generally govern the removal of metallic parameters through hydroxide formation, with overall percentage removals ranging 88 – 100 % achieved for the AMD parameters. The removal kinetics for SO$_4^{2-}$ was modelled using two approaches yielding rate constant values of 1.65 and 1.53 L/day.mol respectively, thereby confirming the authenticity of SO$_4^{2-}$ removal kinetics experimental data. The study findings generally provide insights into better understanding of the potential use of BOF slag, including its limitations for passive AMD remediation, as part of addressing this challenge in South Africa. In this regard, passive treatment system utilizing BOF slag as neutralization material would have potential application in mine closure.

Key words: slag, characterization, quality, experimental, modelling, kinetics
1. Introduction

Gold mining in South Africa over the past century has resulted in the Witwatersrand (divided into East, West, Far West and Central Rand basins) gold bearing reef yielding 40% of all the gold ever mined on earth (Hanlon, 2010). While this has benefited the country economically, such extensive mining has also significantly altered the groundwater hydrology of the basin resulting in generation of low pH effluent rich in ferrous iron, sulphate and heavy metals, generally known as acid mine drainage (AMD). In this regard, AMD from the lowest lying mine shafts in the West Rand basin started decanting at a rate of 15–35 ML/day in 2002 (Coetzee et al., 2004) posing threats to the Krugersdorp Game Reserve and the Cradle of Humankind World Heritage Site. Moreover, extensive coal mining activities are current operational based on the thermal power dependence of South Africa, and this poses future AMD challenges, particularly in the Mpumalanga province. Globally AMD has already been identified as a major environmental problem facing the mineral industry (Ribet et al., 1995) resulting in serious and sometimes permanent ecological damage (Micera and Dessi, 1988); with widely studied and reported detrimental environmental effects (Baird, 1995; Bell et al., 2002).

As part of the efforts to come up with an everlasting solution on AMD in South Africa, short term interventions dealing with uncontrolled AMD decant and long term interventions seeking a permanent solution regarding AMD desalination have been outlined (Department of Water Affairs, 2013). The short-term interventions are based on the South African Government-appointed Inter-Ministerial committee recommendations (Coetzee et al., 2010), to urgently construct a 20 ML/d emergency AMD neutralization plant. In this regard, the Council for Scientific and Industrial Research (CSIR) have successfully developed innovative technologies on AMD neutralization (Geldenhuys et al., 2003), with full scale operational plants worldwide and such technology has become the basis for the short-term intervention in the Western Basin. However, implementation of the short-term interventions, though urgent and necessary at the moment, these do not comprehensively address the significant sludge generation associated with AMD neutralization. Moreover, based on the current learnings from AMD challenges resulting from 100 year of gold mining, similar challenges are projected in coal mining upon their future closure. Therefore, there is still need to continue investigations into alternative ways on AMD remediation, particularly options that are simple and cost effective. In this regard, passive treatment approaches become economically attractive, providing low cost solutions, particularly for the treatment of waters with low acidity, low flow rates where the key chemical outcome is to achieve a near neutral pH and associated low metal concentrations. When used in isolation, passive treatment systems have proven to be most successful at addressing post mining closure, particularly at some coal mines.

Basic oxygen furnace (BOF) slag is a solid residue generated from basic oxygen furnaces during steelmaking processes with an estimated 12 million tons (Mt) and 8 Mt generated annually in Europe and United States, respectively (Proctor et al., 2000; Motz and Geiseler, 2001). In South Africa, the steelmaking industry generates about 4 million tons of by-products from steel making each year, 600 000 tons of which is BOF slag. This is partially
reused in the steel making process because of minor elements contamination, with a significant proportion stockpiled at various sites across the country. In this regard, recycling of BOF slag (Lekakh et al., 2008; Doucet E.F., 2010; Gunning et al., 2010), remains globally restricted, thereby limiting the quantity of BOF slag that can be charged back into the blast furnace (Topkaya et al., 2004). In order to avoid landfilling, the steelmakers usually try to process the slag into useful materials. Thus, BOF slag has been shown to be suitable in various construction applications because of its high strength and durability, and can potentially replace gravel and rock (Motz and Geiseler, 2001). However, the use of BOF slag in road construction, particularly in the South African context has been restricted because of undesirable volume instability (volumetric expansion and disintegration) of the slag aggregate, attributable to hydration of free lime and magnesium oxides in the slag (Mikhail and Turcotte, 1995). However, South Africa being a mineral-rich country, the use of BOF slag for passive remediation of AMD resulting from mining operations, has potential for an environmentally sustainable solution where one waste material could be used for treatment of another. This potential arises from the significant quantities of CaO and MgO present in BOF slag. The potential of using steel slags for neutralization of industrial effluents has previously been described by Cunha et al. (2008a, 2008b). These steel slags generally exhibited a high neutralization capacity and a slower rate of dissolution which are conducive features for passive neutralization.

