REPURPOSING PYRITE FROM COAL WASTE

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

Sustainable management of coal waste is a global environmental concern for collieries worldwide. South African regulatory framework is comprehensive on environmental management of mining activities, taking a cradle to grave approach which puts the mining industry under pressure to adopt more proactive ways to deal with mine waste. In South Africa, coal waste streams are currently one of the largest industrial wastes, yet only limited studies have been done to evaluate their potential for repurposing.

This study aims to provide a proof of concept to demonstrate the feasibility to concentrate pyrite contained in South African coal wastes and recover iron-based coagulants in support of recovery of valuables from local coal downstream emissions. This approach has the potential to improve resource efficiency and provide opportunities for coal mines to enhance their financial viability through product diversification. Furthermore, the establishment of a secondary economy also stimulate enterprise development and economic development in support of addressing unemployment, poverty and inequality for local communities past the perceived mine ‘end-of-life’.

The technical feasibility on the use of dense medium separation to concentrate pyrite from South Africa coal discards was investigated by using sink and float studies. The coal discard fractions of from the sink and float studies were characterized and future applications are suggested based on emerging and established technologies.

Relative densities lower than 2.2 g.cm^{-3} represent 69.9% of the bulk mass with 25.5% and 0.7% sulphur and ash content respectively, as well presenting 22.3 MJ.kg^{-1} in terms of gross calorific value. Based on the theorical recovery of the sink and float studies, this fraction complies with market standards for thermal coal. Approximately 2% in mass (>2.7 g.cm^{-3}) presents as a sulphide-rich fraction with a total sulphur content of 34.7% and a pyritic sulphur content of 33.3%, representing a total and pyritic sulphur recovery of 42.4% and 45.3% respectively. The removal of the pyritic fraction in coal discards causes a significant reduction in the acid generation potential and neutralizing reagent consumption in ARD treatment facilities. In addition, the recovered pyrite concentrate could be converted into valuable products such as ferrous sulphate, sulphuric acid and iron oxides which can be utilized as raw materials in other industrial sectors.

The development of the proof-of-concept for coagulant production was divided in two phases. Under phase one it demonstrated the feasibility to produce ferrous sulphate crystals using South African coal waste with a total sulphur content of approximately 30%. In a second moment, the ferrous sulphate crystals developed from coal waste were used to obtain a ferric iron-based coagulant that was tested on a synthetic wastewater.

A 20 g/L ferrous iron solution with potential for melanterite recovery was produced by acid leaching under abiotic conditions and its was mixed with ethanol to obtain ferrous sulphate crystals. Elemental speciation was conducted to compare the ferrous sulphate produced from coal wastes with ferrous sulphate analytical grade and the results indicated that the products have similar purity grades. The ferrous sulphate crystals were then further oxidized to produce a ferric-iron based coagulant with ferric-iron concentrations of approximately 100 g/L of ferric iron. The coagulant obtained from high-sulphur coal discards was tested on a synthetic wastewater. The results indicated 99% of phosphorous removal and a decrease in the chemical oxygen demand from 109 to 22 ppm, representing a reduction of 80%.

According to the results, it was possible to isolate a pyritic material from coal waste with potential for further processing using bio hydrometallurgical approaches in order to develop an alternative route to recover ferrous sulphate crystals to be used as raw material for the production of ferric based coagulant. The validation results demonstrated that the coagulant has potential to remove metals and phosphorous from wastewater improving the quality of the final effluent.

Pyrite concentration and optimization studies in order to enable technological transfer are identified as future work recommendation. Yet, the use of iron enrichment to recovery phosphorus in form of Vivianite from municipal wastewater is an emerging research field that could be also explored.

Apart from improving resource efficiency and providing opportunities for coal mines to enhance their profitability through product diversification, the proposed approach also presents environmental benefits. These include a reduction in the net volume of waste requiring disposal, a reduction in acid generation potential of coal discards and related treatment costs as well as a reduction in long-term liabilities.

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LINKED OUTPUTS

Gcayiya, M., J.R. Amaral Filho., and S.T.L. Harrison. On the production of sulphur and iron-based materials from pyrite contained in South African coal waste. In: *SAIMM Mineral research conference*, Cape Town, 11-12 November 2019.

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ACRONYMS & ABBREVIATIONS

ABA	Acid Base Accounting
ANC	Acid Neutralisation Capacity
ARD	Acid Rock Drainage
ASTM	American Society for Testing and Materials
COD	Chemical Oxygen Demand
CWSF	Coal Waste Storage Facility
DI water	De-ionized water
DMS	Dense Medium Separation
D_{50}	PSD where 50% of the material is less than the stated size
HF	High-Flow
MPA	Maximum Potential Acidity
MWSF	Mine Waste Storage Facilities
NAF	Non-Acid Forming
NAG	Net Acid Generation
NAPP	Net Acid Production Potential
PAF	Potentially Acid Forming
REE	Rare Earth Elements
UCT	University of Cape Town
UFRGS	Federal University of Rio Grande do Sul
USGS	United States Geological Survey
WRC	Water Research Commission, South Africa
XRD	X-rays diffraction
XRF	X-rays fluorescence

GLOSSARY OF TERMS

Cradle-to-grave: is an assessment which considers impacts at each stage of a product's life-cycle, from the time natural resources are extracted from the ground and processed through each subsequent stage of manufacturing, transportation, product use, and ultimately, disposal.

Circular Economy: A circular economy is a model of production and consumption, which involves sharing, leasing, reusing, repairing, refurbishing and recycling existing materials and products as long as possible.

Mesophilic Bacteria: A group of bacteria that grow and thrive in a moderate temperature range between 20°C and 45°C.

Run-of-Mine: ore in its natural, unprocessed state.

Vivianite: hydrated iron phosphate mineral found in a number of geological environments.

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CHAPTER 1: BACKGROUND

1.1 Introduction

Society is moving towards the development of a circular economy with resource cycles moving towards closure. Therefore reusing, recycling and repurposing of wastes becomes increasingly important. This is driven by the limited availability of natural capital in the earth's ecological, biological and physical systems, and by the effect on quality of life and on wealth generation. An objective of the circular economy is to maximize the life expectancy of resources, minimizing (or preferably eliminating) waste production and consequent environmental risks. In water-scarce South Africa, reducing environmental risks to precious water resources is especially important.

Despite of its commitment to implement a lower carbon economy, over 70% of South Africa's primary energy needs are still derived from coal (Bahrami et al., 2018). To achieve market standards, the run-of-mine (ROM) coal in South Africa is mostly washed, and following beneficiation, a significant part of the total mass is disposed in mine waste storage facilities (MWSF) such as dump deposits and tailings dams. Moreover, no economic value is recovered from the waste and the risk of generating the well-known socioenvironmental impacts and economic liabilities such as acid rock drainage (ARD) from these wastes persists (Chugh and Behum, 2014; North et al., 2015; Ojonimi et al., 2021).

South African coal mining operations still rely on costly end-of-pipe management approaches to coal waste disposal and ARD treatment. MWSF seepages generate thousands of cubic meters of highly concentrated ARD with pH values around 2 daily, releasing tons of iron, sulphur, and other elements of value into natural systems and causing the well-known environmental impacts, economic costs, and environmental liabilities. ARD treatment techniques, such as lime neutralization and precipitation, are extensively used to mitigate such impacts. These consume large amounts of expensive reagents and energy while generating significant quantities of sludge which have to be managed. These methods are only effective in reducing ARD risks in the short term. Thus, preventive measures which can minimise the generation and subsequent dispersion of ARD from waste coal or reduce the amount of acid generating material present in the disposed waste are key for a sustainable MWSF closure (Kotsiopoulos and Harrison, 2018a; Mjonono et al., 2019).

In addition to reducing ARD risk/concentration, the integration of a sulphide removal step into the beneficiation circuit offers the opportunity for value recovery and enhanced resource efficiency whilst removing most of the acid generating material (Amaral Filho et al., 2013; Harrison et al., 2013). In short, the repurposing of acid generating minerals, such as pyrite, would reduce the environmental damage caused by coal waste storage facilities, the volume of coal waste disposed and the amount of reagents required for ARD treatment (Amaral Filho et al., 2017; Weiler et al., 2016).

Improved coal waste management offers potential for the retrieval of value from coal waste by repurposing of associated materials to other uses consistent with the circular economy concept. The potential for separation of sulphides from processing wastes and its application as an effective means to reduce or even remove ARD risks has been demonstrated in WRC K5/1831, WRC K5/2231 and WRC K5/2580. Previous research has shown that through biohydrometallurgical processes the pyrite contained in coal discards can be isolated and converted into valuable products including, but not limited to, ferrous sulphate, sulphuric acid, iron oxides and ferric coagulants (Lopes, 2017; Villetti, 2017).

The current South African regulatory framework has a comprehensive ‘cradle to grave’ approach to environmental management of mining activities, pressurizing the mining industry to adopt more proactive ways to deal with mine waste. This supports the development and implementation of sustainable solutions to the production of valuable materials from the pyritic fraction. This can include iron-based coagulants largely used for water and wastewater treatment. Ideal practice is to separate pyrite rich waste from other waste fractions using mineral processing operations such as flotation and dense medium separation. This reduces the acid generation potential of rest of the coal waste. The pyritic portion can then be repurposed to obtain products with aggregated market value. Using this sustainable approach, the principle of waste minimization is used in conjunction the repurposing of waste materials into products of value.

This project aims to provide a proof of concept to demonstrate the feasibility of concentrating pyrite contained in South African coal waste to recover iron-based coagulants. This approach has the potential to improve resource efficiency and provide opportunities for coal mines to enhance their profitability through product diversification. The establishment of a secondary economy also creates employment opportunities for local communities past the perceived mine ‘end-of-life’.

The proposed approach also has long-term benefits in line with sustainability concepts:

- a reduction in the net volume of waste requiring disposal, thereby reducing land usage and preventing the ongoing generation of leachates containing polluting components, particularly acid rock drainage;
- a source of pyrite for recovering of iron, sulphur and other valuable metals;
- a source of high ash material for safer disposal or future research development for repurposing;
- a source of ferric-based coagulant to be used in water and wastewater treatment;
- a source of ferrous sulphate to be used in agriculture and chemical industries;
- human capital development for the environmental management, sustainability science and technology sectors.

1.2 Project Scope

In this study, the proof-of-concept of recovering pyrite from coal waste and its further processing into crystals of ferrous sulphate is explored as an option for providing a source of ferric-based coagulant for wastewater treatment. Resolution of the following specific objectives form the focus:

- identify key opportunities to obtain metal-sulphur based concentrates for the valorisation of coal mine waste in the South African context;

- techno-environmental characterization of the coal waste and materials produced;
- production of ferrous sulphate heptahydrate and ferric-based coagulant;
- compare ferrous sulphate crystals developed from coal waste with commercially available ones;
- indicate the potential for upscale and technology transfer.

CHAPTER 2: LITERATURE REVIEW

2.1 Coal waste and sulphide repurposing opportunities

Lloyd (2000) reported that in 1990 43 million tons of coal waste material was discarded into waste dumps in South Africa. While in 2001 the Department of Minerals and Energy reported that about 53.8 million tonnes of coal waste were produced that year (Department of Minerals and Energy, 2001). By 2011, close to 1.5 billion tons of coal discard were estimated to be have been generated in South Africa, produced in excess of 60 Mt annually (Belaid et al., 2013). While these large amounts of material both increase the operational costs and negatively affect the environment through their long-term legacy, they contain significant amounts of usable coal as well as other minerals of interest such as pyrite, carbonates and aluminium silicates which can be recovered through the application of approaches in line with circular economy principles (Harrison et al., 2013; Lloyd, 2000; North et al., 2015). Amaral Filho et al. (2013), illustrated that by processing coal waste discards with a total sulphur content of ~7% using well-known gravity concentration techniques, such as dense medium separation, three distinct density fractions can be obtained. Based on their technological characterization, the fractions with low and medium relative densities can be used as raw material for power generation and in the construction sectors respectively (Argane et al., 2015a; North et al., 2015). The fraction with highest density was rich in sulphur, with a pyrite content higher than 70% which has potential to generate an induced ARD for further applications. Through biohydrometallurgical processes, the leachate can be converted into valuable products including, but not limited to, ferrous sulphate, sulphuric acid and iron oxides (Lopes, 2017; Runkel and Sturm, 2009; Vigânico, 2014). The final waste material is depleted in sulphur with reduced ARD risks, and potential to be further re-purposed (Oliveira et al., 2012; Patricio Ferreira et al., 2021).

The isolation of pyrite-rich waste from waste dumps brings not only environmental benefits, but also an integrated management of the pyrite in the collieries which could contribute to the sulphur-related industry in South Africa. According to the (Department of Mineral Resources, 2012), commercial deposits of elemental sulphur are currently still unknown in South Africa; however, sulphur in pyritic form is found in numerous deposits in South Africa. Most of the known pyrite deposits have not been exploited for economic gain. Many of these deposits also contain other potentially valuable minerals and pyrite can be recovered as a by-product. Examples of these include the auriferous conglomerates of the Witwatersrand and coal deposits in Mpumalanga and Waterberg.

