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USING FROTH FLOTATION TO MITIGATE ACID ROCK DRAINAGE RISKS WHILE RECOVERING VALUABLE COAL FROM ULTRAFINE COLLIERY WASTES

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DEDICATION

TO MY CHILD DOXA

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ABSTRACT

The South African coal processing sector generates more than 12 million tons of ultrafine slurry per annum, the majority of which is disposed of in slimes dams. These ultrafine coal wastes contain sulfide-bearing minerals, particularly pyrite, which oxidize and give rise to acid rock drainage (ARD) resulting in extensive and prolonged contamination of local ground and surface waters. Currently, the operations still emphasise an end-of-pipe approach in their management of ARD, with the focus largely on chemical or biological treatment techniques or their combination. In addition to the excessive cost of this approach, the generation of ARD is a long-term problem (tens to hundreds of years) resulting in the challenge of achieving sustainable closure solutions within the resource lifetime. The elimination of the threat of acid generation *before* disposal of the coal wastes would be an important development as it would have a major beneficial impact on water quality and aquatic systems in these areas and would facilitate closure solutions. The simultaneous recovery of a saleable coal product would be an added economic incentive and would improve resource productivity.

This dissertation presents the results of an investigation to develop a two-stage flotation process to produce: (i) a low-volume sulfide-rich concentrate that can be treated chemically or biologically or disposed of in a contained manner; (ii) a high-volume (low sulfur) benign tailings, with low ARD potential compared to conventional tailings; and (iii) a coal concentrate that has added value on account of its low sulfur and ash content. Success requires integration of flotation, aqueous chemistry and mineral bioleaching expertise.

The approach adopted in this exploratory study entails coal flotation in the first stage, which takes advantage of its natural hydrophobicity. The recovered clean coal can be converted into saleable product through the application of dewatering: it can be blended into a middlings coal and sold via the already established export market. Hydrophilic gangue material reports to the tailings, from where, in the second stage of the proposed approach, the remaining sulfides are removed selectively, also by flotation. A small amount of acid-generating material is produced, leaving behind a large-volume benign tailings fraction with reduced ARD risk on a long term basis. The potential environmental risks that may be associated with the low-volume sulfide-rich concentrate may be reduced through its subsequent bio-desulfurization.

Laboratory-scale batch flotation experiments were carried out on a sample of coal ultrafines, using oily and oleic acid collectors to float coal, and xanthate collectors to remove acid-

generating sulfides. The overall coal flotation results indicated that the coal was difficult to float in the presence of dodecane or kerosene as collector, arguably due to its petrographic composition (high inertinite content), high ash content and oxidation due to weathering. To improve the recovery and yield of coal, oleic acid was used as collector and gave much better results in terms of yield. As an illustration, at a dosage of 2.89 kg/t oleic acid, the yield of clean coal was 55.98% at an ash content of 18.1%, down from 34.4% ash content in the feed.

The desulfurization of coal was investigated through laboratory batch flotation tests using potassium xanthate amyl (PAX) as sulfide collector. Direct sulfide flotation might be useful in cases of coal processing wastes with little or no economical value, but which nevertheless represent a risk of perpetual pollution to the environment. Staged addition of PAX enhanced total sulfur recovery and reduced the sulfur content in the tailing, but a significant amount of coal also reported to the concentrate, indicating inadequate depression of the coal.

The results of laboratory batch flotation tests to investigate the two-stage flotation process showed that a low-sulfur tailings (0.38% S) can be produced, together with a clean coal stream with a low ash content (13.54%) and a low volume sulfide-rich fraction (2.68% total sulfur). The majority of the original feed reported to the tailings of the second stage (67.2%) and was characterized by a high ash (40%) content. The clean coal had a low sulfur content of 0.48% S. The two-stage process was investigated with dodecane as coal collector; the use of oleic acid would probably have produced even better results. However, no attempt was made in this research to optimize the reagents.

Acid generating potential tests were carried out on the feed and products of the two-stage process. The combination of net acid generation (NAG) and acid base accounting (ABA) showed that the final (low-sulfur) tailing was non acid-forming. The feed and the sulfide-rich fraction were found to be potentially acid generating. The samples were also subjected to a new biokinetic test, which provides enhanced insight over the conventional static tests. The pH profiles of the biokinetic tests over a period of 76 days were consistent with the trends in the ANC results. However, the biokinetic tests provided additional extended data over the static tests, particularly in terms of the rate of release of neutralization capacity and of acidification as well as the potential for the sample to acidify. These are critical data for prediction of behavior in the field.

Recommendations to continue this work include confirming the results on samples from different coalfields, and optimising the flowsheet in terms of reagents and operating conditions. The potential to upgrade the high sulfur coal stream through bio-desulfurization also needs to be explored in depth.

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ABBREVIATIONS

GENERAL TEXT

ABA	acid base accounting – acid prediction test method
AMD	acid mine drainage
ANC	acid neutralizing capacity
ARD	acid rock drainage
ASTM	American Society for Testing and Materials
CV	calorific value
Eh	redox potential
ISO	International Organization for Standardization
IWRI & EGi	Ian Wark Research Institute and Environmental Geochemistry International
PAX	potassium amyl xanthate
MIBC	methyl isobutyl carbinol
MPA	maximum potential acidity
NAF	non-acid forming
NAG	net acid generation
NAGpH	pH of the NAG liquor after digestion
NAPP	net acid producing potential
NNP	net neutralization potential
NP	neutralization potential
PAF	potentially acid forming
ROM	run-of-mine
SABS	South African Bureau of Standard
SANS	South African National Standard
SEX	sodium ethyl xanthate

SIBX	sodium isobutyl xanthate
UC	uncertain or unclassified
US EPA	United States Environmental Protection Agency
XRD	X-ray Diffraction

UNITS OF MEASUREMENT

μm	micrometer – unit of length ($1\mu\text{m} = 10^{-6}\text{m}$)
g	gram – unit of mass ($1\text{g} = 1000\text{mg} = 10^{-3}\text{kg}$)
g/cm^3	gram per cubic centimetre square – unit of concentration
h	hour – unit of time
$\text{kg H}_2\text{SO}_4/\text{t}$	kilogram of sulfuric acid per ton
kg	kilogram – unit of mass ($1\text{kg} = 1000\text{g}$)
kg/t	kilogram per metric ton – unit of concentration ($\text{kg}/\text{t} = \text{g}/\text{kg}$)
kJ/kg	megajoule per kilogram – unit of energy
L	litre – unit of volume ($1\text{L} = 1000\text{ mL}$)
L/min	litre per minute – unit of flow rate
mg/L	milligram per litre – unit of concentration ($\text{mg}/\text{L} = \text{g}/\text{cm}^3$)
min	minute – unit of time
mm	millimetre – unit of length ($1\text{mm} = 10^{-3}\text{ m}$)
Mt	million metric tons – unit of mass ($1\text{Mt} = 10^6 = 10^9\text{ kg}$)
mV	millivolt – unit of potential
$^{\circ}\text{C}$	degree Celsius (centigrade) – unit of temperature
pH	measure of acid concentration ($-\log(\text{H}^+)$)
rpm	revolutions per minute – unit of rotational speed

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

1.1.1 Coal ultra-fines in South Africa

Conventional coal beneficiation generates large quantities of wastes in the form of overburden, discards and ultra-fine slurries. The South African coal processing sector currently generates more than 12 million tons of ultrafine slurry per annum, the majority of which is disposed of in slimes dams. The large increase in fine and ultrafine coal has been attributed to the mechanization and automation techniques currently employed in coal mining (Bunt, 1997). There is a growing realization in the South African coal industry that the reclamation and treatment of the ultrafine coals are difficult and expensive, due to the requirement of dewatering to dry the product (Franzidis, 1992). This is despite the fact that the quality of the ultrafines is generally comparable to that of the run-of-mine; the air dry calorific value is typically between 20-27 MJ/kg. At the same time the air-dry sulfur content is typically 0.6-2.2%. It is this sulfur in the ultrafine coals that contributes to the environmental problems of acid rock drainage (ARD), once these coals are discarded. Coal ultrafines are more exposed to oxidation and as a consequence are more likely to generate ARD than coarse coal discards due to their size, their large surface area and the liberated state of the sulfur-bearing minerals. ARD is a big problem in coal mining areas, even now; it results from the oxidation of sulfide minerals, in particular pyrite, in an oxidizing environment.

Coal ultrafines are produced in most washing plants during the pre-screening of the run-of-mine; in a few they are generated as tailings from flotation. Due to their fine size, coal ultrafines are expected to contain a large proportion of liberated material with the potential to produce a very low ash content product. Unfortunately, their beneficiation has not been successful in the South African coal processing sector, and they are either added to middlings material for use as thermal coal or discarded. Although initiatives have been taken to improve the disposal of coal wastes over the past years, the long-term risks associated with these practices are often not very well understood. Geldenhuis and Bell (1998) highlighted the shortfall of current disposal methods by showing that most of the ARD in

several mines in the Witbank coalfield was emanating from old opencast workings, which had been backfilled.

It is important to clarify that coal is central to the economy of South Africa. According to the South Africa Yearbook (2009/2010), coal is the primary source of energy (77%), and will remain the major energy source into the foreseeable future, owing to its relative abundance and low cost. As a consequence, many more coal ultrafines will be generated in the years to come. A need arises to control and improve the way in which these processing wastes are discarded so as to avoid and limit the environmental degradation they may cause in the future; i.e. there is a need to consider the desulfurization of these ultrafines before disposal.

1.1.2 Environmental issue associated with coal ultrafines

Martin *et al.* (2002) described the management of tailings from mining operations as the most significant environmental liability, particularly with regards to leaving a negative legacy for future generations. As with many other mine and processing wastes, coal ultrafines contain sulfide-bearing minerals, particularly pyrite, which oxidize and give rise to acid rock drainage (ARD) under conventional disposal conditions. The release of salt and heavy metal bearing ARD to the surrounding environment results in extensive and prolonged contamination of local ground and surface waters.

Globally, many authors have described the occurrence of ARD as the largest major environmental issue facing the mining industry (e.g. Gray, 1997; Broughton and Robertson, 1992; Benzaazoua *et al.*, 2000). In South Africa, concern has been growing over this issue and many studies have highlighted the legacy of many abandoned and operating mine sites producing ARD. These represent the source of ongoing environmental degradation of surface and ground water as well as soil (Naicker *et al.*, 2003; Tutu *et al.*, 2008). Unfortunately, there is often a marked lag time between the disposal of sulfidic wastes and the appearance of adverse environmental impacts. In other words, the occurrence of ARD can be rapid, or it may take years or decades to reach its full potential depending, for example on the mineralogical composition of the wastes (EPA, 2000).

Where no effective control measures are in place, acid rock drainage poses a serious threat to the receiving environment, resulting in elevated levels of environmentally hazardous trace elements and sulfate salts in the water. These have a detrimental effect on water quality and on the aquatic ecosystems in downstream environments (Lefebvre *et al.*, 2001). These dissolved pollutants include mainly metals such as lead, copper, silver, manganese, cadmium, zinc, and iron (Geldenhuis and Bell, 1998; Tiwary, 1999).

Other environmental impacts associated with the coal ultrafines in slimes dams may include the possibility of spontaneous combustion and the associated atmospheric pollution. Spontaneous combustion and burning of coal have been reported in many coalfields in South Africa, particularly in Witbank and Sasolburg (Bell *et al.*, 2001; Pone *et al.*, 2007). In coal wastes, spontaneous combustion may take place by oxidation of organic matter when the rate of heat generated exceeds the rate of heat dissipation. Other processes include oxidation of inorganic coal-bearing phases, such as pyrite, which may provide the necessary heat for self-ignition (Querol *et al.*, 2011).

Termination of the process of ARD generation is challenging once started; consequently, long term treatment is required to protect the receiving environment from undesirable impacts (Sapsford *et al.*, 2009). Up to the present time, South African coal mining and processing operations still emphasise an end-of-pipe approach in their management of ARD, with the focus being largely on chemical or biological treatment techniques or both. However, treatment of the acidic effluent has significant cost and long-term liability implications. Skousen *et al.* (1998) indicated that mining companies operating in acid-generating districts may face the prospect of continual treatment of heavily acidified water with the associated financial liabilities. By way of contrast, the environmentally-aware option focuses on maximizing the prevention approach which goes upstream to manage the pollution at source, thereby minimizing the need for treatment. Prevention of ARD production is preferred over treatment and has the potential to result in substantial environmental and economic benefit. The elimination of the threat of acid generation before disposal of the coal wastes is a much needed development with potential for a major beneficial impact on water quality and aquatic systems in mining areas and to facilitate closure solutions. Regulations regarding environmental pollution are becoming increasingly stringent, thus cost-effective methods to prevent ARD generation at source would be preferable.

As recognition of ARD issues grows in South Africa (Geldenhuis and Bell, 1998; Bell *et al.*, 2001), there is a need to consider both mitigation of pollution problems in perpetuity and the recovery of the valuable coal in these wastes. The development of cost-effective and environmentally responsible strategies for the management of coal ultrafines through the application of a two-stage flotation process could prevent the major environmental risks of ARD associated with their disposal, as well as provide economic benefit and improved resource utilisation as a result of recovering valuable coals from these wastes. This development could be incorporated into an integrated waste management scheme, which would ensure both the efficient recovery of valuable coal from the ultrafines and the production of a low-volume tailings that could be disposed of without environmental harm.

The legacy of many abandoned and operating mine sites producing ARD, which is the source of ongoing environmental degradation of rivers in South Africa, provides an incentive for improving mine waste disposal using alternative innovative technologies such as desulfurization that will address the ARD challenges and meet changing environmental objectives.

1.1.3 Desulfurization and coal flotation overview

ARD generating wastes can be effectively managed by selectively removing sulfur-bearing minerals prior to their disposal; thereby restricting their exposure to oxidizing conditions. Desulfurization of coal can be achieved by chemical, bacterial or physical removal of sulfur. Chemical and biological desulfurization can remove both organic and sulfide sulfur, however these are not cost effective in comparison to the physical process, which only removes sulfide-sulfur during beneficiation. As an illustration, mineral particles containing sulfur may be removed by gravity separation due to their relatively high density compared to coal. However, the efficiency of separation by density processes falls rapidly for fine particles smaller than 100 μm , because of their low particle settling velocities. Instead separation processes based on differences in particle surface properties, such as froth flotation, are suggested.

In view of its proven nature, froth flotation should be a viable method of coal ultrafine beneficiation in South Africa (Horsfall *et al.*, 1986). Flotation is the only method used in the beneficiation of ultrafine coal on a commercial scale worldwide, and much work has been done on the beneficiation of South African coal ultrafines by flotation (Fickling, 1985; Anderson, 1988; Harris *et al.*, 1994; Harris and Franzidis, 1995; Opperman *et al.*, 2002;). However, little is known about the desulfurization of coal processing wastes by flotation. Desulfurization of coal can take place by depressing the sulfide minerals or pyrite, and floating coal, or by depressing coal and floating pyrite (Laskowski, 2001). In each case, the desulfurization level is predetermined by the proportion of sulfide minerals in the ultrafine coal and its acid neutralization potential. Importantly, the tailing produced through desulfurization needs to have enough buffering capacity to safely counteract its acidity potential to meet the minimum requirement for safe disposal.

To date no in-depth research on the recovery of coal ultrafines for the mitigation of ARD risks appears to have been done in South Africa. In an attempt to fill the gap, some preliminary studies on desulfurization of ultrafines were undertaken with limited scope and resources as an undergraduate project at the Department of Chemical Engineering at the

University of Cape Town (Nchabeleng and Shabalala, 2009). The feed coal used in this investigation did not exhibit acid-generating characteristics, and no significant total sulfur removal took place through reverse flotation. However, the overall results of this earlier work provided a basis for both a more fundamental investigation into the technical feasibility of desulfurization of coal with environmental benefits, and the development of appropriate process routes as well as conceptual approaches for minimizing the risks of ARD generation over the long-term, through the production of a coal tailings waste which is depleted in sulfide-bearing minerals.

Consideration of the above suggests that there are environmental and economic benefits in processing coal ultrafines further because of their large content of liberated and high grade coal in comparison to the coarse discards. The reclamation of these otherwise waste products provides potentially cost effective and environmentally attractive solutions for the management of ARD. In doing so, it may be feasible to reduce the environmental footprint of coal mines as far as ARD is concerned. Furthermore, it will result in the recovery of substantial amounts of energy that are currently wasted and the marked reduction in the amount of ultrafine wastes to be handled and disposed of. The following section addresses in more detail the development of a conceptual approach to recovering valuable coal that is currently wasted, and identifies a suitable process route that may be able to control or reduce the ARD impacts to an environmentally acceptable level.

1.2 APPROACH TO COAL RECOVERY AND ARD MITIGATION

The previous section has highlighted a number of relevant points regarding the potential environmental impacts and financial liabilities of ARD associated with the conventional disposal of coal ultrafines which does not always comply with acceptable environmental standards over the long-term. Growing recognition of ARD issues in South Africa provides an opportunity to develop, from a scientific standpoint, a conceptual approach applicable to treating typical coal ultrafines from South African coalfields, for the mitigation of pollution problems in perpetuity and recovery of valuable coal in these wastes through flotation techniques.

1.2.1 Problem Statement

It is worthwhile to recapitulate that wastes generated throughout coal processing operations may contain sulfur-bearing minerals, which are a permanent source of environmental issues

once disposed of in conventional ways. The mining industry is constantly facing major environmental challenges related to the occurrence of ARD and metal leaching to surface and ground waters as well as soil. ARD occurrence may not become apparent for many years, but once initiated can continue for decades. The current practice of ARD management by means of end-of-pipe approaches does not eliminate the long-term environmental risk associated with the disposal of coal processing wastes and does not guarantee a “walk-away” solution. Furthermore, the coal ultrafines that are currently being disposed of have as much CV as the ROM coals, i.e. they can be considered a potential source of additional revenue to the mining industry if beneficiated.

There is therefore an opportunity in South Africa to investigate the development of more efficient, cost-effective and environmentally sound process routes that will on the one hand minimize the production of ARD, so that the large deposits of coal that exist in South Africa can be mined without harming the environment; and, on the other hand, recover, through the application of flotation techniques, valuable coal that is currently wasted.

1.2.2 Research approach

The recovery of coal by flotation is possible due primarily to the inherent floatability of coal and secondly to the use of reagents to promote the flotation process. Nevertheless, South African coals, referred to as Gondwana coals, are generally more difficult to float than Northern Hemisphere coals as a result of their petrographic composition, with high content of inertinite, and their deterioration on exposure to weathering. In addition, coal beneficiation in South Africa is made more difficult by the large quantity of mineral matter, which is finely disseminated in these coals. Regardless of this, many researchers have shown that South African coal ultrafines can be beneficiated by flotation using both conventional and column flotation (Horsfall *et al.*, 1986; Anderson, 1988; Stonestreet, 1991; Bunt, 1997). These flotation processes aim at beneficiating coal by removing ash-forming minerals, while desulfurizing flotation focuses on selective removal of sulfide minerals, especially pyrite, which are the major environmental problem in ARD generation.

The consideration of the characteristics of South African coals constituted a key determinant in the selection of the mitigation process route and had a major impact on the selection of the case study sample for this dissertation. Figure 1.1 shows two process routes designed for selective removal of sulfide minerals and recovery of valuable coal as initially proposed by Harrison *et al.* (2010). Each option or process route is a two-stage flotation process

aimed at the optimum removal of the sulfide-bearing minerals and recovery of valuable products that are present in coal ultrafines.

