

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

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12
13 **ABSTRACT**

14 This study investigated the passive neutralization of acid mine drainage (AMD) using basic
15 oxygen furnace (BOF) slag as neutralization agent over 90 days, with monitoring of the
16 AMD quality parameters and assessment of their removal kinetics. The AMD quality was
17 observed to significantly improve overtime with most AMD parameters removed from the
18 influent during the first 10 days. In this regard, removal of acidity, Fe(II), Mn, Co, Ni and Zn
19 was characterized by fast kinetics while removal kinetics for Mg and SO₄²⁻ were observed to
20 proceed slowly. The fast removal kinetics of acidity was attributed to fast release of alkalinity
21 from the slag minerals under mild acidic conditions of the AMD utilized resulting in rapid
22 consumption of AMD acidity. The removal of AMD acidity through generation of alkalinity
23 from BOF slag passive treatment system was also observed to generally govern the removal
24 of metallic parameters through hydroxide formation, with overall percentage removals
25 ranging 88 – 100 % achieved for the AMD parameters. The removal kinetics for SO₄²⁻ was
26 modelled using two approaches yielding rate constant values of 1.65 and 1.53 L/day.mol
27 respectively, thereby confirming the authenticity of SO₄²⁻ removal kinetics experimental data.
28 The study findings generally provide insights into better understanding of the potential use of
29 BOF slag, including its limitations for passive AMD remediation, as part of addressing this
30 challenge in South Africa. In this regard, passive treatment system utilizing BOF slag as
31 neutralization material would have potential application in mine closure.

32
33 **Key words:** slag, characterization, quality, experimental, modelling, kinetics

34 1. Introduction

35

36 Gold mining in South Africa over the past century has resulted in the Witwatersrand
37 (divided into East, West, Far West and Central Rand basins) gold bearing reef yielding 40 %
38 of all the gold ever mined on earth (Hanlon, 2010). While this has benefited the country
39 economically, such extensive mining has also significantly altered the groundwater
40 hydrology of the basin resulting in generation of low pH effluent rich in ferrous iron, sulphate
41 and heavy metals, generally known as acid mine drainage (AMD). In this regard, AMD from
42 the lowest lying mine shafts in the West Rand basin started decanting at a rate of 15–35
43 ML/day in 2002 (Coetzee *et al.*, 2004) posing threats to the Krugersdorp Game Reserve and
44 the Cradle of Humankind World Heritage Site. Moreover, extensive coal mining activities are
45 current operational based on the thermal power dependence of South Africa, and this poses
46 future AMD challenges, particularly in the Mpumalanga province. Globally AMD has
47 already been identified as a major environmental problem facing the mineral industry (Ribet
48 *et al.*, 1995) resulting in serious and sometimes permanent ecological damage (Micera and
49 Dessi, 1988); with widely studied and reported detrimental environmental effects (Baird,
50 1995; Bell *et al.*, 2002).

51 As part of the efforts to come up with an everlasting solution on AMD in South
52 Africa, short term interventions dealing with uncontrolled AMD decant and long term
53 interventions seeking a permanent solution regarding AMD desalination have been outlined
54 (Department of Water Affairs, 2013). The short-term interventions are based on the South
55 African Government-appointed Inter-Ministerial committee recommendations (Coetzee *et al.*,
56 2010), to urgently construct a 20 ML/d emergency AMD neutralization plant. In this regard,
57 the Council for Scientific and Industrial Research (CSIR) have successfully developed
58 innovative technologies on AMD neutralization (Geldenhuys *et al.*, 2003), with full scale
59 operational plants worldwide and such technology has become the basis for the short-term
60 intervention in the Western Basin. However, implementation of the short-term interventions,
61 though urgent and necessary at the moment, these do not comprehensively address the
62 significant sludge generation associated with AMD neutralization. Moreover, based on the
63 current learnings from AMD challenges resulting from 100 year of gold mining, similar
64 challenges are projected in coal mining upon their future closure. Therefore, there is still need
65 to continue investigations into alternative ways on AMD remediation, particularly options
66 that are simple and cost effective. In this regard, passive treatment approaches become
67 economically attractive, providing low cost solutions, particularly for the treatment of waters
68 with low acidity, low flow rates where the key chemical outcome is to achieve a near neutral
69 pH and associated low metal concentrations. When used in isolation, passive treatment
70 systems have proven to be most successful at addressing post mining closure, particularly at
71 some coal mines.

72 Basic oxygen furnace (BOF) slag is a solid residue generated from basic oxygen
73 furnaces during steelmaking processes with an estimated 12 million tons (Mt) and 8 Mt
74 generated annually in Europe and United States, respectively (Proctor *et al.*, 2000; Motz and
75 Geiseler, 2001). In South Africa, the steelmaking industry generates about 4 million tons of
76 by-products from steel making each year, 600 000 tons of which is BOF slag. This is partially

77 reused in the steel making process because of minor elements contamination, with a
78 significant proportion stockpiled at various sites across the country. In this regard, recycling
79 of BOF slag (Lekakh *et al.*, 2008; Doucet E.F., 2010; Gunning *et al.*, 2010), remains globally
80 restricted, thereby limiting the quantity of BOF slag that can be charged back into the blast
81 furnace (Topkaya *et al.*, 2004). In order to avoid landfilling, the steelmakers usually try to
82 process the slag into useful materials. Thus, BOF slag has been shown to be suitable in
83 various construction applications because of its high strength and durability, and can
84 potentially replace gravel and rock (Motz and Geiseler, 2001). However, the use of BOF slag
85 in road construction, particularly in the South African context has been restricted because of
86 undesirable volume instability (volumetric expansion and disintegration) of the slag
87 aggregate, attributable to hydration of free lime and magnesium oxides in the slag (Mikhail
88 and Turcotte, 1995). However, South Africa being a mineral-rich country, the use of BOF
89 slag for passive remediation of AMD resulting from mining operations, has potential for an
90 environmentally sustainable solution where one waste material could be used for treatment of
91 another. This potential arises from the significant quantities of CaO and MgO present in BOF
92 slag. The potential of using steel slags for neutralization of industrial effluents has previously
93 been described by Cunha *et al.* (2008a, 2008b). These steel slags generally exhibited a high
94 neutralization capacity and a slower rate of dissolution which are conducive features for
95 passive neutralization.