Best practice in management of coal discards considers primarily the reduction of downstream emissions. Therefore, the technological and environmental characteristics of both new and existing waste material is fundamental to decisions aiming to minimise mine waste through “near zero mine waste” strategies (Kinnunen and Kaksonen, 2019; Tayebi-Khorami et al., 2019). The improvement in the efficiency of combustion technologies has made the use of old mineral processing plants for remining of CWSF a reality in South Africa. However, the focus is still only on thermal recovery and other opportunities are not considered. Potential exists to integrate mineral processing techniques with waste repurposing and value recovery. Several studies have demonstrated that pyrite oxidation using biohydrometallurgical processes is possible as a route to recover a variety of products that can be utilised as raw material in other industrial sectors (Figure 2-1) .

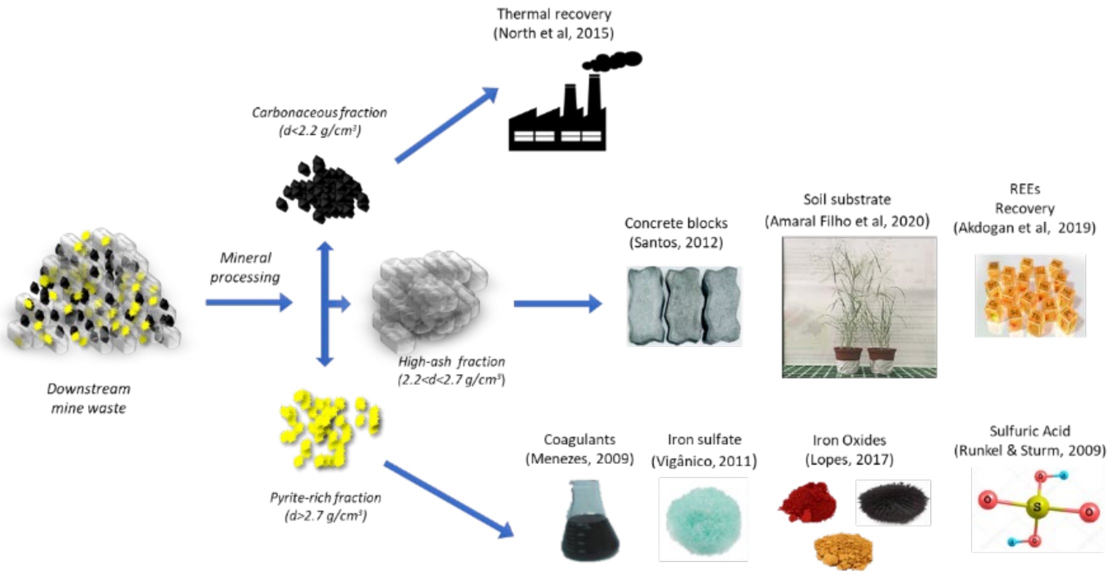


Figure 2-1 Two-stage process to repurpose coal waste including established and emerging technologies to produce metal and sulphur-based materials from pyrite concentrates

These products may include magnetic materials such as magnetite and ferrite, as well as pigments like goethite and hematite (Lopes, 2017). Magnetite has applications in the production of ferrofluids which are used in the coal processing industry to adjust the density of medium suspensions (Love et al., 2005), as supports for medicinal products (Kumar and Mohammad, 2011), as contrast agents in medicine (Elias and Tsourkas, 2009), and as an adsorbent material in the treatment of liquid effluents (Acisli et al., 2017; Ahmed et al., 2013). The most commonly used route for magnetite synthesis is the co-precipitation of ferrous and ferric ions in alkaline pH conditions, due to the simplicity and efficiency of this synthesis method (Laurent et al., 2008). However, in the presence of other metals magnetic ferrites may form and therefore the synthesis of magnetite is usually conducted from pure materials (Nikolic et al., 2014) such as: $FeCl_3.6H_2O$, $FeCl_2.4H_2O$ and $FeSO_4.7H_2O$ (Ahmed et al., 2013; Petcharoen and Sirivat, 2012; Šutka et al., 2014). Some studies have reported the use of iron mining residues (Kumar et al., 2015; Wu et al., 2011) and recovery of iron present in the effluent from processing of coal mine tailings (Vu et al., 2010) for magnetite production.

According to Vigânico (2014), melanterite can be produced from bioleaching of a pyritic sample with 39% sulphur content, through the application of a two-stage process. Bioleaching was initially performed to produce a ferric iron rich solution, thereafter, 99% of the ferric iron was reduced to ferrous iron under anaerobic (anoxic) condition. However, the final product contained metals such as Al, Mn, Zn, As, Pb, among others which was associated with the bulk pyritic coal waste, making it difficult to produce a high purity product. To address the purity issues ethanol was used to precipitate the dissolved ferrous ions as ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) and following recrystallization the purity of the salt produced from the coal waste improved and was comparable to commercially available $FeSO_4.7H_2O$

products. As a main finding, the overall process needed further fundamental understanding especially relating to the micro-biochemical reactions to improve overall system kinetics and efficiency improvement to improve the final product quality (Colling et al., 2017).

In line with the approach suggested above, and to minimise the potential for ARD generation from sulphidic coal waste rocks in SA, the pyritic portion can be removed and repurposed for value addition before disposal. Pyrite-rich fractions of waste rock can be recovered by gravimetric or physiochemical separation processes so that the reject waste rock presents a lower sulphidic content and lower potential for acid generation. This separation is possible through the repurposing of current coal processing DMS units. Applying this approach to coal waste in SA would avoid considerable environmental impact and add value to the mineral coal production chain.

2.2 Pyrite bio-hydrometallurgical aspects

When not exposed to water and oxygen, pyrite is a non-toxic and stable compound widely used for the manufacture of sulphuric acid and sulphur dioxide as well as to produce fertilizers. Studies have also demonstrated the potential for use of pyrite in the production of photovoltaic and lithium batteries (Altermatt et al., 2002; Siyu et al., 2009). However, when not managed properly pyrite will generate ARD with the well-known socio-environmental and economic costs. (Fortes et al., 2021), showed that more than 7000 t/year of Mg, 4700 t/year of Al, 3700 t/year of Mn, 34 t/year of Co, 2.3 t/year of Sb, and around 24 t/year of rare earth elements (REE), are discard into the environment in the Iberian Pyritic Belt. Considering the market metal prices for 2019, the resources contained in the evaluated lixiviates have a potential value of around 95 million USD.

Hydrometallurgy techniques, use an aqueous medium to concentrate a compound or element of interest in solution and when the process is also driven by microorganisms is called biohydrometallurgy (Atlas and Bartha, 1993).

Pyrite is an abundant mineral in the earth and its reactivity under weathering conditions has been thoroughly studied and is considered being is the major source of ARD formed from coal processing wastes (US Environmental Protection Agency, 1994). Pyrite leaching is a complex biogeochemical process that occurs when the mineral surface is exposed to water and air according to the following reactions (Kontopoulos, 1998; Salomons, 1995).

In ARD formation pyrite (FeS_2) oxidizes in the presence of water to ferrous ions (Fe^{2+}), acidic ion (H^+) and sulphates (SO_4^{2-}). Equation 1 demonstrates the chemical weathering reaction responsible for the acid forming reactions, usually occurring abiotically. However, depending on pH and redox potential values the presence of microorganisms may also be observed.

$$2\,FeS_2 2 + \frac{7}{2}O_2 + H_2O \rightarrow \mathrm{Fe}^{2+} + 2\,SO_4^{2-} + 2\,H^+ \quad (1)$$

By keeping the redox potential of the system over 500mV, the ferrous ions are oxidized to ferric ions (Fe^{3+}) (Equation 2), and acidity increases. With the pH lower than 3.5 the Fe^{2+} oxidation will occur at very slow rates.

$$\mathrm{Fe}^{2+} + \frac{1}{4} O_2 + H^+ \rightarrow \mathrm{Fe}^{3+} + \frac{1}{2} H_2O \quad (2)$$

At pH values below 4.5, ferric iron becomes the dominant oxidant, oxidizing pyrite according to the reaction shown in Equation 3. In natural disposal systems, the ARD reactions are catalysed by acidophiles such as *Acidithiobacillus ferrooxidans* (Fe and S oxidizer), *Acidithiobacillus thiooxidans* (S oxidizer) and *Leptospirillum ferrooxidans* (Fe oxidizer).

$$FeS_2 + 14\ \mathrm{Fe}^{3+} + 8\ H_2O \rightarrow 15\ \mathrm{Fe}^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (3)$$

If pH increases to above 3, the Fe^{3+} hydrolysis forms hydroxide precipitates (Figure 2-2) and generates more acidity ions (Equations 4 and 5) (Parbhakar-Fox and Lottermoser, 2015)

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

$$\mathrm{Fe}^{3+} + 2\ H_2O \rightarrow FeoOH + 3\ H^+ \ (5)$$

Other secondary acid-forming sulphates reported to occur in weathered coal and coal wastes include alunite ($KAl_3(SO_4)2(OH)_6$), melanterite ($FeSO_4{\cdot}7H_2O$) and schwertmannite ($Fe_8O_8(OH)_6(SO_4){\cdot}nH_2O$). These metastable sulphur species generate acid when they convert to more stable ferric hydroxides and oxides (Miller, 2008; Stewart et al., 2006a).

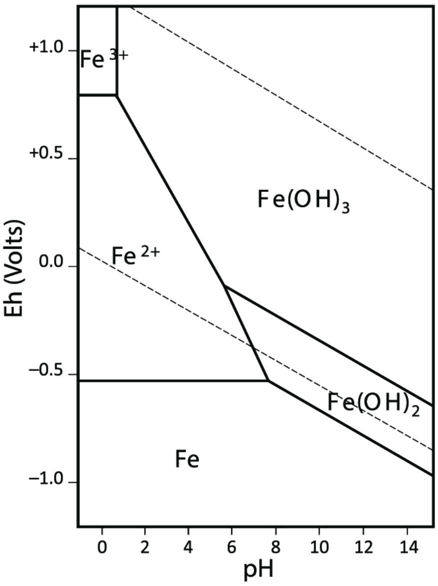


Figure 2-2 Stability-field diagram for aqueous ferric-ferrous system (Hem and Stumm, 1961)

The cyclic oxidation of pyrite and generation of ferric ions can continue for decades, or even centuries, producing more acid and sulphates which can contaminate water bodies if not contained. The isolation of pyrite from coal waste and its further processing in controlled environments can avoid the waste of tons of sulphur and iron that could be redirected to other industrial processes.

2.3 Ferrous sulphate and its applications

Ferrous sulphate is widely used as a flocculating agent in wastewater treatment (Metcalf et al., 2004). Barbosa Mazza et al (2020) used hydrogen peroxide to oxidise ferrous sulphate crystals to produce a ferric based coagulant with environmental benefits. Another field where ferrous sulphate heptahydrate is widely applied is in agriculture where it is used as a soil fertilizer and iron supplement to prevent plant chlorosis virus, commonly known as yellow leaf disorder in vegetables (Zheng-qing and Cang-zhen, 1982). According to (Moodley et al., 2019), millions of dollars were lost in the agricultural industry due to chlorosis virus. This virus, caused by the deficiency of iron in crops, is a serious threat in the commercial agricultural industry and smallholder agriculture related businesses. Additionally, ferrous sulphate is also used to deter snails that harm plants, especially in the early stages of growth (Gázquez et al., 2021a). Ferrous sulphate has also been used in the pharmaceutical industry in drug formulations employed to treat anaemia, both in humans and animals, and other diseases linked to a nutritional deficiency of elemental iron (Santiago, 2012). The Portland cement industry also applies ferrous sulphate as a hexavalent chromium reducing agent for cement and concrete production (Klemm, 1994).

The most common method used for the industrial production of ferrous sulphate heptahydrate is through acid dissolution of high purity metallic iron in hot sulphuric acid to generate an effluent containing a high concentration of iron, sulphate and acidity. This acidic effluent is evaporated and crystallised to form ferrous sulphate (U.S. EPA, 1978). Ferrous sulphate heptahydrate also known as melanterite, green vitriol or copperas, is a greenish blue salt commercially produced as a by-product in the manufacturing of titanium dioxide (Gázquez et al., 2021b) and in steel pickling with sulphuric acid (Kehrmann, 2005; U.S. EPA, 1978). In this project we propose using the iron and sulphate rich solution from the leaching of pyritic coal discards for the production of ferrous sulphate crystals with application in water treatment.

Apart from ferrous sulphate, used in several industrial sectors as, for example, food supplements, agriculture (Ozores-hampton, 2013) or reagents for the Fenton reaction in advanced wastewater treatment (Tchobanoglous et al., 2004), the ferrous sulphate obtained from coal waste may be further processed to produce ferric based coagulants (Menezes et al., 2016; Villetti, 2017).