The current study has therefore investigated passive neutralization of AMD using BOF slag as neutralization material from an experimental and modelling perspective. Overall, a better understanding of insights into the assessment of BOF slag for passive AMD neutralization will provide critical knowledge into the potential use of this abundant waste material as an alternative, particularly for post mine closure in a country that continues to seek an everlasting solution to the AMD challenge.

2. Materials and methods

2.1. Feedstock

AMD containing acidity of about 1813±246 mg/L CaCO₃ equivalent, 630±24 mg/L Fe(II), 2903±49 mg/L SO₄²⁻, pH ranging 5.0±0.1 – 6.0±0.1, and metals; Ca (733±33 mg/L), Mg (243±34 mg/L), Mn (51±1 mg/L), Co, Ni & Zn (0.2±0.01 – 0.3±0.01 mg/L) as given in Table 1 was collected from the Witwatersrand’s Western Basin and used as feed water. BOF slag of particle size range 3 – 14 mm and composition given in Table 2 was collected from a major South African Iron and Steel making company and used as the neutralization material during passive treatment. Organic matter collected from a contamination-free natural forest on campus was used as top layer above the BOF slag to control the redox state of the system and also minimise armouring so as to extend the life expectancy of the passive treatment system as recommended by Taylor et al. (2005). While the inclusion of the organic material in a
passive system was standard as per literature, its characterization was beyond the scope of the study.

2.2. Equipment

Passive AMD neutralization using a 500 L BOF slag alkalinity producing system as given in Figure 1 was used. The 500 L container was used as a passive AMD neutralization system, with feed AMD introduced as influent while neutralized AMD was collected as effluent. A Toledo Auto-titrator was used for the determination of pH, acidity and alkalinity, while a HaCH DR 3900 spectrophotometer was used for SO$_4^{2-}$ determination at 450 nm.

![Figure 1. Schematic representation of the BOF slag-based passive neutralization system](image)

2.3. Experimental procedure

The 500 L container used as passive neutralization system was filled with fully characterized BOF slag of particle size range 3 – 14 mm and covered with plastic. A layer of organic material (not characterized) was placed on top of the BOF slag in accordance to the recommendations by Taylor et al. (2005) (Figure 1). Feed AMD (~ 400 L) was pumped into the model pit and allowed to slowly soak through the organic material and BOF slag until the AMD filled up the container to achieve the required hydraulic head. Three sample aliquots were collected from the feed AMD before the BOF slag-based alkalinity producing passive system was left to undergo passive AMD neutralization. Sample aliquots of AMD effluent were collected on specific days as triplicates over a 24-hr period during the passive AMD neutralization period of 3 months for the experimental determination of selected AMD based quality parameters as given in Table 1. BOF slag was characterized for both major and trace elements before and after AMD neutralization using X-ray fluorescence (XRF). Kinetic modelling was conducted using two approaches (logarithmic plot of concentration ratio vs time & non-linear regression analysis) fitting SO$_4^{2-}$ experimental data to a second order kinetics model, postulating SO$_4^{2-}$ removal reaction as an elementary second order reaction.
2.4. Analytical procedure

Feed AMD quality was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian: Vista Pro CCD Simultaneous ICP-OES). The pH, acidity, alkalinity of the AMD were determined using a Mettler Toledo Auto-titrator following filtration. Fe(II) was determined using standard permanganate titrimetric technique (Standard Methods for the Examination of Water and Wastewater, 1992) while SO$_4^{2-}$ was determined using a HaCH DR 3900 spectrophotometer at 450 nm. BOF slag was characterized for major and trace elements using XRF (PANalytical Epsilon 3 XL, Almelo, Netherlands).