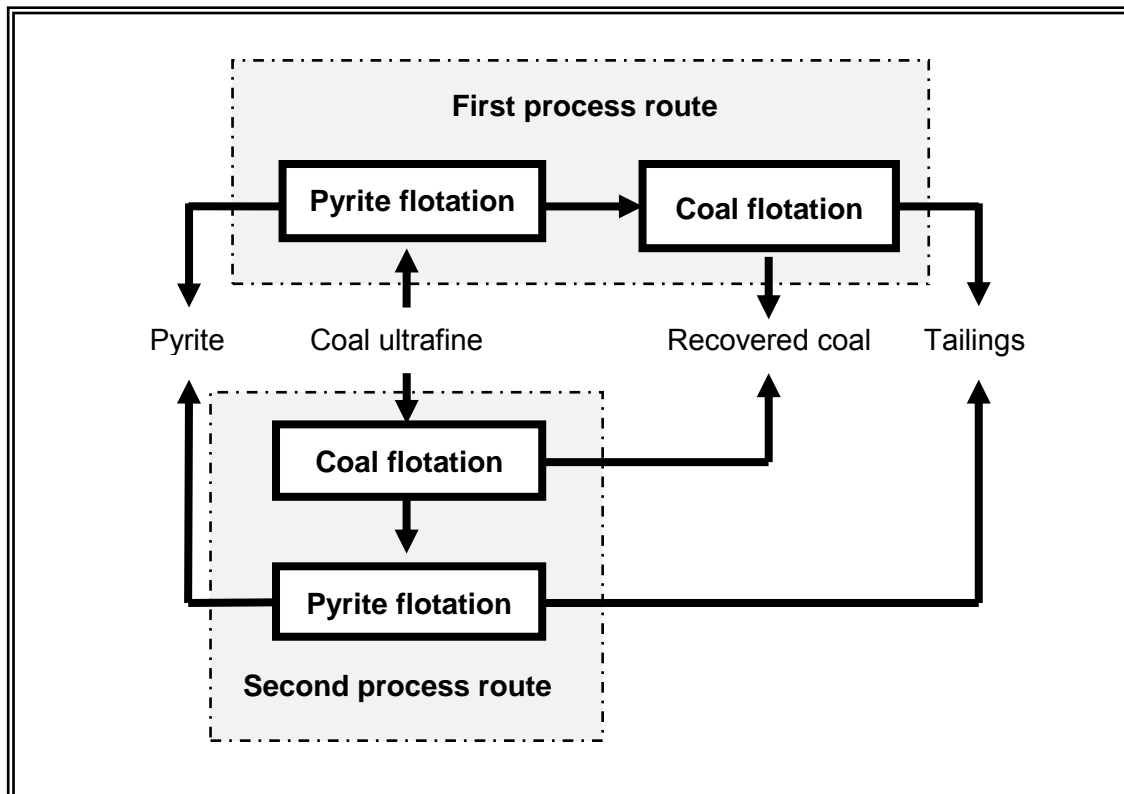


Figure 1.1: Process routes for reclaiming coal ultrafines and mitigating associated environmental impacts in two-stage processes.

The first process route involves the selective removal of sulfide minerals in the first stage, which is followed by coal flotation to recover the valuable coal. This process route would eventually be less viable due to the likely challenges of subsequently floating coal that might have been exposed to a depressant, such as dextrin.

The second process route, which constitutes the conceptual approach explored in this investigation as shown in Figure 1.2, entails coal flotation in the first stage. This takes advantage of its natural hydrophobicity: hydrophilic gangue material reports to the tailings, while the recovered clean coal can be converted into saleable product through dewatering; after which it can be blended into a middlings coal and sold via the already established export market (Reddick *et al*, 2007; Reddick *et al.*, 2008). In the second stage of the proposed approach, sulfides remaining in the first stage tailing are removed selectively, also by flotation. A small amount of acid-generating material is produced leaving behind a benign

tailings fraction with reduced ARD risk on a long term basis to meet the steadily tightening standards. The potential environmental risks that may be associated with the low-volume sulfide-rich concentrate may be reduced through its subsequent bio-desulfurization. It should be pointed out that this flowsheet differs from the previous two-stage flotation process (Miller, 1975), in which sulfides were floated from the coal concentrate rather than the tailing.

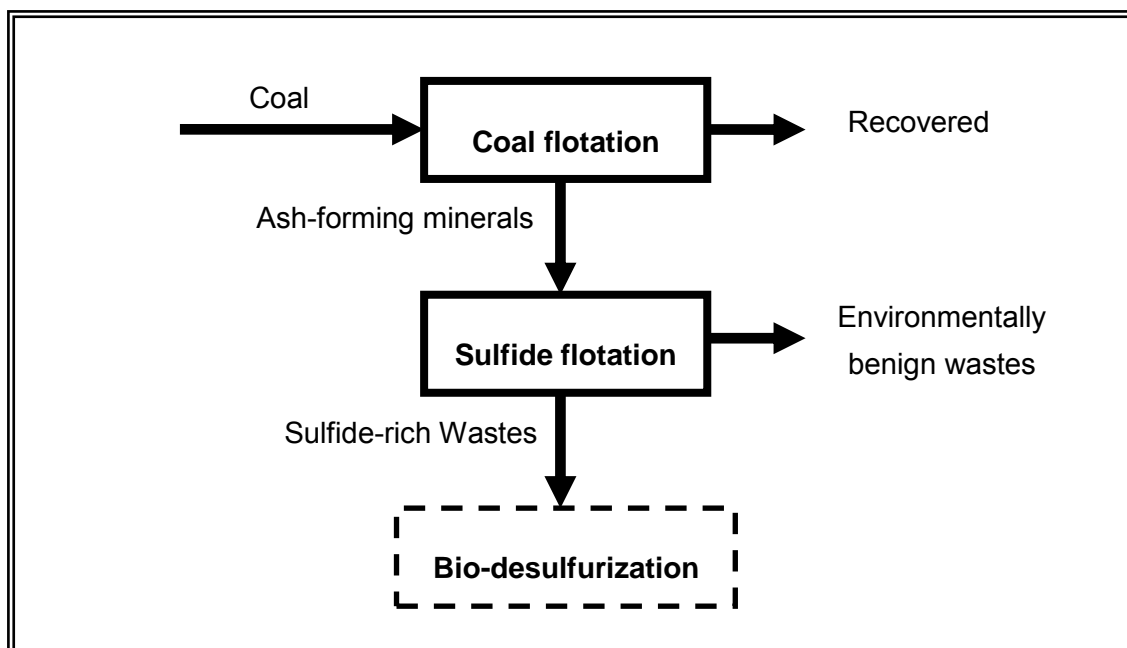


Figure 1.2: Adopted conceptual approach aimed at recovering coal and mitigating ARD risks in a two-stage process

1.2.3 Hypothesis

The above approach provides the motivation to formulate a hypothesis in order to address the long-term ARD risks associated with coal ultrafines disposal: a two-stage flotation process can effectively eliminate the major environmental risks of ARD associated with the disposal of coal ultrafines, as well as provide economic benefit as a result of recovering valuable coals from these wastes.

1.2.4 Objectives and scope of the investigation

The main objective of this research is to develop a desulfurizing flotation process for selectively removing acid-generating materials, in this situation pyrite, from ultra-fine coals and simultaneously recovering saleable coal from these wastes.

Despite the fact that the current investigation has been driven primarily by environmental considerations, there are economic advantages from removing sulfur from the ultrafine coals as well. Beneficiation of coal ultrafines would have financial incentives in terms of income that could be earned versus the present cost of disposal and the potential financial implications of remediation in the case of ARD occurrence. In the context of cleaner production in the South African coal mining industry, the desulfurized ultrafine coals could be converted into saleable product through the application of dewatering techniques (Reddick *et al.*, 2008). In this case, the beneficiated and dewatered ultrafine coals could be added to the middlings coal, and sold via the already established export market (Reddick, 2006).

In the light of the research aims, the scope seeks to approach ARD prevention by reducing the risk through selective removal of the material implicated in the ARD generation process. The desulfurization of coal is investigated systematically through batch flotation tests under various conditions to determine the technical feasibility of selectively removing acid-generating materials from coal ultrafines. This investigation aims to fulfil the requirements of study towards a master's degree of science in Chemical Engineering and the scope is designed as such.

The current study is largely laboratory-based and entails both flotation and ARD prediction tests. Laboratory-scale batch flotation tests have been conducted on a coal fine-to-ultrafine sample from a colliery in the Middelburg area to determine the effects of key parameters on (i) the extent of sulfide sulfur removal in a desulfurization (reverse) float; and (ii) the extent of coal recovery in a direct coal float. Static and biokinetic tests were used to predict the acid generation potential of the feed and flotation outputs. These tests are described in detail in Chapter 2 below. Thus, the experimental work involved flotation and assessment of the acid forming characteristics of the sulfide-rich and sulfide-lean fractions produced, with regard to their environmental impacts at disposal sites.

This study is limited to coal materials and focuses on the ultrafines derived from the processing of run-of-mine (ROM) coal. The study does not attempt to optimise the desulfurizing flotation process; however, satisfactory conditions were explored for maximum recovery of valuable coal in direct flotation and selective removal of sulfide-bearing mineral to an environmentally acceptable level.

1.3 DISSERTATION LAYOUT

The approach taken to fulfil the main objectives and scope of this investigation, as presented in the previous sub-section, is closely reflected in the dissertation structure. The next Chapter outlines the findings of a relevant and concise literature survey, undertaken to offer critical evaluation and draw conclusions on current knowledge and understanding with regard to ARD, the prediction of acid potential, as well as factors affecting coal floatability. Chapter 3 outlines the experimental methods and procedures. The results and discussions of the coal flotation and ARD prediction tests are presented in Chapters 4 and 5. Chapter 4 presents the of the coal, sulfide and stage-wise flotation tests, while Chapter 5 discusses the acid prediction tests, including static and biokinetic, performed on the flotation outputs and feed. The major findings of the research are summarised in Chapter 6, which also includes recommendations for further work.

University of Cape Town

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

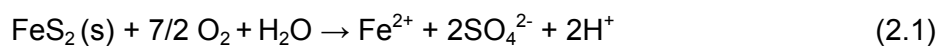
This chapter presents an overview of the available literature relevant to the mitigation of acid rock drainage and coal flotation. The survey begins by describing the fundamental concepts of ARD, its formation, way of preventing it and ways of predicting it using static and kinetic tests; the mineralogy and petrography of coal are then discussed. This is followed by a broad discussion of South African coals with respect to the reserves and characteristics. Finally, since this research seeks to develop a flotation circuit dedicated to maximum recovery of valuable coal from the ultrafines, a thorough review is given regarding the floatability of coal and coal-sourced pyrite.

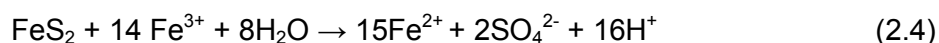
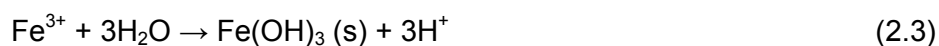
2.2 FUNDAMENTAL CONCEPT OF ACID ROCK DRAINAGE

2.2.1 Formation of ARD

Acid rock drainage (ARD), previously referred to as acid mine drainage (AMD), is an acidic, sulfate and metal laden water that results from exposure of sulfide minerals, in particular pyrite, to oxidizing conditions (Gazea *et al.*, 1996; Akcil and Koldas, 2006). Acid rock drainage typically has pH values below 2.3, acidity levels near 5000 mg/L, and anionic concentrations (mostly sulfate) exceeding 10000 mg/L (Brown, 1996).

Although acidic drainage occurs as a result of naturally occurring processes, its activity is accelerated by land disturbance such as mining operations through exposure of acid-generating minerals at the surface of the earth. Acidity around coal mines is principally due to the oxidation of pyrite, FeS₂, which is commonly associated with coal. The oxidation of pyrite illustrates the generation of acid rock drainage very well, as described by four the general equations below.





Ferrous iron produced by pyrite oxidation is oxidized to ferric iron according to reaction (2.2) depending on the concentration of oxygen, pH and activity of iron-oxidizing bacteria such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* in the surrounding environment. These acidophilic autotrophic bacteria utilize ferrous iron and sulfur compounds as their energy source (Natarajan, 2008). The conversion of ferrous iron to ferric iron and its subsequent hydrolysis generate acidity as well. Ferric iron that has been generated from reaction (2.2) will participate in the oxidation of additional pyrite according to reaction (2.4). The rate of acid formation is rapid in the last step and is limited by the concentration of ferric iron (Ferguson and Erickson, 1987).

It is important to note that three forms of sulfur occur in coal, i.e. sulfate, organic, and pyritic. Sulfate sulfur results from pyrite oxidation and is found in small amounts in freshly mined coal. Organic sulfur is chemically bound to coal molecules and has little to no effect in terms of acid generation. Sulfides, in particular pyrites, are the predominant form of sulfur found in coal and are responsible for the bulk of the acid generated. Table 2.1 shows a list of some of the sulfide minerals associated with coal which may also contribute to acid generation and heavy metal dissolution (Skousen *et al.*, 1998).

Table 2.1: Some important metal sulfides which occur in coal mining regions (Skousen *et al.*, 1998; Ward, 2002)

Mineral	Chemical Composition	Mineral	Chemical Composition
Pyrite	FeS ₂	Molybdenite	MoS ₂
Marcasite	FeS ₂	Millerite	NiS
Pyrrhotite	Fe _(1-x) S	Galena	PbS
Chalcocite	Cu ₂ S	Sphalerite	ZnS
Covelite	CuS	Arsenopyrite	FeAsS
Chalcopyrite	CuFeS ₂	Stibnite	SbS

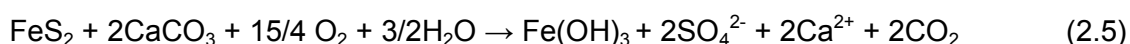
The acid water resulting from the oxidation reactions leads to dissolution of other common contaminants, such as aluminium and manganese, and occasionally other metals such as copper, zinc, and nickel, which are associated with sulfur-bearing minerals in coal. The type and amount of sulfide materials and the presence or absence of neutralizing materials determine the acidity levels, metal composition and concentration. In general, sulfide rich and carbonate poor materials are expected to produce acidic drainage. In contrast, alkaline rich materials, even with significant sulfide concentrations, often produce net alkaline water.

2.2.2 Factors influencing ARD generation

The potential for coal processing wastes to generate acid and release contaminants largely depends on site-specific factors, which can be classified as primary, secondary, and physical factors. Recognition of these factors is critical to both prediction of acid generation potential and evaluation of technically and economically efficient control measures.

The primary factors, also referred to as generation factors, determine the ability of the material to produce acid drainage. These factors include sulfide minerals, oxygen, water, ferric ions, and iron-oxidizing bacteria (Ferguson and Erickson, 1987). Water and oxygen are the principal driving forces for ARD generation; they are provided to the acid generating materials by the external environment. Water serves several roles in the acid production system, acting as a reactant, as a reaction medium, and as a product transport system (Van Niekerk *et al.*, 2008; EPA, 1994).

Regardless of sulfide minerals, ARD may not happen at a mine site owing to the presence of the secondary factors. These factors are the neutralizing materials, which act to control the oxidation reactions. Therefore, the balance between the rate of acid generation and neutralization reactions will determine the acidity of the drainage (Lapakko, 2002). The most effective neutralizing minerals are those containing calcium carbonate (CaCO_3) and magnesium carbonate $\text{CaMg}(\text{CO}_3)_2$, including magnesite (MgCO_3) and ankerite ($\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$). Equation 2.5 represents the dominant acid-neutralizing reaction of calcium carbonate:



Calcium carbonate minerals dissolve more rapidly than other carbonate minerals. Other minerals such as silicates can also neutralize acid, however their rates of dissolution and consequently acid neutralization are slow compared to carbonate minerals. As an illustration,

Lapakko (2002) reported that the dissolution rate of calcium carbonate at near neutral pH is roughly 7 orders of magnitude faster than the dissolution of silicate such as plagioclase-feldspars. Siderite, on the other hand, has a slower rate than calcite, and does not provide net acid neutralization under oxidizing conditions. This understanding is key to the accurate determination of the acid neutralizing capacity of a sample and the prediction potential of a sample (Skousen *et al.*, 1997).

The tertiary physical factors affecting acid drainage include the physical characteristics of the material, the way in which the acid-generating and acid-consuming materials are placed, as well as the local hydrologic regime in the surrounding area. Consideration of the physical aspects of the mineral materials such as particle size, permeability, and physical weathering characteristics is very important in terms of acid generation potential. As an illustration, the relationships between particle size, surface area, and oxidation play a significant role in the acid prediction methods. Fine grain material may limit air diffusion and water flux, whereas very coarse material exposes less surface area. However, deep percolation of water and oxygen is possible in coarse-grained waste resulting in exposure of more materials. In addition, the effects of liberation and mineral association are also important. Disseminated pyrite associated/rimmed with calcite is likely to be much less acid generating than liberated pyrite (Ferguson and Erickson, 1987; Salomons, 1995).

2.2.3 Environmental impact of acid rock drainage

The oxidation of sulfide minerals and subsequent mobilization of environmentally hazardous trace elements can result in contamination of aquatic ecosystems. The occurrence of ARD can cause the release of metals and sulfates into the surrounding environment. As mentioned earlier in Section 1.1.2, dissolved metals in acid drainage may include lead, copper, silver, manganese, cadmium, iron, and zinc, among other metals associated with sulfur-bearing minerals in coal (EPA, 2000). Although acid may be neutralized by the receiving environment, some of these dissolved metals may remain in solution.

Extensive investigations have been carried out in South Africa on the pollution problems arising from mining activities. Geldenhuis and Bell (1998) indicated that several mines in the Witbank coalfield in South Africa are affected by acid rock drainage, which has led to deterioration in the water quality in many surface streams. Naicker *et al.* (2003) studied the impact of acid rock drainage on surface and ground water, as well as soils in and around the mining areas in Johannesburg. The study revealed that the ground water within the mining

district was heavily contaminated and acidified as a result of the oxidation of pyrite contained within tailing dumps, and had an elevated level of heavy metals.

More recently, Tutu *et al.*, (2008) investigated water quality from mine tailings in the same area in relation to spatial distribution and seasonality. Water quality was found to be the lowest in the immediate vicinity of dumps, but water quality improved downstream due to the presence of carbonate material. Oberholster *et al.* (2010) studied the relationships between water quality and the phytoplankton within the riverine zone of Lake Loskop to evaluate the impacts of acid rock drainage and high nutrient concentrations. They reported that higher concentrations of metal ions and sulfate had adverse effects on certain phytonplankton.

2.2.4 Prevention of acid rock drainage

One of the areas in which there has been considerable progress is the understanding of the factors which control the rate and extent of ARD initiation. This understanding has improved the ability to design effective control techniques. ARD control strategies, referred to as 'at-source' control methods, are carried out to treat the acid-generating materials to anticipate acid formation. On the contrary; treatment methods target remediation through addition of chemical-neutralising agents (Johnson and Hallbert, 2005).

The oxidation of pyrite and subsequent conversion occurs through the chemical equations (2.1) to (2.4) presented in Section 2.2.1. The generation of ARD will be retarded or prevented if any of the processes represented by these equations are slowed down or completely stopped. For example, if the sulfide minerals are non-reactive or if the coal contains alkaline material in sufficient quantity to neutralize the acid, ARD will not take place. Furthermore, removal of air and/or water from the system, two of the three main components, would retard the oxidation of ARD. Consequently, methods used to prevent ARD generation aim to exclude one or more components that result in oxidation, while remediation techniques involve collection and treatment of ARD.