2.4 Iron based coagulants

Coagulants are chemical reagents widely used in water and wastewater treatment, that have the ability to destabilize non-sedimentable colloidal particles. These compounds, usually metal salts, modify the physicochemical conditions, breaking down the stability of the colloid to promote the formation of precipitates. The coagulant facilitates the separation of the colloidal particles from the liquid medium for later precipitation and solid-liquid separation (BRATBY, 2006; Tchobanoglous et al., 2004). Most of the coagulants available commercially are aluminium and iron based, usually aluminium sulphate ($Al_2(SO_4)_3.14H_2O$) or ferric chloride ($FeCl_3.6H_2O$). However, other commercial coagulants are emerging including aluminium polychloride, ferric sulphate ($Fe_2(SO_4)_3.9H_2O$) and ferrous sulphate ($FeSO_4.7H_2O$). Some organic coagulants are also currently being used, for example Tanfloc which is a tannin-based coagulant (Sánchez-Martín et al., 2010). It is reported that residual amounts of aluminium in drinking water are detrimental to human health, causing neurological diseases with a link to Alzheimer’s disease (Rondeau et al., 2000). Iron salts such as ferric sulphate (FS), ferric chloride (FC) and ferrous sulphate (FS) are therefore preferred alternatives to aluminium-based coagulants.

Iron-based coagulants, as mentioned with regard to ferrous sulphate in Section 2.3, are commonly produced through acid dissolution of iron scraps or iron ore (Tchobanoglous et al., 2004). Recent research has shown that it is possible to produce iron salts such as poly-ferric sulphate (PFS) and poly-alumino-iron sulphate (PAS) and ferrous sulphate (FS) coagulants by selective precipitation of the metals present in ARD (Menezes et al., 2010, 2009; Rao et al., 1992). The precipitation was achieved by increasing the pH using basic compounds such as sodium hydroxide to precipitate dissolved metals as hydroxides. These iron hydroxides were then dissolved in sulphuric acid to obtain an iron solution. Menezes et al. (2009) investigated the potential to selectively precipitate iron from ARD and produced inexpensive poly-ferric sulphate chemical coagulant (PFS) and following wastewater treatment tests it proved as efficient as commercial coagulants. However, significant amounts of contaminants such Al, Ca, Mn, Pb and Zn were present in the final product.

2.5 Project description and aims

In this project, the downstream waste management approach described in Section 2.1 was followed. The methodology was applied to South African coal discards to identify the possibilities of producing a pyrite enriched stream to be used to obtain a concentrated iron and sulphate solution using biohydrometallurgical processes as detailed by Colling et al. (2011) and Vigânico et al. (2011). We report the gravimetric separation of coal waste to obtain a pyrite enriched fraction of coal waste reported in CHAPTER 3, thus demonstrating the generation of the iron and sulphate rich stream (Oliveira et al., 2016). Production of an iron sulphate coagulant following leaching of pyritic coal waste is reported in CHAPTER 4: Precipitation of the iron sulphate salt from the leachate is reported in CHAPTER 5 The water treatment study is presented in CHAPTER 6.

CHAPTER 3: PYRITE ENRICHMENT OF SOUTH AFRICAN COAL WASTE BY GRAVIMETRIC SEPARATION

3.1 Background and objective

In this section the technical feasibility of concentrate pyrite from South Africa coal discards is demonstrated. Gravimetric separation of coal discards produces fractions of varying density each with potential for further application (Amaral Filho et al., 2017a). Through their characterization and evaluation of techno-environmental aspects, future applications are suggested based on emerging and established technologies.

3.2 Experimental approach

The coal discards used in this study were collected from a dense medium separation unit on a colliery within the eMalahleni region in Mpumalanga. Sink and float studies were performed to assess the coal accessibility through gravity concentration.

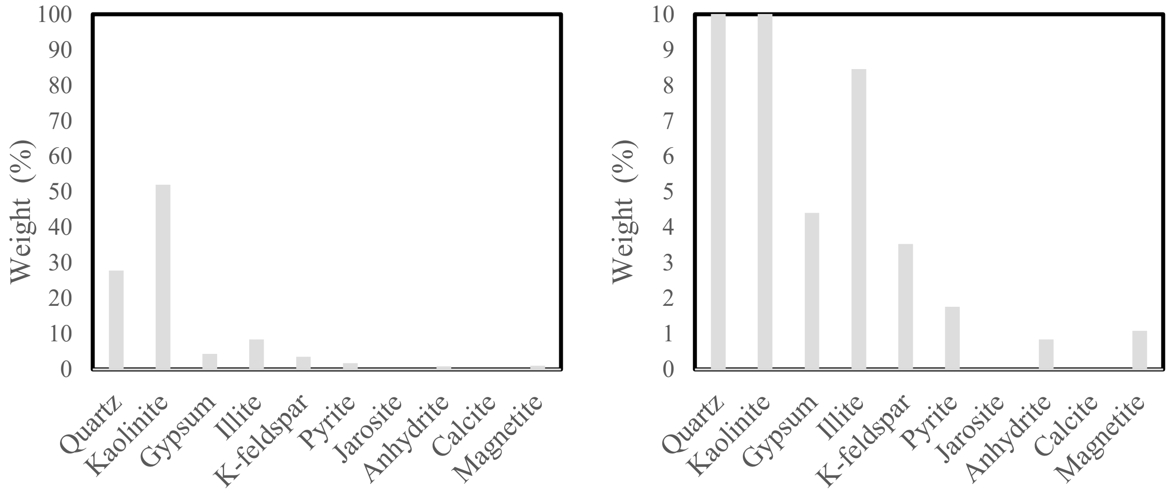


Figure 3-1 presents the mineralogical composition of the bulk sample. The findings from the ARD static tests conducted on the bulk samples are presented in Table 3-1, and suggest that the samples are potentially acid forming. This characteristic can be attributed to the presence of pyrite in the bulk sample (Figure 3-1).

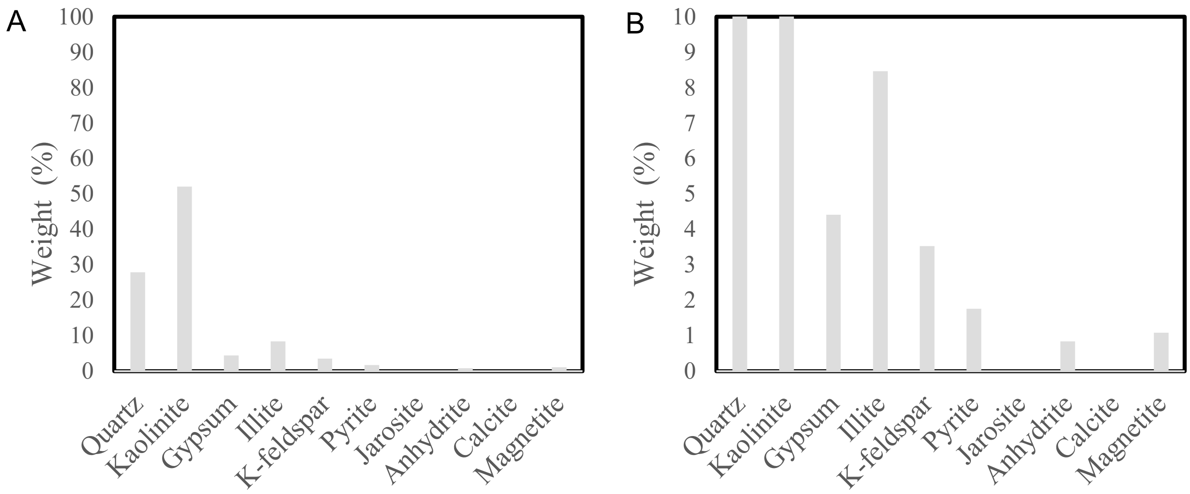


Figure 3-1 Semi-quantitative XRD results in the coal discards bulk sample. A: Weight (%) scaled 0 to 100%. B: Weight (%) 0 to 10%

Table 3-1 Acid base accounting test (Miller et al., 1997; Stewart et al., 2006) results showing the total sulphur (S), maximum potential acidity (MPA), acid neutralizing capacity (ANC), net acid producing potential (NAPP) for coal discards. PAF = potential acid forming.

Sample name	**Total S** (%)	**MPA**	**ANC** (kg H2SO4.t^{-1})	**NAPP**	**ARD classification**
Bulk sample	1.6	49.9	3.9	45.9	PAF

Sink-float tests, or washability studies, are widely used in the mining industry, since they estimate the accessibility of a mineral of interest through the gravity concentration (De Souza et al., 2012). In order to determine the densimetric distribution of the discards and its re-purposing potential, the samples were sieved (+2.0-50.8 mm) and sent for float and sink studies according to the guidelines from ASTM D4371-2012 (American Society for Testing and Material, 2007). Mixtures of heavy liquids at densities of 1.8; 2.0; 2.2; and 2.7 g.cm^{-3} were used in this study. The five fractions obtained from sink and float studies were homogenized and prepared for techno-environmental characterization. Each fraction was analysed in terms of proximate and ultimate analysis, sulphur forms and gross calorific value. The total sulphur content was determined according to ASTM D4239:1997. The sulphur speciation was conducted according to ASTM D 4239. The ash analysis of the fractions obtained was carried out using ASTM D3174-2012. Proximate analysis was performed according to ASTM D5373-16. Static ABA methods are widely used as a screening procedure. In this study, the static tests were performed by modified acid-base accounting (MABA) (Stewart et al., 2006) to determine the balance between acid production and consumption (neutralization) by the mineral components of the samples. The particle size of the samples was reduced to less than 0.25 mm. Acidity potential (AP) was determined based on total sulphur analysis for ABA and sulphide sulphur for MPA.

3.3 Results and discussion

The sink and float studies resulted in five fractions, with characterisation summarised in Table 3-2. As observed, the three fractions with lower densities are lower in ash with higher calorific value. In this instance, if blended, the fractions with density <2.2 g.cm^{-3} represent 69.9% of the bulk mass with 25.5% and 0.7% sulphur and ash content respectively. In terms of gross calorific value, the blended fractions with densities lower than 2.2 g.cm^{-3} present an average value of 22.3 MJ.kg^{-1}, with a recovery higher than 95%. Based on the theorical recovery of the sink and float studies, this fraction complies with market standards for thermal coal according to Table 3-3.

Table 3-2 Sink and float test-work results in terms of mass recovery, calorific value, and ultimate and proximate analysis.

Density fraction (g.cm^{-3})	**Mass (%)**	**Proximate analysis (%)**				**Ultimate analysis (%)**				**CV** (MJ.kg^{-1})
		Ash	**FC**	**Moisture**	**VM**	**C**	**H**	**N**	**S**	
-1.8	58.5	19.6	53.2	2.7	24.5	60.5	3.3	1.6	0.5	24.6
-2.0+1.8	3.5	49.4	25.3	1.8	23.5	42.0	2.7	1.2	0.4	13.1
-2.2+2.0	7.9	59.1	18.4	2.2	20.3	35.0	2.4	1.0	2.8	9.4
-2.7+2.2	28.1	80.4	1.4	1.6	16.6	12.7	1.6	0.5	1.5	1.2
+2.7	2.0	60.6	11.2	1.7	26.5	11.4	0.9	0.4	34.7	8.8

Table 3-3 South African ROM (run-of-mine) coal characteristics and market requirements for washed coal (Steyn and Minnitt, 2010)

	ROM coal	**Thermal coal**
Sulphur (%)	0.5-15	0.7-1
Calorific Value (MJ.kg-1)	16-21	19-27
Ash (%)	20-40	20-30

Approximately 2% in mass (>2.7 g.cm^{-3}) presents as a sulphide-rich fraction with a total sulphur content of 34.7% and a pyritic sulphur content of 33.3%.

Table 3-4, representing a total and pyritic sulphur recovery of 42.4% and 45.3% respectively. Weiler et al. (2016) and Kazadi Mbamba et al. (2011) demonstrated that the removal of the pyritic fraction in coal discards causes a significant reduction in the acid generation potential and neutralizing reagent consumption in ARD treatment facilities. In addition, the recovered pyrite concentrate could be converted into valuable products such as ferrous sulphate, sulphuric acid and iron oxides which can be utilized as raw materials in other industrial sectors (Colling, 2014; Lopes, 2017; Vigânico, 2014).

