Design of Acid Mine Drainage Remediation Plant

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

BACKGROUND

Mining is an essential global industry that has given rise to multiple downstream processes – extractive metallurgy, minerals processing and wide-ranging metal production – that are vital to almost all aspects of human life (farming, healthcare, communication, water, energy supply, transport, space technology and construction) (International Council on Mining and Metals, 2018; Park, Baltazar, Jeon, Li & Seno, 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 this industry contributes more than 7% of their annual gross domestic product (GDP) (Ranjan, 2018). Despite its acknowledged economic contributions however, mining also causes significant environmental degradation and generates multiple waste streams that are disposed of in tailings dams or stored in impoundments. Acid mine drainage (AMD) is an example of one such mining waste and the amount of this that is produced daily as well as the high cost associated with its treatment, has necessitated the development of new, viable and cost-effective remediation schemes (Moodley, Sheridan, Kappelmeyer & Akcil, 2018). In this regard, waste valorisation/beneficiation has potential in (i) assisting AMD remediation schemes to remain economical, as well (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) is a final waste material in the steel making process and contains high concentrations of oxides which have the ability to substantially increase the pH and alkalinity of acidic waters (Naidu, Dyk, Sheridan & Grubb, 2018; Naidu, Dyk & Sheridan, 2018). It is in need of further processing before it can be re-used in the construction and building sector (Ding, Cheng, Liu & Lee, 2017). BOFS cannot be used directly in construction due to volume instability problems that arise due to its high oxide content (Jiang, Ling, Shi & Pan, 2018). Thus, the treatment of AMD using BOFS as a lime substitute could potentially result in two valorised waste products, AMD treated or pre-treated to reusable water standards and BOFS treated to be reused as an aggregate in the construction industry.

This research investigated AMD treatment or pre-treatment using BOFS by assessing the extent of remediation achieved in a laboratory (1-25 ℓ/day) and pilot scale (200-1000 ℓ/day) system. Another industrial by-product, sugarcane bagasse, was 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 and alkalinity rise of the system were determined in order to evaluate the effectiveness of the scheme. Dissolution of the BOFS in the system was also assessed to determine the reduction of free oxide content in BOFS that causes volume instability. Following the collection and interpretation of laboratory and pilot scale data, a larger scale design for the process was proposed.

AIMS

The following were the aims of the project:

1. To perform preliminary laboratory studies which will provide information for the design of a pilot plant unit.
2. To design a pilot process for treating 1000 ℓ /day of AMD on site.
3. To construct the pilot plant to treat 1000 ℓ /day of AMD.
4. To monitor the pilot plant in order to assess performance over a 6-month period.
5. To design and prepare a process for scale up of the original pilot plant to be based on site.

METHODOLOGY

Different methods were used to assess and achieve each of the aims listed. The methodology has thus been divided into the preliminary phase (which included a laboratory scale phase) and the pilot scale phase.

Phase 1 – Preliminary Phase

1. Determine the mechanism and kinetics of BOFS dissolution
2. Determine the mechanism and kinetics of precipitation reactions
3. Determine the functionality of sulfate reduction at large scales using sugarcane bagasse
4. Design, construction and optimization of laboratory scale system

Phase 2 – Pilot scale and larger scale phase

1. Design, construction and optimization of a process for treating 1000 ℓ/day of AMD on-site
2. Propose a design for a larger scale plant using findings from Phase 1 and 2 to treat more than 1000 ℓ/day

These aims were partially or fully achieved to allow a larger scale design to be developed.

RESULTS AND DISCUSSION

The results from the laboratory scale plant and the findings from the preliminary experiments were favourable and sufficient to inform the design of the larger pilot plant. AMD was treated to a maximum efficiency of 99% SO_4^{2-}, Al and Fe removal, 93% Mn removal, 81% Mg removal and pH buffering occurred from approximately 2.4 to 7 in the laboratory scale processes. The system was versatile and was able to treat two different AMD types to a level of 99% Al removal, 98% Fe removal, 93% Mn removal and 42% Mg removal. It was also versatile in that the pH level could be altered depending on desired outlet quality (higher pH's could be achieved via the addition of more BOFS or by allowing a longer reaction time in order to achieve different metals removal capacities). The pilot scale design was changed slightly by using different volumes for different reactors (the biological reactor increased in size relative to the settling tank, etc.) and by changing the pH setpoint in order to lower the recycle rate and ensure some metals were still present in the biological reactor (the pH setpoint was lowered such that less metals would precipitate as sulfate and hydroxide species in the settling tank, leaving some to facilitate the removal of sulfide via precipitation in the subsequent DSR reactor).

During the operation of the pilot plant, complementary experiments were also undertaken. The results from both of these operations in conjunction with the original results were used to inform the larger scale design. The extent of treatment of AMD at the pilot plant (treating 200-1000 ℓ/day) scale was evaluated and determined to have a maximum removal capacity of 97% for Al, 87% for Fe, 100% for Mn and 87% for SO_4^{2-}. The final design was altered slightly from the initial laboratory scale design and the pilot scale design to promote further treatment and reduce energy costs related to pumping and recycling.

GENERAL

All aims were addressed and achieved.

CONCLUSIONS

The final design differed from the original design in the following ways: (i) it did not make use of a recycle effluent stream, (ii) it did not include a secondary settling vessel or a tertiary biological vessel. By assessing the results from the various stages of research comprising the study, it was concluded that the combination of the two waste materials (sugarcane bagasse and basic oxygen furnace slag) was successful in the treatment of acid mine drainage – however the extent of treatment due to the biological step (sugarcane bagasse and sulfate reducing bacteria (SRB)) was deemed poor or low, as sulfate and metal removal during this step were not solely attributed to DSR (due to the suspected inability of the system to maintain a suitable chemical oxygen demand (COD) to sulfate ratio). Nevertheless, all combinations that were explored yielded favourable results overall (improvement of water quality and water treated to an acceptable standard based on the needs of the mine). The configuration that yielded the best results was suggested for the final design. It should be noted that the bulk of the treatment occurred in the BOFS treatment step and this treatment extent could be changed easily by controlling pH levels (by controlling the addition of BOFS). Thus, the different modules in the process can also be used in isolation as pre-treatment steps – treating AMD at mine sites for reuse as process water, agricultural water or as a pre-treatment step before entering into traditional wastewater treatment plants (WWTP).

RECOMMENDATIONS

The main recommendation for the upscale design (final aim of the project) is that a full analysis of the site of implementation be done beforehand in order to (i) determine the quality of effluent water that is needed, (ii) determine what particle size would be best suited to the quality of AMD at site and the geographical area, and (iii) check the conditions in terms of power availability and safety in the area. These factors will determine which of the proposed designs to use. In addition, further studies regarding the optimization of the process control aspect and the use of spent BOFS as an aggregate will need to be conducted to improve the efficiency and optimization of the overall system. It is also recommended that the treated water be used for agricultural purposes as it is nutrient rich.

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ACRONYMS & ABBREVIATIONS

AMD	Acid mine drainage
ARD	Acid Rock Drainage
BOFS	Basic oxygen furnace slag
CMR	Continuously mixed reactor
CSTR	Continuously stirred tank reactor
DR	Direct Reduction
DSR	Dissimilatory sulfate reduction
EAFS	Electrical Arc Furnace Slag
EDA	Energy Dispersive X-Ray Analysis
GDP	Gross Domestic Product
GHG	Green House Gas
HDPE	High density polyethylene
HDS	High density sludge
HRT	Hydraulic Residence Time
LLDPE	Linear low-density polyethylene
LRS	Ladle Refining Slag
PBR	Packed bed reactor
PFD	Process Flow Diagram
PFR	Plug flow reactor
SA	South Africa/n
SRB	Sulfate reducing bacteria
SS	Stainless Steel
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
UN	United Nations
USA	Unites States of America
VFA	Volatile Fatty Acid
WWTP	Wastewater Treatment Plant

CHAPTER 1 BACKGROUND

1.1 INTRODUCTION

Mining activity has been a vital element in the development and advancement of the South African (SA) economy for over a century (Durand, 2012), with excavation and mineral extraction occurring at numerous sites across the country. Much wealth has been generated because of the gold, coal, iron ore and copper mining industries and as of 2020, these sectors still play an important role in ensuring the country's position in the global market. Mining activities, however, tend to have notable impacts on the environment and have also resulted in multiple problems that have had adverse effects on both the environment and the population of SA. One such problem is that of Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD) (McCarthy, Africa & Africa, 2011).

Globally, AMD has long been considered an environmental hazard (Sheoran & Sheoran, 2006) due to its long term impacts on waterways and to the biodiversity of ecosystems that rely on these waterways (Akcil & Koldas, 2006). The United Nations (UN) has recently classified AMD as the second biggest problem that the Earth faces (Tuffnell, 2017) and there are multiple abandoned mine sites in countries such as Australia, Canada and the United States of America (USA) which are also affected by this environmental challenge (Naidoo, Manders, Godfrey & Hobbs, 2009). For SA, AMD presents a particular problem, as the minerals found here account for a large portion of the world's mineral reserves: gold, platinum-group metals, chrome ore, manganese ore, zirconium, vanadium and titanium (Ministry of Economic Development NZ Petroleum & Minerals, 2013). For this reason, mining of these minerals is critical to the SA economy (Kearney, 2012). This is juxtaposed with regional water scarcity issues wherein the leaching and extraction of these minerals from mines (whether open pit or shaft mines) is a complicated process which often results in waste water and effluent that can impact surface waters (Akcil & Koldas, 2006). Accordingly, focus has shifted to mining companies and mine managers controlling AMD release, in an attempt to minimize their impact on the environment (Morrissey, 2003). Thus, a cost-effective treatment system is strongly needed within the SA context.

Two industrial by-products are regionally available in SA in large volumes with the potential to remediate AMD: Basic Oxygen Furnace Slag (BOFS) and sugarcane bagasse (the shredded cane stalk material remaining after sugar extraction) (Grubb, Landers & Hernandez, 2000; P. Ziemkiewicz, 1998; P. F. Ziemkiewicz, Skousen & Simmons, 2003). Name and Sheridan (2014) conducted a study on the use of BOFS and stainless steel (SS) slag obtained from Harsco Mineral and Rail. They determined that BOFS had significant potential as a reagent for treating AMD and could potentially be used to replace lime as a primary neutralizing reagent in many AMD treatment schemes. The BOFS – according to their study – could effectively remove all iron from solution and demonstrated removal of sulfate to a final concentration of approximately 400 mg/ℓ from a starting concentration of 6000 ppm (>90% removal).

Other research has shown that sugarcane-bagasse has the potential to serve as a host media for sulfate-reducing bacteria (SRB) which have the ability to remediate raw, untreated AMD (pH~3), to levels below 400 ppm of sulfate by converting it to sulfide in a process known as dissimilatory sulfate reduction (DSR) (Canfield, 2004). Sulfide can then form insoluble precipitates (Grubb et al., 2018, 2000; Ali Hussain & Qazi, 2016) which effectively remove them from solution, lowering the sulfur content. Thus, using BOFS and bagasse either together or in series could have significant advantages for purposes of improving water quality. Interestingly, the coal-based AMD challenges and sources of BOFS and sugarcane bagasse are all co-located within south-eastern Mpumalanga and Kwa-Zulu Natal in SA.

Combination of these by-products resulted in an overall treatment system that consisted of four processes which were chemical and biological in nature; (i) the pH rise of treated water via alkalinity addition through contact with BOFS particles, (ii) sedimentation of metals and sulfates in the AMD via precipitation reactions facilitated by the rise in pH and the presence of counter-ions in the solution, (iii) production of sulfide and reduction of sulfate via DSR through the action of SRB using waste sugarcane bagasse as a substrate, and (iv) the subsequent precipitation of metal sulfides. Some of these processes had been studied in depth (DSR and precipitation reactions) and some had only been the subject of preliminary studies at the time of this project. However, the conjoining of the processes into one system as well as research into the mechanisms of the various processes made the proposed study novel for a number of reasons:

a. The determination of the kinetics of BOFS dissolution in any medium was novel as it had yet not been studied.
b. The determination of the kinetics of the precipitation reactions that occur after pH rise in AMD using BOFS as a source of alkalinity had not been studied and was thus novel.
c. The determination of the SRB functioning in a BOFS neutralized solution had not been studied.
d. These three processes had never been used in conjunction before, and the simultaneous optimization of these processes with the objective of remediating AMD at a large scale resulted in a novel study.

1.2 PROJECT AIMS

The following were the aims of the project as stipulated by the original WRC proposal:

1. To design a pilot process for treating 1000 ℓ/day of AMD on site.
2. To construct the pilot plant to treat 1000 ℓ/day of AMD.
3. To monitor the pilot plant in order to assess performance over a 6-month period.
4. To design and prepare a process design for scale-up of the original pilot plant to be based on site.

1.3 SCOPE

This study involved the conceptualization, the preliminary testing, the design, construction, operation and monitoring of a laboratory and a pilot plant AMD remediation system which used waste and by-products from the steel and sugar industries. This study was initially scheduled to span over a period of two years (2017-2018), however administrative constraints necessitated the extension of the project by one year. Preliminary experiments and a small-scale process were tested at the premises of the University of the Witwatersrand before a larger scale (200-1000 ℓ/day of AMD) was proposed. Thereafter, the project was based at a coal mining waste site in Witbank, Mpumalanga. The mechanism of treatment, the materials used in construction, the kinetics of the various reactions and the process control philosophy are aspects that were addressed in this study.

1.4 LIMITATIONS

The design of the larger scale plant was not tested and was based purely on data obtained from the laboratory and pilot-scale plants. The processing of the sludge produced as a by-product was not tested and was only discussed theoretically. Additionally, the further use of sugarcane bagasse as a fuel source after use as a substrate in the system was not tested and has also only been discussed theoretically

CHAPTER 2: LITERATURE REVIEW

This Chapter has sections that were sourced from a review article that was prepared as part of this project (Tamlyn Sasha Naidu, Sheridan & Dyk, 2020).

2.1 ACID MINE DRAINAGE

AMD or ARD is formed when rocks and waste mine materials that contain sulfidic components, oxidize on exposure to water or air (Naicker, Cukrowska & McCarthy, 2003). Pyrite, the main component that contributes to the formation of AMD, is found largely in both coal and gold mining sites, but it is also found in smaller quantities in other metal ores. Waters that have been contaminated with AMD are characterized by a low pH, high acidity and high concentrations of sulfates and metals such as iron, manganese, aluminium, magnesium, calcium and iridium (Feng, Deventer & Aldrich, 2004). Polluted waters very often require treatment before release into the environment or reuse at the mine site (Peppas, Komnitsas & Halikia, 2000; Potgieter-Vermaak, Potgieter, Monama & Van Grieken, 2006).

In the past, AMD was commonly left untreated (Diz, 1997), however, during the last ten years, water scarcity issues (both surface and groundwater impacted by AMD) have served as a major motivation to address point and non-point sources of AMD in north and north-eastern SA (Gauteng, Mpumalanga and Limpopo). Polluted water is generated at multiples coal field sites in these areas in the volumes of tens of Mℓ/day. Globally, AMD has also been brought to the forefront of water scarcity issues, with the UN declaring it the second largest problem facing the Earth (Tuffnell, 2017). For these reasons, treatment of AMD has become the topic of much research and investigation over the past decade.

Treatment of AMD (treatment that addresses heavy metals, sulfate concentration, toxins and pH level) generally incorporates many different steps and processes (Macías et al., 2012), each process targeting at least one problematic aspect of the acidic water. Main aspects of treatment involve raising the pH of the system (neutralization), removing high concentrations of heavy and other toxic metals and sulfate, and removing any other toxins and contaminants which may be present in the water and which are specific to the area and type of mine from which it was generated. A critical part of any treatment method is also management of any waste that may be produced (Ryan, Kney & Carley, 2017).

Many different treatment schemes can be used to either repurpose or recycle waste elements of active and passive treatment options. The following sections briefly present the treatment of different detrimental characteristics of AMD.

2.1.1 AMD pH Characteristics

AMD is characterized by a low pH which results in a harsh, highly acidic environment. Raising the pH of AMD using alkaline materials is a traditional, commonly used active treatment method in industry (Singh & Rawat, 1985), with lime being the economically preferred alkaline reagent in many parts of the world (M M Matlock, Howerton & Atwood, 2002). Although lime is preferred, other substances – such as caustic soda – are also used (Sapsford, Santonastaso, Thorn & Kershaw, 2015), but are generally disregarded due to their high cost. The cost of reagents in conjunction with the host of other problems encountered during slaking and dosing (such as the requirement of large doses, size of the particle needed to provide the appreciable surface area and the production of secondary waste products (Matthew M. Matlock, Howerton & Atwood, 2001)) has given rise to much research into alternative methods which can reduce the cost, reduce the secondary waste production and reduce the amount of reagent needed for treatment (M M Matlock et al., 2002; Othman, Sulaiman & Sulaiman, 2015).

The use of metallurgical slag as an alkaline source for pH rise in acidic waters is classified as one such alternate method of dosing. Work has been done previously that indicates pH rise and metal precipitation can be accomplished to a large degree in batch scale operations (Name & Sheridan, 2014). Much work has also been done which confirms the effectiveness of slag use as an alkaline reagent in other systems such as acidic soils, and if these effects can be mimicked in the proposed system, pH rise should be achieved quickly and have the added benefit of the treated water being desirable for use in agriculture (Stanojković, Maksimović, Jošić & Pivić, 2014). The physiochemical properties of metallurgical slag offer high potential for use in agricultural systems as it contains varying concentrations of trace elements which have low bioavailability in soils – this may open up more avenues for reuse of this material or treated AMD after they have been processed in the system.

Metallurgical slags could also potentially be a better reagent than other alkaline materials, due to the fact that they are undesirable by-products of another process (steel making process). This means little to no overall cost would be associated with the sourcing of this reagent (the by-product is cheaper than lime and can also potentially be sold after use in the system as an aggregate for use in concrete, cement or road ballast). The cost of lime (as dolomite, calcite, gypsum or hydrated lime) ranges between R203 and R533 per 1000 kg (Kalkor, 2020), whereas the price of BOFS (with different particle size ranges) is R146 per 1000 kg (Vermeulen & Phoenix Slag Services, 2018). In addition to being cheaper than lime, the use of BOFS in particular, would effectively utilize a secondary mining related by-product in the treatment of AMD – contributing to alleviating the strain placed on the environment by mining and its subsidiary processes. The spent BOFS has the potential to be used in many areas after being used for AMD treatment. Re-use as a road ballast is already established but due to the high free calcium oxide content in the slag (which results in swelling over time), use as an aggregate which results in volumetric instability, is objectionable (Reddy, Pradhan & Chandra, 2006). If the oxides were leached out of the slag before use as a road ballast, this disadvantage could be eliminated.

The pH of systems that use metallurgical slags as an alkaline reagent can easily exceed 12 (depending on the amount of slag used and the period of exposure) (Name & Sheridan, 2014), but the treatment method proposed herein will facilitate a pH rise within the 5-8 range. BOFS has been discussed in detail in Section 2.2.

2.1.2 Heavy Metal Concentration

AMD streams are also characterized by high concentrations of heavy metals, the most predominant of which are Iron and aluminium, which can occur in concentrations in excess of 1000 mg/ℓ. Other metals, such as zinc, magnesium, manganese, calcium, cadmium, lead, nickel, chromium and copper also commonly occur, generally in lower concentrations, but always depending on the type of mine and geographical area in which it is situated.

Because of their high solubility in aquatic environments, heavy metals can easily be absorbed by living organisms (Barakat, 2011), causing disturbances in their natural functioning which can result in illness, mutation and death (Malkoc & Nuhoglu, 2006). Control of metals concentration in water bodies is therefore essential, and many regulations and laws are in place that govern the maximum metal content that can be contained in industrial wastewater discharges. Government agencies give limits for the concentrations of metals, taking into consideration the effect they have on biological organisms. A concentration of below 10 mg/ℓ is allowable for iron and aluminium (Department of Water Affairs and Forestry, 1996), and the total electrical conductivity reading (which is an indicator of total dissolved solids (TDS) and mineralization in a water sample) should not exceed 70 mS/m (Fatoki & Awofolu, 2004). Mining water waste streams will invariably contain larger quantities of metals than this, and thus removal of these metals before allowing the mine water to enter back into a natural water body is required. Several treatment methods are currently used by mines for metal removal. These include precipitation using pH altering methods (as mentioned previously), solvent extraction and ion exchange (Zhang et al., 2016). Metal removal is generally a costly process and even when passive and low-cost methods are used to remove the metals, there remains the problem and added cost of waste management. New methods that aim to provide more effective, cheaper means to facilitate metal removal that result in less waste production are thus continuously being researched and improved.

One such method, biomaterial adsorption and accumulation (a process that uses biological waste materials such as eggshells (Zhang et al., 2016) or dead biomass containing lipids and proteins (Kaduková & Virčíková, 2005) to remove heavy metals) is reported to be highly effective. This is because biomaterials are benign, abundant and cost effective. Adsorbent loss in these methods however are high and continual replenishing needs to be undertaken in order to maintain a process (Chern & Chien, 2002). In addition, the sourcing of the adsorbents is difficult and expensive. Another method, removal via ion exchange resins, is a well-developed method of treatment for heavy metal rich waters. The use of resins is beneficial as there is the potential of lowering costs of treatment via product recovery (DeSilva, 1996). Ion exchange, however, is a costly option and large treatment volumes (which are needed) are difficult to accomplish. Resins are also highly specific (meaning multiple resins may be needed to remove all undesirable contaminants in a water stream) and can be easily fouled which increases the cost of maintenance (Alchin, 2006).

The use of waste metallurgical slag as an adsorbent and alkaline reactant is useful as it is readily available in large quantities, and many steel companies are actively pursuing methods in which to eliminate this by-product – making sourcing of the reagent much easier. Use of metallurgical slag has been approved in biological systems (soil systems) (Aydilek, 2015; Strandkvist, 2016) and thus incorporation of this treatment into the treatment program will allow for further biological means, in particular sulfate reducing bacteria (SRB), to be used to further lower or polish the sulfate content of the AMD.

The precipitation of metals in the proposed process will be facilitated by pH rise. Metal hydroxides, sulfates and oxides form at different pH's and will precipitate out of the solution in a settling tank. Iron precipitates form at pH's greater than 3.5 and aluminium precipitates form at pH's greater than 5 (Balintova & Petrilakova, 2011). A pH of greater than 7 should therefore almost completely remove these two metals. Manganese begins to precipitate at between pHs of 6.5 and 9, and copper precipitates between the pH's of 4 and 6. Magnesium begins precipitation at a pH of 8 (Irving, 1926; Yamagata & Paschoal, 2001). Magnesium and manganese will therefore only partially precipitate at a pH of 7.5. This research incorporates the use of a DSR system for sulfate removal and thus sulfides will also be present in the system for the metal ions to bind to and precipitate with and thus precipitation of metals will occur faster. Hydrogen sulfide reacts with dissolved metals in the AMD via the reaction shown in Equation [2.1] (Taylor, 2005):

$$H_2S + M^{2+} \rightarrow MS + 2H^+ \qquad [2.1]$$

At suitable pH's this results in the precipitation of metals as metal sulfides (this is discussed in detail in section 2.1.3 below).

2.1.3 Sulfate Concentration

The final aspect of treatment involves the removal of sulfate from the AMD stream. Sulfate control in mine waters is primarily achieved by one of two methods: removal through membrane separation of salts from water or removal of sulfate by salt precipitation through ion exchange. Other methods and technologies that are used to a lesser degree are permeable reactive barriers, bioremediation (in particular, biological reduction technologies) and dosing technologies which allow for the formation of insoluble mineral precipitates (Bowell, 2004). This research will incorporate biological reduction and formation of insoluble metal precipitates (as mentioned in the previous section). The formation of insoluble metal precipitates will facilitate the bulk of the treatment and the biological reduction will act as a further "polishing" step.

2.2 BIOLOGICAL SULFATE REDUCTION USING SUGARCANE BAGASSE

Bioremediation processes (processes which use living organisms to combat the harmful effects of AMD) can function naturally or can be enhanced by supplementing the process with electron acceptors, nutrients or by altering other factors (Lin & Lin, 2005). In the case of biological sulfate reduction for AMD treatment, this process can be enhanced by providing a carbon source and by maintaining a favourable pH level – due to the excessive presence of sulfate in AMD streams, supplementing the process with more electron acceptors is not necessary. Other than the presence of a substrate and a favourable pH level, biological sulfate reduction relies almost solely on the presence of different sulfate reducing microorganisms, which are able to live together within the reaction vessel (Goldhaber, 2003). SRB are the most ubiquitous of the sulfate reduction facilitating organisms (Keller, Wall & Chhabra, 2011), but other types of microorganisms may be present in these types of systems that will assist either directly with the sulfate reduction or indirectly via creating a greater availability of nutrients. Competition between microorganisms (methanogenic organisms) in this environment may also be a factor (Jing et al., 2013).

SRB are suitable for AMD treatment as they are able to oxidize organic matter, produce bicarbonates that raise pH and the alkalinity of the media in which they reside, and reduce any sulfates which are present to sulfides under anaerobic conditions (Zagury, Neculita & Management, 2007). Sulfides can then combine with metals to form insoluble metal sulfides. The sulfate reduction reaction is described in Equation [2.2] (Hu, Xu & Chen, 2020):

$$SO^{2-}{}_4 + 2C_{(organic)} + H_2O \rightarrow H_2S + 2HCO_3 \qquad [2.2]$$

Sugarcane bagasse is the chosen organic carbon source used in this research. Sugarcane plants have considerable economic significance in multiple countries, being the principal feedstock for sugar and ethanol production (Souza, Grandis, Leite & Buckeridge, 2014). Two main wastes are generated in sugarcane processing, namely bagasse and straw. Sugarcane bagasse is the solid, fibrous waste from sugarcane milling. It consists of fibre bundles vessels, parenchyma, and epithelial cells (Bizzo, Lenço, Carvalho & Veiga, 2014). It is produced in large amounts around the globe, with a reported production of 280 million tons/year (Ortiz & Oliveira, 2014). The main re-use avenue for sugarcane bagasse is as a source of energy and electricity in sugarcane mills (Dantas, Legey & Mazzone, 2013), however other avenues include use in biorefineries in the production of bio-ethanol, use in paper and animal feeds manufacturing (Tongaat Hulett & Department of Energy (RSA), 2013) and there has also been research where bagasse has shown potential in the treatment of AMD (Bardone et al., 2014; Cherubini, 2010; Westensee et al., 2018).

The effectiveness of SRB at reducing sulfate depends on the population size, the pH and temperature of the solution, the exposure to air and the distribution of the SRB throughout the reaction vessel or bioreactor. It is also dependent on the composition of the microbial community present in the system. Different strains of SRB function optimally over a range of pHs and thus selection of the suitable strain or even cultivation thereof is essential before commencement of treatment. There are many different genera of SRB that can utilize a wide variety of carbon containing substances as electron acceptors and donors (A. Hussain & Qazi, 2012). Different SRB strains have a greater affinity for different carbon sources, such as aromatic hydrocarbons, alkanes and alkenes (Aeckersberg, Rainey & Widdel, 1998). In general, low-molecular weight organic compounds or simpler sugars are better substrates for SRB (Ali Hussain & Qazi, 2016). SRB also do not function at very low or high temperatures and thus the system should ideally be kept at normal temperature (Yuan, Chen, Tsai & Chang, 2016). Sulfate removal also occurs via metal sulfate precipitation as mentioned.

It is important to note that the concentration of different sulfur species within solution is dependent on pH. At pH levels between 0 and 4, H_2S is predominant; at pH levels between 9 and 14, HS^- is the predominant species and at pH levels above 13, S^{2-} is the predominant species. The reactions [2.1], [2.3] and [2.4] can occur with each of the species to form metal sulfides. Manganese and magnesium sulfides reportedly exhibit high solubility at pH levels below 7, thus these metal sulfides are not expected to precipitate (Lewis, 2010).

$$S^{2-} + M^{2+} \rightarrow MS(s) \qquad [2.3]$$

$$HS^- + M^{2+} \rightarrow MS(s) + H^+ \qquad [2.4]$$

2.3 BASIC OXYGEN FURNACE SLAG

Like mining, the iron and steel manufacturing industries are fundamental to the economies of many countries (RSA Department of Trade and Industry, 2018). They provide the basic materials needed for the development and maintenance of infrastructures, vehicles, buildings, industrial facilities, and many other daily necessities (Ko, Chen & Jiang, 2015). Global steel production has been growing rapidly for the past 60 years – in 1967, the total world steel production was reported to be just less than 500 million tonnes (World Steel Association, 2017), but during 2015, the total steel production was reported to be 1599.5 million tonnes, showing an increase of more than 200% in 48 years. This number increased substantially again in 2016, where 1666.2 million tonnes of crude steel was reported to have been produced (Worldsteel Association, 2016).