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

102

103 **2. Materials and methods**

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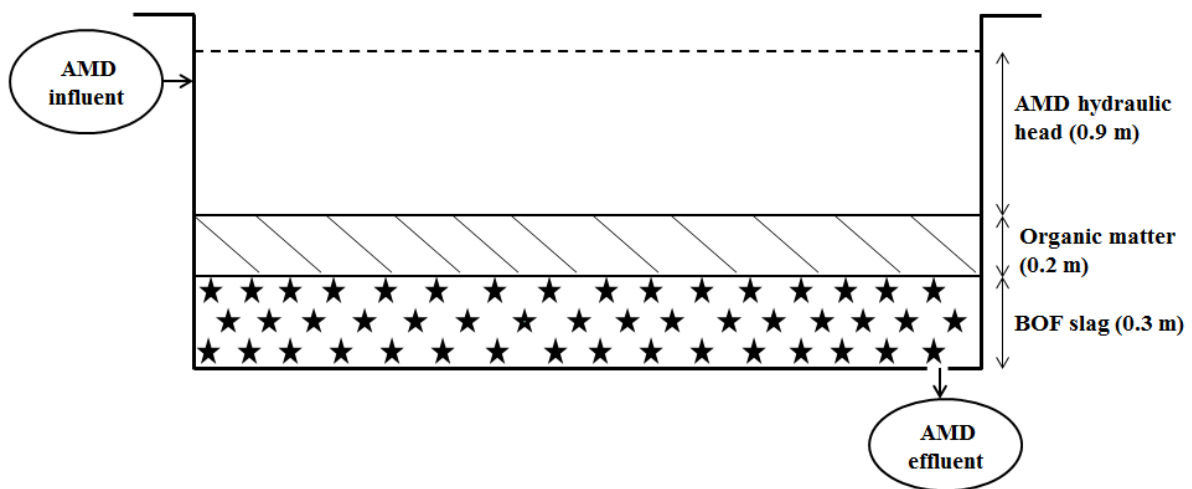
105 *2.1. Feedstock*

106 AMD containing acidity of about 1813 ± 246 mg/L CaCO₃ equivalent, 630 ± 24 mg/L Fe(II),
107 2903 ± 49 mg/L SO₄²⁻, pH ranging $5.0 \pm 0.1 - 6.0 \pm 0.1$, and metals; Ca (733 ± 33 mg/L), Mg
108 (243 ± 34 mg/L), Mn (51 ± 1 mg/L), Co, Ni & Zn ($0.2 \pm 0.01 - 0.3 \pm 0.01$ mg/L) as given in **Table**
109 **1** was collected from the Witwatersrand's Western Basin and used as feed water. BOF slag of
110 particle size range 3 – 14 mm and composition given in Table 2 was collected from a major
111 South African Iron and Steel making company and used as the neutralization material during
112 passive treatment. **Organic matter collected from a contamination-free natural forest on**
113 **campus was used as top layer above the BOF slag to control the redox state of the system and**
114 **also minimise armouring so as to extend the life expectancy of the passive treatment system**
115 **as recommended by Taylor *et al.* (2005). While the inclusion of the organic material in a**

116 passive system was standard as per literature, its characterization was beyond the scope of the
117 study.

118
119 **2.2. Equipment**

120 Passive AMD neutralization using a 500 L BOF slag alkalinity producing system as
121 given in Figure 1 was used. The 500 L container was used as a passive AMD neutralization
122 system, with feed AMD introduced as influent while neutralized AMD was collected as
123 effluent. A Toledo Auto-titrator was used for the determination of pH, acidity and alkalinity,
124 while a HaCH DR 3900 spectrophotometer was used for SO_4^{2-} determination at 450 nm.
125



126 **Figure 1.** Schematic representation of the BOF slag-based passive neutralization system

127

128 **2.3. Experimental procedure**

129 The 500 L container used as passive neutralization system was filled with fully
130 characterized BOF slag of particle size range 3 – 14 mm and covered with plastic. A layer of
131 organic material (not characterized) was placed on top of the BOF slag in accordance to the
132 recommendations by Taylor *et al.* (2005) (Figure 1). Feed AMD (~ 400 L) was pumped into
133 the model pit and allowed to slowly soak through the organic material and BOF slag until the
134 AMD filled up the container to achieve the required hydraulic head. Three sample aliquots
135 were collected from the feed AMD before the BOF slag-based alkalinity producing passive
136 system was left to undergo passive AMD neutralization. Sample aliquots of AMD effluent
137 were collected on specific days as triplicates over a 24-hr period during the passive AMD
138 neutralization period of 3 months for the experimental determination of selected AMD based
139 quality parameters as given in Table 1. BOF slag was characterized for both major and trace
140 elements before and after AMD neutralization using X-ray fluorescence (XRF). Kinetic
141 modelling was conducted using two approaches (logarithmic plot of concentration ratio vs
142 time & non-linear regression analysis) fitting SO_4^{2-} experimental data to a second order
143 kinetics model, postulating SO_4^{2-} removal reaction as an elementary second order reaction.

144

145

146 2.4. Analytical procedure

147 Feed AMD quality was determined using inductively coupled plasma optical emission
148 spectrometry (ICP-OES) (Varian: Vista Pro CCD Simultaneous ICP-OES). The pH, acidity,
149 alkalinity of the AMD were determined using a Mettler Toledo Auto-titrator following
150 filtration. Fe(II) was determined using standard permanganate titrimetric technique (Standard
151 Methods for the Examination of Water and Wastewater, 1992) while SO_4^{2-} was determined
152 using a HaCH DR 3900 spectrophotometer at 450 nm. BOF slag was characterized for major
153 and trace elements using XRF (PANalytical Epsilon 3 XL, Almelo, Netherlands).

