ACID BIO-DESULPHURISATION OF COAL DISCARDS USING A HEAP LEACHING APPROACH

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SYNOPSIS

The extraction and processing of coal generate substantial amount of wastes, which include waste rock, coal discards, and coal fines, posing significant environmental risks. The presence of sulphidic minerals, particularly pyrite, in these wastes can lead to the formation of acidic runoffs, known as acid rock drainage (ARD), when exposed to moisture and oxygen. While physical separation can effectively remove sulphides from fine coal waste, it is more challenging for coal discards and waste rock due to their low liberation. This necessitates either costly physical liberation processes followed by separation or removal through chemical reactions.

The management of ARD pollution involves both prevention and treatment strategies. ARD prevention focuses on minimizing the interaction between oxidants and sulphide-bearing minerals to reduce the formation and release of acidic compounds. Whilst ARD treatment aims at neutralizing the acidic effluent produced and precipitating dissolved metals. Treatment methods are divided into active, and passive approaches based on available resources and pollution severity. Active treatment requires continuous use of alkaline chemicals, incurring significant long-term expenses. Passive treatment systems utilize natural chemical and biological processes to mitigate acidity and precipitate metal pollutants.

Heap bioleaching, a technology commonly used in recovering base metals from low-grade metal sulphide ores, offers a sustainable approach to accelerate the reaction of pyritic fractions within coal discards. This method enables the removal of sulphides in solution under controlled conditions, thereby mitigating ARD over the mine's lifespan. Heap bioleaching is cost effective and readily implementable and so holds promise as an economical alternative to traditional ARD treatment methods. Moreover, the accelerated removal of sulphides through bioleaching could yield environmentally benign coal discards with potential value.

The desulphurization process in heap bioleaching is sustained by microorganisms capable of oxidizing iron and sulphur. Iron oxidizers assist in regenerating Fe^{3+} from Fe^{2+}, while sulphur-oxidizing microorganisms generate sulphuric acid from elemental sulphur and sulphides. These reactions sustain the highly acidic environment, require to the continuous oxidation and leaching of pyrite.

This thesis presents a proof-of-concept experiment aiming to test the feasibility and efficacy of accelerated desulphurisation as an ARD prevention method. The study was conducted in laboratory-scale columns simulating waste heaps over a period of 380 days, using coal discards from the Emalahleni region of Mpumalanga, South Africa. The results demonstrated

successful sulphur removal with 50% desulphurisation achieved within 250 days, with a terminal duration of approximately 600 days.

Post-leaching characterization of the discards showed a significant reduction in the acid generating potential. With static tests displaying a gradual decline in the acid producing potential over time and categorizing the leached discard as non-acid forming after 380 days of irrigation. Biokinetic tests confirmed the significant depletion of the pyritic content in the coal discards further supporting the discards reduced risk of ARD generation.

These findings underscored the potential of heap bioleaching as a viable strategy for desulphurising of high sulphur-containing coal discards during the mine's operational lifespan, potentially enabling their repurposing as saleable coal or safer disposal methods.

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Firstly, to God Almighty whose grace has sustained me throughout this season.

To my beloved wife, your love, patience, and unwavering belief in me have been my source of strength.

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Thank you.

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Olivier Tambwe

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Declaration

I hereby declare that aspects of the research conducted this Masters study and presented in this dissertation have already been published in the form of a technical report to the sponsor and a journal publication, by invitation following presentation at the International Biohydrometallurgy Symposium. The publications in which research from this Masters dissertation is presented are as follows:

- Technical report for the Water Research Commission of South Africa: Kotsiopoulos, A., Amaral Filho, J., Broadhurst J.L., Mjonono D., Tambwe O., Gcayiya M., Ngoma E., Mostert L., and Harrison S.T.L. 2022. "Preventing Acid Rock Drainage Generation from Coal Waste Rock: Comparing long-term efficacy and techno-economic considerations." Final Report prepared for the Water Research Commission (2761). (Chapter 7)
- Journal publication:

  Tambwe, O., Kotsiopoulos A and Harrison S.T.L. 2020. "Desulphurising high sulphur coal discards using an accelerated heap leach approach." Hydrometallurgy. 197(May):105472. DOI: 10.1016/j.hydromet.2020.105472

I affirm that the work reported in the aforementioned publications is mine and was conducted as part of this Masters study under the guidance of my supervisor, Prof. Susan T.L. Harrison.

These publications, based on this dissertation, have contributed to and extended the body of knowledge upon which this dissertation builds.

Olivier Tambwe

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Abbreviations and acronyms

ABA	Acid base accounting
ABS	Autotrophic basal salt
ANC	Acid neutralising capacity
ARD	Acid rock drainage
CCBE	Covers with capillary barrier effects
CPB	Cement Paste Backfills
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
LOI	loss on ignition
MPA	Maximum potential acidity
NAF	Non-acid forming
NAG	Net acid generation
NAG_{pH}	pH of the solution following NAG test
NAPP	Net acid producing potential
PAF	Potentially acid forming
PLS	Pregnant leach solution
PSD	Particle size distribution
ROM	Run-of-mine
SHT	Self-heating temperature
XRD	X-ray diffraction
XRF	X-ray fluorescence

1 Introduction

1.1 Background

Coal mining operations generate large amounts of sulphidic wastes resulting from the removal of excess material to access the coal seam as well as the upgrading of the coal product through the beneficiation process. These wastes constitute a significant environmental hazard, presenting risks such as land degradation and ecosystem destruction, through land footprint, spontaneous combustion, leaching, and dust evolution leading to air and water pollution. As the sulphide-bearing overburden, waste rocks, and tailings are exposed to oxygen and moisture, acidic runoff known as acid rock drainage (ARD) is produced, contaminating adjacent water bodies with high levels of acidity, dissolved metals and soluble sulphates which lead to long-term increased overall salinity (Opitz et al., 2015).

Coal contains several types of sulphur including organic sulphur, molecularly bound into the coal, sulphates, usually present in trace amounts, and sulphides such as pyrite (FeS_2) (Speight, 2021). During the primary stage of ARD development, the initial reaction mechanism revolves around the oxidation of pyrite by molecular oxygen. Yet, as the environment becomes increasingly acidic, ferric ion (Fe^{3+}), generated at an enhanced rate through the microbially catalysed oxidation of ferrous ion (Fe^{2+}), becomes the main oxidising agent (Kotsiopoulos & Harrison, 2017). Iron oxidising microorganisms help the conversion of Fe^{2+} to Fe^{3+} thus sustaining the overall environment acidification. On the other hand, sulphur oxidisers play an essential role in converting sulphur species into sulphuric acid (Hogg, 2013).The elevated levels of acidity promote metal leaching and metal mobility, resulting in the accumulation of metals in soil and water, consequently harming ecosystems.

Management of ARD pollution demands both preventative and treatment strategies. Prevention approaches aim towards safely disposing of mining wastes to minimize the risk of ARD generation. To achieve this, methods such as co-disposal and blending, covers and cement paste backfills are utilised (Harrison et al., 2013; Kotsiopoulos & Harrison, 2017; Kotsiopoulos & Harrison, 2018; Harrison et al., 2020). Conversely, ARD treatment processes, which include passive and active processes, attempt to neutralise the produced acidity, and contain the leached metal ions. These may involve, for example, chemical precipitation of metal sulphates followed by biological sulphate reduction for elemental sulphur recovery (Marais et al., 2020).

Removing sulphides from mine wastes can effectively remove the risk of ARD generation as this eliminates the primary source of ARD production permanently (Benzaazoua et al., 2000;

Harrison et al., 2013). Coal desulphurisation methods include physical, chemical, and biological methods. While physical and physico-chemical methods rely on specific gravity and surface properties (Hesketh et al., 2010; Kazadi Mbamba et al., 2012; Riazi & Gupta, 2015), chemical desulphurisation uses agents which preferentially react with pyrite and organic sulphur without altering the coal matrix (Xia & Xie, 2017). Lastly, biological methods use microorganisms to break down sulphur compounds (Gonsalvesh et al., 2008).

The inoculum type, pH, temperature, Fe^{2+} and Fe^{3+} ions concentration, and coal particle size are some of the key parameters controlling the biodesulphurisation of coal (Çelik et al., 2019). The process has typically been carried out in stirred tank reactors. These units offer the opportunity to readily adjust process operating conditions to maximise sulphur removal. However, the construction, operation and maintenance costs of the equipment hinder the process economic feasibility, particularly in waste processing. Heap bioleaching offers a much more cost-effective alternative, the technology has been successfully applied to the extraction of metals from low-grade sulphidic ores (Watling, 2006; Harrison, 2016). Given its ability to minimise the energy cost associated with comminution, aeration and stirring in tank leaching, heap bioleaching exhibits promise as an optional approach for expediting the leaching process of mining wastes, such as coal discards, with specific aim of facilitating the leaching within life of mine under controlled conditions, to enable preparation of materials with potential to re-purpose and to prevent long-term ARD generation.

1.2 Problem statement

The mining and processing of coal generates substantial amounts of wastes in the form of sulphide-bearing waste rocks and tailings posing a significant environmental hazard, including the long-term generation of acid rock drainage (ARD). To mitigate this risk, sustainable and cost-effective prevention methods are needed, particularly through risk reduction through sulphide removal prior to long-term disposal or, preferably, re-purposing. Controlled, accelerated leaching of coal discards using heap bioleaching presents potential as such a means and further research on this approach is required to address its feasibility and benefit.

1.3 Research objectives, hypothesis, and key questions

1.3.1 Objective and scope

The primary aim of this dissertation is to investigate the efficiency and efficacy of accelerated leaching of high sulphur coal discards, prior to long-term disposal or re-purposing, as an ARD prevention approach. The scope of this study is focussed on the assessment of the leachability of high sulphur coal discards.

1.3.2 Hypothesis

Accelerated heap bioleaching of coal discards constitute a viable long-term ARD prevention technique, as efficient desulphurisation of coal discards with high pyritic sulphur content can be achieved in packed bed of coal discards during the life of the mine. Through this desulphurised discards can either be discarded with reduced risk or re-purposed, while the sulphate and metal rich leachate can be further processed for recovery of chemical fractions.

1.3.3 Key questions

The present study aims at addressing the following key questions:

- To what extent can sulphur be removed from the coal discards through accelerated heap bioleaching?
- Under what time frame can the coal discards be non-acid generating when desulphurised using heap bioleaching?
- What challenges does accelerated heap bioleaching of coal discards present as an ARD prevention method?
- What opportunities are available for re-purposing of the iron and sulphur rich PLS released and the residual desulphurised coal discards?

1.4 Thesis structure

A schematic outline of the dissertation structure is provided in Figure 1-1. Chapter 1 provides the project background, problem statement as well as the objectives. Chapter 2 conducts a critical review of the relevant literature, including ARD generation, characterisation, treatment, and prevention. Chapter 3 describes the materials, experimental procedure, and outlines the analytical methods used in the study. Chapter 4 presents the results of the proof-of-concept column bioleaching of the coal discards, addressing the extent and time of the accelerated leach (Key Questions 1 & 2) as well as challenges presented (Key Question 3). Chapter 5 presents the characterisation results of the coal discards post-leaching, demonstrating the efficacy of the leaching process as well as the potential for re-purposing or risk-reduced disposal (Key Questions 1 and 4). Further, the potential for repurposing leachate solution is presented (Key Question 4). Finally, Chapter 6 gives the research outcomes and concludes with final comments on the significance of the study and recommendations for potential future research.

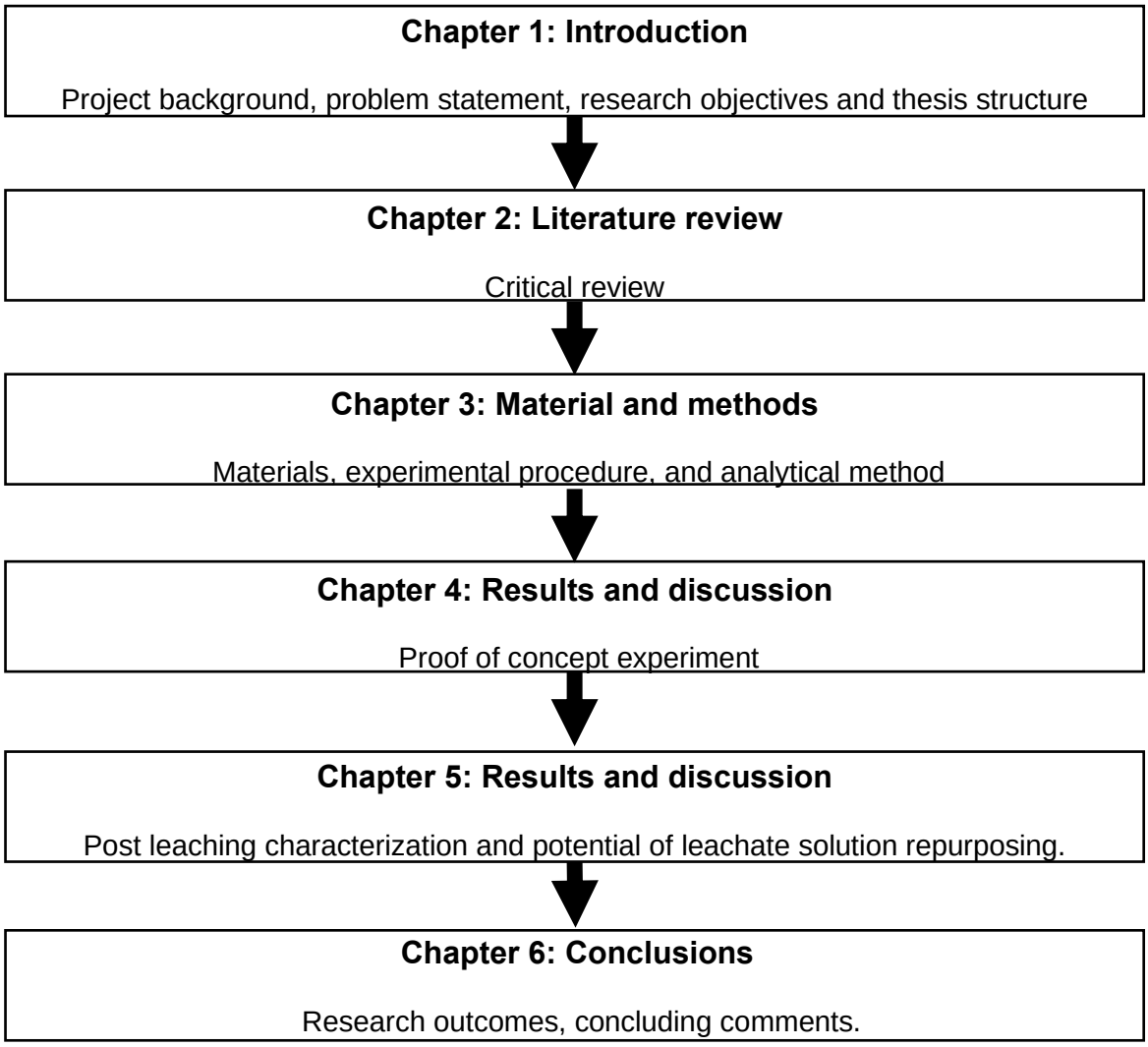

Figure 1-1:Schematic outline of thesis structure.

2 Literature review

2.1 Coal processing

Coal is an organic sedimentary rock formed when vegetation decomposes and is altered by compaction, warmth, and pressure (Speight, 2005). Coal is the world most abundant fossil fuel and has been the most important resource for energy supply (Klein et al., 2001). Coal is primarily used for electricity production, but the synthesis of liquid gasoline from coal has been an appealing alternative to ease the strain on crude oil as the only supply of automotive fuel (Ghosh & Prelas, 2009). However, as renewables supply is growing the contribution of coal to the South African energy mix is set to decrease.

2.1.1 Background on South African coal industry

South African coals are commonly low in both pyritic and organic sulphur (Snyman & Botha, 1993), with sulphur content in raw coal ranging between 1 and 4% (Jeffrey, 2005a). Extractible coal in South Africa has however been found to hold a high ash content ranging up to 65% (Eberhard, 2011). Ash is an inorganic and non-combustible residue, coal value is therefore significantly reduced when excess ash is generated following its combustion, (Subba Rao & Gouricharan, 2016), hence a limit is placed on the ash content of saleable coal.

In South Africa coal is mined in several coalfields (Figure 2-1) located mainly in the Free States, Gauteng, Mpumalanga as well as the north-western part of KwaZulu-Natal (Jeffrey, 2005b) (Pinetown et al., 2007) . The primary utilisation of South Africa's coal consumption is dedicated to electricity production (Eberhard, 2011). In South Africa, coal has assumed a pivotal role as the primary energy source, representing more than 90% of electricity generation (DMRE South Africa, 2020). However, more stringent greenhouse gas emission reduction regulations, will intensify the drive towards renewables, recognizing the continued importance of coal in the transition period as well as the expected ongoing use of coal in coal-rich nations in a high development phase for 10s of years, while also prioritizing the management of historic reserves for a sustainable energy future. Approximately 46% of the annual South African coal production is allocated to electricity generation, 26% is exported, 18% is used for synthetic fuel production and the remainder is consumed domestically in different industries (Steyn & Minnitt, 2010).

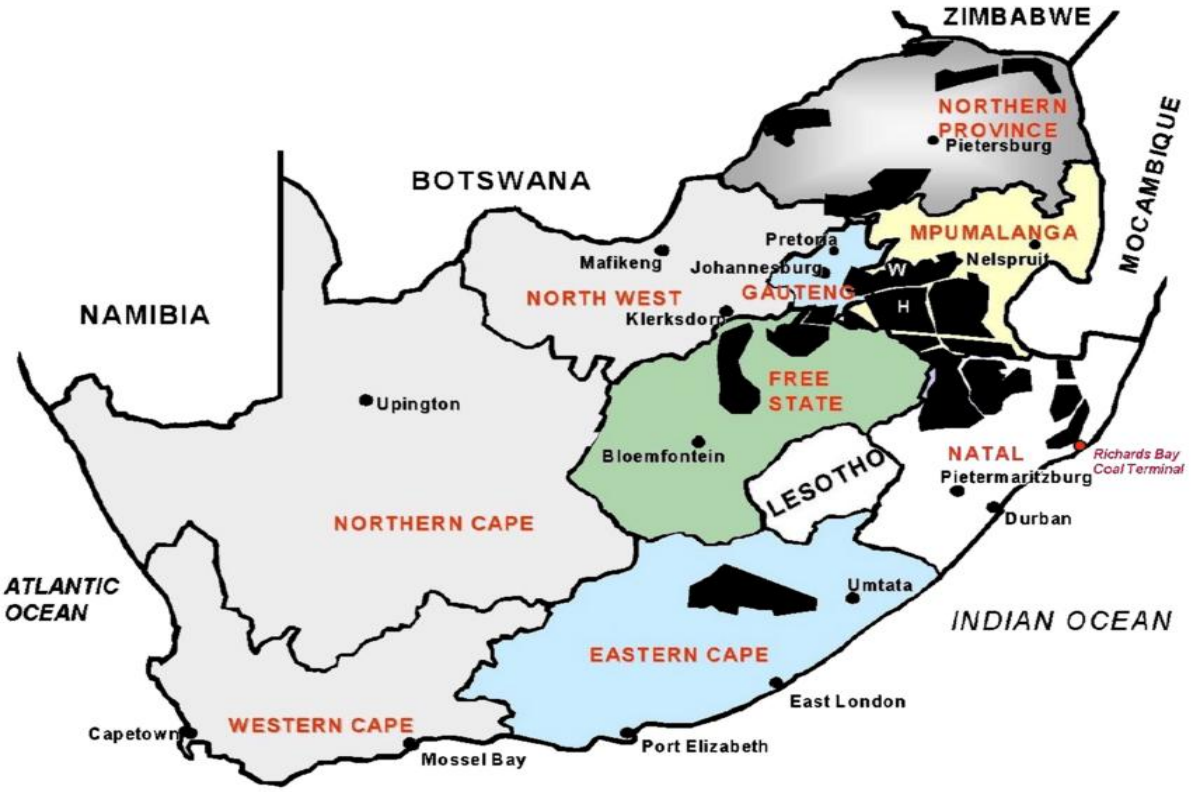

Figure 2-1: Distribution of South African coal fields (Pinetown et al., 2007)

2.1.2 South African coal mineralogy

Coal is mostly made up of the fossilised remains of plant detritus that have been chemically altered throughout geological time (Osborne, 2013). It contains both inorganic micro-constituents which are made up of various minerals, and organic micro-constituents which are divided into 'macerals' deriving from maceration of plant matter (Thomas, 2013). Macerals are grouped into **inertinite** from oxidised plant detritus, and fossilised charcoal, **exinite** (liptinite) from spores, resins, and cuticles, as well as **vitrinite** from woody materials (Van Niekerk et al, 2010; Speight, 2005). Coals often consist of associations of macerals which have distinct physical and chemical characteristics.

