

Integrated removal of inorganic contaminants from Acid Mine Drainage using BOF Slag, Lime, Soda ash and Reverse Osmosis (RO): Implication for the Production of Drinking Water

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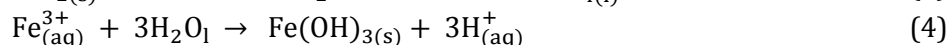
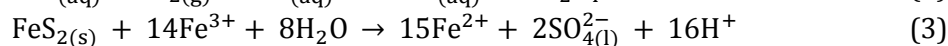
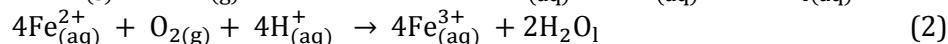
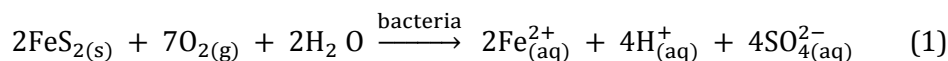
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Abstract This study evaluated the interaction of acid mine drainage (AMD) with Basic Oxygen Furnace (BOF) slag. The reaction proved that pH \geq 10, and 99% metals removal and 75% sulphate removal were achieved. Sulphate concentration was reduced from 18000 to 4000 mg/L hence requiring another purification technology. Hardness was reduced using lime and soda ash. Reverse Osmosis (RO) was used to further clean the water to drinking standard. A single pass two element RO system was simulated in Reverse Osmosis System Analysis (ROSA). The produced water complied with the South African National Standard (SANS) 241 Drinking Water Specifications.

Key words Acid mine drainage; Basic Oxygen Furnace (BOF) slag; inorganic contaminants; neutralization

Introduction

Sulphides bearing mineral exposed during mining activities are prone to react with water and oxygen during rainfall and underground leakages hence leading to the formation of acid mine drainage. In most instances, the formation of AMD can be represented by the following chemical equations (1 – 4) (Masindi 2016; Masindi et al. 2015c):



Due to the nature of a host rock, the resultant mine effluents is rich in Sulphate, Fe, Al, Mn and traces of other constituents (Clyde et al. 2016). For the interest of the public and environmental protection, this mine water need to be treated prior discharge (Pozo-Antonio et al. 2014). South Africa has advanced significantly in terms of mine water treatment (Masindi 2016). Mainly they rely on the use of raw limestone and lime for mine water treatment (Bologo et al. 2012; Maree et al. 2013), this technology has been successfully proven and it is commonly used in mining industries. The only limitation of limestone is partial removal

of contaminants from mine effluents and the limitation of reaching $\text{pH} \leq 7$ (Masindi et al. 2015a). Lime is very effective but cost factor limit its application because it is generated from calcination of limestone (Maree et al. 2013). Moreover, the generated sludge contains hazardous materials that can degrade the environment and pose serious health risk to aquatic and terrestrial organisms (Masindi et al. 2015c). To minimise the use of virgin materials for mine water treatment and to foster the process of sustainable development, several waste material had to be applied to remediate mine water. Masindi (2016) successfully used cryptocrystalline magnesite tailings for mine water treatment. Name and Sheridan (2014) used metallurgical slags for mine water treatment but they did not explore the chemistry thereof. Another study also explored the application of BOF slag for mine water treatment (Lee et al. 2016). This study, therefore, attempt to explore the chemistry of BOF slag and the resultant products and processed water after interacting with AMD. BOF slag is rich in Fe and Ca hence making it much easier to recover magnetite and gypsum (Belhadj et al. 2012). Geochemical model will be employed to point out the mineral phases that are likely to form during the interaction of BOF slag and AMD.

Materials and methods

Materials

BOF slag was collected from a Steel industry in South Africa. Field AMD samples were collected from a coal mine in Mpumalanga Province, South Africa. BOF slag samples were milled to a fine powder using a Retsch RS 200 vibratory ball mill for 15 minutes at 800 rpm. Thereafter, it was passed through a $32 \mu\text{m}$ particle size sieve to get the desired size. The samples were kept in a zip-lock plastic bag until utilization for AMD treatment.

Characterisation of aqueous samples

pH, Total Dissolved Solids (TDS) and Electrical Conductivity (EC) were monitored using CRISON MM40 portable pH/EC/TDS/Temperature multimeter probe. Aqueous samples were analysed using ICP-MS (7500ce, Agilent, Alpharetta, GA, USA). The accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards.

Mineralogical, elemental and microstructural properties

Mineralogical composition of BOF slag and resulting solid residues was determined using XRD. Elemental composition was determined using XRF, the Thermo Fisher ARL-9400 XP+ Sequential XRF with WinXRF software. Morphology was determined using HR-SEM (JOEL JSM – 7500F, Hitachi, Tokyo, Japan). Crystallography and micrographs of cryptocrystalline magnesite were also ascertained using HR-TEM (JEM – 2100 electron microscope, Angus Crescent, Netherland).

