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

John N. Zvimba, Njabulo Siyakatshana and Matlhodi Mathye

ABSTRACT

This study investigated passive neutralization of acid mine drainage using basic oxygen furnace slag as neutralization material over 90 days, with monitoring of the parameters' quality and assessment of their removal kinetics. The quality was observed to significantly improve over time with most 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 slag minerals under mildly acidic conditions of the influent water. The removal of acidity through generation of alkalinity from the passive treatment system was also observed to generally govern the removal of metallic parameters through hydroxide formation, with overall percentage removals of 88–100% achieved. The removal kinetics for SO_4^{2-}/Co was modelled using two approaches, yielding rate constant values of 1.56 and 1.53 L/(day mol) respectively, thereby confirming authenticity of SO_4^{2-}/removal kinetics experimental data. The study findings provide insights into better understanding of the potential use of slags and their limitations, particularly in mine closure, as part of addressing this challenge in South Africa.

Key words | characterization, experimental, kinetics, modelling, quality, slag

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 million litres per day (ML/d) 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 currently operational because of 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 & 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 for 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 for 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, 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 for coal mines upon their future closure. Therefore, there is still need to continue investigations into alternative ways of 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 and 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 AMD problems after mine closure, particularly at some coal mines.

Basic oxygen furnace (BOF) slag is a solid residue generated during steelmaking processes with an estimated 12 million tons (Mt) and 8 Mt generated annually in Europe and the United States, respectively (Proctor et al. 2000; Motz & 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 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 & 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 & 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 for the potential use of this abundant waste material as an alternative, particularly following mine closure in a country that continues to seek an everlasting solution to the AMD challenge.

**MATERIALS AND METHODS**

**Feedstock**

AMD containing acidity of about 1,813 ± 246 mg/L CaCO₃ equivalent; 630 ± 24 mg/L Fe(II); 2,903 ± 49 mg/L SO₄²⁻; pH from 5.0 ± 0.1 to 6.0 ± 0.1; and metals Ca (733 ± 33 mg/L), Mg (243 ± 34 mg/L), Mn (51 ± 1 mg/L); Co, Ni and 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.

**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 5900 spectrophotometer was used for SO₄²⁻ determination at 450 nm.
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 with 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 specified days 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, and non-linear regression analysis) fitting SO₂/C₀⁴ experimental data to a second order kinetics model, postulating SO₂/C₀⁴ removal reaction as an elementary second order reaction.

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, and alkalinity of the AMD were determined using a Mettler Toledo auto-titrator following filtration. Fe(II)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feed AMD</th>
<th>WHO* (DWA)² limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.9 ± 0.1</td>
<td>6.0–9.0</td>
</tr>
<tr>
<td>Acidity (mg/L)</td>
<td>1,813 ± 246</td>
<td>NA</td>
</tr>
<tr>
<td>Fe(II) (mg/L)</td>
<td>628 ± 24</td>
<td>0–0.3 (0–0.1)</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>2,905 ± 49</td>
<td>0–500</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>733 ± 33</td>
<td>0–32</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>243 ± 34</td>
<td>0–30</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>51 ± 1</td>
<td>0–0.1 (0–0.05)</td>
</tr>
<tr>
<td>Co (mg/L)</td>
<td>0.5 ± 0.01</td>
<td>NA</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>0.32 ± 0.01</td>
<td>NA</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>0.17 ± 0.02</td>
<td>NA</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>&lt;0.03</td>
<td>NA</td>
</tr>
<tr>
<td>Si (mg/L)</td>
<td>&lt;0.02</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 1 | Feed AMD quality before and during passive neutralization

<table>
<thead>
<tr>
<th>Component</th>
<th>Before neutralization (wt. %)</th>
<th>After neutralization (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>15.7</td>
<td>16.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.47</td>
<td>0.52</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.12</td>
<td>7.62</td>
</tr>
<tr>
<td>Fe₂O₃</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>Na₂O</td>
<td>0.37</td>
<td>1.49</td>
</tr>
<tr>
<td>K₂O</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>SO₃</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>H₂O</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>
was determined using standard permanganate titrimetric technique (APHA/AWWA/WEF 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, The Netherlands).

RESULTS AND DISCUSSION

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 and 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 and Mn, while Co, Ni and 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. Conversely, 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 (1,813 ± 246 mg/L), Fe(II) (628 ± 24 mg/L), SO$_4^{2-}$ (2,903 ± 49 mg/L), Mg (245 ± 34 mg/L), Mn (51 ± 1 mg/L), Co (0.5 ± 0.01 mg/L), Ni (0.32 ± 0.01 mg/L) and Zn (0.17 ± 0.02 mg/L) 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 Equation (4), while aluminium at neutral pH values (5–9) precipitates as hydroxide according to Equation (5).

