Acid Mine Drainage Pilot Remediation System using Waste Products from the Steel Manufacturing and Sugar Industries ◉

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Abstract

Acid mine drainage (AMD) has long been considered a global environmental hazard due to its long-term detrimental effects on waterways and the ecosystems that reside within them. The amount of AMD produced daily as well as the high cost associated with treatment has led the United Nations to classify AMD as the second biggest problem that the Earth faces. As such, new cost-effective remediation methods are strongly needed. This research involves such a method and focuses on the operation of a waste beneficiation treatment scheme that is being tested at pilot-scale. It incorporates the use of two waste-products which are produced in many AMD-affected countries: steel slag and sugarcane bagasse. The study has confirmed the potential of these products in the treatment of AMD through a two-step, chemical and biological process. Slag eluate contacted with raw AMD is used to initially buffer the AMD solution and precipitate potentially toxic metals in a sedimentation tank. Overflow from the sedimentation tank is then passed through a packed bed containing sugarcane bagasse inoculated with sulfate reducing bacteria as a polishing step to remove sulfate, precipitate metal sulfides and elevate pH to near neutral conditions. A portion of the effluent is recycled through a packed bed of slag to create the eluate for pre-treatment of the raw AMD solution. The AMD used in these experiments was characterized by pH 2.6; 174 mg/L Al, 245 mg/L Ca, 4289 mg/L Fe, 334 mg/L Mn, 415 mg/L Mg and 16333 mg/L SO_4^{2-}. Operation of the pilot scale system treating 200-1000 L/day has thus far shown maximum Al, Fe, Mn and SO_4^{2-} removals of 97%, 87%, 100%, and 87% respectively. The dissolution of the slag and the alkalinity generation was found to occur mainly due to CaO and MgO dissolution. The SRB functioned in the slag eluate and a maximum sulfate reduction of 76% was found in the bioreactors. If optimized correctly, this treatment scheme could be implemented at mine sites throughout the world where these waste products are regionally available and could serve as either a low-cost pre-treatment program, or as a way for mines to recycle their acid waste for use as process or agricultural water.

Keywords: BOF Slag, Sulfate reducing bacteria, dissimilatory sulfate reduction, pilot plant

Introduction

Mining is an essential global industry that gives rise to multiple downstream processes, such as extractive metallurgy, minerals processing and general metal production that are vital to almost all aspects of human life - farming, healthcare, communications, water, energy supply, transport, space technology, and construction (International Council on Mining and Metals 2018; Park et al. 2019). Mining is a large source of wealth in many areas, with countries such as Zambia, Chile, Peru, Ukraine, Uzbekistan, South Africa, Australia, and Kazakhstan all reporting that mining contributes more than 7% of their annual gross domestic product (GDP)

(Ranjan 2019). Despite its acknowledged economic contributions, mining also causes substantial environmental degradation and generates huge amounts of wastes that are disposed of in tailings dams or stored in impoundments. Acid mine drainage (AMD) is an example of one such mining waste. The amount of AMD produced daily as well as the high cost associated with its treatment has necessitated new, viable and cost effective remediation schemes (Moodley 2018). In this regard, waste valorization/beneficiation has potential in (i) assisting AMD remediation schemes to remain economical, as well as in (ii) contributing to the alleviation of the burden of solid waste management in countless other industries (removal of secondary pollution which has multiple social and environmental benefits) (Nayak & Bhushan 2019).

Basic oxygen furnace slag (BOFS), containing high concentrations of oxides which have the ability to substantially increase the pH and alkalinity of acidic waters (Naidu et al. 2018a; Naidu et al. 2018b) is a final waste material in the steel making process that is in need of further processing before it can be re-used in the construction and building sector (Ding et al. 2017). BOFS cannot be used directly in construction due to volume instability issues that arise because of its high oxide content (Jiang et al. 2018). The treatment of AMD using BOFS as a lime substitute could potentially result in two valorized waste products, AMD treated to reusable water standards and BOFS treated to be reused as an aggregate in the construction industry.

This research investigates AMD treatment using BOFS by assessing the extent of remediation achieved in a pilot scale (200-1000 L/day) system. Another industrial by-product, sugarcane bagasse, is also used in the study to further remediate AMD after the BOFS treatment step and the efficacy of this biological treatment step is also evaluated. The aluminium, calcium, iron, manganese, magnesium and sulfate removal efficiency as well as the pH rise of the system are determined in order to evaluate the effectiveness of the scheme. Dissolution of the BOFS in the system is also assessed to determine the reduction of free oxide content in BOFS that causes volume instability.