Table 3-4 Results of sulphur speciation assays of the five density fractions obtained from sink-float studies

Density fraction (g.cm^{-3})	**Sulphur forms** (%)		
	Elemental S	**Sulphate S**	**Sulphide S**
-1.8	0.01	0.1	0.4
-2.0+1.8	0.01	0.1	0.3
-2.2+2.0	0.01	0.6	2.1
-2.7+2.2	0.01	0.2	1.4
+2.7	0.01	0.7	33.3

The results of the subsequent static ARD tests, conducted on the density fractions (after density separation), are summarised in Table 3-5. A comparison of the static test results indicates that the fraction of -2.7+2.2 density has a 3-fold higher ANC and consequent lower acid production (NAPP) than the bulk discards, due to the presence acid neutralizing minerals (Table 3-5). The material with intermediate density (2.2 < d < 2.7 g.cm^{-3}) had an ash content of 80% and a total carbon content of 12.7%, while comprising 28% of the mass of the bulk material. Approximately 28% of the total sulphur reported to this fraction. Further washability studies should be conducted to evaluate the potential for sulphur recover from the 2.5 and 2.6 g.cm^{-3} density fractions. The reported high-ash content in these fractions signifies the presence of substantial mineral matter which may be used for several ends including soil fabrication, safer co-disposal or as aggregate in Civil Engineering (Amaral Filho et al., 2017; Argane et al., 2015; Firpo et al., 2015; Harrison et al., 2013; Kotsiopoulos and Harrison, 2018; Santos et al., 2013).

Table 3-5 Acid base accounting test results showing the total sulphur (S), maximum potential acidity (MPA), acid neutralising capacity (ANC), net acid producing potential (NAPP) for coal discards. PAF = potential acid forming. AF = acid forming

Density fraction (g.cm^{-3})	**Total S** (%)	**MPA**	**ANC**	**NAPP** (kg H_2SO_4/t)	**ARD Classification**
-1.8	0.5	15.30	17.80	-2.50	Uncertain
-2.0+1.8	0.4	45.90	4.40	41.50	PAF
-2.2+2.0	2.8	85.70	0	85.70	PAF
-2.7+2.2	1.5	18.45	13.10	5.35	Uncertain
+2.7	34.7	1061.80	0	1061.80	AF

Table 3-6 Major mineral phases as weight % found in the fraction obtained from dense medium separation studies

Mineral phase	**Density fractions** (g/cm^{-3})				
	-1.8	**-2.0+1.8**	**-2.2+2.0**	**-2.7+2.2**	**+2.7**
Quartz (SiO_2)	8.4	8.8	7.6	72.0	21
Kaolinite ($Al_4Si_4O_{10}(OH)_2.H_20$	75.2	40.0	82.9	22.3	2.8
Mica ($Al_2K_2O_6Si$)	14.3	4.5	7.2	2.5	1.6
Feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$	-	1.9	-	-	-
Kalsilite ($KAlSiO_4$)	-	-	-	-	0.8
Pyrite (FeS_2)	-	-	--	2.8	57.3
Gypsum ($CaSO_4.2H_2O$)	1.3	0.8	0.8	0.5	0.7
Anhydrite ($CaSO_4$)	0.8	0.0	1.6	-	-
Jarosite ($KFe_3(SO_4)_2(OH)_6$)	-	9.8	-	-	1.1
Melanterite ($FeSO_4.7H_2O$)	-	2.7	-	-	-
Szomolnokite ($Fe(SO_4).H_2O$)	-	-	-	-	6.6
Goethite ($FeO(OH)$)	-	-	-	-	7.3
Phosphoferrite ($(Fe,Mn)_3(PO_4)_2.3H_2O$)	-	-	-	-	0.8

3.4 Conclusion

The above approach demonstrates potential environmental and economic benefits through fractionation of coal waste. Firstly, the removal of the sulphide component from the bulk coal discards using gravity concentration techniques prior to disposal presents significant reduction in acid generation potential from the bulk ash fraction while also recovering a low-sulphur clean coal of acceptable calorific value.

The separated low volume sulphur-rich concentrate can be desulphurised to prevent environmental risks associated with its disposal. Alternatively, it can be disposed with containment. Economic benefits can be achieved by converting the iron-sulphur components in this high-sulphur fraction into valuable products or into raw materials for utilisation in other industrial sectors.

This study presents an approach for the handling of downstream coal discards through the removal of the pyritic component using gravity concentration enabling recovery of multiple products, thereby minimizing waste for final disposal and improving resource efficiency. The results obtained support the feasibility of the two-stage concentration process for concomitant long-term removal of ARD risk, reduction of long-term liabilities associated with its management and treatment, and potential for value recovery in terms of combustible coal and additional products.

CHAPTER 4: IRON-RICH LEACHATE PRODUCTION FROM SOUTH AFRICAN COAL WASTE

4.1 Background and objective

The results from CHAPTER 3 demonstrated that is possible to recover a pyrite concentrate with over 60% of pyrite content (up to 35% total sulphur) from bulk SA coal discards containing as little as 1.6% of total sulphur. In order to investigate the feasibility of producing a ferric based coagulant by bioleaching pyritic concentrates from coal waste, samples were sourced and an experimental plan was based studies conducted on Brazilian high-sulphur samples (Lopes, 2017; Villetti, 2017). Demonstration of this approach using South African coal waste is key to determining its feasibility as a commercial application. South African coal waste may present specific challenges based on composition which may affect the acid generation kinetics.

4.2 Experimental approach

Figure 4-1 illustrates the overall experimental approach followed in this study. Sampling was conducted by visual and hand sorting. The coal discard samples with average diameter between 2 and 50 mm were collected manually through visual identification from a coal waste storage facility located in a colliery in eMalahleni area, Mpumalanga Figure 4-2. The initial sample obtained presented approximately 20% of total sulphur. Further hand sorting was conducted to obtain a fraction with sulphur content higher than 30%.

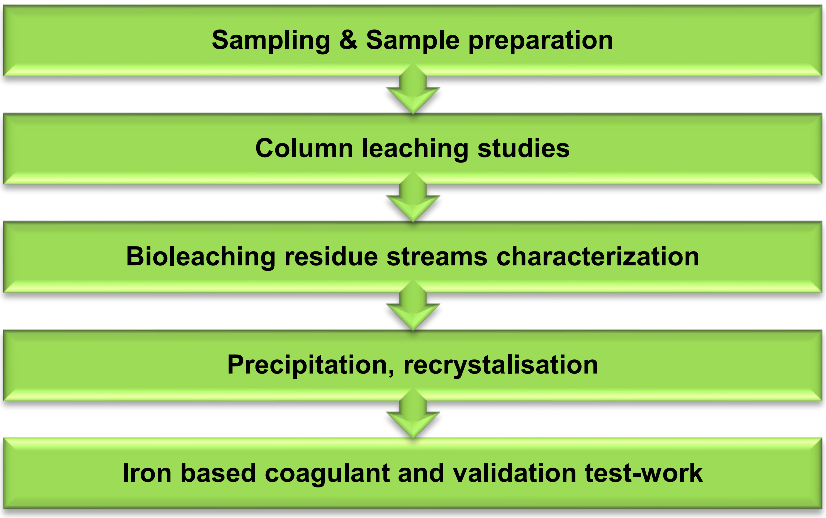


Figure 4-1 Experimental test-work for the proof-of-concept to produce Ferrous sulphate heptahydrate crystals and ferric-based coagulants

Figure 4-2 Hand-picked material collect from a coal waste storage facility in Mpumalanga area.

Leaching experiments to concentrate iron and sulphur in solution were carried out using four laboratory scale glass columns (30 cm high and 7 cm in diameter) constructed as packed bed reactors and filled with 500 g of high-sulphur coal waste rock. Columns were irrigated in closed circuit as depicted in Figure 4-3.

The particle size of coal used corresponded to 1/7 to 1/10 of the column diameter to enable contacting to be regular. For this, each sample was representatively split, crushed and screened to achieve a 2-6 mm size fraction and stored in re-sealable plastic bags for laboratory leaching column studies. For characterization studies a fraction of each sample was further crushed to particle size less than 37 µm and homogenized. Coal waste characterization was conducted in terms of ARD static tests according to (Miller, 2008) and mineralogy using SEM and XRD techniques at the Department of Chemical Engineering, UCT. Total sulphur was obtained according to ASTM (ASTM, 2012). Following column packing, 1 L of deionized water was introduced and recirculated at a constant flow rate. The system was corrected for evaporation with water and acidified water and the leachates were analysed weekly in terms of iron speciation, sulphate, and redox potential over 500 days.

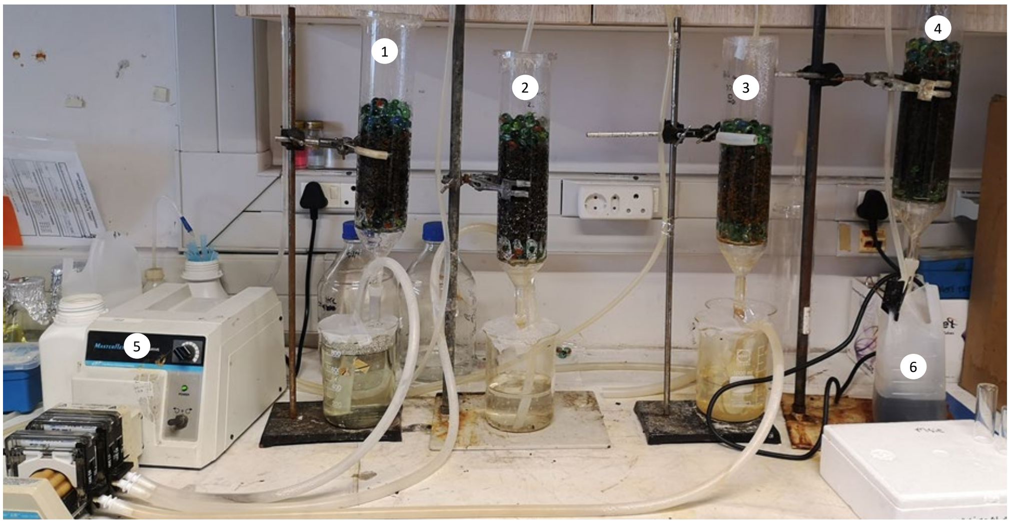


Figure 4-3 Experimental set-up on day 1 for iron leaching experiments of coal waste samples with various % of sulphide content. The pH of the leftmost column was adjusted by the addition of sulphuric acid to maintain the pH below 1.3, while the rightmost column was irrigated at a faster rate than the other columns for the first 50 days. 1)

Based on previous studies (Villetti, 2017), an initial investigation of the effects of flow rate on the system kinetics was evaluated. Initially, for 20% S coal waste samples, a 0.12 L/min (CW20% – A) and 2 L/min (CW20% – B) flow rate was used. After day 50, no effect of the flow rate in the system was noticed and the flow rate of the HF column was adjusted to 0.12 L/min.

In contrast with the worked carried out in Brazil (Lopes, 2017; Villetti, 2017), where in the first week redox potential and pH values reached ~700 mV and ~2, respectively, following 12 days of experiments, no acid formation was noted in any of the columns containing SA samples. In order to speed up iron dissolution, one of the columns packed with coal waste with 30% of total sulphur had its pH adjusted using P.A. H_2SO_4 at pH 1.3 (CW30% – B). The pH was kept lower than 1.3 to avoid jarosite formation, as its precipitation reduces ferric iron available and can passivate the available mineral surface reducing sulphide and ferrous iron oxidation. After pH stabilization at 1.3, the correction of system water evaporation was conducted using acidified water (pH 1.3). The acidified water addition stopped on day 234. From day 234 the water evaporation correction was then conducted using DI water for column "CW30% – B".

For the non-acidified columns, the total water in the system was periodically totally replaced (1 L) to allow the removal of any compounds with acid neutralising capacity (ANC) which may have been washed from the waste samples.

The experimental details of column operation and water replacement information used for the leaching columns are found in Table 4-1 and Table 4-2.

Table 4-1 Samples used and experimental approached followed for column leaching studies. CW = coal waste

Columns identification	Total Sulphur	Flow rate	Inoculation	pH controlled	Description
CW20% – A	22.3%	0.12 L/min	Yes – day 352	No	Hand-picked from dump deposit
CW20% – B		2 L/min for 50 days, and 0.12 L/min after day 50	No	No	
CW30% – A	28.8%	0.12 L/min	No	No	Concentrate from bulk sample
CW30% – B		0.12 L/min	No	Adjusted to 1.3 on day 12	

Table 4-2 Water replacement strategy conducted for ANC removal on the non-acidified columns.

Column	Amount of water replaced (L/kg)	Last day of water replacement	pH on the last day of water replacement
CW20% – A	72	172	5.4
CW20% – B	114	175	5.2
CW30% – A	100	172	5.3

4.2.1 Improved leaching by microbial inoculation

The results from the initial high sulphur coal waste leaching studies suggest that the hand-picked South African coal waste sample used had a high pyritic content, but also contained significant amount of acid neutralizing compounds. For samples with similar mineralogical composition, the use of DMS as reported in CHAPTER 3 will improve the separation of the pyritic fractions within the coal waste from minerals components rich in ANC.