The inorganic matter in coal is its non-combustible fraction, which commonly consist of minerals such as calcite, siderite, quartz, clay, as well as pyrite and marcasite (Swaine, 1990). Mineral components can also be incorporated into coal organic structures, such as the organic sulphur found into macerals (Speight, 2012). Overall, the presence of minerals reduces the coal calorific value and coking properties (Osborne, 2013).

Coal is classified by type, rank, and grade. The coal type refers to its petrography which indicates the kind of plant residue from which it was formed (Osborne, 2013). Coal rank is the percentage of volatile matter it contains. Coals are commonly ranked as anthracite, bituminous, subbituminous, or lignite. The calorific value of coal rises as the proportion of volatile mater decreases (Speight, 2005). The grade of coal determines its economic value for a specific use. It is a measure of the coal quality, and it refers to the sulphur content, the ash fusion temperature, and the quality of trace elements in coal (Speight, 2012).

South African coals are Gondwana coals, which are mineral-rich, difficult to beneficiate, and have a wide range of rank and organic matter content (Falcon & Ham, 1988) (Sanders & Brookes, 1986). Minerals contained in South African coals are often deeply imbedded in the coal structure (Speight, 2012). This significantly affects beneficiation as minerals are often difficult to remove in the process due to their small size and dissemination. Additionally, minerals such as quartz are abrasive thus accelerating equipment wearing (Subba Rao & Gouricharan, 2016).

2.1.3 Impact of sulphur on coal processing and consumption

Pyritic sulphur serves as the predominant sulphide in coal; other forms of sulphur commonly found in coal include organic sulphur as well as sulphates. Other sulphide minerals including galena (PbS) and sphalerite [(Zn, Fe) S], are often found as well (Klima, Arnold & Bethell, 2012). Sulphate minerals include gypsum ($CaSO_4.2H_2O$), its anhydrite ($CaSO_4$), barite ($BaSO_4$), as well as several iron sulphates (Prayuenyong, 2002). The coal matrix contains a complex structure wherein organic sulphur is covalently bonded, making it an integral component. As a result, the physical removal of organic sulphur from coal by separation is challenging in comparison to pyritic sulphur (Subba Rao & Gouricharan, 2016).

The conversion of sulphur contained in coal to sulphur dioxide during combustion decreases its energy yield. Further, sulphur dioxide is a pollutant gas which is the main cause of acid rain (Speight, 2012: Aller et al., 2001). Sulphuric acid and hydrogen sulphide result from high sulphur coal combustion. Moreover, carbon dioxide, a by-product of the coal combustion reaction, is the principal contributor to the greenhouse effect (Mishra et al., 2014). Additionally, acid rock drainage is induced by sulphide minerals, notably pyrite, being exposed to oxygen and moisture and undergoing oxidation during and after mining operations or in mine waste dumps (Thomas, 2013). This is the main cause of water contamination from coal mining.

2.1.4 Coal beneficiation and waste generation

Coal beneficiation

Mined coal, often referred to as “run-of-mine coal” or ROM coal, is made up of different size fractions and contains undesired impurities. Coal beneficiation (washing) entails all the activities required to make the ROM coal marketable and of consistent quality (Speight, 2016).

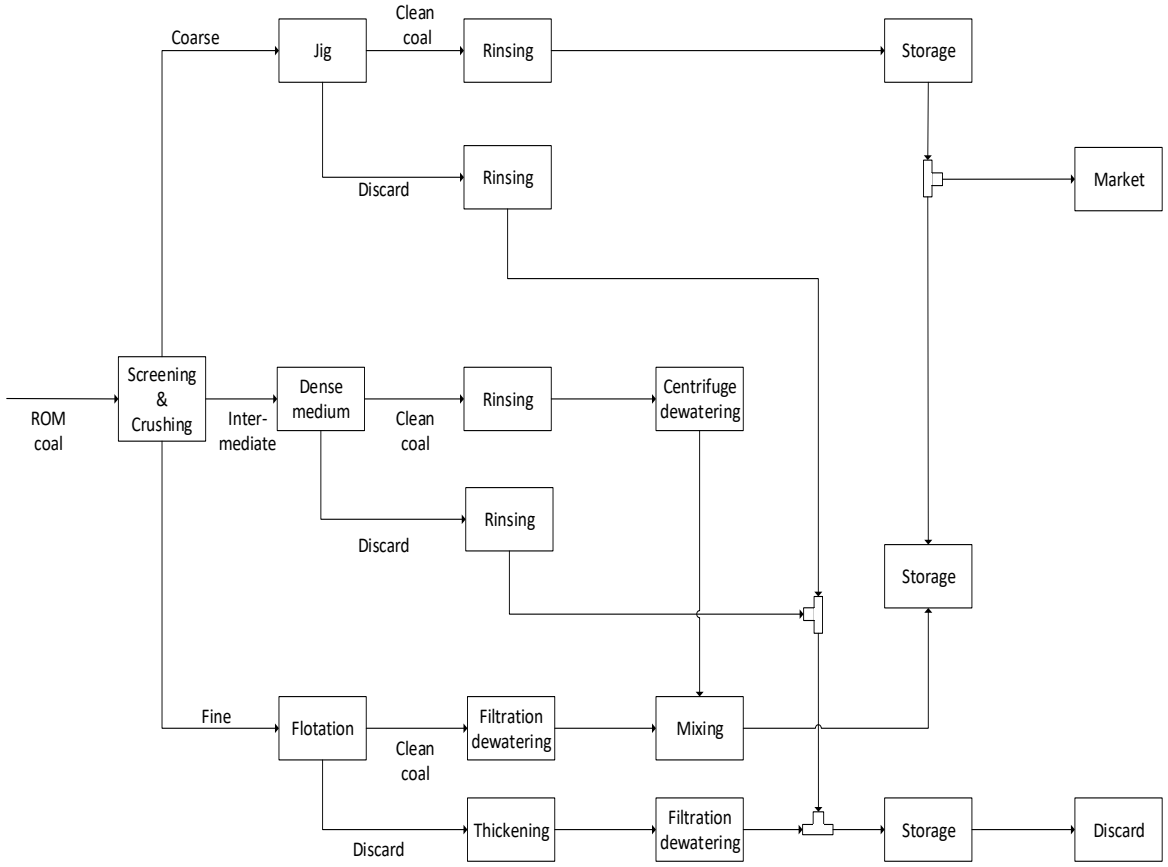

Figure 2-2: Typical coal beneficiation plant flowsheet adapted from (Chiang & Cobb, 2000)

Coal beneficiation, commonly referred to as coal preparation, aims to enhance the calorific value of coal for immediate utilization in steam and power generation, as well as for diverse applications including chemical feedstock, liquefaction, and gasification (Speight, 2012). Coal combustion flue gases contain sulphur oxides (SO_x), nitrogen oxides (NO_x), and hazardous metal compounds due to the presence of pollutants such as sulphur, nitrogen, and ash yield (Chiang & Cobb, 2000); these may be reduced through appropriate coal beneficiation. Coal beneficiation relies on size and density differences. Figure 2-2 depicts a standard coal beneficiation plant, with the various coal size fractions treated using different beneficiation

techniques. Coal is reduced in size and screened before the separation of impurities, dewatering, and drying.

Coarse coal (**150-10 mm**): Coarse coal is washed using gravity-based separation equipment, such as jigs (Subba Rao & Gouricharan, 2016). Natural drainage and filters are used to dewater coarse coal following separation, this depending on the mode of transit and application (Chiang & Cobb, 2000).

Intermediate coal (**10-0.6 mm**): Gravity separation is similarly used to clean intermediate coal. Dense medium baths, concentrating tables, and cyclones are utilised to accomplish this. Next, the coal is dewatered via sieve bends or centrifuges (Osborne, 2013).

Fine coal (**0.6-0.15 mm**): Fine coal can be treated using a range of technologies depending on economic feasibility. Efficient removal of impurities is achieved using non-gravimetric washing methods, such as froth flotation. Fraction of fine coal passing through 0.15 mm are referred to as ultra-fines and are typically processed similarly to fines. For fine coal dewatering, more complex mechanical devices such as centrifuges and vacuum filters are needed. To achieve acceptable moisture content, thermal drying is often required additionally (Leonard, 1991).

Coal beneficiation wastes

Significant quantities of waste are produced during coal mining activities. The extraction of coal necessitates the movement of substantial volumes of soil, while cleaning procedures facilitate the separation of non-combustible substances from coal. Depending on the source, a coal preparation plant can reject 20 to 50% of the run-of-mine coal it processes as waste (Osborne, 2013). Coal mining and beneficiation operations are related to a variety of wastes (Speight, 2012), namely:

- **Overburden**: Consists of the soil, rock, and other minerals that lie above the coal seam.
- **Coal discards**: Refers to poor quality coal often containing stones and rocks with high ash and sulphur content. As a result of beneficiation, discards contain high mineral concentrations (Kundu et al., 2021).
- **Coal tailings**: Refers to fine and ultra-fine coal particles (slurries) generated from the de-sliming process in the coal preparation plant.

The bulk of well-liberated coals in the coal-producing regions of the world have already been mined (Klima et al., 2012; Osborne, 2013). Coals in South Africa are mostly poorly liberated and require substantial crushing prior to washing (de Korte, 2010). Consequently, the extraction and processing of South African coal result in the generation of significant amount

of waste. These are typically piled in discard dumps or pumped into slurry pounds without sufficient consideration for their impending long-term environmental impact. Nonetheless, stringent environmental regulations have forced mining operators to implement more sustainable waste management practices (DME, 2001). The disposal of coal processing waste presents a significant hazard to nearby communities and ecosystems due to their capacity to generate acid rock drainage with associated metal deportation, thereby contaminating soils, as well as surface and groundwater sources (Younger et al., 2002).

Characterisation of the various types of South African coal processing wastes is shown in Table 2-1.

Table 2-1: South African coal waste characteristics (DME, 2001)

Coal waste	**Discards**	**Ultra-fines**
Calorific value (MJ/kg)	11 – 14	20 – 27
Sulphur (%)	1 – 5	<2
Fixed carbon (%)	18 – 24	41 – 56
Volatiles (%)	16 – 24	41 – 56
Ash (%)	30 – 60	10 – 50

The relatively high sulphur content (mostly pyritic) constitutes the primary environmental concern posed by coal processing waste material. When pyrite (FeS_2) is exposed to water and air, it produces sulphuric acid (H_2SO_4) and iron hydroxide [$Fe(OH)_2$]. Additionally, acidic leachate causes heavy metals to dissolve, which seep into surface and ground water, disrupting marine habitats (Speight, 2012).

Ultra-fine slurries have a non-negligible calorific value (Table 2-1), they have potential to be recovered as fuel for combustion in power plants. However, efficient dewatering of the slurry is required for this waste management solution to be environmentally and economically sound (Klima et al., 2012).

2.2 ARD generation

2.2.1 Formation of ARD resulting from sulphide oxidation.

ARD formation entails the oxidation of sulphide minerals; the reaction is carried out through both chemical and biological means with the involvement of biological oxidation having a rate determining impact (Jiao et al., 2023):

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+$$ Eq 1

The reaction that converts Fe^{2+} to Fe^{3+} consuming protons is as follows:

$$4\,Fe^{2+} + 4\,H^+ + O_2 \rightarrow 4\,Fe^{3+} + 2\,H_2O$$ Eq 2

The Fe^{3+} ion possesses the capability to function as an electron acceptor in the context of further pyrite oxidation, or alternatively, it can engage in a hydrolysis reaction with water, resulting in the release of further protons in the following manner:

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+$$ Eq 3

$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_3 + 3\,H^+$$ Eq 4

Sulphur oxidising micoorganisms allow the regeneration of the protons as:

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$$ Eq 5

The overall reaction is acid froming:

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,SO_4^{2-} + 16\,H^+$$ Eq 6

The coexistence of water and oxygen enhances the process of pyrite oxidation, resulting in the formation of Fe^{2+} ions. These ions subsequently undergo further oxidation to Fe^{3+} according to Eq. 1 and Eq. 2. Iron-oxidising micro-organisms catalyse this process, these microorganisms use Fe^{2+} as an energy source by oxidising it to Fe^{3+} (Hogg, 2005).

The initial stage in the progression of ARD involves oxidation facilitated by the presence of oxygen. Once underway, Fe^{3+} quickly becomes the dominant oxidising agent under acidic conditions (Eq. 3), and thus further oxidises pyrite. The oxidation reaction is regulated by the acidity of the environment, whereby the interaction between Fe^{3+} and water leads to the formation of ferric hydroxide (Eq. 4) with the removal of ferric iron by precipitation as $Fe(OH)_3$ when the pH exceeds 3.5. This compound is accountable for the distinctive red colour observed in waters contaminated with ARD. Proton regeneration is catalysed by sulphur oxidising microorganisms as they add oxygen to reduced sulphur species such as thiosulphate (Eq. 5). This allows the leaching of acid soluble minerals. When assessing the overall reaction

(Eq. 6), the process results in acid formation. Hence the very acidic environment is created by the foregoing reactions.

2.2.2 Factors influencing ARD formation.

Microbial activity

Acidophilic micro-organisms catalyse sulphide mineral oxidation, speeding up the process by several orders of magnitude (Johnson & Hallberg, 2003). Microorganisms involved in the oxidation of sulphide minerals include iron-oxidising micro-organisms (e.g., *Leptospirillum ferriphilum* and *Leptospirillum ferrooxidans*), sulphur-oxidising microorganisms (e.g., *Acidithiobacillus thiooxidans*), as well as iron- and sulphur-oxidising micro-organisms (e.g., *Acidithiobacillus ferrooxidans*).

Iron-oxidising microorganisms usually live in acidic (pH lower than 4), aerobic environments rich in both reduced-iron and -sulphur compounds. Microorganisms classified as *A. ferrooxidans, L. ferrooxidans and L. ferriphilum* are the main species competing for their communal substrate, Fe^{2+} (Schaechter et al., 2013). However, *A. ferrooxidans* is a chemolithoautrophic bacterium as it generates energy from the oxidation of Fe^{2+}, as well as that of elemental and partially oxidised sulphur. The oxidation of Fe^{2+} to Fe^{3+} allows a rapid oxidation of sulphide minerals, as Fe^{3+} is a strong oxidant. Iron-oxidising microorganisms and in many cases archaea, therefore, enable the oxidation of sulphide minerals using an indirect mechanism (Watling, 2006).

Sulphur oxidising microorganisms use sulphur compounds as sources of energy (Lederberg, 2000). These metabolic abilities can be found in extremely acidic environments, which often contain elevated concentrations of inorganic substrate (Schaechter et al., 2013). Sulphur-oxidising microbes allow the oxidation of polysulphides and elemental sulphur to sulphate. *Acidithiobacillus ferrooxidans* can oxidize both Fe^{2+} and sulphur compounds. The sulphur oxidisers: *Sulfobaccillus sp., Acidithiobacillus caldus and Acidithiobacillus thiooxidans* are three of the most common microorganisms found in heaps and dumps (Watling, 2006).

Acidophilic microorganisms accelerate the solubilisation of metal sulphides, causing acid rock drainage. They essentially produce the leaching chemicals as well as the environment in which the leaching reaction occurs (Rawlings, 2005).

Ambient conditions

The production of ARD is significantly influenced by the environmental conditions surrounding exposed sulphide-bearing ore. The three basic factors of climate that govern rock weathering are the amount of precipitation relative to evaporation, humidity, and temperature (Plumlee &

Travis, 1999). The weathering of minerals is a key factor in understanding acid rock drainage, since disintegration of the rocks containing metal sulphides accelerate the rate of acid generation through the increase in reactive area (Matsumoto et al, 2017).

The rate of sulphide mineral oxidation is enhanced in humid climate, as high humidity and warm temperatures constitute favourable conditions for microorganisms responsible for the leaching reactions (Borek, 1994). Dry climates tend to favour lower pH and higher metal contents in waters affected by ARD. This is explained by the lower dilution caused by fresh water and the intensified evaporation-induced concentration of acidic substrates and metals (McCarthy, 2011; Nordstrom, 2009)

Mineralogy of mine wastes

The physical and chemical properties of mineral wastes exert a significant influence on both the abundance and rate of ARD formation. The acid producing potential arising from the presence of sulphides, such as pyrite, within the waste is offset by the occurrence of acid neutralizing reactions following the dissolution of acid-consuming gangue minerals (Becker et al., 2015). Acid generating minerals are mainly constituted of iron sulphides, characterised by metal/ sulphur ratios of less than 1 and sulpho-salts such as enargite (Cu_3AsS_4) (Nordstrom & Alpers, 1999). A variety of carbonates (calcite, dolomite), aluminium hydroxide, ferric oxyhydroxide, silicates and aluminosilicate minerals provide the most important pH-buffering reactions in mineral deposits as they react to consume the acid generated during sulphide oxidation (Plumlee, 1997).

The techniques employed to extract and process minerals during mining exploitation greatly affect the nature and volume of ARD generation. The two major factors contributing to this are the amount of disturbance generated and the amount of mineralised rock exposed to weathering (Plumlee, 1997).

2.3 Characterisation of ARD

Ensuring the reliable prediction of the prospective development of ARD derived from ores abundant in sulphides or mining byproducts is of utmost importance to facilitate suitable remediation measures within the affected area. The assessment of the quantities of acid-generating and acid-neutralizing constituents present within the mineral composition is employed to delineate minerals with potential acid-generating capabilities. The introduction of acidic conditions can be alleviated through the dissolution of acid-neutralizing minerals, e.g., carbonates present in the mineral structure (Benzaazoua et al., 2000). While both the extent of these reactions and their relative rates are of importance in these predictions, characterisation of waste mineralogy with respect to ARD potential has traditionally only

considered the relative extent of these reactions when reacted to completion (Harrison et al., 2020).

2.3.1 Static characterization

The primary objective of static ARD characterisation tests is to determine the maximum potentials for acid production and acid neutralization (Lapakko & Lawrence, 1993). These assays are quite straightforward and provide a screening tool for mineral characterisation, with a result that requires additional characterisation work. However, standard static tests have intrinsic constrains, such as: (i) their inability to accurately replicate natural conditions in terms of fluid extraction and pH, (ii) their tendency to overestimate potential acidity due to inadequate consideration of the sample's mineralogical composition, (iii) they do not consider the role of ARD forming microorganisms (Parbhakar-Fox & Lottermoser, 2015).

Acid Base Accounting

The acid base accounting (ABA) assays quantify the disparity existing between components that generate acid and those that consume acid within a mineral. The outcome is classified into three categories: "acid-forming," "non-acid forming," or "uncertain" (Stewart, Miller & Smart, 2006). The ABA test presents findings in terms of net acid producing potential (NAPP), which refers to the difference between the maximum potential acidity (MPA) and the acid neutralising capacity (ANC) (Broadhurst et al., 2013). The NAPP is quantified as the equivalent weight, measured in kg, per ton of H_2SO_4 (Azcue et al., 1999).

$$\mathrm{NAPP} = \mathrm{MPA} - \mathrm{ANC} \qquad \text{Eq 7}$$

where: $\mathrm{MPA} = \%S \times 30.6$ kg H_2SO_4 / ton

ABA

Net Acid Generation

Using H_2O_2 as an oxidant, net acid generation (NAG) assays assess the acid production potential by allowing both acid generating and acid neutralising reactions to happen concurrentlyFeS2+15⁄2⁄$H_2O_2 \rightarrow \mathrm{Fe(OH)_3} + 2\,\mathrm{SO_4^{2-}} + 4\,\mathrm{H^+} + 4\,\mathrm{H_2O}$

Eq 8) (Broadhurst et al., 2013). To measure the sample equivalent NAPP, the solution pH (NAG_{pH}) is first recorded, then the solution is back titrated to a pH of 4.5, followed by a second titration to pH 7.0 (Stewart et al., 2006).

$$\mathrm{FeS_2} + \frac{15}{2}\mathrm{H_2O_2} \rightarrow \mathrm{Fe(OH)_3} + 2\,\mathrm{SO_4^{2-}} + 4\,\mathrm{H^+} + 4\,\mathrm{H_2O} \qquad \text{Eq 8}$$

The standard NAG test produces a higher level of precision when determining the potential for acid formation in the field compared to the ABA test as it gives an explicit empirical assessment of total sample reactivity (Charles et al., 2015). However, due to organic acid effects, the NAG method may exaggerate the acid producing ability of materials with low acid generating potential (Broadhurst et al., 2013).

Static ARD classification

Results obtained from static ARD tests provide broad guidelines for ARD production and enable the comparison of different samples. A table (such as Table 2-2) or a graph (such as Figure 2-3) are commonly used to summarise the results of ABA and NAG tests to better visualise the sample's acid producing potential.