Although the steel industry provides substantial employment in the world's top producing countries, namely China, Japan and India (Sawe, 2017), it is also responsible for large amounts of waste material generation, energy consumption and CO_2 emissions. The proper and efficient reduction and management of waste production, energy use and greenhouse gas (GHG) emissions are essential to achieving sustainable development. Improper management impacts on environmental and public health and affects the development and improvement of future generations. For this reason, research has been conducted in this industry with the aim of (i) reducing energy consumption and lowering CO_2 emissions and (ii) combatting, eliminating or reducing waste and re-using or recycling waste materials and by-products.

2.3.1 Solid waste generation

The steel industry is responsible for large amounts of solid waste generation, primarily in the form of steel slag. The worldwide output of steel slag is reported to be over 1600 million tons annually (Liu & Wang, 2017). Slag is a glass (Huang et al., 2013) or gravel like by-product that is left over in steel making processes after the desired metal has been smelted or separated from its ore (Humbert, 2019). It can be categorized by either the process in which it was generated (BOFS, electrical arc furnace slag (EAFS), ladle refining slag (LFS)), or by the type of steel produced in said process (carbon steel slag or stainless-steel slag) (Liu & Wang, 2017; Ndlovu, Simate & Matinde, 2017; Yi et al., 2012). Countries such as Japan, Germany and France have found multiple reuses for their slag production and report waste material reusability rates of close to 100%. However, there are still countries that struggle with managing the waste production from this industry (Yi et al., 2012). China was responsible for approximately half the world's steel production in 2010 (Allen, 2010), and generates large amounts of slag that do not currently have reuse avenues. In 2015, 120 million tonnes of steel slag were produced in China with another 1 billion tonnes already accumulated in landfills or in stockpiles where metallic elements present in the slag can leach out and have the potential to cause environmental and health problems (Evarts, 2017; Mo et al., 2017).

Two types of by-product are produced during steel and iron manufacturing, (i) blast furnace slag (BF-S) combined with BOFS and (ii) converter or refining slag. In 2008 between 230-280 Mt of BOFS and 130-200 Mt of converter slag were produced globally (Kuwahara & Yamashita, 2013) and current estimates put slag generation at between 200 and 250 kg per tonne of steel that is produced (Kumar, Sah, Sanyal & Prasad, 2019). As discussed, slag which is not reused is generally placed in landfill sites which are not closed off or isolated from the surrounding environment. When water comes into contact with the slag, a solution high in alkaline content is produced. When this water seeps back into the environment it has detrimental side effects for aquatic and terrestrial animal and plant life in the surrounding areas (Souter & Watmough, 2017). This is considered the most widespread and chronic impact of alkaline wastes from the steel industry (Gomes, Mayes, Rogerson, Stewart & Burke, 2016).

2.3.2 Impact of slag on the environment

The geochemical behaviour and characteristics of the alkaline leachate seeping from landfill sites and stockpiles depends on many factors, including (W. M. Mayes, Younger & Aumônie, 2008; William M. Mayes & Younger, 2006): (i) the chemistry (pH, conductivity, etc.) of the water before it comes into contact with the slag; (ii) the composition and age of the slag contained in the landfill site; (iii) the flow rates, redox status, and residence time of the water (known as hydrogeological factors); (iv) the nature of any other steel mill wastes also present in the land fill site; (v) the chemical and physical properties of the surrounding ground and lastly, (vi) the chemistry of the body of water that eventually receives the leachate. Alkalinity generation generally arises from two processes: (i) the rapid hydration and dissociation of calcium and magnesium oxide, and (ii) the slower dissolution of Ca-silicate minerals (like rankinite, larnite and akermanite) (Gomes et al., 2016). The release of metals or elements from slags that contribute to alkalinity generation can cause environmental problems such as water and soil pollution (Shen & Forssberg, 2003). There are many impacts of alkaline leachate waters which include increased water pH, increased COD, increased oxygen depletion, increased salinity, and increased metal concentrations (W. M. Mayes et al., 2008; William M. Mayes & Younger, 2006). In conjunction with these effects, mineral precipitation also occurs and can suffocate or smother macroinvertebrate communities as well as reduce light penetration into water bodies, further amplifying any ecological impact of the leachate release (Hull, Oty & Mayes, 2014). For these reasons, along with the need to reduce the environmental impact of the steel manufacturing industry as a whole, metallurgical slag reuse and recycling is considered to be essential.

There are two main processes used in the production of steel: (i) primary steel production which uses iron ore as the main raw material (this includes BF and BOF processes (Steenkamp & Preez, 2015)), and (ii) the direct reduction (DR) process and electric arc furnace (EAF) process. The latter two processes require much less capital than the BF and BOF processes and involves using a combination of steel scrap and iron ore that will be reduced in the DR process (Tanaka, 2015) and purified in the EAF process. At present, steel production in high output countries, such as in China and Japan, mainly use iron ore as raw materials via the primary BF and BOF route (Wei et al., 2017).

2.3.3 The Basic Oxygen Furnace (BOF)

The BOF process forms part of the primary steel production route, which also incorporates the BF process. In a BF, the iron ore, limestone and fuel are continuously supplied through the top section of the furnace, while heated air is forced into the lower section (Geerdes, Toxopeus & Van der fliet, 2009). The end products are usually molten metal and slag, of which the former is fed into a BOF and the latter is considered a waste material or by-product of the process. If the carbon content in steel is too high it could result in defects such as inclusions and blowholes which form during solidification, thus the BOF process is essential in steelmaking as it lowers the carbon content of the molten alloy and changes it into low-carbon steel (Kloppers & Fedotova, 2001). The BOF is essentially a converter in which heat is internally generated by the oxidation of impurities that are found within the molten slag. Along with the molten slag, oxygen is also added to the charge and this leads to the formation of iron oxide and carbon monoxide (which are exothermic reactions). Within the furnace, the temperature level or amount of heat produced is determined by the rate of oxidation of metals and the temperature of molten iron which is received from the BF (Remus & Roudier, 2010; Yildrim & Prezzi, 2009). Due to the increasing amount of accumulated scrap metal, scrap is also sometimes added into the BOF, making up 20 to 30% of the entire charge. Lime and fluorspar (the commercial name for calcium fluorite (Masoudi, Ezzati & Moradzadeh, 2017)) are added to the furnace to form a slag which contains the impurities that are removed from the molten slag. When the carbon content of the molten metal is reduced to a sufficient level, the steel is tapped into a ladle and cast continuously.

At the end of the BOF process, the liquid steel and slag form an immiscible layer which is first separated and then tapped into ladles and slag pots. The BOFS pots are transported to further processing facilities or directly to solidification and casting facilities, after which they are sent to a disposal or storage site (Ndlovu et al., 2017). The composition of the hot metal from the BF process, the scrap metal that was added and the chemical reactions that occur during the BOF cycle will determine the composition of the slag as well as the amount produced (Remus & Roudier, 2010; Yildirim & Prezzi, 2011). The BOF process has not undergone any fundamental changes in the last 20 years: the same processes that occur in steel processing plants today were used then (Barker, Paules, Rymarchyk & Jancosko, 1998).

2.3.4 Composition and characteristics of BOFS

The characteristics and composition of BOFS varies largely from site to site, as well as over different time periods at the same site. This is due to the varying nature of the sources of ore and scrap used in the process and thus the varying characteristics of the chemical reactions and mechanisms that occur (Teir, Eloneva, Fogelholm & Zevenhoven, 2007). In general, all BOFS tend to have a high basicity or alkalinity ratio (due to the nature of impurities found in the ore) and a high FeO content (Ndlovu et al., 2017; Remus & Roudier, 2010; Reuter, Xiao & Boin, 2004). The alkalinity in slag is found in compounds such as CaO, MgO and SiO2 in varying degrees (T.S. Naidu et al., 2018).

2.3.5 Uses of BOFS

Steel Slag reuse generally falls into three main areas of application (Piatak, Parsons & Seal, 2015):

- Slag as a construction material,
- Metal recovery from slag
- Slag use in environmental remediation applications

Of particular interest in this study, is the use of BOFS as a construction material and as an environmental remediation reagent.

2.3.6 Concrete Aggregates

Due to increased environmental concerns and more restrictive regulations in some counties (China and India), a substitute for sand and gravel as natural aggregate use in the civil construction and concrete industries is highly sought after (Somvanshi, 2015; Wang, 2016). Since more than 15 million tons of natural aggregate resources like gravel, limestone and other rocks are used annually, the search for natural aggregate replacement has become an important and urgent issue (Ding et al., 2017). Like steel, concrete is a major construction material, reportedly the most widely and extensively used man-made material in the world (Brito & Saikia, 2012). This large scale production of concrete has many negative environmental effects, some of which arise from the concrete industry’s use of natural stones as aggregates (Brito & Saikia, 2012).

Concrete comprises of three major fractions, namely aggregate, binder and water – aggregate constitutes approximately 75% of the total concrete volume and therefore plays a vital role in the performance of the final concrete product (Brito & Saikia, 2012). Concrete properties such as workability, strength, dimensional stability and durability are all, in part, due to the quality and characteristics of the aggregate used. Conventional concrete contains sand as fine aggregate and gravel (in various sizes) as coarse aggregate. Materials that are used as aggregates are mined, and this process as well transporting the aggregate to the cement plant, are both fuel and labour intensive (Ayenagbo, Kimatu, Gondwe & Rongcheng, 2011). For this reason, the use of waste materials as an aggregate is an attractive alternative to traditional aggregate avenues.

BOFS is an example of a waste material that has shown potential for use as an aggregate substitute in concrete. The physical properties of slag are highly comparable to those of natural aggregates. The California bearing ratio, compressive strength, and Mohs' scale of hardness value of slag are even reported to be better than that of natural aggregate (Ding et al., 2017). In addition to this, the Toxicity Characteristic Leaching Procedure (TCLP) test showed that there are no toxic materials which exist in BOFS that can be classified as general industrial waste (Yildrim & Prezzi, 2009). The bulk density of BOFS qualifies it for use as a construction material and the L.A. Abrasion and crushing indices indicate that BOFS has good crushing and abrasion resistance. Studies report that these qualities, amongst others, make it suitable for use in concrete (Manso, Polanco, Losañez & González, 2006; Maslehuddin, Sharif, Shameem, Ibrahim & Barry, 2003). When compared to limestone and basalt, a BOFS mix showed comparable results for fatigue life, low temperature cracking resistance, water sensibility, and high temperature stability (Xue, Wu, Hou & Zha, 2006).

A drawback that has been reported in the use of BOFS as an aggregate is that it contains many hydratable oxides. These can result in volumetric instability or expansion (as shown in Figure 1) – a characteristic not allowable in concrete aggregates for safety and structural soundness.

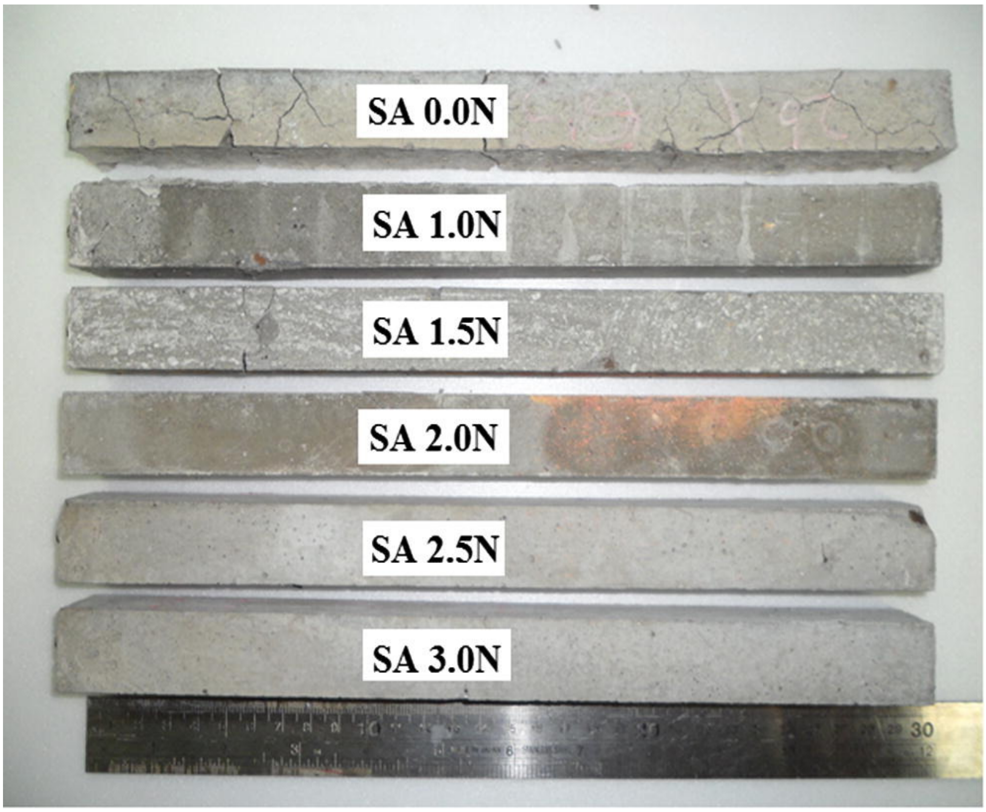

Figure 1: Concrete mixtures made with BOFS that had been chelated with oxalic acid after four days of steam curing process (Ding et al., 2017)

This remains an issue and studies are currently underway that aim to remove or lower the free lime content of the slag before use as a concrete aggregate. By reducing the hydratable oxide content through attrition and chelating processes (using oxalic acid as a chelating agent), the volume expansion of BOFS decreases from 4.7% to 2.8% (approximately a 40% volume expansion reduction). Aside from possible volume instability, the physical and mechanical properties of cement mortars made with BOFS has great potential as a civil construction resource (Ding et al., 2017). A depiction of the effect of volume instability is shown clearly in Figure 1, where different concentrations of oxalic acid were used to chelate the BOFS prior to preparation of the concrete mixture. Sample SA 0.0N contained slag that was not pre-treated at all and the subsequent samples (from top to bottom) show samples which received increasing pre-treatment. Understandably, volume instability is a major issue in the reuse of slag in cement, concrete and road filler and more research is needed to combat this. Use of oxalic acid as an oxide removing agent is clearly effective, but very costly. Use of a waste acidic material (such as AMD) may reduce the cost of pre-treatment of BOFS.

In this regard, the converse treatment of AMD using BOFS as a lime substitute could potentially result in two valorised waste products, (i) AMD treated to reusable water standards and (ii) BOFS treated to be reused as an aggregate in the construction industry. Using BOFS as an AMD treatment reagent could contribute to developing a circular economy in the AMD remediation field and lower the cost of pre-treatment for both AMD and BOFS.

2.4 SUMMARY OF COMBINED PROCESS

The design proposed for the purposes of remediating AMD with respect to pH level, sulfate and metal content, includes the use of sugarcane bagasse (due to its availability of organic carbon) as a substrate for SRB, and BOFS as a neutralizing agent for AMD. Using both these products in a treatment scheme, could potentially lower the sulfate and metal concentrations of AMD to allowable limits (agricultural, potable or for use as process water) and increase the pH to near neutral conditions. The substrate is not limited to sugarcane bagasse however, and other waste organic sources of carbon can be used for this application.

These waste/by-products were tested individually and then in conjunction to assess their ability to remediate AMD and to establish a working, effective design that could be deployed at mining wastewater sites. The methodology that was followed to establish the design is discussed fully in Chapter 3.

CHAPTER 3: DESIGN METHODOLOGY

3.1 INTRODUCTION

In order to properly determine a feasible and working design for a combined biological and chemical AMD treatment system, a number of preliminary small-scale, batch experimental steps were taken to inform a larger scale design. The treatment or pre-treatment extent of volumes of below 100 mℓ of AMD was initially determined and these results were used to formulate a design scheme that could eventually potentially treat up to 10 000 ℓ/day. Batch experimental tests led to a continuous process that could treat between 1 and 25 ℓ/day which was monitored continuously for over a 1-year period. The results and observations from this study were used to inform the design of a larger scale plant, designed to treat between 250 and 1000 ℓ/day. This plant was constructed and then monitored for a period of 8 months. During this period, complementary data were also obtained from additional batch studies. The results from all studies have been used to inform the design of a plant that can treat up to 10 000 ℓ/day plant. This section briefly summarizes each step of the process undertaken to advise a final design. **This section refers solely to the design methodology – detailed descriptions of the materials and methods used for laboratory work, field work and complementary data are provided in the relevant chapters (Chapters 4-6).**

3.2 PRELIMINARY EXPERIMENTS

Initial batch and continuous experiments were undertaken to determine the manner in which the BOFS and sugarcane bagasse could be combined to achieve maximum treatment. This phase included combining the two materials in one reaction vessel and then combining them in series, to determine which configuration would yield the most favourable results.

During this phase it was observed that (i) precipitation of various metal salts occurred rapidly during a pH rise and (ii) SRB functioning was inhibited by the low pH of raw AMD. The findings suggested that introducing the AMD directly into the system (into direct contact with the BOFS or sugarcane bagasse) would not be an option. This was due to the fact that the AMD had too low of a pH (it would kill any bacteria present in the sugarcane bagasse reactor and thus render this treatment null) and upon exposure to BOFS would precipitate metal oxides and sulfates almost instantaneously (resulting in a layering or armouring of the BOFS particles and preventing further release of alkaline components). A recycle stream (containing treated water) was conceptualized to combat the issues of armouring of the slag and potentially toxic shocking the biological system containing SRB.

A schematic which shows the preliminary design configuration is presented in Figure 2.

3.2.1 Schematic representation of preliminary design

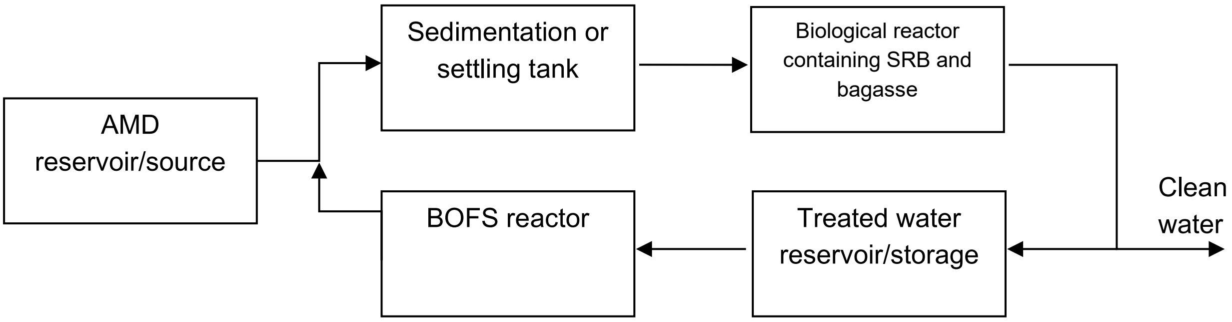

Figure 2: Preliminary design block flow diagram

This recycle stream necessitated the use of clean water for start-up procedures but allowed for less manual work to be done with regards to removing precipitate/sedimentation that had formed and replacement of the slag. Figure 2 describes the configuration that was proposed – and initially tested – to prevent precipitation and toxic shock of the system. Instead of entering the system in direct contact with one of the reagents, the raw AMD is mixed in a settling tank with the slag eluate. The water in this tank undergoes precipitation reactions (due to the increase in pH), removing a large amount of sulfates and various metal species. The water exiting the tank thus has an increased pH and is of significantly better quality – making it suitable for further treatment using biological means. Under the action of sulfate reduction, the sulfate and any metals still contained in the AMD are removed and the water exiting the biological reactor is considered treated. This water can be released back or can enter the system again as a recycle stream, coming into contact with BOFS in a BOFS packed bed reactor. This water has a very low concentration of sulfates and metals and thus precipitation and armouring of the slag does not occur.

3.3 LABORATORY SCALE (1-25 ℓ/DAY)

The preliminary design (discussed in section 3.2) was tested in a continuous laboratory-scale setup for a period of a year. The remediation setup comprised of two pumps and a number of process vessels (an AMD feed tank, slag vessels, sedimentation vessels, primary and secondary DSR vessels, water reservoir and outlet storage tank) which were sealed and anaerobic. The typical setup is shown in Figure 3, where S1-S5 denote sampling points.

Multiple configurations were tested:

- Vessels of different sizes
- Different reactor types
- Vessels in series
- Different qualities of AMD
- Different particle sizes of BOFS and
- Different reaction times.

Data was obtained from these configurations that assisted in informing the larger scale design.

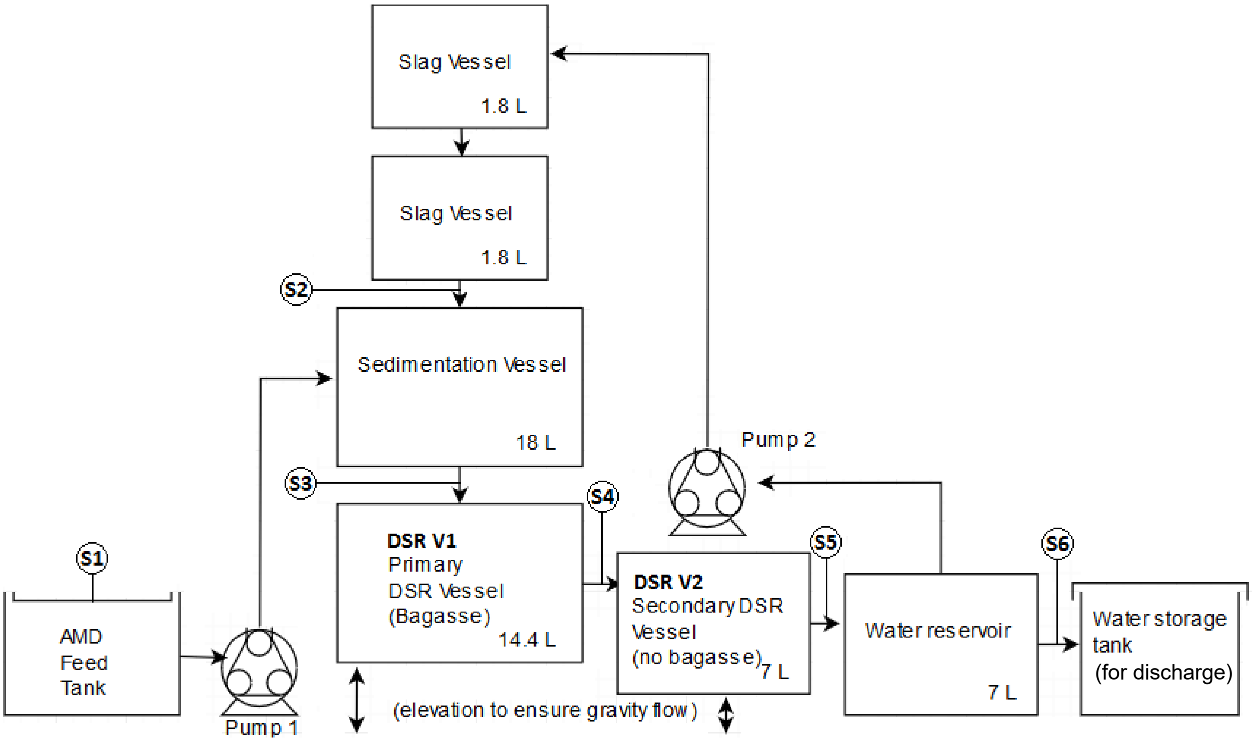

Figure 3: Laboratory scale set-up with vessels and sampling points denoted

AMD was treated to a maximum efficiency of 99% SO_4^{2-}, Al and Fe removal, 93% Mn removal, 81% Mg removal and pH buffering from approximately 2.4 to 7. The system was versatile and was able to treat two different AMD types to a level of 99% Al removal, 98% Fe removal, 93% Mn removal and 42% Mg removal. The main observations that altered the large-scale design were (i) the pH control data and (ii) the dissolution of the slag data. The pH levels played an important role in the treatment extent, with the pH affecting the amount of sulfate and metals removed in the settling/sedimentation phase, as well the functioning of the biological reactor. If the pH is not properly controlled in the settling tank (via determining and maintaining the correct mixing ratio between AMD and slag eluate), then the treatment extent is affected in this vessel as well as in all subsequent vessels. Low pH in the settling vessel, results in less precipitation and a higher concentration of sulfates and metals entering into the biological reactor. If the feed into the biological reactor has a low pH, the SRB in this vessel are affected (Ayangbenro, Olanrewaju & Babalola, 2018) and the sulfate reduction rate will be lowered, again leading to a higher a concentration of metals and sulfates in the discharge water. Higher concentration of metals and sulfates into the BOFS reactor will result in precipitation and possible armouring of the slag in this vessel – reducing further dissolution of pH raising or alkaline reagents. Thus, maintaining the desired pH in all vessels is of vital importance to ensuring functionality of the system.

For this reason, the following changes were introduced into the final design:

(i) The slag vessel contained an excess of slag of different particles sizes to ensure a continuous dissolution and a constant supply of high-pH, high-alkalinity eluate. A larger vessel size was proposed for this reactor.

(ii) The area and volume of the settling tanks were increased to allow for greater settling. This was also done to combat any slight variations in pH that may occur in this vessel, allowing more time for precipitation to occur and more time for smaller particles to settle. The controlled pH setpoint in the settling vessel was also changed to a lower pH (5). A pH of 5 would allow for a lower ratio of mixing between the AMD and slag eluate streams, as well as ensuring that enough dissolved metal species enter into the biological reactor to act as counterions for the precipitation of sulfide components.

(iii) The proportional size of the biological vessels (where sulfate reduction take place) were increased and the amount of bagasse used (in proportion) was also increased. A larger quantity of bagasse meant that the carbon source was available in excess and did not act as a limiting factor. The larger amount of bagasse also meant more hydrogen acceptors were present in this biological reactor which could play a role in offsetting any minor pH variations that occurred.

(iv) Lastly, a H_2S scrubber was added to combat any H_2S that could be liberated from the biological reactor. H_2S production was not an issue in the smaller scale design and was not envisioned to be an issue in the larger scale design either (due to the maximum amount of sulfide generation being within allowable limits). However, to negate any uncontainable H_2S release, the scrubber (a 200 L plastic drum) contains water, hydrogen peroxide or ammonia. Gas from the bagasse reactors was directed into the base of the vessel and allowed to bubble through the liquid. H_2S gas exhibits high dissociation and reactivity, and the gas will react with the scrubbing liquid to form sulfuric acid and water. The tank used was constructed from polyethylene to prevent degradation of the vessel via corrosion. The scrubber is represented by symbol R-107 in Figure 4.

3.4 PILOT SCALE (200-1000 ℓ/DAY)

Following the design and successful operation of the laboratory scale process, the plant designed to treat 200-1000 ℓ/day of AMD was constructed at a site in eMalahleni, South Africa. The site comprises of two dams which are used concurrently to contain seepage from a large mine tailings dump.

The system operated as follows (referring to Table 1 and Figure 4): AMD (stream 1) was pumped into an initial sedimentation vessel (R-102A/B) where it was mixed with a slag eluate stream (stream 10) from the slag chamber (R-101A/B). The slag eluate stream had a high 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 increased, causing (i) precipitation reactions and (ii) removal of dissolved metals and sulfates in the solution via gravitational settling. The outlet from the sedimentation section (stream 3) contained significantly less sulfate and metal ions and was at a higher pH (close to neutral). This stream entered the biological reactors (R-104, R-105, and R-106), the first two of which contained sugarcane bagasse. The outlet from R-106 (stream 6) entered a water reservoir (TK-101) where the treated water was stored. Water from TK-101 either overflowed into the AMD dam or was recycled into R-101A where it underwent a reaction with the BOFS.

All vessels were sealed and R-107 acted as a H_2S scrubber. Vessels marked B were replacement vessels that were included in the design and were to be used when cleaning of the system occurred. When sludge build up (of precipitates) occurred in R-102A and R103-A, the inlet and recycle flow (stream 1 and 10) could be redirected to R-102B and R-103B to allow for continuous operation. In a similar way, when slag replacement had to occur in R-101A, stream 7 could be redirected to R-101B (already containing slag). Due to operational limitations (discussed in Chapter 5), these vessels were never used, with sludge removal and slag replacement occurring in intervals during the operational period.