3. Results and discussion

3.1. AMD and BOF slag characterization

Table 1 shows the feed AMD quality before AMD passive neutralization using BOF slag and the AMD effluent quality at different time points: 1 day, 1 week, 1 month, 2 months & 3 months during passive neutralization. Table 2 shows the chemical composition for BOF slag, while Figure 2 shows the XRF scan for BOF slag before and after AMD neutralization. It can be seen from Table 1 that the major AMD parameters include Fe(II), acidity, SO$_4^{2-}$, Ca, Mg & Mn, while Co, Ni & Zn constituted minor AMD parameters. From Table 2, the major components of BOF slag include SiO$_2$ (15.7%), Al$_2$O$_3$ (9.12%), Fe$_2$O$_3$ (24.7%), MnO (3.44%), MgO (6.44%) and CaO (36.5%). Thus, CaO and MgO constitute the alkalinity producing components of BOF slag useful for AMD neutralization. On the other hand, Al$_2$O$_3$, MnO, SiO$_2$ and Fe$_2$O$_3$ make up undesirable slag minerals that may contribute to contamination of neutralized AMD through metal leaching (Engström et al. 2013). Based on Table 1, the AMD quality was observed to improve during passive neutralization as the initial feed acidity (1813±246), Fe(II) (628±24), SO$_4^{2-}$ (2903±49), Mg (243±34), Mn (51±1), Co (0.3±0.01), Ni (0.32±0.01) and Zn (0.17±0.02) significantly decreased over the neutralization period. This change in AMD quality is attributed to the removal of metals via metal hydroxide formation as the pH of the feed AMD increases from 5.9 to 9.6 upon contact of AMD with the BOF slag bed. The general dissolution of slag minerals and the subsequent consumption of acidity during AMD neutralization have been described by Engström et al. (2013), and are based on; for calcium; the formation of Ca$^{2+}$, for aluminium; the formation of Al$^{3+}$ and for magnesium the formation of Mg$^{2+}$ according to Equations. (1) – (3). The silica released from the silica-containing minerals dissolves in water according to Eq. (4), while aluminium at neutral pH values (5 – 9) precipitates as hydroxide according to Eqn. (5).

\[
\text{CaO(s) + 2H}^+(aq) \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} \tag{1}
\]

\[
\text{MgO(s) + 2H}^+(aq) \rightarrow \text{Mg}^{2+} + \text{H}_2\text{O} \tag{2}
\]

\[
\text{Al}_2\text{O}_3(s) + 6\text{H}^+(aq) \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O} \tag{3}
\]
$\text{SiO}_2(s) + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4(aq)$  \hspace{1cm} (4)

$\text{Al}^{3+}(aq) + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3(s) + 3\text{H}^+(aq)$  \hspace{1cm} (5)

$\text{Si(OH)}_4(aq) \rightarrow \text{Si(OH)}_3^- (aq) + \text{H}^+(aq)$  \hspace{1cm} (6)

$\text{Al(OH)}_3(s) + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_4^- (aq) + \text{H}^+(aq)$  \hspace{1cm} (7)

**Table 1.** Feed AMD quality before and during passive neutralization

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feed AMD before neut.</th>
<th>1 day</th>
<th>1 week</th>
<th>1 month</th>
<th>2 months</th>
<th>3 months</th>
<th>WHO(^c) (DWA)(^b) Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.9±0.1</td>
<td>7.4±0.2</td>
<td>8.5±0.5</td>
<td>7.6±0.1</td>
<td>8.9±0.1</td>
<td>9.6±0.1</td>
<td>6.0 - 9.0</td>
</tr>
<tr>
<td>Acidity</td>
<td>1813±246</td>
<td>53±20</td>
<td>39±1</td>
<td>12±10</td>
<td>0</td>
<td>0</td>
<td>NA</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>628±24</td>
<td>237±110</td>
<td>126±14</td>
<td>74±21</td>
<td>46±8</td>
<td>37±16</td>
<td>0 - 0.3 (0 - 0.1)</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>2903±49</td>
<td>248±34</td>
<td>1865±55</td>
<td>1530±64</td>
<td>1164±17</td>
<td>783±100</td>
<td>0 - 500</td>
</tr>
<tr>
<td>Ca</td>
<td>733±33</td>
<td>940±80</td>
<td>870±68</td>
<td>299±4</td>
<td>353±20</td>
<td>179±12</td>
<td>0 - 32</td>
</tr>
<tr>
<td>Mg</td>
<td>243±34</td>
<td>202±2</td>
<td>131±39</td>
<td>51±1</td>
<td>33±0</td>
<td>16±1</td>
<td>0 - 30</td>
</tr>
<tr>
<td>Mn</td>
<td>51±1</td>
<td>20±6</td>
<td>1.2±0.7</td>
<td>0.9±0.1</td>
<td>0.4±0.1</td>
<td>0.1±0.01</td>
<td>0 - 0.1 (0 - 0.05)</td>
</tr>
<tr>
<td>Co</td>
<td>0.3±0.01</td>
<td>0.04±0.02</td>
<td>0.01±0.003</td>
<td>0.008±0.003</td>
<td>0.009±0.001</td>
<td>0.005±0</td>
<td>NA(^c)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.32±0.01</td>
<td>0.05±0.01</td>
<td>0.017±0.002</td>
<td>0.007±0.001</td>
<td>0.009±0.001</td>
<td>0.008±0.001</td>
<td>NA(^c)</td>
</tr>
<tr>
<td>Zn</td>
<td>0.17±0.02</td>
<td>0.02±0</td>
<td>0.02±0</td>
<td>0.02±0</td>
<td>0.02±0</td>
<td>0.02±0</td>
<td>0 - 3 (0 - 0.5)</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;0.03</td>
<td>-</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>-</td>
<td>&lt;0.03</td>
<td>NA</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;0.02</td>
<td>-</td>
<td>1.3±0.3</td>
<td>4.1±2.0</td>
<td>-</td>
<td>8.1±2.0</td>
<td>NA</td>
</tr>
</tbody>
</table>

\(^a\)WHO - World Health Organization (WHO) (2011)

\(^b\)DWA - Department of Water Affairs (DWA) of South Africa (1996)

\(^c\)NA - not available.