In this study, we visually identified and hand-picked coal waste with high sulphur, however the acid neutralizing material reduced the leaching kinetics achieved in the column leaching experiments. By replacing the leachate solution with fresh water, the immediately accessible ANC was removed which resulted in a decrease of the leachate pH (Figure 4-6). On day 352 the 20%S column (Table 4-1) previously irrigated with deionised water was inoculated with a mesophilic biooxidation community of microorganisms with 10^{10} cells/kg of coal waste to accelerate pyrite dissolution. The microbial consortium has been fully characterised by quantitative polymerase chain reaction (qPCR) and comprises an approx. 1:1 ratio of the iron oxidising species *Leptospirillum ferriphilum* and the sulphur oxidising species *Acidithiobacillus caldus*. The culture is maintained in 1 L continuously stirred tank reactor (CSTR) at approx. 30°C with weekly feeding by removing a fifth of the reactor volume and replacing it with fresh nutrient solution and 1% (w/v) pyrite concentrate. This mixed mesophilic culture will be supplemented with a 1:1 mixture of iron and sulphur oxidising *Sulphobacillus* spp, *Sb. thermosulphidooxidans* and *Sb. benefaciens*.

4.3 Results and discussion

4.3.1 Pyritic material characterization

The hand-picked bulk samples from the dump deposit presented a lower sulphur content and higher acid neutralizing capacity when compared with the sample with relative density of 2.7 g.cm^{-3} from the dense medium separation (DMS) studies (CHAPTER 3). As expected, the total sulphur (Table 4-2) indicates the samples contained pyritic material, confirmed through the XRD results showed in the Table 4-3, presenting up 74% of pyrite content. However, the results for ABA test also indicate the presence of acid neutralizing material on the hand-picked samples. The samples obtained by sink and float studies presented no acid neutralizing capacity.

Table 4-2 Total sulphur content and ARD static ABA static test results of the bulk hand-picked samples from dump deposit and +2.7 g.cm-3 obtained in the sink-float studies, only hand-picked samples were used on the pyrite leaching and ferrous sulphate production studies.

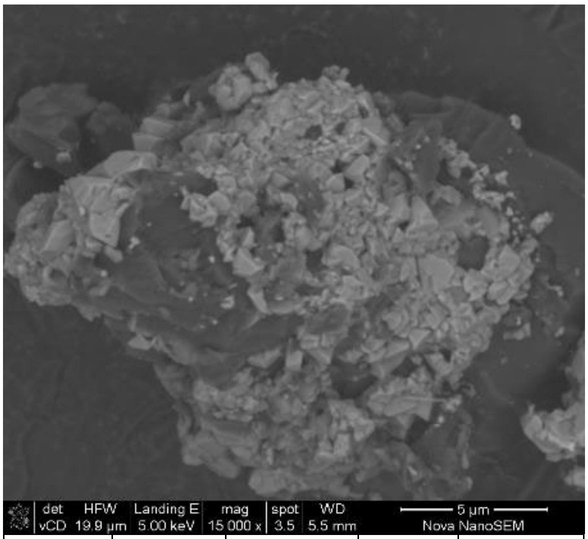
Samples	**Total S** (%)	**ABA** (Kg.H_2SO_4/t)		
		MPA	**ANC**	**NAPP**
Hand-picked from dump deposit	22.3	709.9	127.7	582.3
DMS +2.7	34.7	1061.80	0	1061.8

The mineralogical results presented in Table 4-3, confirm that pyrite is the major mineral phase found in both samples used in this study. The high pyrite content demonstrates potential for sulphur and iron recovery using biohydrometallurgical approaches. The presence of acid neutralizing material such as gypsum, dolomite and calcite is also observed. After further manual sorting (Section 4.2), the proportion of pyrite in the samples increased from 51.1% to 74.0%. When compared with the samples concentrated using heavy-liquids (DMS +2.7), as described in the previous chapter, the samples hand sampled presented a higher content of acid neutralizing material such as carbonates and metal based hydroxides.

Table 4-3 Mineral composition of bulk hand-picked compared to DMS +2.7 g.cm^{-3} samples determined by XRD analysis

Mineral	**Hand-picked from dump deposit (A)**	**Hand-picked from dump deposit (B)**	**DMS +2.7**
Quartz – SiO_2	14.3	3.0	21.0
Muscovite – $KAl_2(AlSi_3O_{10})(F,OH)_2$, or $(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$	2.0	-	1.6
Kaolinite – $Al_2(Si_2O_5)(OH)_4$	3.3		2.8
Feldspar – $KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$	1.2	-	-
Calcite – $CaCO_3$	8.4	2.2	0.8
Dolomite – $CaMg(CO_3)_2$	7.4	5.0	
Pyrite – FeS2	51.1	74.0	57.3
Gypsum – $CaSO._{4}\cdot 2H_2O$	2.4	13.4	0.7
Bassanite $Ca(SO_4)\cdot 0.5H_2O$	6.1	-	
Jarosite – $KFe^{3+}{}_3(OH)_6(SO_4)_2$	3.8	-	1.1
Szomolnokite – $Fe^{2+}(SO_4)\bullet(H_2O)$	-	-	6.6
Goethite – $Fe^{3+}O(OH)$	-	-	7.3
Chlorite (Mg,Fe)3(Si,Al)4O10(OH)2·(Mg,Fe)3(OH)6	-	1.1	-
Gibbsite – $Al(OH)_3$	-	1.4	-
Phosphoferrite – $3(Fe^{2+}{}_{0.75})3(Mn^{2+}{}_{0.25})(PO_4)_2\bullet 3(H_2O)$	-	-	0.8

The results for the SEM and EDS analysis are presented in the Figure 4-4 and complementary SEM images are presented in the Figure 4-5. Chemical composition results, using EDS for identification, showed the presence of sulphur (13.6%wt) and iron (15.1%wt) indicating again the presence of pyrite. By observation is possible to identify a significant amount of coal attached to the pyrite grains, which is further confirmed by the amount of carbon (35.7%wt).



C (%)	O (%)	Mg (%)	S (%)	Fe (%)
35.7	35.3	0.2	13.6	15.1

Figure 4-4 Scanning Electron Microscopy (SEM) image and chemical composition by energy-dispersive X-ray spectroscopy (EDS) results for the samples hand-picked from dump deposit containing 29% of total sulphur. Results in % weight.

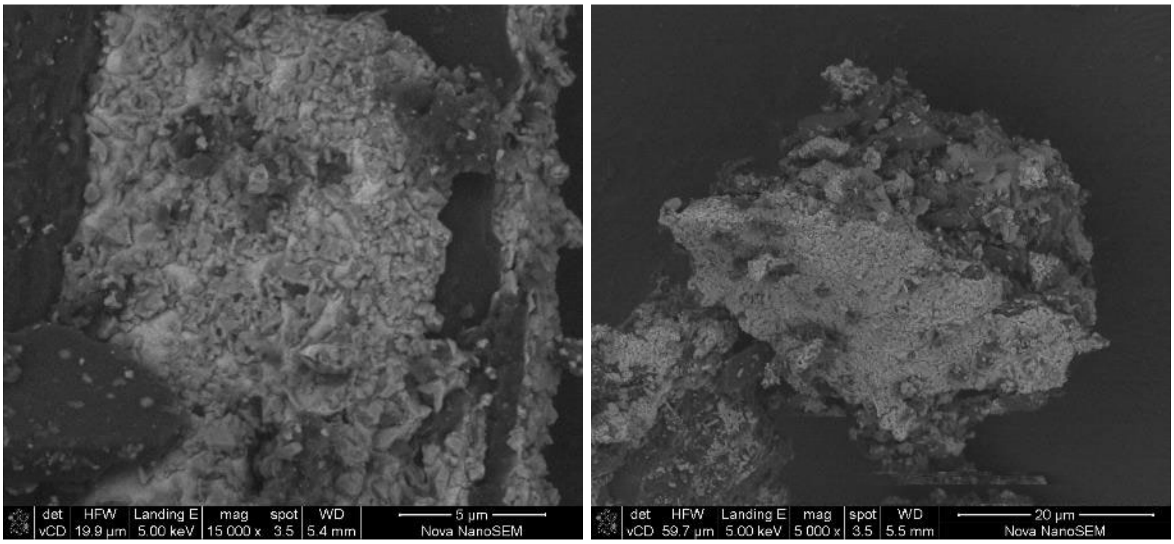


Figure 4-5 Scanning Electron Microscopy (SEM) images for the 30% total sulphur samples.

4.3.2 Pyrite leaching experiments

The results of the pH fluctuations of leaching are given in Figure 4-6. It is observed the flow rate of the system had no effect on the pH. As expected from the characterization assays, the results suggest coal samples used in this study presented significant acid neutralising capacity due to the presence of acid consuming material. As an effect, a rapid increase in solution pH was observed from day 1 to day 10 (Figure 4-6) and this is attributed to dissolution of carbonate containing minerals, particularly calcite and dolomite. At Ph >2, under increasing alkaline conditions, total iron concentration precipitated in the solution. The pH controlled strategy, in the form of sulphuric acid addition (30%CW – B), resulted in an immediate and sharp decrease in the pH of the leachate generated from this column. Acid addition was performed periodically until the day 56, when the pH stabilized at under pH 1.3. The pH was kept below

1.5 to avoid jarosite formation, as its precipitation reduces soluble iron in solution and can passivate the available mineral surface reducing sulfide oxidation. Until day 234 the correction of evaporation was made by adding acidified water (pH 1.3), and after, the addition of acid was discontinued, and DI water was used to evaporation correction.

The effect of water replacement in the system for alkalinity removal can be observed from day 50 (CW20% – A and B, and CW30% – A), reaching pH levels under 5 after 260 days for the 3 non-pH-controlled columns.

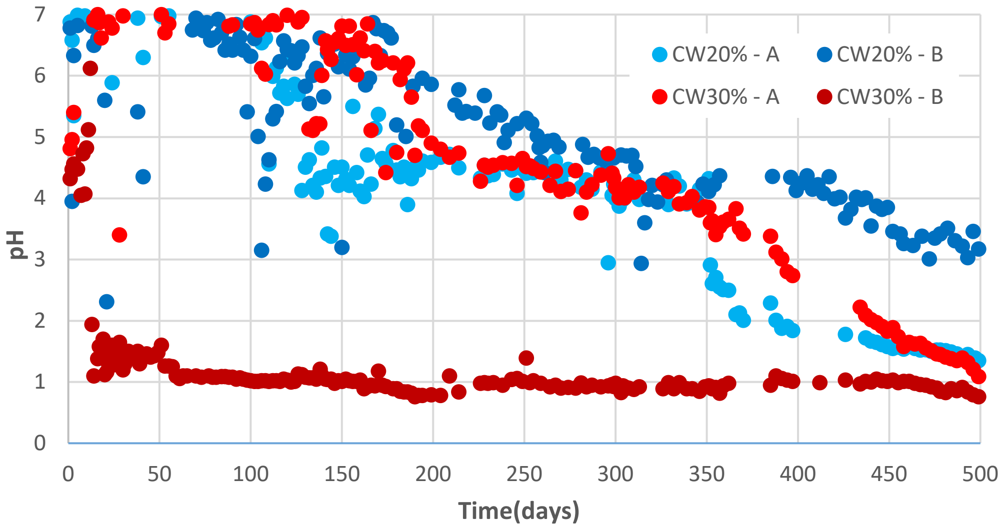


Figure 4-6 Profile showing the pH fluctuations over 500 days of leaching experiments.

Redox potential profiles showing the fluctuations over 500 days are presented in Figure 4-7. The presence of alkaline minerals inhibits microbial activities, preventing the oxidation reactions driven by endemic microorganisms. According to Villetti, 2017 the acid forming reactions in Brazilian samples, depleted of acid neutralizing capacity, started immediately, and after seven days of leaching the leachate pH dropped from 7 to 1.2 with the redox potential increasing to 635 mV. In the South African samples, from day 1 to 12, the redox potential of the leachate sample decreased with increase in solution pH. From day 12, after acid addition in the form of sulfuric acid addition to the 30% sulphide sample (30%CW – B), the redox potential increased to about 400 mV and remained stable thereafter, ideal condition for Fe^{2+} solubility (Figure 2-2).

The inoculated system (CW20% – A) reached 541 mV after inoculation indicating microbial activity in the system, 10 days after inoculation reached 571 mV and after 100 days of inoculation, the redox potential stabilized at values over 700mV. The redox profile for both non-inoculated and non-pH-controlled columns demonstrated that under pH 3 an increase of microbial activity occurs, driven by endemic microorganisms.

The dissolution of neutralising materials from coal waste led to build-up of considerable concentrations of salts especially heavy metals which had an inhibited effect on microbial growth and ferrous iron oxidation.