Table 2-2 NAPP and NAG_{ph} results classification (Opitz, 2013) after (Stewart et al, 2006).

NAPP Result [kg H_2SO_4/ ton]	**NAG_{pH} Results**	**Sample Classification**
NAPP≤ 0	$NAG_{pH} \geq 4.5$	Non-acid forming
NAPP≤ 0 & $NAG_{pH} \leq 4.5$ or NAPP ≥ 0 & $NAG_{pH} \geq 4.5$		Uncertain
NAPP≥ 0	$NAG_{pH} \leq 4.5$	Acid forming

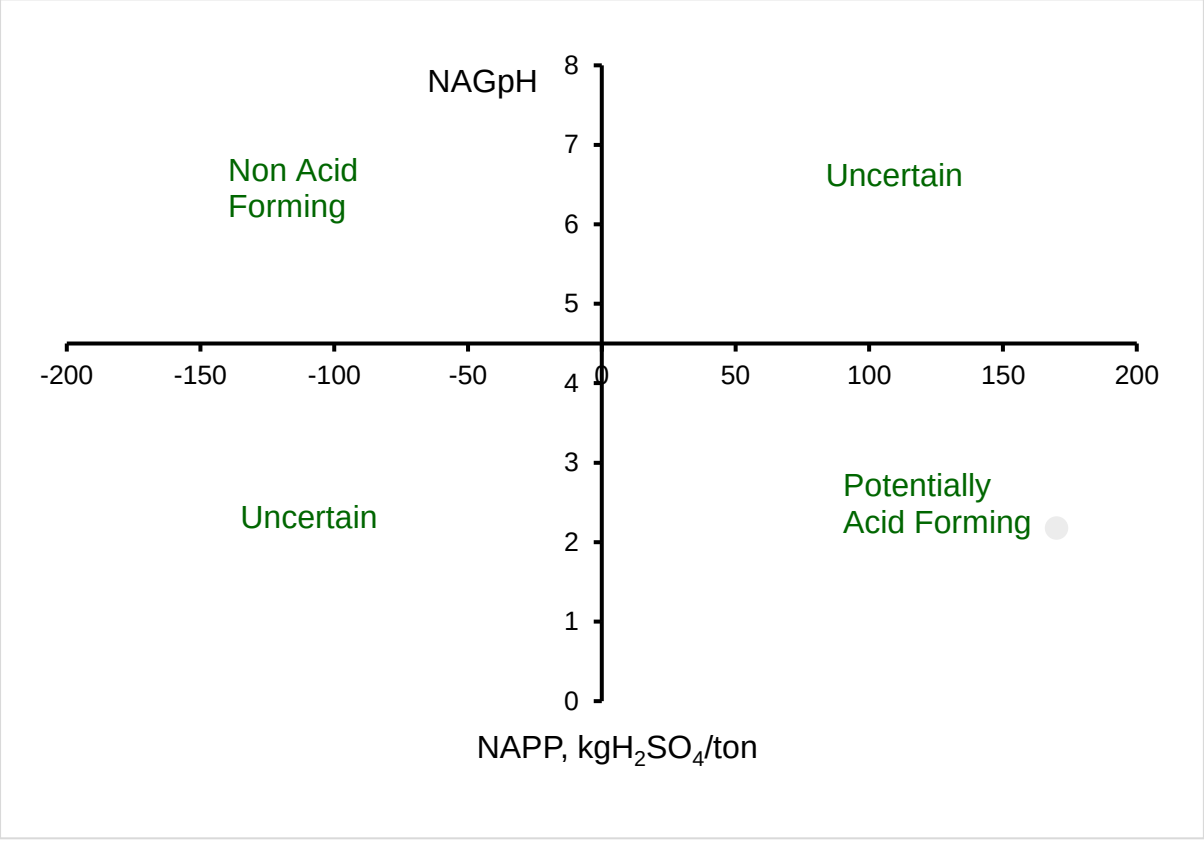

Figure 2-3: Combined static test classification plot (Stewart et al, 2006)

2.3.2 Kinetic characterisation

Kinetic ARD characterisation tests aim to mimic the cyclic wetting/drying and flushing of minerals. These fluid parameters provide a more accurate assessment of the duration of possible ARD generation (Parbhakar-Fox & Lottermoser, 2015). Leach column tests and humidity cell tests are two of the most utilised kinetic tests. In standard tests (humidity cells; ASTM D5744-96), samples are subjected to oxidation, and washed with deionised water after a set amount of time (Dold, 2017).

Some of the shortcomings related to this method include the extended time frame required to perform the test as it takes months to years to obtain meaningful results, the fact that they do not account for microbial activity and are difficult to reproduce (Broadhurst et al., 2013; Harrison et al., 2013; Harrison et al., 2020a; Stewart et al., 2006).

2.3.3 Microbial characterisation

The microbial contribution in ARD generation is overlooked by static and kinetic ARD characterisation tests. The acid-producing capacity of mineral wastes has been assessed using shake flask experiments, which include microbial activity monitoring (Bruynesteyn & Hackl, 1982). These tests suffer from several limitations. Firstly, they utilise a single microbial species, thereby disregarding the intricate impact of microbial activity on ARD generation. Secondly, they neglect to consider the relative reaction rates of acid generation and neutralisation, further diminishing their comprehensiveness. To tackle these obstacles, the UCT biokinetic test was developed with the intention of incorporating the influence of microbial activity in the formation of ARD and providing quantitative information pertaining to the kinetics of acidification and neutralisation reactions that occur after mineral liberation. The inception of this concept was initially introduced by (Hesketh et al., 2010a) and further expounded upon by Broadhurst et al., 2013; Opitz et al., 2016; Opitz et al., 2018; and Guseva et al., 2021.

2.4 ARD prevention and treatment

The management of ARD pollution includes both prevention and treatment strategies. ARD prevention methods focus on minimising the interaction between oxidants and sulphide-bearing minerals, with the goal of reducing the formation and release of acidic compounds. On the other hand, treatment methods use chemical agents to effectively neutralise the acidity generated by ARD and restrict the release of metal ions into the environment.

2.4.1 ARD prevention

Covers

Cover systems are placed over sulphur-bearing mineral wastes to decrease their acid-generating potential. Covers aim to limit the oxygen migration to the underlying acid producing waste material as well as to function as a water infiltration barrier. Cover systems are classified based on their specific design objectives. Oxygen transport and oxygen consuming barriers are obtained by laying a cover composed of oxygen consuming materials such as wood wastes or other organic debris (Bussière et al., 2004). Infiltration barriers use components with low permeability such as clay soils to minimize moisture flux by providing a low conductivity layer, thus isolating the acid-generating materials from water (MEND, 2004). The selection of a cover system is dictated by economic considerations as well as technical feasibility factors such as the waste material type (tailings, waste rock) and reactivity, the site hydrogeologic setting, and climate conditions (Demers et al., 2008).

Acid-producing tailings are often disposed in pounds or lakes, which constitute water covers (Skousen et al., 2019). Submerging mineral wastes prevents acid generation by effectively constituting an oxygen barrier and reducing the wastes reactivity (MEND, 2004). Covers comprised of desulphurised tailings are used as an alternative to water covers to minimize the oxygen migration to acid-generating mine wastes (Demers et al., 2008). Cover systems consisting of desulphurised tailings layers offer both economic and environmental benefits due to the abundant availability of tailings on mining sites. By incorporating these tailings into the ARD prevention strategy, the need for additional land disturbance is avoided. The integration of desulphurised tailings as a substitute for fine-grained soils in covers with capillary barrier effects (CCBE) is a widely embraced approach due to its effectiveness in mitigating ARD (Bussière et al., 2004). When fine particles are layered on top of coarse particles, the capillary barrier effect arises due to their difference in size distribution (Lessard et al., 2018).

Co-disposal and blending

Mineral wastes are typically deposited in dumps with porous structures; this promotes water permeation, oxygen diffusion, and subsequently facilitates the infiltration of water and diffusion of oxygen. Such conditions contribute to the generation of ARD. However, the generation of ARD can be effectively prevented by co-disposing benign materials alongside acid-generating waste rock and discards. This practice reduces the permeability of the waste materials, thereby restricting the access of oxygen, water, and other aggressive oxidants to the mineral surface of the waste, consequently mitigating the occurrence of ARD (Kotsiopoulos & Harrison, 2017). The acid-generating waste rock and non-toxic tailings are co-disposed in one of two arrangements: a layered configuration, characterized by their alternating deposition in

distinct strata, or a blended packing configuration, where the waste rock and benign tailings are thoroughly mixed to form a homogeneous amalgamation (Wickland et al., 2006a; Wickland et al., 2006b). Kotsiopoulos & Harrison (2017) examined the efficacy of co-disposing coal interburden with benign tailing in preventing ARD. The tailings were acquired from the previous flotation of ultrafine coal for desulphurisation purposes (Kazadi Mbamba et al., 2012). Long-term results pointed to a successful neutralisation of the acid-generating waste rock with either layered or blended configurations. This was owing to decreased permeability, effluent flow limitation, structural integrity of the ore deposit as well as the desulphurised tailings' neutralisation capacity (Kotsiopoulos & Harrison, 2018).

Mjonono et al., (2019) investigated several packing configurations to optimise the efficiency of coal waste rock and coal fines co-disposal. Decrease in voidage between coal waste rock particles allowed an increase in bed stability thus a more effective ARD prevention. Co-disposing waster rock and benign tailings presents important environmental and economic advantages. The tailings fill the gaps between the waste rock, restricting air and oxygen flow, therefore preventing the generation of ARD. The mixture of tailings and the waste rock results in enhanced stability, thereby reducing the probability of experiencing catastrophic liquefaction failure. Moreover, co-disposal eliminates the necessity for a tailings dam, thereby alleviating the associated high maintenance costs (Wickland et al., 2006b).

Cemented paste backfill

Backfilling is a crucial process employed to mitigate the detrimental ecological impact arising from the discharge of mining wastes. This is accomplished by placing the waste back into the cavities created after mineral extraction. This technique provides numerous benefits, including enhanced ground stability, heightened security of mining infrastructure, augmented productivity, diminished land requisites, minimised disturbances associated with tailings disposal, and, therefore, reduced expenditures pertaining to environmental management, rehabilitation, and mine closure (Dorricott & Grice, 2002). Cemented paste backfills (CPB) have been increasingly used in underground mines as a structural support and can serve as both an ARD prevention method by stabilising the pollutants contained in the wastes and as a sustainable alternative to traditional mine waste disposal methods. CPB are typically made of wet tailings (75 – 85 % solids), a binding agent (3 – 7 wt%) and water (Benzaazoua et al., 2008). The performance of the backfill in terms of strength and stability can be significantly influenced by the physical, chemical, and mineralogical properties of its constituent components, thereby posing a potential risk of collapse (Ercikdi et al., 2009). Several additives such as powdered fly ash, Portland cements, and blast furnace slag obtained from smelting processes are commonly employed as binding agents. However, it is crucial to note that the

formulation and utilisation of CPB composites necessitate rigorous techno-economic analysis (Belem & Benzaazoua, 2008).

2.4.2 ARD treatment

ARD pollution treatment methods focus on the neutralisation of the acidic effluent generated and dissolved metals precipitation to meet specified limits. A wide range of treatment processes are used and are commonly categorized as active and passive approaches, contingent upon the availability of resources and the magnitude of the pollution. Continuous applications of alkaline chemical reagents are required for active ARD treatment (Johnson & Hallberg, 2005). Active treatment, while effective, incur significant expenses due to their long-term nature, spanning decades and entailing substantial investments in equipment, chemicals, and manpower (Skousen et al., 1998). Passive treatment systems, in contrast, do not rely on frequent chemical inputs. Instead, they harness naturally occurring chemical and biological mechanisms to counteract acidity, facilitate oxidation or reduction of metal pollutants, and induce their precipitation (Skousen et al., 2017).

Active treatment

Various chemicals commonly used in active treatment methods include limestone, soda ash, hydrated lime, caustic soda, and ammonia. The selection of an appropriate alternative is influenced by several technical and economic factors, such as acidity levels, flow rate, effluent metal concentrations, as well as the cost of reagents, labour, equipment, and the duration of treatment required (Skousen et al. 2000). A typical ARD chemical treatment facility consists of an input pipe or drain to allow the entry of contaminated water, storage tanks designed to contain the reagents utilised in the treatment process, a settling pond intended for the collection of precipitated metals, and an outflow point where water samples are regularly examined to ascertain compliance with predetermined contaminant thresholds (Skousen et al., 2019).

Much research has been presented on the use of biological sulphate reduction for the conversion of sulphate to either sulphides with metal recovery as metal sulphides or to elemental sulphur. While this has been applied to treatment of sulphate rich process effluents, its cost has, to date, not enabled its use for treatment of ARD.

Passive treatment

While active ARD treatment techniques demand a constant allocation of chemicals in addition to the lasting energy and labour input, passive ARD treatment systems offer minimal operating costs and require only intermittent maintenance with little additional energy supply (Park et al., 2019). Passive ARD treatment strategies use natural processes to neutralise acidity and

precipitate metal contaminants. The design and selection of an adequate passive ARD treatment strategy relies on the site characteristics as well as effluent volume and chemistry. Passive ARD treatments strategies are classified as biological or geochemical (Skousen et al., 2017). Biological passive ARD treatment methods such as aerobic and anaerobic wetlands use organic matter to allow the microbial reduction of sulphates and the absorption of metal pollutants. Geochemical technologies include anoxic limestone drains, open limestone channels and leach beds. These methods use basic substances such as steal slag or limestone, mixed with the polluted waters, to neutralise the effluent acidity (Skousen et al., 2000). Marais et al. (2020) proposed a semi-passive approach to achieve biological sulphate reduction and partial sulphate oxidation in linear flow channel reactors. This technology has demonstrated to be an effective mitigation strategy to ARD pollution with the added benefit of elemental sulphur recovery (Marais et al, 2022).

2.5 Bioleaching

Bioleaching refers to processes that extract metals from low-grade ores or waste by oxidising the metals using microorganisms, in particular acidophilic microorganisms, and generating soluble compounds (Hogg, 2013). Bioleaching processes are conducted in highly aerated, open non-sterile environments such as continuous flow stirred tank reactors, heaps, or irrigated dumps (Rawlings & Johnson, 2007; Harrison, 2016).

2.5.1 Chemical mechanism

Bioleaching mechanisms are often categorised as contact and non-contact leaching to convey information about the physical location of the cells involved in the reactions. Contact bioleaching involves an electron transfer directly from the microorganisms to the metal sulphide to which they are adhering. Non-contact bioleaching occurs through Fe^{3+} ions acting on the mineral as the metal sulphide-oxidising agent; these Fe^{3+} ions are produced by oxidation of Fe^{2+} ions, either by planktonic microorganisms or those adhering to the mineral surface but not necessarily adhering directly to the mineral sulphide (Vera et al, 2013).Two distinct indirect chemical pathways describe metal sulphide leaching: the thiosulphate and polysulphides mechanisms, and both depend on the mineral species involved (Schippers & Sand, 1999).

The thiosulphate pathway takes place on leaching acid-non-soluble metal sulphides. It consists of a series of electron extractions, where hydrated Fe^{2+} ions oxidise the disulphide component of FeS_2 to a sulphonic acid group. The bond between the iron and the two sulphur

atoms is severed, resulting in the production of hydrated Fe^{2+} ions and thiosulphate (Vera et al, 2013). Thiosulphate is next reduced to tetrathionate, which is in turn decomposed to produce elemental sulphur, sulphide, pentathionate and trithionate (Rohwerder et al., 2009). Eq 9 and Eq 10 outline the overall thiosulfate pathway.

$$FeS_2 + 6\,Fe^{3+} + 3H_2O \rightarrow {S_2O_3}^{2-} + 7\,Fe^{2+} + 6H^+ \quad (1) \qquad \text{Eq 9}$$

$${S_2O_3}^{2-} + 8\,Fe^{3+} + 5H_2O \rightarrow 2{SO_4}^{2-} + 8\,Fe^{2+} + 10H^+ \quad (2) \qquad \text{Eq 10}$$

Acid soluble minerals such as pyrrhotite (Fe_2S_8), troilite (FeS), sphalerite (ZnS), hauerite (MnS_2), galena (PbS), and chalcopyrite ($CuFeS_2$) in contrast are solubilised by a combination of electron extractions by Fe^{3+} and proton assault. This breaks the bond between the metal and sulphur component. However, the sulphur component is concurrently oxidised in the presence of Fe^{3+} to form the free sulphur molecule which is then reduced to polysulphides and polysulphides radicals as shown in Eq 11 & Eq 12 (Huang & Li, 2014).

$$MS + 6\,Fe^{3+} + H^+ \rightarrow M^{2+} + 0.5H_2S_n + 6\,Fe^{2+} \quad (n \geq 2) \qquad \text{Eq 11}$$

$$0.5H_2S_n + Fe^{3+} \rightarrow 0.125S_8 + Fe^{2+} + H^+ \qquad \text{Eq 12}$$

$$1.5O_2 + 0.125S_8 + H_2O \rightarrow {SO_4}^{2-} + 2H^+ \qquad \text{Eq 13}$$

2.5.2 Microorganisms in bioleaching

Bioleaching processes are catalysed by certain microorganisms (microorganisms and archaea) using reduced iron and sulphur compounds as an energy source. Their aerobic oxidation provides electrons, which they use to produce adenosine triphosphate (ATP), while CO_2 from air provides the required carbon source for the typical autotrophic or mixotrophic species (Schaechter et al., 2013). Biooxidation of pyrite has often been linked to *Acidithiobacillus (At.) ferrooxidans* and *Acidithiobacillus (At.) thiooxidans* (Edward et al., 2022). Several commercial processes have been developed to use microbial consortiums including *Leptospirillum ferrooxidans, L. ferriphilum, At. Thiooxidans, At. Caldus* and *At. Ferrooxidans* to act as the biological catalyst is pyrite oxidation (Vardanyan et al., 2015).

Sulphur-oxidising microorganisms, including *At. Caldus* and *Sulfobacillus sp.*, play a crucial role in mineral decomposition by producing sulphuric acid from sulphides and elemental sulphur (Rawlings & Johnson, 2007).

2.5.3 Effect of temperature

Bioleaching is facilitated by a chemical leaching reaction coupled to microbial oxidation of ferrous iron to produce Fe^{3+} and reduced sulphur compounds to produce H^{+}. The impact of temperature is found on both components of the leaching process and is assessed using kinetic studies. On average, the pace of chemical reactions is multiplied by two for every 10 °C rise in temperature (Rawlings et al., 2003). Although the rates of chemical reactions improve as the temperature is raised, various microbial communities have temperature optima, hence the active microbial communities involved in the process change as the temperature vary (Olson et al., 2003). Microorganisms may be classified broadly according to the temperature range wherein they thrive. While not strictly established, the temperature-based classifications are as follows: psychrophiles (15 °C), mesophiles (15–40 °C), moderate thermophiles (40–60 °C), thermophiles (60–80 °C), and hyperthermophiles (>80 °C) (Plumb et al., 2008). Leaching processes operated at higher temperature thus require the involvement of thermophilic microorganisms. The transition of microbial community composition as temperature rises is well demonstrated by Tupikina et al. (2013). Microorganisms that thrive at high temperatures are often found in mining areas and natural hot-springs, and they include species with a sulphur-based metabolism (Lederberg, 2000).

2.5.4 Effect of Fe^{2+} and Fe^{3+} ion concentrations

Where the sulphidic mineral is well liberated and in good contact with the lixiviant, bioleaching is controlled by the activity of iron- and sulphur-oxidising microorganisms, which promote the regeneration of Fe^{3+} and acid throughout the leaching process (van Hille et al., 2010). The oxidation of Fe^{2+} to Fe^{3+} ion (Eq. 2), therefore, plays a crucial role in determining the process efficiency. Under aerobic conditions, Fe^{2+} readily oxidises to Fe^{3+} with oxygen as the electron acceptor. However, at lower pH, Fe^{3+} become the electron acceptor, oxidising pyrite to generate Fe^{2+} (Hesketh et al., 2010b). Optimal bioleaching conditions require fast Fe^{2+} to Fe^{3+} oxidation and are thus characterised by high redox potential (> 650 mV) (Watling, 2006).

2.6 Desulphurisation of coal

Removal of pyritic and organic sulphur present in coal is essential to increasing its economic value and has become an even more crucial part of coal processing as increasingly stringent

environmental regulation targeting pollutants such as sulphur oxide are implemented. Coal desulphurisation can be achieved using various technologies which include physical (mechanical), chemical and biological processes (Speight, 2016).