The prevention approach represents the best strategy and most preferable option, because it holds the key to the mitigation of acid rock drainage (Natarajan, 2008). At-source control of ARD has more advantages than treatment options. The process of ARD generation is extremely difficult to stop once started and the long-term treatment of acid rock is required to protect the receiving environment from adverse impacts (Sapsford *et al.*, 2009). Skousen *et al.* (1998) indicated that coal mining companies operating in an acid-generating area often treat ARD. Consequently, they may face the prospect of long-term to indefinite treatment of

acid water and its associated financial liabilities. However, ARD prevention at source will help reduce handling, treatment, and disposal cost and also will reduce the generation of acidic leachates (Komnistas *et al.*, 2001). Because regulations regarding environmental pollution are becoming more stringent, cost-effective approaches to ARD prevention and mitigations at source would be preferable.

2.2.4.1 Approaches to ARD prevention and mitigation

The role of mitigation measures, as far as ARD is concerned, involves maintaining or controlling the rate of sulfide mineral oxidation so that ARD formation is prevented or reduced to minimal or acceptable levels. The principle of preventing the generation of acid rock drainage from sulfide sources may involve one of the following mechanisms (INAP, 2009):

- Minimization of oxygen diffusion into the mass of sulfide minerals;
- Elimination of water infiltration into concentrates, tailings or waste rocks;
- Isolation of sulfide containing wastes before disposal;
- Control of pH by addition of lime, limestone, phosphates, fly ash etc.;
- Use of bactericides to inhibit the action of iron-oxidizing bacteria;
- Removal of acid-generating material from waste prior to disposal.

Broughton and Roberton (1992) have highlighted three key factors required in the early stage of chemical oxidation, viz. reactive sulfides, oxygen and water. The prevention of ARD impact from mining wastes will focus primarily on the mineralogy of the potentially acid-generating material and the availability of water and oxygen. Many methods are currently being used in the mining industry aimed at reducing the environmental impact of sulfide mining wastes by eliminating one or more of the essential components, or by controlling the environment around the sulfide grain.

2.2.4.2 Overview of ARD preventive methods

This subsection presents a summary of some of ARD prevention methods available for prevention and mitigation of ARD. These methods may include water cover, soil cover, blending, backfill etc. Recently, environmental desulfurization has been proposed as an emerging technology in the prevention of acid rock drainage (Bois *et al.*, 2004; Hesketh *et al.*, 2010a). Some of the current preventive techniques used the mining industry are described below.

It is now recognised that the reduction of the rate of acid generation in mine spoils can be accomplished by exclusion of oxygen, which is most effectively achieved by under water storage or saturated layering. When stored under water, sulfide mine wastes are largely chemically stable owing to the unavailability of oxygen in the resulting anaerobic conditions (Morin, 1993). Specific factors required in the selection of the most appropriate method are well-documented in Broughton and Robertson (1992). Due to the fact that wind and waves may cause the re-suspension of tailings under water, and in order to improve the efficiency of water covers, tailings are covered with a layer of sediment or organic material that presents the advantage of limiting oxygen diffusion (Skousen *et al.*, 1998).

Alternatively, the oxidation reaction can be slowed down by placing problematic wastes under covers to prevent the oxygen diffusion into reactive sulfide mineral wastes. Covers are materials characterized by low permeability and high compaction, and they are generally used to rehabilitate tailing disposal areas that are potentially acid-generating (Demers *et al.*, 2008). Covers may comprise low sulfide content waste rock or organic materials. Peppas *et al.* (2000) showed that the application of an organic cover can act both as an oxygen-consuming and physical barrier, thus minimizing the oxidation of the underlying sulfide materials. Furthermore, metals can be precipitated as sulfides and oxyhydroxides within the organic matter. The application of an organic cover may improve the aesthetics of the reclaimed area by establishing a vegetative layer on top due to the presence of nutrients. The presence of toxic elements in the organic cover, i.e. sludge from a wastewater plant, may pose potential health and environmental risks; the treatment of sludge from the wastewater plant is necessary before use (Peppas *et al.*, 2000).

ARD production can also be minimized by blending acid-generating and acid-consuming materials to produce environmentally benign composites. The objective of blending is to balance alkaline and acid-generation potential to minimize the risk of net acid generation. In the coal industry, fly ash or kiln dust may provide a useful source of alkalinity which can be incorporated into pyritic overburden and coal waste spoils to minimize acid drainage potential (Johnson and Hallberg, 2005). Mixing of alkaline materials, such as limestone, is currently the most common method of controlling ARD generation at-source. However, the effectiveness of this method is still questionable in controlling ARD due to the limited solubility of limestone under equilibrium conditions near neutral pH and the tendency to armour with ferric hydroxide precipitates. As a result, the rate of reaction of the coated limestone with ferric hydroxide is inhibited and production of neutralizing capacity is reduced. In addition if blending is not done properly, toxic heavy metals contained in the fly ash can cause environmental concerns (Evangelou, 1995; Vandiviere and Evangelou, 1998).

An alternative to blending technology is to add solid-phase phosphates to pyrite mine waste to precipitate iron (III) as ferric phosphate, thereby reducing its potential to act as an oxidant of sulfide minerals. Evangelou (2001) studied the application of soluble phosphate together with hydrogen peroxide which oxidizes pyrite, producing ferric ion, which in turn reacts with phosphate to produce a surface protective coating of ferric phosphate.

Another technique used to control ARD formation is backfill, which involves placing some or all of the mine processing wastes back into the voids created by the mining operations, thus isolating them from the oxidizing conditions (Benzaazoua *et al.*, 2008). High strength in backfill is generally achieved by adding more binder, consequently resulting in high cost. There are different types of backfill: hydraulic fill, paste fill, rock fill, blended fill, etc. A phenomenon known as sulfate attack takes place in backfill made of tailings from sulfide, reducing the strength of the backfill significantly (Dorricott and Grice, 2002).

Oxidation of sulfide minerals in backfill is considered one of the main environmental concerns since it can affect the water quality. Ouellet *et al.* (2006) investigated the evolving reactivity of highly sulfidic cement over time using oxygen consumption tests. They found that the addition of binder in the paste backfill reduces the migration and consumption of oxygen through the backfill, and consequently limits the formation of acid rock drainage.

Finally, inhibition of pyrite oxidation can be achieved by bactericides involving the application of anionic surfactants, which are highly toxic to iron- and sulfur-oxidizing bacteria. Anionic surfactants can be used to control bacteria that catalyze the conversion of Fe^{2+} to Fe^{3+} , thereby controlling pyritic oxidation. The amount of acid generated from pyritic materials can be reduced or eliminated by inhibition of the iron-oxidizing bacteria (Johnson and Murray, 1997). The inhibition of ARD generation by bactericides presents only a short-term strategy used to delay the onset of oxidizing conditions. Sand *et al.* (2007) reported a six-year study on mitigation of ARD in large lysimeters. Their results showed that an addition of sodiumdodecylsulfate (SDS), a bactericide, partly reduced the activity and number of *Acidithiobacillus ferrooxidans* but did not kill the bacteria. As a result, the release of metals, heavy metals and sulfate from the mine waste was not significantly reduced.

2.2.4.3 Desulfurization of wastes

Ziemkiewicz and Skousen (1996) indicated that some of the methods described above are only partially successful and have been considered as failures because they do not demonstrate a complete control of acidity produced at site. More recently, desulfurization

has been suggested as a new approach for controlling and minimizing ARD production from mine spoils; it involves the separation of acid generating sulfide tailings by means of froth flotation (Benzaazoua *et al.*, 2000). As a result, the non-acid generating fraction does not represent a long-term liability, which is in fact considered as the main environmental benefit of using this emerging preventive approach (Bois *et al.*, 2004). The selective removal of pyrite, which is the primary component, will completely stop reaction (2.1), which leads to the formation of ARD. This method produces low sulfur content and sulfide-rich portions as schematized in Figure 2.1, where NP and AP represent the neutralizing potential and acid potential, respectively.

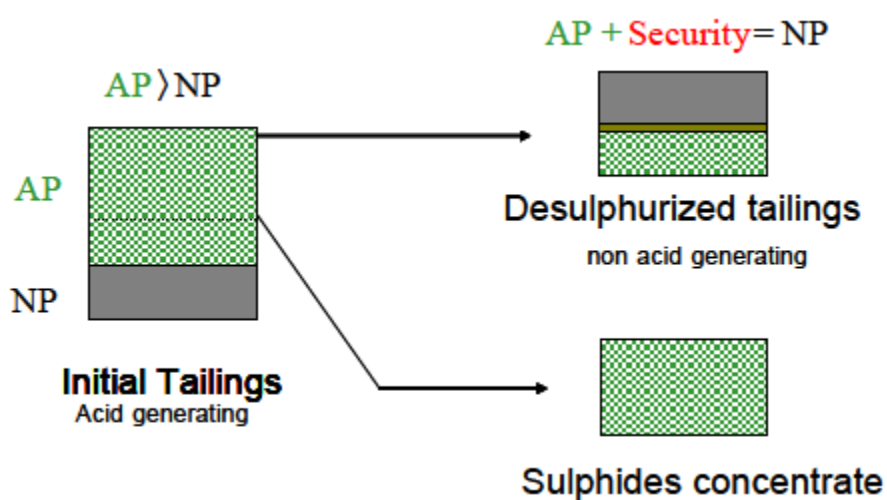


Figure 2.1: Scheme illustrating the environmental desulfurization principle (Bois *et al.*, 2004). NP and AP represent the neutralizing and acid potentials, respectively.

With this approach, it is possible to substantially reduce the volume of acid generating mine tailings, which can be managed effectively in terms of their acid-generating potential (Benzaazoua *et al.*, 2000; 2008). More recently, under the same scenario Hesketh *et al.* (2010a) studied the abatement of the generation of acid rock drainage from copper sulfide tailings through an integrated waste management scheme. This study showed that the technical feasibility of the selective removal of pyrite from tailings depends on the amount of collecting agent during flotation. In addition the geochemical ARD prediction tests at laboratory-scale revealed that the flotation residue with a sulfur grade of 0.2 % was classified as non-acid forming.

Various options exist for disposing safely of the desulfurized tailings. According to Bois *et al.* (2004), the desulfurized tailings can be used as a moisture retention layer in a cover with capillary barrier effects to prevent acid rock drainage. The sulfide concentrate can be used

for paste backfill materials. When mixed with binders, they give good long term results in terms of mechanical stability. A column test investigation conducted by Demers *et al.* (2008) revealed that ARD generation can be effectively prevented by the use of desulfurized tailings as cover material in monolayer cover systems combined with water table elevation. On the other hand, the concentrate from desulfurization, even if sulfide-rich, has been shown to produce high quality backfill, a well established waste management technology.

Desulfurization by means of flotation may lead to a major reduction in costs related to the supply and transportation of natural materials (such as clay and gravel) required in the application of other AMD prevention technologies. Economic analysis has shown that the implementation of this new technology is comparable to other technologies with significant environmental benefits as shown in Figure 2.2 in which CCBE stands for covers with capillary barrier effect.

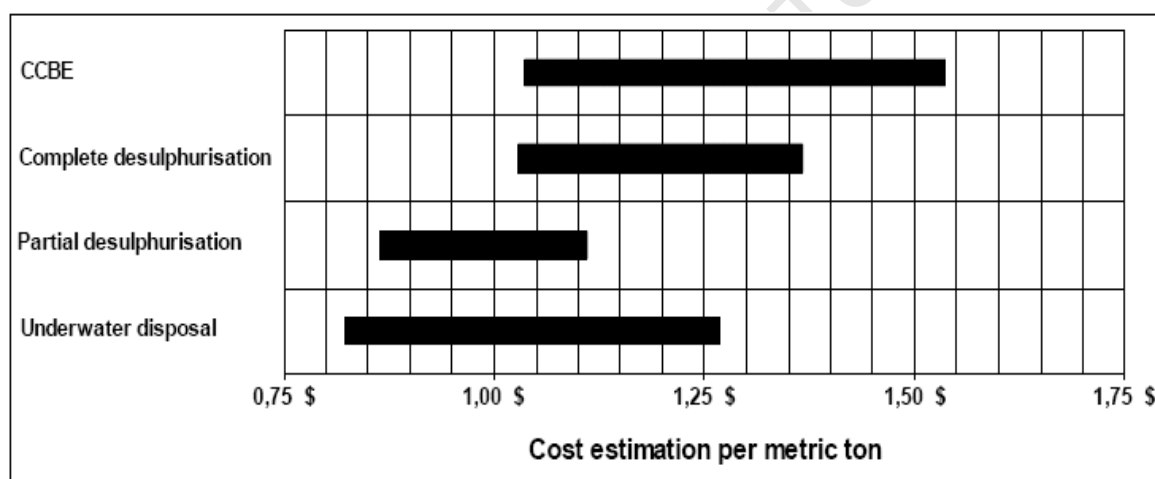


Figure 2.2: Comparison of cost estimations of desulfurization compared with other ARD prevention methods (Benzaazoua *et al.*, 2000; Bois *et al.*, 2004).

2.2.5 Acid generation prediction

The prediction of the potential for a mineral material to generate acid and release metal is an important component in controlling ARD production from both an environmental and an economic perspective (Broughton and Robertson, 1992). Prediction testing of acid generation materials can significantly reduce long-term environmental and associated financial liabilities. Different techniques can be used in the prediction of acid generation potential and drainage water quality: geographical comparisons; geological models; geochemical static tests, geochemical kinetic tests and mathematical models (Coastech

Research, 1991; EPA, 1994). In the scope of the present work, only static tests and kinetic tests are summarized in the following sections.

Static tests are used as a preliminary indicator to identify the materials that may have acid generation potential; they determine the balance between potentially acid generating and potentially acid consuming minerals in a sample. Overall, acid-producing minerals are reactive sulfide minerals, whereas acid-neutralizing minerals are primarily carbonates, even though hydroxides, silicates and clays are able to provide neutralization potential. Mineralogical knowledge of the material is an important adjunct to the chemical tests. Static tests are quite simple, rapid and relatively inexpensive to conduct. There are a number of static test procedures that are used to determine the proportions of acid-generating and consuming minerals; each of these procedures addresses the same variables, but varies in procedure. If the waste is potentially acid-generating, it will possibly require a method of disposal to either prevent acid generation or to mitigate its impacts on the surrounding environment (Lawrence and Scheske, 1997; Price *et al.*, 1997).

2.2.5.1 Acid-base accounting

Acid-base accounting (ABA) is the most commonly reported laboratory procedure for the prediction of ARD risks because it is simple, relatively cost-effective and reliable (Lawrence *et al.*, 1989). Frequently referenced to as the source document, Sobek *et al.* (1978) formally presented a step-by-step laboratory procedure for the ABA assessment associated with mine overburden. This method involves a comparison of the maximum potential acidity (MPA), typically estimated from the total sulfur in the sample, with the acid neutralization capacity (ANC). The net acid production potential (NAPP) or net neutralization potential (NNP) of a sample is given by the difference between the MPA and the ANC (EPA, 1994; Stewart *et al.*, 2006).

The acid neutralizing minerals (expressed as neutralization potential, NP or acid neutralizing capacity) are determined by titration of the sample either by direct titration with acid, or acidification and back titration with base. The neutralization potential is determined first by a simple fizz test to select the acid strength and amount to use in the next step. The mineralogical composition of the sample is a key factor as it indicates the sources of neutralizing and acid potentials of a sample (Paktunc, 1999). For example, of the many types of neutralizing minerals present, carbonates and exchangeable bases are the only alkaline compounds in sufficient quantity in most coal wastes. Furthermore, the presence of organic sulfur in coal, non-acid generating sulfur-bearing minerals such as gypsum, and the

presence of siderite (iron carbonate) can greatly compromise the reliability of the laboratory determination of ANC (Stewart *et al.*, 2003).

In the standard determination of ANC, it is assumed that all the sulfur in the sample is reactive. This assumption does not take into account the presence of gypsum and other sulfur minerals that are not oxidized in the test. The ABA test has been criticized because of its tendency to overestimate the acid neutralization potential of a sample. This is because of the use of a strong acid, which may dissolve minerals that would not otherwise react to maintain drainage pH which is within an environmentally acceptable range; and the use of boiling acid. Another shortfall concerns the contribution from metal hydroxides that precipitate during the titration with sodium hydroxide resulting in underestimation of the ANC value (EPA, 1994).

Stewart *et al.* (2003) indicated that the ANC test does not provide any indication regarding the reactivity of the acid neutralising material in a given sample, and that the lag time associated with ARD generation is not determined in the NAPP value. In addition, Weber *et al.* (2004a) reported that the ANC of a sample containing significant amounts of siderite (iron carbonate) as conducted in the standard ABA can be overestimated. Siderite does not contribute to the buffering capacity of a sample, because the alkalinity produced during digestion is neutralized by acidity upon oxidation of Fe^{3+} iron to Fe^{2+} and subsequent hydrolysis.

Skousen *et al.* (1997) pointed out that the hydrogen peroxide (H_2O_2) method more accurately portrays the neutralizing capacity of a sample than the standard Sobek method. The modified H_2O_2 ANC test is a refinement test developed to overcome the effects of siderite on the determination of ANC value. In the H_2O_2 method, a small amount of 30% hydrogen peroxide is added to the filtrate of HCl digested mixture to cause the oxidation of ferrous iron to ferric iron before back-titration. In this case, the mixture has a more accurate neutralizing capacity with no siderite interference. However, the addition of H_2O_2 can cause the dissolution of any reactive sulfide such as framboidal pyrite, thereby generating sulfide acidity, which can result in negative ANC. A better approach involves filtration of the sample before back titration and addition of H_2O_2 reduces the opportunity for dissolution of pyrite (Skousen *et al.*, 1997; Weber *et al.*, 2004b). Stewart *et al.* (2003) also investigated the effects of siderite on the ANC test. They concluded that the standard ANC test is inappropriate for samples with more than 15% w/w siderite, which requires a more complex method with larger amounts of hydrogen peroxide for the complete oxidation of ferrous iron.

2.2.5.2 Net acid generation test

The net acid generation (NAG) is a direct determination of the ability of a sample to produce acid through sulfide oxidation and also provides an indication of the reactivity of the sulfides and the availability of neutralizing materials. The test does not measure the total sulfur or sulfide content, but it is rather based on the reactivity of the sulfides. This test entails the addition of hydrogen peroxide to a sample to encourage rapid oxidation of sulfide minerals, in particular pyrite. The resulting acid is neutralized by carbonates present in the sample and the net acidity remaining after reaction is determined by titration with sodium hydroxide. A benefit of the NAG test compared to the ABA test, described in the previous section, is that it mimics the reaction of MPA and ANC, determining a single value without bias towards acid generation. In addition, sulfur assay is not required (Lawrence *et al.*, 1989; EPA, 1994).

Weber *et al.* (2004b) indicated that the NAG test, performed on samples with high content of framboidal pyrite, requires sequential addition of H_2O_2 in order to achieve the complete oxidation of sulfide minerals present and to avoid catalytic decomposition of peroxide. As a rule, the sequential NAG testing is used to provide the total acid producing potential for samples typically when pyritic sulfur is less than 7% (Stewart *et al.*, 2006). The sequential NAG test is a multi-stage procedure involving a series of single addition tests on the one sample until such time that catalytic decomposition does not occur, or when the pH NAG solution is greater than 4.5 (IWRI and EGi, 2002).