Table 1: Description of process flow diagram elements in Figure 4

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

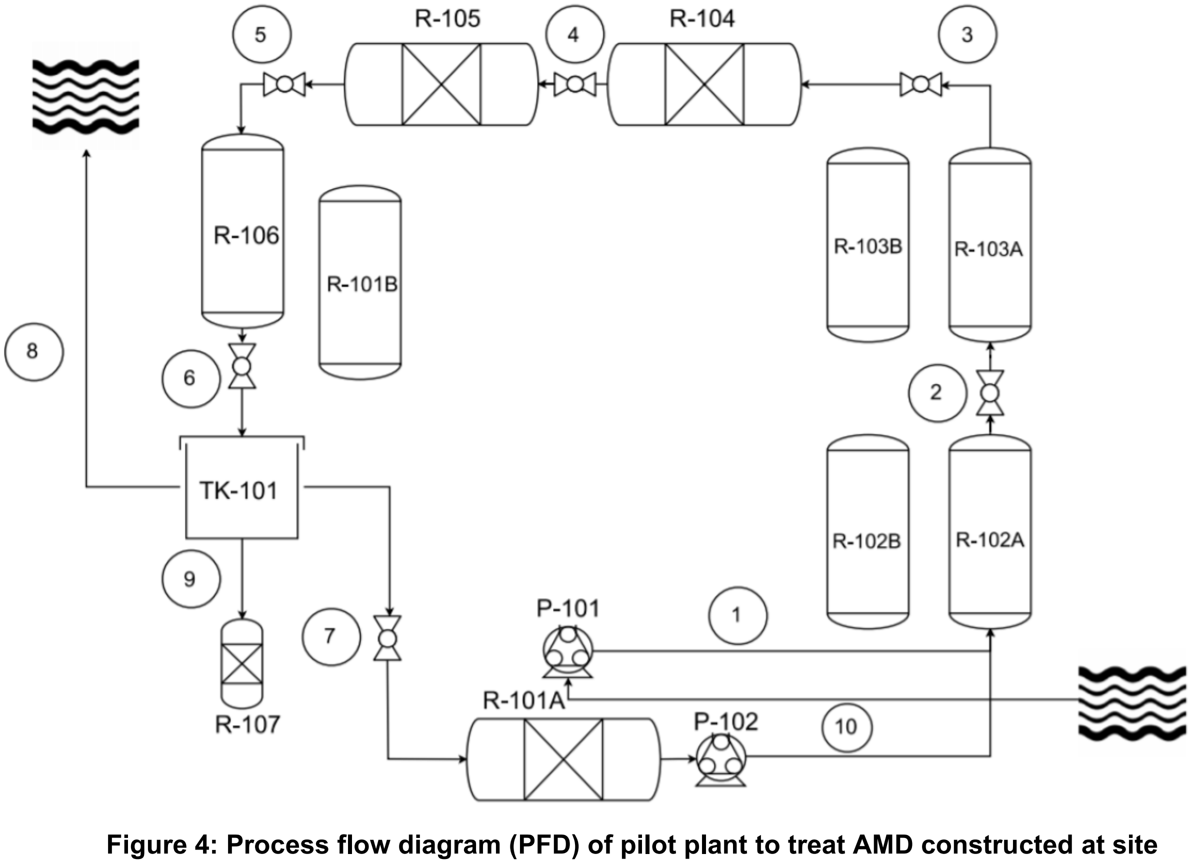

Figure 4: Process flow diagram (PFD) of pilot plant to treat AMD constructed at site

A process control element was used to vary the ratio of slag eluate (stream 10) to AMD feed (stream 1) that was mixed (and underwent a titration reaction) in the sedimentation vessels (R-102 and R-103) in order to maintain a pH of 5 in these vessels. A pH of 5 was chosen to (i) keep the recycle flowrate at a sustainable level, (ii) allow for ideal functioning of SRB, 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 5.

Figure 5: AMD remediation pilot plant at mine dam site (photographs taken by authors)

The extent of treatment of AMD at the pilot plant (200-1000 ℓ/day) scale was evaluated 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 in the BOFS neutralized solution and the biological reactors showed a maximum sulfate removal of 76%. These were comparable to the laboratory scale data obtained, however significant differences were noted which were attributed to multiple technical issues which were experienced at site. These are discussed in Chapter 5.

3.5 COMPLEMENTARY EXPERIMENTS

Further experiments conducted during the pilot scale period included (i) determining the dissolution mechanism of the slag in the medium used, (ii) determining the alkalinity content of the precipitate which formed in the settling tank and (iii) determining the best process control configuration to maintain the ideal pH. These were relevant as the dissolution of the slag which produces hydroxyl units in the system to increase the pH of the AMD, is the limiting factor. It was found that the alkalinity (and ability to in increase the pH of the system) was much higher when BOFS was dissolved directly in AMD as opposed to when dissolved in water or treated water. It was also found that smaller particle sizes of slag, although exhibiting a much quicker dissolution rate, cemented in liquid when left stagnant which prevented further dissolution. The smaller particle sizes also remained suspended in the liquid for longer periods of time and partially dissolved slag particles were frequently found in the sediment which formed at the bottom of the settling tanks. The sedimentation therefore contains a large amount of alkaline material which can be recycled to act as a pH raising reagent in the system. The process control mechanism was also investigated and a proportional only controller with pH controlled in the slag reactor as opposed to the settling tank was found to operate the best.

The findings and observations from each section have been used in the proposal of a design to treat 10 000 ℓ/day.

3.6 ANALYTICAL TECHNIQUES

The following analytical techniques were used to obtain measurements throughout the project period.

- Metal concentrations (Al, Ca, Fe, Mg, Mn) were measured with an Agilent 2000 series atomic spectrometer (AAS). Samples were filtered with 0.45 µm filters, diluted on a 1:3 ratio with deionized water and acidified with 0.6 mℓ of nitric acid prior to analysis. This was done to measure the difference in concentration in dissolved and precipitated metals in the samples. Sludge samples were acidified using nitric acid prior to measurement.
- Sulfate and sulfide concentrations were measured using turbidimetric spectrophotometric tests (using a Merck Spectroquant Pharo 300) (American Public Health Association, 1975; Center for bioprocess engineering research, 2016). Samples were filtered and sometimes diluted before testing to ensure concentrations were within an accurate range.
- A Scanning Electron Microscope (SEM) (FEI Quanta 200 ESEM) was used to investigate the surface of the slag particles. Standard concentration solutions were used for each test to obtain relevant calibration equations. Samples were mounted onto a metal plate using carbon tape and coated with carbon and gold palladium. Energy Dispersive X-Ray Spectroscopy (EDS) was used/performed during SEM analysis to determine the elemental composition on the slag surface (this was a qualitative assessment).
- XRD and Rietveld quantification analyses were done externally to determine the mineralogical composition of the slag. XRD sample preparation included grinding 3 g of sample and spiking it with fluorite on a 90:10 weight basis. Bagasse characterization data was obtained from the sugar mill. A Siemens D500 computer automated diffractometer was used to perform XRD.
- The pH and oxidation reduction potential (ORP) were measured using a DF Robot combined pH and ORP meter.

- Alkalinity/Acidity was measured using potentiometric titration. The titration sample (20 mℓ) was continuously stirred and an initial pH determined and 0.02 N H_2SO_4 was added in varying proportions and pH was monitored until a pH of 4.5 (for total alkalinity calculations) was achieved. The total volume of H_2SO_4 added was recorded and used in calculating total alkalinity using equation [3.1]. For acidity, 0.1 N NaOH solution was used as a titrant.

  $$Total\ alkalinity/acidity\ as\ CaCO_3 = \frac{(B/A)\times N\times 50\times 1000}{ml\ sample} \qquad [3.1]$$

  Where B is the total volume of standard acid used in titration to pH 4.5 or A is the total volume of standard base used, N is the normality of the standard solution of the acid or the base titrant, 50 is the mg equivalent of $CaCO_3$ and 1000 is used to convert from mℓ to ℓ (Smith, 2018).
- Flowrates were determined via calibrations of the peristaltic pumps which were used.
- Particle size distributions were obtained from Phoenix Slag Services.
- COD measurements were obtained using 1 ml sample together with Merck Millipore COD reagents 1.14679.0495 (A) and 1.14680.0495 (B) as well as COD cell test kit 114690. These were premixed solutions containing potassium dichromate that reacted with oxidizable material contained in the test sample. The solution containing both sample and reagents were heated to 148°C and then cooled before being tested. The concentration of unconsumed yellow $Cr_2O_7^{2-}$ ions was then determined photometrically (Merck Spectroquant ® Pharo 300) and using stoichiometry, giving the mg/ℓ of COD of the sample (Center for bioprocess engineering research, 2016; Decker, Askew & Merck, 2017).

3.7 SUMMARY

A summary of the design methodology is as follows:

- Testing/evaluation of individual reagents (sugarcane bagasse with SRB and BOFS) to determine their efficacy and ideal conditions.
- Combining the reagents to determine the most feasible model for combined treatment.
- Testing the model at a laboratory scale (treating up to 25 ℓ/day)
  - Identifying shortcomings, proposing alternatives and testing alternatives
  - Proposing a model/design for the larger scale (pilot) plant based on findings
- Designing, constructing, and monitoring the pilot scale design (treating up to 250-1000 ℓ/day)
  - Identifying shortcomings, proposing, and testing alternatives where possible
- Proposing a design for a large scale (treating up to 10 000 ℓ/day) plant based on the findings from the previous steps.

CHAPTER 4: LABORATORY-SCALE PLANT

4.1 INTRODUCTION

The construction and operation of a laboratory-scale plant was essential to the design process, as this allowed for the behaviour of the system to be monitored and improved before proposing a larger scale design based on the initial concept. The laboratory scale processes were tested over a period of 156 days and assessed multiple different aspects of operation, namely: reactor type, particle size, pH dependency and variation in feed quality. As discussed in Chapter 2, the data obtained from the laboratory work was used to compile a pilot scale design. This section discusses the focal merits of the laboratory phase of the work. This small-scale study has also been the basis of a journal article and a conference paper (Naidu et al., 2018; Naidu, Van Dyk, Sheridan & Grubb, n.d.).

4.2 METHODOLOGY

As mentioned in Section 3.2, initial testing (conducted prior to laboratory scale design) revealed the shortcomings of introducing the AMD into contact with either the BOFS or the SRB and sugarcane bagasse directly. The schematic shown in Figure 2 was thus followed, whereby a recycle stream of treated water was reacted with BOFS and then used as a titrant for AMD. The (approximately) neutral water that was generated as a result of this reaction was then passed through the sugarcane bagasse and SRB. In this way, denaturing of both reagents (BOFS and sugarcane bagasse with SRB) was avoided.

Plastic vessels (to avoid corrosion) were used as reactors during the laboratory scale investigation. Vessels contained in the laboratory plant are listed below with volumes in brackets:

- Sedimentation vessel/settling tank (18 ℓ)
- Primary biological (sulfate reduction) vessel containing sugarcane bagasse (14.4 ℓ)
- Secondary biological (sulfate reduction) vessel/sulfide precipitation vessel (7 ℓ)
- Water reservoir/storage tank (7 ℓ)
- 2 x Slag packed bed reactors (PBR) containing BOFS (1.8 ℓ) (this was changed to a 1 ℓ continuously stirred tank reactor (CSTR) during operation).

The setup also consisted of 2 peristaltic pumps and a pH controller which controlled the pH at a set-point via on-off control. This set-point was changed throughout the operation.

The initial performance of the process was tested by operating the system under different process conditions for a total of 106 days. COD was measured in the liquid from the biological reactor containing bagasse before operation began. BOFS particles were replaced, and sizes changed on Day 33, from size 1 (8,000 µm <d<13,000 µm) to size 2 (1,700 µm <d<3,350 µm), and on Day 64 from size 2 to size 3 (d< 1,000 µm) (particle size ranges were achieved using sieve analysis). On Day 64 the BOFS reactor type was changed from a PBR to a CSTR to eliminate blockages due to the small particle size. The raw AMD was changed on Day 70 from Type A to Type B (the compositions of the different AMD are shown in Table 2). Samples were taken from sample points at different positions in the process (as shown in Figure 3) and analysed for metal, sulfide and sulfate content as well as pH and redox/ORP. Following this, the plant was run for a period of a further 50 days using a CSTR and size 3 (d< 1,000 µm) BOFS in order to assess pH control functionality and options.

Table 2: Composition and pH of AMD sourced from two different AMD sources in eMalahleni, Mpumalanga, South Africa

AMD Type	pH	Aluminium (mg/ℓ)	Calcium (mg/ℓ)	Iron (mg/ℓ)	Magnesium (mg/ℓ)	Manganese (mg/ℓ)	Sulfate (mg/ℓ)
Type A	2.44	434.89	110.83	3039.60	105.67	88.29	12955.62
Type B	2.47	497.25	175.38	3506.88	94.04	197.68	5199.92

SRB was cultivated separately using a solution of sodium sulfate and sodium acetate (using a 0.7 g COD/g sulfate concentration) and then added to the AMD solution (SRB solution to AMD was mixed with a 1:2 ratio). Sulfide production and sulfate reduction (concentrations) were used as indicators of SRB activity. This inoculum was then added to the biological reactor containing sugarcane bagasse. SRB cultures were sourced from previous experiments which had used mud sediment from Emmarentia Dam in Randburg, South Africa.

4.3 REACTOR TYPE

BOFS dissolution was not found to occur sufficiently in unagitated systems and thus a constant flow or constant agitation was required to achieve the necessary level of reaction – corresponding to a rise in alkalinity and pH of the system. In this regard, two types of reactors were investigated – a CSTR and a PBR.

4.3.1 Packed Bed Reactor

The system was initially designed to house a PBR which would facilitate the acid-base reaction between the BOFS and the AMD/treated water. Use of a PBR was tested initially in the continuous process using the configuration showed in Figure 3 and monitored over a period of time. Treated water from the reservoir was pumped into this reactor and came into contact with the BOFS where a dissolution reaction took place. The pH, metal and sulfate content was observed for this period and it was found that without agitation of the slag, the pH did not reach a level high enough to titrate the AMD to the desired pH. The recycle ratio could not be sustained by the low concentrations of hydroxide groups found in the BOFS eluate from this reactor – i.e. because dissolution of the slag was not occurring sufficiently (due to the reactor type and BOFS particle size), the amount of hydroxide units in the slag eluate was not enough to fully neutralize the AMD to the desired pH.

Thus, either a higher recycle ratio (and conversely a longer reaction time in the slag reactor) needed to be used, or a way to increase the dissolution of the slag needed to be implemented.

The PBR used in the laboratory had a small volume in relation to the total volume of the system and did not contain enough BOFS (or water) to facilitate the required rise in pH. As the requirement of the system grew (AMD needing higher and higher volumes of slag eluate to be neutralized), the flowrate through the PBR increased – effectively decreasing the residence time and the time allowed for the dissolution reaction (this meant that the solution did not have a high enough pH and there were not sufficient hydroxyl units in the solution to increase the alkalinity of the AMD by the required amount). It was concluded that for a PBR to be effective, it would have to (i) contain a substantial excess of BOFS and (ii) be of a great enough volume that water contained within this chamber would have enough time to allow dissolution of the BOFS and generate sufficient alkalinity to neutralise the AMD.

It was also found that particle size played an important role in dissolution. When an assortment of particle sizes (including fines or particles with a diameter less than 1 mm) were used as the packing material, hindrance of flow due to cementation was observed in the reactor. When only larger particle sizes (particles with a diameter of 1 cm or above) were used, void space and flow did not present any problems as no fines were present to create cementation and hinder flow. In addition, the space between particles increased allowing for constant and uniform flow through the reactor. The pH increase of the water entering the reactor, however, was very low when larger particles were used. This was attributed to the decreased surface area of the BOFS particles. It was noted that in situations of high flowrate (turbulent flow), cementation was not an issue and the fine particles remained suspended in the solution.

Residence times of between 44 and 4 days were achieved for different conditions – smaller particle sizes of slag exhibiting better performances in terms of recycle rate and residence times. The flowrates and residence times are presented in Table 3 below.

Table 3: Residence time, recycle ration, and flowrates of inlet and recycle streams in system for different particle sizes and AMD qualities

AMD Type	Size class and Particle Size (µm)	AMD flowrate (ℓ/Day)	Recycle flowrate (ℓ/Day)	Residence Time (Days)	Recycle Ratio
A	1 (8 µm < d< 13 µm)	1	24.48	1.69	24.48
A	2 (1.7 µm < d< 3.35 µm)	2.18	24.48	1.61	11.23
A	3 (d < 1 µm)	3.76	24.48	1.43	6.51
B	3 (d < 1 µm)	10.42	24.48	1.16	2.35

4.3.2 Continuously Stirred Tank Reactor

The PBR reactor was replaced with a CSTR during the operation of the laboratory scale system. This was done to increase the alkalinity of the BOFS eluate and thus increase the pH of the system. A dosing system was used whereby BOFS fines were added to the CSTR at intervals in order to maintain the pH in the settling tank at a certain level. This system was highly effective and increased the efficiency of the system by 3.76 (3.76 times more AMD could be treated to the same conditions using the CSTR than when using the PBR) and thus in terms of treatment capacity, the CSTR was more effective. This system, however, was more energy intensive as a dosing schedule needed to be determined and energy was used to constantly agitate or stir the system. Using fines which are suspended in fluid also did not allow for a complete dissolution reaction to occur and the sedimentation in the settling tank will contain a high concentration of partially dissolved BOFS particles. In order to minimize reagent loss in relation to this, it was proposed that a recycle stream may need to be added to the system, whereby the sludge which forms in the settling tank is used again as an alkalinity source due to its content of unreacted BOFS. This is similar to a high-density sludge (HDS) system which is discussed in Chapter 7, Section 7.3.3.

4.3.3 Summary (Reactor Type)

Due to the increased energy demands and impracticality of agitation at a large scale, the PBR design was used for the pilot scale set-up. The volume of the tank (in relation to the rest of the plant) was increased, as well as the amount of BOFS in the vessel. This was done to combat the initial issues experienced with the PBR in the laboratory scale system.

4.4 PARTICLE SIZE

BOFS is available in a variety of different particle sizes from different steel manufacturing sites. The typical size distribution found at the Phoenix Slag Services site is shown in Table 4 and all particle sizes cost the same (R146 per ton (Vermeulen & Phoenix Slag Services, 2018)). Different size classes (mentioned above and shown in Table 3) were tested in the BOFS reactor in order to ascertain which particle sizes were best suited to treat AMD. When the recycle rate was kept constant, it was found that a smaller particle size coupled with agitation allowed for better performance in the system in terms of lower residence times – this is shown in Table 3.

Due to the distribution of the BOFS found at the Phoenix site, as well as the impracticality of using a constantly agitated vessel for large volumes, an assortment of large and fine particle sizes was initially used for the pilot scale design. It was deemed necessary to use particles with a diameter of 13.2 mm and below as this was the size class that Phoenix Slag Services indicated they would be most likely to supply on a continued basis. Particles with a diameter of below 13.2 mm were thus used and further divided into 3 classes (1, 2 and 3 representing the larger, medium and smaller particles in this range). Particles were divided into further groups as these size classes each have different uses as aggregates.

Table 4: Particle size distribution of BOFS from Phoenix Slag Services

Size Group	Diameter (mm)	Mass (g)	% Distribution
1	37.5 < d	0	0
2	26.5 < d < 37.5	0	0
3	19 < d < 26.5	0	0
4	13.2 < d < 19	470.5	25.8
5	4.75 < d < 13.2	999.2	54.9
6	2 < d <4.75	316.6	17.3
7	0.425 < d < 2	28.5	1.6
8	0.075 < d < 0.425	2.5	0.1
9	d < 0.075	2.3	0.1

The residence time calculations took into account the recycle stream flowrate. The particle size classes 1, 2 and 3 that were used in the study, correspond to size groups 5, 6 and 7 + 8 + 9 from the original distribution, respectively.

4.5 pH DEPENDENCY

The pH in the system was of vital importance to the extent of treatment achieved in each vessel. As discussed briefly before (in Chapter 3), the pH in the settling tank determined the amount of metals and sulfates which are removed, the pH in the biological reactor determined the functioning of the SRB and the pH of the slag eluate determined the recycle ratio and rate of the treated water going back into the system. For this reason, determining an ideal pH level was essential.

The metal species contained within the AMD precipitated out of solution at different pHs. The calcium which entered the system via dissolution of the slag was also able to precipitate out of solution due to the availability of excess sulfate which acted as a counterion at certain pHs. This is shown in Figure 6.

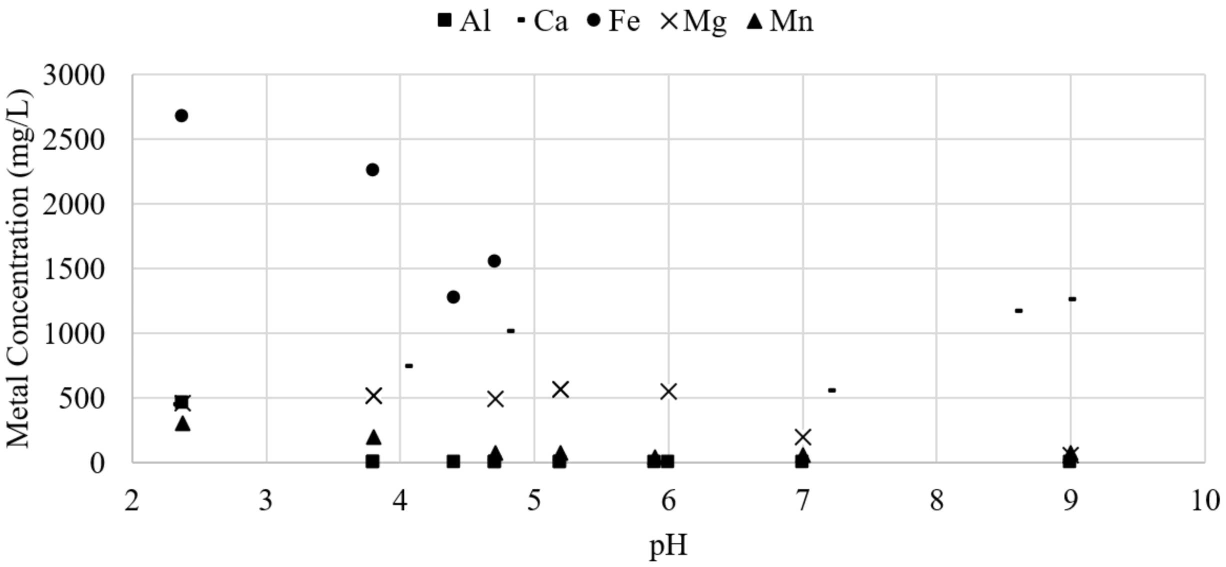

Figure 6: Dissolved metal concentration in AMD solutions at different pH levels when pH is altered using BOFS fines

As depicted, the ideal pH for removal of all prominent dissolved metals in AMD occurs at a pH of 7. During the first stage of the biological process however, organic acids are released into the system from the bagasse which lowers the pH slightly. Because of this, it was initially theorized that a set level of 9 should be achieved in the settling tank. This was tested and deemed too energy intensive (due to the high recycle rate) to be feasible. A pH of 7 was therefore chosen for subsequent experiments. This pH was able to be maintained, however it was found that a higher degree of metals and sulfate could be removed in the biological reactor if a higher concentration of metals were available to bond with the sulfidic components produced as a result of DSR. Thus, a pH of 5 was chosen as the setpoint in the settling tank for the design of the pilot plant. This would have the added benefit of lowering the recycle rate – effectively increasing the amount of water treated and decreasing the energy consumption of the plant. The pH dependency is linked closely to the process control philosophy and mechanism. This is discussed in detail in Chapter 5.

4.6 VARIATION IN FEED QUALITY

During operation of the laboratory scale system, two different types of AMD were tested. The composition and characteristics of which are shown in Table 2. The two different AMD sources had similar pH levels but different metal and sulfate concentrations. Behaviour of the system when treating the two AMD's were different, but the same (or very similar) conditions were able to be maintained in each case. The treatment efficiency of Type B AMD was approximately 2.77 times better than the treatment efficiency of Type A AMD (2.77 times more AMD was able to be treated using a constant recycle flowrate of 24 ℓ/day). This indicated that the design of the system and the process control was versatile and could potentially be implemented at different sites with different AMD qualities.

4.7 SUMMARY/SUMMATION OF TREATMENT

As mentioned, different types of AMD were tested in the laboratory scale configuration (the characteristics and composition of these AMDs are given in Table 2) as well as different particle sizes (size 1, 2 and 3 as shown in Table 3). The main/overall results of the conceptualized design testing these different variables over the experimental period were favourable, with removal of most metals and sulfates occurring to levels of over 90%. The total removal of the prominent metals and sulfate from the system when different particle sizes and different AMD qualities is shown in Figure 7. Relative standard deviation (RSD), mean and number of repetitions (sampling times) are shown in Table 5. As depicted, all metals and sulfates (with the exception of Mg and Ca) were found to have an average of > 90% removal for all configurations of particle size and AMD type. Ca increased in concentration for all configurations which is attributed to the continuous influx of Ca into the system from the dissolution of the calcium oxide in the BOFS (discussed in Chapter 6). A value of 2.61 mg/ℓ of COD was found in the primary bioreactor before testing – giving a COD measurement of 12.56 mg COD/kg of bagasse. Bagasse was not replaced during the 106 day period and thus (according to the COD to sulfate ratio of 0.7) the sulfate removed in this reaction could not be attributed solely to biological sulfate reduction. It was determined that some reduction did occur – due to the presence of sulfide components – however further precipitation of sulfates could also have occurred in the bioreactors, as well as adsorption.

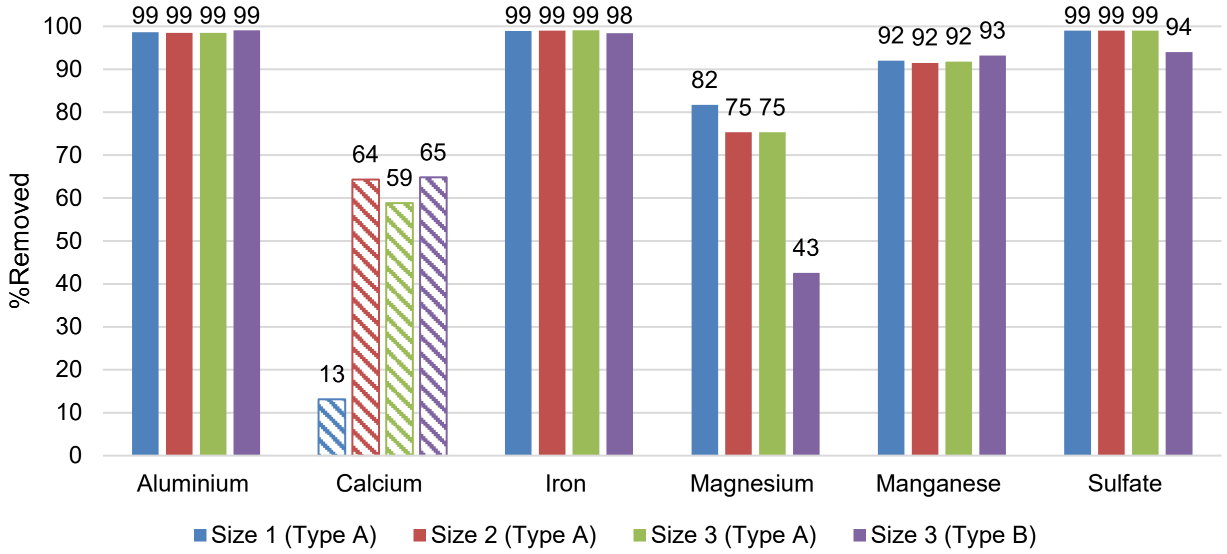

Figure 7: Percentage of (i) removal of total Al, Fe, Mg, Mn and sulfate in the laboratory scale system when different particle sizes and AMD qualities are used, and (ii) addition of Ca to the treated water due to BOFS dissolution (data prepared using averages for the 106-day period)

Mg removal was also not as high as the other metals, due firstly to the dissolution of magnesium oxides in the BOFS and also due to the pH in the system not being high enough to facilitate complete precipitation. The operation of the system was considered a success with the data being obtained giving valuable information regarding necessary changes that would have to be made in the large-scale design. RSD values show that the outlet conditions were not constant during the operation of the plant.