2.6.1 Physical coal desulphurisation

Physical desulphurisation of coal occurs during coal beneficiation due to specific gravity and differences in surface properties between coal and pyritic sulphur (Riazi & Gupta, 2016). Gravity separation is accomplished through the use of concentrating tables, jigs, and dense medium processes, thereby allowing the retrieval of thermal coal possessing a lower specific gravity ranging from 1.30 to 1.70 in contrast to pyrite, which has a higher specific gravity range of 4.95 to 5.10 (Osborne, 2013).

Driven by surface property differences between coal and pyrite, separation by flotation is one of the most extensively used desulphurisation methods in industry (Riazi & Gupta, 2016). The process typically requires the conditioning of the coal surface within the slurry, adhesion of hydrophobic coal particle to gas bubbles which float to the top of the flotation cell and create a stable coal-rich froth layer, while gangue minerals report to the tailings (Chiang & Cobb, 2000).

Although physical desulphurisation methods are efficient in removing pyrite and sulphates, organic sulphur separation from coal requires more aggressive processes (Laskowski, 2001).

2.6.2 Chemical desulphurisation of coal

Chemical desulphurisation involves the use of compounds selectively reacting with pyritic and organic sulphur whilst not affecting the coal matrix. The operations are often carried out at high temperature and pressure (Subba Rao & Gouricharan, 2016). Methods include acid and alkaline leaching, H_2O_2 oxidation, and solvent extraction. Acid and alkaline leaching consist of combining coal with either acidic agents such as hydro-chloric acid, nitric acid, hydrofluoric acid, ferric chloride, or alkaline compounds such as potassium hydroxide, and sodium hydroxide to extract sulphur while the mixture is stirred or heated (Ghosh et al., 2015).

Although effective in removing both inorganic and organic sulphur, chemical desulphurisation methods are energy intensive, application in industry is limited due to the high capital expenditure required (Xia & Xie, 2017).

2.6.3 Biological desulphurisation of coal

Biological desulphurisation processes leverage microorganisms for the degradation of sulphur compounds, offering a range of advantages compared to conventional physical and chemical approaches. Notably, these methods involve reduced capital and operating costs, attributed

to the minimal energy loss incurred during treatment. This cost-effectiveness stems from the use of ambient temperatures and atmospheric pressure, which facilitate efficient and economical operation (Gonsalvesh et al., 2008). Available technological options for biodesulphurisation of coal include heap leaching, leaching in lagoons and leaching in a stirred-tank reactor (Acharya et al., 2004). Coal particle size is a key factor influencing the efficiency of stirred tank reactor microbial desulphurisation. Size must typically be reduced to an extremely fine level to allow optimal pyrite liberation, particulate suspension, and microbial contact (Harrison, 2016; Çelik et al., 2019). Using stirred tank reactors, biological desulphurisation of finely ground coal has been conducted giving pyritic sulphur removal efficiencies as high as 90% (Rossi, 2013). In general, biodesulphurisation methods allow the removal of most pyritic sulphur. Organic sulphur removal is more challenging and requires the use of specific bacterial strains, such as those from the genera *Paenibacillus* and *Rhodococcus* (ElSawy & Gray, 1991).

2.7 Physio-chemical factors influencing heap bioleaching of coal discards

Heap bioleaching involves piling up crushed ore or, in this case, crushed coal discards atop an impermeable surface, while percolating a lixiviant through the packed bed and capturing the pregnant leach solution for further processing to recovery metals or sulphur or both. This approach presents itself as a cost-effective substitute for stirred-tank leaching, as it necessitates significantly reduced capital and operational expenditures (Bartlett, 1997; Petersen, 2016). The efficiency of heap bioleaching is contingent upon physical, chemical, and biological factors. Particle size, temperature and rate of irrigation are key physico-chemical factors influencing the heap leaching process (Cara et al., 2005).

2.7.1 Particle size

Particle size distribution (PSD) and its porosity significantly influences the extent of mineral liberation in heap leaching operations. PSD affects the fluid flow pattern inside the ore bed which subsequently determines the efficacy of contact between the leach solution, the ore particles, microbes, and mineral grains to be leached (Fagan-Endres et al., 2017). To explore the leaching of sulphic minerals for either metal recovery or sulphide removal or both, the impact of grains particle size has been explored using laboratory-scale column leach reactors. A smaller grain size would have the advantage of facilitating leach solution access to targeted mineral. However, this is negated by higher energy cost required for size reduction and increased leach solution consumption (Bartlett, 1997). Further, in heap leaching operations,

finer particle sizes are likely to reduce the bed's overall permeability to air and leach solution. Increasingly the importance of the nature of size reduction is being considered to recognise the potential for increasing liberation of the mineral grain through a combination of size reduction and porosity enhancement (Dobson et al., 2017; Fagan-Endres et al., 2017).

Particle size similarly impacts coal desulphurisation as it does metal leaching from low grade ores (Andrews et al., 1993). Particle size, coal type, coal porosity, liberation and exposed surface area are key parameters affecting coal desulphurisation. Smaller particle size and increased porosity mean larger exposed surface area thus improved liberation and more efficient sulphur leaching (Orsi et al., 1991). Additionally, smaller particle size allows better microbial access to the mineral site (Klein, 1998), speeding up desulphurisation and decreasing residence time.

Although it is favoured for better sulphur removal, finer coal particle sizes should be avoided since they increase the likelihood of poor bed permeability. In contrast, larger particle sizes prevent adequate pyrite or sulphur accessibility thus slowing the desulphurisation process (Andrews et al., 1993). Finding the smallest particle size that can successfully be desulphurised while preventing waterlogging in the bed is the necessary compromise required for the selection of a particle size in coal heap leaching operations. Agglomerating the finer particles generated during comminution is a potential solution to avoiding bed silting and maintaining adequate bed permeability. Further enhancing particle porosity while limiting size reduction can be advantageous.

2.7.2 Temperature

Heap bioleaching reaction rate is temperature dependent, as temperature enhances reaction rates both chemical and biological reaction rates, and hence metal and sulphur extraction (Section 2.5.3). Temperature regulation in heap leaching operations is achieved through the control of evaporation, accomplished by adjusting parameters such as heap height, irrigation rate, and aeration rate (Scheffel, 2002). Bench-scale column leach experiments have shown that temperature increases sulphur removal efficiency from coal (Aller et al., 2001; Morán et al., 1997). However, at higher temperatures, e.g. over 70 °C, lower oxygen, and carbon dioxide solubility may result in mass transfer constraints (Boogerd et al., 1990).

While optimising temperature in coal bioleaching operations, the risk of spontaneous combustion should always be considered. Spontaneous combustion of coal occurs during oxidation under specific conditions related to coal rank, particle size, moisture content, aeration, and temperature (Speight, 2005). Substances susceptible to spontaneously ignite have a self-heating temperature (SHT) at which they would begin to burn (Pone et al., 2007).

As coal reaches its SHT, the oxidation process will intensify, raising temperature and resulting in combustion (Kaymakçi & Didari, 2002). The implementation of covers, artificial barriers, and periodic compaction mitigate the risk of spontaneous combustion in coal stockpiles by inhibiting microbial oxidation (Fierro et al., 1999). Where accelerated oxidation is desired, the balance between optimising biological oxidation and controlling temperature is required.

2.7.3 Rate of irrigation

Efficient heap bioleaching entails counter-current flow of oxygen and leach solution through unsaturated void spaces in the ore bed (Petersen, 2016). As the leach solution perchlorates through the heap, a buoyancy gradient caused by variations in air temperature and composition drives air movement upwards (Bartlett, 1997). Ensuring even application of the irrigating solution across the heap is key. Spray or drip irrigation configurations are frequently used on heaps subject to operating conditions (Manning & Kappes, 2011). Standard irrigation rates in heap leaching range from 5 to 20 L/m^2/h (Petersen, 2016; Petersen & Dixon, 2007).

Higher irrigation rates imply that more solution meets the minerals, therefore improving leaching efficiency. However, irrigation rates close to 20 L/m^2/h are likely to decrease the microbial population due to cell detachment (Chiume et al., 2012). Conversely, low irrigation rates may lead to soluble salt build-up and high osmotic potential, negatively affecting microbial activity (Rawlings & Johnson, 2007; Edward et al., 2022). Selection of an adequate irrigation rate for a particular heap bioleaching operation is done through rigorous column leach reactor experiments.

Liquid holdup, the ratio of the heap liquid content to its overall volume, is essential in understanding heap leaching flow behaviour (Andrews et al., 1993). Liquid hold-up controls particle mass transfer, wetting efficiency, and liquid residence time distribution. Higher irrigation rates may generate liquid hold-up which threatens the bed structural integrity (Ilankoon & Neethling, 2012). The interaction between irrigation rate, fluid properties, packing on moisture content and residence time has been explored by Odidi et al., 2023ab.

2.8 Coal heap bioleaching experiments

Heap bioleaching presents potential to provide an economical and efficient technological option for the desulphurisation of coal and its wastes, whereas stirred-tank leaching requires milling of the coal waste and maintaining the entire coal mass in suspension. The latter present high capital and operating costs. It is proposed that heap leaching offers a simple and inexpensive alternative (Cara et al., 2005). Still, industrial implementation of coal

desulphurisation by heap bioleaching is rare due to, among other technical constraints, the lengthy residence time required to achieve adequate sulphur removal (Tillet & Myerson, 1987).

Studies have investigated the efficiency of coal desulphurisation using bench-scale leach column reactors simulating a vertical cross-section of a heap from top to bottom. A key factor affecting the process efficiency is the inoculum type; microbial consortia comprising iron- and sulphur oxidising microorganisms have yielded satisfactory results (Cara et al., 2003).

Inocula constituted of microorganisms native to the coal sample itself have been explored. Morán et al., (1997), achieved 46% of pyritic sulphur removal after 42 days of irrigation with a leach solution at pH 1.5. An enriched native mixture of chemolithotrophic microorganisms was also used by Gòmez et al., (2004), as inoculum to desulphurise a coal sample with 3.11 % total sulphur content, achieving 30% of pyritic sulphur removal after 60 days. Aller et al., (2001), used an enriched native inoculum to investigate the effect of temperature and pH on the desulphurisation efficiency. An optimum pH of 2.0 was found and decreasing temperatures were shown to reduce the sulphur removal.

A pilot heap leaching plant obtained was irrigated for 161 days, at which point 39% of pyritic, and 23% of total sulphur had been removed from the pilot heap made up of 6 tons coal with initial total sulphur content of 2.88%. The operation was conducted using a mixed culture of native microorganisms isolated from the coal (Cara et al., 2005). No data was presented on the quality of the residual coal or coal waste from these studies.

2.9 Summary of literature review

This literature review has presented an overview of the commonly used ARD prevention and treatment methods applicable to coal and its wastes. ARD is generated from coal wastes when pyrite found in these wastes is exposed to air and water, this results in the leaching of metals and other contaminants. Approaches to prevent ARD generation attempt to minimise the exposure of sulphide-bearing mineral to oxidant or to remove the sulphide present in the coal or coal waste. On the other hand, ARD treatment methods use chemicals or microbial processes to neutralise the produced acidity, recover the sulphur fraction to a different phase and contain the released metal ions.

Accelerated leaching of coal discards in heaps provides potential as a simple and cost-effective means of preventing ARD formation from these wastes. The effectiveness of coal heap leaching depends on physico-chemical and biological factors which include particle size, temperature, rate of irrigation, Fe^{2+} and Fe^{3+} ion concentration and inoculum type. Laboratory scale studies have shown the efficiency of heap bioleaching in desulphurising coal. However, the long residence time required to obtained satisfactory sulphur removal constitute a major

hurdle to the industrial application of the process. Literature suggests that technological advances and optimal process design would be required to implement heap bioleaching as an effective ARD mitigation method for coal wastes on a large scale.

In this dissertation, this potential is explored further to investigate the efficiency and efficacy of accelerated leaching of high sulphur coal discards, prior to long-term disposal or re-purposing, as an ARD prevention approach. The study focuses on both the extent and rate of leaching of the coal discards, the nature of the components of the leachate, and particularly the quality of the residual coal discards, both in terms of responsible disposal and in terms of re-purposing of the coal waste.

3 Materials and Methods

The experimental work in this study involved several steps. First, the mineral characterisation of the coal discards sample was conducted. This was followed by the characterisation of ARD generation potential. Next, the discards were leached in laboratory scale column reactors, with rate and extent of leaching explored following microbial inoculation with comparison to controls using the native microorganisms and an abiotic control. Lastly, the leached coal discards were characterised to assess the extent of desulphurisation and determine the acid producing capacity.

3.1 Materials

3.1.1 Coal discards sample and characterisation methods

The leaching experiment utilized coal discards sourced from the Emalahleni region of Mpumalanga, South Africa. The sulphur content of the coal discards was determined to be 10.4% by weight using the LECO S32 sulphur analyser, which adheres to the (ASTM D4239, 2018) standard high temperature method. The mineral composition was assessed using X-ray diffraction; EVA and TOPAS software were used to identify and quantify the minerals present. EVA supports all Bruker detectors and XRD scan types, offering a wide range of analytical capabilities, from data reduction and basic scan evaluation to detailed peak analysis, phase identification, quantification, and determination of crystallinity and crystallite size. TOPAS, a profile-fitting software, excels in quantitative phase analysis, microstructure analysis, and crystal structure analysis, uniquely integrating various profile-fitting techniques (Brucker). The composition of the samples, prepared as pressed pellets, was analysed utilizing X-ray fluorescence (XRF) spectrometry in the Department of Geological Sciences at the University of Cape Town, using a Panalytical Axios XRF spectrometer equipped with a rhodium end-window X-ray tube. Elemental analysis on the coal discards samples was conducted using inductively coupled plasma-mass spectroscopy (ICP-MS) at the Mintek Analytical Laboratory, University of Stellenbosch, using standard equipment and procedures.

3.1.2 Inoculum

The mixed stock culture used as inoculum was made up predominantly of a sulphur and iron-oxidising microorganisms, namely, *Acidithiobacillus caldus* and *Leptospirillum ferriphilum*, constituting 54.2% and 44.1% respectively. A semi-batch stirred tank reactor was used to grow

the inoculum culture at a temperature of 35 °C. A pyrite concentrate was used as the growth medium, and the culture was removed (30%) and replenished on a weekly basis.

3.2 Experimental apparatus

This project utilised a set of column reactors of 100 mm internal diameter available at the Centre for Bioprocessing Engineering Research (CeBER) at the University of Cape Town, to investigate the removal of sulphur from coal discards using bioleaching. The equipment has been extensively used as part of previous studies on hard rock ore bioleaching, allowing for comparison with a large collection of previous recoded data (van Hille et al., 2010; Chiume et al., 2012; Tupikina et al., 2011,2013).

Figure 3-1 and Figure 3-2 show the CeBER bioleaching column reactors. The five columns used for this study, were made up of PVC pipe with length of 500 mm and internal diameter of 100 mm., fitted with flanged top and bottom plates. The pipe was mounted on a stand and the packed material sat on a porous metallic plate with a diameter of 100 mm, located 435 mm form the top of the column. The columns were equipped with internal and external temperature probes, placed within the ore bed and on the external surface of the column respectively. The temperature inside the column could be regulated through an external heating coil and was measured at the centre point.

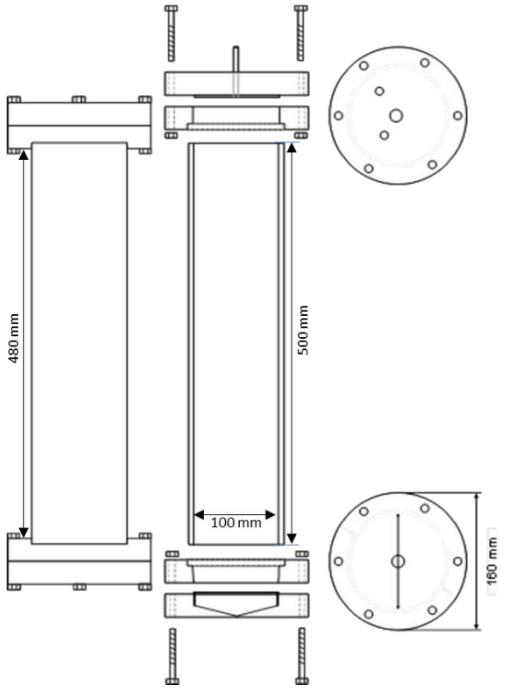

Figure 3-1: Schematic representation of CeBER bioleaching column reactor.

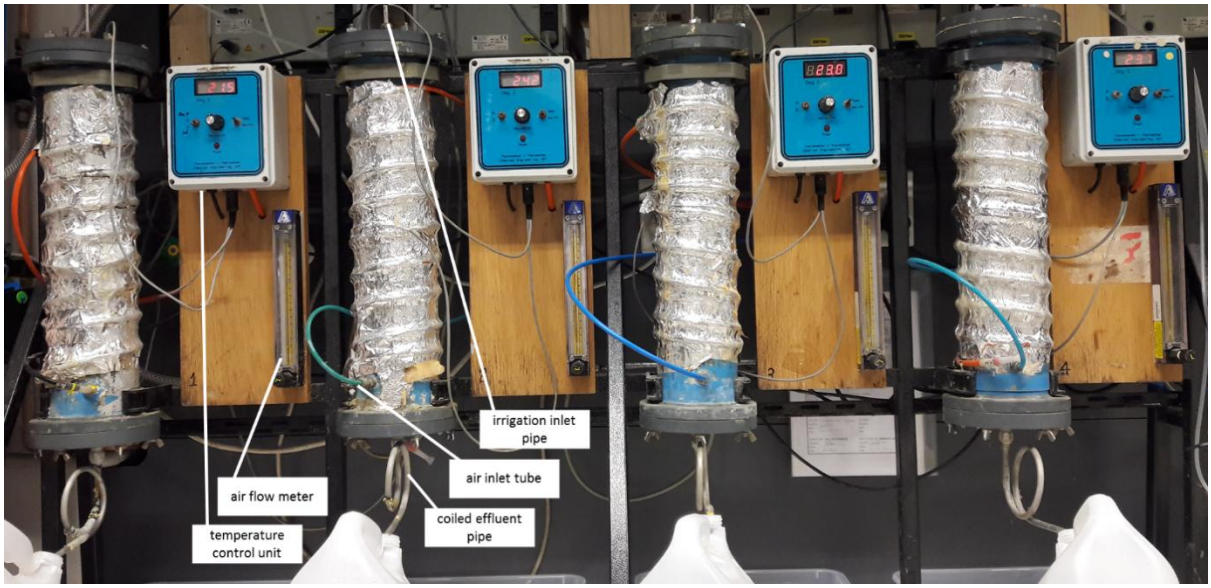

Figure 3-2: The CeBER bioleaching column reactors.

To provide adequate drainage, the baseplate was covered with marbles prior to the bed being packed on top of it. The bed was then topped with an additional layer of marbles to ensure smooth flow and good distribution of the leaching solution, entering from a single point. A Masterflex peristatic pump was used to continuously irrigate the bed with single flow-through and no recirculation to enable controlled conditions. The leach solution was collected at the base of the column where the effluent pipe was coiled to prevent air loss. Aeration was supplied from the bottom of the columns through an air distributor; a rotameter was used to control the air flow.

3.3 Experimental procedures

3.3.1 Coal discards sample preparation

The particle size distribution of the sample was determined subsequent to the passage of the coal discards through a 22.4 mm sieve, the d_{20} was measured at 3.7 mm and d_{50} as well as d_{80} at 9.0 and 14.3 mm respectively. The coal discards were agglomerated using 8 kg 98% H_2SO_4 per ton, holding finer particles together to promote better permeability.

3.3.2 Column tests experiment

Loading the columns

During agglomeration, the coal discards sample underwent inoculation with a mixture containing 10^{12} cells per ton. Each of the five columns employed in the investigation was filled

with ~ 3 kg of a representative portion of the agglomerated coal discard sample. This led to the establishment of a height-to-diameter ratio (H/D) of 3.6 in the column.

Column setup and leaching operation

The column setup is presented in Table 3-1, it consisted of five columns including a pair of control columns that were not inoculated. One of the two control columns was irrigated with acidified water at pH 1.5, while the other with deionised water at pH 7.0. Additionally, the setup comprised triplicate inoculated columns irrigated with acidified water at pH 1.5. The acidified water pH was set to 1.5 using 98% concentrated H_2SO_4 (Merck), and nutrients at various concentrations were added to the mixture (Table 3-2). Irrigation was done continuously from the top of each of the five column reactors at a rate of 5 L $m^{-2}h^{-1}$.

Table 3-1: Column setup

Columns	Irrigation	Inoculation
Column 1 (C1)	Acidified salts solution (pH 1.5)	Inoculated
Column 2 (C2)	Acidified salts solution (pH 1.5)	Inoculated
Column 3 (C3)	Acidified salts solution (pH 1.5)	Inoculated
Control water (CW)	Deionised water	Non- inoculated
Control acid water (CA)	Acidified salts solution (pH 1.5)	Non-inoculated

Table 3-2: Nutrients concentration in acidified water leaching solution.