One potential limitation of the NAG test is that it may underestimate acid production by creating the possibility that some acid generating material may be incorrectly classified as non-acid-generating. Furthermore, the prediction of ARD potential for coal rejects and tailings can be unreliable due to high concentrations of organic carbon present, which may interfere with NAG test results (Miller, 2008).

2.2.5.3 Classification of static tests

Lawrence *et al.* (1989) showed that the choice of one particular test procedure alone is not likely to provide a definitive assessment of whether a particular sample is acid-generating. They suggested that a combination of two or more tests will provide a more confident and reliable assessment. To this end, the NAG test is usually used in conjunction with other static methods, such as the NAPP determined by the ABA method. However, classifying samples based on the results of these tests does not exactly predict, but rather gives an indication of acid generation. Figure 2.3 gives an ARD classification plot showing the NAG

test results in conjunction with NAPP values. There are three zones in the plot: potentially acid forming (PAF), non-acid forming (NAF) and uncertain (UC).

According to the plot, a sample is classified PAF when it has a positive NAPP and $\text{NAGpH} \leq 4.5$, and NAF when it has a negative NAPP and $\text{NAGpH} \geq 4.5$. When there is an apparent conflict between NAPP and NAGpH, the samples are classified in the uncertain domain: when NAPP is positive and $\text{NAGpH} \geq 4.5$, or when the NAPP is negative and $\text{NAGpH} < 4.5$ (Miller, 2008).

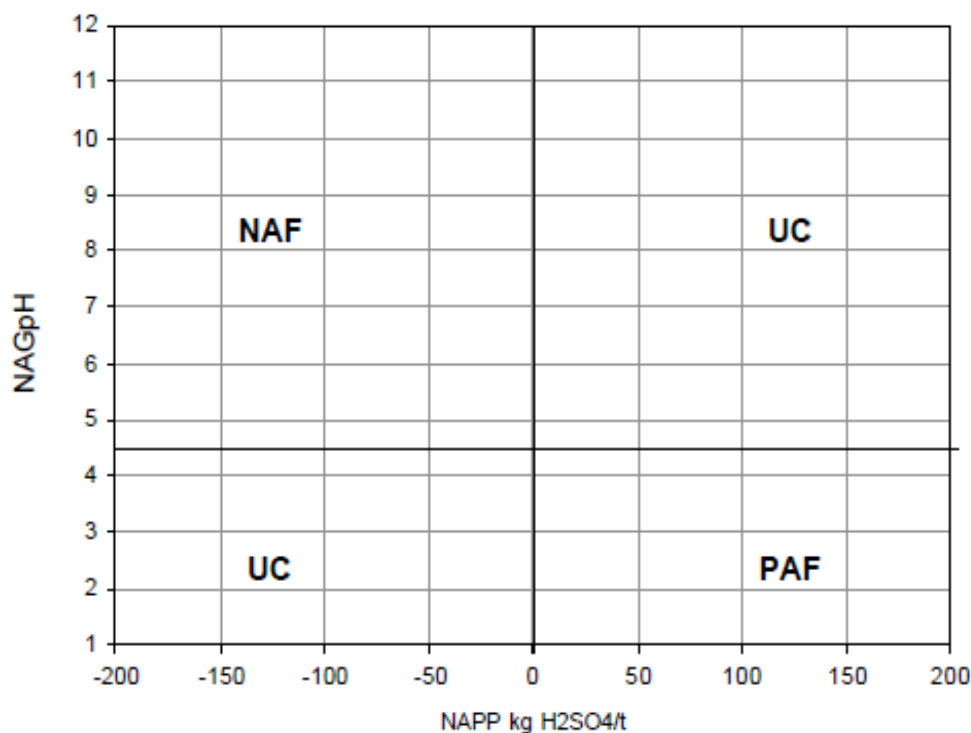


Figure 2.3: ARD classification plot showing NAGpH versus NAPP, with ARD classification domain indicated (Miller, 2008).

2.2.5.4 Biological shake flask tests

Static prediction techniques have limitations; they are qualitative only and cannot be used in the prediction of drainage water quality. They provide some useful information on overall potential independent of time and rate (Broughton & Robertson, 1992). By the way of contrast, kinetic tests attempt to mimic the natural oxidation reactions of the field environment and provide information on the rate of sulfide oxidation and therefore acid generation, as well as an indication of drainage water quality (Sapsford *et al.*, 2009). Kinetic tests can provide prediction information including: the relative rates of acid generation and

neutralization, which determines geochemical conditions; the time to ARD onset; and, finally, the drainage chemistry and the resulting downstream loadings for the predicted geochemical conditions (Price *et al.*, 1997). A thorough discussion on kinetic tests would be beyond the scope of this work, however, a comprehensive review of the use of humidity cell and similar leaching tests for the prediction of ARD is well-documented in Sapsford *et al.* (2003).

Hesketh *et al.* (2010b) indicated that both static and kinetic tests do not account for microbial factors, nor the relative kinetics of acid-generating and acid-consuming reactions across the range of material present, and they do not provide information on the lag associated with ARD onset due to the establishment of populations of ferrous iron- and sulfur-oxidizing bacteria. Although the British Columbia Research Confirmation Test, a type of kinetic test, can assess the ability of sulfur-oxidizing bacteria to oxidize the sulfide minerals, the results may be unrealistic due to initial acidification of the sample (Lawrence *et al.*, 1989).

The biokinetic test, a prediction method under development at the University of Cape Town, provides valuable information on the potential and likelihood of acidification due to microbial colonisation and the relative kinetics of acid-neutralizing and acid-generating reactions. Furthermore, the biokinetic test can enhance the results of the static tests by providing informative data on microbial activity and their role in the kinetics and mechanisms involved in ARD production (Hesketh *et al.*, 2010b). The biokinetic test involves the addition of 7.5 mL inoculums of sulfur- and ferrous iron-bacteria to a flask containing 7.5 g of finely ground sample. The pH and metals in solution are monitored every 2 to 4 days to assess bacterial growth until such time as their values remain constant. The biokinetic test is used to classify mine wastes on the potential to generate acid; and it is especially intended to confirm the results of static tests.

In summary, ARD prediction plays a key role in waste management and ARD control at source. Underestimation of the acid-generation or overestimation of neutralization can lead to incorrect decisions regarding ARD prevention or waste disposal. To this end, results from static tests in combination with biokinetic tests were used in this dissertation to classify the feed and flotation product samples in terms of ARD generation potential.

2.3 COAL MINERALOGY AND PETROGRAPHY

Knowledge of the coal mineralogy and petrography is of great practical importance in the cleaning and utilization of coal as well as in the prevention of long-term impacts. In addition,

the interpretation of acid prediction tests described above requires consideration of the mineral composition of the sample. In this section the petrographic and mineralogical nature of coal is discussed and attention is drawn to the characteristics of South African coals with regards to their beneficiation.

2.3.1 Coal Rank

The extent of alteration or the degree of coalification of the original plant material, from which the varieties of coal were derived, determines the coal composition and properties. The coal rank indicates the stage of transformation reached by a particular coal. The original material decayed to form peat, which then passed through one or more degrees of alteration to give one of the varieties of coal, i.e. lignite, sub-bituminous coal, bituminous coal, semi-anthracite and anthracite. Semi-anthracites and anthracites are termed high-rank coals due to their high level of alteration. Medium-rank refers to bituminous coal, while lignite and sub-bituminous are termed low-rank coals. The high- and medium-rank of coals are often referred to as hard or black coal and the low-rank as brown coal (Laskowski, 2001).

2.3.2 Coal composition

2.3.2.1 Organic components of coal

Coals are heterogeneous, complex and non-crystalline macromolecules consisting of two classes of material: organic components or macerals, and mineral matter. The nature of coal such as rank and type, and its value in various utilizations, are fundamentally defined by the organic particles (Ward, 2002; Demirbas, 2002). The organic components of coals are classified into different types with distinct chemical and physical properties due to differences in the original plant materials and the extent of metamorphism (Honaker *et al.*, 1996). Coal is often highly variable even when it originates from the same source (Naik *et al.*, 2005). The macerals are classified into three groups on the basis of their physical and chemical properties, as follows:

- (i) *Vitrinite* – derived from plant cell substances and comprising the most abundant macerals in coal. The measurement of vitrinite reflection is commonly used in the determination of coal rank. These macerals vary in appearance from being completely without structure to exhibiting well-discernible tissues. As the rank increases, the reflectance of vitrinite group macerals increases. Vitrinite is the major

maceral group in humic coal and contributes significantly to its behavior in industrial processes such as flotation (Jiménez *et al.*, 1998).

- (ii) *Exinite* – derived from secretions and waxy coatings of plants, and lower in reflectance than *vitrinite*. These macerals have low reflectance (dark in reflected light), a high relief, and high volatile matter content. They are relatively sparse in humic bituminous coals (Falcon, 1978)
- (iii) *Inertinite* – with or without recognizable plant structures, and lower in reflectance than *vitrinite*. The cell structure of wood is often seen and it becomes harder as the reflectance increases. Inertinite has a high carbon and lower volatile matter content than *vitrinite*, but it is richer in oxygen than *vitrinite* or *exinite*. As a result, it has low floatability (Falcon, 1978).

The bands of macerals, which can be distinguished by the naked eye, are called lithotypes; they are known as vitrain, durain, clarain and fusain (Laskowski, 2001).

2.3.2.2 Mineral components of coal

Mineral matter refers to the different inorganic materials found in coal. Coal preparation processes upgrade the raw coal by reducing the proportion of its inorganic impurities considerably. The beneficiation of coal is therefore dependent upon the amount, distribution and association of mineral matter. The most common minerals in coal include quartz, clay minerals (especially kaolinite and illite), feldspars, carbonates such as siderite, calcite and dolomite; and sulfide minerals (Ward, 2002; Pinetown et al, 2007).

Among other mineral matter found in coal seams, sulfur is probably the one constituent of coal with most environmental concern in terms of acid generation. Sulfur in coal can occur as organic sulfur, sulfate sulfur, and sulfides (pyrite and marcasite). Sulfate sulfur is usually only found in minor quantities in fresh coal and other undisturbed pyrite-containing rocks, and is commonly the result of weathering and recent oxidation of sulfide sulfur (Kawatra and Eisele, 2001). Sulfide sulfur represents the dominant form of sulfur in the majority of coal and associated rocks. It is the sulfur form of greater concern in terms of its potential to generate ARD. Of all the sulfide minerals that may be present in coal, pyrite predominates and is the major acid producer.

A study conducted by Kgabi *et al.* (2009) on five coal-producing regions in South Africa revealed that the Fe-bearing compounds found are pyrite, ankerite, illite, and jarosite, with pyrite as the main mineral matter. Pyrite is usually intimately associated with the organic

components of the coal deposit occurring, for example, within individual vitrinite bands (Ward, 2002). Liberated pyrite can be separated from coal by gravity concentration methods owing to its high density of 5 g/cm^3 compared to the density of coal ranging between 1.3 to 1.5 g/cm^3 . However, gravity concentration becomes inefficient for particles finer than $100 \mu\text{m}$; flotation is rather used to desulfurize these particles from coal (Laskowski *et al.*, 2007).

While pyritic sulfur can be separated from coal, organic sulfur is combined with the organic constituents of coal and organically bound within the coal. Organic sulfur is only found in appreciable quantities in coal beds and in other carbonaceous rocks. Generally, the organic sulfur component is not chemically reactive and has little or no effect on acid-generating potential (Skousen *et al.*, 1998).

2.4 COALS IN SOUTH AFRICA

Coal is the main energy source in South Africa and provides about 77% of the country's total energy needs. South Africa is ranked sixth in the world in economically recoverable coal reserves (34,224 Mt in 2005) and fifth globally in annual production (245 Mt in 2005) (Van Niekerk *et al.*, 2008).

2.4.1 Petrographic characteristics of South African coal

The coal in South Africa is low-rank, low-grade, low in calorific value, inertinite-rich and possesses high mineral matter content. Only a small proportion of the reserves may be classified as top-grade metallurgical coking coal and anthracite (Falcon, 1977). In general, the rank of coal found in South Africa increases from West to East. The coal of the Free State and the Karoo Basin is low rank. The coals in certain parts of Kwazulu Natal (now mostly mined out) were very high rank coals, while the Mpumalanga and Northern Province coals are higher rank.

As can be seen from Table 2.2, the Gondwana coals of the Southern Hemisphere and India are quantitatively and qualitatively different from those of the Carboniferous and Tertiary in the Northern Hemisphere, as a result of differences in the vegetation and the climate between the two hemispheres. Furthermore, South African coals tend to be chemically rather than physically changed, because of their shallow burial depth (and hence a lack of pressure effect) as well as temperature effects caused by widespread igneous intrusions (Fickling, 1985).

Table 2.2: Average macerals proportions of three principal coal source regions (after Falcon, 1977)

Macerals	Reactivity	Location		
		Carboniferous coals, Germany	Permian, South Africa	Permian Tertiary, America
Vitrinite	Reactive	70	40	82
Exinite	Reactive	15	0	40
Inertinite	Non to partially reactive	15	60	10
Minerals	Non-reactive	3	14	2

In South Africa, as in other Gondwana countries, analysis of coals in terms of macerals, structure, and behavior shows that the coals contain mainly inertinite which, except for semi-fusinite and macrinite, is unreactive; while the Northern Hemisphere, or Laurasian, coals are rich in vitrinite, which are known to be highly reactive (Sanders and Brookes, 1986).

One of the most considerable differences between the Northern Hemisphere Carboniferous and Southern Hemisphere Gondwana coals is in the mineral matter content. More than 75% of South Africa's coals have ash content higher than 21.5 percent (Falcon, 1977). The most abundant minerals in South African coals are clay minerals (primarily kaolinite and illite), together with carbonates (calcite, dolomite, ankerite and siderite), sulfides, quartz and glauconite. Pyrite is the most abundant sulfide mineral, although marcasite is present. Hematite is the principal iron oxide present. Phosphate minerals such as apatite may be present as submicroscopic grains and occur occasionally along with other heavy minerals such as tourmaline, rutile and zircon (Geldenhuis and Bell, 1998).

2.4.2 South Africa coal reserves

The main coal deposits of South Africa are in the Karoo Basin (Pinetown *et al.*, 2007). South Africa has approximately 75 % of Africa's coal reserves, contained in nineteen coalfields, located mainly in KwaZulu-Natal, Mpumalanga, Limpopo, and Free State, with lesser amounts in Gauteng, the North-West Province and the Eastern Cape. Over 95% of South African coal reserves are bituminous with about 2% being anthracite (Kershaw and Taylor, 1992). Based on recent data, the total remaining recoverable reserves of coal in South Africa are estimated at 51 billion tons (Jeffrey, 2005). This suggests that more coal ultrafines will be

generated in the process of beneficiating the huge coal reserve, with a possibility of harming the environment if there is no efficient method to reduce associated ARD risks to an acceptable level.

2.4.3 Coal preparation in South Africa

As South African coals often have high mineral matter contents, coal preparation or washing plays a significant role in the removal of inert mineral matter from these coals. In general, reduction of mineral matter is needed for coking coal and for many export steaming coals in South Africa (Kershaw and Taylor, 1992). Coal preparation normally relies on gravity separation, owing to the large density differences between organic coal substances and associated mineral matter. The distribution of the latter within the coal determines the effectiveness of coal washing. The difficulty of beneficiation for many Gondwana coals is due to the large quantity of mineral matter, which is finely disseminated, and to high inertinite content. Inertinite macerals tend to have a higher density than vitrinite. The ash content of the discard is relatively low for much of the Gondwana coal, resulting in significantly higher coal losses (Sanders and Brookes, 1986; 1987).

The beneficiation methods depend largely on the particle size of the coal to be washed. In South African coal washing plants, jig washers or dense medium baths are used to clean coarse coal (+6.3 mm). These operate on differences in relative density between the coal and the mineral matter. Small coal (-6.3 + 0.5 mm) is cleaned in dense medium cyclones, which use a suspension of very fine magnetite in water to achieve a medium of the required density for separation. Fine coal (<0.5 mm) is usually screened out of the small coal dense medium cyclone feed, because it cannot be recovered with the use of magnetite. In some plants, it is washed in spiral concentrators or by froth flotation, but in many others it is either discarded or dewatered and added unbeneficiated to a beneficiated product. Separation methods based on relative density cannot be used to treat the ultrafine coal (<0.15 mm). Instead, processes based on differences in surface properties such as flotation or oil agglomeration, are used. Franzidis (1992) reported that only 12% of South African plants treated the coal ultrafines by means of flotation, while all other washing plants disposed of the ultrafines.

The most intensively beneficiated coals in South Africa were the Natal high-rank coals, which have been mined out. Coking, steaming and anthracite coals were mined in Natal and most of these were washed. Generally, Kwazulu Natal coals were relatively easy to clean with jigs, dense-medium separation and froth flotation being used. The Free State coals

cannot be beneficiated to high grade product and are the least beneficiated South African coals, because of their low-rank and high mineral matter content. Coals from the important Highveld (Transvaal) coalfield are mainly used unbeneficiated for power generation and for export. Coals from the Northern Province coalfields, for example Waterberg, require extensive washing including froth flotation of the fines, especially if these are used to produce coking coals (Kershaw and Taylor, 1992).

2.5 COAL FLOTATION AND FACTORS AFFECTING COAL FLOATABILITY

2.5.1 Overview of froth flotation

Froth flotation is a separation process based on the differences in surface properties of particles in various fine-sized minerals (Wills, 1997). Froth flotation depends heavily on the treatment of the minerals with reagents to cause the preferential attachment of hydrophobic particles to air bubbles, which aggregate and then rise through the pulp to the surface. In the froth flotation process, the material is ground to liberate particles of the materials to be separated. Generally, flotation involves addition of reagents such as collector and frother, which are mixed with the slurry while aerated and stirred at the same time. Collector reagent is selectively adsorbed on the surface of the hydrophobic minerals which then become attached to the ascending air bubbles where they are collected on the surface in the form of froth.

The selectivity of the separation is dependent upon differences in particle surface properties. The water-loving (hydrophilic) minerals are wetted by the aqueous phase and do not attach to air bubbles, remaining in suspension in the body of the pulp to be carried off as underflow (Miller and Deurbrouck, 1982). Many coals can be easily floated with only a frother and fuel oil, owing to their natural hydrophobicity. In coal flotation, the organic matter is usually transferred to the float fraction, leaving the ash-forming minerals in the pulp or tailing. This is referred to as a direct flotation as opposed to reverse flotation, in which the mineral matter is separated into the froth (Stonestreet and Franzidis, 1988, 1992, Stonestreet, 1991; Pawlik and Laskowski, 2003).

The essential difference that exists between coal and ore flotation is that only the fine fraction of coal, not suitable for gravity concentration, is treated by flotation. In the flotation of ore, the entire tonnage is ground to fine size, both to liberate it and to make it fine enough for

flotation (Aplan, 1976). In other words, flotation in coal beneficiation plays a supplementary role to specific gravity separation processes for coarse coal and middlings.

2.5.2 Factors affecting coal floatability

The coal flotation process is a complicated system involving several phases influenced by many factors including the nature of the coal and the associated pyrite, the particle size, the kind and the amount of reagents, the collection time, and the hydrodynamic variables (Hirt and Aplan, 1981). A detailed review of the various phases in the coal flotation pulp, their interactions with each other and how these interactions affect the flotation process is well-documented in Polat *et al.* (2003). A description of all the factors affecting the flotation of coal is beyond the scope of this work. However, some of the factors such as rank, type of coal and the effect of reagent addition are presented below for discussion purposes.