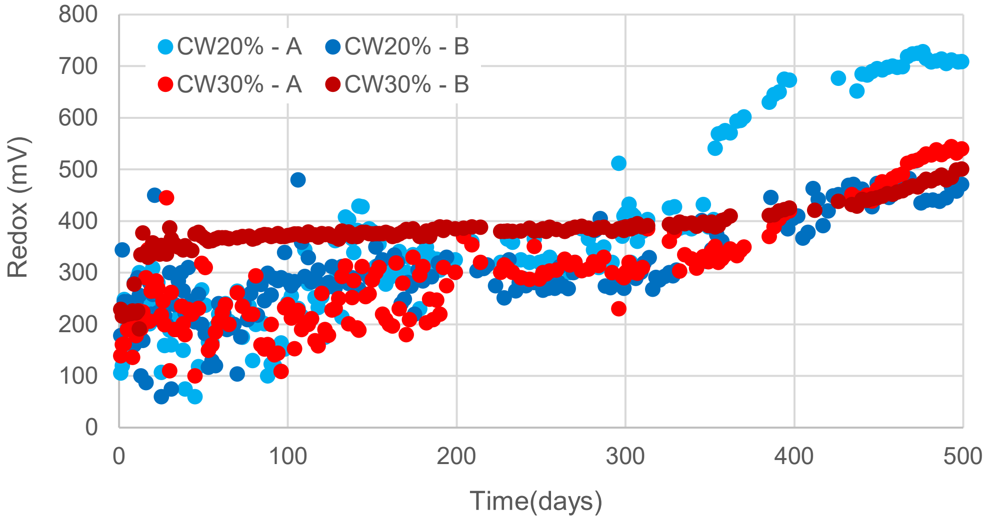


Figure 4-7 Redox potential fluctuations over 500 days of leaching experiments.

The lack of stable increase in the ferric iron concentration confirms inactivity of endemic iron and sulphur oxidising microorganisms and that may be caused by toxicity of metal ion concentrations (Mg^{2+}, Ca^{2+}, Al^{3+}, etc.). It is observed that the inoculation increases the microbial activity for the CW20% – A column. In the column “CW30% – B” once acid addition ceased (day 234), 50% of the leachate was replaced for DI water. The diluted solution created adequate conditions to microbial metabolism and the oxidation reactions catalysed by endemic bacteria increased the amount of ferric iron in solution when pH reach values lower than 3. “CW30% – A” column presented similar behaviour, when the aqueous medium became suitable for microbial metabolism.

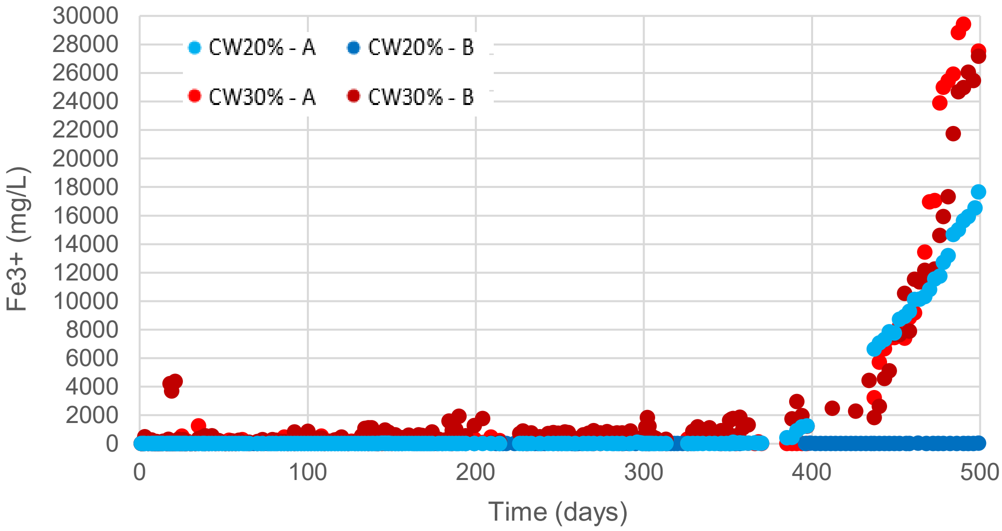


Figure 4-8 Ferric iron content in leachate generated from leaching columns over 500 days.

Despite the possibility of the use of bio-induced ARD with high ferric iron content as coagulant for physico-chemical wastewater treatment, the presence of contaminants is still a concern (Colling et al., 2011; Menezes et al., 2010). By producing a ferrous sulphate solution for melanterite crystal formation undesired elements are selectively separated. In this proof-of-concept study, ferrous iron and sulphate are the components of interest.

Figure 4-8 presents the leaching profiles for ferrous iron and Figure 4-10 the sulphate concentration in solution after 500 days of experiments. From day 10, with increased acidity and availability of protons H+ (oxidising agent), after the addition of acid, the chemical leaching reaction of sulphide mineral via polysulphide pathway was catalysed. At redox potential below 400 mV, and pH lower than 3, ferrous iron dominated in the leached solution generated through abiotic acid leaching (Figure 2-2). After discontinuing the use of acidified water for evaporation correction, a reduction in the concentration of ferrous iron is observed due to the oxidation reactions driven mostly by microorganisms. Therefore, the results for CW30% – B indicate that ferrous in solution is a result of acid leaching under abiotic conditions.

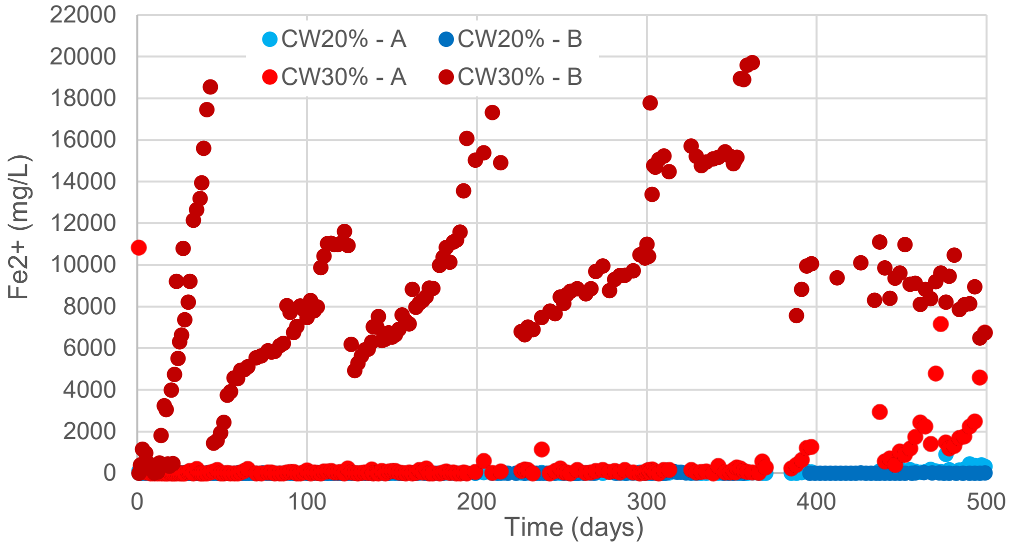


Figure 4-9 Ferrous iron content in leachate generated from leaching columns over 500 days.

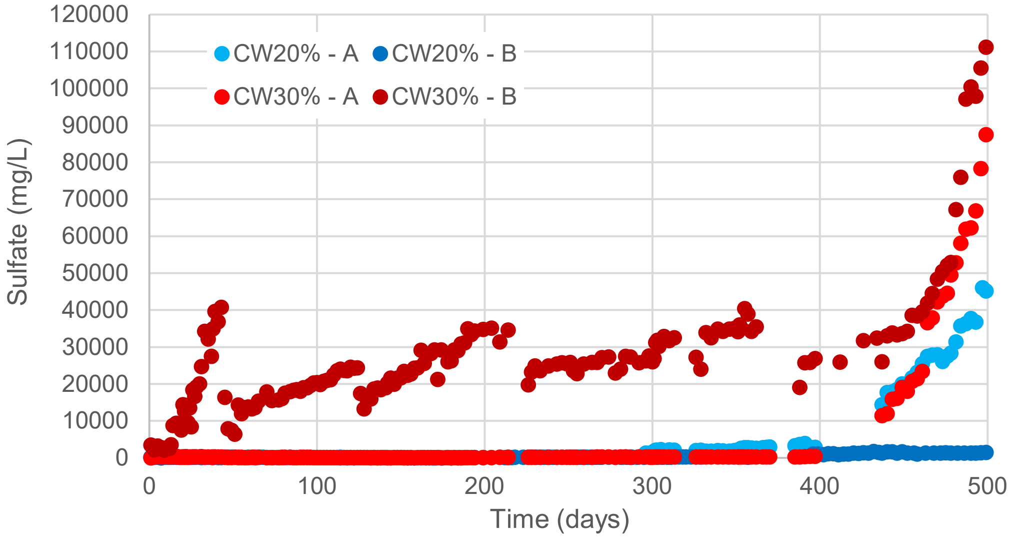


Figure 4-10 Sulphate content in leachate generated from leaching columns over 500 days.

Aliquots of a ferrous iron rich solution were collected from the pH-controlled leaching of column "CW30%-B". Samples for precipitation and crystallization studies were collected on days 43 and 124, 226 and 385. The solutions were characterized and used to investigate production of an iron-rich coagulant from South African coal waste for water treatment studies. These results are reported in CHAPTER 5 and CHAPTER 6.

Figure 4-11 shows the appearance of columns after 385 days experiments and Figure 4-13 shows one of the ferrous sulphate rich solutions used in the precipitation studies.

Figure 4-11 Leachate solutions generated after 430 days of experiments. From left to right: CW30%-B; CW20%-A; CW30%-A; CW20%-B.

Figure 4-12 Leachate solutions generated after 530 days of experiments. From left to right: CW30%-B; CW20%-A; CW30%-A; CW20%-B.

Figure 4-13 Ferrous iron rich leachate solution generated from pH-controlled column and used for crystallization studies.

Iron removal considerations

According to the XRD results, the columns packed with coal waste containing 22% total sulphur had 51% pyrite, whilst columns containing coal waste with 29% total sulphur had 75% of pyrite in their mineral composition, giving a total mass of iron of 119 g for the CW20% columns and 175.1 g for the CW30% columns.

Table 4-4 presents the calculated total iron in the samples and the total iron removed after 500 days of experiments.

Table 4-4 Total iron removal after 500 days of leaching. Considering pyrite (FeS2) contains 46.67 percent iron and 53.33 percent sulphur by weight %

	pyrite content (%)*	calculated total iron in the column (g)	iron removal after 500 days (%)
CW20% – A	51	119.0	17
CW20% – B			<1
CW30% – A	74	175.1	29
CW30% – B			34

*according to XRD results

According to the total iron profiles (Figure 4-14), after 500 days of experiments 34% of the total iron had been removed from the system in the column “CW30% – B”. If considering only the acid leaching performed abiotically (up to day 400), 20% of the total iron had been removed. In contrast, 14% of the total iron was removed in the last 70 days of experiments under biotic conditions driven by iron-oxidizers endemic bacteria.

The influence of the bacterial activity on iron removal is also observed in the inoculated column (CW20%-A). In the columns the microbial mentalism has started at pH lower than 3. The microbial oxidation in the inoculated columns occurred under higher redox potential (~700mV) conditions when compared with the non-inoculated columns (CW30%-A and CW30%-B), where the microbial oxidation is observed under redox potential higher than 450 mV.

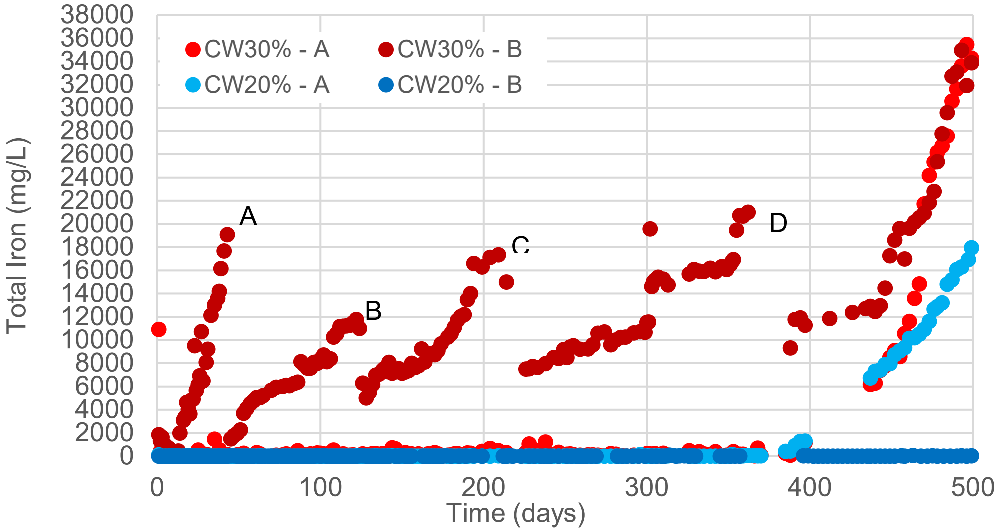


Figure 4-14 Total iron content in leachate generated from leaching columns over 500 days, and sampling points (A, B, C and D) for ferrous sulfate crystals precipitation and crystallization studies

Moreover, the removal of iron and sulphur from coal waste will decrease the acid forming reactions making the material safer for disposal as well decreasing the amount of neutralizing reagents used for ARD water treatment. The potential for repurposing and its benefits in terms of safer disposal should be further evaluated after the recovery of iron and sulphur.