In the biological vessels, sulfate removal occurred at a lower rate than the settling vessel, accounting for less than 2% of overall sulfate removal. Sulfate removal in the biological vessels could have been achieved via sulfate reduction, sulfate precipitation, sulfide precipitation as well as adsorption of sulfate or sulfide to the surface of the organic carbon source.

Table 5: Standard deviations and repetitions for outlet conditions from laboratory scale plant operation

Size 1/Type A				Size 2/Type A			
Metal/ Component	**Mean (mg/ ℓ)**	**Repetitions**	**RSD**	**Metal/ Component**	**Mean (mg/ ℓ)**	**Repetitions**	**RSD**
Aluminium	6.08	24	0.28	**Aluminium**	6.72	10	0.06
Calcium	121.75	24	0.33	**Calcium**	182.09	10	0.04
Iron	31.31	24	0.66	**Iron**	29.95	10	0.52
Magnesium	18.89	24	1.07	**Magnesium**	26.11	10	0.49
Manganese	6.92	24	0.42	**Manganese**	7.52	10	0.31
Sulfate	168.53	24	0.52	**Sulfate**	157.13	10	0.40
Sulfide	3.77	3	0.47	**Sulfide**	7.24	10	0.55
Vanadium	0.05	8	0.20	**Vanadium**	0.05	10	0.00
pH	7.42	24	0.09	**pH**	7.10	10	0.07
Size 3/Type A				**Size 3/Type B**			
Metal/ Component	**Mean (mg/ ℓ)**	**Repetitions**	**RSD**	**Metal/ Component**	**Mean (mg/ ℓ)**	**Repetitions**	**RSD**
Aluminium	6.63	8	0.03	**Aluminium**	4.44	12	0.14
Calcium	176.64	8	0.06	**Calcium**	288.93	12	0.10
Iron	27.42	8	0.24	**Iron**	57.53	12	0.50
Magnesium	26.11	8	0.49	**Magnesium**	53.98	12	0.19
Manganese	26.28	8	0.16	**Manganese**	13.34	12	0.25
Sulfate	130.32	8	0.10	**Sulfate**	287.77	12	0.13
Sulfide	7.18	8	0.26	**Sulfide**	1.26	3	3.83
[redacted]	[redacted]	[redacted]	[redacted]	**Vanadium**	0.05	12	0.20
pH	7.09	8	0.03	**pH**	6.92	12	0.22

A 35%, 29%, 35% and 16% sulfate removal was achieved across DSR vessel 1 for size 1 (8,000 µm <d< 13,000 µm), size 2 (1,700 µm <d< 3,350 µm), size 3 (d< 1,000 µm) particle size and Type B AMD respectively. DSR vessel 2 had a lower sulfate removal percentage than DSR vessel 1. Sulfide was detected in the biological vessels over the 106-day period which confirmed the occurrence of sulfate reduction. The lower overall sulfate removal for Type B AMD was attributed to a change in conditions – SRB may need to acclimatize to the new conditions over a period of time before maximum sulfate reduction can occur.

CHAPTER 5: PILOT SCALE PLANT

5.1 INTRODUCTION

After operation of the laboratory scale work, the initial design was modified and used in the construction of a pilot plant at a coal dump site in Witbank, Mpumalanga. This section discusses the operation of the plant at the site with regards to technical issues that were experienced, data obtained and any findings or observations that were made which have contributed to the design of the 10 000 ℓ/day plant. This work was also used as the basis of a conference paper (Tamlyn S. Naidu, Sheridan, Van Dyk & Higginson, 2019). The design used is shown in Figure 4 in Chapter 3.

5.2 METHODOLOGY

Data obtained from the laboratory scale operation allowed changes to be made to the design where necessary. Vessel sizes were increased to allow for larger areas for settling and the availability of more carbon for the SRB in the biological reactor. The full design methodology and sizing for the pilot scale plant can be found in Appendix A. The biological reactors used in the pilot scale were each inoculated with 100 ℓ of inoculum before operation commenced. This inoculum was cultivated in 25 ℓ vessels using the same methodology as described in Section 4.2.

5.2.1 Construction and Commissioning

The system was constructed using 2200 L chemical and heat resistant plastic (linear low density polyethylene (LLDP)) vessels as the reactors and JoJo tanks for the water reservoir and H_2S Scrubber. Construction took place over a 4-month period from January 2018 to April 2018. The system was tested with water at the Phoenix Slag Services site in Wadevile before being transferred to the site in March. Once the equipment had been transported and connected at the site, clean water was needed in order to provide a sufficient volume of water (of the right composition) to be used as the recycle stream. AMD could not be used as this would result in possible fouling of the BOFS and poisoning of the SRB in the biological reactors. Clean water was not available at site and process water had to be used instead. This water had a pH of 3 and was contaminated by various metals and sulfate which caused thick layers of precipitation over the BOFS that prevented the dissolution of the slag and the raise in the pH of the system. This delayed the optimal performance of the plant for a period of time. The plant operated for a total of 196 days.

5.2.2 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 6.

Table 6: 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 onwards	0	2400	5.4

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

5.3 EXTENT OF REMEDIATION

The inlet quality of the AMD changed continuously but had an average concentration and pH as shown in Table 7. The change in inlet concentration may have contributed to the variation in treatment extent over the remediation period. 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 the subsequent dissociation that results in the release of hydroxide units. The fluctuation in pH and metals across the system over time (as shown in Figure 8 and Figure 9) is attributed to the varying amount of oxide containing BOFS particles that come into contact (and are able to react) with the AMD.

Table 7: Average composition and pH of AMD in storage dams

Component	Concentration (mg/ℓ)	RSD
Al	177.4	0.59
Ca	237.4	0.56
Fe	4320.1	0.07
Mn	331.3	0.42
Mg	412.5	0.25
SO_4^{2-}	16301	0.07
V	0.07	0.1
pH	2.6	0.07

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.

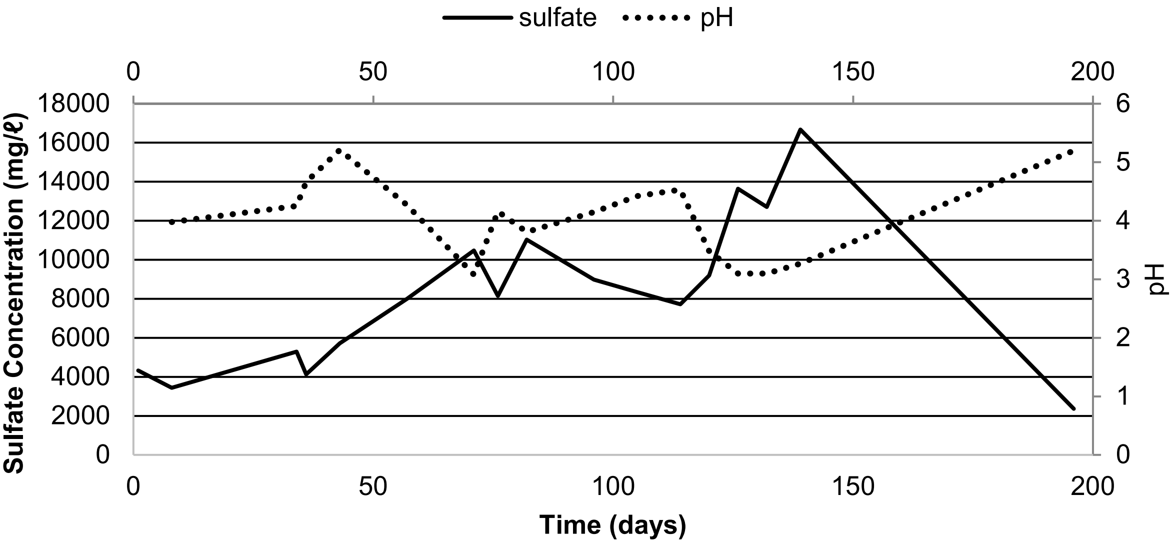

Figure 8: pH and sulfate concentration of the treated water from the pilot scale plant over the 196-day period (samples taken from TK-101-treated water reservoir)

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.

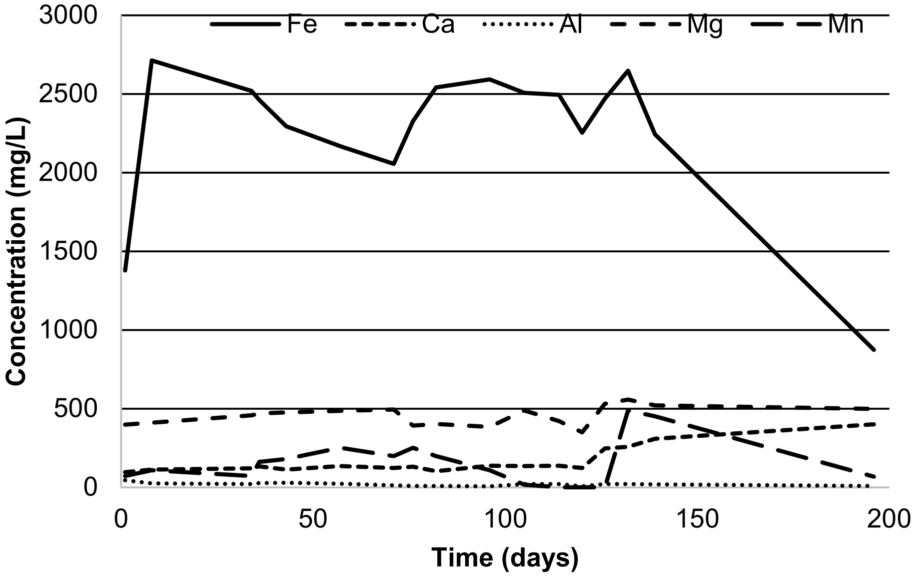

Figure 9: Metal concentrations in the water reservoir (TK-101) over the 196-day period

Effects of precipitation were 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 Figures 8 and 9). 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 sulfates and metals, and pH levels between 4 and 7 allow for optimum SRB activity. The extent of treatment in each vessel at the end of the 196-day period is shown in Table 8 in terms of % removal of each component (based on the initial and last reading). Bold indicates an increase in concentration.

Table 8: Extent of remediation across each process vessel (%removal of components) where bold text indicates an increase in concentration and plain text indicates a decrease

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 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 of operation time (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 increased 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).

5.4 TECHNICAL AND SITE ISSUES

Multiple site related issues affected the functioning of the pilot plant. These included the lack of continuous power, lack of clean water and lack of security. Multiple thefts at the site resulted in the aeration of the system (when vessel covers were stolen) and eventually in the collapse of the reactors (when the reactor steel supports were stolen). Theft of power cables in October 2018 resulted in a complete ceasing of operation of the plant as the site management were unable to indicate when power would be restored after a period of 2 months.

These issues are summarised below:

- **Power outages**

  Start-up was aimed to take 21.5 days with the AMD pump pumping at 600 ℓ/day and the slag recycle pump, pumping at between 2000 and 3000 ℓ/day. This was not achieved due to power outages at site, and this process took approximately 34 days. Power outages at the plant site occurred frequently and resulted in a complete shutdown of the pumps which disrupted the continuous flow of AMD feed and recycle in the system. These outages led to a delay in the pilot plant start-up period from 21.5 days to 34 days as the pumping rate of 600 ℓ/day AMD and the slag recycle of 2000 and 3000 ℓ/day was not continuously maintained. Theft of power cables eventually necessitated shut down of the plant as the mine indicated they could not commit to re-establishing power at the site.
- **Theft at site**

  Anaerobic conditions were aimed to be kept stable, however due to theft at site this was not possible for a period of 2 weeks. The vessel covers were stolen and this allowed aeration of the biological system for a two-week period which compromised the anaerobic nature of the bioreactors. To address the problem, the covers were replaced with clear cheap plastic sheeting; the mine was informed of the incident and security measures to protect equipment of a valuable nature were increased (motion detections sensors were provided by the mine and the pumps and process control system were secured in locked enclosures).
- **Poor mobile network connectivity**

  Access to site via remote control was aimed to be established from the onset of operation in order to continuously monitor the plant. This was established but was not constant due to data interruptions at site. The network connectivity at site was erratic and remote access to the system was not sustainable using a data connection. This limited plant monitoring, as problems which arose at site were only identified during the weekly visits. Data had to be collected weekly with monitoring and remote access and control occurring only sporadically.
- **No potable water on site.**

  The desired pH was envisioned to be reached after 4 days, however due to the slag armouring or coating, alkalinity accessibility was limited, and the desired pH was not achieved. The system was designed for start-up with 13 000 litres of clean water, however, due to the isolation of the site and lack of access to clean water, process water (with a pH of 3 and high sulfate and metal content) was delivered to site and was used instead. This led to a large amount of precipitation and armouring of the top layer of slag in the slag vessel which in turn led to poor release of the oxide compounds in the slag (which were responsible for the pH increase). This greatly limited the operation of the plant as oxide release was dampened in the system, preventing pH rise of the AMD entering the plant. This was rectified by removing the layer of precipitate that had formed and was preventing oxide release. The particle size of slag that was used was also not ideal for use in a packed reactor. The slag may have hindered the flow of liquid through the slag reactor. As a result, diffusion and dissolution of the alkalinity generating compounds of the slag in the liquid did not occur at fast-enough rates (similarly to what was found in the laboratory scale process). This limited the pH rise of the recycle stream and the sedimentation vessel. The hindrance of flow was due to cementing and compacting of the smaller particle sizes of slag (during the removal of the precipitation layer, hard, compacted layers of slag were found). Larger particle sizes were then added and were used to ensure more accessibility of the liquid to the slag and maintain better flow through the reactor.

The operation of the pilot plant indicated that the design was functional at larger scales and exhibited similar and comparable results to the ones obtained from the laboratory scale plant.

CHAPTER 6: COMPLEMENTARY DATA

6.1 INTRODUCTION

During the operation of the pilot scale plant, a number of laboratory scale experiments were undertaken to further investigate the mechanisms of sulfate removal, metal removal and pH rise in the system. It was also necessary to investigate the process control mechanism, as this played a large role in the effective functioning of both the small and large-scale plants. Findings from these complementary studies are discussed in this section. These findings have also been used to inform the 10 000 ℓ/day design. The results from these experiments were used to form the basis of a peer reviewed conference paper which has been published in the 2020 SAIMM Mine Tailings conference proceedings (Tamlyn S. Naidu, Chauhan, Xiong, Sheridan & van Dyk, 2020). A summary of the findings is presented below:

6.2 METHODOLOGY

6.2.1 Slag dissolution

Experimentation was done (on three size classes of slag: (i) class 1-2 mm to 3.35 mm in diameter; (ii) class 2-4.75 mm to 6.7 mm in diameter and (iii) class 3-6.7 mm to 9.5 mm in diameter) to further understand the dissolution kinetics of BOFS and to ascribe a suitable model to predict the extent of dissolution of BOFS in media of different pH levels or acidity/alkalinity measurements. Slag leaching tests were conducted to ascertain the mechanism of dissolution. Slag samples and leaching liquids (water, AMD and hydrochloric acid) were weighed and measured out such that the liquid to solid ratio remained constant at 10:1. Initially, 40 g of slag and 400 mℓ of liquid were used, thereafter, 80 g of slag and 800 mℓ of liquid were used. The liquid was placed into a 1000 mℓ beaker on a magnetic stirrer, at 200 rpm and room temperature, and the pH probe was inserted into the liquid. The pH of the liquid after slag was added, was monitored continuously. 1 mℓ of the leaching liquid was removed as aliquots at varying time intervals for AAS analysis and titration samples of 20 mℓ of the leaching liquid was removed at 20 seconds into the experiment and at the end once pH stability was attained. The leached slag was put into an oven for drying at 50°C. Experiments were replicated, and where necessary multiple experiments were run to ensure change in volume after sampling did not affect the experiment. Other experiments were run using the same methodology with different volumes and masses of BOFS and leaching liquid. Lagergren and shrinking core kinetic models were applied to the data obtained from these experiments. A comparison between lime and BOFS was also performed using data from literature.

6.2.2 Precipitate formation

Sludge formed in the various reactors was collected, acidified and assessed using the AAS procedure. This was done to determine what types of precipitates had formed. The BOFS particles from the slag dissolution reactions were also assessed using SEM and EDS. A review/literature-based study was conducted alongside these tests to determine the likely mechanism of precipitation.

6.3 MECHANISM OF pH INCREASE

6.3.1 Comparison of lime and BOFS

An important thing to note in the comparison between lime (quicklime or hydrated lime) and BOFS is the availability of free lime in the sample (components that are available to hydrate and raise the pH of the media). Lime and free lime generally refer to the CaO component of the sample, however BOFS contains multiple other units in oxide and silicate form that dissolve in liquid media and contribute to the neutralization or pH rise of the media. Table 9 shows an approximate availability of oxides (that can readily hydrate in liquid media) in lime and BOFS. Although the free lime content in BOFS is 13%, this only refers to the components found on the surface of the solid particle. As dissolution occurs (largely following Lagergren kinetics (Tamlyn S. Naidu et al., 2020)), more oxide components become available. The size of the BOFS particle used will also affect the amount of free oxide content – smaller particles have a larger availability of neutralizing/alkaline components than larger particles.

Table 9: Free oxide content in quicklime, hydrated lime and BOFS with particle aperture between 2000-3350 microns (determined via SEM and Energy dispersive X-ray analysis (EDA)) where Wollastonite found on the surface of the particle was not considered a free oxide (due to it's insolubility in water) *(Tolonen, Sarpola, Hu, Rämö & Lassi, 2014)*.

Alkaline material	Oxide content (Total %)	Free oxide content (%)
Quicklime	94	91
Hydrated lime	73	71
BOFS	87	13

Although the free oxide content of BOFS is significantly less than that of normal quicklime or hydrated lime, the BOFS still exhibited success in neutralizing AMD. 80g of slag was able to raise the pH of a sample of Type A AMD with an initial pH of 2.44 to (i) a pH of 7 in 540 minutes and (ii) a pH of 10 in 1365 minutes. This is shown in Figure 10. The experiment shown in Figure 10 was repeated multiple times and it was observed that the pH in the system did not stabilize, even after 72 hours of reaction time.

The pH rise was directly related to (i) the volume of AMD, (ii) the composition of AMD, (iii) the amount of BOFS, (iv) the particle size of the BOFS and the (v) allowed reaction time. For example, 15 g of slag fines (aperture of 1000 microns or less) was able to increase the pH of 1500 ml of Type B AMD (significantly lower initial sulfate and iron concentration) to a pH of 7 in 55 minutes, and similarly 67 g of fine BOFS was able to raise 200 ml of this Type B AMD to a pH of 7 in 5 minutes.

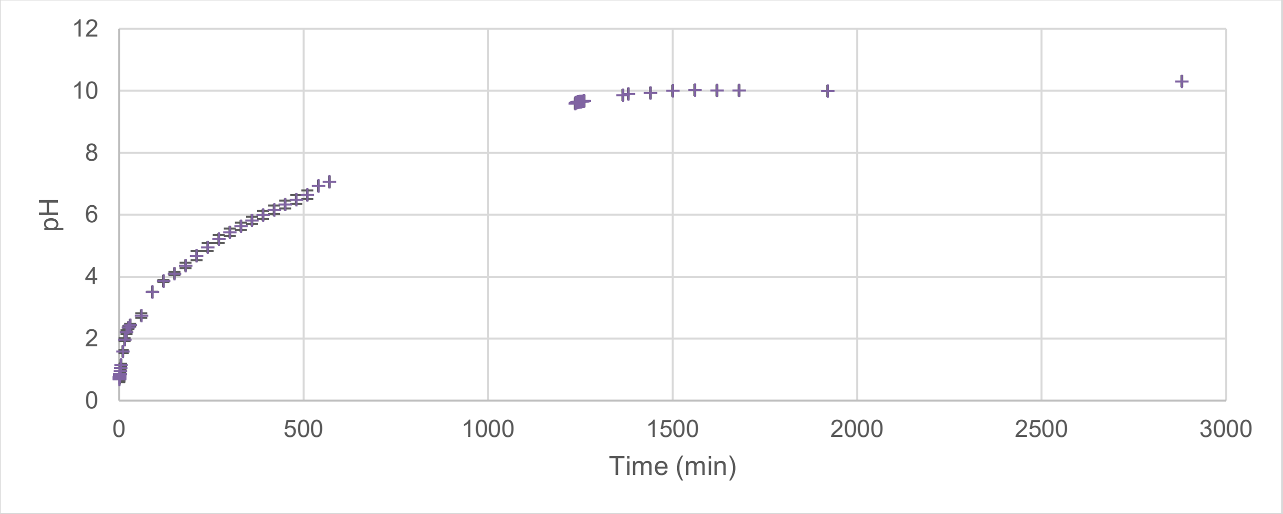

Figure 10: pH change over time in 800 ml of AMD in a constantly agitated reactor when 80 g of slag with particle aperture between 2000-3350 microns has been added.

The alkalinity addition corresponding to the last data point collected in the experiment shown in Figure 10, was 2897 units of alkalinity as $CaCO_3$ in mg/L.

The dissolution of BOFS in an acidic medium is the main mechanism of pH rise in the system, with the secondary/supporting mechanism being the hydrolysis of the sugarcane bagasse in the biological reactor.

Table 10: Oxide content of BOFS used in the experiment

Oxide	wt.%
CaO	41.6
Fe_2O_3	20.5
SiO_2	14.4
MgO	7.2
Al_2O_3	2.8
SO_3	0.4
Loss on ignition (LOI)	5

As shown in Table 8 (Chapter 5) and Figure 7 (Chapter 4), 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, magnesium and other metal oxides (Gomes et al., 2016). The BOFS obtained directly from Phoenix Slag services was assessed for oxide content and shown to contain 41.6 mass% CaO and 7.2 mass% MgO (shown in Table 10) (XRD was performed following the procedure found in Chapter 3 (section 3.6)). The main components of BOFS were Ca, Fe, Si, Al and Mg oxides and thus Ca and Mg concentrations were primarily used as an indication of dissolution extent, as Fe and Al formed precipitated at the pH levels that were reached in the solutions. The hydration, dissolution and dissociation reactions that bring about alkalinity from CaO and

MgO are described by Equations [6.1] to [6.4]. The iron oxide and aluminium oxide compounds also undergo dissociation similar to calcium and magnesium oxide. However, as mentioned, these components cannot be measured in the solution as they have already formed insoluble compounds and precipitated due to the pH levels that are reached in the system.

$$CaO + H_2O \leftrightarrow Ca(OH)_2 \qquad [6.1]$$

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^- \qquad [6.2]$$

$$MgO + H_2O \leftrightarrow Mg(OH)_2 \qquad [6.3]$$

$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^- \qquad [6.4]$$

The concentrations of H^+ ions (obtained from pH measurements in the media) over time were also used to study the dissolution kinetics (using equation [6.5]). $[H^+]$ was used as this was representative of the dissolution of all oxidic compounds in the slag, regardless of pH.

$$[\mathrm{H}^+] = 10^{-\mathrm{pH}} \qquad [6.5]$$

6.3.2 Chemisorption Behaviour

Equations [6.6] to [6.10] show the Lagergren pseudo-1st order, pseudo-2nd order models, and shrinking core diffusion through liquid film, diffusion through the ash layer and chemical reaction models that were applied and evaluated to the experimental data, respectively. It should be noted that (i) agitation was used in the batch experiments which reduced the liquid film layer diffusion limitations and (ii) BOFS dissolution is not limited to only the kinetic models tested in this report.

$$\ln\left(\frac{\mathrm{C_t - C_e}}{\mathrm{C_o - C_e}}\right) = -\mathrm{k_{1,obs}t} \qquad [6.6]$$

$$\frac{1}{\mathrm{C_o - C_e}} - \frac{1}{\mathrm{C_t - C_e}} = \mathrm{k_{2,obs}} \qquad [6.7]$$

$$\mathrm{k_f t = X} \qquad [6.8]$$

$$\mathrm{k_d t} = 1 - 3(1 - \mathrm{X})^{0.67} + 2(1 - \mathrm{X}) \qquad [6.9]$$

$$\mathrm{k_r t} = 1 - (1 - \mathrm{X})^{0.33} \qquad [6.10]$$

It was observed that the chemical reaction model did not apply to the water and the AMD dissolution cases. Diffusion through the ash layer was found to apply best to water for Ca (all size classes) and Mg (size class 3) release from the BOFS. $[H^+]$ kinetics were used to represent the experiment and a pseudo-1st order Lagergren model was seen to apply more often. The larger particle sizes underwent a lower rate of dissolution than the smaller particle sizes of BOFS. This can be seen in the pH data obtained over time for dissolution of different particle sizes shown in Figure 11.

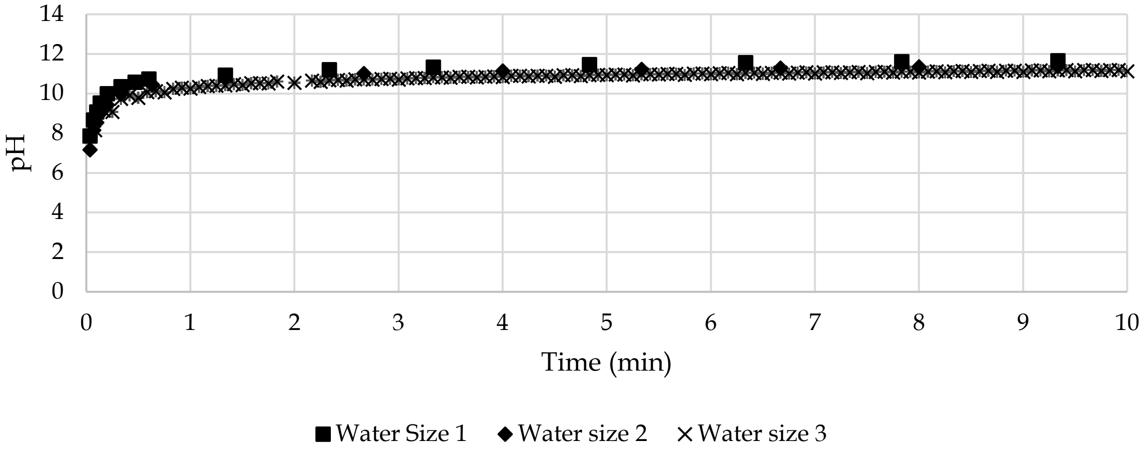

Figure 11: pH in water solutions during dissolution of BOFS of different particle sizes

6.3.3 Alkalinity

The alkalinity and acidity of water, HCl and AMD were measured before and after reaction with BOFS of size class 1 (diameter from 2 mm to 3,35 mm) using titration methods. The total alkalinity and acidity calculated is summarized in Figure 12.

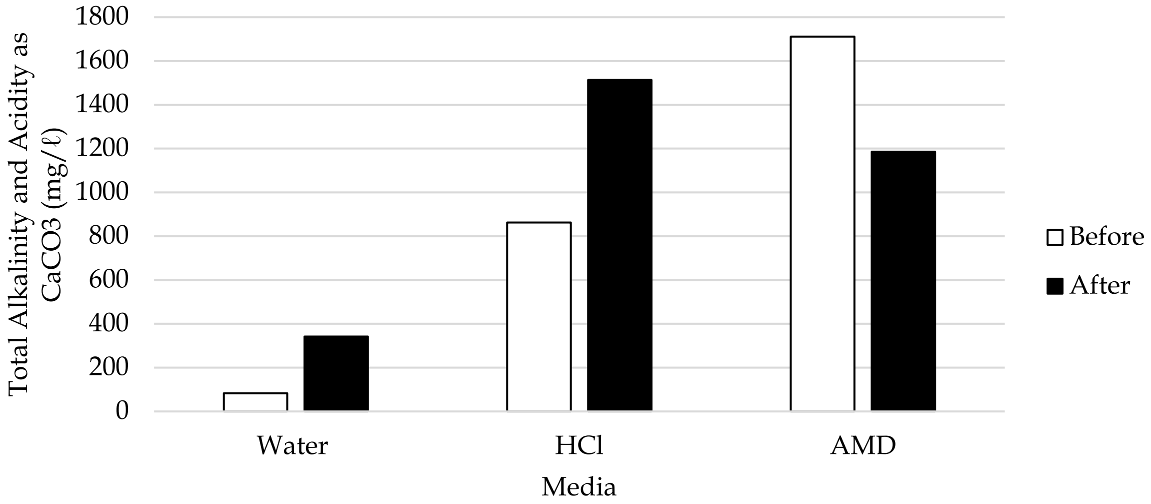

Figure 12: Total acidity in 800 mℓ of water, HCl and AMD solutions before reaction with 80 g of BOFS total alkalinity after as $CaCO_3$

As shown in Figure 12, the acidity in water before the BOFS reaction and the alkalinity after the BOFS reaction are much lower than the acidity and alkalinity of both acidic media. This indicates that more BOF dissolution occurs in acidic media than in neutral solutions. For application in AMD treatment, this potentially means that AMD should be reacted directly with the slag instead of using a recycle stream (as used in the laboratory and pilot-scale systems). Paradoxically, armouring of BOFS particles, which is due to precipitation of various compounds that form during neutralization reactions, prevents the direct contact between AMD and BOFS. This was observed during SEM testing.