2.5.2.1 Effect of coal rank

As stated previously in Section 2.3.1, rank refers to the level of coalification. The behavior of coal in a flotation process is largely dependent on the rank of coal, which may characterize the inherent floatability. Gutierrez-Rodriguez *et al.* (1984), using contact angle measurements, indicated that the degree of hydrophobicity of various coals decreased with decreasing rank, fixed carbon and total carbon content, and with increasing oxygen and hydroxyl content. As an illustration, the bituminous coals used to produce coke present easy floatability and high hydrophobicity, while the low-rank sub-bituminous coals, containing greater amounts of oxygen, float poorly. For higher-rank coals, the reagent consumption in flotation is low because of the natural hydrophobicity of the coal. However, for low-rank coals containing greater amounts of oxygen, oily collectors will not spread on the surface of the coal particles, which leads to poor performance and large reagent dosage requirements (Laskowski, 2001).

2.5.2.2 Effect of petrographic composition

As mentioned previously in Section 2.3.2.1, macerals are grouped as vitrinite, exinite and inertinite and they behave differently in flotation as a result of their different surface properties. Studies on petrographic composition in relation to flotation properties have indicated that vitrinite and exinite groups of macerals have better response than the inertinite group (Hower *et al.*, 2000; Jena *et al.*, 2008). These studies are in agreement with the findings of Arnold and Aplan (1988), who investigated the behavior of coal macerals using

the contact angle to quantitatively determine their hydrophobicity. They found that the order of decreasing floatability was as follows: liptinite>vitrinite>inertinite. In fact, inertinite-rich coals are readily oxidized upon exposure to weathering conditions, thus resulting in poor floatability due to the presence of oxygen functional groups, most commonly, carboxyl, phenolic and carbonyl functionalities on the surface of coal particles.

2.5.2.3 Coal flotation reagents

In the operation of coal flotation plants, the acquired floatability resulting from the use of flotation reagents is as important as the natural floatability or hydrophobicity. The most used reagents in coal flotation are listed in Table 2.3. In general, the reagents used in coal flotation may include collector, frother, depressant and promoters depending on the rank and degree of oxidation of the coal.

Table 2.3: Coal flotation reagents (Laskowski, 2001)

Type	Flotation reagents	Functional group	Examples	Action
Nonpolar (water insoluble)	Collectors	-	Kerosene; fuel oil	Through selective wetting and adhesion of oil drops to coal particles
Surface active (water soluble)	Frothers	Hydroxyl; nitrogenous	Aliphatic alcohols; pyridine containing tar oils	Frothers with some collecting abilities. Also improve emulsification of oily collectors
Emulsifiers (Soluble in oily collector)	Promoters	Hydroxyl; carboxyl; nitrogenous	Polyethoxylated alcohols, fatty acids	Facilitate collector emulsification and its spreading over coal surface
Inorganic (water soluble salts)	Modifiers	-	NaCl, CaCl ₂ ; Na ₂ SO ₄ ; H ₂ SO ₄ ; CaO; Ca(OH) ₂	Promoters; pH regulators; sulfide depressants
Protective colloids	Depressants	Hydroxyl; carboxyl	Polymers; starch, dextrin, carboxymethyl cellulose	Modifiers; coal depressants

The collector is used to render the coal surface more hydrophobic. The high-rank coals, unless oxidized, are highly hydrophobic and are normally floatable without a collector and pulp conditioning (Miller and Deurbrouck, 1982). In practical flotation tests, a small amount of fuel oil such as kerosene or fuel is added with a frother to increase the rate of coal flotation, to serve as a frother extender, to float coarse particles or to float less hydrophobic macerals. Furthermore, oily collectors may be used to float slightly locked particles to achieve a high recovery or yield of coal (Aplan and Arnold, 1991). The amount of oil required for a given coal depends on the coal rank and will increase as the rank decreases. However, Gupta *et al.* (2009) indicated that the flotation performance of fine coal declines on increasing collector dosage from low level to high level. This is due to the coverage of mineral particle surfaces by collector at higher dosage.

Many collectors besides fuel oil and kerosene can be used in coal flotation. Jia *et al.* (2000) reported that the addition of oxygenated functional groups to the collector molecule markedly enhances the flotation of lower rank and oxidized coals. To the lists of coal collectors should be added non-ionic collectors such as fatty acids (Denby *et al.*, 2002). Sis *et al.* (2003) found in laboratory investigations that ionic collectors reduced the ash content significantly better than the non-ionic collectors, but their yields were significantly lower.

Other type of reagents, such as frothers, are used to facilitate air dispersion into fine bubbles, and to stabilize the froth. The effect of frothers on bubble size is a result of their ability to reduce bubble coalescence. The most commonly used frothers are the short chain alcohols such as MIBC (methyl isobutyl carbinol). Since MIBC has no collecting properties for coal and is not adsorbed on the coal surface, the quantity required for an easily floatable coal would be somewhat lower, compared to other types of frothers with collecting properties such as pine oil (Aplan, 1976). Gupta *et al.* (2007) studied the effect of frothers on foam stability, bubble size and coal flotation. They pointed out that MIBC (least surface active) is the most effective frother in terms of bubble size reduction and is very selective and appropriate for the flotation of ultrafines.

Other possibilities for coal flotation would be the flotation of the sulfides and associate gangue minerals by using depressants (Stonestreet and Franzidis, 1988). A depressant inhibits flotation of a given mineral; its function is opposite to that of a collector. Any reagents which will oxidize the surface of coal, thus destroying its natural hydrophobicity, may be considered as a potential coal depressant. Usually coal is depressed in the pulp in reverse flotation, during which the mineral matter associated with coal are recovered in the froth. For this purpose, a large number of reagents may be used to depress coal including starches, in

particular dextrin, and the natural and synthetic polymers such as polysaccharides as well as oxidizing and reducing agents. Inorganic salts such as stannous, hypophosphorous acid and potassium permanganate can also depress coal. In some instance, the pH of the pulp may also be considered as a coal depressant, since recovery decreases at low and high pH values (Aplan, 1976).

Mineral matter that gives cause environmental concern, such as pyrite, can be depressed during coal flotation. In pyrite depression the use of lime, sodium cyanide and the oxidation products of pyrite, ferrous and ferric sulfate, have been shown to be effective (Laskowski, 2001). Perry and Aplan (1985) have been shown that polysaccharides and xanthated polysaccharides are good pyrite depressants during coal flotation. However, care needs to be taken when using these depressants because most pyrite depressants are also coal depressants at a similar, though usually higher, concentration. For example, many common starches are pyrite depressants at ≈ 0.1 kg/t, but at 0.3-1.0 kg/t they are coal depressants (Purcell and Aplan, 1991). Another approach in depressing pyrite during coal flotation involves pyrite surface alteration followed by the use of a specific depressant for this new surface (Gasiorek, 1997; Kang *et al.*, 2007).

The ash-forming minerals also influence the wetting properties of coal; the greater the ash content, the less hydrophobic the coal sample is due to the fact that silicates and other ash-forming minerals are readily wetted by water and cause slime coatings on coal particles leading to less recovery (Jena *et al.*, 2008). Consequently, a large amount of reagents are required to float high-ash coal.

2.5.3 Flotation of low rank and oxidized coals

Most coals, in particular low rank, are susceptible to oxidation by weathering, which begins as soon as the coal is mined and proceeds during transportation and storage. Weathering of coal is a naturally occurring process resulting from the oxidation of coal in the presence of moisture and oxygen. Oxidation involves a physico-chemical adsorption of oxygen on the surface of coal, and as a result increases the number of oxygen functional groups on the coal particle's surface. These oxygen groups such as carboxyl, phenolic, carbonyl, and hydroxyl groups increase the number of hydrophilic sites on the coal surface, resulting in reduced wettability and hence floatability (Jia *et al.*, 2000; Somasundaran *et al.*, 2000; Polat *et al.*, 2003). The effects of surface functional groups on coal flotation behavior have been well-reviewed (Fuersternau *et al.*, 1983). These functional groups were found to control both

coal wettability through the balance of hydrophobic/hydrophilic sites and flotation kinetics by their influence on surface charge.

In general, low rank coals are readily oxidized and lose much of their floatability (Jena *et al.*, 2008). The effect of oxidation on coal surface can be very considerable. Sarikaya (1995) reported that the flotation recovery of coal decreased from 95% to 24% upon oxidation for bituminous coal, using alcohol type frother only. Tao *et al.* (2002) conducted a flotation study of refuse coal slurry, which underwent heavy oxidation in a tailing pond for more than 30 years. They pointed out that a poor recovery was obtained even in the presence of high dosage of conventional reagents such as #2 fuel oil and MIBC, due to the weak affinity of heavily oxidized coal surfaces to air bubbles.

A number of investigators have attempted to improve the performance of desulfurization for difficult-to-float and oxidized coals. For example, the floatability of oxidized coal can be enhanced by pre-treating with an aliphatic alcohol such as butanol prior to flotation (Demirbas, 2002). Jena *et al.* (2008) studied the flotation characteristics of oxidized high ash sub-bituminous coal using a non-conventional reagent known as black oil to enhance the floatability. The floatability of these oxidized coals was improved by modifying the surface characteristics and/or enhancing particle-reagent interactions. The addition of oxygenated functional groups to form coal collector molecules, such as tetrahydrofurfuryl ester surfactants, was found to be more effective in the flotation of oxidized coal than using conventional collectors such as dodecane (Jia *et al.*, 2000, 2002).

The use of pitch additive in dry grinding is another approach that may improve the flotation recovery of a difficult-to-float coal in the presence of a typical collector such as kerosene, while maintaining satisfactory reduction in mineral matter (Kang *et al.*, 2007). Ateşok and Çelik (2000) studied the flotation of oxidized coal with a collector molecule to which oxygenated polar groups were added to provide a means for it to hydrogen bond with the oxygenated surface sites on the coal. They concluded that when the coal surface is heavily oxidized, or for a low-rank coal, an oxygenated functional group on the collector chain will greatly enhance the coal recovery.

Zhao *et al.* (2008) and Çınar (2009) investigated the flotation behavior and hydrophobicity of low-rank coal by low-temperature heat pre-treatment. The heat treatment increased the floatability of low-rank coal owing to the decrease in oxygen-containing groups in coal. The treatment of coal at low temperature (105°C) for 4h improved the coal floatability even without using any collector in both column and mechanical cell flotation.

2.5.4 Desulfurizing flotation

As discussed previously, removal of sulfur from coal ultrafines prior to disposal is essential for reducing associated environmental impacts. Despite the fact that coal flotation is effective in removing ash-forming minerals from coal, it does not normally remove all sulfur-bearing minerals associated with coal in conventional practice. Of the three forms of sulfur in coal (organic sulfur, sulfate sulfur and pyrite), only pyritic sulfur can be substantially removed by physical methods based on gravity separation. The efficiency of these methods falls rapidly when the particle size becomes smaller than 150 μm . Consequently, separation processes such as froth flotation, which utilise the surface properties of coal, are used.

Desulfurization of coal by chemical and microbial coal cleaning processes has been shown to remove both pyrite and organic sulfur, but the operating cost is much higher compared to the physical techniques. The most suitable method for removal of pyritic sulfur from coal is froth flotation (Sis *et al.*, 2003). Since pyrite may be finely disseminated in coal, there is a need for the feed material to be ground to a size at which mineral matter is sufficiently liberated from the coal. There are three methods by which pyritic sulfur can be rejected during coal flotation. The first method consists of flotation circuitry (including froth sprinkling). In this case, the coal froth concentrate is sprayed with water to wash free, or dislodge from the froth, the less hydrophobic coal-pyrite particles and clay slimes which have been entrained (Miller and Deurbrouck, 1982). In the second method, the desulfurization of coal by flotation can take place by depressing pyrite with the concomitant flotation of coal. Pyrite depression involves changing the surface properties of pyrite particles to make them more water-loving (hydrophilic) and hence less floatable. Although the flotation of pyrite in ore processing can be effectively depressed by a wide range of depressants such as alkaline solutions, these pyrite depressants are not very effective in coal flotation. This is due to the fact that coal-source pyrite behavior is known to be different to ore-source pyrite, and its depression is much more difficult in coal flotation than in ore flotation (Perry and Aplan, 1985). Lastly, separation of coal from its refuse may be achieved by depressing coal and floating pyrite in a reverse flotation (Purcell and Aplan, 1991; Demirbas, 2002).

A study conducted by Hirt and Aplan (1991) indicated that the rejection of pyrite is best facilitated by the use of starvation quantities of a non-oily frother-collector system, a short flotation time, a low aeration rate and a low impeller speed. Regardless of the optimisation of these process variables, a small portion of the pyrite in fine-size coal can still report to the coal product. Miller (1975) indicated that the difficulty in rejecting pyrite during coal flotation is due to the fact that either the pyrite is floating as a result of being locked in floatable coal,

or being entrained (fine liberated pyrite). More recently Kawatra and Eisele (1997) conducted a study to demonstrate the mechanisms by which pyrite particles were reaching the froth phase during coal flotation. They pointed out that pyrite can become naturally hydrophobic at neutral pH owing to the formation of hydrophobic elemental sulfur as a result of pyrite oxidation.

In an attempt to remove as much finely disseminated or locked pyrite in the froth as possible, Miller (1975) proposed a stage-wise flotation process. In the first stage, most of the coal is collected in the froth, whereas some of the coarse pyrite, and most of the ash-minerals are rejected. MIBC was selected as frother, because it provides a stable froth without exhibiting strong collecting properties. The remaining pyritic materials are then floated from the first-stage clean coal product in the presence of a sulfide collector, a frother and coal depressant such as dextrin. The two-stage method is suitable for coal containing finely disseminated or unliberated pyrite that cannot be removed by conventional flotation. It was found that under these conditions up to 80% of pyritic sulfur was removed from some coals in pilot plant operations using 0.25 to 0.5 kg/t of amyl xanthate.

It has been established that coal-source pyrite is much less floatable with the conventional sulfide collector, xanthate, than ore pyrite. For example, the amount of PAX consumed in a reverse flotation was greater in coal-pyrite flotation, than in ore-pyrite flotation. The high consumption of PAX has been attributed to surface heterogeneities, such as clay inclusions in the marcasite component causing the coal-pyrite particles to be hydrophilic. It was found that coal-pyrite flotation was best performed near neutral pH, with performance dropping off at both high and low pH values (Miller and Deurbrouck, 1982).

Various other methods have been investigated to improve the desulfurization of fine coal. For example, flotation of ultrafines that have been pre-treated in an ultrasonic-conditioning device showed increased yield of coal as well as selectivity compared to untreated samples (Kang *et al.*, 2007; Amini *et al.* 2009). Furthermore, coal desulfurization by means of flotation can be enhanced by bioadsorption of oxidizing bacteria such as *Acidithiobacillus ferrooxidans*, to modify the superficial properties of pyrite particles from hydrophobic to hydrophilic. The study by Zhu *et al.* (2002), comprising adaptation of active thiophilic bacteria to coal pyrite by exposing the bacteria to pyrite under conditions favourable for bacteria activity and growth, showed that the micro-organisms were able to decrease the hydrophobicity of pyrite. Gasiorek (1997) investigated the desulfurization of coal by conventional flotation and bioflotation. They reported that bacteria were more successful in changing the characteristics of the pyrite surface, rendering it hydrophilic, thus decreasing

the recovery of sulfur in the biological process significantly. A more recent study (Amini *et al.*, 2009) indicated that the recovery of sulfur decreased by about 14% in the biological process compared to conventional flotation.

Conditioning of oxidized coal by electrolytic reduction has been also shown to improve the floatability of coal. Jia *et al.* (2000) investigated the effect of electrolytic reduction on the desulfurizing flotation of coal. The results showed a reduction in the number of oxygen-functional groups on the coal surface and an improvement on the hydrophobicity of coal, and reduction of the initial oxidation products on the pyrite surface. Zhu and Zhu (2003) studied the desulfurization of coal by electrochemical reduction flotation in an aqueous NaCl solution by combining the effect of electrochemical desulfurization and electrolytic reduction. They reported that electrochemical reduction enhanced the removal of pyrite from coal due to conversion of hydrophobic pyrite coal to hydrophilic through an increase in the concentration of hydroxyl groups and aliphatic moieties and a corresponding decrease in carboxyl groups.

To date no in-depth research on the desulfurization of coal ultrafines by froth flotation appears to have been done in South Africa. In an attempt to fill the gap, some preliminary studies on desulfurization of ultrafines were undertaken as an undergraduate project in the Department of Chemical Engineering at the University of Cape Town (Nchabeleng and Shabalala, 2009) with limited scope and resources. The removal of the sulfur containing components by flotation was investigated. Laboratory-scale flotation tests were carried out to investigate the effects of frother addition and collection period on froth stability and sulfur recoveries. The results indicated that no significant removal of total sulfur took place through reverse flotation. Nevertheless, both the visual observations and net acid generation (NAG) prediction test results indicated appreciable separation of sulfide sulfur (pyrite) from other (organic) sulfur forms, with the majority of the acid-forming pyrite reporting to the concentrate fraction during flotation. ARD assessment tests indicated that the small volume sulfide-rich concentrate was highly acid-generating with NAGpH of 2.7 from the feed NAGpH of 5.2. Furthermore, a slight increase in the NAGpH of the flotation tailings was observed (to 6.5), as a result of floating the sulfide sulfur.

This preliminary study did not provide sufficient justification for development of the desulfurization approach by flotation, due to the fact that the feed coal used in this investigation did not exhibit acid-generating characteristics. However, the overall results of this earlier work provided a basis for a more fundamental investigation into the technical feasibility of coal desulfurization to minimize the risks of ARD generation over the long-term, through the production of a coal tailings waste which is depleted in sulfide-bearing minerals.

2.6 CHAPTER SUMMARY

The preceding sections have reviewed the major literature findings pertinent to this present research. The review has highlighted the fundamentals of ARD generation with regards to its formation, prevention and the methods used for its prediction. Because ARD occurrence is an environmental liability faced by mining companies all over the world, new approaches need to be developed to reduce the pollution of the receiving environment to an acceptable level. Current practices of controlling the generation of ARD are in some cases not successful. There is therefore a need for more effective preventive methods. Consideration of these emerging methods may reduce the long-term impact associated with sulfide-containing wastes in the coal mining and processing sectors.

To have a better understanding of the material under investigation, the composition and characteristics of coal have been discussed briefly, with an emphasis on the behavior of coal in South Africa in relation to its floatability. Coal is currently one of the most important commodities in South Africa, and with an ever-increasing world demand for coal, unbeneficiated coal ultrafines can become important targets for more revenues in coal mining. Regardless of the low-rank and the readily oxidized nature of most South African coal, many studies undertaken in South Africa reveal that froth flotation, during which the coal is usually transferred to the froth leaving the ash-forming minerals in the pulp or tailing, is a viable method for the beneficiation of coal ultrafines.

Because of the increased need to meet the demand of coal for energy in South Africa, the amount of ultrafines generated is expected to increase in the foreseeable future. For this reason, efficient approaches are required to ensure the optimal use of valuable coal resources that are currently discarded, while reducing the environmental footprint of coal mines as far as ARD is concerned.