**Table 2.** BOF slag chemical composition (%) for major elements before and after AMD neutralization

<table>
<thead>
<tr>
<th>Component</th>
<th>Before neutralization (wt. %)</th>
<th>After neutralization (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>15.7</td>
<td>16.2</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.47</td>
<td>0.52</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>9.12</td>
<td>7.62</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>24.7</td>
<td>24.4</td>
</tr>
<tr>
<td>MnO</td>
<td>3.44</td>
<td>3.25</td>
</tr>
<tr>
<td>MgO</td>
<td>6.44</td>
<td>5.31</td>
</tr>
<tr>
<td>CaO</td>
<td>36.5</td>
<td>37.9</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.37</td>
<td>1.49</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>0.65</td>
<td>1.00</td>
</tr>
<tr>
<td>LOI</td>
<td>1.94</td>
<td>1.66</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>0.41</td>
<td>0.50</td>
</tr>
<tr>
<td>Total</td>
<td>100.2</td>
<td>100.2</td>
</tr>
</tbody>
</table>
The dissolution of silica is the only pH-independent reaction during AMD neutralization, while precipitation of aluminium hydroxide generates acidity. Under alkaline pH (>10.0) the silica and aluminium react further with release of more acidity, but this is not experienced under the conditions of the current study, since a maximum pH of 9.6 was reached. In this regard, the release of acidity from Eqn. 5 as Al\(^{3+}\) is removed from AMD via hydroxide precipitation created a natural pH buffer that delayed attainment of alkaline conditions that would result in the release of undesirable soluble Al(OH)\(_4^-\) species, thereby reintroducing removed Al\(^{3+}\) back into the neutralized AMD as given in Equation. 7. The determination of Al, total Fe (result not shown in Table 1) and Si in three samples selected over the entire study period confirmed that no Al (<0.03 mg/L) and Fe (0.07 mg/L) was released with only Si increasing from less than 0.02 mg/L at the beginning of neutralization to 8.1±2.0 mg/L at the end of AMD neutralization. The release of Si into the AMD effluent therefore confirms the pH-independent dissolution of silica from BOF slag during passive treatment, and is the only major limitation identified in this study.

A comparison of the concentration for the effluent AMD parameters given in Table 1 to those published by WHO (2011) shows that most parameters (pH, acidity Mg, Mn, Co, Ni, & Zn) are either within the acceptable WHO limits or removed to zero levels following three months of passive neutralization. In this regard, acidity, Fe(II), SO\(_4^{2-}\), Mg, Mn, Co, Ni and Zn decreased from 1813±246, 628±24, 2903±49, 243±34, 51±1, 0.3±0.01, 0.32±0.01 and 0.17±0.02 mg/L to 0, 37±16, 783±100, 16±1, 0.1±0.01, 0.005±0, 0.008±0.001 and 0.02±0 mg/L respectively. This represented percentage removal efficiencies of 100, 94.1, 73, 93.4, 99.8, 98.3, 97.5 and 88.2% for acidity, Fe(II), SO\(_4^{2-}\), Mg, Mn, Co, Ni and Zn respectively, suggesting a potential simple and cost effective solution for post mine closure in the South African context. In a previous study (Zvimba et al. 2013), a 97% removal of Fe(II) in a sequencing batch reactor over 30 min with aeration, reactor stirring and using commercial CaCO\(_3\) as neutralization agent was reported. The currently reported Fe(II) removal of 94% over 3 months closely compares to the previously reported data, with the slight deviation suggesting the impact of operating parameters such as aeration, stirring and the nature of neutralization agent. However, passive neutralization of AMD using BOF slag has significant potential as a cost effective and sustainable option that can be considered for mine closure, considering the energy intensive nature of other alternatives such as reverse osmosis (RO). The significant overall percent removal of SO\(_4^{2-}\) (73%) is rather surprising as SO\(_4^{2-}\) removal through gypsum crystallization is generally governed by the solubility of gypsum (K\(_{sp}\) = 9.1 × 10\(^{-6}\)) which is a function of SO\(_4^{2-}\) and Ca\(^{2+}\) concentrations as well as the ionic strength. In this regard, the removal of SO\(_4^{2-}\) from AMD containing 2903±49 mg/L resulting in final SO\(_4^{2-}\) levels of about 783±100 mg/L at the end of the study strongly suggests the role of other removal mechanisms such as adsorption within the BOF slag bed during passive neutralization. The removal of SO\(_4^{2-}\) has been previously reported to decrease from 3,800 to 2,500 mg/L during AMD neutralization using CaCO\(_3\) in a sequencing batch reactor, with further SO\(_4^{2-}\) removal to 1,368 mg/L only achieved following addition of more soluble Ca(OH)\(_2\) (Zvimba et al. 2013). These findings suggest that SO\(_4^{2-}\) removal via adsorption in a sequencing batch reactor maybe disrupted by both aeration and stirring. Therefore, further optimization of SO\(_4^{2-}\) removal during passive AMD neutralization that integrates adsorption
and crystallization should be considered as part of further investigations, and this could be a major breakthrough for AMD desalination.