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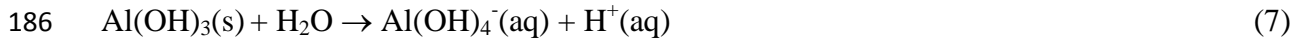
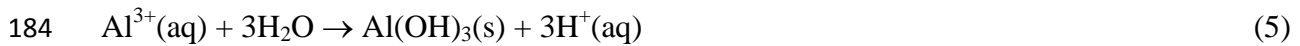
155 3. Results and discussion

156 3.1. AMD and BOF slag characterization

157 Table 1 shows the feed AMD quality before AMD passive neutralization using BOF
158 slag and the AMD effluent quality at different time points; 1 day, 1 week, 1 month, 2 months
159 & 3 months during passive neutralization. Table 2 shows the chemical composition for BOF
160 slag, while Figure 2 shows the XRF scan for BOF slag before and after AMD neutralization.
161 It can be seen from Table 1 that the major AMD parameters include Fe(II), acidity, SO_4^{2-} , Ca,
162 Mg & Mn, while Co, Ni & Zn constituted minor AMD parameters. From Table 2, the major
163 components of BOF slag include SiO_2 (15.7%), Al_2O_3 (9.12%), Fe_2O_3 (24.7%), MnO
164 (3.44%), MgO (6.44%) and CaO (36.5%). Thus, CaO and MgO constitute the alkalinity
165 producing components of BOF slag useful for AMD neutralization. On the other hand, Al_2O_3 ,
166 MnO, SiO_2 and Fe_2O_3 make up undesirable slag minerals that may contribute to
167 contamination of neutralized AMD through metal leaching (Engström *et al.* 2013). Based on
168 Table 1, the AMD quality was observed to improve during passive neutralization as the initial
169 feed acidity (1813 ± 246), Fe(II) (628 ± 24), SO_4^{2-} (2903 ± 49), Mg (243 ± 34), Mn (51 ± 1), Co
170 (0.3 ± 0.01), Ni (0.32 ± 0.01) and Zn (0.17 ± 0.02) significantly decreased over the neutralization
171 period. This change in AMD quality is attributed to the removal of metals via metal
172 hydroxide formation as the pH of the feed AMD increases from 5.9 to 9.6 upon contact of
173 AMD with the BOF slag bed. The general dissolution of slag minerals and the subsequent
174 consumption of acidity during AMD neutralization have been described by Engström *et al.*
175 2013), and are based on; for calcium; the formation of Ca^{2+} , for aluminium; the formation of
176 Al^{3+} and for magnesium the formation of Mg^{2+} according to Equations. (1) – (3). The silica
177 released from the silica-containing minerals dissolves in water according to Eq. (4), while
178 aluminium at neutral pH values (5 – 9) precipitates as hydroxide according to Eqn. (5).

179





187

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

Parameter	Feed AMD						WHO ^a (DWA) ^b Limit
	before neut.	1 day	1 week	1 month	2 months	3 months	
pH	5.9±0.1	7.4±0.2	8.5±0.5	7.6±0.1	8.9±0.1	9.6±0.1	6.0 - 9.0
Acidity (mg/L)	1813±246	53±20	39±1	12±10	0	0	NA
Fe(II) (mg/L)	628±24	237±110	126±14	74±21	46±8	37±16	0 - 0.3 (0 - 0.1)
SO ₄ ²⁻ (mg/L)	2903±49	2482±34	1865±55	1530±64	1164±17	783±100	0 - 500
Ca (mg/L)	733±33	940±80	870±68	299±4	353±20	179±12	0 - 32
Mg (mg/L)	243±34	202±2	131±39	51±1	33±0	16±1	0 - 30
Mn (mg/L)	51±1	20±6	1.2±0.7	0.9±0.1	0.4±0.1	0.1±0.01	0 - 0.1 (0 - 0.05)
Co (mg/L)	0.3±0.01	0.04±0.02	0.01±0.003	0.008±0.003	0.009±0.001	0.005±0	NA ^c
Ni (mg/L)	0.32±0.01	0.05±0.01	0.017±0.002	0.007±0.001	0.009±0.001	0.008±0.001	NA ^c
Zn (mg/L)	0.17±0.02	0.02±0	0.02±0	0.02±0	0.02±0	0.02±0	0 - 3 (0 - 0.5)
Al (mg/L)	<0.03	-	<0.03	<0.03	-	<0.03	NA
Si (mg/L)	<0.02	-	1.3±0.3	4.1±2.0	-	8.1±2.0	NA

189 ^aWHO - World Health Organization (WHO) (2011)

190 ^bDWA - Department of Water Affairs (DWA) of South Africa (1996)

191 ^cNA - not available.

192

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

Component	Before neutralization (wt. %)	After neutralization (wt. %)
SiO ₂	15.7	16.2
TiO ₂	0.47	0.52
Al ₂ O ₃	9.12	7.62
Fe ₂ O ₃	24.7	24.4
MnO	3.44	3.25
MgO	6.44	5.31
CaO	36.5	37.9
Na ₂ O	0.37	1.49
K ₂ O	<0.01	<0.01
P ₂ O ₅	0.17	0.19
Cr ₂ O ₃	0.14	0.14
SO ₃	0.65	1.00
LOI	1.94	1.66
H ₂ O	0.41	0.50
Total	100.2	100.2

194

195 The dissolution of silica is the only pH-independent reaction during AMD
196 neutralization, while precipitation of aluminium hydroxide generates acidity. Under alkaline
197 pH (>10.0) the silica and aluminium react further with release of more acidity, but this is not
198 experienced under the conditions of the current study, since a maximum pH of 9.6 was
199 reached. In this regard, the release of acidity from Eqn. 5 as Al^{3+} is removed from AMD via
200 hydroxide precipitation created a natural pH buffer that delayed attainment of alkaline
201 conditions that would result in the release of undesirable soluble $\text{Al}(\text{OH})_4^-$ species, thereby
202 reintroducing removed Al^{3+} back into the neutralized AMD as given in Equation. 7. The
203 determination of Al, total Fe (result not shown in Table 1) and Si in three samples selected
204 over the entire study period confirmed that no Al (<0.03 mg/L) and Fe (0.07 mg/L) was
205 released with only Si increasing from less than 0.02 mg/L at the beginning of neutralization
206 to 8.1 ± 2.0 mg/L at the end of AMD neutralization. The release of Si into the AMD effluent
207 therefore confirms the pH-independent dissolution of silica from BOF slag during passive
208 treatment, and is the only major limitation identified in this study.