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

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

\[
\text{Al}_2\text{O}_3(s) + 6\text{H}^+(aq) \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O} \quad (3)
\]

\[
\text{SiO}_2(s) + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4(aq) \quad (4)
\]

\[
\text{Al}^{3+}(aq) + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3(s) + 3\text{H}^+(aq) \quad (5)
\]

\[
\text{Si(OH)}_4(aq) \rightarrow \text{SiO(OH)}_3(aq) + \text{H}^+(aq) \quad (6)
\]

\[
\text{Al(OH)}_3(s) + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_4(aq) + \text{H}^+(aq) \quad (7)
\]
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 Equation (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) and Si in three samples selected over the entire study period confirmed that no Al (<0.03 mg/L) or 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 the World Health Organization (WHO 2011) shows that most parameters (pH, acidity Mg, Mn, Co, Ni, and Zn) are either within the acceptable WHO limits or removed to zero levels following 3 months of passive neutralization. In this regard, acidity, Fe(II), SO$_2^-$/C0$_4^-$, Mg, Mn, Co, Ni and Zn decreased from 1,813 ± 246, 628 ± 24, 2,903 ± 49, 243 ± 54, 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$_2^-$/C0$_4^-$, Mg, Mn, Co, Ni and Zn respectively, suggesting a potential simple and cost-effective solution following 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 the 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. The significant overall per cent removal of $\text{SO}_4^{2-}$ (73%) is rather surprising as $\text{SO}_4^{2-}$ removal through gypsum crystallization is generally governed by the solubility of gypsum (solubility product constant $K_{sp} = 9.1 \times 10^{-6}$), which is a function of $\text{SO}_4^{2-}$ and $\text{Ca}^{2+}$ concentrations as well as the ionic strength. In this regard, the removal of $\text{SO}_4^{2-}$ from AMD containing $2903 \pm 49$ mg/L, resulting in final $\text{SO}_4^{2-}$ levels of about $785 \pm 100$ 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 $\text{SO}_4^{2-}$ 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 $\text{SO}_4^{2-}$ removal to 1,368 mg/L only achieved following addition of more soluble $\text{Ca(OH)}_2$ (Zvimba et al. 2013). These findings suggest that $\text{SO}_4^{2-}$ removal via adsorption in a sequencing batch reactor may be disrupted by both aeration and stirring. Therefore, further optimization of $\text{SO}_4^{2-}$ 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 and 3 and Figure 2, shows no significant changes in the BOF slag chemical composition, and this suggests 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.

### Acidity, sulphate and metal removal kinetics

Figure 3 shows the observed data for acidity, $\text{SO}_4^{2-}$ and metal 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 and Zn is characterized 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.

However, the removal kinetics for Mg and $\text{SO}_4^{2-}$ during AMD neutralization appeared to initially proceed much more slowly during the first 15 days. From Figure 3, the removal of Mg and $\text{SO}_4^{2-}$ 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 $\text{SO}_4^{2-}$ from AMD proceeds via gypsum crystallization, a process generally associated with slow kinetics (Geldenhuys et al. 2003). However, the fact that $\text{SO}_4^{2-}$ was overall removed from $2,903 \pm 49$ mg/L to $783 \pm 100$ suggests 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

<table>
<thead>
<tr>
<th>Table 3</th>
<th>BOF slag chemical composition for trace elements before and after AMD neutralization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
</tr>
<tr>
<td>Before neutral (mg/L)</td>
<td>&lt;5.00</td>
</tr>
<tr>
<td>After neutral (mg/L)</td>
<td>&lt;5.00</td>
</tr>
<tr>
<td>Mg</td>
<td>La</td>
</tr>
<tr>
<td>Before neutral (mg/L)</td>
<td>&lt;5.00</td>
</tr>
<tr>
<td>After neutral (mg/L)</td>
<td>&lt;5.00</td>
</tr>
<tr>
<td>Sn</td>
<td>Sr</td>
</tr>
<tr>
<td>Before neutral (mg/L)</td>
<td>11.2</td>
</tr>
<tr>
<td>After neutral (mg/L)</td>
<td>6.43</td>
</tr>
</tbody>
</table>
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).

\[
2\text{Fe}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow 2\text{Fe}^{3+}(\text{aq}) \tag{8}
\]

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, and 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:

\[
3\text{Ca(OH)}_2(\text{aq}) + 3M(\text{SO}_4)(\text{aq}) \rightarrow 3\text{CaSO}_4(\text{s}) + 3\text{M(OH)}_2(\text{s}) \tag{9}
\]

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 the current study therefore provide 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 following 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 the current study, it presents sustainability opportunities for the suggested methodology.