Nutrients	Concentration (mg/ L)
$FeSO_4.7H_2SO_4$ (500 mg/L Fe^{2+})	2.5
$(NH_4)_2SO_4$	183.3
$NH_4H_2PO_4$	60.5
K_2SO_4	11.2

Column In-bed sampling

The method outlined by Chiume et al., (2012), was applied to perform in-bed sampling of the columns. This method involves using an apparatus to sample the ore bed. The in-bed sampling device consists of a screw mechanism, two sections, and a slot designed to hold a metal plate that functions as a slicer. To begin, the base of the column is opened, and the supporting perforated plate is carefully removed to prevent the ore from spilling. The in-bed sampler is then secured to the column. Using the screw mechanism, the packed ore bed is gradually lowered until it reaches the second section. A metal slicing plate is then inserted into the slot, cutting across the ore bed horizontally. The screw is fully lowered to transfer the lower

portion of the ore bed into the second compartment of the sampler, which is then detached. A sample of the ore remaining in the second compartment is manually removed for analysis. The second section is reattached, and the screw is lifted until the ore bed reaches the metal slicing plate. The slicing plate is removed, and the ore bed is carefully returned to the column. Finally, the sampling device is removed, the bottom plate of the column is reinstalled, and normal operation resumes.

For each of the sampling performed, the column of coal discards was lowered to enable approximately 500 g of leached coal discards to be extracted as a slice from the middle region of the column bed without its unpacking.

3.4 Characterisation of the ARD Generation Potential

3.4.1 Static Test

The net acid producing potential (NAPP) was calculated by deducting the acid neutralising capacity (ANC) from the maximum potential acidity (MPA) (Skousen et al., 1998) Stewart et al., 2006). The NAPP of the coal discards was determined using acid base accounting (ABA) tests. The MPA is estimated based on the sulphur content of the coal discards (LECO S632 Sulphur Analyser). This technique operated under the assumption that all sulphur present in the coal waste consisted of pyritic and oxidizable compounds. Estimation of the discards ANC was obtained through the reaction of the sample with HCl, followed by a subsequent back titration with NaOH (0.5 M), as per the process described by Skousen et al. (1998). This method is commonly used to evaluate the potential environmental impact of coal discards on water quality (Skousen et al., 1998; Stewart et al., 2006).

The coal discards net acid generation (NAG) was assessed using H_2O_2, which enabled simultaneous acid neutralising and acid producing reactions to take place (Broadhurst et al., 2013). The mixture was back titrated with H_2O_2 to a pH of 4.5, considering acidity produced from sulphate oxidation. The final NAG (NAG_{pH}) was then determined through an additional titration to pH 7.0 (Hesketh et al., 2010a).

The sample was found to have an acid neutralising capacity (ANC) of 54 kgH_2SO_4 per ton and a maximum potential acidity (MPA) of 224.4 54 kgH_2SO_4. This was consistent with the fact that approximately 4% of the coal discards content was made up of gypsum, which is not able to generate acid. The principal contributor to the MPA was found to be pyrite with more than 96% of the total sulphur content. The static test characterisation plot, which combines both the net acid generating potential (NAG_{pH}) and net acid producing potential (NAPP), was used

to evaluate the overall acid producing potential of the sample. A classification plot allows the visualization of the final result (Stewart et al., 2006) as show in Figure 3-3.

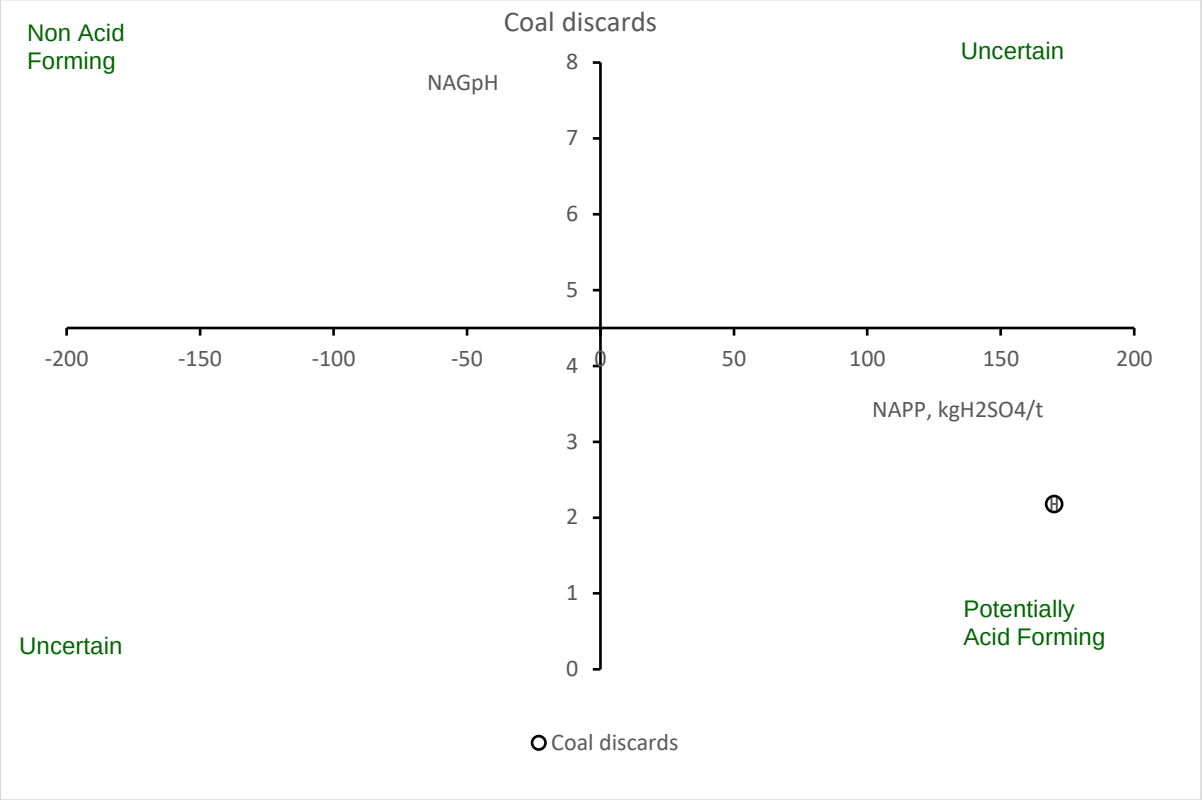

Figure 3-3: Coal discards static test characterisation plot.

3.4.2 Biokinetic tests

Typical tests evaluating the ARD potential frequently overlook the contribution of microorganisms during the ARD generation process as well as the relative rates of neutralisation and acidification (Opitz et al., 2015). The UCT biokinetic test is a method that has been developed specifically to address this issue. The test is designed to accurately account for the microbial activity that can contribute to ARD production, and to provide data on the relative rates of acidification and neutralisation (Hesketh et al., 2010a; Broadhurst et al., 2013).

The coal discard samples were milled to 100% passing 75 µm. Then, 7.5 grams of the milled samples were placed in 250 mL Erlenmeyer flasks and mixed with 150 mL of autotrophic basal salt (ABS) medium at pH 2.0. The mixed microbial culture used in the column experiment at a concentration of 10^9 cells was used to inoculate each one of the flasks. Once inoculated, the

flasks were placed in an orbital shaking incubator at a temperature of 37 °C and set to 150 rpm for 90 days. The purpose of this was to mimic the conditions that would occur in an ARD environment.

3.5 Analytical procedures

3.5.1 Solution pH and redox potential

A Metrohm 713 meter was utilised to measure the leachate solution pH. The device was calibrated between pH 1.0, 4.0 and 7.0. A Metrohm 827 was used to measure the leachate solution redox potential using a Ag/AgCl reference electrode.

3.5.2 Iron concentration

The leachate solution Fe^{2+} concentration was determined using the 1,10-phenanthroline method with the aid of a spectrophotometer. Total Fe concentration was obtained via the same method after addition of excess hydroxylamine, the Fe^{3+} concentration was assessed by subtracting the Fe^{2+} from the total Fe concentrations (APHA/AWWA/WEF, 2017).

3.5.3 Sulphate concentration

The concentration of sulphate in solution was determined using the turbidometric analysis described in (APHA/AWWA/WEF, 2017). A spectrophotometer was used to perform the absorbance measurements at a wavelength of 420 nm. Sulphate concentration was determined by converting the recorded absorbance values using a sulphate calibration curve.

3.6 Evaluation of desulphurisation

The daily mass of sulphur removed was estimated by measuring the sulphate concentration in the pregnant leach solution. The mass of sulphur removed was calculated as the difference in sulphate concentration between the leachate and inlet solution multiplied by the irrigation rate (Eq.14)

$$Mass\ of\ S\ removed\ per\ day = (S_{conc} - S_{conc-inlet}) \times Irrigation\ rate \quad \text{Eq 14}$$

$$\%\ S = \frac{Mass\ of\ S\ removed\ per\ day}{Mass\ of\ coal\ discards\ loaded\ in\ the\ column\ reactor} \quad \text{Eq 15}$$

The percentage of sulphur removed was then determined by dividing the daily mass of sulphur removed by the total mass of coal loaded in the column reactor (Eq.15). The cumulative percentage of sulphur removed was tracked throughout the course of the experiment.

4 Desulphurisation of coarse coal discards through bioleaching

In this chapter, the potential of using accelerated heap bioleaching as a means of preventing ARD is explored. To accomplish this task, column reactors at a laboratory scale were utilized. The key metric in determining the success of the experiment was the amount of pyrite that was leached from the coal discards. In the experiment, the coal discards were exposed to different irrigation conditions to investigate weathering and the potential to accelerate desulphurisation under acidic conditions. All columns were prepared and packed using coal discards agglomerated with 8 kg concentrated H_2SO_4 per ton. The first non-inoculated control column was irrigated with deionised water (CW) to investigate the potential of acidification under normal weathering conditions. The second non-inoculated control column was irrigated with acidified water (CA), aimed at exploring the influence of native microorganisms in the acidification process. Lastly, results from the triplicate columns (C1, C2, C3) inoculated with a consortium of iron- and sulphur oxidising microorganisms and irrigated with acidified water were analysed and compared to those of CA to evaluate the impact of inoculation on the extent of desulphurisation.

4.1 Characterisation of the coal discards

4.1.1 Particle size distribution

The coal discards sample was constituted of coarser particles as demonstrated by its particle size distribution (PSD) (Figure 4-1). The PSD was determined by the sieving method (ASTM D4749-87, 2012) and indicated that 10% of the sample was smaller than 2.2 mm, 50% was smaller than 11 mm and 80% was smaller than 28 mm. Hence the sample was mostly constituted of coarse particles (Leonard, 1991).

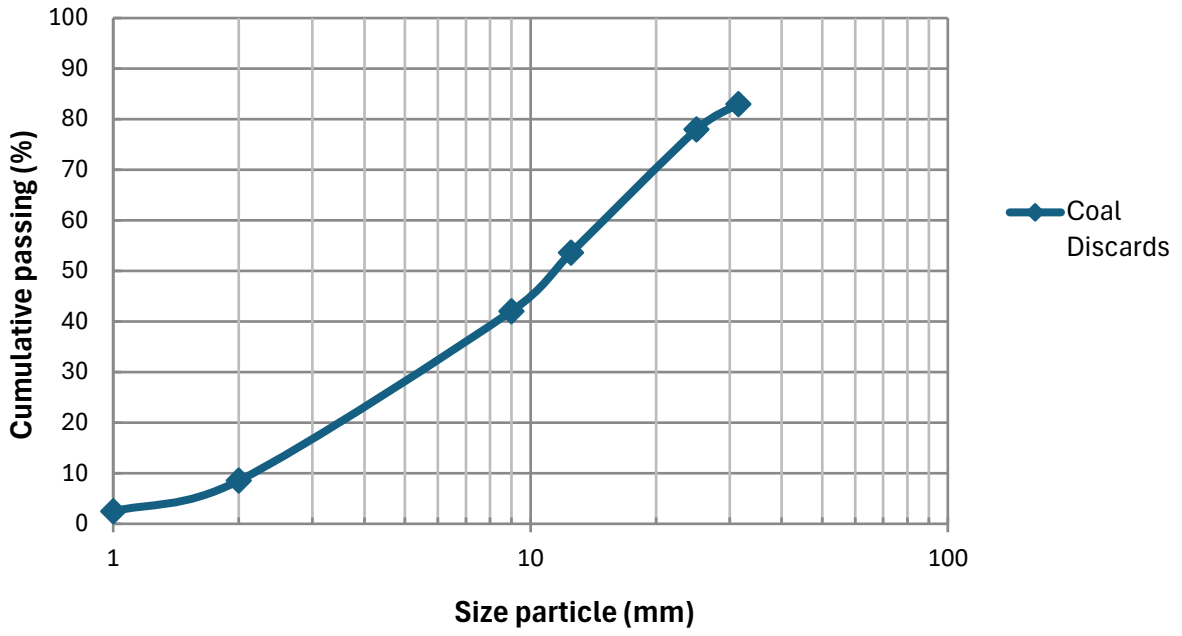

Figure 4-1: Particle size distribution of coal discard sample.

4.1.2 Coal discards mineralogy

The coal discards were characterised using by the LECO analyser, XRD, XRF and ICP-MS. LECO analysis revealed a total sulphur content of 10.4% and XRD confirmed that pyrite was the main mineral sulphide at a concentration of 11.4% (Table 4-2). The sulphur speciation analysis, presented in Table 4-1, indicated that the pyritic S content was 6.3% which relates well to the pyrite content. Further, it confirmed the presence of both non-acid sulphates as well as organic sulphur which present a low risk of acid generation.

Table 4-1: Coal discards sample sulphur speciation analysis

Sulphur forms	% Sulphur	% out of Total Sulphur
Pyritic	6,3	60,7
Acid Sulphate	0	0,2
Non-Acid Sulphate	1,4	13,6
Total Sulphate	1,4	13,8
Low risk	1,2	11,7
Total Sulphur	10,4	100

The XRD results, shown in Table 4-2, indicate quartz (21.3%) and kaolinite (39.8%) as the major silicate-based gangue mineral phases. Further they highlight the most important acid neutralising minerals such as calcite and gypsum, with kaolinite, illite and anhydrite also likely contributing neutralising capacity.

XRF analysis substantiated XRD results revealing a noticeable concentration of SiO_2 and Al_2O_3 in the coal discards sample (Table 4-3).

Rare earth elements (REE) are widely utilised in various industrial applications such as defence, energy, and technology. Coal and coal by-products represent a promising secondary source for the extraction of REEs, and ongoing research aims to optimise and commercialise processes (Nawab & Honaker, 2023). Elemental analysis results showed high concentrations of cerium, lanthanum, and yttrium in these coal discards, as presented in Table 4-4.

Table 4-2: Coal discards sample X-ray diffraction (XRD) analysis

Mineral	Composition	Concentration (wt%)
Quartz	SiO_2	21.28
Kaolinite	$Al_2Si_2O_5(OH)_4$	39.77
Gypsum	$CaSO_4.2H_2O$	7.97
Illite	(K,H3O)(Al,Mg,Fe)2(Si,Al)4O10[(OH)2,(H2O)])	12.71
K-feldspar	$KAlSi_3O_8$	2.86
Pyrite	FeS_2	11.40
Jarosite	$Kfe^{3+}3\ (SO_4)_2\ (OH)_6$	2.13
Anhydrite	$CaSO_4$	0.45
Calcite	$CaCO_3$	1.43

Table 4-3: Coal discards sample X-ray fluorescence (XRF) analysis

Mineral	Composition	Concentration (wt%)
Aluminium oxide	Al_2O_3	14,28
Calcium oxide	CaO	2,39
Chromium (III) oxide	Cr_2O_3	0,01
Iron (III) oxide	Fe_2O_3	8,30
Potassium oxide	K_2O	0,98
Magnesium oxide	MgO	0,58
Manganese (II) oxide	MnO	0,02
Sodium oxide	Na_2O	0,08
Phosphorus pentoxide	P_2O_5	0,12
Quartz	SiO_2	33,85
Titanium dioxide	TiO_2	0,71
	L.O.I.	37,77
Sum Of Conc.		99,09

Table 4-4: Coal discards sample rare earth (REE) elements analysis

Elements		Concentration (ppm)
Scandium	Sc	9,36
Yttrium	Y	22,46
Lanthanum	La	28,70
Cerium	Ce	66,20
Praseodymium	Pr	6,90
Neodymium	Nd	25,39
Samarium	Sm	5,11
Europium	Eu	0,89
Gadolinium	Gd	4,28
Terbium	Tb	0,69
Dysprosium	Dy	4,39
Holmium	Ho	0,83
Erbium	Er	2,55
Thulium	Tm	0,38
Ytterbium	Yb	2,60
Lutetium	Lu	0,36
Thorium	Th	13,69

4.2 Investigating Accelerated Bioleaching of Coal Discards in Columns

The column tests were continuously conducted over a period of 380 days (see Table 3-1). Regular measurements were performed to monitor the process, including pH, redox potential, and concentration of Fe^{3+} within the effluent solution. In addition, in-bed sampling of the columns was conducted on C3 on day 144, and on day 297 for both C1 and CA. Characterisation of the leached discards was performed once the experiment was concluded; these analyses are reported in Chapter 5.

The pH of the pregnant solution from the water-irrigated, neutral non-inoculated control CW was observed to increase sharply, reaching a maximum of 3.9 by Day 30 of the leaching experiment (CW in Figure 4-2). This rise in pH levels can be ascribed to the displacement of the agglomerating acid solution during irrigation and the dissolution of acid-neutralising minerals from within the coal discards. The initial volume of liquid used for agglomeration is

roughly 0.6 L while the irrigation process at 5 L $m^{-2}.h^{-1}$ equates to provision of 0.94 L of irrigant per day, giving an indication of the dilution effect. The acid-neutralising minerals present in the coal include calcite, gypsum, and kaolinite. The rise in pH can be credited to the solubilisation of said minerals, as agglomeration is believed to have initiated the acid-consuming reaction. However, after this initial increase, the pH of the solution began to decrease, falling to 3.0 and 2.3 at the Days 60 and 170, respectively. The decrease in pH was accompanied by an acceleration of the oxidation rate, as reflected in the redox potential rising from 570 mV to 660 mV between the 50th and 100th days (Figure 4-3). The increase in Fe^{3+} concentration also confirmed the accelerated oxidation process (CW in Figure 4-5). The results pointed to a gradual acid-generating process confirming the potential of the discards for ARD generation when exposed to natural oxidants.

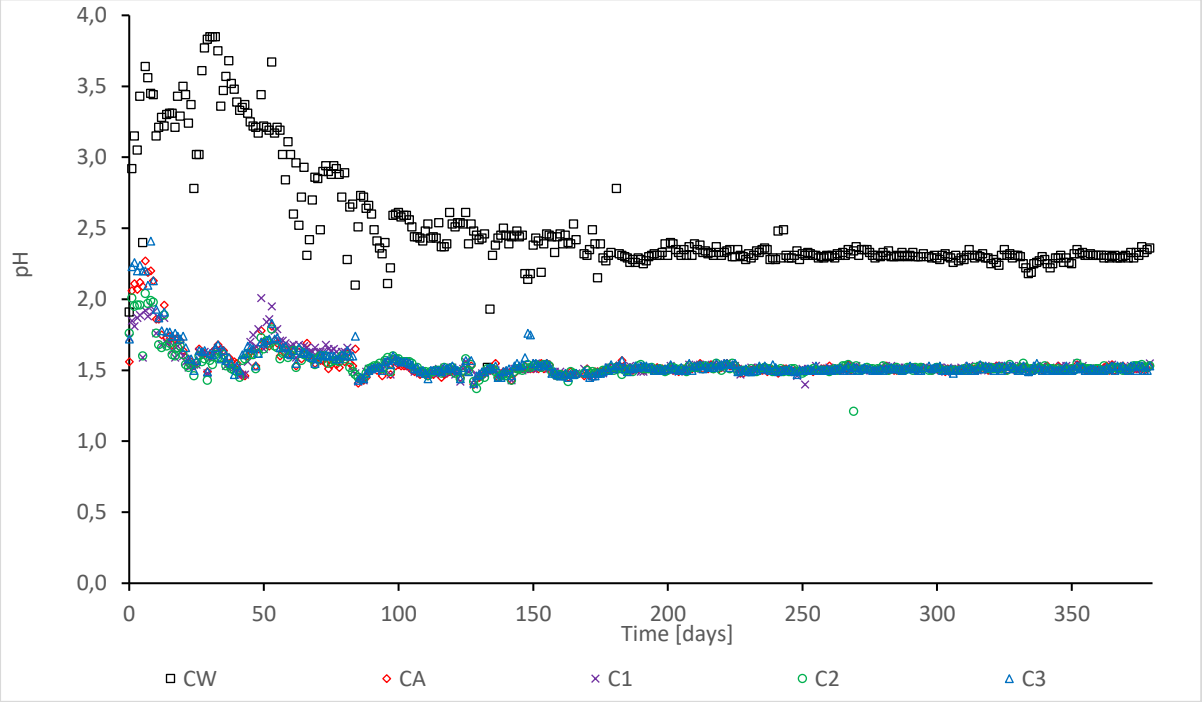

Figure 4-2: pH of the effluent solution from the accelerated coal column leach experiments.