Overall, a comparison of the major and trace elements composition in BOF slag before and after AMD neutralization as given in Tables 2, 3 and Fig. 2 shows no significant changes in the BOF slag chemical composition, and this suggest insignificant metal leaching over the study period. This is a critical outcome as it suggests the potential disposal of the BOF slag-organic material-sludge residue by filling the mine voids as a sustainable approach beyond AMD treatment and recovery of clean water.

Table 3. BOF slag chemical composition (%) for trace elements before and after AMD neutralization

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Ba</th>
<th>Bi</th>
<th>Br</th>
<th>Cd</th>
<th>Ce</th>
<th>Cl</th>
<th>Co</th>
<th>Cs</th>
<th>Cu</th>
<th>Ga</th>
<th>Ge</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before neutral. (mg/L)</td>
<td>&lt;5.00</td>
<td>149</td>
<td>&lt;5.00</td>
<td>&lt;5.00</td>
<td>8.92</td>
<td>106</td>
<td>757</td>
<td>171</td>
<td>&lt;5.00</td>
<td>5.22</td>
<td>&lt;5.00</td>
<td>61</td>
<td>4.47</td>
</tr>
<tr>
<td>After neutral. (mg/L)</td>
<td>&lt;5.00</td>
<td>189</td>
<td>&lt;5.00</td>
<td>&lt;5.00</td>
<td>9.58</td>
<td>94.5</td>
<td>729</td>
<td>177</td>
<td>2.33</td>
<td>7.41</td>
<td>1.22</td>
<td>56</td>
<td>11.2</td>
</tr>
<tr>
<td>Hg</td>
<td>La</td>
<td>Lu</td>
<td>Mo</td>
<td>Nb</td>
<td>Nd</td>
<td>Ni</td>
<td>Pb</td>
<td>Rb</td>
<td>Sb</td>
<td>Sc</td>
<td>Se</td>
<td>Sm</td>
<td></td>
</tr>
<tr>
<td>Before neutral. (mg/L)</td>
<td>&lt;5.00</td>
<td>166</td>
<td>&lt;1.00</td>
<td>8.94</td>
<td>87.4</td>
<td>73.9</td>
<td>74.8</td>
<td>185</td>
<td>30.3</td>
<td>4.8</td>
<td>40.2</td>
<td>&lt;5.00</td>
<td>&lt;5.00</td>
</tr>
<tr>
<td>After neutral. (mg/L)</td>
<td>&lt;5.00</td>
<td>167</td>
<td>&lt;1.00</td>
<td>7.96</td>
<td>88.3</td>
<td>58.1</td>
<td>73.2</td>
<td>162</td>
<td>28.9</td>
<td>6.5</td>
<td>29.6</td>
<td>&lt;5.00</td>
<td>&lt;5.00</td>
</tr>
<tr>
<td>Sn</td>
<td>Sr</td>
<td>Ta</td>
<td>Te</td>
<td>Th</td>
<td>Tl</td>
<td>U</td>
<td>V</td>
<td>W</td>
<td>Y</td>
<td>Yb</td>
<td>Zn</td>
<td>Zr</td>
<td></td>
</tr>
<tr>
<td>Before neutral. (mg/L)</td>
<td>11.2</td>
<td>124</td>
<td>6.62</td>
<td>&lt;5.00</td>
<td>20.5</td>
<td>&lt;5.00</td>
<td>&lt;5.00</td>
<td>470</td>
<td>24</td>
<td>&lt;5.00</td>
<td>&lt;5.00</td>
<td>101</td>
<td>19.7</td>
</tr>
<tr>
<td>After neutral. (mg/L)</td>
<td>6.43</td>
<td>123</td>
<td>4.88</td>
<td>&lt;5.00</td>
<td>16.9</td>
<td>&lt;5.00</td>
<td>&lt;5.00</td>
<td>578</td>
<td>19.9</td>
<td>&lt;5.00</td>
<td>&lt;5.00</td>
<td>117</td>
<td>14.2</td>
</tr>
</tbody>
</table>
Figure 2. XRF pattern for BOF slag (a) before and (b) after neutralization