Methods

Following the design and successful operation of a laboratory scale process using the same concept (Naidu et al. n.d.), a plant designed to treat 200-1000 L/day of AMD was constructed at a mine tailings dam in Emalahleni, South Africa. The dam site, shown in Figure 1, comprised of two dams which are used concurrently to contain seepage from a large mine tailings dump situated at a coal mine.

The chemical composition of the water contained within the dams changes constantly due to the varying nature of the coal tailings dump (new waste is continuously added to the dump and water seeps through this, entering the dam) as well as due to climactic conditions. The pilot plant was designed to account for the varying inlet quality so as not to effect the sensitive biological systems present in the process.

The system operates as follows (referring to Table 1 and Figure 2): AMD (stream 1) is pumped into an initial sedimentation vessel (R-102A/B) where it is mixed with a slag eluate stream (stream 10) from the slag chamber (R-101A/B). The slag eluate stream has high

Figure 1 (1-2) *Joint AMD dams in Emalahleni, South Africa where pilot plant is constructed (photographs by authors)*

pH, alkalinity and hydroxide content due to reaction between the AMD and the oxides contained within the slag. When mixed with the AMD in R-102A/B and R-103A/B, the pH of the resulting solution increases, causing (i) precipitation reactions and (ii) removal of dissolved metals and sulfate in the solution via gravitational settling. The outlet from the sedimentation section (stream 3) contains substantially less sulfate and metal ions and is at a higher pH (close to neutral). This stream enters the biological reactors (R-104, R-105, and R-106), the first two of which contain sugarcane bagasse which act as a substrate (carbon source) for sulfate reducing bacteria (SRB). SRB are sensitive to extreme pH levels and thus the neutralization of the AMD in the sedimentation vessels (R-102, R-130) allows for SRB functioning. The biological reactors are responsible for facilitating further sulfate ion removal via dissimilatory sulfate reduction (DSR). The outlet from R-106 (stream 6) enters a water reservoir (TK-101) where the treated water is stored. Water from TK-101 either overflows into the AMD dam or is recycled into R-101A where it undergoes a reaction with the BOFS. All vessels were sealed and R-107 acted as a H2S scrubber. Vessels marked B are replacement vessels.

Process control was setup to control the ratio of slag eluate (stream 10) to AMD feed (stream 1) in the system in order to maintain a pH of 5 in the sedimentation vessels (R-102A and R-103A). A pH of 5 was chosen to (i) keep the recycle flowrate at a sustainable level, (ii) allow for ideal functioning of the biological

entities (namely sulfate reducing bacteria (SRB)) which function best at a pH between 4 and 7, and (iii) allow for a suitable amount of precipitation of metals in the bioreactors (metals need to be present in the bioreactors to allow for metal sulfide precipitation). A depiction of the layout of the plant is shown in Figure 3.

Data collected from the plant for a 196-day period is discussed in the Results and discussion section below.

Results and discussion
Flowrate and residence time
The total volume of the system was approximately 13 000 L. Flowrates and residence times for the period are displayed in Table 2.

From day 120 onwards, the residence time for both the slag eluent and AMD streams was 5.4 days or lower. The flowrate into the system was determined by process control operation.

Extent of remediation
The inlet quality of the AMD changed continuously but had average Al, Ca, Fe, Mn, Mg, SO_4^{2-} and V concentrations of 174 ± 99.8, 245 ± 128.4, 4289 ± 313.3, 334 ± 136.0, 415 ± 104.2, 16333 ± 1072 and 0.06 ± 0.01 mg/L respectively. The average pH of the untreated AMD was 2.6. The pH levels changed across each vessel as well as over time, but the average pH in each vessel was 5.4 (R-101), 3.2 (R-102), 3 (R-103), 4.6 (R-104), 4.6 (R-105), 4 (R-106) and 4 (TK-101). The change in pH of the AMD is due to hydration reactions that occur between the AMD and the BOFS and

Table 1 Description of Process flow diagram elements (Figure 2)

Diagram Number	R-101A/B	R102A/B	R103A/B	R-104	R-105	R-106	R-107	TK-101	P-101	P-102
Element	Slag reactor and replacement	First sedimentation vessel (and replacement)	Second sedimentation vessel (and replacement)	Biological Reactor 1	Biological Reactor 2	Biological Reactor 3	Hydrogen Sulfide Scrubber	Water reservoir	AMD Pump	Recycle pump