6.3.4 BOFS Surface Morphology

The layer of precipitation that formed on the surface of the BOFS reactor is shown in Figure 13. SEM images of the particles before and after reaction with water, HCl and AMD were obtained and are shown in Figure 14. The slag leached by water and the untreated BOFS look similar, with slightly more porosity being seen in the water leached slag.

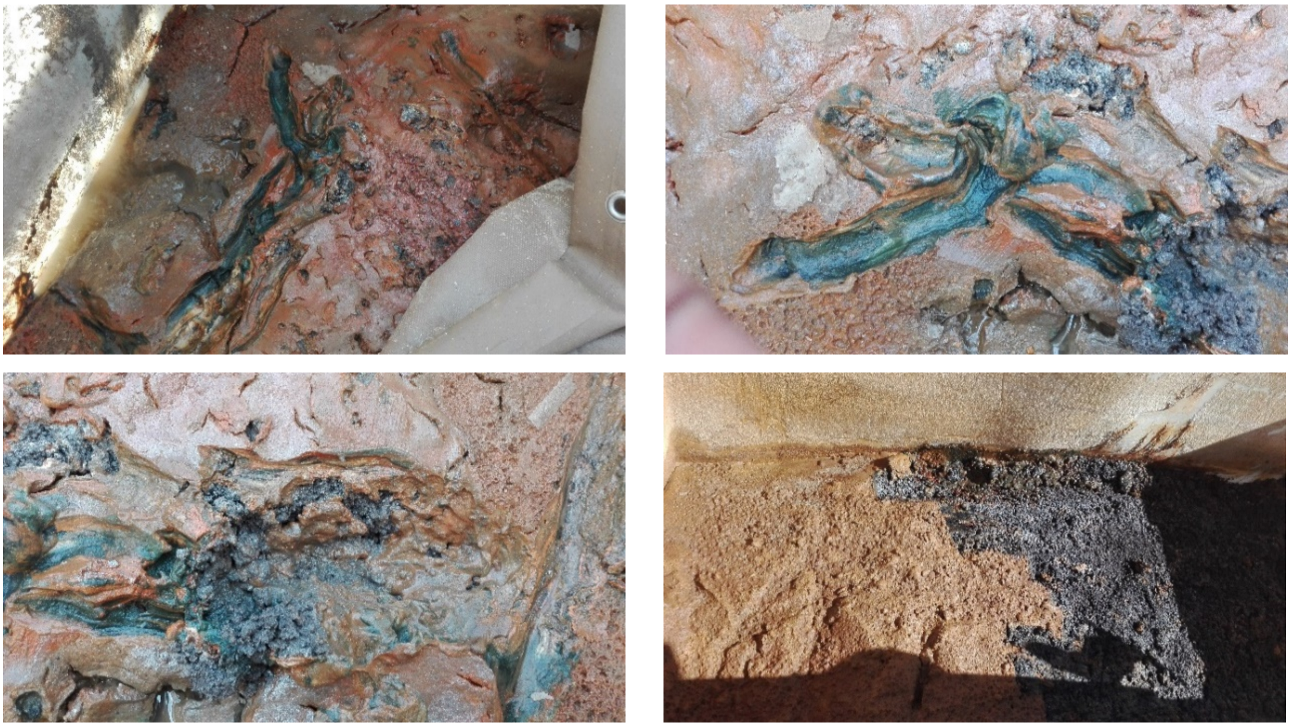

Figure 13: Precipitation layer on top of the BOFS in the BOFS reactor

The particles leached in HCl ((v) and (vi)) display more precipitation spots (shown by the lighter colour) and the AMD particle (iii) appears to be coated in a distinct layer identified as gypsum. It is evident that a coating of precipitates formed on the surface of the BOFS particles which were reacted with acidic media. This coating or armouring of the BOFS particles was observed in the continuous process and had a significant impact on the accessibility of the slag to react with the AMD. An agitated system could be used to prevent settling of the precipitate – in this case a recycle stream would be rendered null.

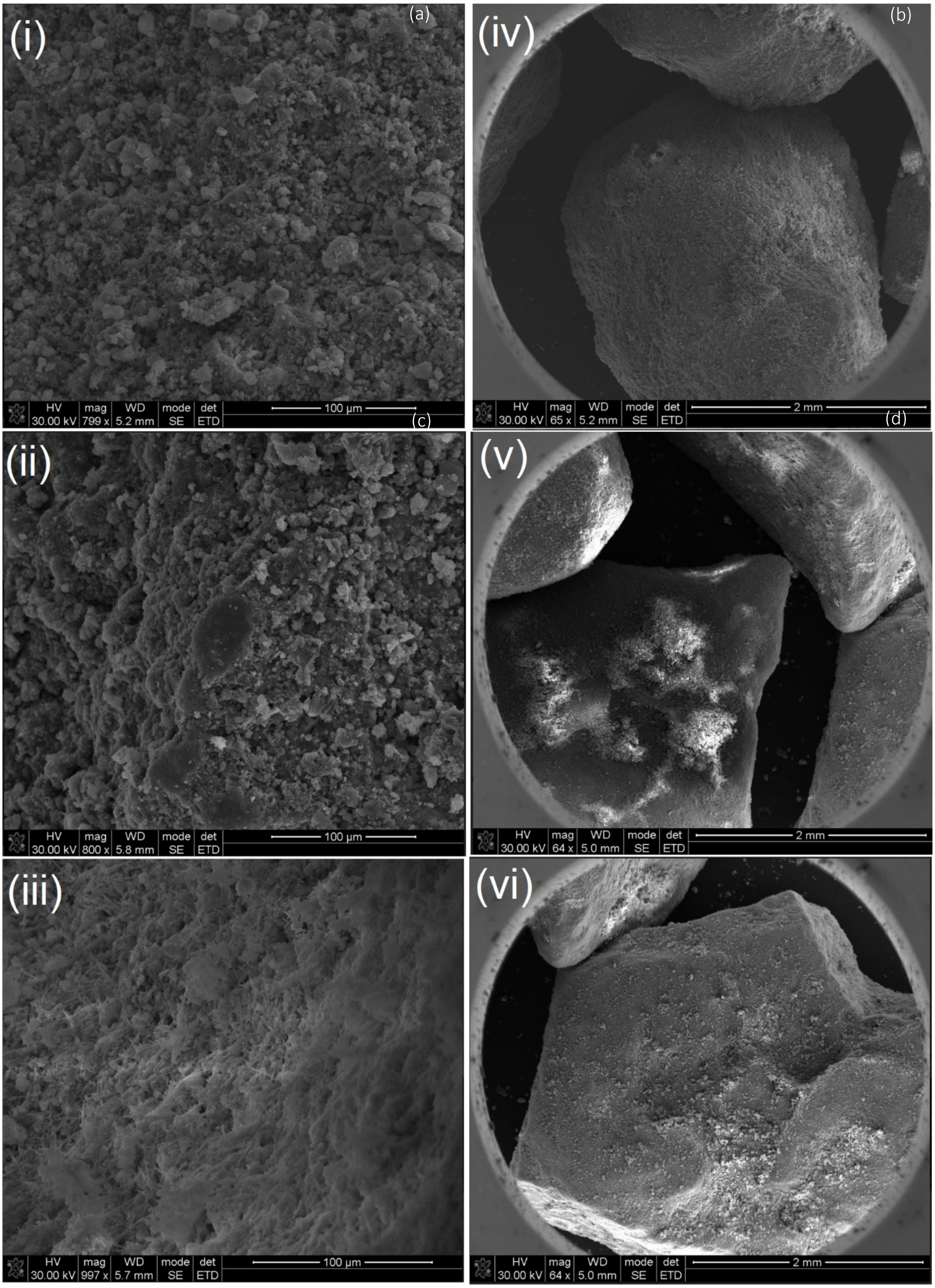

Figure 14: SEM images of (i) and (iv) unreacted BOFS; (ii) water leached BOFS; (iii) AMD leached BOFS; (v) and (vi) HCl leached BOFS

6.3.5 BOFS Dissolution in Pilot and Laboratory Scale Operation

During the operation of both the laboratory and pilot-scale plants, it was observed that the pH of the system was the variable that the concentrations of metals and sulfates were dependent on. The pH, in turn, was dependent on the rate of dissolution of the BOFS.

BOFS dissolution was thus deemed the limiting factor and efforts were made to increase it by (i) increasing the amount of BOFS used, (ii) decreasing the particle sizes used and (iii) changing the reactor type from packed bed reactor (PBR) to a continuously stirred or agitated reactor (CSR). Each of these changes yielded positive results in that the rate of dissolution increased and more AMD could be treated per unit time.

In the pilot-scale system, it was noted that the calcium concentration increased with pH – an indication that the dissolution of CaO contributed to the rise in pH. Other elements (Al, Fe and even Mg) could not be assessed, as all these elements formed insoluble compounds at the pH levels that were reached. The normalised (to 100%) removal or increase in concentration through leaching from the slag is shown in Figure 15.

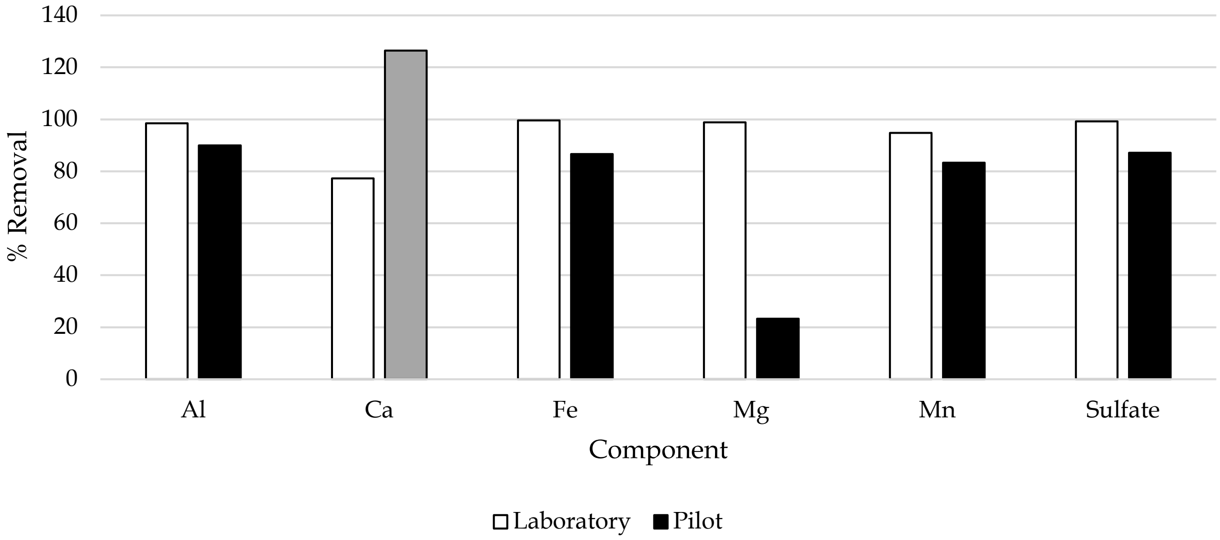

Figure 15: Removal (%) of Al, Ca, Fe, Mg, Mn and Sulfate across the laboratory and pilot-scale systems with Ca exhibiting an increase in the pilot-scale system (shown in grey)

As seen, the Ca concentration increased by 126% in the pilot-scale system yet decreased in the laboratory scale system. This was expected as the ratio of BOFS to AMD in the pilot scale system was much higher than that of the laboratory scale system. This ratio was changed to decrease the limiting reagent behaviour of the BOFS dissolution – the BOFS was present in excess in the pilot-scale plant whereas in the laboratory plant it was a limiting reagent. The Mg removal was also much lower in the pilot-scale and again this was due to the presence of excess BOFS as well as the low pH levels in the pilot-scale that did not cause Mg to form insoluble precipitates. Apart from the Ca and Mg, the pilot scale and laboratory processes functioned comparably.

According to the data obtained from the laboratory and pilot-scale systems, the treatment scheme designed to remediate AMD using BOFS and sugarcane bagasse were effective and a significant improvement in the quality of the polluted water, as well as a substantial dissolution of oxides into the solution from the BOFS, was found. BOFS was effective in raising the pH of the AMD, as well as the other media (HCl, water), to ranges between 10 and 12, however the increase in alkalinity of the media was dependent on the initial acidity of the solution – the pH rise occurred fastest in water, however, greater release of alkaline elements were achieved in more acidic media. The Lagergren kinetic model presented a more accurate fit of the data than the shrinking core model, with the pseudo-first-order model seeming to better apply to acidic media using $[H^+]$ decrease and the pseudo-second-order model found to apply better to a neutral solution. Assessing the dissolution of Mg and Ca oxides individually, showed converse results, with dissolution in acidic media fitting the pseudo-second-order model better and dissolution in neutral media fitting the pseudo-first-order model better.

Shrinking core model fits were achieved in certain cases, though more accuracy in model fitting can be achieved by factoring in other variables that influence kinetics (such as temperature and pressure). The kinetic rate constants were estimated from the batch tests done, however, pH dependency was not considered in this study. By using pH buffered solutions the primary mineral kinetics may be estimated with more accuracy (Windt et al., 2011). The higher dissolution rate being found in acidic media than in water can be seen in Figure 16, where the concentration of Ca and Mg ions in solution are much higher in AMD than in water after being reacted with BOFS at the same conditions for the same period of time.

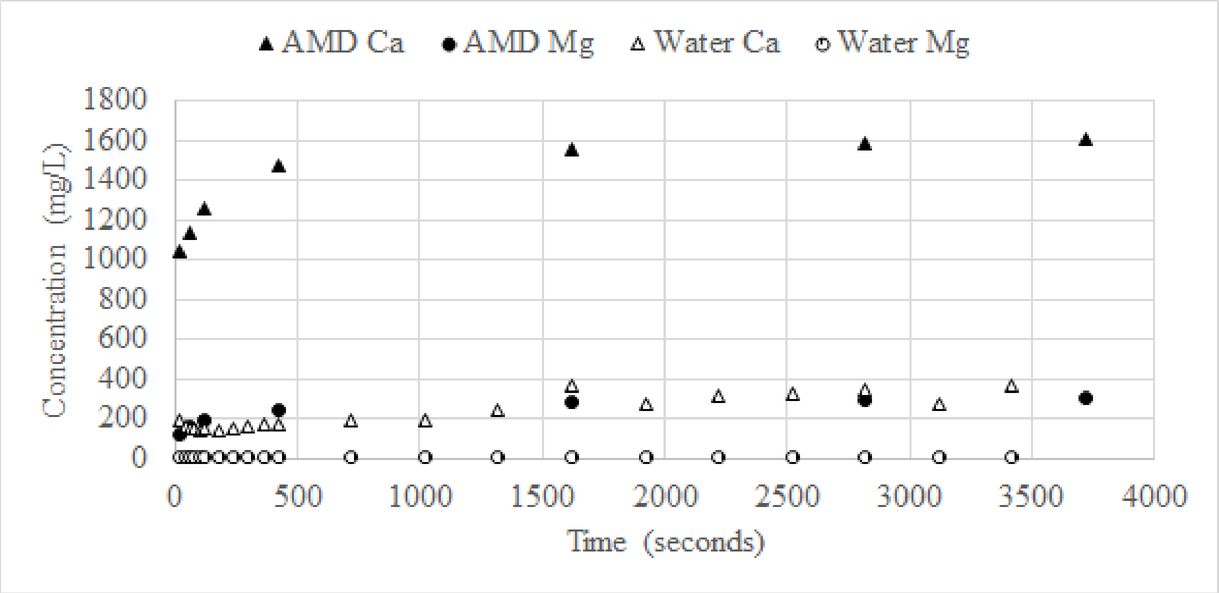

Figure 16: Concentrations of Mg and Ca ions in water and AMD solutions that are reacted with slag fines in a CSTR

This corresponds to the findings from alkalinity measurements taken in water, AMD and HCl media after reaction with BOFS for a period of time (Figure 12). The pH in each of the systems were different (the pH in the water system was the highest, followed by HCl and then AMD) after the same reaction time with the same mass of BOFS and the alkalinity readings indicate that although a lower pH is recorded in the acidic media, the solutions have a higher alkalinity than that of water. This explains the large amount of water (recycle stream) that is needed to neutralize the AMD. These observations support and explain the findings from the laboratory scale set-up which indicated that a lower recycle rate was maintained when fine particles of BOFS were stirred into the AMD. It indicates that dosing may be a less energy intensive option to using large particle sizes and a recycle stream.

6.4 MECHANISM OF SULFATE AND METAL REMOVAL

Sulfate and metals were removed from the system via precipitation reactions followed by sedimentation that occurs under the action of gravity. Due to the relatively low concentrations of sulfide that were found in the biological reactors (shown in Chapter 4) as well as the high flowrates through the plant (low residence times), SRB functioning likely did not solely account for the sulfate removal over the biological reactors. The main sulfate removal mechanism was through precipitation via pH rise and this may have continued through the biological reactors. The precipitation reactions that could have occurred are discussed below.

6.4.1 Aluminium

The initial concentration of aluminium in the AMD (Type A) was 434 mg/L. Aluminium in acidic media most commonly forms an aqueous cation, with an oxidation number of +3 (Harding, Johnson & Janes, 2002). Addition of an alkaline material (which will hydrate and dissociate to form hydroxide units) to the solution, will first precipitate an insoluble aluminium hydroxide (by Equation 4):

$$Al^{3+}(aq) + 3OH^{-}(aq) = Al(OH)_3(s) \qquad [6.11]$$

This was considered the main mechanism of aluminium removal in the system. It is important to note that both aluminium oxide and hydroxide species are amphoteric in nature. In acidic solutions, they will dissolve and assist with neutralizing the acid (by Equation 5):

$$Al(OH)_3(s) + 3H^{+}(aq) = Al^{3+}(aq) + 3H_2O(l) \qquad [6.12]$$

Excess hydroxide units in the solution could also cause the aluminium hydroxide to form a tetrahydroxyaluminium ion via Equation 6:

$$Al(OH)_3(s) + OH^{-}(aq) = [Al(OH)_4]^{-}(aq) \qquad [6.13]$$

Aluminium sulfate or sulfide could also potentially form as there is an excess of sulfate ions in the AMD. However, aluminium sulfate has a very high K_{sp} (69.2) which means it will not precipitate. Similarly, aluminium sulfide, also with a very high K_{sp} is rapidly hydrolysed in an aqueous solution to form aluminium hydroxide and hydrogen sulfide gas – thus it is unlikely that removal of aluminium occurred in this manner. Aluminium was removed from the solution almost completely (to a concentration of 10.7 mg/L) at a pH of 3.8 and redissolution did not occur even at a pH level of 9.

6.4.2 Calcium and Magnesium

Calcium and magnesium were present in the AMD at a concentration of 110 mg/L and 115 mg/L respectively. Calcium (as well as magnesium) was also added to the solution through the dissolution (hydration and dissociation) of the BOFS. Calcium and magnesium in aqueous solutions are found in the form of a positive cation with an oxidation number of 2+. Both calcium oxide and calcium hydroxide have an intermediate solubility in water and calcium will not precipitate out of solution as either of these species. Calcium sulfate has a higher Ksp than calcium hydroxide (experimentally exhibiting a solubility of 0.274% w/w compared to calcium hydroxide which exhibited a solubility of 0.12% w/w in water at 20°C (Royal Society of Chemistry, 2020)), however due to the saturation of the solution with sulfates (initial Type A AMD concentration of 12955 mg/L) and the reaction of the hydroxyl group with multiple other elements – the bulk of the calcium removal is achieved via gypsum precipitation. Despite the precipitation of calcium sulfate, the calcium concentration increased in the system with increasing pH.

When the BOFS comes into contact with liquid, hydration will take place and calcium hydroxide will form. If this hydrated BOFS is then exposed to air, carbon dioxide will react with this to form calcium carbonate (by Equation 7) which has a low solubility in water:

$$Ca(OH)_2\ (aq) + CO_2\ (g) = CaCO_3\ (s) + H_2O\ (l) \qquad [6.14]$$

The pH raising capacity of the BOFS in neutral solutions will thus be lowered if this occurs, however further reaction with an acidic media can result in the formation of carbon dioxide and water (Equation 8):

$$CaCO_3\ (s) + 2H^+\ (aq) = Ca^{2+}\ (aq) + CO_2\ (g) + H_2O\ (l) \qquad [6.15]$$

It is thus recommended to keep the BOFS dry before use as a reagent, and once it is in use keep the particles submerged. Magnesium is most likely removed from the solution in the form of magnesium sulfate (which has a solubility of 33.7% w/w in water) and magnesium hydroxide (which is soluble in acidic solutions but less so in basic solutions (Royal Society of Chemistry, 2020)). Magnesium decreased in solution at a pH of 9 (to a concentration of 61.7 mg/L).

6.4.3 Iron

Under acidic conditions, the most stable oxidation state of iron is 2+. If the AMD is aerated then the redox potential of the water is such that it allows for oxidation of the ferrous iron (2+) contained in the solution to ferric iron (3+) which can then precipitate as iron hydroxide, $Fe(OH)_3$ via reactions described by equations 9 and 10 (Silver, 2012).

$$4Fe^{2+} (aq) + 3O_2 (g) + 2H^+(aq) = 2Fe^{3+} (aq) + H_2O (l) \quad [6.16]$$

$$Fe^{3+} (aq) + 3OH^- (aq) = 2Fe(OH)_3 (s) \quad [6.17]$$

Fe^{3+} has a low solubility at certain pH levels and generally precipitates out of solution. In the case that the system is anaerobic and if excess CO_3^{2-} is available in the solution (as may be the case if BOFS is hydrated and then exposed to air) the $Fe(HCO_3)_2$ salt is formed. Upon exposure to air this leads to the formation of FeCO3 and then to iron (III) oxide. During experiments, iron was almost completely removed at a pH of 7 (from an initial concentration of 3039 mg/L to 0.289 mg/L).

6.4.4 Manganese

Under acidic conditions, the most stable oxidation state of manganese is 2+. In this reduced (Mn^{2+}) state, manganese is moderately soluble in the form of $MnSO_4$ and thus very little Mn removal is attributed to $MnSO_4$ formation and precipitation. At pH levels of 8 and above, manganese can precipitate as $MnCO_3$ and $Mn(OH)_2$. In aerated systems (under oxidizing conditions), Mn in the 3+ and 4+ can also form MnO_2, Mn_2O_3 and Mn_3O_4 even at lower pH levels – compounds which are all insoluble in water. It should be noted that is iron (II) is present in solution manganese will not precipitate at neutral conditions. Manganese in the system decreased from 88 mg/L to 52 mg/L at a pH level between 6 and 9. It should be noted that initially manganese increased in the system – this could be attributed to dissolution of manganese containing compounds in the BOFS (XRF analysis shows MN makes up 3% by weight of BOFS).

6.4.5 Sulfate

Sulfate in the system is likely to form any of the compounds found in Table 11 below. The most likely way that sulfate is removed is via the precipitation of calcium sulfate.

Table 11: Solubility of sulfate compounds % weight/weight in water at 25°C

Magnesium Sulfate	33.7
Manganese (II) Sulfate	62.9
Iron (II) Sulfate	26.3
Calcium Sulfate	0.274
Iron (III) Sulfate	Slightly soluble
Aluminium Sulfate	36.4

The counterions which form part of the sulfate compounds which are presented in Table 11 (predominantly Calcium and Magnesium) become abundantly available in the solution through the dissolution and leaching of the BOFS. Once present in solution they can then bind with the sulfate ion to form a nearly insoluble product. The solubility of each sulfate compound of note (compounds which have been identified in the sample) is shown in Table 11, however it is likely that a small percentage of sulfate is also removed via formation and settling of small amounts of other compounds. The sulfate in the system

6.4.6 Sediment/precipitate formed

An SEM was used on the precipitate which had formed on the surface of the BOFS particle. This precipitate is shown in Figure 17. An EDA was also performed on the sample.

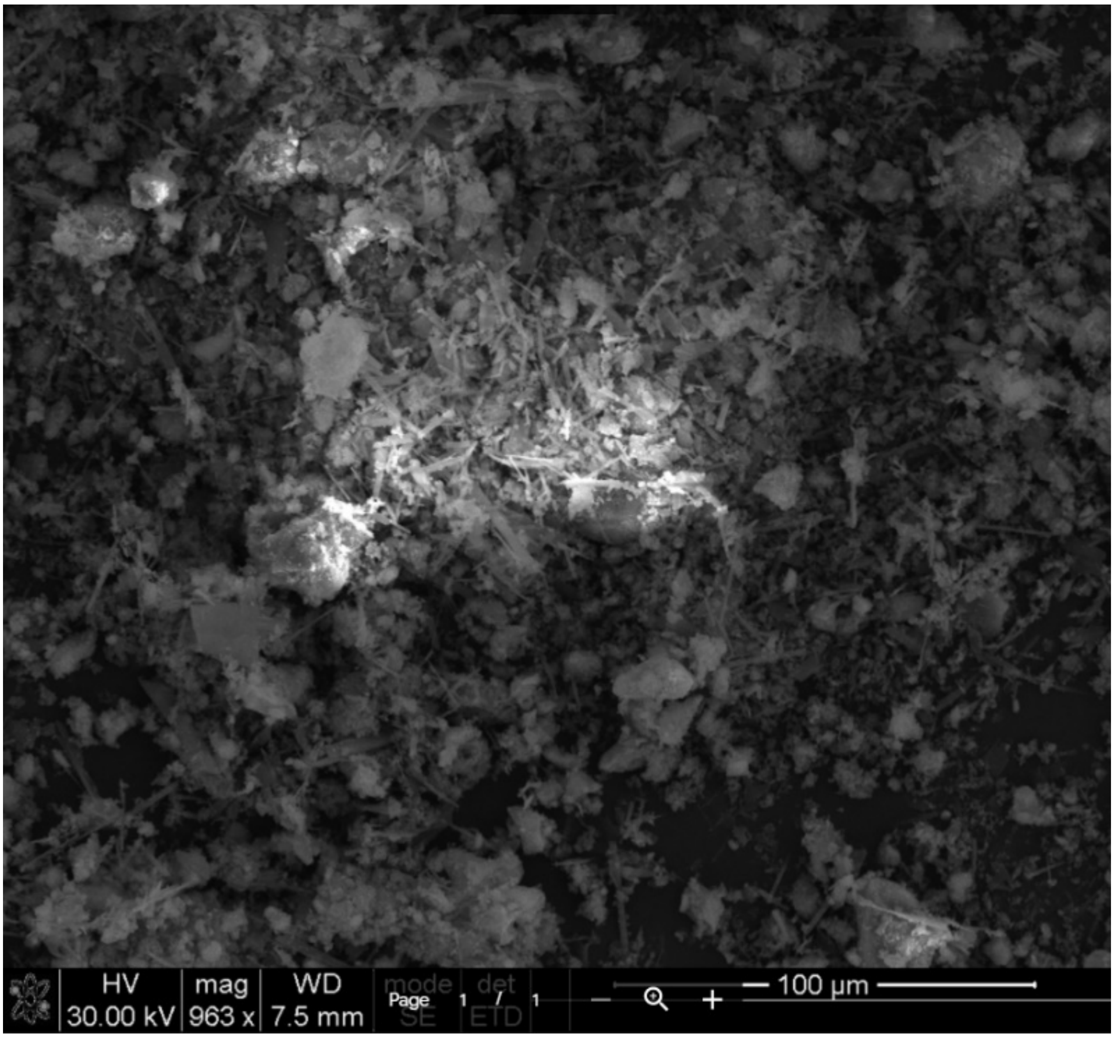

Figure 17: SEM of precipitate formed after reaction of BOFS and AMD for a period of 32 hours.