209 A comparison of the concentration for the effluent AMD parameters given in Table 1
210 to those published by WHO (2011) shows that most parameters (pH, acidity Mg, Mn, Co, Ni,
211 & Zn) are either within the acceptable WHO limits or removed to zero levels following three
212 months of passive neutralization. In this regard, acidity, Fe(II), SO_4^{2-} , Mg, Mn, Co, Ni and Zn
213 decreased from 1813 ± 246 , 628 ± 24 , 2903 ± 49 , 243 ± 34 , 51 ± 1 , 0.3 ± 0.01 , 0.32 ± 0.01 and
214 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
215 mg/L respectively. This represented percentage removal efficiencies of 100, 94.1, 73, 93.4,
216 99.8, 98.3, 97.5 and 88.2% for acidity, Fe(II), SO_4^{2-} , Mg, Mn, Co, Ni and Zn respectively,
217 suggesting a potential simple and cost effective solution for post mine closure in the South
218 African context. In a previous study (Zvimba *et al.* 2013), a 97% removal of Fe(II) in a
219 sequencing batch reactor over 30 min with aeration, reactor stirring and using commercial
220 CaCO_3 as neutralization agent was reported. The currently reported Fe(II) removal of 94%
221 over 3 months closely compares to the previously reported data, with the slight deviation
222 suggesting the impact of operating parameters such as aeration, stirring and the nature of
223 neutralization agent. However, passive neutralization of AMD using BOF slag has significant
224 potential as a cost effective and sustainable option that can be considered for mine closure,
225 considering the energy intensive nature of other alternatives such as reverse osmosis (RO).
226 The significant overall percent removal of SO_4^{2-} (73%) is rather surprising as SO_4^{2-} removal
227 through gypsum crystallization is generally governed by the solubility of gypsum ($K_{\text{SP}} = 9.1$
228 $\times 10^{-6}$) which is a function of SO_4^{2-} and Ca^{2+} concentrations as well as the ionic strength. In
229 this regard, the removal of SO_4^{2-} from AMD containing 2903 ± 49 mg/L resulting in final
230 SO_4^{2-} levels of about 783 ± 100 mg/L at the end of the study strongly suggests the role of other
231 removal mechanisms such as adsorption within the BOF slag bed during passive
232 neutralization. The removal of SO_4^{2-} has been previously reported to decrease from 3,800 to
233 2,500 mg/L during AMD neutralization using CaCO_3 in a sequencing batch reactor, with
234 further SO_4^{2-} removal to 1,368 mg/L only achieved following addition of more soluble
235 $\text{Ca}(\text{OH})_2$ (Zvimba *et al.* 2013). These findings suggest that SO_4^{2-} removal via adsorption in a
236 sequencing batch reactor maybe disrupted by both aeration and stirring. Therefore, further
237 optimization of SO_4^{2-} removal during passive AMD neutralization that integrates adsorption

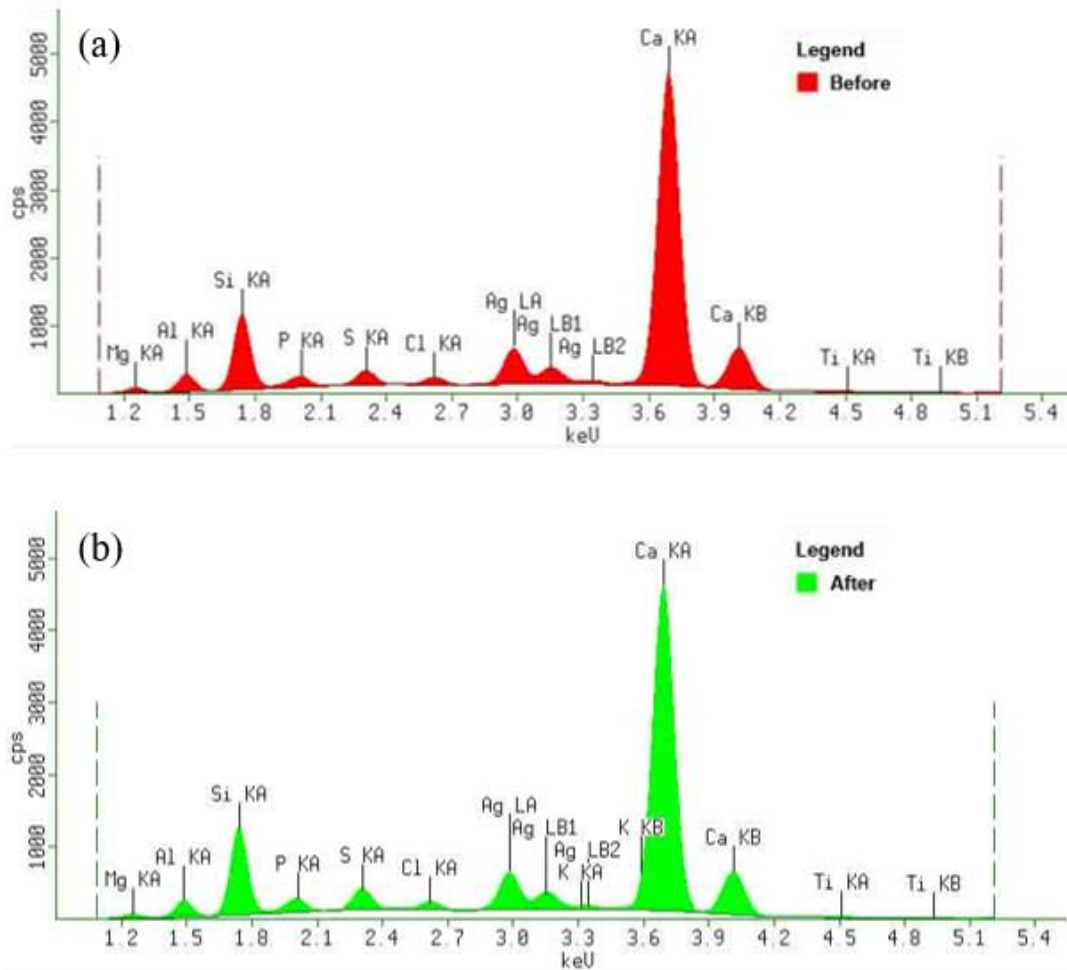
238 and crystallization should be considered as part of further investigations, and this could be a
 239 major breakthrough for AMD desalination.