4.5 Conclusion

A Ferrous iron rich solution with potential for melanterite recovery was produced by acid leaching South African high-sulphur wastes under abiotic conditions. However, The high level of gangue materials in pyrite-rich coal discards and the need to recycle the irrigant to achieve high concentration of ferrous sulphate solution significantly affected the efficiency of leaching by buffering acid produced from dissolution of sulphide. The presence of gangue materials lowered the rate of pyrite leaching, thus resulting in low iron-sulphur oxidation due to poor kinetics. In addition, carbonate containing materials resulted in notable increase in solution pH profile during first 20 days that led to precipitation of iron concentration in solution. The dissolution of acid neutralising materials such as dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) from coal discards led to build-up of considerable concentrations of salts especially toxic metals (Mg^{2+}, Ca^{2+}, Al^{3+}) and that inhibited microbial activity and ferrous iron oxidation. Pyrite oxidation occurs in higher rates when driven by microorganisms under aerobic conditions, as soon as solution pH drops from 3, and redox potential higher than 450mV.

CHAPTER 5: FERROUS SULPHATE PRECIPITATION FROM IRON-RICH LEACHATE

5.1 Background and objectives

The sulphate precipitation technique using ethanol forms a compound with the general formula $M_2+SO_4.nH_2O$, where M = metal ion (Fe^{2+}, Mg^{2+}, Zn^{2+}, Ca^{2+}, etc.). Ethanol precipitates metal sulphate compounds from acidic solution depending on their concentrations in solutions(Aktas, 2011). The ethanol precipitation technique only precipitates metal sulphates that are in high concentrations in acidic solutions and this property allows selective recovery of high purity material from impurities with low concentrations.

According to Vigânico, (2014), ferrous sulphate can be precipitated from ferrous and sulphate rich solutions through the addition of ethanol in a 1:1 ratio. The precipitate can then be recovered using simple solid-separation techniques as filtration or evaporation, with the possibility of recovering the ethanol. This approach was tested using the ferrous and sulphate rich solution produced from the pH controlled 30% S coal waste column (CW30% – B) on days 43 and 124, 226 and 385.

5.2 Experimental approach

This chapter presents a method for the precipitation of ferrous sulphate heptahydrate using ethanol. A schematic of the phases of the experimental approach is given in Figure 5-1. In the first phase of the experimental work, acid leaching of pyrite-rich coal discards in column leach experiment resulted in the recovery of ferrous and sulphur rich leachates containing up to 19 g/L ferrous iron (Figure 4-13). During the second phase of the experimental work the ferrous sulphate contained in the four collected samples was selectively precipitated using ethanol absolute (99.5%, v/v) in a 1:1 volumetric ratio (Aktas, 2011). Precipitation, Phase 3, was conducted through agitation in Erlenmeyer flasks for 20 min at room temperature. The mixture was stirred to increase the speed of ferrous sulphate precipitation using a magnetic stirrer bar and plate. In Phase 4, the precipitate was recovered by filtration using standard 11 µm pore filter paper (diameter 150 mm). After filtration the solid material was washed twice with 50% ethanol (v/v), dried at room temperature and subsequently weighed, and prepared for further analysis. For samples A and B mineralogical composition was analysed by X-ray diffraction (XRD). On the ferrous sulphate crystals obtained from study B and D, XRF analysis was used for identification of major elements and ICP-MS was used for identification of minor and trace elements. For the sake of comparison, elemental composition of analytical grade ferrous sulphate heptahydrate was also examined.

In the Table 5-1 is found the experimental conditions used for the crystallization and precipitation studies in the 4 different samples collected.

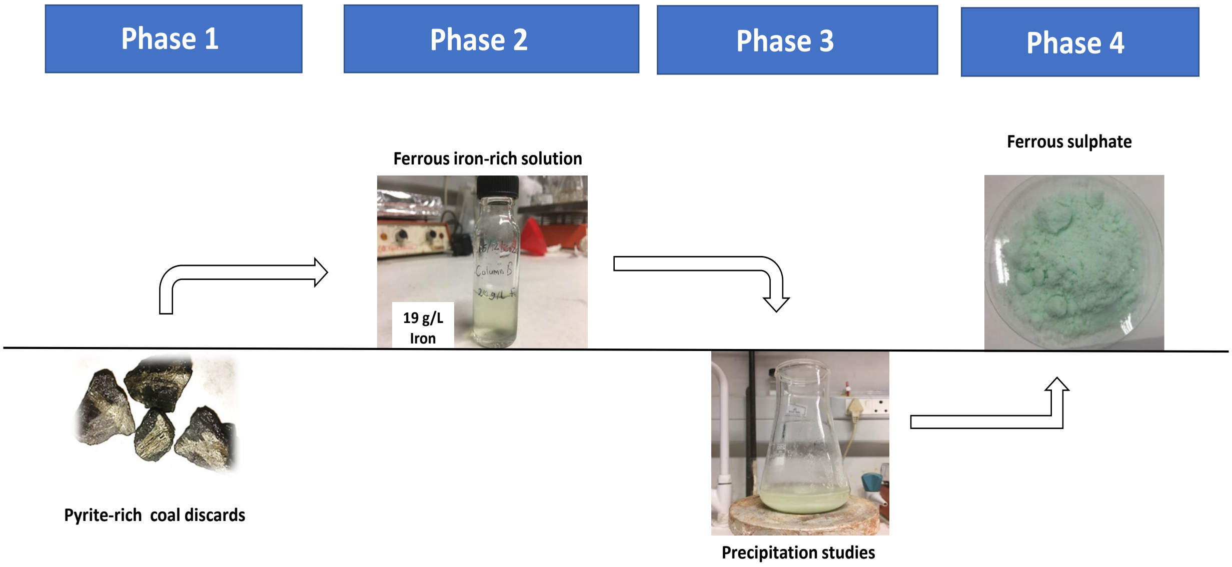


Figure 5-1 Experimental approach followed to precipitate and recover ferrous sulphate from the leach ate solution generated from the pH controlled 30% S coal waste leaching column reported in CHAPTER 3.

Table 5-1 Precipitation studies conducted on the liquor samples collected from day 48 and 130

Precipitation studies	**A**	**B**	**C**	**D**
Sampling day	43	124	226	385
Forced evaporation (Yes/No)	N	Y	N	N
Initial volume (mL)		200	200	500
Final volume (mL)		93		
Ferrous Initial concentration (mg/L)		10 933		
Ferrous Final concentration (mg/L)	18 600	17 015	15 000	17 692
Sulphate Initial concentration (mg/L)		24 342		
Sulphate Final concentration (mg/L)	40 711	46 970	34 605	36 250
Amount of leachate used for precipitation (mL)	45	60	180	500
Ferrous sulphate crystals recovered from above (g)	4	5	7	20

5.3 Results and discussion

Figure 5-2 and Table 5-2 Semi-quantitative XRD results for precipitation studies display the XRD pattern of the final product recovered from leachate collected on day 43 and day 124. As shown above, the final product precipitated on day 124 contained lower levels of impurities when compared with the ferrous sulphate heptahydrate recovered from leachate collected on day 43. The XRD analysis of precipitated crystals in Study A showed that the material was mostly Hexahydrate ($MgSO_4 6H_2O$) and this indicated that the dissolution of dolomite and chlorite (magnesium bearing minerals) by acidified irrigant, released Mg^{2+} ions into the solution as shown in Eq. 6.

$$CaMg\ (CO_3)2 + H^+ \rightarrow Ca^{2+} + Mg^{2+} + HCO_3^- \qquad (6)$$

An increase in Mg^{2+} concentration in the effluent solution favours the formation of magnesium containing final product, as explained in the literature, ethanol only precipitates metal-sulphates that are in high concentration in acid solution (Aktas, 2011). When ethanol was added in Fe^{2+}, Mg^{2+} and Ca^{2+} rich solution, the reaction favoured the formation of Hexahydrate (67%) and Melanterite (30%) and this indicates that Mg^{2+} ions were in high concentration.

The consistently low pH profile between day 49 and 124 indicates that most carbonate containing minerals were dissolved during first 49 days of acid leaching. When fresh feed was introduced on day 50, a notable increase in ferrous iron concentration was observed. Impurity detected in the final product recovered from leachate collected on day 124 was gypsum as shown on Table 5-2. Gypsum formation was attributed by Ca2+ ions released from dissolution of dolomite $CaSO_4.2H_2O$ and calcite $CaCO_3$. The released Ca^{2+} ions reacted with CO_3^{2-} ions and acid to form calcium sulphate, carbon dioxide and water according to Eq. 7.

$$Ca^{2+} + CO_3^{2-} + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \qquad (7)$$

$CaSO_4$(s) combine with water molecules to form gypsum ($CaSO_4.2H_2O$). Nevertheless, 88% of the crystals precipitated was confirmed by X-ray Diffraction to be Ferrous sulphate heptahydrate. Thus, the method used in this study showed selective precipitation of ferrous sulphate heptahydrate.

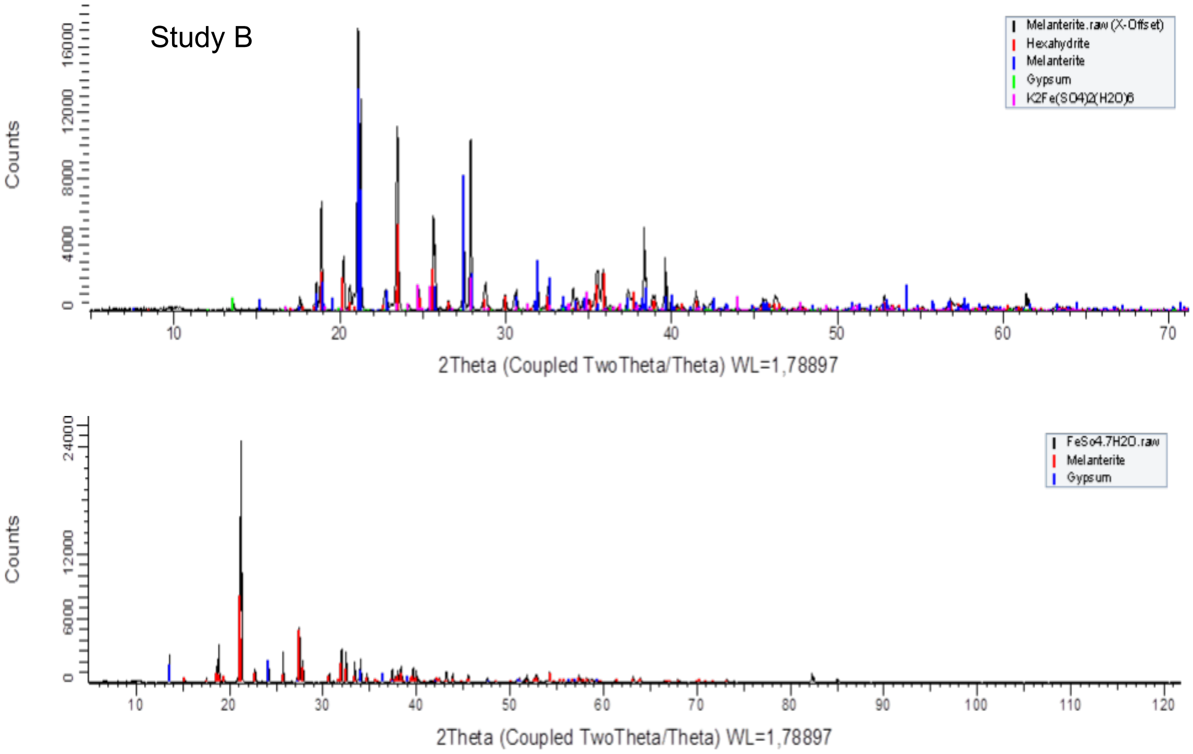


Figure 5-2 XRD patterns profiles for the ferrous sulphate produced in this study. Study A – Sampled on day 43; Study B – sampled on day 124.

Table 5-2 Semi-quantitative XRD results for precipitation studies

	Chemical formula	Study A	Study B
Melanterite	$FeSO_4.7H_2O$	30	88
Hexahydrite	$MgSO_4.6H_2O$	67	0
Gypsum	$CaSO_4.2H_2O$	2	12
Hexahydrate iron (II) sulphate-dipotassium	$K_2Fe\ (SO_4)_2(H_2O)_6$	1	0

The results for elemental speciation for samples collect on day 124 (Study B) and 385 (study D) are shown in Table 5-3 (majors) and Table 5-4 (minors and traces). As observed, samples from study D presented higher amounts of iron and lower contents of undesired elements such as Al and Si. In terms of minor and traces elements, the same trend is observed indicating the improvement of the ferrous sulfate quality over time. Despite to the increase on Pb and Ni and Zn from study B to D, all the other major, minor and trace elements are found in lower concentrations in Study D. Yet, when compared with ferrous sulfate P.A., the ferrous sulfate produced from the solution collected on the day 385 (Study D) presented similar grade purity, even presenting lower concentrations of undesired elements related to metal surface treatment such as Al, Cr, Cu, Zn, and Ni.