The results from the SEM and AAS run on the acidified precipitate, showed that aluminium, calcium, iron, magnesium, manganese and silicate had all precipitated. The SEM and EDA were able to identify oxides and silicates but not sulfates or hydroxides, however it is likely (given the chemistry of the AMD solution and the difference in initial concentration and pH and final concentration and pH) that the majority of precipitates formed were sulfates and hydroxides.

6.5 PROCESS CONTROL MECHANISM

Multiple process control configurations were tested on the system to ascertain which control mechanism best allowed the process to maintain a constant, desired pH. The diagrams (Figure 18 and 19) show the different configurations that were tested, where pHT denotes the position of the pH transmitter and pHC denotes the position of the pH controller.

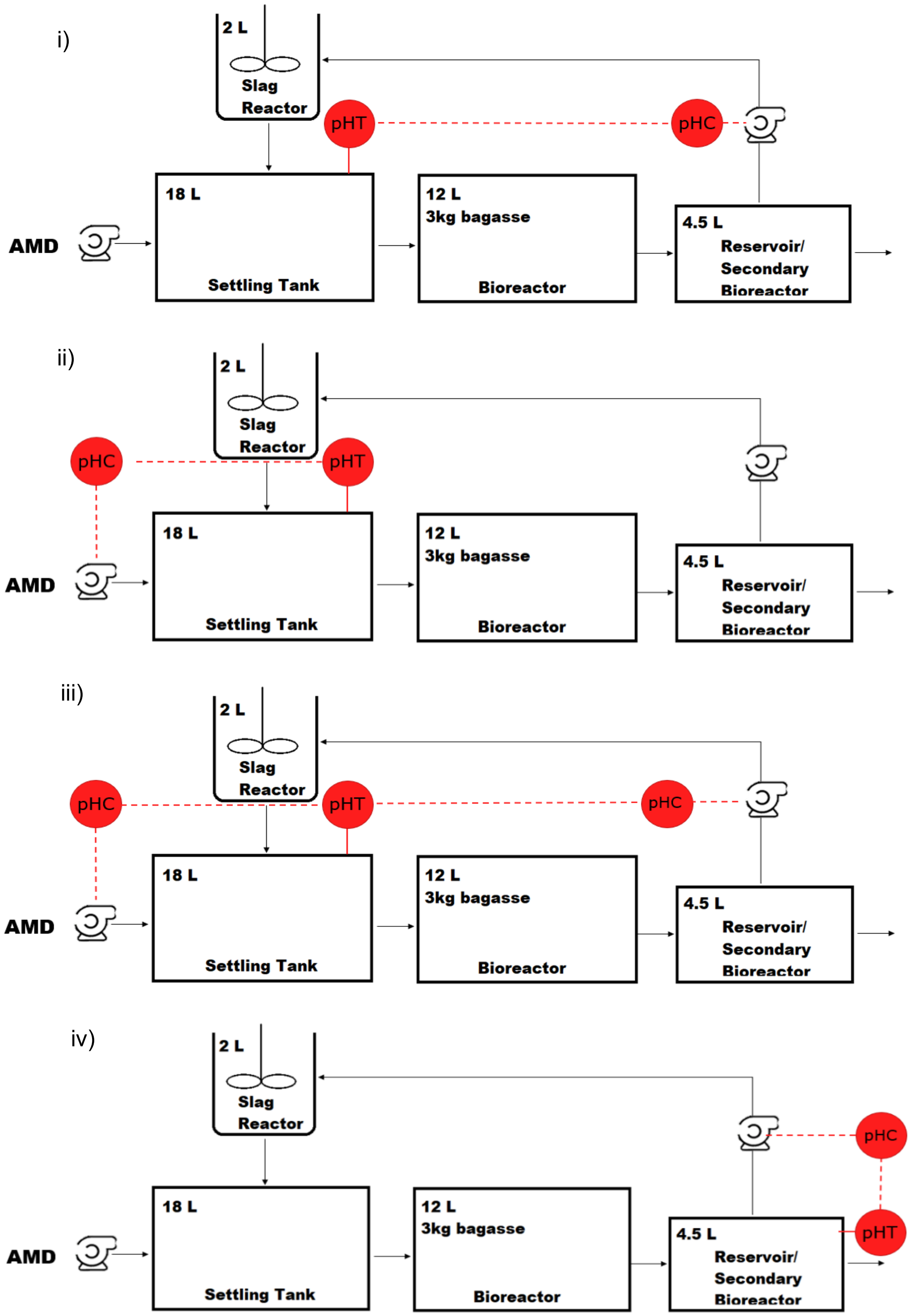

Figure 18: (i) Process control with recycle flowrate controlled using the pH in the settling tank; (ii) Process control with the AMD flowrate controlled using the pH in the settling tank; (iii) Process control with both the AMD and recycle flowrates being controlled using the pH in the settling tank; (iv) Process control with recycle flowrate controlled using the pH in the secondary bioreactor

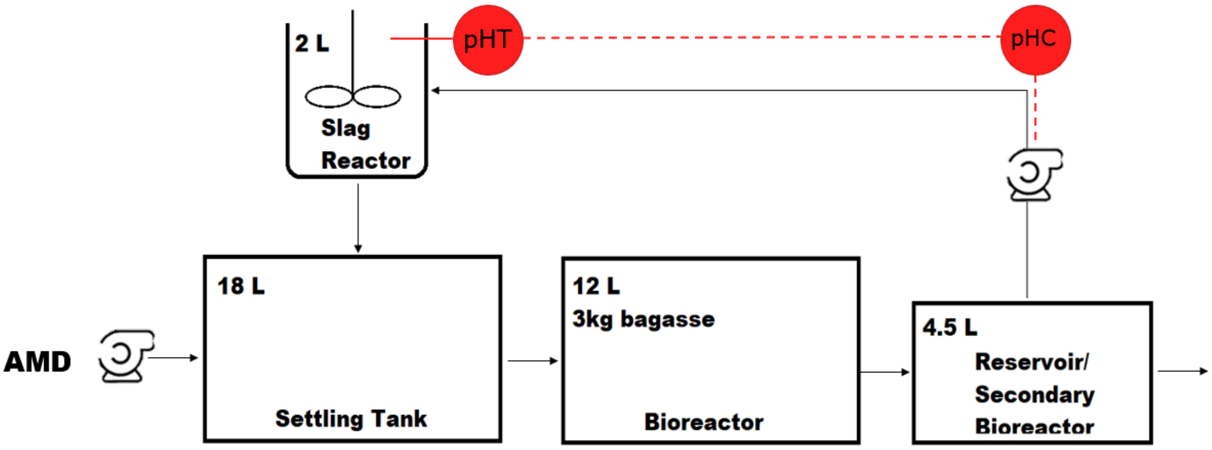

Figure 19: Process control with the recycle flowrate controlled using the pH setpoint in the slag reactor

The configuration shown in Figure 19 functioned the best with regards to maintaining a constant pH in the specified vessel. In addition to this, a proportional only control scheme was suitable for the pH control when this configuration was used. Proportional control does not incorporate integral or derivative control and makes it marginally easier to configure. The recycle flowrate (which was linked to the AMD flowrate) could also be maintained at a fairly constant rate when a proper dosing schedule was followed.

CHAPTER 7: PROPOSED DESIGN FOR SCALE UP

7.1 INTRODUCTION

Using the data and findings obtained from the studies conducted and discussed in Chapters 2-5, a design for a larger scale plant is proposed in this section. The design is a general proposal for a plant that will treat more than 1000 ℓ/day and less than 10 000 ℓ/day of AMD with a quality similar to that found at site (Type A AMD). Some design elements have not been changed due to seamless functioning of these sections of the plant in the laboratory and pilot scale trials, but all reactors and vessels are discussed in detail. In some instances, a technical design is not proposed and a descriptive design is provided instead. A simple schematic of the proposed design is shown in Figure 22. The process control philosophy for the proposed plant is also discussed in this section. The design is proposed to be modular, as the treated water from each vessel has reuse avenues, and thus the mine or site in question may need to only deploy part of the treatment program to achieve the desired treatment extent.

7.2 SETTLING TANK

The initial settling tank designs did not display any issues during the operation of the laboratory or pilot scale plants; thus the design of this section can remain largely the same. There are some design considerations to consider and these are discussed.

7.2.1 Primary settling tank(s)

The rectangular tanks that were used during the pilot study functioned well, however for the larger scale design a circular settling tank is proposed due to the lower frequency of maintenance and ease of sludge removal found when using this type of settler. The main considerations of a circular sedimentation/settling tanks (method of introducing flow, energy dissipation, flow distribution and sludge removal) are discussed:

7.2.1.1 Method of introducing flow

If a circular tank is used, the AMD and slag eluent mixture must be introduced in the centre of the tank (Tchobanoglous et al., 2014). Periphery addition is sometimes used but primary settling tanks generally favour the centre tank addition design. The pipe used to transport the water to the centre of the tank can be (i) suspended from a bridge above the reactor or (ii) fixed in place beneath the reactor floor. It is suggested that the feed pipe enters the settler from the bottom as this nullifies the need for large energy dissipation devices (discussed in 7.2.1.2). The proposed vessel set-up is shown in Figure 20.

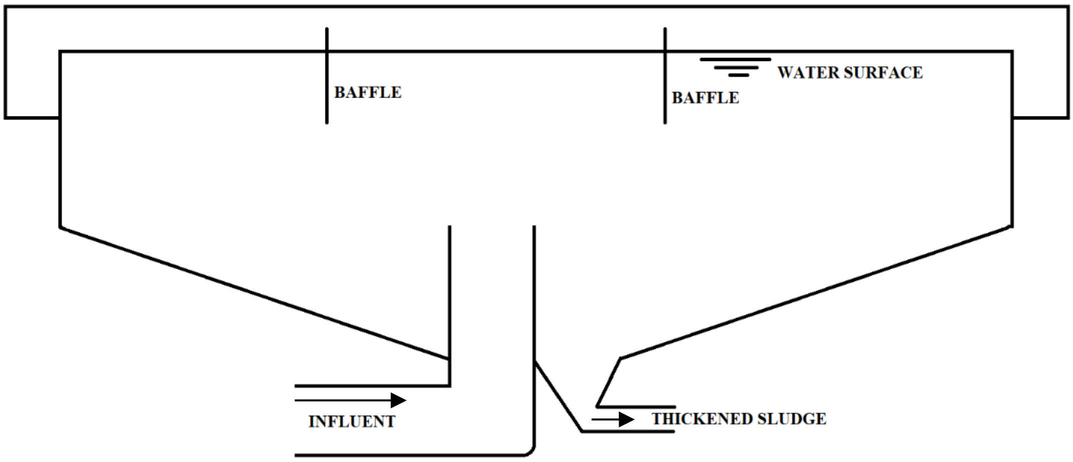

Figure 20: Basic design of the proposed settling vessel

7.2.1.2 Energy dissipation and flow distribution

An energy-dissipating device would have to be used in conjunction with the centre tank addition design when water is added from above the reactor. This design will allow the settling tank to receive influent from the centre column and discharge it tangentially into the top section of the settling tank. It is also proposed to include baffles in the construction of the primary settler in order to direct the flow of the clarified water (this is shown in Figure 20).

7.2.1.3 Sludge removal

In order to facilitate sludge removal, the bottom of the circular settling tank needs to be sloped to form an inverted cone structure. The solids that form and settle at the bottom of the tank can be scraped or can flow to a small hopper located at the bottom of the tank in the centre. To minimize the cost of sludge removal, an airlift pump can be used periodically to remove the sludge contained in the hopper.

Findings from the assessment of the sludge in the primary settling tanks from the laboratory and pilot scale studies indicated that a significant amount of alkalinity remains in the sedimentation layer or sludge blanket and this could be used as an additional pH raising reagent. If this sludge is recycled back into the settling tank or slag reactor before being removed, further reaction between BOFS particles and AMD can occur, reducing the amount of fresh slag needed during replacement. The recycling can be facilitated by a sludge outlet stream that leads either directly to the slag reactor or to a rotary vane feeder which will dose the slag reactor.

7.2.1.4 Sizing

Using the same design principle as followed for the pilot scale plant (scaling up), the area needed for the settling tank (to facilitate settling for a flowrate of 10 000 ℓ/day) is 48.2 m^2 (the surface area for the pilot plant was 4.82 m^2). It is thus proposed that 5 settling tanks each with a diameter of 3.6 m be used for the larger design. The allowable detention time in a settling tank is usually < 8 hours, however the pilot scale which had detention time of > 8 hours functioned well in terms of settling, thus a height of 1 m is deemed acceptable for the settling vessels.

7.2.2 Secondary settling tank

A rectangular tank was also used for the secondary settler to both facilitate further sulfate reduction and to remove any remaining metal sulfides or biological matter that had formed in the biological section of the plant. This vessel was tested at laboratory and pilot scale and the removal capacity was comparatively low, with the concentration of some ions increasing in the system instead of decreasing. For this reason, a secondary settler is deemed unnecessary for the application of the design. However, should secondary filtration be required (this will be based on the quality of the effluent needed) it is recommended that a packed bed filter or a high-pressure sand filter is used.

7.2.2.1 Packed bed filter

This filter will make use of a packing material to remove biological components from the treatment scheme by means of the formation of a biofilm on the packing material of choice. Research done on the BOFS indicates that it contains small amount of chromium and nickel that may act as an anti-microbial substance. If a packed bed filter is used as a form of removal of biological matter from the outlet stream, it is suggested that BOFS be used as part of the packing material.

7.3 BOFS REACTOR

There were multiple issues relating to the BOFS reactor that were experienced during the laboratory and pilot scale studies – the main issue being that of mass transfer between the BOFS and the treated water. It was discovered that treated water which had a significantly lower acidity and higher pH than untreated AMD, was not as effective at dissolving the BOFS as raw AMD was. This caused the ratio between the recycle stream and the feed stream to be very high (high recycle compared to a low AMD inlet). When AMD was added directly to the slag, the alkalinity release and dissolution occurred much faster and to a higher degree. The pH of the AMD thus rose higher and more quickly than when AMD was mixed in the settling tank with slag eluent. Adding AMD directly to the slag, however, introduced the armouring and precipitation problem, whereby precipitation that formed either coated the slag particles, significantly lowering or preventing further dissolution, or formed a thick layer or precipitate/sedimentation on the surface of the BOFS bed, again preventing access to fresh BOFS. When AMD was added directly to the slag, then an agitated system was needed to keep the precipitated metal salts suspended in solution until it the liquid reached the settling tank. For the purposes of the upscale design, a continuously mixed reactor is proposed. The other option (a packed bed reactor) is also discussed briefly.

7.3.1 Continuously mixed or stirred tank reactor

An abrasion resistant tank fitted with a rubber coated stirrer will need to be used for this application. AMD will be pumped into this tank at a fixed rate with the addition of fine BOFS being controlled via pH control of the CSTR or the settling tank. The addition of the slag will be facilitated by a rotary vane feeder. The fines used will need to be less than 0.8 mm in diameter which will ensure that these particles remain suspended in the solution and do not settle in the reactor. During laboratory scale operation it was found that the particles sized between 0.8 and 1 mm settled in the CSTR. Using this option will give more control of operation and easier materials handling. The recycle stream will also be rendered null in this instance.

7.3.1.1 Sizing

It must be noted that sizing of this reactor may change with changes in site (AMD quality and BOFS particle size), different treatment requirements (composition of outlet stream) and modularity of the plant (whether or not the process includes all three process vessels – BOFS chamber, settling tank and DSR chamber). For application at the Type A AMD Dam site – treating AMD with all processes (BOFS, settling and DSR chambers) – the sizing is done according to the results from lab experimentation.

During experimentation, 1 g of BOFS (aperture size between 2000 and 3350 µm) was required to increase the pH of AMD to 7 in 540 minutes. The size of this reactor would thus need to be 3750 L to facilitate the treatment of 10000 ℓ/day with a dosing rate of 694.44 g/min or 1000 kg per day. This dosing schedule must be followed when no sludge recycling is done.

7.3.2 Packed bed reactor

The alternative would be to use a PBR packed with larger sized particles and containing no fines. This option will require a slag replacement schedule and a recycle stream as AMD will not be pumped directly into this chamber. If this option is used, it is recommended that an additional CSTR is used to stir the AMD into the slag eluent before it enters the settling tank to promote further reaction between the BOFS eluent and the AMD.

7.3.2.1 Sizing

In the case where a PBR is chosen as the BOFS reactor, the reactor will have to be constructed in a modular fashion to allow for removal and replacement of the slag at intervals. The reaction time allowed will dictate the size of the reactor – lower reaction times will mean a larger reactor. It should also be noted that as the “free lime” or accessible oxides at the surface of the BOFS particles get consumed, the reaction time will increase.

Taking this into account, 3 reactors each 2000 ℓ in volume, containing 2000 kg each of BOFS (aperture size between 2000 and 3350 µm) are proposed for this larger scale design. The BOFS should be placed in permeable bags (500 kg) or crates that can be lifted via crane. This sizing mimics the pilot scale design, but contains more BOFS of a larger particle size, and allows for a maintenance/replacement schedule.

7.3.3 High density sludge process

Sludge recycling (discussed in the settling tank section (7.2.1)) may necessitate the use of a high-density sludge (HDS) process. This process incorporates two additional vessels aimed at maximizing the use of the BOFS before disposal. In this process the sludge which is extracted from the settling tank must be added to a vessel which contains fresh BOFS. This forces contact between the solids and promotes coagulation of fresh BOFS particles onto the recycled precipitates and unreacted BOFS particles – (the fact that the fresh and recycled particles are combined will force the precipitation reactions to occur on the surface of the existing particles, thereby increasing their size and density). This vessel will then lead into the BOFS reactor vessel where AMD can be added and the process can occur normally. A further vessel which is aerated can then also be added to promote oxidation of ferrous iron to ferric iron. A schematic of this system is shown in Figure 21.

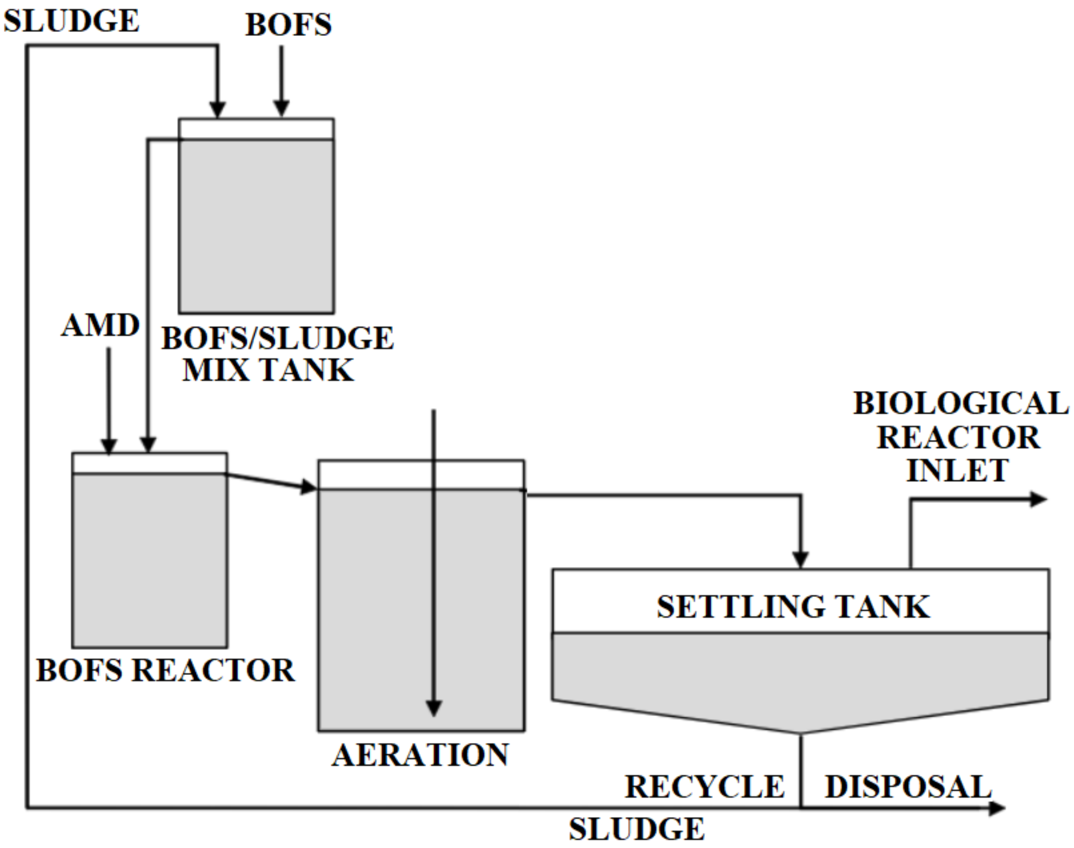

Figure 21: Schematic of HDS system with recycle stream proposed to be used in the larger scale design, using BOFS as a lime source

7.4 BIOLOGICAL REACTORS

Biological sulfate reduction may not have been the sole cause of the sulfate removal across the biological reactors, due to (i) low sulfide levels, (ii) high flowrates and (iii) low COD from the available sugarcane bagasse. This was the main issue which was found during the operation of the biological reactors at the laboratory or pilot scales. It is thus recommended that the design for these reactors change in terms of sizing and amount of bagasse added. These reactors will operate as (i) sealed downflow or up-flow pack bed reactors or (ii) plug flow closed reactors and contain sugarcane bagasse as a packing. The bagasse will have to be replaced at intervals and the spent bagasse can be used as a fuel source or disposed of. The design of the biological section differs from the pilot plant design in that it only contains two reactors. The third reactor has been deemed unnecessary as a sulfate reduction reactor and as a secondary settling vessel. As discussed, a secondary settler or filter can be added easily to the design if the effluent water quality needs to be improved.

A hydrogen sulfide scrubber is still part of the biological reactor design and acts as a precautionary system.

7.4.1.1 Sizing

Approximately 72% of sulfate removal occurred due to pH rise as a result of BOFS dissolution in the pilot scale plant. Using the average AMD concentration of 16301 mg/ℓ, this would mean a further 4564 mg/ℓ of sulfate remained in the solution. In order to lower this to within irrigation water standards (576 mg/ℓ – discussed in Chapter 9 (Rodda, Armitage & Carden, 2014)), a further 3988 mg/ℓ will have to be removed via sulfate reduction in the biological reactors. The maximum COD measured in the biological reactor was 12 g/kg of bagasse, literature however, reports sugarcane bagasse as having 18g of COD/kg of bagasse (Vats, Khan & Ahmad, 2019). Using this value and taking the ratio of COD:sulfate as 0.7:1 – conservatively, 1550 kg of bagasse will be needed daily to treat 10000 ℓ/day of AMD. This will mean a regular replacement schedule. Using a 2-day hydraulic residence time (HRT), the combined volumes of the biological section will need to be 20 000 ℓ. This can achieved using a modular approach, which will also make replacement of bagasse easier to facilitate.

7.5 SCHEMATIC OF PROPOSED DESIGN

The diagram in Figure 22 and Table 12 shows a basic representation of the layout of the proposed design. The design is much simpler than both the laboratory and the pilot scale processes and does not incorporate a recycle stream. However, it should be noted that this process can function with the use of a recycle stream in conjunction to a PBR BOFS reactor using large particles of BOFS (as opposed to a continuously stirred reactor using fine particles). If this design is preferred, then the same layout as the pilot plant will be used.

Table 12: Description of schematic of upscale design shown in Figure 22

Diagram Number	R-101	R-102	R103	R-104	R-105	P-101	P-102
Element	Slag reactor	Clarifier/Settling Tank	Biological Reactor 1	Biological Reactor 2	Hydrogen Sulfide Scrubber	AMD Pump	Recycle pump (rotary vane pump)

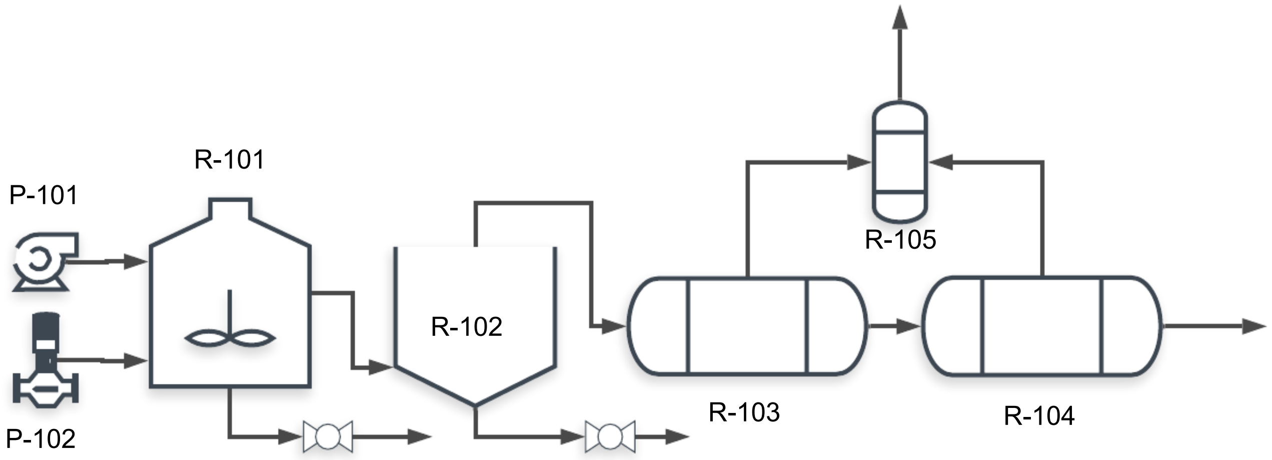

Figure 22: Schematic of proposed larger scale (10000 ℓ/day) design

7.6 PROCESS CONTROL

The mechanism proposed to be used for the process control over the larger system is as follows:

- The pH in the slag reactor will be monitored and transmitted to a programmable logic controller (PLC)
- The PLC will alter the speed of the rotary vane pump used to dose the slag reactor based on the pH chosen as the setpoint and how different the measure pH is to this value.
  - If the pH in the vessel is higher than the setpoint, the speed of the pump will decrease and if the pH is lower than the setpoint, the speed of the pump will increase
- Proportional only control can be used for this set-up.

7.7 MATERIALS OF CONSTRUCTION

Where possible, the equipment must be constructed out of LLDPE or HDPE. If this is not an option, the equipment will need to be rubber lined and coated. The pump used to pump the AMD will have to be peristaltic to ensure no corrosion occurs due to exposure of highly acidic waters over long periods of time.

7.8 COSTING OF REAGENTS

As mentioned in Section 2.1.1, the cost of lime (as dolomite, calcite, gypsum or hydrated lime) ranges between R203 and R533 per 1000 kg (Kalkor, 2020), whereas the price of BOFS (with different particle size ranges) is R146 per 1000 kg (Vermeulen & Phoenix Slag Services, 2018). When using a CSTR with no recycle HDS stream, the cost of reagents per day to treat AMD in this reactor would be R146. This will likely be lower due to the HDS as well as the fact that the waste or by-product generated in this reactor is valuable as an aggregate.

The cost of sugarcane bagasse is reported as approximately R1300/1000 kg (Gralimex Import, 2017). This means that per day, the cost for biological treatment would be R2015.

CHAPTER 8: WASTE GENERATION, DISPOSAL AND RE-USE ROUTES

8.1 AVENUES FOR SLUDGE RE-USE

The sludge produced in the system due to pH change and precipitation is rich in sulfates and minerals with a particularly high composition of calcium sulfate, making it ideal for agricultural use. This sludge could be used (i) as a source of calcium and sulfur for plant nutrition, (ii) for improving the quality of acidic soils, (iii) for treating aluminium toxicity (although the sludge does contain aluminium components, the gypsum content may be enough to negate this (Wulff-zottele et al., 2014)), (iv) for improving soil structure, (v) for improving water filtration and (vi) for preventing runoff and erosion. The sludge will also have remnants of the BOFS and multiple studies have shown that BOFS is suitable for soil amendments, treatments and nutrient support (Goodarzi & Salimi, 2015; Pistocchi et al., 2017; Tsai & Kao, 2009).

If sludge is not reused in this manner, it will need to be disposed of or stored in an impoundment. However, it should be noted that if an HDS process is implemented, the amount of sludge (needed to treat larger volumes of water) will be much less due to the recycling of the sludge. This also means the waste sludge will be more chemically stable and contain less leachable components – making waste disposal marginally safer than traditional lime dosing plants (Kuyucak, Lindvalf, Serrano & Oliva, 2012).