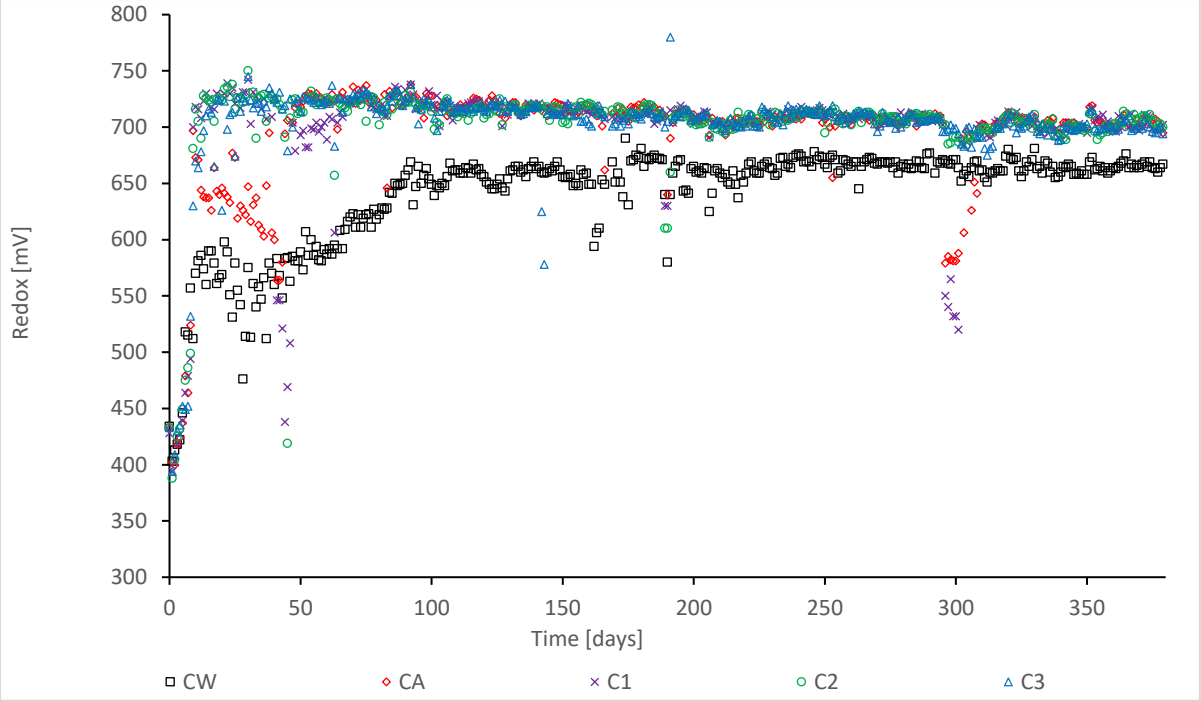

Figure 4-3: Redox potential profiles of the effluent solution from the accelerated coal column leach experiments.

Results from the non-inoculated, acid-irrigated control column CA column indicated that the effluent solution showed a clear pattern of variations in pH levels, redox potential, and iron concentration. At the start of the experiment, the effluent solution pH rapidly increased from 1.5 to 2.5 after 10 days. Following this initial increase, the pH subsequently decreased, remaining in the range between 1.5 and 1.7 around Day 30. Further, evidence of Fe^{2+} oxidation could be observed from the CA effluent solution redox potential at this point; it increased to 640 mV after 12 days and remained at this level up until Day 38.

On the 74th day, a notable rise in the redox potential was observed, remaining within the range of 710-730 mV thereafter (Figure 4-3). These results suggested the existence of iron-oxidising species within the coal discards that can become dominant and actively responsible for the Fe^{2+} oxidation. The accelerated oxidation in the CA column indicated the presence of native iron and sulphur oxidising microorganisms. Typically harboured in coal mines, these acidophilic microorganisms fix carbon dioxide and use inorganic electron donors as their energy source, forming Fe^{3+} and H^{+} (Schaechter et al., 2013). Fe^{3+} is favoured to be the primary oxidising agent because of acidification from the oxidation of the coal discards (Kotsiopoulos & Harrison, 2017), further decreasing the effluent solution pH below 2.3 thus enhancing the discards desulphurisation.

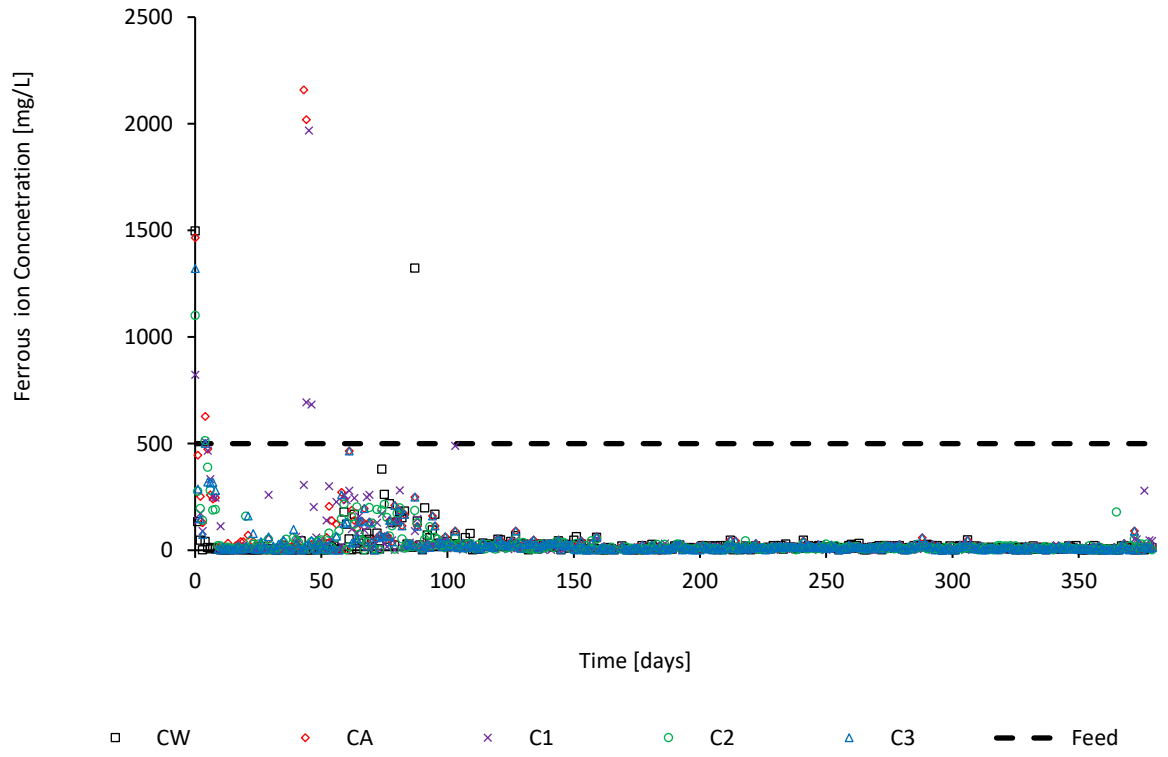

Figure 4-4: Ferrous iron concentration profiles of the effluent solution from the accelerated coal column leach experiments.

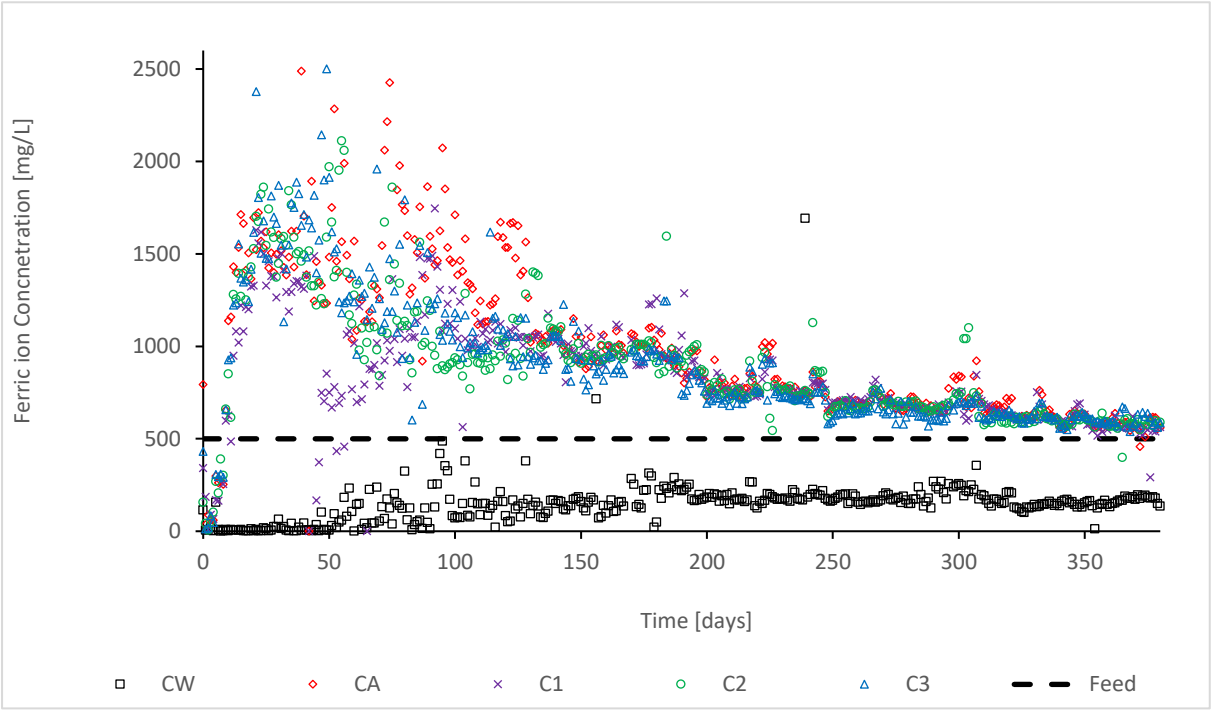

Figure 4-5: Ferric iron concentration profiles of the effluent solution from the accelerated coal column leach experiments.

In Figure 4-4, the graph illustrates the levels of Fe^{2+} found in the effluent solution, while the dotted line represents the Fe^{2+} concentration in the irrigating solution. Throughout the experiment, Fe^{2+} concentration in the PLS consistently stayed below the irrigating solution concentration of 500 mg/L. This consistent pattern suggests the presence of a thriving microbial community capable of oxidizing iron in each column.

The triplicate inoculated columns, C1, C2, and C3, showed successful desulfurization through the results obtained. After a modest initial increase in pH of the effluent solutions from the three columns reaching a maximum at 2.2 on Day 6 due to the neutralising capacity of the discards, the pH decreased over the period Day 6 to Day 25, by which point it was in the range of 1.5 to 1.6 whereafter it stayed in this range (Figure 4-2). The redox potential and Fe^{3+} concentration measured in the effluents of C1, C2 and C3 indicated fast onset of iron oxidation.

The redox potential started out below 400 mV but rose in all three column effluent solutions to above 700 mV after 14 days. It then stabilised between 695 and 730 mV for the remainder of the experiment. This is supported by Fe^{3+} concentration in the leachate increasing to a maximum of 1800 mg/L between 20 and 40 days, before decreasing to around 1000 mg/L by days 70-150, and gradually decreased further over time, likely due to the low solubility of ferric iron as well as the depletion of readily leachable pyrite in the coal discards with time.

A noticeable decrease in the redox potential of the effluent solution from the C1 column was recorded on day 43, decreasing from around 700 mV to reach 440 mV (Figure 4-3). The cause of this decline was a sudden rise in temperature within the column, which depleted the microbial community responsible for catalysing the oxidation reaction. This temperature increase, reaching 55°C, was triggered by a disruption in irrigation. The oxidation of pyrite is an exothermic reaction, and the irrigant contributes to removing heat formed from the coal bed. This occurrence highlights the critical importance of appropriate aeration and irrigation measures to prevent the occurrence of spontaneous combustion in coal heap bioleaching operations.

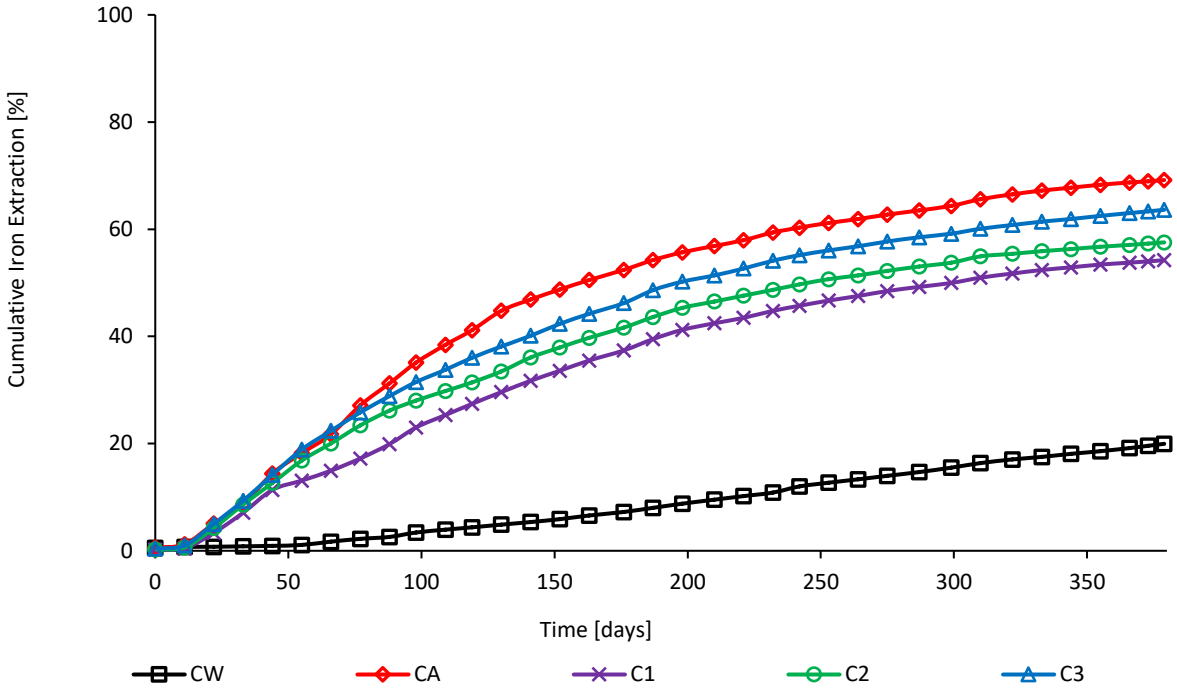

Figure 4-6: The total amount of iron extracted was calculated using the iron concentration measurements from the column reactors effluent solutions.

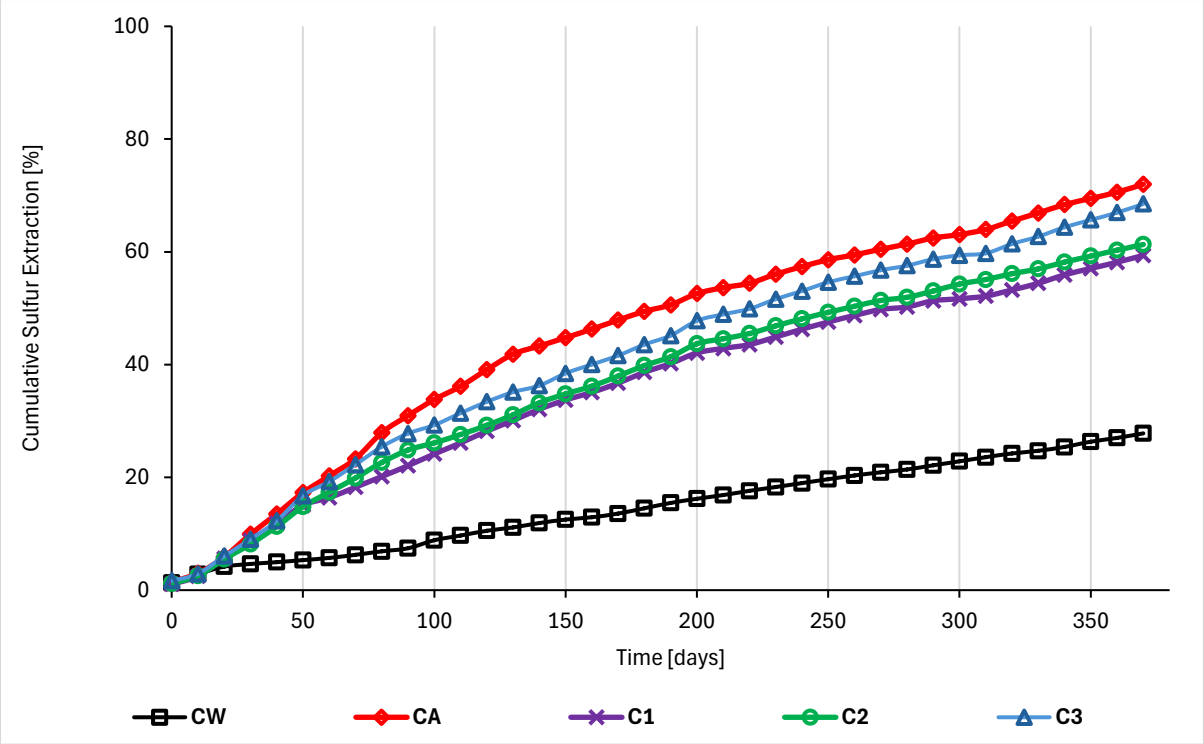

Figure 4-7:The total amount of sulphur extracted was calculated using the sulphate concentration measurements from the column reactors effluent solutions.

In-bed samples of the coal discards bed were collected from the C3 column on Day 144 and from the CA and C1 columns on Day 297 as per the procedure detailed by Chiume et al. (2012), to evaluate the effectiveness of the coal discards desulphurisation. A portion of this solid sample was subjected to LECO analysis and the results showed a substantial drop in sulphur content in the sampled coal discards (Table 4-5). Sulphur content in the coal discards decreased over the duration of the tests. From an initial concentration of 10.40% to 6.97% in the sample taken from the C3 on Day 144 and to 5.40% and 4.78% in the samples collected from the C1 and CA respectively on Day 297. The in-bed sampling procedure, however, resulted in a temporary disruption to the microbial activity in the columns owing to suspension of irrigation for a short period and physical motion in the bed; this can be observed from the effluent solution redox potential. Within a 10-day period, the microbial communities were able to recover, and leaching performance returned to levels prior to the disturbance.

Table 4-5: Sulphur removal results measured from samples taken from the C3, C1 and CA columns on days 144 and 297.

Sample	Sulphur (%)	*Sulphur removed (%)*	*Sulphur removed as % pyritic S present initially*	Leaching duration
Coal discards	10.40	0.00	0.0	0
C3	6.97	3.43	54.0	144
C1	5.40	5.00	79.4	297
CA	4.78	5.62	89.2	297

Despite the interruption brought about by the sudden temperature variation and the collection of samples within the bed, evidence of Fe^{2+} oxidation in C1, C2, C3 could be observed. This was demonstrated by the high redox potential of the columns' leachate solutions, which remained between 695 and 730 mV from 14 days until the end the experiment (Figure 4-3). The high concentration of Fe^{3+} also suggested a strong rate of microbially catalysed leaching, with concentrations remaining above 1000 mg/L in the effluent solutions of all three columns for the first 150 days of the experiment (Figure 4-5). The results indicated that the inoculation did not significantly influence the degree of sulphur removal in the columns. Evidence of iron- and sulphur-oxidising microorganisms activity in the CA column is substantiated by the first stage of redox potential increase to around 650 mV (Figure 4-3). The subsequent slow rise in redox potential measured in the column could be attributed the increasing establishment of the microbial culture as the Fe^{3+} concentration increased, thus providing favourable conditions.

The cumulative amount of iron and sulphur leached from the coal discards in both the non-inoculated and inoculated columns is shown in Figure 4-6 and Figure 4-7 respectively. It was compiled considering the effluent solution iron concentrations and the irrigation rate to the columns. Over the course of the experiment the iron concentration in the leachate solutions from C1, C2, C3 and CA steadily decreased, going from 1800 mg/L to under 560 mg/L after 350 days, which gave an indication of gradual depyritization of the coal discards, resulting in less accessible pyrite in the coal discards and so less leaching each day. The cumulative percentage of iron removed reached between 30 and 40% after 100 days; thereafter the rate of removal slowed such that between 54 and 64 % was leached by the end of the experiment. These resulted were confirmed by the LECO analysis of the leached coal discards performed as the tests were concluded.