Table 5-3 XRF results for precipitation study B, study D and commercial ferrous sulphate heptahydrate

(%)	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2	L.O.I.
Study B	bdl	0,4	bdl	16.0	bdl	8,91	0,2	0.1	0,2	bdl	0,0	73.4
Study D	0.1	0,1	bdl	33,9	0,0	0,1	0,0	0,0	0,0	0,0	0,0	66.4
Ferrous Sufate P.A.	0.2	0,1	bdl	31,8	0,0	0,1	0,0	0,0	0,0	0,4	0,0	67.5

Table 5-4ICP-MS results for precipitation study and commercial ferrous sulphate heptahydrate.

element	Study B	Study D	Ferrous Sufate P.A.	element	Study B	Study D	Ferrous Sufate P.A.
Sc	1,8	0,3	0,4	Pr	0,9	0,1	0,1
V	13,4	9,2	9,1	Nd	5,3	0,3	0,3
Cr	14,2	12,6	28,9	Sm	1,8	0,1	0,1
Co	26,4	5,5	11,1	Eu	0,5	0,0	0,0
Ni	33,2	51,8	312,4	Gd	3,0	0,1	0,1
Cu	929,0	220,2	372,6	Tb	0,5	0,0	0,0
Zn	16,8	215,7	456,3	Dy	2,9	0,0	0,1
Rb	0,4	0,2	0,3	Ho	0,5	0,0	0,0
Sr	134,5	4,9	1,1	Er	1,4	0,0	0,1
Y	14,6	0,2	0,5	Tm	0,2	0,0	0,0
Zr	2,0	8,0	26,6	Yb	1,0	0,0	0,0
Nb	0,1	0,7	0,5	Lu	0,1	0,0	0,0
Mo	1,3	0,7	0,8	Hf	0,1	0,2	0,6
Cs	0,3	0,0	0,1	Ta	0,0	0,0	0,0
Ba	15,9	5,5	4,7	Pb	1,7	167,8	102,1
La	1,8	0,2	0,2	Th	1,2	0,1	0,1
Ce	5,9	0,6	0,6	U	0,1	0,1	0,1

5.4 Conclusion

A strategy to lower the concentration of impurities in solution by introduced fresh feed on day 43 improved the quality of final product from 37% (study A) to 88% (study B), according to the XRD results. The XRD analysis results for study B did not contain any magnesium material as opposed to study A. Further elemental characterization indicated a further improvement in quality over time. The final product obtained from the pyrite acid leaching collecting after 385 days presented similar grade when compared to the Ferrous Sulfate P.A, analysed. The quality of ferrous sulphate heptahydrate produced can be improved by purifying the compound through recrystallization, a method widely used to extract impurities from salts.

CHAPTER 6: FERRIC BASED COAGULANT PRODUCTION AND VALIDATION IN APPLICATION OF WASTEWATER TREATMENT

6.1 Background and Objective

The production of ferric coagulant from ferrous sulphate crystals occurs through the oxidation of ferrous ions, for example using sulphuric acid and hydrogen peroxide, a well-known oxidizing reagent, or a microbially catalysed iron oxidation process. This step is recognized as being critical for coagulant production. Previous studies by Villetti (2017), have demonstrated the feasibility of coagulant production from ferrous sulphate crystals, using water, sulphuric acid and hydrogen peroxide, resulting in a coagulant with an iron concentration close to 12%. Key variables in attaining the required purity of this project will not be determined in this proof-of-concept.

6.2 Experimental approach

Coagulant production was conducted by oxidizing the laboratory produced ferrous sulphate crystals according to the method by Villetti (2017). The oxidizing reagents used were chosen based on the low cost associated with acquiring them. Many parameters can contribute to the production of high-quality ferric sulphate coagulant, however, no optimisation of the parameters were performed in this study.

Ferric coagulant was produced using ferrous sulphate crystals originating from a ferrous rich solution obtained from the acidic leaching of pyrite rich coal waste as described in Section 5.2. The ferrous sulphate crystals were dissolved in deionised water with the addition of sulphuric acid. Oxidation was achieved by the addition of hydrogen peroxide 200 volumes. Following oxidation, iron speciation in the coagulant was conducted to inform the amount of reagent needed for treatment.

The ferric sulphate coagulant was tested with a 1 L neutralization-coagulation-precipitation conducted on a synthetic wastewater. Synthetic wastewater was produced in the laboratory by introducing 500 g of organic compost into 5 L of water. After 24 h the solution was filtered and used for preliminary test-work.

Wastewater treatment was conducted by adding 400 ppm of coagulant in the synthetic wastewater. The pH was adjusted to 8 followed by fast agitation for 3 min and slow agitation for 5 min. The sedimentation step was performed for 10 min. Filtration was conducted for solid-liquid separation. Raw and treated wastewater samples were then subjected to water quality analysis of pH, COD, redox potential, total iron, total phosphorous, conductivity and turbidity.

6.3 Coagulant production and wastewater treatment

A ferric sulphate coagulant was produced from ferrous sulphate crystals as shown in Figure 6-1 and described by Equation 8:

$$FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \tag{8}$$

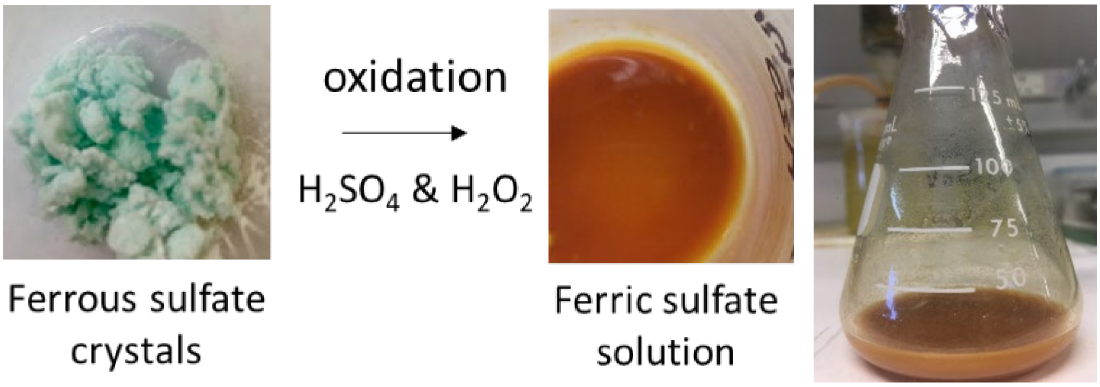


Figure 6-1 Oxidation of ferrous sulphate crystals to produce a ferric sulphate solution using H_2SO_4 and H_2O_2 as oxidants.

The ferric sulphate (96 g/L and pH 2), was used directly as a coagulant and applied to the treatments as described above, and the visual effect after coagulation-precipitation can be observed in theFigure 6-2 and

Figure 6-3.

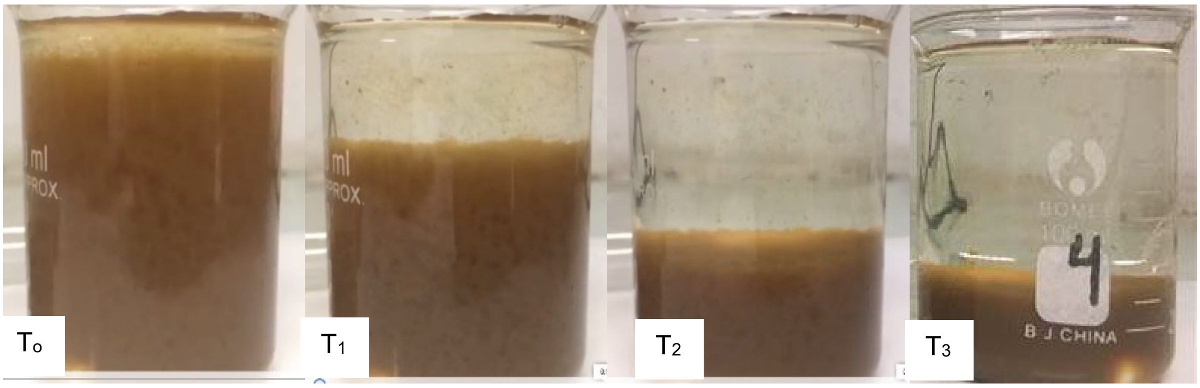


Figure 6-2 Sedimentation step on the synthetic wastewater treatment. T = time after agitation step. T_0 = 0 sec; T_1 = 60 sec; T_2 = 180 sec; T_3 = 600 sec.

Figure 6-3 Colour removal from synthetic wastewater after solid-liquid separation

Water analysis results presented in Table 6-1 demonstrate that despite the increase in the total dissolved solids indicated by electric conductivity (EC) results, most of the parameters analysed in this proof of concept showed an improvement after the wastewater treatment using the coagulant produced from SA coal wastes. The use of iron enrichment in wastewater treatment to recover phosphorous in the form of vivianite is a promising research field and should be considered for future work (Wang et al., 2019; Wilfert et al., 2016; Wu et al., 2019).

Table 6-1 Water analysis results before and after coagulation-neutralization-precipitation-filtration water treatment.

Water quality parameter	**Synthetic wastewater**	
	Before treatment	**After treatment**
pH	7.6	7.5
EC (mS/m)	44.2	239.0
Redox	199.0	224.0
COD (mg/L)	109.0	22.0
Iron (Fe) total mg/L	0.25	0.12
Phosphorus (P) Total (mg/L)	2.1	<0.2
Turbidity (NTU)	3.3	0.7

6.4 Conclusion

The iron-based coagulant obtained from ferrous sulfate crystals by leaching coal waste presented iron concentration of 96 g/L. The coagulant was tested in a synthetic wastewater produced using organic compost. The results indicated that after treatment there a decrease in COD, iron and phosphorus concentrations. Phosphorous recovery from wastewater using Fe is an emerging research field and should be considered as future work. Further optimization should be conducted to evaluate the performance of other and cheaper oxidizing reagents, e.g. sodium hypochlorite or microbial oxidation catalysts.

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

In this proof-of-concept study, preliminary desktop studies indicated that by applying mineral processing techniques, such as dense medium separation using iron-silicon suspensions it is possible to concentrate pyrite from coal waste. This pyrite enriched concentrate can then be used for several ends, whilst most of the neutralizing minerals present reported to the residual waste stream to result in a waste with less ARD forming related risks.

Sink-and-float test-work involving density separation using heavy organic liquids has showed that is possible to obtain a pyrite rich stream with roughly 70% of pyrite in densities higher than 2.7g.cm^{-3}. The pyrite rich-stream is depleted of acid neutralizing material after densimetric concentration.

In this proof-of-concept research, pyrite has shown promising results in terms of producing a low pH, and sulphur and iron-rich solution by bio-leaching coal waste material with up to 30% of total sulphur.

The presence of acid neutralizing minerals such dolomite and calcite in South African coal waste inhibits the microbial activity and oxidation reactions responsible ferric iron formation and the use of gravimetric separation should be considered since it selectively isolates pyrite reducing the undesired acid consuming material.

By leaching South African high-sulphur coal waste discards in a packed bed reactor under abiotic conditions ferrous sulphate solution with up to 20 g.L^{-1} is generated. By adding ethanol P.A. into the ferrous rich solution, in 1:1 ratio, ferrous sulphate crystals are formed with potential for be used as raw material for industrial sectors.

The quality and purity of ferrous sulphate crystal is function of the gangue material present in the pyrite concentrate and its quality increases over time. The grade of the ferrous sulfate crystals produced from the leachate obtained from coal waste and collected on day 385 is comparable to the analytical grade ferrous sulphate evaluated in this project.

The ferrous sulphate crystals obtained from coal waste were processed to produce a ferric-iron based coagulant which was used for validation studies. The iron-based coagulant obtained from ferrous sulfate crystals by leaching coal waste presented iron concentration of 96 g/L. The coagulant was tested in a synthetic wastewater produced using organic compost. The results indicated 99% of phosphorous removal and a decrease in the chemical oxygen demand from 109 to 22 ppm, representing a reduction of 80. Turbidity and iron removal were also observed after treatment.

Pyrite concentration and optimization studies in order to enable technological transfer are identified as future work recommendation. Yet, the use of iron enrichment to recovery phosphorus in form of Vivianite from municipal wastewater is an emerging research field that could be also explored.

Apart from improving resource efficiency and providing opportunities for coal mines to enhance their profitability through product diversification, the proposed approach also presents environmental benefits. These include a reduction in the net volume of waste requiring disposal, a reduction in acid generation potential of coal discards and related treatment costs as well as a reduction in long-term liabilities.

The proper management of downstream emissions is primary to address the challenges faced by the mining industry, therefore understanding the technological and environmental characteristics of the disposed material is fundamental to make decisions regarding the opportunities for strategies to minimise mine waste, i.e. “towards zero mine waste” strategies.

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