Table 2 Flowrate and Residence Time in System

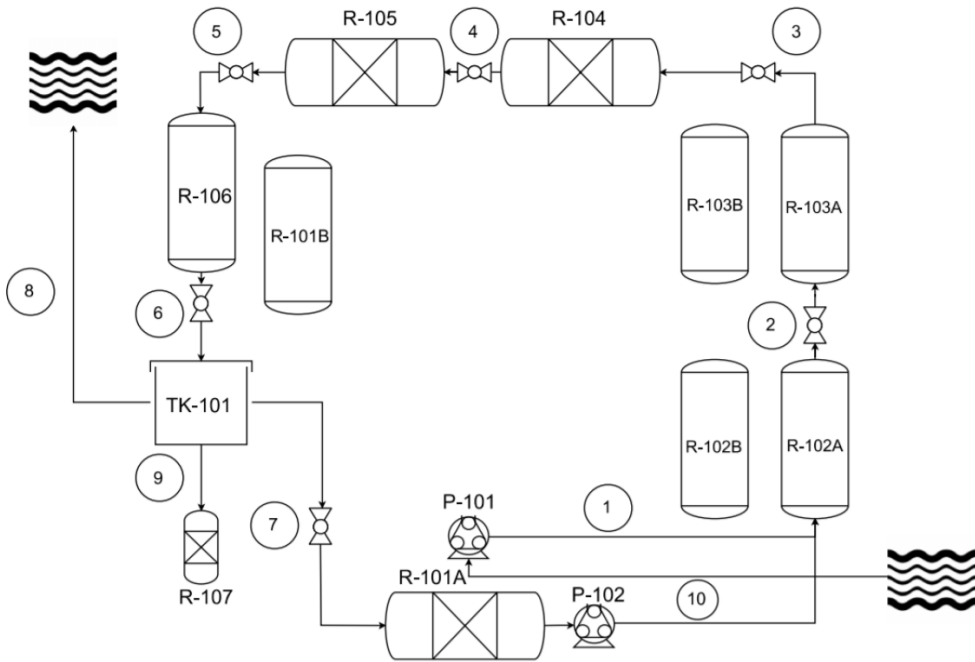| Time Period (days)	Flowrate of AMD (L/day)	Flowrate of Slag Eluent (L/day)	Residence Time (AMD and Slag Eluent) (days)
34	600	1000	8.1
34-43	270	1000	10.2
43-76	270	1200	8.8
76-120	270	2000	5.7
120-139	0	2400	5.4

Figure 2 Process flow diagram (PFD) of pilot plant to treat AMD constructed at site

Figure 3 (1 and 2) AMD remediation pilot plant at mine dam site (photographs taken by authors)

the subsequent dissociation that results in the release of hydroxide units. The fluctuation in pH across the system over time (as shown in Figure 4) is attributed to the varying amount of oxide containing BOFS particles that come into contact (and are able to react) with the AMD. This varying amount is determined by the process control over the plant. When the pH of the sedimentation vessel (R-102) is lower than 5, the flowrate of the entering slag eluate (stream 10) increases until it reaches a maximum of 2400 L/day and the flowrate of the AMD stream (stream 1) decreases until 0 in order to facilitate a higher ratio of slag eluate to AMD. For pH levels higher than 5 the opposite is true. Process control over the system became automatically effective after

120 days and thus fluctuations occurred. In addition to this, precipitation and settling in the BOFS reactor limited the release of further oxides. This was combatted by removing sedimentation and allowing only treated water (with a lower ion content and thus less ability to form precipitates) to flow through the BOFS reactor. The metal and sulfate levels across the system fluctuate along with pH levels (as shown in Figure 4). Metal and sulfate concentrations are dependent on the pH levels, making pH control in the system extremely important. High pH levels allow for more precipitation reactions to occur, removing a higher quantity of sulfate and metals, and pH levels between 4 and 7 allow for optimum SRB activity.
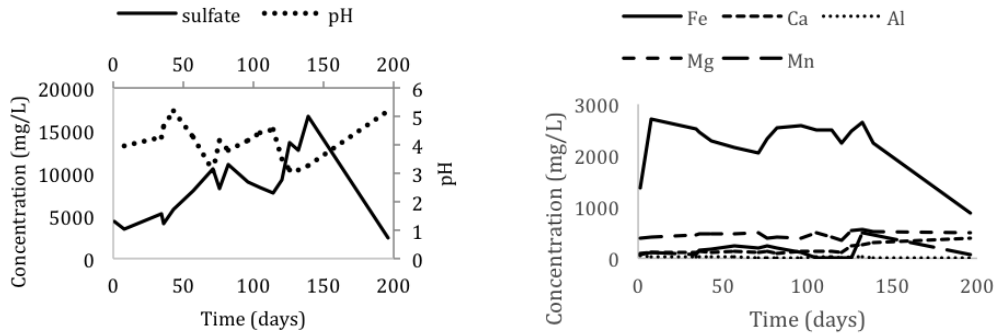
Figure 4 (1) pH and sulfate concentration in the water reservoir (TK-101) over the 196-day period (2) Metal concentrations in the water reservoir (TK-101) over the 196-day period