Interacting BOF slag and AMD

Coal AMD samples were treated at optimized conditions in order to assess the effectiveness of BOF slag. This is a succession study from a study that focused on the chemistry of AMD post contacting the BOF slag. The resultant solid residue after treatment of field AMD was

characterized in an attempt to gain an insight as to the fate of chemical species. Name and Sheridan (2014) reported that the optimum conditions for remediation of acid mine drainage using BOF slag is 60 min of shaking time and 100g/1 L S/L ratios. Jafaripour et al. (2015) reported that 15 mins was enough for the removal of heavy metals from acid mine drainage using BOS sludge. For the purpose of this study 60 mins and 100g/1 L S/L ratios will be used to determine the efficiency of BOF slag for high sulphate and Fe-rich coal mine water.

ROSA membrane analysis

Permeate Flux reported by ROSA is calculated based on ACTIVE membrane area. Reverse Osmosis System Analysis for FILMTEC™ Membranes, ROSA version 9.1 Configuration with DB U399339_359.

Proposed AMD treatment network

The schematic presentation of the BOF, lime, soda ash and RO treatment is shown in fig. 1.

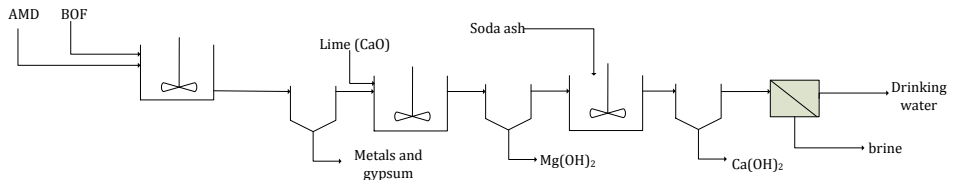


Figure 1 Schematic presentation of the proposed treatment process

Results and discussion

Production of drinking water using BOF slag and Reverse Osmosis system

The chemical profile of raw coal AMD, BOF reacted-AMD, lime and soda ash softened water, and DWS/SANS standards is shown in tab. 1.

The initial pH of acid mine drainage was 7.5 prior treatment hence indicating that there was potential neutralisation of mine water by natural processes (tab. 2). After contacting the BOF slag with AMD at 100g/1L solid to liquid ratio the pH increase to 13, thereafter, the introduction of lime and soda ash showed no difference in the residual pH. An increase in pH was directly proportional to alkalinity which increased from 20 to 1995 after contacting the BOF slag. It was insignificantly increased to 2004 and 2090 after adding lime and soda ash respectively. Total dissolved solids (TDS) and Electrical Conductivity (EC) were also directly proportional; this may be attributed to dissolution of neutralizing agents thus releasing elements to water. Thereafter, the introduction of lime and soda ash did not have impacts on the TDS and EC hence that some elements were being removed in each stage approach. Lime was added to remove sulphate and soda ash was added to remove the Ca. The total hardness was observed to be high in the Gold mine water (>1500), after contacting the BOF slag, it was observed to have increased hence indicating possible dissolution of Ca and Mg species and mineral phases. The levels of metal species were observed to have decreased after contacting all the neutralising

agents. The reduction of Fe and other chemical species may also be described by the potential formation of magnetite. Sulphate was also observed to have decreased after contacting the BOF slag hence indicating the possibility of gypsum recovery. Similar results were obtained by Masindi et al. (2015). All the parameters complied with SANS 241 water quality guidelines except for sulphate, cobalt, and sodium. Alkalinity, EC, and TDS were also above the prescribed limits. After using the ROSA software for cleaning up the water from BOF slag, Lime and soda ash, the resultant water quality water meeting the prescribed limits as recommended by the SANS 241 water quality guidelines (tab. 2).

Table 1 Chemical profile of raw coal AMD, BOF reacted-AMD and DWS/SANS standards

Parameters	AMD	BOF	Lime	Na ₂ CO ₃	Units	SANS standards
Alkalinity CaCO ₃ as Mg/L	<5.0	11	2004	2090	mg/L	≤120
pH (25°C)	2	8	13	13	-	≥5 to ≤9.7
Electrical Conductivity (EC)	960	470	800	920	mS/cm	≤170
Total Dissolved solids (TDS)	36000	13000	4300	4600	mg/L	≤1200
Total Hardness	3131	5080	3200	<0.5	mg/L	-
Aluminium	500	<0.70	<0.5	<0.5	µg/L	≤300
Iron	6000	<0.80	<0.5	<0.5	µg/L	≤300
Manganese	125	20	<0.5	<0.5	µg/L	≤100
Sodium	30	50	200	2000	mg/L	≤200
Potassium	2	10	20	20	mg/L	≤20
Calcium	500	800	1300	<0.5	mg/L	≤300
Magnesium	480	700	<0.5	<0.5	mg/L	≤400
Cobalt	25	<0.35	40	30	µg/L	≤0.2
Copper	1.5	<0.40	<0.5	<0.5	µg/L	≤2000
Lead	5	<0.10	<0.5	<0.5	µg/L	≤10
Nickel	30	<0.40	<0.5	<0.5	µg/L	≤70
Zinc	200	<0.60	<0.5	<0.5	µg/L	≤5
Cadmium	10	<0.20	<0.5	<0.5	µg/L	≤3
Silicon	30	1.5	0.1	0.3	mg/L	≤6
Sulphate	18000	4570	2000	2000	mg/L	≤500