The theoretical time required for the coal discards to become non-acid forming can be estimated based on the overall acid-forming reaction (Eq 16). By applying reaction stoichiometry and assuming an average daily pyrite consumption rate of 31.4 mg per hour in

each column—estimated from the average concentration of ferric hydroxide in the leachate solution—the timeframe required for the coal to be non-acid forming can be predicted. Assuming that coal is non-acid forming when the pyrite content falls below 0.3% by weight, the coal in the columns would theoretically reach this state in approximately 322 days.

After 380 days, the CA column exhibited an iron removal efficiency of approximately 69.2%, with the total sulphur removed at 60.1%. Should only pyritic S be removed, this represents a removal of 99.7% of pyritic S. Should both pyritic and sulphate-S be removed, this represents 78.0% removal of these fractions. From the C1, C2 and C3 columns the amount of iron removed was 54.2%, 57.5%, and 63.6% respectively. The extent of desulphurisation (as a % of total S) of the coal discards after 380 days amounted 61.6% from C1, and 63.5% from C3. Of the pyritic and sulphate sulphur present, these removals equate to 80.0 % and 82.5 % respectively. Using linear extrapolation of the cumulative percentage of iron leached the terminal duration of the tests were estimated i.e. the time required for complete desulphurisation of the coal discards. The coal discards in the CA column would take 577 days to be completely desulphurised, while those in C1, C2 and C3 would take between 526 and 655 days assuming all sulphur present can be removed.

Comparing the non-inoculated and inoculated columns, it was evident that microorganisms naturally found in the coal discards were predominantly present in the column reactors. This was corroborated by cell count done on the leached samples after 380 days, which showed between 7.0-7.5 $\times$ 10^{17} cells/ton for C1 and C3, as well as about 5.8 $\times$ 10^{17} cells/ton for CA. Eventually, the microbial population in the CA column likely predominated over the added inoculum in the enhanced oxidation of Fe^{2+} to Fe^{3+} the principal oxidant. The CW column findings revealed that acidic conditions were crucial for the initiation of oxidation. After 380 days, the results indicated low iron and sulphur removal with 20 and 30% respectively. The disparity between iron and sulphur removal rates might have indicated precipitation of iron-containing compounds such as jarosite; ferric iron precipitation is enhanced at pH above 2.0 and the pH of the water-irrigated column did not reduce below pH 2.5. This pH will impact both the availability of Fe^{3+} as leach agent and the composition of the community of microorganisms available to regenerate this ferric leach agent.

4.3 Conclusions

Accelerated heap bioleaching leaching presents a promising avenue for the efficient removal of readily leachable sulphur from coal discards. Results have shown that a significant portion of the leachable sulphur could be removed within 100 days of irrigation. Further, leachable sulphur contained in the coal discards was essentially depleted after 380 days of leaching. A

general time frame of about two years could therefore be recommended to achieve efficient sulphur removal.

Although inoculation facilitated the initiation of the leaching process, accelerating pyrite oxidation, and consequently sulphur removal, the presence of indigenous microorganisms in the coal discards potentially better suited for oxidising pyrite suggests that inoculation may not be required for large scale operation which could assist in decreasing cost. Alternatively, the use of an inoculum developed from the indigenous community may be advantageous.

Results have shown that lower pH levels, less than 2, greatly enhance the efficiency of the leaching process. The acidic environment is advantageous to iron- and sulphur-oxidisers due to Fe^{3+} availability. Therefore, maintaining acidic conditions is critical in achieving effective sulphur removal.

5 Characterization and potential for re-purposing of post-leaching coal discards and leachate solution

5.1 Post-leaching static test characterization

An assessment of the coal discards potential to generate acid was carried out through static tests performed before, during and after the leaching experiment. Samples were obtained from column C3 following a period of 144 days of irrigation, C1 and CA after 297 days, and from all three columns after 380 days. Although XRD analysis of the unleached coal discards confirmed the presence of acid-neutralising compounds, they were not able to offset the acid producing capacity. The unleached coal discards had a net acid producing potential (NAPP) of 170 kg H_2SO_4/ton, which was consistent with the discard's pyrite concentration of 11.4%.

Table 5-1: Static tests results from coal discards sample prior- and post-leaching. Acid neutralising capacity (ANC), maximum potential acidity (MPA)

Sample	Sulphur (%)	Leaching duration (days)	MPA (kg H_2SO_4 / ton)	ANC (kg H_2SO_4 / ton)
Coal discards	10.40	0	224,4	54,4
C3	6.97	144	213,5	179,5
C1	5.40	297	165,5	174,5
CA	4.78	297	145,7	170,1
C1	3.99	380	122,1	247,6
CA	4.15	380	127,0	205,3
C3	3.80	380	116,3	238,7

The coal discards prior- and post-leaching ANC and MPA are shown in Table 5-1. An increase in the ANC can be observed coupled with a decrease in the MPA. The sample collected from C3 on day 144 had a MPA of 213.5 kg H_2SO_4/ton which decreased to 116.3 kg H_2SO_4/ton by day 380. Samples collected from C1, and CA had MPAs of 165.5 and 145.7 kg H_2SO_4/ton respectively at day 297, decreased from 224.4 kg H_2SO_4/ton pre leaching. These similarly decreased to 122.1 kg H_2SO_4/ton for the sample from C1 and 127.0 kg H_2SO_4/ton for the sample from CA by day 380.

On the other hand, an increase in ANC values can be observed in the samples post leaching. On day 297, samples from C1 and CA yielded ANC values of 174.5 and 170.1 kg H_2SO_4/ton

respectively, confirming the increase in neutralising capacity reaching 205.3 and 238.7 kg H_2SO_4/ton after 380 days of leaching.

Table 5-2: Static tests results from coal discards sample prior- and post-leaching. Acid Base Accounting and Net Acid Generation (NAG) methods were performed, PAF= potentially acid forming, NAF= non-acid forming, NAPP = net acid producing potential.

Sample	Sulphur (%)	Leaching duration (days)	NAGpH	NAPP (kg H_2SO_4/ ton)	ARD Classification
Coal discards	10.40	0	2.18 ± 0.01	170.00	PAF
C3	6.97	144	4.80 ± 0.02	34.00	UNC
C1	5.40	297	4.73 ± 0.04	-8.91	NAF
CA	4.78	297	4.68 ± 0.02	-24.40	NAF
C1	3.99	380	5.35 ± 0.01	-125.49	NAF
CA	4.15	380	4.97 ± 0.03	-78.33	NAF
C3	3.80	380	5.14 ± 0.01	-122.40	NAF

Table 5-1 shows the results of the static tests carried out on samples collected during and after the experiment. A clear decreasing trend in the acid generating potential can be observed. The sample obtained from C3 collected on day 144 had a NAPP of 34 kg H_2SO_4/ton and was labelled as uncertain (Figure 5-1). By day 380, the NAPP decreased to -122.40 kg H_2SO_4/ton, leading to the sample categorization as non-acid forming. On day 297, samples from C1 and CA yielded NAPP values of -8.91 and -24.40 kg H_2SO_4/ton respectively, indicating a general decline of the acid generating capacity of the discards and a categorisation of non-acid forming. The aforementioned trend was corroborated by the samples collected on day 380 from the three columns, which indicated non-acid forming potential (Figure 5-1).

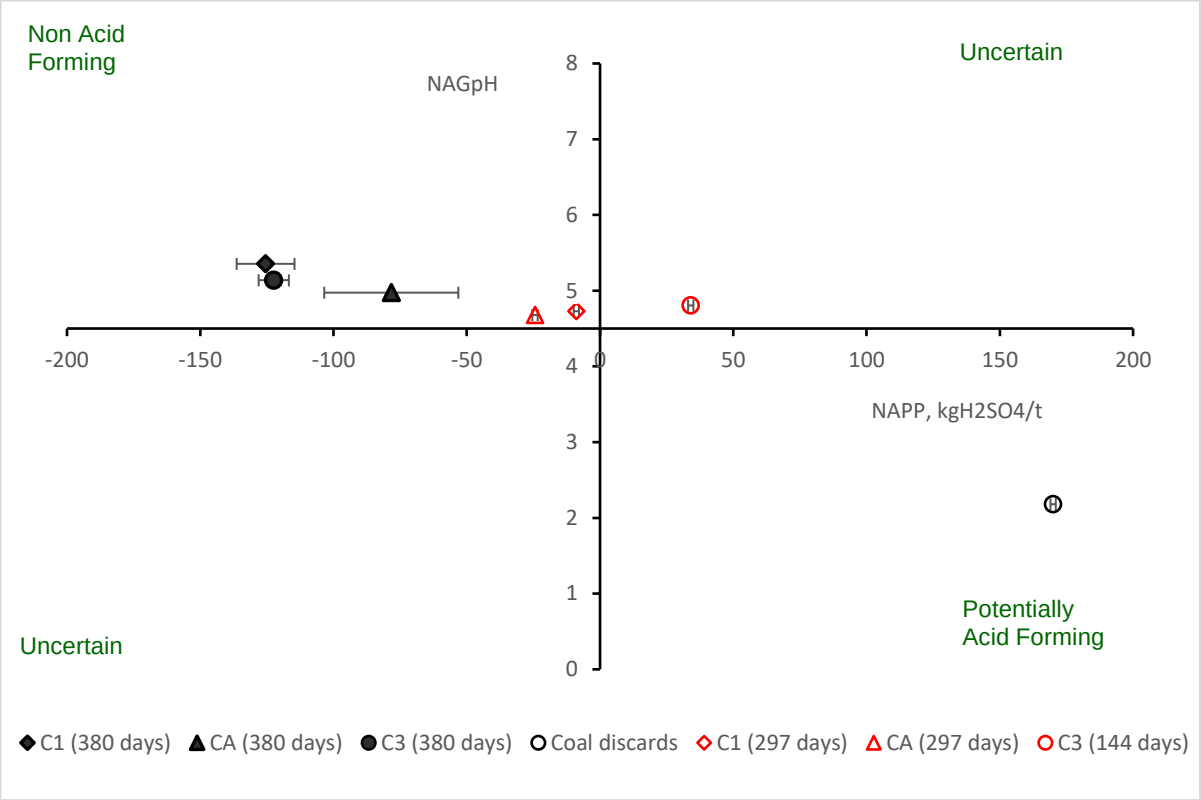

Figure 5-1: Static test classification of coal discards before and after leaching, error bars indicate standard deviation

5.2 Post-leaching biokinetic test characterization

It is recognised that the static tests do not take into consideration relative rates of acidification and neutralisation, nor the impact of microbial activity. Biokinetic tests were conducted to assess the pace of acid generation and consumption over an extended duration while accounting for the microbial activity promoting the Fe^{2+} oxidation. Both the samples obtained from columns C1, C3, and CA leached for 380 days and the unleached coal discards were analysed over a period of 90 days. The pH (Figure 5-2), redox potential (Figure 5-3), Fe^{2+} and Fe^{3+} concentration (Figure 4-4 and Figure 5-5) were continuously monitored, thereby providing a comprehensive analysis of the pyrite oxidation process.

The pH in the biokinetic test on the unleached coal discards experienced an initial rise, peaking at pH 2.2, due to acid-neutralizing reactions. These reactions were found to align with the neutralizing capacity observed in XRD analysis and static tests. Subsequently, the pH declined reaching approximately pH 1.8 by day 17 (Figure 5-2), providing evidence of swift oxidation occurring in the coal discards, specifically targeting the sulphide minerals. The pH remained

stable around 1.8 for the remainder of the experiment. The increase in alkalinity corresponded with lower redox potential values (Figure 5-3). This is corroborated by the higher Fe^{2+} concentration at the onset of the test (Figure 5-4), while higher redox potential values reflected the subsequent oxidation reaction phase. The Fe^{3+} concentration profile demonstrated a net increase from day 17, confirming the onset of microbially catalysed oxidation of Fe^{2+}. The biokinetic tests conducted on the unleached discards supported the static tests results, indicating that the discards had some, but limited, acid neutralising capacity while they demonstrated significant acid producing potential.

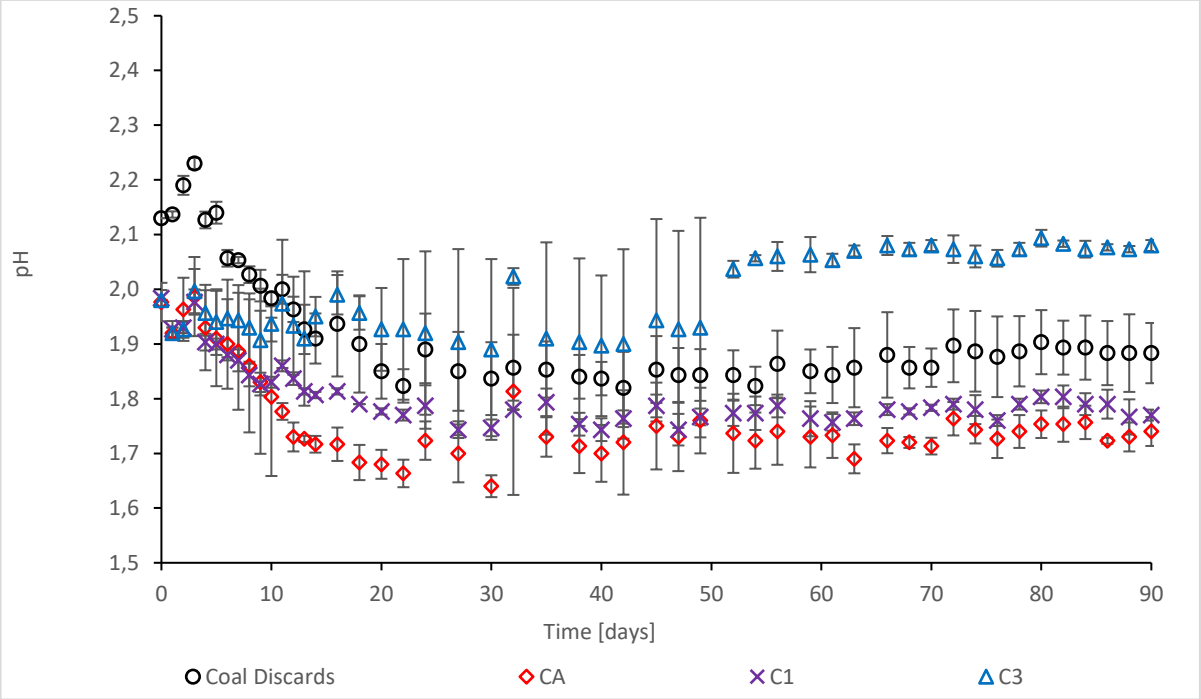

Figure 5-2: Biokinetic tests pH profile, error bars depict standard deviation.

For the sample collected from column CA after 380 days of leaching, the pH profile exhibited a notable reduction in comparison to that of the unleached coal discards. Specifically, the pH value decreased from 1.98 at the beginning of the tests to 1.73 on day 12 (Figure 5-2), ultimately reaching a minimum of 1.6 on day 30. No period of neutralisation was observed at the start of the test, demonstrating that the limited acid neutralisation was removed during the accelerated leach treatment.

This trend was validated by the redox potential profile, which indicated a steady increase up to 670 mV (Figure 5-3), and the Fe^{3+} concentration, which markedly increased to 600 mg/L by day 30 (Figure 5-5). The acid-generating capacity observed in the CA sample is believed to

be the consequence of the reduction in its acid-neutralizing components during the leaching procedure and the enhanced availability of its pyrite constituents owing to milling before the biokinetic tests which ensures liberation of the pyrite.

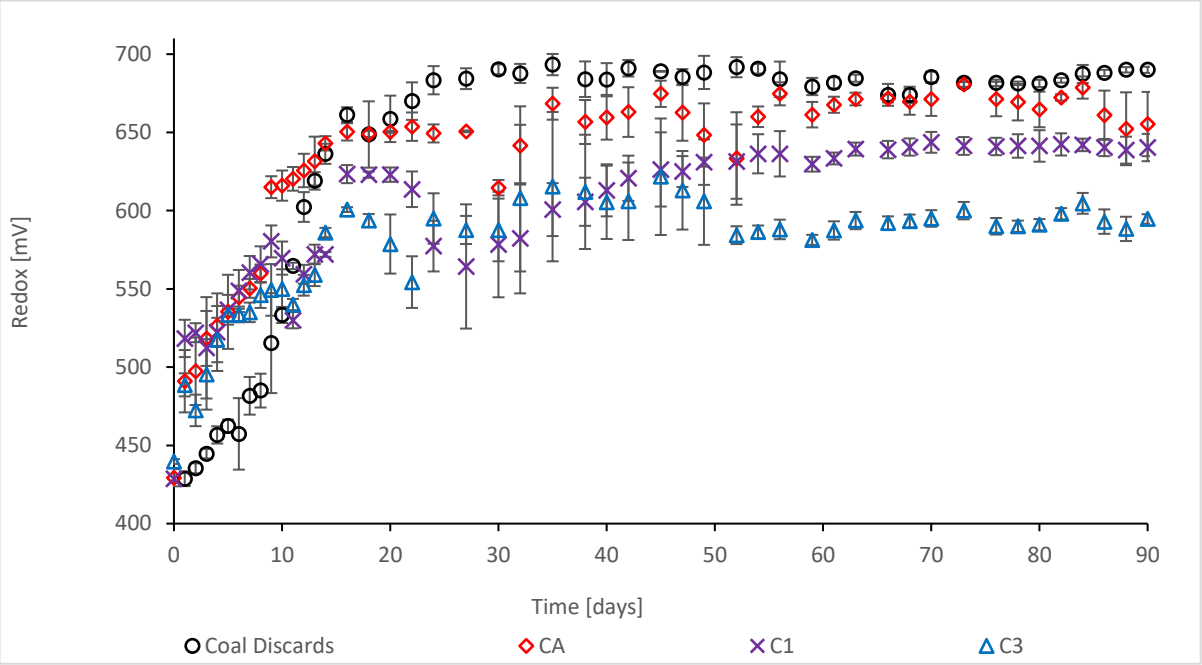

Figure 5-3: Biokinetic tests redox potential, error bars depict standard deviation.

Samples obtained from columns C1 and C3 exhibited a notable decline in their ability to generate acidic conditions. In column C3, the pH profile initially ranged from 1.9 to 2.0 during the initial 50 days of leaching (Figure 5-2). However, it subsequently increased and remained stable between 2.0 and 2.1 for the remaining duration of the tests. On the other hand, the pH profile of the C1 sample decreased from approximately 2.0 to 1.7 and then fluctuated within the range of 1.7 to 1.8. Notably, despite an increase in its redox potential from 430 mV to 623 mV in the initial 16 days of the experiment (Figure 5-3), the redox potential of the C1 sample decreased to 563 mV by day 27. This decrease coincided with an increase in pH, suggesting a reduction in its capacity to generate acidity. Subsequently, the redox potential increased to 650 mV as the remaining capacity to neutralize acidity was depleted. Furthermore, the levels of Fe^{3+} in the samples from C1 and C3 consistently exhibited values lower than 250 mg/L over the entire duration of the investigation as depicted in Figure 5-5. This confirms the significant depletion of the pyritic content in the samples and further supports their reduced ability to generate acid.

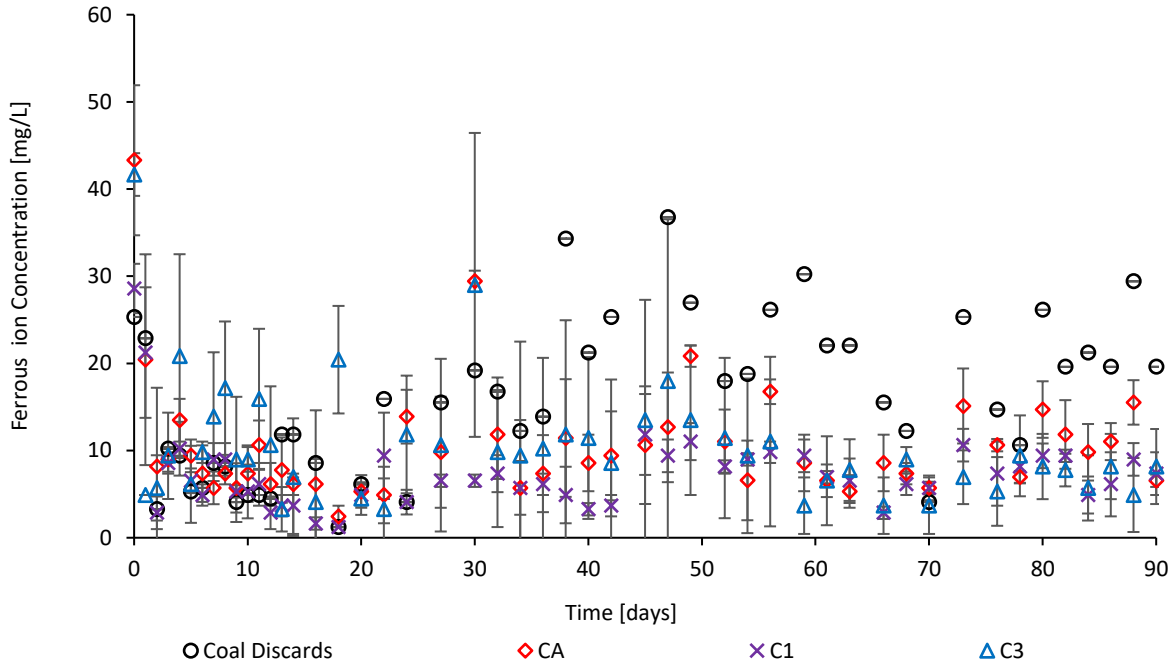

Figure 5-4: Biokinetic test Fe^{2+} profiles, error bars depict standard deviation.