The review has also comprehensively discussed the approaches available for the desulfurization by flotation of low-rank and difficult-to-float coals, such as those that are present in South Africa. As already discussed, coal is floatable due to its natural hydrophobicity; however many factors such as surface oxidation, particle size, and coal rank may reduce the performance of coal flotation and increase the pyrite recovery in the froth. Both pyrite and coal exhibit some degree of hydrophobicity. Although pyrite depressants have been used successfully in ore flotation, they seem to be inadequate and ineffective in the direct flotation of coal. This has been attributed to a lack of pyrite liberation and the difficulty of pyrite depression in direct flotation. The efficiency of coal pyrite separation can

be improved by floating pyrite and depressing coal in the pulp. In reverse flotation, the clean coal is recovered in the tailings as product, while the minerals present in coal are floated.

The findings of this literature review, in particular the preliminary work on the desulfurization flotation of South African ultrafine colliery wastes, provide the basis for investigating a new two-stage flotation approach, in which coal is floated in the first stage by taking advantage of its natural hydrophobicity; while hydrophilic gangue material reports to the tailings. The second stage entails the selective removal of sulfides remaining in the first stage tailing. A small amount of acid-generating material is removed to leave behind a benign tailings as the majority fraction with reduced ARD risk on a long term basis.

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CHAPTER 3

EXPERIMENTAL WORK PROTOCOL

3.1 INTRODUCTION

As stated previously in Section 1.2.4, the main objective of this research was to investigate the mitigation of acid rock drainage by means of flotation and, simultaneously, recover valuable coal products. The experimental work involved carrying out a series of flotation tests to investigate to some extent the recovery of valuable coal from ultrafine wastes, and the separate, selective removal of acid generating materials from these tailings; and determining the ARD generation potential of all the product streams to evaluate the effectiveness of the process.

This present chapter gives a description of the experimental work including the coal sample characterization, the flotation procedures and the ARD prediction tests. Flotation experiments included both coal and sulfide flotation tests; while the acid prediction tests included the acid base accounting (ABA), net acid generation (NAG) and the newly developed biokinetic tests.

3.2 COAL SAMPLE CHARACTERIZATION

The characterization of the coal sample under investigation included particle size and ash-by-size determination of the as-received and rod-milled coal waste sample, flotation release analysis, petrographic analysis, sulfur speciation analysis, ultimate and proximate analyses as well as X-ray diffraction (XRD) analysis.

3.2.1 Coal used in this investigation

The experimental work was carried out using an inertinite-rich, medium rank bituminous waste coal. A 50 kg sample of dried thickener underflow (roughly 98.4% passing 850 μm) was received from a processing coal plant in the Middleburg area, South Africa. The thickener underflow coal was selected on the basis that it constitutes the stream that is non-

beneficiated in most South African coal washing plants and is a potential source of environmental pollution as far as ARD generation is concerned. Since this work was driven by environmental considerations and the mitigation of ARD was the primary focus, the coal sample was selected based on its acid generating capacity due to the presence of sulfide minerals.

The ultrafine coal slimes sample received was thoroughly mixed using a riffle, a manually operated device that divides a sample into halves. The whole sample was passed through the riffle three times, recombining the halves each time. The sample division was accomplished using the riffle and power-driven rotary sample dividers or splitters. A large number of sub-samples of approximately 1 kg each were split by the rotary splitter for milling in the rod mill to produce material suitable for both characterization and flotation tests. Immediately prior to flotation, each 1 kg sub-sample was milled in a stainless steel mill (257 mm internal diameter, 293 mm length) with ten 25 mm (diameter) by 288 mm (length) stainless steel rods. The mill was operated at 80 rpm for 20 minutes to reach approximately 75% passing 150 μm .

The rod-milled samples were weighed to provide the required mass for preliminary characterization work or flotation experiments. For example, for a pulp density of 6.67%, 0.2 kg was used, and for 10%, 0.3 kg was used. The weighed milled samples were sealed in plastic bags.

All of the research work described in this dissertation was conducted on this thickener underflow coal. The aim was to establish the procedure and determine the recovery of valuable coal for one coal; the same procedures could then be extended (by future researchers) to other coal ultrafines from different South African coalfields.

3.2.2 Particle size analysis

The particle size analysis was carried out at the Mineral Processing Laboratory in the Chemical Engineering Department at the University of Cape Town. The primary aim of the particle size analysis was to obtain quantitative data about the size distribution of particles in the coal sample as-received and after rod-milling. The dry test sieving method was used for this purpose based on the method described in ISO 153:1993 (SANS 1953:1993). The screen sizes used were 850, 600, 425, 300, 212, 150, 106, 75, and 53 μm . The 9 sieves were arranged in a stack with the coarsest sieve on the top and the finest on the bottom. The ratio of aperture widths of adjacent sieves was based on the square root of 2. A tight-fitting

pan was placed below the bottom sieve to receive the final undersize; a lid was placed on top of the coarser sieve to prevent escape of sample. 120 g of coal sample was placed in the uppermost sieve, and the stack was then placed in an automatic shaker which vibrated in a vertical plane. After 20 min, the stack was taken apart and the amount of coal material retained on each sieve weighed. The results were expressed in terms of the percentage mass of coal remaining on sieves of different aperture sizes. Ash analysis was also performed on each size fraction.

3.2.3 Flotation release analysis

In an attempt to determine the maximum possible performance that could be achieved through the direct flotation of the rod-milled coal, a flotation release analysis was performed on a subsample of the coal. Reagents used were dodecane as collector, and MIBC as frother (see Section 3.3.2.1 below). The first rougher flotation step of the release analysis procedure involved the separation of combustibles from non-combustibles. The combustible-rich rougher concentration was then progressively cleaned; a minimum of 12 cleaner floats was performed, progressively re-floating coal froth products to collect only coal particles that were fully hydrophobic. Concentrates were re-floated each time and the tailings were kept for analysis, until the final product consisted of only the strongly floatable material.

The flotation procedure used in the release analysis test was the same as the flotation methodology described below in section 3.3.2.2, except that incremental starvation amounts of reagents were added to the cell to collect all floatable coal. Once the initial concentrate had been recovered, a cleaner flotation step was conducted without changing the operating conditions. The tails were removed each time and the concentrate reintroduced into the cell. This process was continued until such a time that as much of possible of the hydrophobic coal had been recovered, i.e. 12 cleaner floats. The final cleaner concentrate, 12 cleaner tails and the rougher tailings were filtered, dried and weighed in order to determine the yield over the duration of the float. Ash analyses were conducted on these samples so as to determine the cumulative concentrate ash contents and calculate the coal recoveries.

3.2.4 Ultimate analysis

A subsample of rod-milled coal was sent to ALS Laboratory group to perform ultimate analysis, which was conducted according to ASTM D 5373. The ultimate analysis included carbon, hydrogen, nitrogen and oxygen. Total sulfur analysis, using thermal decomposition

combustion infrared spectrophotometry, was carried out both at ALS Laboratory according to ASTM D4239:1997 and in the analytical laboratory at the University of Cape Town using a Leco model S 632 sulfur analyzer*.

3.2.5 Proximate analysis

Proximate analysis was carried out on a rod-milled coal sample at the ALS Laboratory in Witbank. In the proximate analysis four constituents, namely moisture, ash, volatile matter and fixed carbon, were determined. The ash and moisture analyses were performed according to ISO 1171:1997 (SANS 131:1997) and ISO 589:2008 (SANS 589: 2009), respectively. The volatile matter content was determined according to ISO 1171:1997. The amount of fixed carbon was obtained by difference.

3.2.6 Forms of sulfur

Sulfur speciation analysis was performed at the ALS Laboratory in Witbank on rod-milled coal samples according to ISO 157:1996. A test portion was extracted from the coal with dilute hydrochloric acid to bring both the sulfate sulfur and the non-pyritic iron into solution. The pyritic iron and sulfur remained in the residue. The sulfate sulfur extracted from the test portion was determined gravimetrically by precipitation with barium chloride. The insoluble residue which was separated by filtration was further extracted with dilute nitric acid to bring the pyritic iron into solution. The amount of iron present was then determined by either titrimetric, calorimetric or atomic absorption spectrometric techniques. The pyritic sulfur content of the original test sample was calculated from this pyritic iron concentration, assuming the 1:2 stoichiometry of FeS_2 . Under the conditions described in the Standard, organic sulfur is insoluble in both dilute hydrochloric acid and dilute nitric acid and was thus determined, by difference, from the total sulfur content and the sulfate and pyritic sulfur contents.

* The value of sulfur content from ALS Laboratory of the same sample was higher compared to that obtained using LECO at the analytical laboratory in the Department of Chemical Engineering at the University of Cape Town. It is worth indicating that the sulfur results obtained from the Leco were used in the flotation experiments and those from ALS Laboratory were used for sulfur speciation.

3.2.7 X-ray Diffraction (XRD) analysis

X-ray Diffraction (XRD) analysis was performed on the rod-milled coal sample at the Catalysis Laboratory in the Department of Chemical Engineering at the University of Cape Town to determine the minerals associated with the coal ultrafines. The sample for XRD analysis was prepared using a McCrone Micronizing Mill. Powder XRD spectra were obtained by using a Bruker D8 Advance powder diffractometer with Vantec detector and fixed divergence and receiving slits with Co-K α radiation. The phases were identified using Bruker Topas 4.1 software and the relative phase amounts (weight %) were estimated using the Rietveld method. The values of Rwp and G.O.F were approximately 9.35 and 1.77, respectively.

3.2.8 Petrographic analysis

A petrographic block of the as-received sample was prepared by the South African Bureau of Standards Laboratories (SABS), Pretoria, in accordance with the ISO 7404-2:1985 and examined under the microscope at Petrographics SA Laboratory. The analysis provided information regarding the organic composition and maturity of the coal.

In order to determine the petrographic composition of the coal, the group maceral analysis was carried out according to ISO 7404-3:1994 and the reactive inertinite macerals were identified according to the method developed by Smith *et al.* (1983) for South African coals. In order to determine coal rank, vitrinite random reflectance measurements were carried out in accordance with the ISO 7404-5:1994. The individual 100 random measurement values were each converted to a maximum value for the sample (in-house method of calculation). The mean maximum reflectance value and the standard deviation of the distribution were calculated as detailed in ISO 7404-5. The percentages of the vitrinite in each step were plotted as a histogram for the sample.

A condition analysis was also performed on the coal. In this type of analysis, the components were quantified using a 500 point-count technique as described in ISO 7404-3:1994.

3.2.9 ARD assessment tests

ARD prediction tests as described in Section 3.4 below were carried out to characterize the acid generating potential of the rod-milled coal sample prior to flotation test work. The

selection of the coal sample to be used in this exploratory study depended largely on its acid-generating characteristics, to suit the main objective of the research.

3.3 FLOTATION METHODOLOGY

Laboratory batch flotation tests were carried out on both the as received coal and the rod-milled coal to determine acceptable conditions for the coal and sulfide flotation processes. Flotation experiments were carried out according to a strict procedure that was maintained throughout the test work.

3.3.1 Flotation cell

A bottom-driven 3 L Leeds-type sub-aeration laboratory batch flotation cell, equipped with electronic impeller speed and air flow rate regulators as represented in Figure 3.1, was used for all testwork.



Figure 3.1: Picture of the laboratory batch Leeds-type cell used for coal and sulfide flotation

3.3.2 Coal flotation

3.3.2.1 Reagents

The collector used in almost all of the coal flotation tests was laboratory grade dodecane, at a dosage varying from 0.70 to 3.72 kg/t; it was supplied by Merck. In order to compare the results obtained with dodecane, kerosene and oleic acid were used in some flotation coal tests; they were supplied by Sigma-Aldrich and May & Baker LTD Dagenham England, respectively.

The frother used exclusively in all the flotation experiments was methyl iso-butyl carbinol (MIBC), supplied by Sigma-Aldrich. This frother is the single most common used frother in coal flotation.

3.3.2.2 Flotation procedure

All the coal flotation tests were carried out at room temperature in the 3 L modified Leeds batch flotation cell. Approximately 1 L of tap water was introduced into the cell; 200 g of coal solids (dry basis) was added; the impeller speed set to 1200 rpm; and the cell was filled to 3 L with additional water. No attempt was made to regulate pulp temperature or pH. The desired quantity of dodecane collector was added to the suspended pulp using a syringe inserted below the pulp surface. After conditioning for 5 min, MIBC frother was added using a micro-syringe (again below the pulp surface). A period of 60 s was allowed for the frother to disperse through the pulp and then the air supply to the flotation cell was turned on and maintained at a flow rate of 5 L/min. The froth was removed manually by means of a scraper designed to cover the full width of the cell at a predetermined depth. In order to ensure reproducibility, scraping was performed at fixed intervals within each concentrate collection.

Four concentrates were collected over fixed intervals in numbered, pre-weighed pans to investigate the flotation kinetics. The total collection time for coal flotation was 5 min. A feed sample was taken before aeration of the pulp and a tailings sample was taken after each test. All batch flotation tests were conducted in duplicate and the reproducibility was found to be within 2% (consequently error bars are not shown on any of the graphs of the flotation results in Chapter 4). Experiments within each subset were performed successively (on the same day) to maintain similar conditions.

3.3.3 Sulfide flotation

3.3.3.1 Reagents

Sodium ethyl xanthate (SEX), sodium isobutyl xanthate (SIBX), and potassium amyl xanthate (PAX) were used as collectors for sulfide minerals. These collectors were supplied by Senmin. MIBC was used as the frothing agent. All sulfide flotation tests were performed using yellow dextrin as coal depressant, supplied by Africa Products (Pty) Limited. Fresh depressant was prepared every second day.

3.3.3.2 Sulfide flotation procedure

The sulfide flotation procedure was the same as for the coal flotation tests except in the following respects. After the pulp had been conditioned with the collector (PAX), the desired quantity of coal depressant (dextrin) was added and conditioned for 5 additional minutes, after which the required amount of frother, MIBC, was added into the pulp with a micro-syringe. A further 60 s of conditioning was allowed before opening the air valve to start aeration. The aeration rate was set at 6 L/min and the impeller speed at 1200 rpm. Four concentrates were collected over a period of 20 minutes.

3.3.4 Analysis of flotation samples

Feed, concentrate and tailings samples from each flotation experiment were filtered and oven dried overnight and weighed before analysis. Sulfur analysis was carried out using a LECO sulfur analyser at the Analytical Laboratory in the Department of Chemical Engineering at the University of Cape Town. The ash analysis was performed according to standard method SANS 131:1997, detailed in Section A.1.1 of Appendix A.

3.3.5 Double-stage flotation

Since the objective of this research was to develop a two-stage process aimed at coal recovery and mitigation of acid risks associated with coal ultrafine waste, a double-stage flotation test was performed so as to prove the conceptual approach described in Section 1.2.2. In the first stage of the selected process route, coal was floated by taking advantage of its natural hydrophobicity, following the procedure outlined in Section 3.3.2.2; pyrite and non-sulfide minerals were left behind in the tailings. The second stage involved a conventional flotation of pyrite and depression of non-sulfide minerals as described in the

sulfide flotation procedure. The residue from the coal flotation test was dried and weighed before being used as feed in the subsequent stage, which was conducted according to the procedure outline in Section 3.3.3.2. The operating conditions for the second-stage test were the same as in the single-stage test to improve the grade of sulfide in the concentrate and keep the yield as low as possible.

3.4 ARD PREDICTION TESTS

The ARD prediction tests were carried out on the rod-milled coal sample and products of the flotation tests.

3.4.1 Acid-base accounting

The acid-base accounting test involved the estimation of both the acid forming and acid neutralizing capacities of a sample in separate tests.

3.4.1.1 Maximum potential acidity (MPA)

The maximum potential acidity (MPA) that can be generated by a sample was determined from the sample total sulfur content. The total sulfur was determined using the high temperature combustion, LECO test (as in Section 3.2.4 above). It was assumed that all the sulfur measured in the sample occurs as pyrite (FeS_2) and that the pyrite reacts under oxidizing conditions to generate acid. The MPA of a sample was calculated from the total sulfur content as described in Section C.1.1 of Appendix C.

3.4.1.2 Acid neutralizing capacity (ANC)

The acid formed as a result of pyrite oxidation will to some extent react with acid neutralizing minerals contained in the sample. This inherent acid buffering capacity of a sample is quantified in terms of the acid neutralization capacity (ANC).

In this research, the ANC of each sample was determined by the H_2O_2 siderite correction ANC test, which was modified from the standard Skousen *et al.* (1998) method in order to improve the efficiency of the test by reducing incomplete Fe hydrolysis of the sample. To account for the presence of siderite that may overestimate the ANC value, a refinement of the Skousen *et al.* (1997) method was used as described by Stewart *et al.* (2006). The method was performed by adding 2 g sample to each of two duplicate Erlenmeyer flasks,

with a third one serving as blank. The amount and strength of added HCl to all the beakers were determined according to the fizz rating as outlined in Table 3.1. The sample was boiled for 5 min, cooled and then filtered to eliminate the possibility of pyrite oxidation associated with H₂O₂ addition. The solution was back-titrated to pH 4.5, then treated with 5 mL of 30% peroxide to enhance the oxidation of dissolved Fe (II) and the precipitation of Fe (III) oxhydroxide. After boiling for a further 5 min and cooling, the solution was back titrated with NaOH to pH 7 to determine the final ANC of the sample. The solution was left for 24 h, the pH adjusted to 7 if required and a further 5mL of H₂O₂ added. This last step was repeated over 72 h. In order to calculate the ANC, a blank test was carried out for each pair of concentrations of NaOH and the amount of acid consumed by the reaction with the sample calculated and expressed in kg H₂SO₄/t. The ANC procedure is outlined in more detail in Section C.1.2 of Appendix C.

3.4.1.3 Fizz rating

The ANC method was conditional upon performing a fizz test to determine the appropriate amount and strength of acid that needed to be used to dissolve the carbonates (Sobek *et al.*, 1978). The fizz ratings were assigned by placing about 0.5 g of sample on aluminium foil, adding one or two drops of 25 % HCl, and then evaluating the reaction qualitatively according to the criteria presented in Table 3.1. The presence of CaCO₃ was indicated by bubbling or audible effervescence.

Table 3.1: Fizz rating and associated HCl volume, and HCl and NaOH concentrations to be used in ANC test (modified Sobek *et al.*, 1978; IWRI & EGI, 2002).

Reaction Scale	Fizz rating	HCl Molarity (M)	Volume (ml)	NaOH Molarity (M)
None	0	0.5	4	0.1
Slight	1	0.5	8	0.1
Moderate	2	0.5	20	0.5
Strong	3	0.5	40	0.5
Very Strong	4	1.0	40	0.5
Carbonate	5	1.0	60	0.5

3.4.1.4 Net acid producing potential (NAPP)

The NAPP represents the balance between the capacity of a sample to generate acid (MPA) and its capacity to neutralize acid (ANC). The NAPP is expressed in units of kg H₂SO₄/t and is calculated as follows:

$$\text{NAPP} = \text{MPA} - \text{ANC}$$

where MPA represents the maximum potential acidity and ANC stands for acid neutralizing potential. If MPA is smaller than the ANC, this indicates that the sample has sufficient ANC to neutralize the acid. Conversely, if the MPA exceeds the ANC then the NAPP has a positive value, which gives an indication that the sample may be acid generating (Stewart *et al.*, 2006).

3.4.2 Net acid generating (NAG)

The tests were used in association with the NAPP to classify the acid generating potential of a sample. In the NAG test, the sample is reacted with hydrogen peroxide to rapidly oxidize any sulfide minerals contained within the sample. During the NAG test both acid generation and acid neutralization reactions occur simultaneously. Therefore, the end result represents a direct measurement of the net acid generated by the sample. This value is commonly referred to as the NAG capacity and is expressed in the same units as NAPP. The NAG test was carried out in two ways, as described in the sections that follow.