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

246

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

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



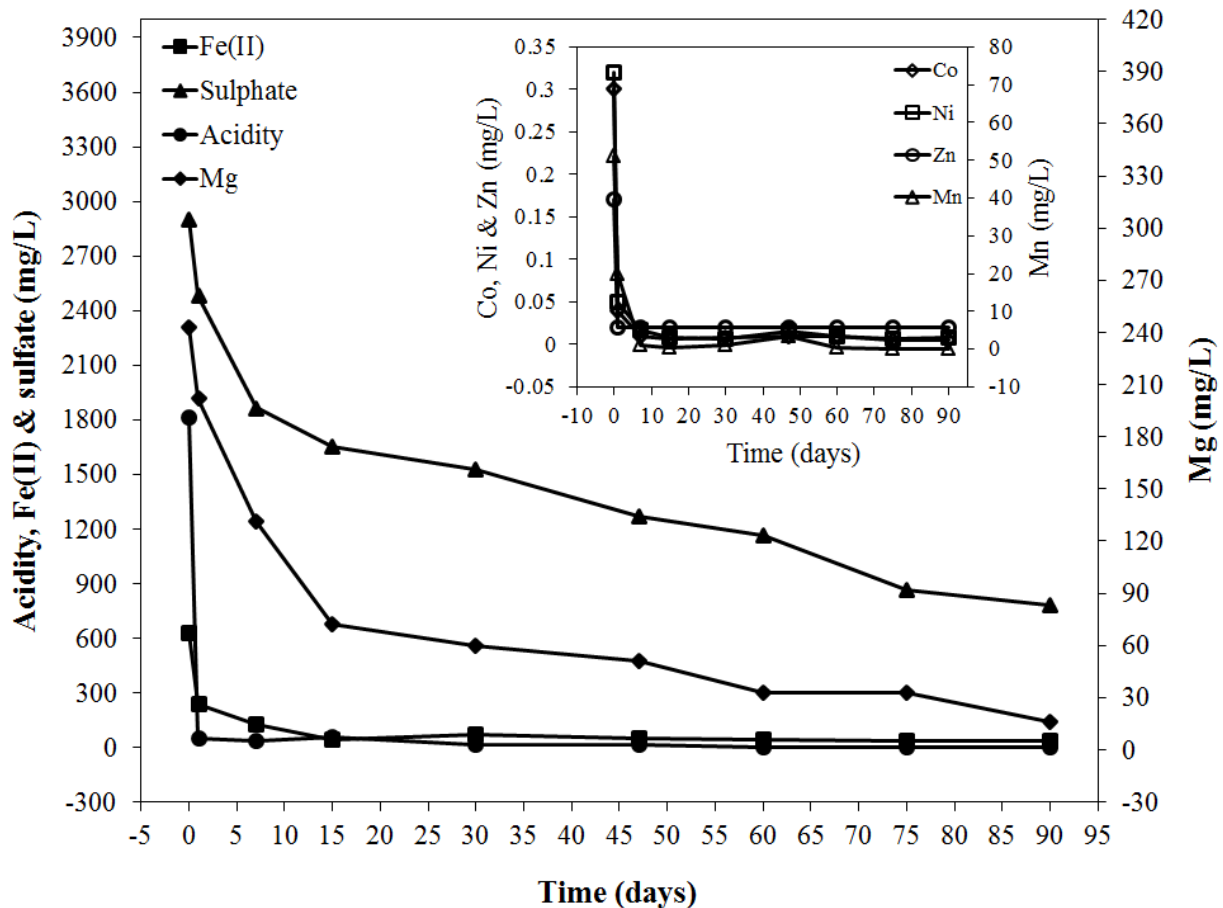
248 **Figure 2.** XRF pattern for BOF slag (a) before and (b) after neutralization

249 *3.2. Acidity, sulphate & metals removal kinetics*

250 Fig. 3 shows the observed data for acidity, SO_4^{2-} and metals removal kinetics during
 251 the passive AMD neutralization using BOF slag as neutralization material. From Figure 3, it
 252 can be observed that removal of acidity, Fe(II), Mn, Co, Ni & Zn is characterised by an initial
 253 rapid decrease of these AMD parameters during the first 10 days of neutralization before
 254 reaching a plateau at almost zero concentration. In this regard, the removal for acidity, Fe(II),
 255 Mn, Co, Ni and Zn was observed to be 97.1, 62.3, 60.8, 86.7, 84.4 and 88.2% respectively by
 256 day 1, and this increased significantly by day 7.

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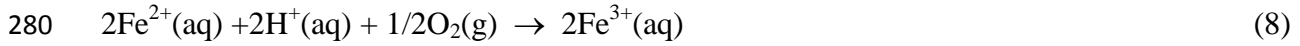


259
 260 **Figure 3.** Acidity, sulphate and metals' removal kinetics during passive AMD neutralization
 261 using BOF slag as alkalinity generating system.

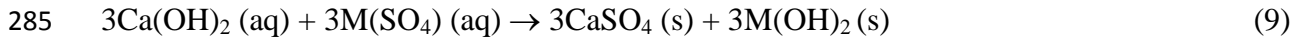
262
 263 However the removal kinetics for Mg and SO_4^{2-} during AMD neutralization appeared to
 264 initially proceed much slower during the first 15 days. From Figure 3, the removal of Mg and
 265 SO_4^{2-} was observed to be 16.9 and 15.5% after day 1 and slightly increased to 46.1 and
 266 35.7% respectively, by day 7. The removal of SO_4^{2-} from AMD proceeds via gypsum
 267 crystallization, a process generally associated with slow kinetics (Geldenhuis *et al.* 2003).
 268 However, the fact that SO_4^{2-} was overall removed from 2903 ± 49 mg/L to 783 ± 100 suggest
 269 additional removal mechanisms such as adsorption in addition to the normal gypsum
 270 crystallization.