8.2 AVENUES FOR WATER RE-USE

The process was designed in such a way that outlet streams from each of the treatment vessels (slag chamber, sedimentation chamber and DSR chamber) can be accessed – i.e. it is a modular system. Thus, depending on the treatment needs of the mine or dam in question, the modules can be replaced, added or omitted as necessary. Each stage in the process achieves a different level of treatment and the outlet from each vessel therefore has different options for reuse. These are discussed below.

8.2.1.1 Drinking/potable water

According to WHO and South African drinking water standards (Table 13) – the quality of water exiting the slag chamber (from the pilot and laboratory scale plants) is not suitable for use as drinking water – thus further treatment is needed before this water is suitable for human consumption. Reverse osmosis, ultra or nanofiltration could be used as further treatment methods for this water. In some instances, mines have water treatment plants on site – however, some streams of AMD are too severely polluted and treatment via the WWTP is not feasible. In these cases, the proposed design/process can be used as a low cost, pre-treatment step before the water enters the established WWTP.

Table 13: WHO and SANS 241 drinking water standards compared to quality of slag vessel outlet

Components	WHO Max (mg/ℓ)	SANS 241 (mg/ℓ)	Pilot Plant (outlet from slag vessel) (mg/ℓ)	Laboratory Plant (outlet from slag vessel) (mg/ℓ)
Aluminium	0.2	0.3	0 (Undetected)	4.94
Calcium	2-80	150	401.96	270.14
Iron	0.3	0.3	50	17.66
Magnesium	20	70	425.97	5.37
Manganese	0.5	0.1	143.53	5.79
Sulfate	500	250	2435	109.11
pH	6.5-8.5	5-9.7	9.06	11.49

(Mamba, Rietveld & Verberk, 2008; Verlicchi & Grillini, 2020; World Health Organization, 2009)

8.2.1.2 Irrigation/Agricultural Water

If the outlet water has the same composition as that of the laboratory plant slag vessel outlet, it can be used for irrigation purposes with just a small amount of pH adjustment (from 11.49 to 8.4) (according to the South African irrigation water standards shown in Table 14). Using the outlet from the primary DSR vessel may be more suitable for this purpose as the concentrations (with the exception of iron) and pH are all within range.

Table 14: South African irrigation water standards compared to quality of slag vessel and DSR vessel outlet

Components	Maximum range of SA irrigation water standards (mg/ℓ)	Pilot Plant (outlet from slag vessel) (mg/ℓ)	Laboratory Plant (outlet from slag vessel) (mg/ℓ)	Laboratory Plant (outlet from Sedimentation vessel) (mg/ℓ)	Laboratory Plant (outlet from DSR vessel) (mg/ℓ)
Aluminium	20	0 (Undetected)	4.94	9.87	5.74
Calcium	824	401.96	270.14	209.92	123.76
Iron	20	50	17.66	62.76	29.82
Magnesium	225	425.97	5.37	59.47	17.67
Manganese	10	143.53	5.79	10.02	7.34
Sulfate	576	2435	109.11	289.17	213.58
pH	6.5-8.4	9.06	11.49	7.28	7.10

(Rodda et al., 2014)

Producing irrigation water from AMD treatment may be a necessary route to take, considering the lack of water resources in some regions where AMD generation poses a serious environmental problem (Martins, Santos, Pires, Barros & Costa, 2010). This option for reuse is recommended (above others), as the treated water from the system contains nutrients from the slag and DSR vessels that could aid in crop growth – reducing the need (and associated cost) of fertilizers. In the case where this system is used for production of water for irrigation purposes, hydraulic residence times will need to be selected to ensure treatment occurs to the acceptable level (complying with maximum recommended values for compounds of interest for waters for irrigation purposes).

8.2.1.3 Process water

Another option for re-use/use of the treated water is use as process water at the mine site. This would include (Water for Africa, 2009):

- Water used for extraction activities
- Water used for beneficiation activities
- Water used for utility areas
- Water used for waste management or tailings areas
- Water used in general site areas

All these activities or areas at a mining site can make use of process water and potable water is not necessarily needed for these purposes. Thus, the treated water from the system could be used in one of these avenues. The mine site in question would have to stipulate whether the composition and quality of the treated or semi-treated water would be suitable for use in these specific areas. Outlet from the sedimentation vessel can also be used as process water depending on the method and purpose of reuse. Partially treated water from the sedimentation vessel will not be suitable for agricultural or drinking water (as shown in Table 14) and will only be viable for process water use or further treatment.

8.3 AVENUES FOR SLAG RE-USE

The spent BOFS from the process is valuable as a construction material and can be used as an aggregate in cement, concrete or as road ballast (Tamlyn Sasha Naidu et al., 2020; Xue et al., 2006). Trade routes will have to be established to transport spent slag; however this material can also be used closer to the mine in the development of tailings dams or impoundments.

CHAPTER 9: SUMMARY

9.1 CONCLUSIONS

The proposed study was envisioned to begin with an initial concept and end with a tangible design of a system that could treat AMD to agricultural or process water standards using the two waste materials, sugarcane bagasse and BOFS. Both the laboratory and the pilot-scale plants were successful, and the final proposed design is based on findings from the previous smaller-scale set-ups. The waste or by-products were successful in remediating AMD in a continuous process and the possibility of upscale of the design is recognised. The following points are presented as the main conclusions of the study:

- The level of metal and sulfate removal in the settling tanks is dependent on the pH in the tank which is dependent on the alkalinity released from the BOFS. If a higher or lower degree of removal is required in this step, the desired pH (which is controlled) can be altered in order to achieve this.
- The biological reactors are designed as a polishing step. The bulk of the removal of the sulfates occur within the settling tanks due to pH rise, but the polishing below 1000 mg/ℓ can only occur in the biological reactors. These reactors function best at pH values between 4 and 8 and the amount of removal of sulfate that occurs in these reactors is based largely on residence time. If a higher degree of sulfate removal is required, the reactors can be made larger or vessels can be added in series to facilitate this. In addition to this, these reactors function best in anaerobic conditions and need to remain sealed. When aeration occurs, previously precipitated compounds can re-dissolve in the solution. These reactors will also need to contain the suitable amount of organic carbon source to allow for the desirable level of sulfate reduction (0.7g COD/g sulfate)
- The particle size of BOFS and whether agitation is present or not, influences how long the liquid must be in contact with the slag to dissolve enough oxides to increase the alkalinity of the system and thus raise the pH. Any particle size can be used, but different reactor types must be used to facilitate this.
- The reaction times found in the systems that were tested were not long enough to completely dissolve the BOFS, even when fine particles were used. Thus, the sludge that forms in the settling tank contains a large amount of alkaline containing particles. This sludge can be recycled and further used as an oxide source before being disposed of. If this option is chosen, an addition of an HDS system must take place.
- The controlled pH can be anywhere in the system, however the recommended vessel for control is the slag reactor.
- Replacement rates for the reagents will vary depending on the treatment volume.
- There are further reuse avenues for all waste streams in this process:
  - The BOFS can be used as an aggregate in construction
  - The bagasse can be used a fuel source
  - The sludge can be further processed to extract valuable rare earth metals

- The treated AMD can be used as agricultural or process water or can enter into a commercial water treatment plant for further remediation

9.2 RECOMMENDATIONS

Further studies regarding the optimization of the process control aspect and the use of spent BOFS as an aggregate will need to be conducted to improve the efficiency of the system. It is also recommended that the treated water be used for agricultural purposes as it is nutrient rich. Previous studies have indicated that BOFS or BOFS leachate can be used as a fertilizer or for soil enrichment and treatment due to the high concentrations of calcium, magnesium and silicates it contains (Ito, 2015; Makabe-Sasaki, Kakuda, Sasaki & Ando, 2012). The treated water also contains some organics, in the form of acids or sugars which is beneficial for the growth of certain plants.

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APPENDIX A: DESIGN DOCUMENT

Design of Acid Mine Drainage Remediation Plant (CONFIDENTIAL)

Kopseer Dam, Witbank

Deliverable No.1

Report
to the Water Research Commission

by

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Project No. KN/NNNN

July 2017

EXECUTIVE SUMMARY

A design for a pilot scale process aimed at remediating 1000 ℓ /day of acid mine drainage at the Kopseer Dam in Witbank, South Africa is presented in detail. The plant design parameters are determined based on a combination of literature, previous lab scale experimental data and space and equipment availability. The plant uses a combination of metallurgical slag and sulfate reducing bacteria cultures to achieve the design aims which are to remediate the acidic water to acceptable grey water standards. The process design includes 8 low-density polyethylene vessels used as reactors and sedimentation tanks which -with the combination of a recycle stream – enables pH rise of the acidic mine water, precipitation of heavy metal sulfate complexes from the AMD and dissimilatory sulfate reduction, which lowers the sulfate concentration to below 100 mg/ℓ. A fraction of the remediated water is recycled back into the process to prevent armouring and deactivation of the slag, and the remaining water enters back into the Kopseer Dam. Construction of the equipment will be done off site, with only setup and pipe connections occurring on site. All on site work will be done in accordance with the Anglo American health and safety protocol.

BACKGROUND

A collaborative project aimed at determining the viability of the combination and large scale of use of metallurgical slag and sugarcane bagasse to remediate AMD.

AIMS

The following are the aims of the project:

1. To perform preliminary laboratory studies which will provide information for the design of a pilot plant unit.
2. To design a pilot process for treating 1000 ℓ /day of AMD on site.
3. To construct the pilot plant to treat 1000 ℓ /day of AMD.
4. To monitor the pilot plant in order to assess performance over a 6-month period.
5. To design and prepare a process for scale up of the original pilot plant to be based on site.

GENERAL

This document serves as the initial design of the pilot plant system to be constructed.

ACKNOWLEDGEMENTS

The project team wishes to thank the following people for their contributions to the project.

Reference Group	**Affiliation**
Others	

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LIST OF FIGURES

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ACRONYMS & ABBREVIATIONS

AMD	Acid Mine Drainage
ARD	Acid Rock Drainage
SRB	Sulfate Reducing Bacteria
DSR	Dissimilatory Sulfate Reduction
HMI	Human Machine Interface
PFD	Process Flow Diagram
P&ID	Piping and instrumentation diagram

CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

This project is a collaboration of the University of the Witwatersrand, Phoenix Slag, Illovo Sugar and Anglo American who all aim to determine the viability of remediating AMD at a large scale in a two-step process which combines the use of metallurgical slags and sugarcane bagasse. Previous laboratory scale experimentation has confirmed the functionality of metallurgical slag as a pH raising agent and the use of sugarcane bagasse as a carbon source for dissimilatory sulfate reduction (DSR). These experiments were done on a smaller scale and the feasibility of the process must be tested at a larger continuous scale in order to confirm its effectiveness and determine whether use as a large-scale remediation option is possible. This report is the first deliverable of the project and summarizes the lab scale experimental process by using the data obtained to design a pilot scale plant.

1.2 PROJECT AIMS

The following are the aims of the project:

6. To perform preliminary laboratory studies which will provide information for the design of a pilot plant unit.
7. To design a pilot process for treating 1000 ℓ /day of AMD on site.
8. To construct the pilot plant to treat 1000 ℓ /day of AMD.
9. To monitor the pilot plant in order to assess performance over a 6-month period.
10. To design and prepare a process for scale up of the original pilot plant to be based on site.

This document serves as fulfilment of the second aim.

1.3 SCOPE AND LIMITATIONS

Experimental data was obtained from batch and continuous lab scale processes and this data was used to determine the parameters for the pilot scale design. The data obtained enabled determination of the relevant operation vessels, as well as sizing and positioning thereof. These experiments were done over a period of one month, but some data from previous studies and literature were also used in the design. The experimental; kinetics used to design the process were sourced over a short period of time and thus allowances had to be made to compensate for the plant operating for a much longer. For this reason all of the equipment sizes have been overestimated depending on literature or data.

1.4 SUMMARY OF WORK TO DATE

Table 1 and Table 2 summarise the work to date, revised due dates and deliverables submitted thus far.

Table 1: Work Completed to date

No.	Task	Summary
1	Preliminary experimentation	Lab scale experimentation to determine parameters of large scale design
2	Initial design of pilot plant	Design document detailing pilot plant specifications
3	Construction of pilot plant at site.	Construction and set-up of plant at site
4	Experimentation, data collection and monitoring at site.	Monitoring and data collection
5	Result over 6 months summary report	Interpretation of 6 months of results
6	Further experimentation and monitoring	Application of any relevant changes and further monitoring
7	Draft Final Report	Draft conclusion
8	Final Report	Conclusion

Table 2: Summary of deliverables

No.	Deliverable	Status	Due Date
1	Initial design of pilot plant	Completed/Submitted	03/07/2017
2	Construction of pilot plant at site.	In progress	01/09/2017
3	Result over 6 months summary report	In progress	02/04/2018
4	Draft Final Report	In progress	03/09/2018
5	Final Report	In progress	03/12/2018

CHAPTER 2: OVERVIEW OF PROCESS

2.1 INTRODUCTION

A process is designed to remediate Acid Mine Drainage sourced from Kopseer Dam, located in Witbank, Mpumalanga. The Dam is a receptacle for acid water waste from coal mines in the area and contains high concentrations of heavy metals and sulfate. The proposed process uses metallurgical slags to raise the pH of the acidic water, allowing metal and sulfate precipitates to form and be removed via gravitational settling. After the pH is raised sufficiently, the water is then directed to a bagasse chamber where the remainder of the sulfate is removed via DSR. The outlet of this chamber is treated water with a relatively neutral pH and low metal and sulfate content. The system will be constructed less than 10m from the Kopseer Dam (CONFIDENTIAL) site and will be monitored for 1 year.

2.2 DESIGN BASIS

Remediation of 1000 ℓ/day of acidic mine water

2.3 DETAILED PROCESS DESCRIPTION

AMD (with pH of 2) from the dam will be pumped into system using a peristaltic pump. The AMD stream is designed be split equally and will both enter sedimentation vessels from the top. The sedimentation vessels are arranged in parallel. Recycled treated water will also enter the sedimentation vessels from the top after being exposed to metallurgical slag which will raise the pH. This high pH water will mix with the acidic (low pH) water, and a mixture with a pH of between 5 and 9 will be obtained (optimal pH will be determined after long term experimentation). At this range of pH's, precipitation of metal sulfate complexes will occur and the sedimentation vessels will facilitate this under the action of gravitational settling.

The water exiting the sedimentation vessel will thus have a lower sulfate and heavy metal concentration than the original AMD. The outlets from the sedimentation vessels will join (after being split in the parallel system) and enters into two DSR chambers arranged in series. These vessels act as biological reactors in which DSR occurs. Sugarcane bagasse is packed into crates and stacked throughout the lengths of the reactors. Space between the crates is allowed.

A by-product of the DSR reaction is sulfide which binds to hydrogen to produce H_2S gas. If the gas concentration nears the allowable threshold, this gas can be directed to a scrubbing unit which oxidizes the sulfide to produce sulfuric acid. The scrubbing unit waste is disposed of in the dam. The reactor outlet enters a secondary sedimentation vessel in which precipitation of metal sulfides can be accomplished. The outlet of this chamber enters a reservoir and is considered the end product – remediated water.

Under the action of a peristaltic pump, some of this water is pumped back into the process, entering first into a slag reactor chamber which is packed with metallurgical slag in crates, and then into the sedimentation vessels to assist with precipitation. The flowrate of this stream is determined via pH control of the sedimentation vessel – if the pH is low, the flowrate of the recycle is increases and vice versa. The recycle loop is necessary as it prevents the armouring of the slag. If low pH AMD is allowed to come into direct contact with the slag, the slag will be coated with metal precipitates and the alkaline reagent will no longer be accessible to raise the pH. All vessels will be sealed (with the exception of the scrubber) and will be covered to prevent UV penetration.
The design of the process is done in detail and presented in Chapter 4.

2.4 COMMISSIONING OF PLANT/START-UP

Th system will need to be commissioned with metal free water to prevent armouring of the slag. A water tank containing clean water will be used initially and will act as the source of the recycle stream until all vessels in the process are filled to capacity and an outlet flow is obtained.

2.5 HEALTH AND SAFTEY

All work done will comply to Anglo Americans health and safety protocols. Medical examinations of all workers allowed on site are being conducted and an environmental and health risk assessment is in the process of being reviewed.

CHAPTER 3: SITE SELECTION AND LAYOUT

3.1 INTRODUCTION

The pilot plant will be constructed at the Kopseer Dam, located in Witbank, Mpumalanga. Topical views of the physical site are shown and discussed and a plant layout diagram, in which the proposed positioning of each vessel used in the plant is shown, is also presented.

3.2 SITE SELECTION

In Figure 1 a top view of the entire dam is shown. The area of construction is outlined.

Figure 1: Top view of Kopseer Dam with area of construction outlined

The dam is situated next to a large mine dump in which slurry and solid wastes are continuously deposited. Liquid mine wastes (consisting mainly of waste water) seep through this dump, leaching out heavy metals and sulfate from the solid wastes. This liquid flows out through the bottom of the dump as toe seepage and is directed towards Kopseer Dam. There is currently no treatment option for this dam and in order to keep from overflowing, the water is continuously pumped out of the dam back into the mine dump. The water in this dam is therefore continuously decreasing in quality and in need of remediation – making it an ideal site for an experimental plant.

The total area of the site selected is approximately 774 m^2 (18 m x 43 m), however only a portion of this is able to accommodate construction due to the positioning of trenches, fences and power equipment already situated at the site which create access constraints A piece of land approximately 5 m x 30 m, with an area of 150 m^2 is proposed to be used for construction, as shown in Figure 2.

Figure 2: Top view of area to be used for construction of pilot plant at Kopseer Dam

All process equipment is proposed to occupy 95 m^2 with the remaining area to be left open for additions or alterations to the process if they are needed.

3.3 PLANT LAYOUT

In Figure 3 below, the proposed plant layout as seen from above is displayed. Vessels have been drawn to scale and labelled in accordance with the process diagrams which will be displayed in

Chapter 4. The electrical housing box has not been sized. This will be done after initial testing of the control equipment.

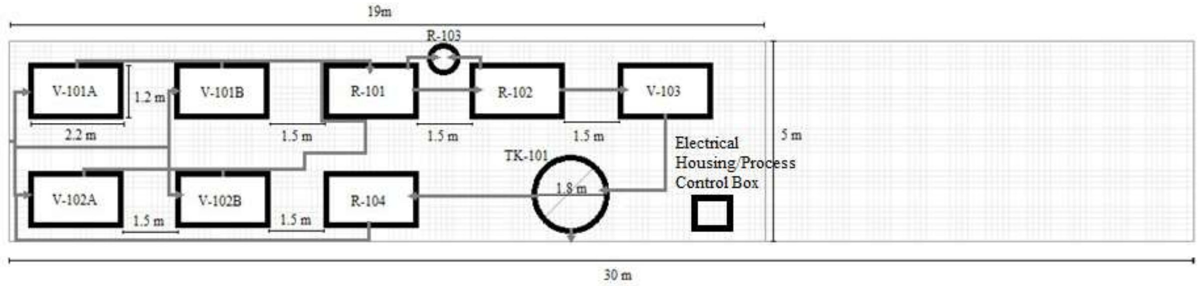


Figure 3: Plant layout top view

The positioning of the piping that is shown in the layout diagram includes silicon, nylon and PVC piping that will be used for construction. Different piping materials will be used for different sections of the plant and this will be further discussed in Chapter 6

CHAPTER 4: PROCESS FLOW DIAGRAMS

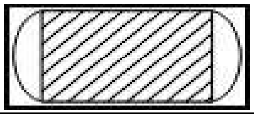
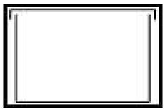
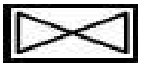
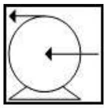
4.1 INTRODUCTION

The designed process is shown in a process flow diagram which details the process diagrammatically

4.2 PROCESS FLOW DIAGRAM (PFD)

In Figure 4, a diagrammatic representation of the process flow and layout of the plant is shown. A key is provided in Table 1 which details and specifies the symbols used in the diagram.

Table 3: Key for Process flow diagram

Representation and description of symbols on PFD	
Symbol/Diagram	**Description**
	Settling Tank/Sedimentation Vessel
	Reaction Vessel
	Storage Vessel
	Valve
	Peristaltic Pump
	Stream Number

In Figure 5, a process flow diagram without symbols is provided. Images of the vessels have been used instead of diagrammatic representations.

P-101	V-101A/B	V-102A/B	R-101	R-102	R-103	V-103	TK-101	P-102	R-104
AMD Feed Pump	Sedimentation Vessel	Standby Sedimentation Vessel	Bagasse Reactor	Secondary Bagasse reactor	Hydrogen Sulfide Scrubber	Secondary Sedimentation Tank	Storage Tank for Remediated Water	Recycle Pump	Slag Chamber

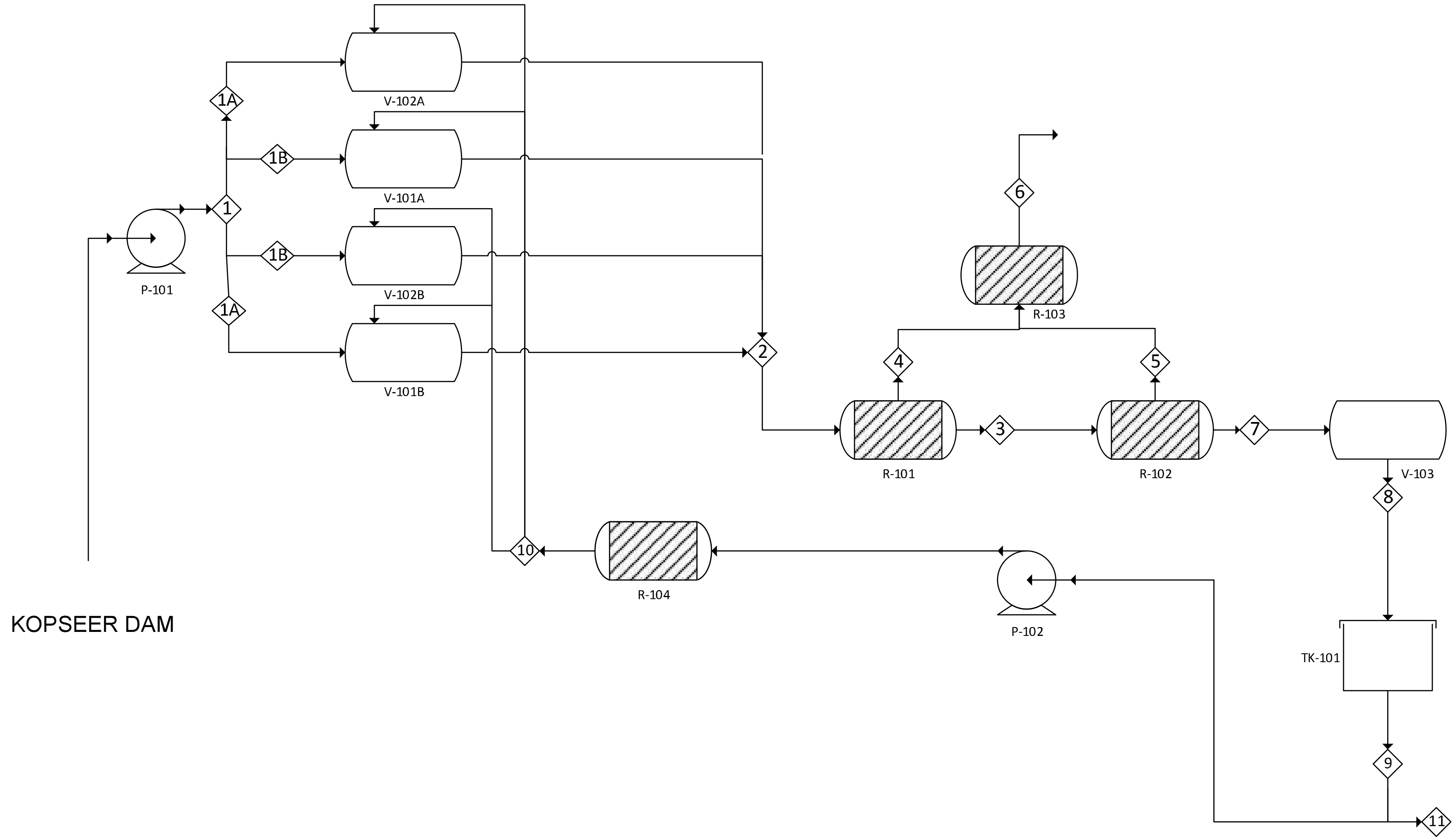


Figure 4: Process flow diagram

P-101	V-101A/B	V-102A/B	R-101	R-102	R-103	V-103	TK-101	P-102	R-104
AMD Feed Pump	Sedimentation Vessel	Standby Sedimentation Vessel	Bagasse Reactor	Secondary Bagasse reactor	Hydrogen Sulfide Scrubber	Secondary Sedimentation Tank	Storage Tank for Remediated Water	Recycle Pump	Slag Chamber

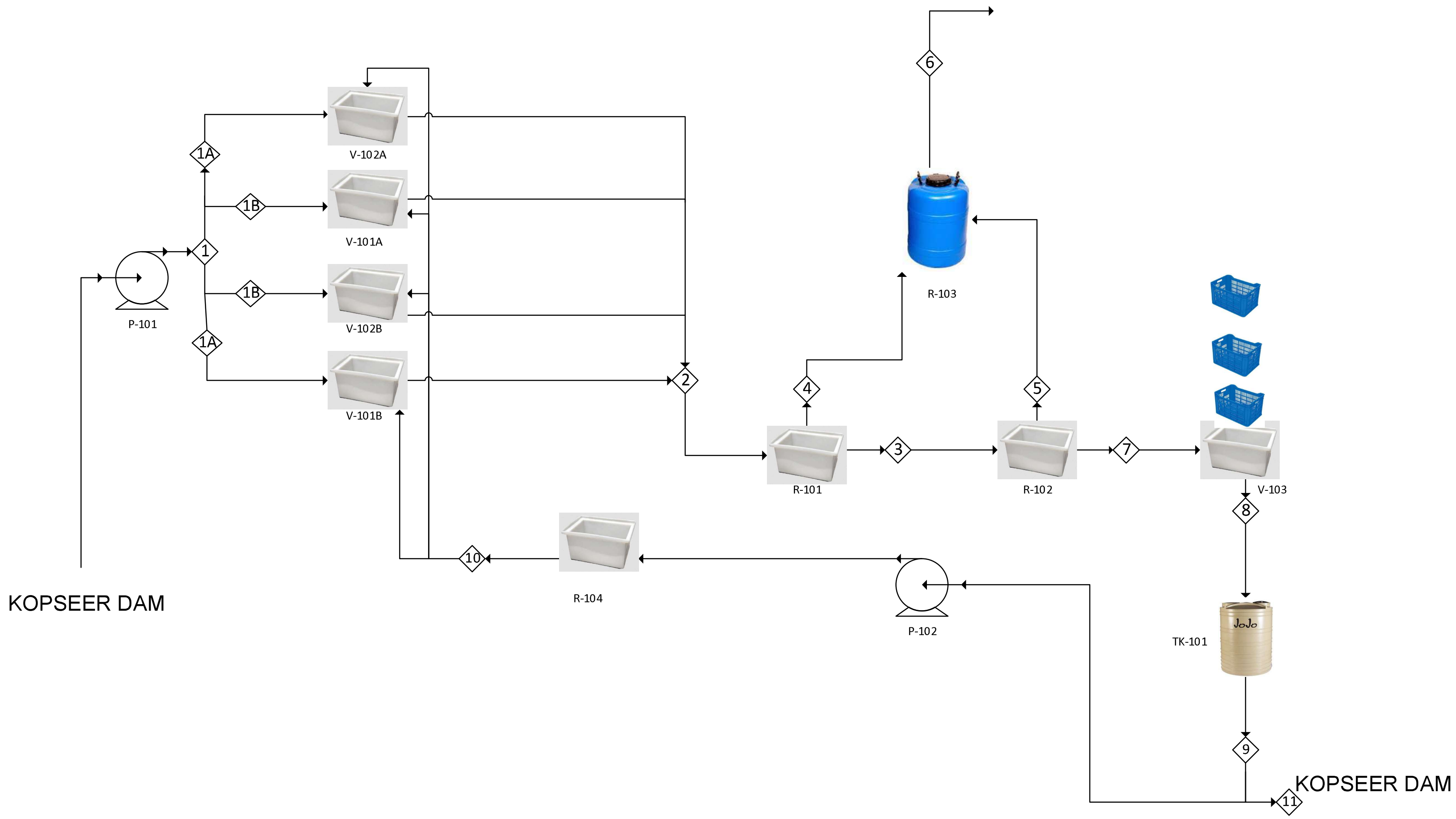


Figure 5: Process Flow Diagram - no symbols

CHAPTER 5: EQUIPMENT DESIGN

5.1 INTRODUCTOIN

All major process equipment (reactors, sedimentation vessels) are sized and described in detail in this section. All reactions and settling will occur in pre-made polyethylene vessels, which are UV and acid resistant. All vessels have the same dimensions; however, sizing is investigated to ensure they adhere to the minimum allowable size for the reactor or settling tank. Where these vessels are not large enough, multiple are used in series or parallel depending on the process. All vessels will be sealed to avoid re-oxidation of any sulfide that may be present in the streams and may be covered to ensure no UV light is able to penetrate through.