**Sulphate removal kinetics**

Sulphate removal is one of the critical indicator parameters 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$_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 1 day. Based on these assumptions, the reaction model can be described as given in Equation (10).

$$\text{Ca}^{2+} (\text{aq}) + \text{SO}_2^- (\text{aq}) \rightarrow \text{CaSO}_4 (\text{s})$$  \hspace{1cm} (10)

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

$$r = k \left[ \text{Ca}^{2+} \right] \left[ \text{SO}_2^- \right]$$  \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 $\left[ \right]$ denotes concentration of species in mol/L. The reaction is assumed to be an elementary reaction between Ca$^{2+}$ and SO$_2^-; hence the order of reaction with respect to each species is unity. The reaction is a bimolecular reaction; hence the value of $[\text{Ca}^{2+}]$ is given by $[\text{Ca}^{2+}]_0 - ([\text{SO}_2^-]_0 - [\text{SO}_2^-])$, where the subscript 0 denotes initial concentration. In the case of SO$_2^-$, following some algebraic manipulation, the reaction rate is designated as given in Equation (12).

$$r = -\frac{d[\text{SO}_2^-]}{dt} = k \left( [\text{SO}_2^-]^2 + [\text{SO}_2^-] \cdot ([\text{Ca}^{2+}]_0 - [\text{SO}_2^-]) \right)$$  \hspace{1cm} (12)

For ease of designation, we denote $X = [\text{SO}_2^-]$, $Y = [\text{Ca}^{2+}]$, and $B = ([\text{Ca}^{2+}]_0 - [\text{SO}_2^-]_0)$ and re-write Equation (12), where $Y_0 \neq X_0$ as given in Equation (13).

$$-\frac{dX}{dt} = k(X^2 + X \cdot B)$$  \hspace{1cm} (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).

$$X = \frac{B \left( \frac{X_0}{X_0 + B} \right)}{e^{\left( \frac{Bt - \ln \left( \frac{X_0}{X_0 + B} \right)}{X_0 + B} \right)} - 1}$$  \hspace{1cm} (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.

**Second order kinetics**

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

$$\ln \left( \frac{X}{Y} \right) = k(X_0 - Y_0)t + \ln \left( \frac{X_0}{Y_0} \right)$$  \hspace{1cm} (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

![Figure 4](https://iwaponline.com/wst/article-pdf/75/5/1014/454335/wst075051014.pdf)

**Figure 4**  | Logarithmic plot of rate data, yielding a rate constant value of $k = 1.56$ [L/day mol].

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the slope is equal to $k(X_0 - Y_0)$, where $X_0$ (sulphate) is known from Table 1, i.e. 2.903 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 mg/L) than the proceeding recording (940 mg/L) for Ca2+ concentrations.

Accordingly, $Y_0$ corresponds to concentration on day 0, and from the extrapolation via logarithmic regression, $Y_0 = 1.066$ mg/L = 0.0266 mol/L. Thus $(X_0 - Y_0) = 0.0036$ mol/L. From this, it then follows that

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

Thus, the value of $k$ determined from the slope in Figure 4 is 1.56 [L/(day mol)].

### Non-linear regression

Unlike the first approach, the second approach focuses purely on the concentration of $SO_2^{4-}$, which is the most accurately measured component and determines 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 focuses on minimizing the sum of squares between the experimental values and model values from Equation (14), was used.

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

where $X_{exp}$ represents experimental values of $[SO_2^{4-}]$ and $X_{mod}$ 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

$$X_{mod}[t, k_0] = X(k_0) + \frac{dX(k_0)}{dk}(k_1 - k_0)$$

where

$$\frac{dX(k)}{dk} = -B^2t_0(e^{Bkt_0}(X_0/X_0 + B)) \left( \frac{X_0}{Bt_0(X_0/X_0 + B)} - 1 \right)^2$$  \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 the rate constant $k$ obtained from non-linear regression (Figure 5) was 1.53 [L/(day mol)]. In this regard, the values of $k$ obtained in both cases correspond very well, confirming the authenticity of $SO_2^{4-}$ removal kinetics experimental data.

### 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 $SO_2^{4-}$ was characterized by initial slow kinetics, Mg was removed to below the acceptable WHO limit while $SO_2^{4-}$ 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 $SO_2^{4-}$ removal kinetics showed that the experimental data fitted the theoretical data and these were 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 following mine closure, possibly in lined neutralization lagoons where longer retention times can be achieved, with potential of using the final residue for mine void filling as a sustainable disposal method. Therefore, the study provides further critical knowledge in understanding more insights into the potential application of the principle of waste as a resource to achieve future sustainability.

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