Table 3 Extent of Remediation across each Process Vessel (%removal of components)
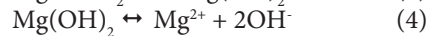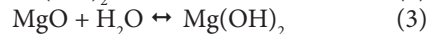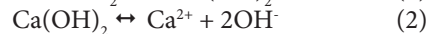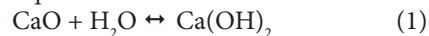
Component	R-102A/B (%)	R-103A/B (%)	R-104 (%)	R-105 (%)	R-106 (%)	TK-101 (%)	R-101A/B (%)
Mn	69,23	70,50	76,51	78,32	77,30	79,90	83,32
Mg	0,79	4,77	0,34	16,06	12,44	19,54	23,31
Al	95,22	95,86	96,61	97,07	96,08	95,45	90,03
Ca	185,32	167,87	69,13	123,12	69,74	62,43	226,45
Fe	56,28	69,72	77,96	82,72	83,39	79,61	86,61
SO_4^{2-}	55,63	72,52	80,24	81,95	83,53	84,69	87,10
pH	5,26	5,34	5,24	5,49	5,11	5,20	7,24

The extent of treatment in each vessel at the end of the 196-day period is shown in Table 3 in terms of % removal of each component (based on the initial and last reading). Bold indicates an increase in concentration.

The extent of remediation changed considerably over time at site, and this was attributed to the fluctuating conditions (changing feed quality, climate and availability of electricity to run equipment). The best treatment (for a combination of components) was observed after approximately 4000 hours (167 days) of operation and showed an 84% removal of sulfate, 80% removal of dissolved Fe, 62% increase of Ca, 95% removal of Al, 20% increase of Mg and a 80% removal of Mn. The maximum removals in terms of Al, Fe, Mn and sulfate were 97%, 87%, 100% and 87% respectively (across different reactors). Vanadium did not exhibit any considerable changes and Mg and Ca concentrations consistently increase in the system. The chemical section of the plant (R-102, R-103) was able to remove up to 72% of sulfate and the biological section (R-104, R-105, R-106) could remove a further 11% (76% sulfate removal over the 3 reactors).

Dissolution of BOFS

As shown in Table 3, the Mg and Ca concentrations increased within the system, confirming the hydration reaction between the treated AMD and the oxidic compounds within the slag. According to literature, alkalinity can be generated from BOFS via hydration followed by dissociation of calcium and magnesium oxides (Gomes et al. 2016). The BOFS contained 41.6 mass% CaO and 7.2 mass% MgO (other oxides are present, but only Ca and Mg have been considered due to the rise in their concentrations). The hydration, dissolution and dissociation reactions that bring about alkalinity from CaO and MgO components are described by Equations 1 to 4.

$$CaO + H_2O \leftrightarrow Ca(OH)_2 \qquad (1)$$
$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^- \qquad (2)$$
$$MgO + H_2O \leftrightarrow Mg(OH)_2 \qquad (3)$$
$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^- \qquad (4)$$

Ca in the system increased by 226% and Mg increased by 23% signifying that CaO and MgO compounds could contribute to the bulk of the pH rise and that oxidic compounds are being removed from the slag.

Conclusions

The extent of treatment of AMD using a two-step, chemical and biological process at a pilot plant (200-1000 L/day) scale was evaluated successfully and determined to have a maximum removal capacity of 97% for Al, 87% for Fe, 100% for Mn and 87% for SO_4^{2-}. SRB functioned well in the BOFS neutralized solution and the biological reactors exhibited a maximum sulfate removal of 76%. Some oxide compounds in BOFS underwent hydration (and subsequent dissociation) reactions with the treated AMD, potentially removing a degree of volume instability from the material. Although ideal functioning did not occur until after 4000 hours of operation, the experiment confirmed functionality of the scheme at a pilot plant scale. Issues relating to the poor performance [sedimentation in BOFS chamber (R-101)] in the first 4000 hours were identified and deemed to be easily correctable. Further work will focus on achieving successful pH control in the system in order to optimize the metal and sulfate removal as well as exploring manners through which to regenerate the sludge produced in the sedimentation vessels.

Acknowledgements

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