Table 2 Chemical profile of RO cleaned water and DWS/SANS 241 water quality standards

Name	Pass Streams (mg/L as Ion)					SANS standards
	Feed	Adjusted Feed	Concentrate Stage 1	Permeate		
				Stage 1	Total	
NH4+ + NH3	0.00	0.00	0.00	0.00	0.00	≤ 1.5
K	9.50	9.50	13.33	0.57	0.57	≤20
Na	54.00	54.00	75.82	3.09	3.09	≤200
Mg	723.00	723.00	1029.92	6.87	6.87	≤400
Ca	844.01	844.01	1202.39	7.77	7.77	≤300
Sr	0.00	0.00	0.00	0.00	0.00	≤6
Ba	0.00	0.00	0.00	0.00	0.00	≤0.5
CO3	0.64	0.64	1.56	0.00	0.00	≤-
HCO3	427.03	427.03	603.79	11.71	11.71	≤-
NO3	0.00	0.00	0.00	0.00	0.00	≤1
Cl	69.23	69.34	97.32	4.04	4.04	≤5
F	0.00	0.00	0.00	0.00	0.00	≤1.5
SO4	4569.98	4569.98	6512.11	38.38	38.38	≤500
SiO2	1.50	1.50	2.12	0.05	0.05	≤6
Boron	0.00	0.00	0.00	0.00	0.00	≤2.4
CO2	70.30	70.30	70.75	70.21	70.19	≤-
TDS	6698.90	6699.01	9538.38	72.47	72.47	≤1200
pH	6.70	6.70	6.80	5.42	5.42	≤5 to 9.7

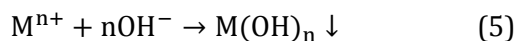
Elemental composition of raw BOF slag and the resultant residues

The elemental composition of raw BOF slag and AMD-reacted BOF slag is reported in tab. 3.

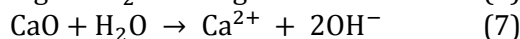
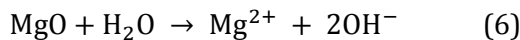
Table 3 Elemental composition of raw BOF slag and AMD-reacted BOF slag

Elements	Raw BOF slag	AMD-Reacted BOF slag
SiO ₂	13.52	11.28
TiO ₂	0.35	0.28
Al ₂ O ₃	7.78	7.59
Fe ₂ O ₃ (t)	25.81	28.55
MnO	4.37	3.60
MgO	7.16	5.91
CaO	38.41	29.69
Na ₂ O	0.33	0.20
K ₂ O	0.04	0.03
P ₂ O ₅	1.198	0.963
CoO	<0.001	0.002
Cr ₂ O ₃	0.168	0.111
CuO	<0.001	0.003
NiO	0.007	0.014
PbO	0.017	0.017
SO ₃	0.608	9.69
V ₂ O ₅	0.128	0.102
BaO	0.019	0.015
ZnO	0.005	0.037
LOI	-0.19	1.97
Total	99.70	100.04
H ₂ O	0.54	7.13

The XRF results revealed that the raw BOF slag consist of Ca, Fe, Si, Al, Mg and Mn as major components. Ca was available at elevated concentration as compared to the rest. After contacting the AMD, the level of alkali and earth alkali metals went down hence indicating dissolution of base cations. Base metals lead to an increase in pH hence precipitating the metals as hydroxide as indicated in the equation below (equation 5).



The dissolution of base cations from BOF slag may be represented by the following equations (Masindi et al. 2015d):



This may lead to an increase in the pH of the aqueous system with the subsequent precipitation of chemical species. An increase in pH of the product water may be due to dissolution of traces of silicates as shown by XRD and XRF and the release of Mg, Ca and Na as revealed by XRF and EDS may also contribute to an increase in pH. Silicate will react with acidity in AMD through ion exchange and partial dissolution hence leading to an increase in pH (Masindi et al. 2015b).



After reacting BOF slag with AMD, the content of S and Fe went up hence indicating possible attenuation of these chemical species from water. This could better be explained by the water quality.

Conclusions

This study further validated that BOF slag can be used for the treatment of very acidic, and metalliferous mine water with a literature breaking sulphate concentration. Reaction of BOF slag and coal mine water led to an increase in pH (≥ 10) and a significant reduction in inorganic species concentrations. Attenuation of sulphate, Al, Mn, Fe and other chemical species was observed to be optimum at 60 min of agitation at S: L ratio of 1 g: 100 mL. Under these conditions, the pH achieved was ≥ 10 , which is suitable enough for metal removal. From This study has further verified that BOF slag has the potential of neutralizing the acidity and attenuating toxic chemical species from coal mine water. The residual alkaline earth metals and sulphate were removed using reverse osmosis (RO) as simulated by ROSA simulation software and the produced water meet the drinking water quality. As such, this study proved that the coupling of RO process to BOF slag and different softeners will produce water of drinking standard.

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