3.4.2.1 Single addition NAG Test

This test involves a single addition of 250 ml of 15% H₂O₂ to 2.5 g of pulverised sample. The solution is allowed to react overnight, and then heated until gently bubbling for approximately 2 h to remove excess H₂O₂ and encourage the release of inherent neutralizing capacity. Once the sample has cooled to room temperature, the pH and the titrated acidity to pH 4.5 and 7 of the mixture are determined in kg H₂SO₄/t (Stewart *et al.*, 2006). The amounts of acidity at pH 4.5 and 7 were calculated as described in Section C.2.1 of Appendix C.

3.4.2.2 Sequential addition NAG test

The sequential addition method was used to overcome the effect of H₂O₂ decomposition, which happens for samples with high sulfide content. The sequential NAG test involves multi-stage addition of a series of single addition NAG tests on the one sample. At the end of

each stage, the sample is filtered and the filtrate is used to determine the NAGpH and titrated pH at 4.5 and 7. The cycle is repeated until the NAGpH is greater than 4.5, or when catalytic decomposition of peroxide does not occur. The overall sequential NAG capacity in kg H₂SO₄/t of the sample is then determined by adding the individual generated acidity obtained at each stage.

3.4.3 Classification of samples

The acid forming potential of a sample was classified based on the acid-base accounting and NAG test results as follows:

1. Barren: essentially no acid generating capacity and no acid buffering capacity.
2. Non-acid forming (NAF): negative NAPP and final NAG pH \geq 4.5
3. Potentially acid forming (PAF): positive NAPP and final NAGpH < 4.5
4. Uncertain (UC): positive NAPP and NAGpH > 4.5, or negative NAPP and NAGpH \leq 4.5

The classification of samples as acid forming, non-acid forming or non-conclusive is described in Table 3.2 for both the NAPP and NAG assays and their combination. This classification is based on the work of Stewart *et al.* (2006).

Table 3.2: Classification for results of static tests (Stewart *et al.*, 2006; Hesketh *et al.*, 2010a)

ARD prediction tests	Result	Units	Classification guideline
Acid Base Accounting (ANC)	NAPP > 20 -20 < NAPP < 20 NAPP < -20	kg H ₂ SO ₄ /t kg H ₂ SO ₄ /t kg H ₂ SO ₄ /t	Acid forming Potentially acid forming (PAF) Non acid forming (NAF)
Net Acid Generation (NAG)	NAG pH < 4 & NAG _{pH7} > 10 NAG pH > 4 & NAG _{pH7} = 5-10 NAG pH > 4	kg H ₂ SO ₄ /t kg H ₂ SO ₄ /t pH	Acid Forming Potentially acid forming (PAF) Non acid forming (NAF)
Combined static tests	NAG pH < 4.5 and NAPP > 0 NAG pH > 4.5 and NAPP < 0		Potentially acid forming (PAF) Non acid forming (NAF)

If these criteria fail, the results are considered uncertain and further testing is required for classification.

3.4.4 Bio-kinetic flask test

The biokinetic test is an emerging protocol under development at the University of Cape Town (Hesketh *et al.*, 2010b), used to classify samples in terms of their potential to generate acid. The biokinetic test extends the findings of the static tests by including the role of microorganisms in the acidification process and providing kinetic data from which the relative rates of neutralization and acidification potential can be ascertained.

For the biokinetic test, 7.5 g samples of flotation feed, concentrate or tailings (particle size < 150 μm) were added into 150 mL autotrophic basal salts medium at pH 2 in a 250 mL Erlenmeyer flask. The media were inoculated with 7.5 mL of an active mixed culture comprising *Acidithiobacillus ferroxidans* (DSM 584), *Leptospirillum ferriphilum* (ATCC 49881), *Acidithiobacillus caldus* (DSM 8584) and *Sulfobacillus benefaciens* (DSM 19468). The flasks were stoppered with cotton wool bungs, weighed and incubated at 37°C on an orbital shaker at 150 rpm for 75 days. Distilled water was added to maintain constant weight during the experiment. The same procedure was used for the biotic tests with pH control and for tests in the absence of bacteria (abiotic tests). In the constant pH tests, drops of sulfuric acid were added from a burette to maintain the pH steady at pH 2.

The onset of bacterial growth was indicated by the appearance of a brown colour in the medium due to the formation of ferric salts. The pH, redox potential and iron concentration in solution were monitored every 2 to 4 days. Ferric iron concentration in solution was measured as the difference between the total and ferrous iron concentrations. The total and ferrous iron concentrations were determined spectrophotometrically using the 1-10 phenanthroline method (Komadel and Stucki, 1988). Redox potential was measured using a Crison ELP 21 Eh meter against a silver/silver chloride reference electrode (+199 mV). The pH was measured using a Metrohm 713 pH meter. The biokinetic test methods are outlined in more detail in Section C.4 of Appendix C and the detailed description of the results is found in Section D.2.2.

CHAPTER 4

RESULTS AND DISCUSSION: COAL CHARACTERIZATION AND FLOTATION TEST WORK

4.1 INTRODUCTION

As stated in Section 1.2.4, the main objective of this research was to develop in concept a desulfurizing flotation circuit aimed at mitigating the generation of ARD risks associated with coal ultrafines, and simultaneously recovering saleable coal from the wastes. In essence the project seeks to investigate whether flotation techniques can be successfully used to recover a saleable coal product from the coal ultrafines arising from mining and processing operations, and remove acid generating materials prior to the disposal of coal flotation residues.

To this end, the recovery and desulfurization of coal through the application of froth flotation techniques was investigated systematically through laboratory batch flotation tests under various conditions in order to determine the technical feasibility of selectively removing the acid-generating materials from coal ultrafines. The effects of key parameters, such as the type and dosages of reagents, and the extent of both coal recovery in a direct coal float, and sulfide sulfur removal from the tailing, were investigated. No attempt was made to optimize the process.

The coal used in this investigation was characterized by means of size, ash-by-size, petrographic, proximate, ultimate and flotation release analyses. This chapter begins by reporting these characterization tests. This is followed by the results of the batch flotation tests performed on subsamples of the coal to determine the recovery of valuable coal. These results are discussed in terms of the recoveries, yields and grades of the final products obtained under different flotation conditions. The results of sulfide flotation from coal in one stage and by stage-wise addition of collector are then presented. Finally the conceptual approach proposed in this work is demonstrated in the two stage-flotation process.

4.2 COAL CHARACTERIZATION RESULTS

4.2.1 Size analysis distribution

The results of the size and ash-by-size distributions of the as-received coal are given in Table 4.1. The results shows that the as-received sample contained a significant amount of ultrafine material (23.64 % passing 106 μm) but that a substantial amount of coarser material was also present (53.77 % greater than 212 μm). The -75 μm fraction had the greatest ash content of 47.6%. The entire sample was rod-milled to 75% passing minus 150 μm prior to flotation (see Table 4.1); the ash content of the -75 μm fraction dropped to 38.6% as a result.

Table 4.1: Size and ash-by-size distribution of the as-received and rod-milled coal waste samples

Size, μm	As-received coal waste		After rod-milling	
	Wt, %	Ash, %	Wt, %	Ash
+850	1.40	22.8	-	-
-850+600	8.10	29.1	-	-
-600+425	14.02	29.5	1.71	33.3
-425+300	15.93	34.6	5.86	32.6
-300+212	14.37	36.8	8.28	39.4
-212+150	11.33	35.6	8.22	42.8
-150+106	11.26	41.7	13.78	39.4
-106+75	6.35	43.6	11.77	40.5
-75+53	7.23	49.1	14.72	37.3
-53	10.06	46.5	35.66	39.1

4.2.2 Proximate and ultimate analyses

The results of the proximate and ultimate analyses together with the calorific value for the feed coal sample are shown in Table 4.2. According to the results, the coal sample used in this study was characterized as having a high ash content of approximately 34.4 % (dry basis) with a gross CV of about 19.02 kJ/kg. The total sulfur content, determined according to ASTM D4239:1997 at ALS Laboratory, was approximately 1.08%.

Table 4.2: Summary of the proximate and ultimate analysis results of the coal sample

a) Proximate analysis % (air-dry basis)	
Ash (bulk)	34.4 ± 0.14
Volatile matter	19.3 ± 0
Moisture	3.8 ± 0.07
Fixed Carbon	42.5 ± 0.07
b) Ultimate analysis % (air-dry basis)	
Total Sulfur	1.08 ± 0.01
Carbon	49.4 ± 0.07
Hydrogen	2.65 ± 0.04
Nitrogen	1.31 ± 0.01
Oxygen	7.36 ± 0.08
c) Calorific value kJ/kg	
	19.02 ± 0.04

4.2.3 Sulfur speciation

Table 4.3 shows the results of the analysis of the forms of sulfur in the coal ultrafines under investigation. The coal sample contained approximately 0.52% of sulfidic sulfur and 0.32% of sulfate sulfur. The amount of organic sulfur, calculated by difference based on the total sulfur (1.08%), was about 0.24%.

Table 4.3: Sulfur speciation of coal sample (ALS Laboratory, Witbank)

Forms of sulfur	Average amount (%)
Sulfide	0.52 ± 0.01
Sulfate	0.32 ± 0.01
Organic	0.25 ± 0.02
TOTAL	1.08 ± 0.04

The proportion of sulfate sulfur indicated that the sample was oxidized: pristine coal contains no or only a negligible proportion of sulfate sulfur. Although the sulfide mineral content in the coal made up a much lower proportion of coal compared to carbon, the other organic elements and the ash-forming minerals, they are an important component because of the

environmental impact related to ARD. Acid prediction tests performed (see section 5.2 below) indicated that the coal sample was potentially acid generating.

4.2.4 X-ray Diffraction

Table 4.4 shows the mineralogical composition of the ultrafine coal waste sample determined using XRD analysis. The XRD results have been manipulated to take into account the presence of amorphous (coal) content using the Parr formulas (ASTM D-388) as follows:

$$mm = 1.08A + 0.55S$$

where mm, A, and S are the weight percent of the mineral matter, ash and total sulfur, respectively.

Table 4.4: Mineralogical characterization of the coal ultrafine waste

Mineral	Chemical composition	Mineral matter content (wt %)	Concentration in coal (wt %)
Quartz	SiO ₂	29.40	11.10
Pyrite	FeS ₂	1.13	0.43
Siderite	FeCO ₃	0.55	0.21
Calcite	CaCO ₃	2.99	1.13
Dolomite	CaMg(CO ₃) ₂	0.33	0.12
Gypsum	CaSO ₄ •2H ₂ O	4.03	1.52
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	59.16	22.33
Epsomite	MgSO ₄ •7(H ₂ O)	1.65	0.62
Jarosite	KFe ³⁺ ₃ (OH) ₆ (SO ₄) ₂	0.76	0.29

The most common carbonate minerals present in the sample were found to be calcite (CaCO₃, 1.13 wt%), siderite (FeCO₃, 0.21 wt%) and dolomite (CaMg(CO₃)₂, 0.12 wt%). Based on the amount of pyrite (0.43 wt%) in the coal sample, the proportion of sulfide sulfur is 0.23 wt%, much smaller than 0.52 wt% that was found in the sulfur speciation analysis (*cf* Table 4.3). This can be explained by the detection limit (about 2-3%) of the XRD instrument.

4.2.5 Petrographic analysis

Petrographic analysis was carried out on the as-received coal by Petrographics SA in Pretoria. Table 4.5 gives a summary of the petrographic analysis. The maceral analysis (percent by volume (mineral matter-free)) indicated the coal sample contained a high proportion of inertinite (76 %) while the total content of reactive macerals, defined as the propensity of the maceral constituents to react to heating, was about 24%, consisting of 21% vitrinite and 3% liptinite. The general condition analysis indicated that a very significant proportion of the coal particles examined displayed cracking and micro-fissures (around 27%) while approximately 11% of the organic particles exhibited signs of severe weathering and general disintegration. The condition analysis has also indicated that some cracking occurred probably during handling and preparation due to the somewhat brittle nature of coal (particularly vitrinite) of this level of maturity. Furthermore, the pyrite present mainly exhibited a “fresh” bright yellow colour (2% of the whole coal). However, reddish-orange oxidized forms of pyrite were sometimes seen (<1%).

Table 4.5: Summary of the major petrographic properties of the coal feed

Petrographic properties	Feed coal
1. Rank (degree of maturity) ISO 11760-2005 Classification of Coals	Bituminous Medium Rank C
2. Mean maximum reflectance % Vitrinite-class distribution	0.83 V 6 to V 11
3. Petrographic composition % by vol.	
4. Maceral analysis (mineral matter-free)	
Total reactive macerals %	24
Vitrinite content %	21
Liptinite content %	3
Total inertinite %	76
Maceral analysis - Total %	100
5. Condition analysis	
"Fresh" coal particles %	62
Cracks and fissures %	27
Severely weathered coal %	11
Condition analysis - Total %	100

4.2.6 Flotation release test

A flotation release analysis was performed on a sample of the coal to determine the optimum performance that could be achieved by batch flotation. The air flowrate and the impeller speed were maintained at 5 L/min and 1200 rpm respectively. The flotation release method is described in Section 3.2.3 above. Starvation amounts of both frother (MIBC) and collector (dodecane) were added. Release analysis results are graphically depicted in Figure 4.1 while the details are given in Section A.2 of Appendix A.

It can be seen in Figure 4.1 that the coal was floatable in the batch cell, although the selectivity was poor. The release flotation curve indicates a theoretical yield of 49.04% at an ash content of 16.37%. It is also possible to obtain a product with an ash content of 12.74% at a theoretical yield of 33.7%.

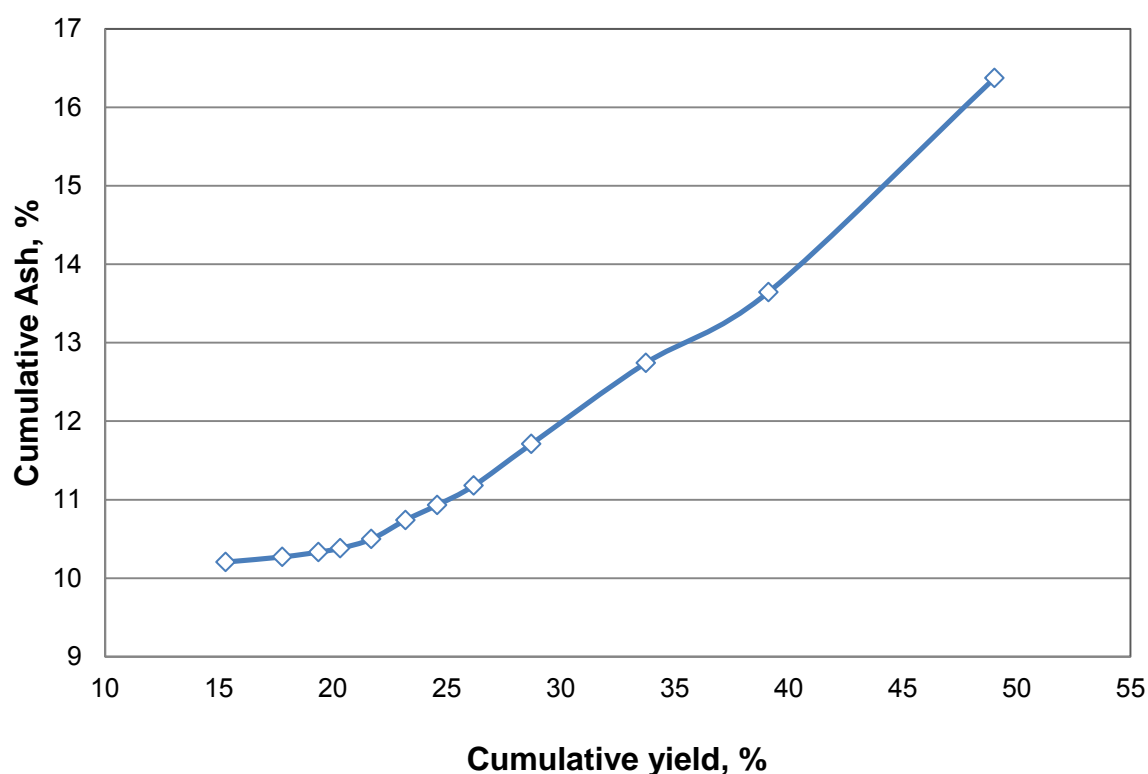


Figure 4.1: Flotation release result of coal sample in the presence of dodecane and MIBC

4.3 COAL FLOTATION RESULTS

The objective of this part of the study was to recover high-calorific value/low-ash content product coal from the coal ultrafine wastes by means of froth flotation and as a result decrease the volume of the discards in the slimes dams. To this end, laboratory batch flotation experiments were carried out on subsamples of the thickener underflow coal according to the procedure outlined in Section 3.3.2.2. The collector type and dosage were varied as was the dosage of the MIBC frother. The air rate and impeller speed were maintained at 5 L/min and 1200 rpm respectively. A pulp density in the region of 6.67 % was used.

The results were evaluated in terms of the yield, combustibles recovery and ash content of the concentrate. It should be pointed out that the term “combustibles” used throughout this section refers to the weight proportion of the sample that was consumed when the material was placed in a muffle furnace. The ash percentage was calculated on a moisture-free basis.

Detailed results of these experiments appear in Section D.1 of Appendix D. For each run the experimental conditions pertaining to that run are presented, together with the flotation results.

4.3.1 Effect of collector addition

Collector addition is a pre-requisite for the effective flotation of most South African coals since they do not float adequately in the presence of a frother alone. The effect of collector concentration was therefore of vital importance and it was studied to determine the extent of coal recovery and the quality of the coal product obtained.

Initial laboratory batch flotation tests were carried out using various dosages of dodecane collector, with no attempt to optimize the process. Figure 4.2 plots the cumulative recovery of combustibles over 5 min of flotation time. The collector dosage was varied from 0.70 to 3.72 kg/t, while the MIBC frother dosage was kept constant at 0.11 kg/t. After 5 min of flotation time, the flotation yield (mass product / mass feed) and recovery (combustible in product / combustible in feed) were only 18.96% and 23.83%, respectively at 1.86 kg/t of dodecane. Doubling the amount of dodecane from 1.86 kg/t to 3.72 kg/t increased the yield and recovery by only 0.76% and 0.93%, respectively. In view of these preliminary results, the coal sample under investigation was considered difficult to float. This is supported by the

flotation separation efficiency, defined as the difference between the combustible recovery and ash recovery, which varied from 8.71% to 15.54% as shown in Table 4.6.