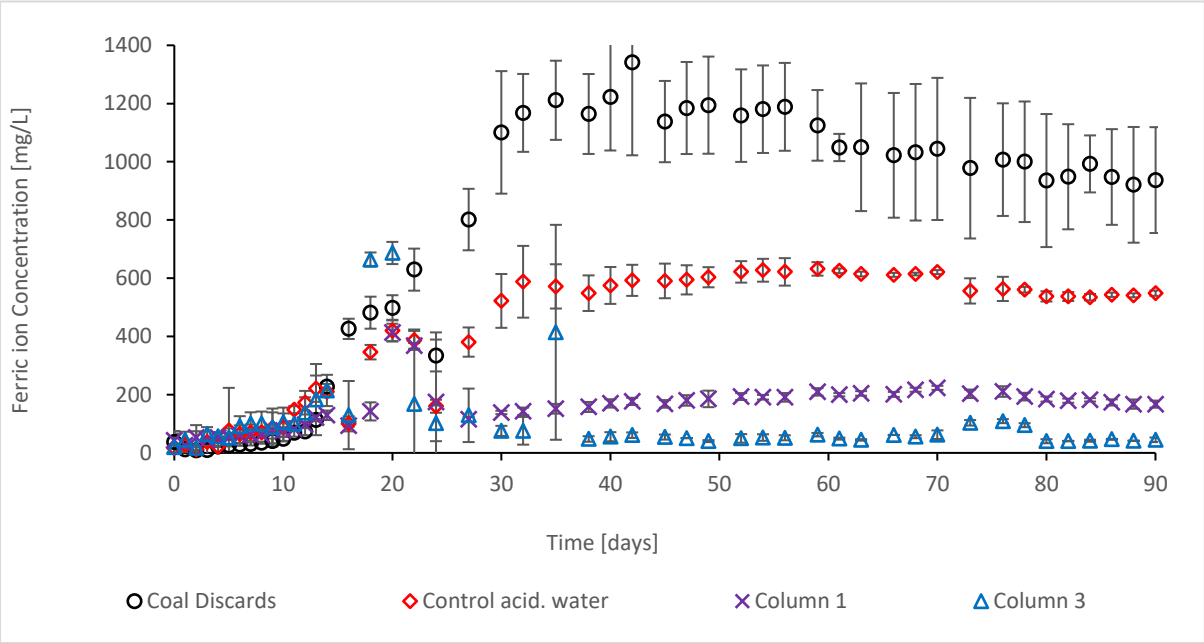

Figure 5-5: Biokinetic test Fe^{3+} profiles, error bars depict standard deviation.

5.3 Calorific value

Table 5-3 presents the calorific value of the initial coal discards sample and the subsequent changes observed after a leaching period of 380 days. The calorific value of coal serves as a direct measure of its heat content, playing a crucial role in determining its economic value (Speight, 2012). Prior to leaching, the discards exhibited a calorific value of 7.89 MJ/kg. The leaching experiment led to a notable increase in calorific value, with measurements of 9.00, 10.52, and 9.04 MJ/kg obtained from samples C1, CA, and C3, respectively, after the 380-day leaching period. This increase in calorific value can be attributed to the reduction in ash and sulphur content achieved during the leaching process.

Table 5-3: Calorific value of coal discards before and after 380 days of leaching

Samples	Calorific value MJ/ kg
Coal discards (pre-leach)	7.86
Expt'l Column 1 (380 days)	9.00
Expt'l Column 3 (380 days)	9.04
Control - Acidified Water (380 days)	10.52

5.4 Potential for value recovery from the leachate solution

The responsible handling of the leachate solution resulting from the coal discards desulphurisation operations and concomitant repurposing of the dissolved constituents is key in ensuring the process sustainability. The potential for value recovery from coal waste and sulphate rich solution has been extensively documented. The leachate solution presents opportunities for the recovery of chemicals such as iron-based coagulants, iron sulphate, iron oxides, sulphuric acid, and extraction of REEs. The desulphurised solid coal wastes hold promise for utilisation in construction, and as soil substrate, amongst others.

Bio-hydrometallurgical extraction of ferric sulphate-rich coagulants has been conducted on coal wastes with varying pyrite concentration (Menezes et al., 2016). Ferric sulphate coagulants with typical commercial grade iron concentration have been produced by leaching coal tailings using packed bed reactor on a laboratory scale (Menezes et al., 2016). Vigânico et al. (2011) suggested an approach coupling a bio-hydrometallurgical process with UV radiation to produce melanterite (ferrous sulphate heptahydrate crystals) from pyrite-rich coal tailings. The study demonstrated the feasibility of producing high purity melanterite from coal tailings thus minimising the waste environmental impact.

Ferreira et al. (2021), explored the potential reuse of pyrite-rich tailings from coal mining by assessing methods for waste valorisation. The tailings underwent consecutive leaching cycles, with resulting pyrite rich leachate solution and solid desulphurised coal waste. The benign coal waste showed promise for energy generation due to its high calorific value. While the pyrite rich leachate solution was treated via partial distillation and ethyl alcohol addition to yield gypsum and ferrous sulphate.

Amaral Filho et al. (2022) explored the application of dense medium separation to recover value from coal discards. The process generated three distinct fractions: a low-density fraction with increased calorific value that could be repurposed for energy use; an intermediate-density fraction, abundant in ash and acid-neutralising minerals, and with low sulphur content that can be re-purposed for road construction, as a construction material or as the base-matrix for soil fabrication; and, finally, a high-density fraction, rich in sulphidic minerals including pyrite from which Fe- and S- rich products can be derived.

REEs, such as lanthanide elements, yttrium and scandium, are vital for the modern technologies, particularly in high technology components necessary for the low carbon economy and for electronic devices (Liu et al., 2023; Smith et al. 2019). Supply of REEs is limited and poorly distributed geographically which has raised interest in their recovery. Despite their abundance REEs are typically dispersed in low concentrations and are often

found in complex mineral matrices, making their extraction and separation both technically challenging and economically demanding. Coal and its wastes present a potential secondary reservoir for the extraction of REEs. Miranda et al. (2022) investigated the use of a trap-extract-precipitate process to extract REEs from coal mine ARD. The study performed a mass and energy balance to evaluate the technology economic and environmental impact. Although results show that the process significantly reduced environmental impact, it required cost optimisation strategies for large scale applications. Smith et al. (2019) compared liquid emulsion membranes and supported liquid membranes with conventional solvent extraction for the recovery of REEs from coal fly ash leachates. It was observed that REE recovery rates in both liquid emulsion membranes and supported liquid membranes processes were influenced by diffusional mass transfer and solvent affinity. These results offer valuable insights for future research, focusing on optimizing separation processes and exploring diverse feedstocks beyond coal ash. Liu et al. (2023) considered the role of organic acids for REE recovery and separation. Increasingly, there is interest in the use of affinity binding of REEs by proteins and peptides and their separation through adsorption columns. The protein lanmodulin, recovered from a species of *Methylobacterium*, is the agent with best known selectivity for REEs currently (Ye et al., 2023), and further research is underway to improve REE recovery through protein adsorption. For this application, coal leachates such as developed through this study have significant potential as a liberated REE source.

Recovery of REEs and their associated value from the leachate prepared through accelerated bioleaching of coal discards during life of mine has potential to both enhance resource efficiency and enable the economics of responsible waste handling. In addition to REE recovery, the re-purposing of Fe and S fractions to further products discussed above is required.

5.5 Conclusions

Results from the static tests performed pre- and post-leaching showed that the leached discards had a lower NAPP and NAG_{pH} than the unleached discards, indicating a significant reduction in the acid producing capacity. While the unleached discards were classified as potentially acid forming, the leached discards were observed to be non-acid forming in samples studied after both 297 and 380 days of irrigation. Biokinetic tests conducted before and after leaching revealed that the leached discards had a lower acid generation and higher acid consumption rate than the unleached discards. This confirmed a substantial depletion of the pyritic content and an increase in the neutralising capacity.

The calorific values of the coal discards pre- and post-leaching gave an indication of the effect of the leaching operation on the discards energy content. The results showed that the leached discards had a slightly higher calorific value than the unleached discards, implying an improvement in the quality of the coal as a result of the leaching process. In this study, the resultant increase in calorific value does not appear high enough for use as an energy source. Instead, use a matrix for soil fabrication may be appropriate; however, with associated density separations, recovery of fractions with energy value may be feasible. Should re-purposing of the solid residue not be feasible, disposal without legacy risks of ARD can be achieved.

Further, in order to ensure the accelerated leaching of the sulphidic fraction of coal discards is feasible, the re-purposing of the leachate is required. Early-stage analysis demonstrates the re-purposing of the Fe and S fractions as pigments, coagulants and other, while value recovery through potential recovery of REEs is recommended for further study.

6 Conclusions and recommendations.

Coal wastes present significant environmental risks, including soil degradation and destruction of the ecosystem. This is due to factors such as land use, spontaneous combustion, leaching, and dust evolution, all contributing to air and water pollution. When exposed to oxygen and moisture, sulphide-bearing overburden, waste rocks, and tailings generate ARD. This polluting ARD affects water sources with elevated acidity, dissolved metals, and soluble sulphates, thereby increasing overall salinity over time. Heap bioleaching presents as a viable alternative to enable the accelerated removal of the sulphur component of the coal discards, preventing long-term ARD potential and opening possibilities for re-use and re-purposing of the fractions otherwise classified as waste. Heap bioleaching has been effectively utilized for extracting metals from low-grade sulphidic ores. With its capacity to reduce energy costs associated with processes like comminution, aeration, and agitation in tank leaching, heap bioleaching shows promise as a potential method for expediting the leaching of the pyritic component, along with other mineral sulphides, from mining wastes, such as discarded coal, within the operational lifespan of a mine under controlled conditions. This approach aims to prepare materials for potential reuse and re-purposing or, where essential, to dispose of a discards fraction of low S content, so as to prevent the long-term generation of ARD.

As outline is Chapter 1, the objective of this study is to investigate the efficiency and efficacy of accelerated leaching of high sulphur coal discards, prior to long-term disposal or re-purposing, as an ARD prevention approach. It was hypothesised that accelerated heap bioleaching of coal discards constitutes a viable long-term ARD prevention technique, as efficient desulphurisation of coal discards with high pyritic sulphur content can be achieved in packed bed of coal discards during the life of the mine. Further, through this, desulphurised discards can either be discarded with reduced risk or re-purposed, while the sulphate and metal rich leachate can be further processed for recovery of chemical fractions. This objective was pursued through experimental work addressing the following research questions:

- To what extent can sulphur be removed from the coal discards through accelerated heap bioleaching?
- Under what time frame can the coal discards be non-acid generating when desulphurised using heap bioleaching?
- What challenges does accelerated heap bioleaching of coal discards present as an ARD prevention method?
- What opportunities are available for re-purposing of the iron and sulphur rich PLS released and the residual desulphurised coal discards?

The experimental work involved initial proof-of-concept research using column reactors at a laboratory-scale to investigate the viability of accelerate heap bioleaching in mitigating ARD. Subsequently, comprehensive static and microbial characterisation of the leached coal discards was conducted. Lastly a brief exploration of the potential of value recovery from the leached solution was presented.

6.1 Research outcomes

6.1.1 Desulphurisation of coal discards

Results from the column irrigated with water (CW) match the leaching behaviour of high sulphur coal discards when exposed to natural weathering conditions. It was observed that as the acid neutralizing potential of the discards depleted, acid production was observed. These results confirmed the lasting impact of ARD as previously studied.

Extensive desulphurisation was successfully accomplished in the acidified columns over the 380 days of leaching. The effluent solution pH first increased, due to the acid consuming reactions, then decreased over time. Evidence of microbial Fe^{2+} oxidation and ferric leaching of the pyritic fraction was observed, as indicated by increase in redox potential and Fe^{3+} concentration. In the inoculated experimental columns, C1, C2 and C3, the iron and sulphur removal efficiency was within the range of 55-69% over 380 days. The time-course profile of desulphurisation indicated rapid initial desulphurisation such that 25 – 40% of the Fe and S were solubilised within 90 to 120 days. Thereafter a slowing of the rate resulted such that 35 – 50% release was achieved by 180 days (i.e. an additional 10% in 90 days), and finally 55 – 70% by 380 days (i.e. an additional 20% in 200 days). By extrapolation, it is proposed that all Fe and S would be removed within 525 to 655 days. However, the required release to ensure environmentally responsible disposal or re-use is unlikely to require complete Fe and S removal.

The effluent solution from the non-inoculated column CA, exhibited a similar pattern of pH change, with an initial increase owing to neutralisation followed by a decrease as acidification set in. The redox potential increased, indicating Fe^{2+} oxidation by iron-oxidising species. Acidification resulted in the dominance of Fe^{3+} as the main oxidising agent, facilitating desulphurisation. Results from the non-inoculated column compared to the inoculated columns pointed to a microbial community native to the coal discards that is likely to develop and colonise the packed coal bed naturally under appropriate acidic conditions and to have played a significant role in enhancing the Fe^{2+} oxidation to Fe^{3+}. In other words, the indigenous

microbial community that would eventually be responsible for long-term acid generation and ARD pollution can be effectively harnessed to enable accelerated leaching and S removal during the life of mine.

6.1.2 Post-leaching characterisation

The acid generating capacity of the coal discards was assessed through static tests conducted before, during and after the leaching experiment. Although XRD analysis confirmed the presence of acid neutralizing compounds in the unleached discards, they were unable to counterbalance the acid-producing capacity. The coal discards had a NAPP of 70 kg H_2SO_4/ton and were acid forming. However, the acid generating potential decreased over time in the accelerated leach environment, with the NAPP decreasing to 34.0 kg H_2SO_4/ton and uncertain acid generating status by 144 days, the range – 9.0 to -24.0 kg H_2SO_4/ton and non-acid-forming status by 297 days and finally reaching -122.40 kg H_2SO_4/ton by day 380 to be classified as non-acid forming.

Biokinetic tests were performed on both the unleached and leached coal discards, to evaluate the pace of acid production and consumption while considering microbial activity promoting Fe^{2+} oxidation. The initial pH of the unleached coal discards rose due to acid-neutralizing reactions, but subsequently declined to around pH 1.8, indicating rapid oxidation powered by sulphide minerals. The redox potential reflected the observed pH results confirming the acid generating potential of the discards.

The leached coal discards from CA produced a significantly decreasing pH profile, matched with increasing redox potential and Fe^{3+} concentration. The observed increase in acid production in the sample was thought to be due to a decrease in its acid-neutralizing components during the leaching experiment coupled with augmented presence of pyrite constituents resulting from milling preceding the biokinetic tests. Samples from C1 and C3 showed declining acid producing capacity, with fluctuation in pH and redox potential. The Fe^{3+} levels remained consistently low in these samples, indicating a depletion of the pyritic content and reduced acid generation.

6.1.3 Key challenges encountered

This study has identified key challenges associated with heap bioleaching of coal discards as an ARD prevention method, including pyrite liberation, operating temperature, and the duration of the desulphurisation process. The low pyrite liberation typically observed in coal discards, which limits the exposure of pyrite surfaces to leaching agents. This reduced exposure decreased the efficiency of sulphur removal and extended the desulphurisation timeline. To address this, pre-treatment methods such as comminution could be explored, but

their technical and economic feasibility must be carefully assessed within the heap bioleaching framework.

Another critical challenge is controlling the temperature during the leaching process. While higher temperatures can accelerate chemical and biological reaction rates, they also increase the risk of spontaneous combustion, a serious concern when handling coal. Ensuring that the heap temperature remains below the coal's self-heating threshold is crucial to prevent combustion while maintaining effective bioleaching activity. Furthermore, the extended time frame required for biological desulphurisation, compared to faster physical or chemical methods, represents a logistical and economic constraint.

6.2 Concluding remarks

This study demonstrated a theoretical validation of the accelerated heap leaching process for the removal of sulphur from coal wastes. Significant desulphurisation was achieved as the column reactors used were operated in an accelerated inoculated environment with continuous acidification achieved through irrigation. The effectiveness of the desulphurisation process was evident through the removal of sulphur and iron from the discards.

Optimisation of the leaching process is required to reduce the timeframe require to prevent ARD pollution from the discards. The results of biokinetic test confirmed that the treated discards were not acid generating. Further, the study indicated that heap bioleaching conducted over a period of approximately one year would be sufficient to eliminate the environmental hazard, even before process optimization.

The uninoculated environment maintained under acidified conditions, showed significant iron and sulphur removal, resulting in non-acid forming behaviour. This suggests the formation of a proficient native microbial culture capable of desulphurising the discards. Inoculated and indigenous microbial communities exhibited different behaviour at the offset of the leaching experiment, where the uninoculated conditions maintained a lower redox potential, indicating a lower capacity for Fe^{2+} oxidation which was subsequently enabled.

Although results from the static test substantiated a transition to non-acid producing status of the leached discards, the sample from CA showed slightly higher residual in the biokinetic test. Additional research would be necessary to analyse the variables that contributed to these findings.

As this study successfully demonstrated the viability of heap bioleaching for desulphurising potential acid-forming coal discards, it is imperative to thoroughly investigate the repurposing of both the leached coal discards and the ferric sulphate rich leachate produced. One potential

option is energy generation using the leached coal discards, while the generated leachate could be utilized to produce iron oxides, iron salts, sulphuric acid.

The findings demonstrated the inherent capacity of the coal discard to generate acidity, which can be mitigated through the leaching process. The decrease in acid generating potential over time suggests a possibility for rehabilitating these discards and reducing their environmental impact.

6.3 Recommendations

Additional investigations into the key parameters influencing the leaching process are recommended:

- Optimisation of coal discards particle size: Particle size significantly influences leaching efficiency with smaller particle size increasing the surface for the leaching solution to react with the coal discards thus accelerating the process. However, finer particle size is susceptible affect permeability thus hindering the flow of leachate and oxygen diffusion. Finding the optimal particle size is therefore key in achieving maximum desulphurisation.
- Microbial consortium: selecting the most suitable microbial strain is crucial to ensuring efficient desulphurisation of the coal discards. Microorganisms native to the coal discards have shown promising results. Further investigations are recommended to understand the diversity and dynamism of these strains and enhance desulphurisation efficiency.
- Leaching solution flowrate and recirculation: further investigations into the effect leaching solution flow rate and recirculation are recommended. Although higher flow rate may improve leaching efficiency, this could affect bed stability. Recirculation of leachate is crucial to concentrating PLS for adequate value recovery. However, recirculation of leaching solution could introduce microbial inhibitors and precipitates negatively affecting microbial community and bed permeability.
- Leaching process duration: exploration of suitable leaching duration is recommended. Although longer duration may improve the process overall efficiency, it implies higher operating costs and potential environmental impact.
- Re-purposing and value recovery: results have shown promise in improved calorific value of leached coal discards making it adequate for energy generation. High-calorific-value desulphurised coal presents a direct opportunity for sale as industrial fuel, while lower-calorific-value desulphurised coal can be repurposed into fabricated

soils, promoting sustainable land rehabilitation. Comprehensive techno-economic analyses should determine the viability of these products as value-added outputs. On the other hand, the leachate solution presented opportunity for the recovery of valuable products. This includes sulphur for agricultural applications, ferric sulphate for coagulants and pigments production, and the recovery of rare earth elements (REEs), which are critical for high-tech industries. Further investigation into the possibilities of re-purposing and value recovery is thus recommend to improve the process economic feasibility and environmental impact.

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7 Experimental results

Please be advised that the experimental results of the dissertation are available on ZivaHub platform. You can access them via the following link:
[https://figshare.com/s/d85d4595aa46be8c2d71]