271 Based on the data given in Figure 3, it appears acidity removal generally governs the
 272 removal kinetics of most metals. In this regard, metal removal is expected to be a result of
 273 metal hydroxide precipitation during AMD neutralization. The dissolution or leaching of
 274 alkalinity producing components would probably be characterized as a surface reaction,
 275 followed by a solid-liquid diffusion process resulting in alkalinity generation and
 276 consumption of acidity as given in Equations. 1 – 3. The consumption of acidity is also
 277 partially enhanced by the acid catalysed oxidation of ferrous iron during AMD neutralization
 278 as given in Equation. 8.

279



281 As the acidity gets rapidly removed from AMD during neutralization as shown in Figure 3;
 282 the pH of the AMD increases as given in Table 1 resulting in removal of metals such as Fe^{3+} ,
 283 Mn, Co, Ni, & Zn as metal hydroxides (Equation 9). However, Mg removal proceeds at a
 284 slower rate as its complete removal is only achieved at pH values greater than 11.



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

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

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

301

302 3.3. Sulphate removal kinetics

303 Sulphate removal is one of the critical indicator parameter of AMD treatment and this is
 304 generally described by Equation. 9. This parameter was modelled as a second order reaction
 305 between dissociated Ca^{2+} cations and SO_4^{2-} anions. The progressive leaching of Ca^{2+} into
 306 solution, according to Equation. 1 can be neglected, since, according to Table 1, the acidity
 307 actually declines dramatically after one day. Based on these assumptions, the reaction model
 308 can be described as given in Equation. 10.



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

311 $r = k[\text{Ca}^{2+}][\text{SO}_4^{2-}]$ (11)

312 Where r is the rate of reaction for any species in the reaction, specified by the stoichiometric
 313 coefficient, k is the reaction rate constant and $[]$ denotes concentration of species in [mol/L].
 314 The reaction is assumed to be an elementary reaction between Ca^{2+} and SO_4^{2-} , hence the
 315 order of reaction with respect to each species is unity. The reaction is a bi-molecular reaction,

316 hence the value of $[Ca^{2+}]$ is given by $\{[Ca^{2+}]_0 - ([SO_4^{2-}]_0 - [SO_4^{2-}])\}$, where the subscript 0
 317 denotes initial concentration. In the case of SO_4^{2-} , following some algebraic manipulation, the
 318 reaction rate is designated as given in Equation 12.

$$319 \quad r = -\frac{d[SO_4^{2-}]}{dt} = k([SO_4^{2-}]^2 + [SO_4^{2-}] \cdot ([Ca^{2+}]_0 - [SO_4^{2-}]_0)) \quad (12)$$

320 For ease of designation, we denote $X = [SO_4^{2-}]$, $Y = [Ca^{2+}]$, and $B = ([Ca^{2+}]_0 - [SO_4^{2-}]_0)$ and
 321 re-write Eq. (12), where $Y_0 \neq X_0$ as given in Equation (13)

$$322 \quad -\frac{dX}{dt} = k(X^2 + X \cdot B) \quad (13)$$

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

$$325 \quad X = \frac{B}{e^{\left(\frac{Bkt - \ln\left(\frac{X_0}{X_0+B}\right)\right)} - 1}} \quad (14)$$

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

329 3.3.1 Second Order Kinetics

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

$$331 \quad \ln\left(\frac{X}{Y}\right) = k(X_0 - Y_0)t + \ln\left(\frac{X_0}{Y_0}\right) \quad (15)$$

332 and thus, a plot of $\ln(X/Y)$ against time (t) provides a straight line from whose slope the rate
 333 constant can be determined. This is shown in Figure 4. From this equation the slope is equal
 334 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
 335 and Y_0 (calcium ions) is extrapolated from the data in Table 1 according to the graph. This is
 336 necessitated by the outlying initial recording on Table 1, i.e. a lower concentration (733) than
 337 the proceeding recording (940) for Ca^{2+} .

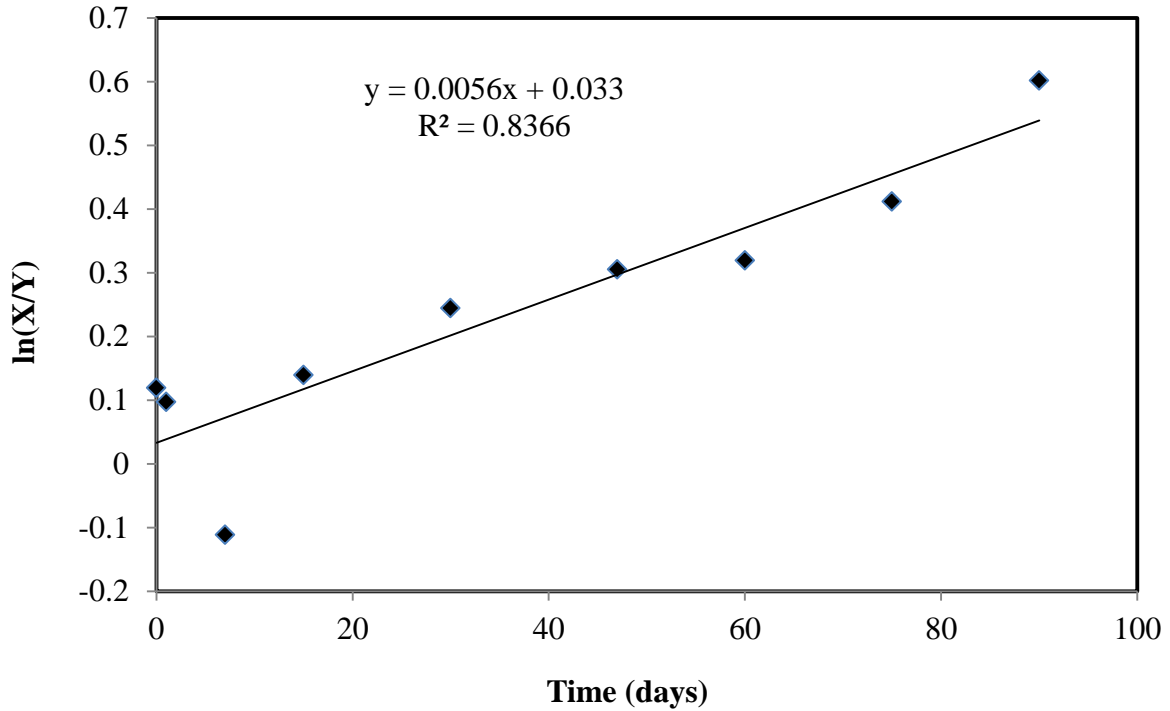
338
 339 Accordingly, Y_0 corresponds to concentration on day 0, and from the extrapolation via
 340 logarithmic regression, $Y_0 = 1066 \text{ mg/L} = 0.0266 \text{ mol/L}$. Thus $(X_0 - Y_0) = 0.0036 \text{ mol/L}$.
 341 From this, it then follows that