3.2. Acidity, sulphate & metals removal kinetics

Fig. 3 shows the observed data for acidity, $\text{SO}_4^{2-}$ and metals removal kinetics during the passive AMD neutralization using BOF slag as neutralization material. From Figure 3, it can be observed that removal of acidity, Fe(II), Mn, Co, Ni & Zn is characterised by an initial rapid decrease of these AMD parameters during the first 10 days of neutralization before reaching a plateau at almost zero concentration. In this regard, the removal for acidity, Fe(II), Mn, Co, Ni and Zn was observed to be 97.1, 62.3, 60.8, 86.7, 84.4 and 88.2% respectively by day 1, and this increased significantly by day 7.
Figure 3. Acidity, sulphate and metals’ removal kinetics during passive AMD neutralization using BOF slag as alkalinity generating system.

However the removal kinetics for Mg and $SO_4^{2-}$ during AMD neutralization appeared to initially proceed much slower during the first 15 days. From Figure 3, the removal of Mg and $SO_4^{2-}$ was observed to be 16.9 and 15.5% after day 1 and slightly increased to 46.1 and 35.7% respectively, by day 7. The removal of $SO_4^{2-}$ from AMD proceeds via gypsum crystallization, a process generally associated with slow kinetics (Geldenhuys et al. 2003). However, the fact that $SO_4^{2-}$ was overall removed from 2903 ± 49 mg/L to 783 ± 100 suggest additional removal mechanisms such as adsorption in addition to the normal gypsum crystallization.

Based on the data given in Figure 3, it appears acidity removal generally governs the removal kinetics of most metals. In this regard, metal removal is expected to be a result of metal hydroxide precipitation during AMD neutralization. The dissolution or leaching of alkalinity producing components would probably be characterized as a surface reaction, followed by a solid-liquid diffusion process resulting in alkalinity generation and consumption of acidity as given in Equations. 1 – 3. The consumption of acidity is also partially enhanced by the acid catalysed oxidation of ferrous iron during AMD neutralization as given in Equation. 8.
As the acidity gets rapidly removed from AMD during neutralization as shown in Figure 3; the pH of the AMD increases as given in Table 1 resulting in removal of metals such as Fe$^{3+}$, Mn, Co, Ni, & Zn as metal hydroxides (Equation 9). However, Mg removal proceeds at a slower rate as its complete removal is only achieved at pH values greater than 11.

$$3\text{Ca(OH)}_2(\text{aq}) + 3\text{M(SO}_4\text{)}(\text{aq}) \rightarrow 3\text{CaSO}_4(s) + 3\text{M(OH)}_2(s)$$  \hspace{1cm} (9)

where M = Al, Fe(II), Mg, Mn, Co, Ni or Zn

Such pH dependent removal of metals has also been previously reported for treatment of acidic wastewaters and AMD neutralization in active mode (Zvimba et al. 2012, 2013), with complete Mg removal only achieved under highly alkaline pH. The pH conditions achieved in current study therefore provides a desirable natural trade-off achievable in BOF slag-based passive systems regarding reaching the right alkaline conditions for acceptable Mg removal without compromising the precipitated Al(OH)$_3$.

Based on the observed AMD parameter removal dynamics, the proposed passive AMD neutralization methodology has potential feasibility for post mine closure, whereby the BOF slag-organic matter-sludge system would be contained in a lined lagoon during passive treatment. Once the BOF slag-organic matter-sludge system is exhausted with confirmation of no metal leaching occurring as observed in the current study, the lagoon can be de-sludged and the remaining residue possibly used to fill in the mine void. If such an approach is successfully implemented based on the outcomes of current study, it presents sustainability opportunities for the suggested methodology.