5.2 SETTLING TANK/SEDIMENTATION VESSEL

This system is represented by symbols V-101A, V-101B, V-102A and V-102B on the PFD and P&ID.

5.2.1 Overview & 2D Diagram

Feed into the settling tank consists of two streams; fresh AMD and recycled treated water which must first enter into the pH raising/slag chamber. Before pH rise occurs, the recycled water is at a pH of 7.5 and contains approximately 11 mg/ℓ of dissolved iron, 200 mg/ℓ of dissolved magnesium and 53 mg/ℓ of dissolved manganese. The sulfate content of this stream is aimed at being kept below 100 mg/ℓ. Calcium content of this stream is high at approximately 500 mg/ℓ. After exiting the slag chamber (before entering the sedimentation tank) the quality and characteristics of this feed changes due to the sudden rise in pH. The calcium content can reach levels of above 1600 mg/ℓ but all other heavy metal concentrations decrease. The settling tank contains a large volume of water moving at a low velocity, as shown in Figure 6.

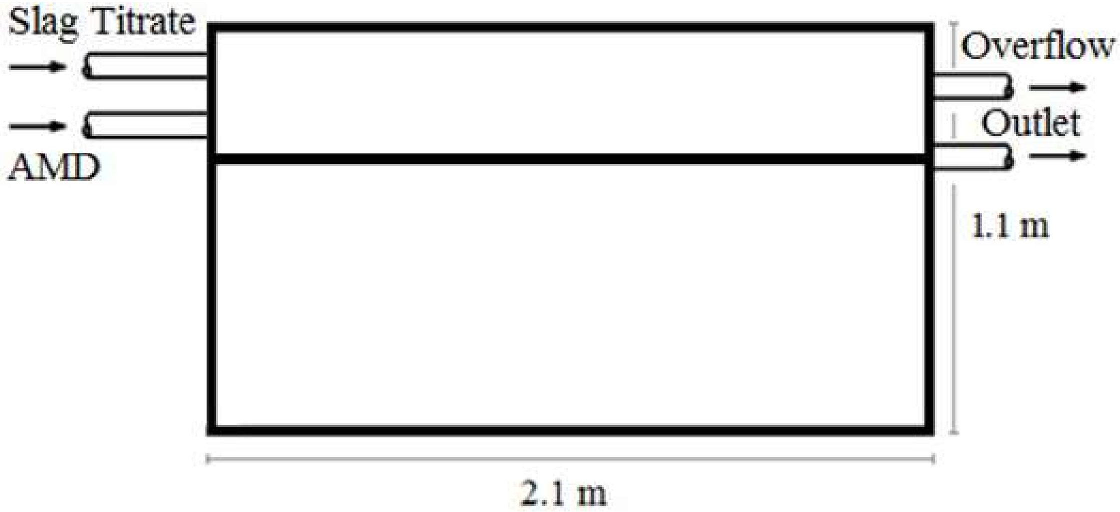


Figure 6: : Gravity Settling tank to be used for heavy metal oxide/sulfate/sulfide/carbonate settling

The low pH AMD and high pH slag titrate would enter the vessel, mix and reach an average pH level. This pH level would be higher than the original AMD pH and thus, following mixing, precipitation of the heavy metals would occur. As the precipitate particles form in the liquid, they would settle (under the action of gravity) to the bottom of the tank. Smaller particles settle at a lower rate and may possibly be carried further forward before they reach the bottom of the tank. The very fine particles are carried away in the liquid overflow. Future designs may incorporate a mechanism which will allow easier separation of the precipitates.

5.2.2 Sizing

The smallest particle (ferric sulfate) was used to determine the ideal size of the sedimentation vessel. Ferric sulfate has a theoretical settling velocity of 0.000288m/min (Haman & Zazueta, 2014), which gives a calculated maximum settling area of 4.82 m^2 (calculations are shown in Appendix B). This value incorporates a safety estimation, as the vessel should be large enough to hold all precipitate that is formed, without causing blockages or overflows. Two vessels will be used, each with a height of 1.1m, a length of 2.1, and a width of 1.2 m, to achieve the desired sedimentation.

5.2.3 Materials & Mechanical Design

According to data obtained from lab scale experiments, a total of 15 kg/day of metal precipitates could potentially be formed and removed in the settling tank when treating 1000 ℓ/day of AMD. For this reason, two sedimentation systems will be constructed; to be used alternatingly, while cleaning of the other occurs. Cleaning of these vessels will occur weekly or when needed to avoid blockages. The inlet into the settling basin will minimize entrance velocities by the addition of a baffle just below the inlet position. This will allow very little turbulence to be created, and will distribute the water across the basin as uniformly as possible. Data obtained from experimentation indicates that precipitation of iron sulfate occurs after 24 hours of pH change. In order to ensure maximum precipitation and removal of metals, the vessel will have a residence time of at least 48 hours.

The material used for the sedimentation chamber will be linear low-density polyethylene (LLDPE) which is resistant to a 70% solution of sulfuric acid. This material will be able to withstand the corrosive nature of the AMD.

5.3 BAGASSE REACTOR

The bagasse reactors are represented by symbols R-101 and R-102 on the plant layout diagram, PFD and P&ID.

5.3.1 Overview & 2D Diagram

The bagasse reactor contains sugarcane bagasse and a culture of sulfate reducing bacteria which enables sulfate reduction. The bagasse is placed in removable, perforated crates and stacked inside the reactor. These racks do not impede flow and allow for spacing between the bagasse stacks to facilitate sulfate reduction. Lab scale experiments have shown greater sulfate removal when liquid is not in direct contact with carbon source. An internal side view of the reactor is shown in Figure 7

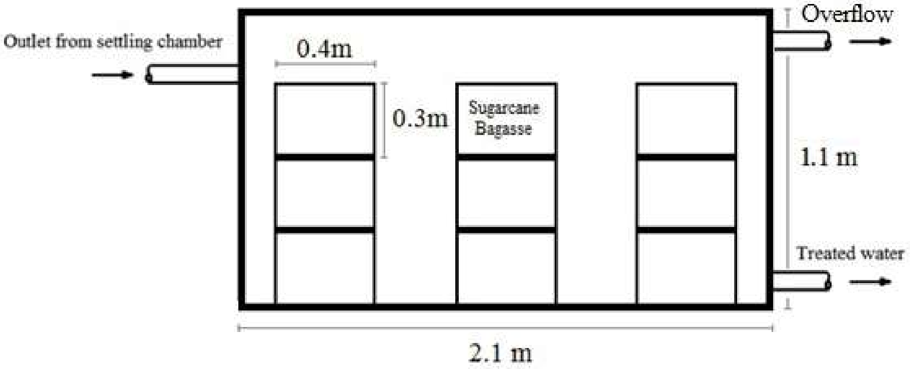


Figure 7: Side view of bagasse reactor

The inlet into the reactor is situated above the base and feeds liquid which flows via gravity out of the main settling tank. A gas vent is fitted to these reactors (which are sealed) and the gas produced from this system is passed through a scrubber before it is liberated into the environment.

5.3.2 Sizing

Using data obtained from experimentation, the volume of the reactor is calculated to be 1650 ℓ. A detailed calculation is shown in Appendix A. The pre-made rectangular vessel with a length of 2.1 m, width of 1.2 m and height of 1.1 m will be used. This size reactor can be used to facilitate the reaction, independent of sugarcane bagasse loading – i.e. providing an alternative carbon source with a negligible volume. Since sugarcane bagasse mass (and relative volume) has to be considered, the experimental data is used to ensure scale up of the reactor is feasible.

Lab scale experimentation has shown a removal rate of sulfate of 22 mg/hour in a 50 Litre vessel with a residence time of 24 hours. If these results are used, a 1000 litre vessel will be needed to treat a flowrate of 1000 ℓ/day of AMD. Thus the proposed reactor vessel will be sufficient for the process. To achieve a final concentration of approximately 100 mg/ℓ only one reactor will be needed, however two of these reactors will be set up in series to facilitate the removal in order to increase the non-contact space between the bagasse and the liquid. In this way, the sulfate removal is theorized to occur at a faster rate.

Both reactors will be inoculated with a functional strain of SRB culture which has been cultivated using Kopseer Dam AMD samples (these cultures are currently being maintained using sodium sulfate and sodium acetate and their functioning is being monitored). Using short term experimental results, a mass of 25 kg of bagasse must be used in each of these reactors to achieve a final sulfate concentration of under 100 mg/ℓ. This mass of bagasse will not be depleted immediately and will take approximately two weeks to degrade. The true replacement schedule is unknown and will form a research question.

All carbon containing compounds within the bagasse can theoretically be used by the SRB. Thus, since the bagasse generally has a water content of 50% or below, theoretically 3 kg of bagasse is needed in total per day to treat 1000 ℓ of AMD. Including an over-estimation parameter to accommodate inefficiency of SRB functioning and cellulose breakdown, 90 kg of bagasse will be needed in total per month. To accommodate this, the bagasse is proposed to be changed every 17 days, pending observation of the system.

5.3.3 Materials & Mechanical Design

The sulfate reduction reaction will occur in two bioreactors arranged in series as opposed to one larger reactor. This is due to the challenges associated with maintaining homogeneity in large systems. The shape of the vessels will be rectangular, each having a height of 1.1 m and a length of 2.1 m. Cell washout will not be prevented, but it is assumed that SRB cell growth is equal to cell wash out.

All parts of the reactors will be constructed from linear low-density polyethylene (LLDPE) which is resistant to 70% sulfuric acid solution. No metals will be used due to the highly corrosive environment. The system will be sealed using pond liner.

5.4 HYDROGEN SULFIDE SCRUBBER

A low risk of hydrogen sulfide being released in a short period of time into the environment is present and for this reason a hydrogen sulfide scrubber is incorporated into the design. To negate any uncontainable H_2S release, the scrubber consists of a 200L plastic drum containing water, hydrogen peroxide or ammonia. Gas from the bagasse reactors will be directed into the base of the vessel and allowed to bubble through the liquid. H_2S gas exhibits high dissociation and reactivity, and the gas will react with the scrubbing liquid to form sulfuric acid and water. The tank used will be constructed from polyethylene to prevent degradation of the vessel. The scrubber is represented by symbol R-103 in the PFD and P&ID.

5.5 SLAG REACTOR

This reactor is represented by symbol R-104 on the PFD and P&ID.

5.5.1 Overview and 2D Diagram

The slag reactor allows a rise in pH of the feed via hydroxide enrichment and hydronium ion depletion. An approximate rate of pH rise has been determined from previous experiments and this rate reduces over time as slag depletion occurs. A large slag reactor is used which will be packed with crates containing slag particles to allow for easier replacement and removal. The reactor is set up as shown in Figure 8 below.

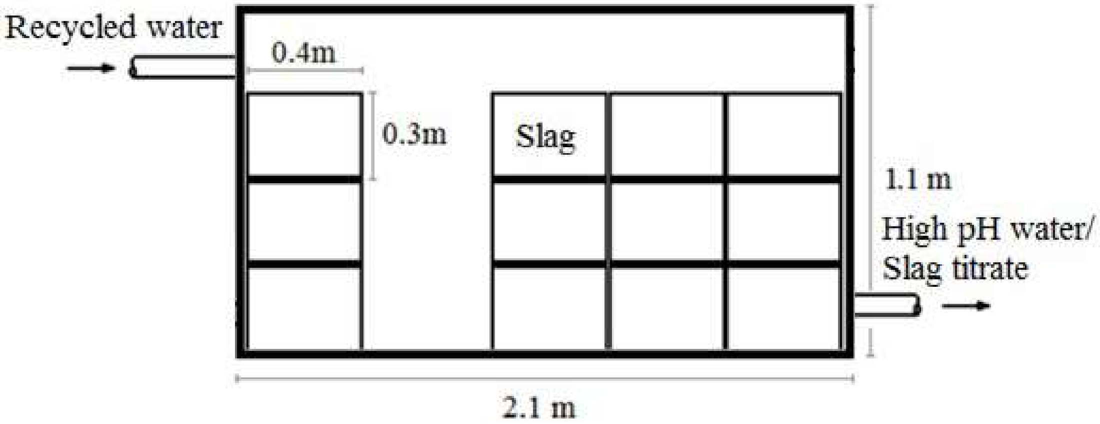


Figure 8: Side view of slag reactor

Each crate will contain 10 kg or more of slag which is above 8mm in aperture. The crates will allow for easy and quick replacement of the slag. The crates act like cartridges and replacement is simple, and requires little power. Settling in the reactor may occur due to the presence of heavy metals, and this can be cleaned out when necessary.

5.5.2 Sizing

Using the data obtained from lab scale experiments, 15 kg of slag should be sufficient to raise the pH of 1000 ℓ of AMD to 9. This is determined using breakthrough curves which saw a drop from pH 11 to pH 10 after treating approximately 100 ℓ of neutral pH water with 300 g of slag. A titration curve was also used to determine the ratio of clean water to AMD needed to reach a pH of 9. A pH of 9 will allow for sufficient heavy metal precipitation and will still be within range of the SRB pH functionality.

A 2,772 m^3 vessel will be used as the slag reactor vessel, which will allow for a maximum of 30 crates. If the reactor is packed to a maximum capacity, 25 kg of slag can be filled in each crate, giving a total slag mass of 750kg. This will allow 50 days of treatment before depletion becomes noticeable. This option is at full reactor capacity and can be used for prolonged periods where regular replacement of slag is not possible or feasible. In order to create ease of replacement for general use however, each crate will only be filled with 10kg, and only 24 crates will be fitted in the reactor - giving a total slag mass of 240 kg. This will be sufficient for 16 days of remediation at the highest recycle rate. Every week 12 crates (120 kg) can be replaced. In this way, the slag would always be present in excess. This would prevent depletion of slag which would result in large increases of the recycle stream flowrate.

5.5.3 Materials & Mechanical Design

The slag reactors will be constructed out of acid resistant plastic (linear low-density polyethylene). The inlet of the reactor will be just above the base of reactor and the outlet will be just below the level of water.

5.6 TREATED WATER RESERVOIR

The reservoir is represented by symbol TK-101 on the PFD and P&ID.

5.6.1 Overview

The treated water will exit the bagasse reactor and enter into a water reservoir which would then drain back into the Kopseer Dam. The reservoir would be sealed and would not allow for hydrogen sulfide gas liberation or oxidation of any sulfide ions. The flow of the recycle stream from the reservoir to the slag reactor is controlled via pH of the settling tank. The outlet water flows back into the Kopseer Dam via an overflow outlet. This overflow would be the product stream of the system.

5.6.2 Sizing

The reservoir will have a volume of 225 L. A Jojo tank will be used as the vessel.

5.6.3 Materials and Mechanical Design

The reservoir will be constructed from acid resistant and UV resistant plastic and will be sealable.

CHAPTER 6: PIPING, VALVES AND PUMPS

6.1 PIPING

Piping will consist primarily of PVC tubing with a small amount of silicon tubing used to pump water from the Kopseer Dam to the settling tank. Nylon tubing may also be used in certain parts of the plant to disallow oxygen from entering the system as this would interfere with the SRB functioning as well oxidize any reduced sulfate in the process. The material used for each piping stream is shown in the table below. The lengths provided are estimations obtained from the plant layout diagram and may increase based on the positioning of the trenches already built on site.

Table 4: Piping materials of different streams and respective lengths

Stream Number	Piping Material	Approximate Length (meters)
1	Silicon	4
1A & 1B	PVC	4
2	PVC	3
3	PVC or nylon	2
4 & 5	Silicon	3
7	PVC or nylon	3
8	PVC or nylon	3
9	PVC or nylon	3
10	Silicon	5
11	Silicon	3

6.2 PUMPING

Pumping will be done using peristaltic pumping to avoid direct contact with any liquid (which will cause corrosion and degradation of materials not resistant to acid). The environment at the dam is highly corrosive and no metal will be used in the construction of the plant. Two peristaltic pumps will be used in the process (P-101 and P-102 in PFD) P-101 will have a constant speed and the speed of P-102 will be controlled via the pH data obtained from the settling tank. Other pumps can be added optionally to

a. pump water from the bagasse chamber into the reservoir
b. pump water from slag chamber to slag chamber
c. pump water from slag chamber into the settling chamber
(all optional pumps can be removed if the plant is setup in a way that allows for gravity flow)

The pumps will be housed in the electrical/process control box which will be constructed of acid and UV resistant plastic.

6.3 VALVES

Multiple polyethylene or Teflon ball and joint valves and three-way valves will be used to control the flow in the system. The flow will be switched off and on depending on configuration and replacement scheduling. Additional clamp valves may be used where necessary to alter and control the flow between the various operations.

CHAPTER 7: CONTROL PHILOSOPHY

7.1 INTRODUCTION

The monitoring and control philosophy will be one of providing a low level of automation and an overview of the status of the various streams within the plant, in terms of pH, temperature and conductivity. Programming of the system will be required to ensure trouble free operation. The following monitoring and controls will be of effect.

1. Flow, pH, temperature and conductivity
2. Drives indications, interlocking and control

7.2 GENERAL PHILOSOPHY

The general interface between the operator and the supervisory system is that plant automation will be geared towards a high level of operator action and low level of automated control.

Automated control will be accomplished via monitoring of the pH inside of the settling tanks. The pH of the settling tank will control the flow of the recycle stream into the slag chamber by controlling the speed of the peristaltic pump (P-102). pH, conductivity and temperature will also be monitored, but these will be purely for recording purposes. Other control aspects may be added as the plant commences operation.

7.3 CONTROL BOX

The operator interface to the plant will consist of visual display units and keyboards. All stream displays will be inside the control housing/box, but there may be some displays situated at the point of analysis for convenience. The interface will enable the operator to start, control and stop the plant as well as allow the operator to monitor the process continuously and remotely. The HMI will provide an alarm display and management system. In addition to this, all digital and some trend displays of certain analogue variable will be accessible to the operator by means of a data logger and a 3G network connection. The software will be designed in such a way to ensure easy back up and restoration.

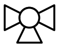
7.4 INTERLOCKS

Interlocks are suitably configured process conditions or integral devices which must signify a healthy plant operational state before a certain piece of equipment can be operated. A process interlock is proposed to be used in the system to stop the AMD and recycle streams if the pH of the water exiting the sedimentation tanks are too low or too high as this will result in death of the SRB.

7.5 PROCESS AND INSTRUMENTATION DIAGRAM

The diagram shown in Figure 9 is a detailed representation of the pilot plant. Valves, sample points, piping and instrumentation are shown. Table 2 provides a key which details the symbols used in the P&ID. All piping and cord will be enclosed in a hard conduit.

Table 5: Key for piping and instrumentation diagram

Utility Connections Key	
Symbol/Diagram	**Description**
SP	Sampling Point
pHT	pH Transmitter
TT	Temperature Transmitter
PT	Pressure Transmitter
CT	Conductivity Transmitter
pHI	pH Indicator
CI	Conductivity Indicator
TI	Temperature Indicator
1	Stream Number
	Butterfly Valve
	3-Way Valve

P-101	V-101A/B	V-102A/B	R-101	R-102	R-103	V-103	TK-101	P-102	R-104
AMD Feed Pump	Sedimentation Vessel	Standby Sedimentation Vessel	Bagasse Reactor	Secondary Bagasse reactor	Hydrogen Sulfide Scrubber	Secondary Sedimentation Tank	Storage Tank for Remediated Water	Recycle Pump	Slag Chamber

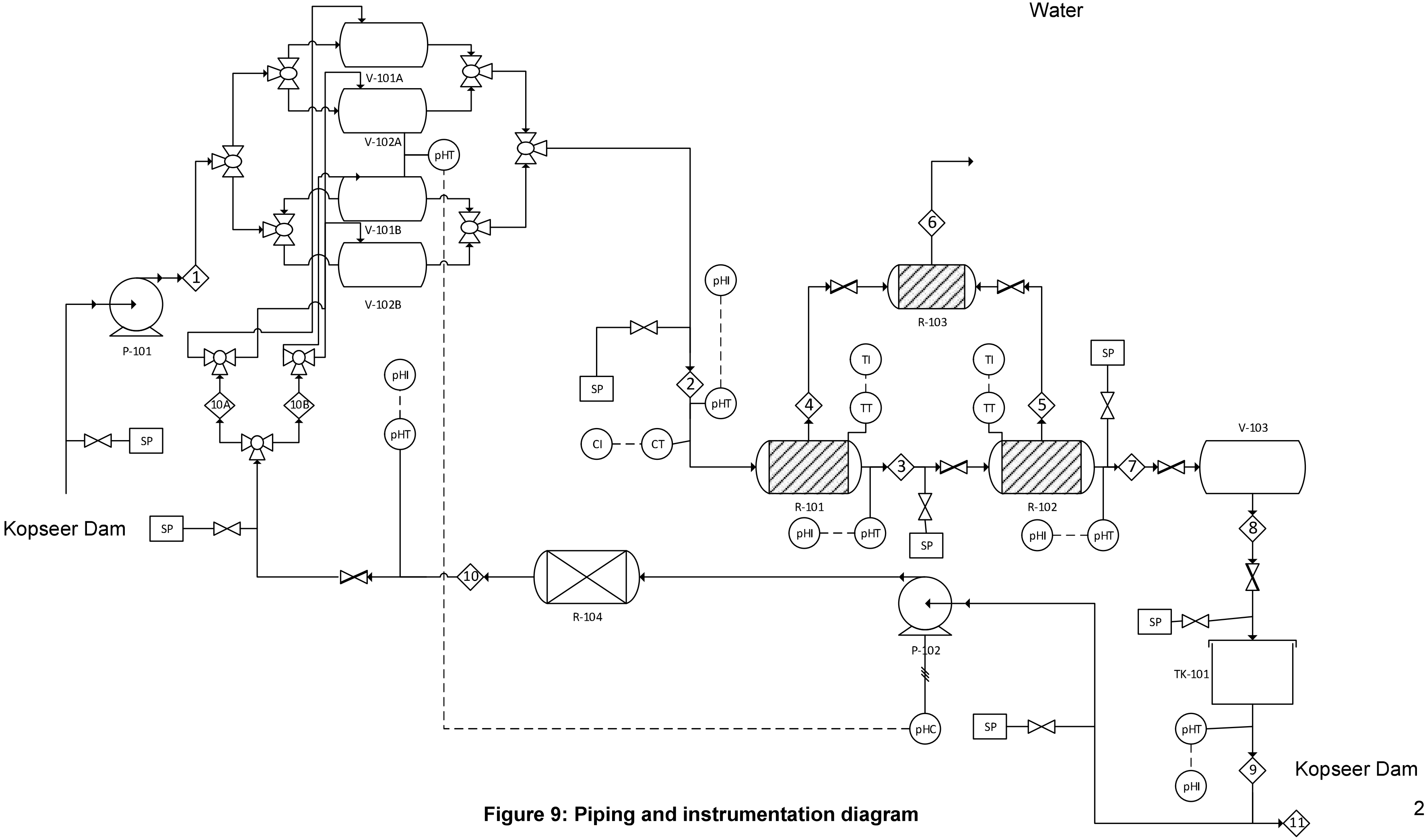


Figure 9: Piping and instrumentation diagram

CHAPTER 8: WASTE MANAGEMENT

Spent slag will be disposed of on site in the large mine dump situated next to dam. Treated water and scrubber water will be disposed of in the Kopseer dam. Both the treated water and the scrubber water are of better quality than the Kopseer Dam water and thus any disposal into the dam is allowable. The waste bagasse will be disposed of in the dam or at mine dump site. Solid precipitate will be disposed of with the slag in the mine dump situated next to the dam. A schedule for waste disposal will be created based on process performance.

CHAPTER 9: COSTING

A list of parts needed to construct the pilot plant, as well as their quantity and cost is provided in the table below. Prices marked with an * have not been quoted for and estimations have been provided in those cases.

Table 6: Parts and pricing list for pilot plant

Part	Description	Quantity	Cost	Supplier	Total
	Plastic rectangular reaction/sedimentation vessel	8	R6000	Pioneer Plastics, 5 Potgieter St, Rosslyn, Pretoria, 0200, South Africa	R48000
	Industrial pH electrode	3	R6000	Hanna Instruments (Pty) Ltd, 6 Vernon Road, Morninghill, South Africa	R18000
	pH electrode + meter	5	R600	Microrobotics South Africa, Centurion	R3000
	pH transmitter	3	R3000	Test & Measurement Instruments cc	R9000
	programmable logic controller	1	R12000	Siemens	R12000

Part	Description	Quantity	Cost	Supplier	Total
	Industrial Conductivity meter	1	R7000	Hanna Instruments (Pty) Ltd, 6 Vernon Road, Morninghill, South Africa	R7000
	Temperature probe and arduino kit	5	R800	Microrobotics South Africa, Centurion	R4000
	Piping	All fittings	*R5000	-	R5000
	Valves	All fittings	*R1500	-	R1500
	Crates	70	R85	Shawson's Plastics, South Africa	R5950
	Pumps	2	*R60000	Watson and Marlow	R120000
	Plastic scrubber vessel	1	R160	Pioneer Plastics, 5 Potgieter St, Rosslyn, Pretoria, 0200, South Africa	R160

Part	Description	Quantity	Cost	Supplier	Total
	Weather meter kit	1	R1300	Microrobotics South Africa, Centurion	R1300
	Aluminium tape	All fittings	*R3000	-	R3000
	Plastic pond liner sheets	All fittings	*R3000	-	R3000
	Water Reservoir	1	R2400	Plumblink, South Africa	R2400
	Electronic Housing	1	R6000	-	R6000
	Laptop	1	R6000	Incredible Connection	R6000
Total (rounded)					R256 000

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APPENDIX A: BAGASSE REACTOR SIZING (LITERATURE BASED)

When conditions are ideal, the size of the reactor(s) (which is modelled as a plug flow reactor) is given by Equation 1 (Fogler, 1999) .

$$V = F_{A_0} \int_0^X \frac{dX}{-r_A}$$

Equation 1

Where:

F_{A_0}	is the initial molar flowrate of sulfate
r_A	is the rate law, and
X	is the desired conversion

$-r_A$ is given by Equation 2 and C_A is given by Equation 3 below.

$$-r_A = kC_A^2$$

Equation 2

r_A is given by Equation 2 and C_A is given by Equation 3 below.

$$C_A = C_{A_0}(1 - X)$$

Equation 3

Using Equation 2 and Equation 3, Equation 1 is simplified to:

$$V = \frac{F_{A_0}}{kC^2_{A_0}} \int_0^X \frac{dX}{(1 - X)^2}$$

A k value from experimental data is determined to be 0.005497 mol/day. X is calculated using an experimental value of sulfate entering the bagasse reactor (approximately 15000 mg/ℓ), and is determined to be 0.93. The initial concentration of sulfate is 15.62 ml/ℓ, and the initial molar flowrate of sulfate is measured as 15.615 mol/day.

APPENDIX B: SEDIMENTATION TANK SIZING

Equation 4 is used to calculate the settling velocity of Iron sulfate (Haman & Zazueta, 2014).

$$V_p = 0.00135\ (d^2)(SG - 1)(0.0254)$$

Equation 4

Where

V_p = settling velocity of particles in water(m/min)

d = particle diameter (microns) (2 micron for ferric sulfate)

SG = specific gravity of particle

$$Area = 1.604\left(\frac{Q}{V_p}\right)$$

Where:

$Area$ is the surface area of the settling tank in ft^2

Q is the flowrate into the tank in gal/min

V_p is the settling velocity of the particle in in/min