$$342 \quad k = \frac{0.0056}{(X_0 - Y_0)} = 1.56 \frac{\text{L}}{\text{mol.day}}$$

344

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

346



347

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

349 *3.3.2 Non-Linear Regression*

350 Unlike the first approach, the second approach focuses purely on the concentration of SO_4^{2-} ,
 351 which is the most accurately measured component and determine the reaction constant.
 352 Because Equation 14 is a non-linear expression in k , the Gauss-Newton non-linear regression
 353 technique as described by Seber & Wild (2003), which focusses on minimizing the sum of
 354 squares between the experimental values and model values from Equation 14 was used.

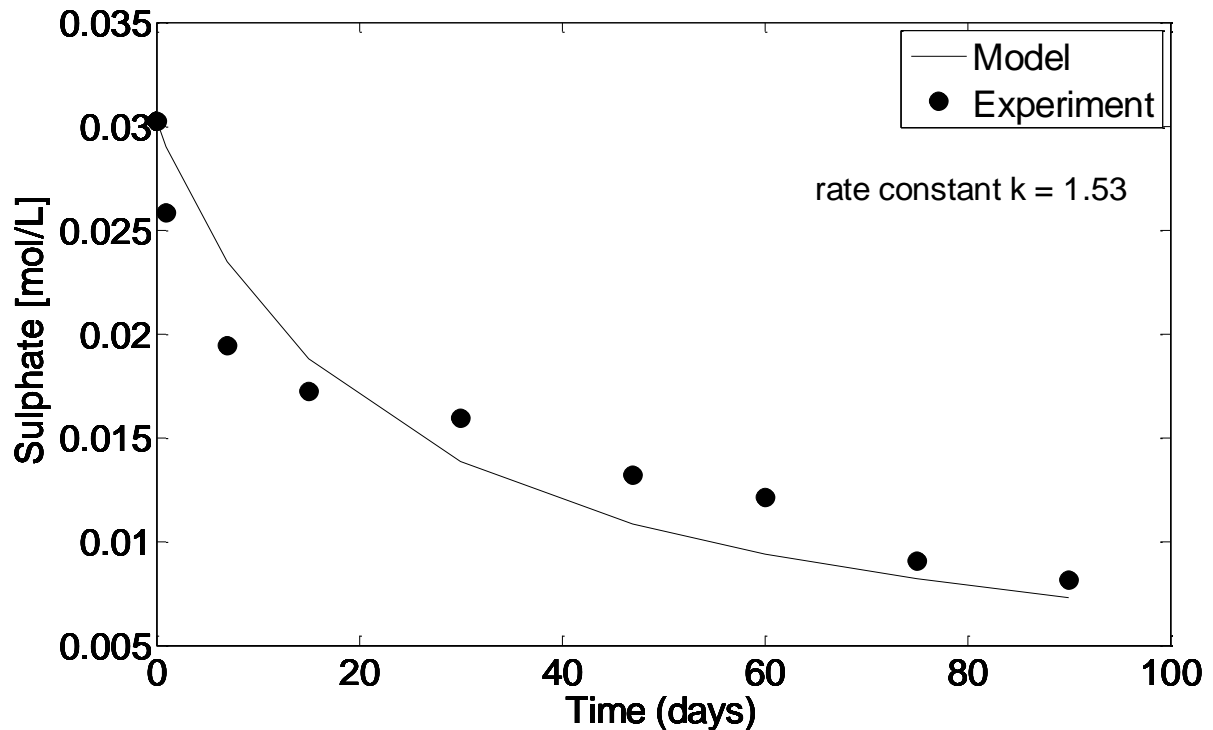
355
$$Q[k] = \sum_i \left(X_{\text{exp}}(t_i) - X_{\text{mod}}[t_i, k] \right)^2 \Rightarrow \min, \quad (16)$$

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

360
$$X_{\text{mod}}[t, k_0] = X(k_0) + \frac{dX(k_0)}{dk} (k_1 - k_0) \quad \text{where} \quad \frac{dX(k)}{dk} = \frac{-B^2 t e^{\left(Bkt - \ln\left(\frac{X_0}{X_0+B} \right) \right)}}{\left(e^{\left(Bkt - \ln\left(\frac{X_0}{X_0+B} \right) \right)} - 1 \right)^2}. \quad (17)$$

361 After setting $(k_1 - k_0) = m$, Equation 17 is substituted into Equation 16 and setting at the
 362 minimum, $dQ/dm = 0$, successive iterations of m are undertaken and produce new and
 363 updated values of k , until a final value of k is obtained at the required tolerance. This was
 364 performed in Matlab, using a specially written code. The value of rate constant obtained from

365 non-linear regression $k = 1.53$ [L/day.mol]. In this regard, the values of k obtained in both
366 cases corresponds very well, confirming the authenticity of SO_4^{2-} removal kinetics
367 experimental data.