### 3.3. Sulphate removal kinetics

Sulphate removal is one of the critical indicator parameter of AMD treatment and this is generally described by Equation 9. This parameter was modelled as a second order reaction between dissociated Ca$^{2+}$ cations and SO$_4^{2-}$ anions. The progressive leaching of Ca$^{2+}$ into solution, according to Equation 1 can be neglected, since, according to Table 1, the acidity actually declines dramatically after one day. Based on these assumptions, the reaction model can be described as given in Equation 10.

$$\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{CaSO}_4(s)$$  \hspace{1cm} (10)

whose second order reaction rate can be written as given in Equation 11.

$$r = k[\text{Ca}^{2+}][\text{SO}_4^{2-}]$$  \hspace{1cm} (11)

Where $r$ is the rate of reaction for any species in the reaction, specified by the stoichiometric coefficient, $k$ is the reaction rate constant and [ ] denotes concentration of species in [mol/L]. The reaction is assumed to be an elementary reaction between Ca$^{2+}$ and SO$_4^{2-}$, hence the order of reaction with respect to each species is unity. The reaction is a bi-molecular reaction,
hence the value of $[\text{Ca}^{2+}]$ is given by \{\([\text{Ca}^{2+}]_0 - ([\text{SO}_4^{2-}]_0 - [\text{SO}_4^{2-}])\}, where the subscript 0 denotes initial concentration. In the case of $\text{SO}_4^{2-}$, following some algebraic manipulation, the reaction rate is designated as given in Equation 12.

$$r = -\frac{d[\text{SO}_4^{2-}]}{dt} = k\left([\text{SO}_4^{2-}]^2 + [\text{SO}_4^{2-}] \cdot ([\text{Ca}^{2+}]_0 - [\text{SO}_4^{2-}]_0)\right)$$

(12)

For ease of designation, we denote $X = [\text{SO}_4^{2-}]$, $Y = [\text{Ca}^{2+}]$, and $B = ([\text{Ca}^{2+}]_0 - [\text{SO}_4^{2-}]_0)$ and re-write Eq. (12), where $Y_0 \neq X_0$ as given in Equation (13)

$$-\frac{dX}{dt} = k(X^2 + X \cdot B)$$

(13)

Using appropriate theories of calculus to integrate in the intervals $[X_0, X]$, and $[0, t]$, results in the expression given in Equation 14.

$$X = \frac{B}{e^{(k/t) \cdot \ln\left(\frac{X_0}{Y_0}\right)}}$$

(14)

Two approaches are followed in the kinetic modelling, firstly, the integral form of the rate equation to demonstrate second order kinetics is used, and secondly Equation 14 to perform non-linear regression is applied. Ideally, values of $k$ from both approaches should correspond.

3.3.1 Second Order Kinetics

According to rate laws (Smith, 1970), for a second order kinetics postulation to hold,

$$\ln\left(\frac{X}{Y}\right) = k(X_0 - Y_0)t + \ln\left(\frac{X_0}{Y_0}\right)$$

(15)

and thus, a plot of $\ln(X/Y)$ against time ($t$) provides a straight line from whose slope the rate constant can be determined. This is shown in Figure 4. From this equation the slope is equal to $k(X_0 - Y_0)$, where $X_0$ (sulphate) is known from Table 1, i.e. 2903 mg/L or 0.0302 mol/L and $Y_0$ (calcium ions) is extrapolated from the data in Table 1 according to the graph. This is necessitated by the outlying initial recording on Table 1, i.e. a lower concentration (733) than the proceeding recording (940) for $\text{Ca}^{2+}$.

Accordingly, $Y_0$ corresponds to concentration on day 0, and from the extrapolation via logarithmic regression, $Y_0 = 1066$ mg/L = 0.0266 mol/L. Thus $(X_0 - Y_0) = 0.0036$ mol/L. From this, it then follows that

$$k = \frac{0.0056}{(X_0 - Y_0)} = 1.56 \frac{L}{\text{mol.day}}$$

Thus, the value of $k$ determined from the slope in Figure 4 is 1.56 [L/day.mol].
Figure 4. Logarithmic plot of rate data, yielding a rate constant value of $k = 1.56\ [\text{L/day.mol}]$

### 3.3.2 Non-Linear Regression

Unlike the first approach, the second approach focuses purely on the concentration of $\text{SO}_4^{2-}$, which is the most accurately measured component and determine the reaction constant. Because Equation 14 is a non-linear expression in $k$, the Gauss-Newton non-linear regression technique as described by Seber & Wild (2003), which focusses on minimizing the sum of squares between the experimental values and model values from Equation 14 was used.

$$Q[k] = \sum_i \left( X_{\text{exp}}[t_i] - X_{\text{mod}}[t_i, k] \right)^2 \Rightarrow \min,$$  \hspace{1cm} (16)

where $X_{\text{exp}}$ represents experimental values of $[\text{SO}_4^{2-}]$ and $X_{\text{mod}}$ represents modelled values (Equation 14) of the same variable. The expression for the model (Equation 14) is approximated by a Taylor expansion truncated by the first derivative with respect to $k$, which is given by;

$$X_{\text{mod}}[t, k_0] = X(k_0) + \frac{dX(k_0)}{dk} (k_1 - k_0) \quad \text{where} \quad \frac{dX(k)}{dk} = -B^2 te^{Bkt - \ln \left( \frac{X_0}{X_0 + B} \right)} \left( e^{Bkt - \ln \left( \frac{X_0}{X_0 + B} \right)} - 1 \right)^2.$$  \hspace{1cm} (17)