368

369 **Figure 5.** Plot of Experimental values of $[\text{SO}_4^{2-}]$ versus kinetic model (Equation 14) after
370 non-linear regression is applied. Value of $k = 1.53$ [L/day.mol]

371

372 4. Conclusions

373 Results from this study showed that for most AMD based parameters; the removal is
374 associated with initial fast removal kinetics with most parameters' removal achieved within
375 10 days of passive AMD neutralization. Although the removal of Mg and SO_4^{2-} was
376 characterized by initial slow kinetics, Mg was removed to below the acceptable WHO limit
377 while SO_4^{2-} was surprisingly removed to levels much lower than those normally achieved in
378 active reactor systems suggesting the role of additional removal mechanisms during
379 neutralization. No significant leaching of BOF slag based toxic metals such as Al was
380 observed during AMD neutralization as passive neutralization was naturally buffered to
381 operate within pH conditions where $\text{Al}(\text{OH})_3$ precipitation was favourable as opposed to Al
382 leaching. However, the pH independent leaching of Si from silica minerals in BOF slag could
383 not be prevented and this was identified as a current limitation associated with passive AMD
384 neutralization using BOF slag, and would require further investigation. Modelling of the
385 SO_4^{2-} removal kinetics showed that the experimental data fitted the theoretical data and this
386 was represented by second order kinetics. Overall, the removal of most AMD parameters
387 during passive AMD neutralization using BOF slag as neutralization material was generally

388 achieved to acceptable WHO limits over 90 days, suggesting potential use of BOF slag for
389 passive AMD treatment for post mine closure, possibly in lined neutralization lagoons where
390 longer retention times can be achieved, with potential of using the final residue for mine void
391 filling as a sustainable disposal method. Therefore, the study provides further critical
392 knowledge in understanding more insights into the potential application of the principle on
393 waste as a resource to achieve future sustainability.

394

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399

400 **References**

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

404 **Baird C. 1995 Environmental Chemistry. W.H. Freeman, New York, pp. 301–302.**

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

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

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

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

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

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

424 Underground Mining Basins, Gauteng Province. Third ed. AMD Feasibility Study: Long
425 Term Solution Newsletter, Pretoria, South Africa, pp. 1–9.

426 Department of Water Affairs (DWA) and Forestry, 1996 South African Water Quality
427 Guidelines, Second ed. Volume 1: Domestic Use. CSIR Environmental Services, Pretoria
428 South Africa.

429 Doucet F. J., 2010 Effective CO₂-specific sequestration capacity of steel slags and variability
430 in their leaching behaviour in view of industrial mineral carbonation. *Minerals Engineering*,
431 **23**, 262–269.

432 Engström F., Adolfsson D., Samuelsson C., Sandström A. & Björkman B. 2013 A study of
433 the solubility of pure slag minerals. *Minerals Engineering*, **41**, 46–52.

434 Geldenhuys A. J., de Beer M. & Hlabela P. 2003 An integrated limestone/lime process for
435 partial sulphate removal. *Journal of Southern African Institute of Mining and Metallurgy*
436 **103**, 345–353.

437 Gunning P. J., Hills C. D. & Carey P. J., 2010 Accelerated carbonation treatment of industrial
438 wastes. *Waste Management*, **30**, 1081–1090.

439 Hanlon T. M. 2010 The impacts of mining legacy in a water-scarce South Africa: An
440 Environmental Security Perspective. MSc Thesis, Department of Geosciences, Oregon State
441 University, USA.

442 Lekakh S. N., Rawlins C. H., Robertson D. G. C., Richards V. L. & Peaslee K. D. 2008
443 Kinetics of aqueous leaching and carbonization of steelmaking slag. *Metallurgical and*
444 *Materials Transactions B* **39B**, 125–134.

445 Micera G. M. & Dessi, A. 1988 Chromium absorption by plant roots and formation of long-
446 lived Cr(V) species: an ecological hazard? *Journal of Inorganic Biochemistry*, **34** (3), 157–
447 166.

448 Mikhail S. A. & Turcotte A.M. 1995 Thermal behaviour of basic oxygen furnace waste slag.
449 *Thermochim Acta*. **263**, 87–94.

450 Motz H. & Geiseler J. 2001 Products of steel slags; an opportunity to save natural resources.
451 *Waste Management* **21**, 285–293.

452 Proctor D. M., Fehling K. A., Shay E. C., Wittenborn J. L., Avent C., Bigham R.D., Connolly
453 M., Lee B., Shepker T.O. & Zak M.A. 2000 Physical and chemical characteristics of blast
454 furnace, basic oxygen furnace and electric arc furnace steel industry slags. *Environmental*
455 *Science and Technology*, **34**, 1576–1582.

456 Ribet I., Ptacek C.J., Blowes D.W. & Jambor J.L. 1995 The potential for metal release by
457 reductive dissolution of weathered mine tailings. *Journal of Contaminant Hydrology*, **17**,
458 239–273.

459 Seber G. A. F. & Wild C. J., 2003 Non-Linear Regression. Wiley Interscience, John Wiley &
460 Sons Inc. New Jersey, USA. ISBN 0-471-47135-6.

461 Smith J.M. 1970 Chemical Engineering Kinetics. 2nd Edition. McGraw-Hill, USA.

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

466 Topkaya Y., Sevin N. & Gunaydyn A. 2004 Slag treatment at Kardemir integrated iron and
467 steel works. *International Journal of Mineral Processing*, **74**, 31–39.

468 World Health Organization (WHO), 2011 Guidelines for drinking water quality, Third ed.
469 incorporating first and second addenda Volume 1 – Recommendations. WHO Press,
470 Geneva.

471 Zvimba J. N., Mathye M., Vadapalli V. R. K., Swanepoel H. & Bologo L. 2013 Fe(II)
472 oxidation during acid mine drainage neutralization in a pilot-scale sequencing batch reactor.
473 *Water Science and Technology*, **68**(6) 1406–1411.

474 Zvimba J. N., Mulopo J., Bologo L. T. & Mathye, M. 2012 An evaluation of waste gypsum-
475 based precipitated calcium carbonate for acid mine drainage neutralization. *Water Science
476 and Technology*, **65**(9), 1577–1582.

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