After setting $(k_1 - k_0) = m$, Equation 17 is substituted into Equation 16 and setting at the minimum, $dQ/dm = 0$, successive iterations of $m$ are undertaken and produce new and updated values of $k$, until a final value of $k$ is obtained at the required tolerance. This was performed in Matlab, using a specially written code. The value of rate constant obtained from
non-linear regression $k = 1.53$ [L/day.mol]. In this regard, the values of $k$ obtained in both cases corresponds very well, confirming the authenticity of $SO_4^{2-}$ removal kinetics experimental data.

![Graph showing sulphate concentration over time](image)

**Figure 5.** Plot of Experimental values of [$SO_4^{2-}$] versus kinetic model (Equation 14) after non-linear regression is applied. Value of $k = 1.53$ [L/day.mol]

### 4. Conclusions

Results from this study showed that for most AMD based parameters; the removal is associated with initial fast removal kinetics with most parameters’ removal achieved within 10 days of passive AMD neutralization. Although the removal of Mg and $SO_4^{2-}$ was characterized by initial slow kinetics, Mg was removed to below the acceptable WHO limit while $SO_4^{2-}$ was surprisingly removed to levels much lower than those normally achieved in active reactor systems suggesting the role of additional removal mechanisms during neutralization. No significant leaching of BOF slag based toxic metals such as Al was observed during AMD neutralization as passive neutralization was naturally buffered to operate within pH conditions where Al(OH)$_3$ precipitation was favourable as opposed to Al leaching. However, the pH independent leaching of Si from silica minerals in BOF slag could not be prevented and this was identified as a current limitation associated with passive AMD neutralization using BOF slag, and would require further investigation. Modelling of the $SO_4^{2-}$ removal kinetics showed that the experimental data fitted the theoretical data and this was represented by second order kinetics. Overall, the removal of most AMD parameters during passive AMD neutralization using BOF slag as neutralization material was generally
achieved to acceptable WHO limits over 90 days, suggesting potential use of BOF slag for
passive AMD treatment for post mine closure, possibly in lined neutralization lagoons where
longer retention times can be achieved, with potential of using the final residue for mine void
taking as a sustainable disposal method. Therefore, the study provides further critical
knowledge in understanding more insights into the potential application of the principle on
waste as a resource to achieve future sustainability.

Acknowledgements

We acknowledge the support of the CSIR, South Africa, for funding the project, the
WATERLAB (Pvt) Ltd for providing analytical data, Phumulani Msomi for assisting with
sample analysis.

References

Standard Methods for the Examination of Water and Wastewater, 1992 19th edition,
American Public Health Association/American Water Works Association/Water
Environment Federation, Washington DC, USA.


Bell F. G., Halbich T. F. J. & Bullock S. E. T. 2002 The effects of acid mine drainage from
an old mine in the Witbank coalfield, South Africa. Quarterly Journal of Engineering
Geology and Hydrogeology, 35(3), 265–278.

Coetzee H., Hobbs P. J., Burgess J. E. Thomas A., Keet M., Yibas B., van Tonder D., Netili
F., Rust U., Wade P. & Maree, J. P. 2010 Mine water management in the Witwatersrand gold
fields with special emphasis on acid mine drainage. Report to the Inter-Ministerial
Committee on Acid Mine Drainage, pp. 1–128.

Coetzee H., Winde F. & Wade P. 2004 An assessment of sources, pathways, mechanisms and
risks of current and potential future pollution of water and sediments in gold-mining areas of
the Wonderfonteinspruit Catchment. Water Research Commission Report No. 1214/1/06,
Pretoria, South Africa.

Cunha M. L., Gahan C. S. Menad N. & Sandström Å. 2008a Leaching behaviour of industrial
oxidic by-products: Possibilities to use as neutralisation agent in bioleaching. Materials
Science Forum, 587–588, 748–752.

Cunha M. L., Gahan C. S., Menad N. & Sandström Å., 2008b Possibilities to use oxidic
by-products for precipitation of Fe/As from leaching solution for subsequent base metal
recovery. Minerals Engineering, 21, 38–47.

Department of Water Affairs (DWA), 2013 Feasibility Study for a Long-Term Solution to
address the Acid Mine Drainage associated with the East, Central and West Rand


Taylor J., Pape S. & Murphy N. 2005 A Summary of Passive and Active Treatment Technologies for Acid and Metalliferous Drainage (AMD), Australian Centre for Minerals Extension and Research (ACMER) Fifth Australian Workshop on Acid Drainage, 29-31 August, Fremantle, Australia.