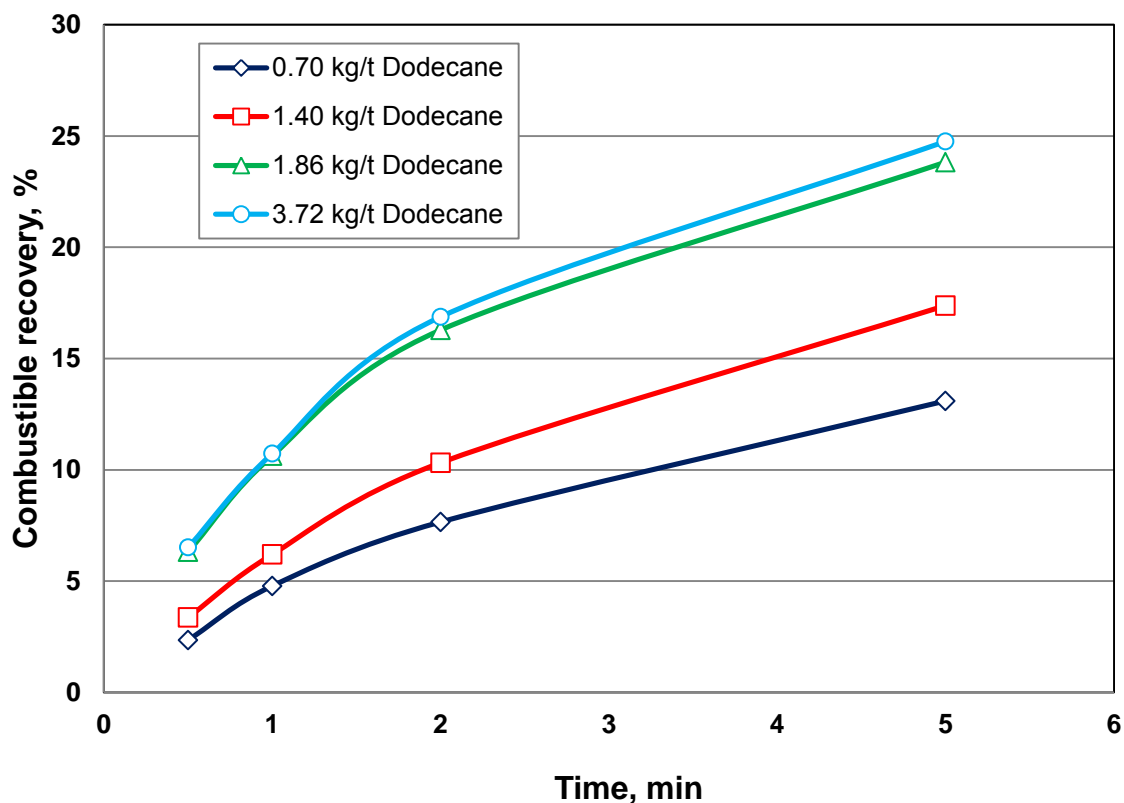


Figure 4.2: Kinetic flotation results for different dosages of dodecane collector. MIBC frother was kept constant at 0.11 kg/t.

Table 4.6: Coal flotation results (after 5 min) with dodecane collector and 0.11 kg/t MIBC frother

Dodecane dosage (kg/t)	Yield (%)	Product sulfur (%)	Product Ash (%)	Separation efficiency (%)	Recovery (%)	
					Combustible	Ash
0.70	10.26	0.32	13.9	8.71	13.10	4.39
1.40	13.67	0.33	14.3	11.38	17.38	6.00
1.86	18.96	0.41	15.3	14.92	23.83	8.90
3.72	19.72	0.40	15.1	15.54	24.76	9.21

Based on these results, an attempt was made to increase the yield and recovery of coal in subsequent flotation tests. The dosage of MIBC frother was increased to a constant value of 0.28 kg/t while the collector dosage was varied from 0.70 to only 2.79 kg/t. Figure 4.3 shows the results obtained under these new conditions. For ease of comparison, the data are also shown in Table 4.7 to give an indication of the grades of clean coal and tailing produced in these tests. Table 4.7 also shows the results of a float test carried out using no dodecane collector, i.e. in the presence of 0.28 kg/t MIBC frother only.

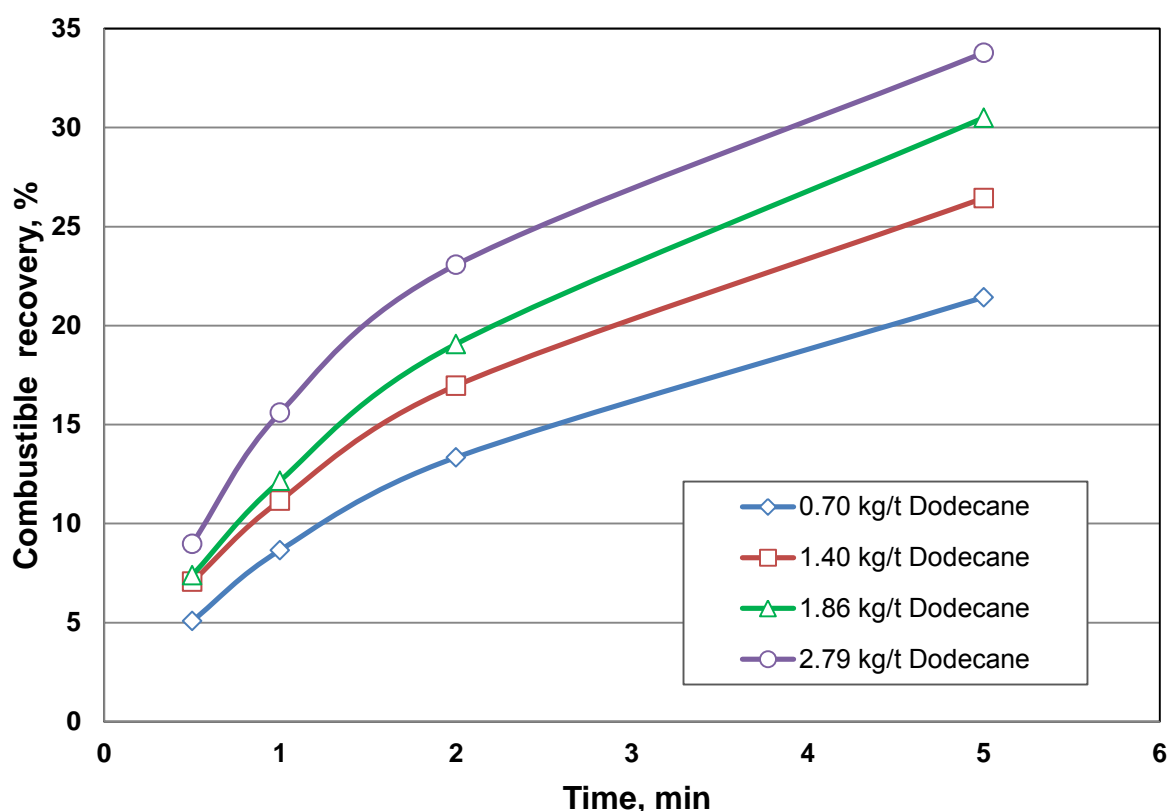


Figure 4.3: Kinetic flotation results for different dosages of dodecane collector. MIBC frother was kept constant at 0.28 kg/t.

For each collector dosage, the recovery increased with the increased dosage of MIBC frother. As an illustration, at 1.86 kg/t dodecane, the recovery varied from 23.83% at 0.11 kg/t MIBC to 30.5% at 0.28 kg/t MIBC; the increase in the recovery was therefore about 6.67%. Under the new reagent conditions, flotation performance increased upon increasing collector concentration from a low to a high level, however not altogether as expected. In the presence of 0.28 kg/t MIBC, The flotation yield and combustible recovery at 0.7 kg/t of dodecane were 17.16% and 21.41%, respectively. In the complete absence of collector, the combustible yield was 7.06% with the highest content of ash (18.1%). This showed that the

addition of dodecane enhanced the hydrophobicity of the coal particles, thus increasing the selectivity between coal particles and mineral matter.

The recovery and yield at the highest dosage of dodecane were 33.79% and 27.37%, respectively. It was again interesting to observe that doubling the amount of dodecane from 1.4 kg/t to 2.79 kg/t increased the recovery by no more than 7.35% and the yield by 6.18%. It was also observed that low dosage of dodecane resulted in poor froth development during the flotation of coal. Increasing dodecane dosage improved the froth structure and stability, resulting in increased coal recoveries.

Table 4.7: Coal flotation results (after 5 min) with dodecane collector and 0.28 kg/t MIBC frother

Dodecane dosage (kg/t)	Clean coal			Tailing			Ash of raw coal (%)
	Yield (%)	Ash (%)	Sulfur (%)	Yield (%)	Ash (%)	Sulfur (%)	
0	7.60	18.1	0.48	92.40	32.6	0.65	33.6
0.7	17.16	15.6	0.46	82.84	35.9	0.83	33.4
1.4	21.19	15.1	0.45	78.81	36.5	0.82	33.4
1.86	24.37	14.0	0.45	75.63	36.9	0.84	33.0
2.79	27.37	15.5	0.47	72.63	37.6	0.87	33.3

In view of these results, the coal sample under investigation was considered difficult to float, as characterized by the low yield and recovery. The reason for the poor recovery of combustibles even in the presence of high concentration of dodecane may be explained by the petrographic composition of the coal (see Table 4.5), which indicates that the coal was low rank and inertinite-rich. Petrographic studies of coal flotation products have indicated that vitrinite and exinite have a better response than inertinite (Jena *et al.*, 2008).

Inertinite-rich coals are readily oxidized upon exposure to weathering conditions, resulting in the formation of hydrophilic oxygen functional groups on the coal surface. Froth flotation is sensitive to factors that may change the surface chemistry of coal, such as the degree of oxidation (Kawatra and Eisele, 2001) which makes the coal more hydrophilic and more difficult to float. It is known that relatively large quantities of oily reagents are required to float oxidized coal (Aplan, 1993; Tao *et al.*, 2002). Although a large quantity of dodecane (≈ 3 kg/t) was used in the testwork described above, the response of the coal slurry to flotation was not appreciable probably due to oxidation of the coal surfaces: petrographic analysis (Table

4.5) indicated that at least 11% of the coal was oxidized. This is consistent with the study conducted by Sarikaya (1995), which suggested that flotation test results can be used as an indication of the degree of weathering.

Additionally, the poor recovery may be due to the high-ash content of the coal sample, about 34 %. Ash-forming constituents also determine coal floatability; the greater the ash content, the less hydrophobic is the coal due to the fact that ash-forming minerals such as silicates and clays are readily wetted by water and cause slime coatings on coal particles, leading to a loss in recovery (Aplan and Arnold, 1991; Jena *et al.*, 2008).

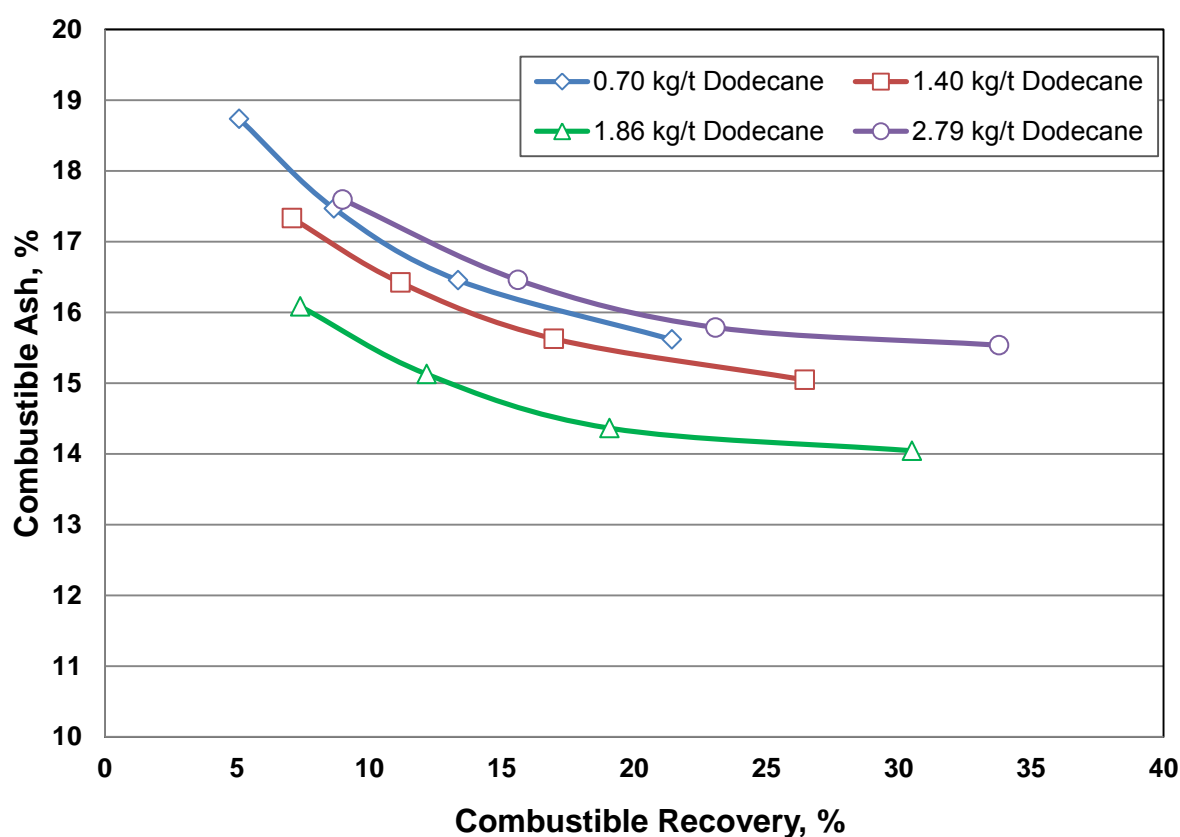


Figure 4.4: Combustible recoveries and ash contents of concentrates during flotation with different dosages of dodecane collector. The MIBC dosage was kept constant at 0.28 kg/t.

Regardless of the poor recovery and yield, the concentrate grade was good (low ash content), ranging from 15.5% to 18.08%, as indicated in Figure 4.4. This indicates that dodecane was able to disperse through the pulp and selectively adsorb onto the surface of the coal ultrafine particles, resulting in increased affinity of the coal particles toward the air bubbles.

However, the addition of dodecane did not stop the sulfur-bearing minerals from floating at the same time as the coal. Table 4.7 shows that the sulfur content of the clean coal was about 0.46% compared to 1.08% in the feed. It may be assumed that the sulfur that reported to the concentrate was in the form of organic and sulfide sulfur (sulfate sulfur would be expected to dissolve in the slurry; hence the poor sulfur mass balance). This unintentional flotation of sulfide mineral during flotation may have been caused by locked particles, excessive collector and/or conditioning promoting the natural floatability of pyrite particles (Aplan, 1993). It is important to note that this study did not attempt the depression of pyrite during coal flotation, because in almost every case a good pyrite depressant is also a good coal depressant at the same or higher reagent concentration (Purcell and Aplan, 1991). Perry and Aplan (1985) indicated that pyrite depression during coal flotation may involve a trade-off between the coal yield and the sulfur content of the floated coal.

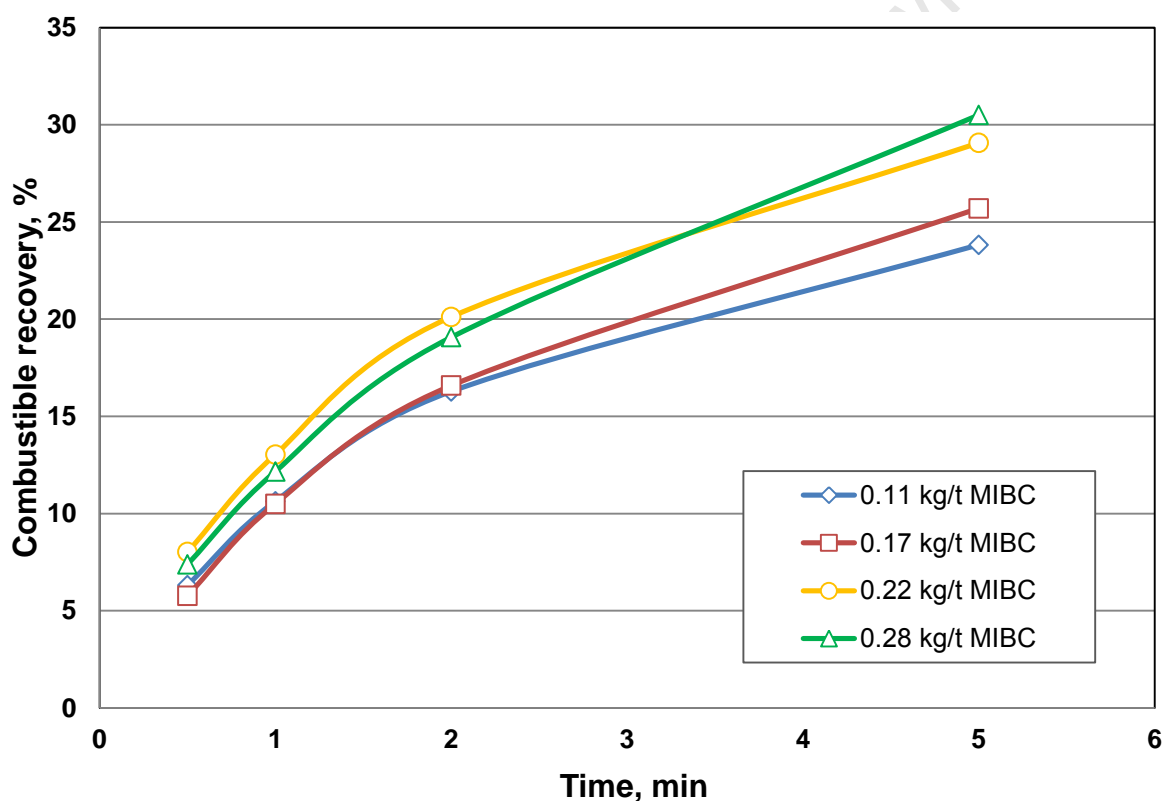
4.3.2 Effect of frother addition

Frothers are used in froth flotation to facilitate the dispersion of air into fine bubbles, to stabilize the froth and to control the bubble size, as a result of their ability to prevent or retard bubble coalescence (Gupta *et al.*, 2009). One of the most effective frothers (MIBC) with low surface activity was used exclusively in this research. A set of experiments was carried out in which the dosage of dodecane collector was kept constant at 1.86 kg/t (which may be considered as the optimum dosage based on the results reported in Figure 4.3 and Table 4.7) while the dosage of MIBC was varied from 0.11 to 0.28 kg/t. The overall effect of increasing the MIBC dosage was to increase the recovery and flotation rate of coal. As can be seen in Table 4.8 and Figure 4.5, the coal recovery showed a noticeable increase for each successive increase in MIBC addition.

The highest combustible recovery (30.50%) and yield (24.34%) were obtained at the highest dosage of the frother (0.28 kg/t). The effect of varying the dosage of frother MIBC on the combustibles recovery and grade are shown in Figure 4.6. Once again it can be seen that the carbonaceous material was not readily floated. At the highest dosage of MIBC, approximately 30.5% of coal was recovered to the concentrate, containing 14% ash. Interestingly, at a low concentration of MIBC, both the grade and the recovery of the concentrate decreased. The decrease in grade is possibly due to hydrogen bonding between MIBC with the hydrated mineral matter (Naik *et al.*, 2005). This shows that coal recovery is dependent on frother concentration in solution and can be reduced by frother adsorption onto coal. Frother dosages must often be increased to an optimum level to ensure adequate recovery of coal without comprising the grade of the valuable coal.

Table 4.8: Coal flotation results (after 5min) with MIBC frother and 1.79 kg/t dodecane collector

MIBC dosage (kg/t)	Clean coal			Tailing			Ash of raw coal (%)
	Yield (%)	Ash (%)	Sulfur (%)	Yield (%)	Ash (%)	Sulfur (%)	
0.11	18.96	15.3	0.32	81.04	35.6	0.73	33.6
0.17	20.45	13.4	0.45	79.55	35.9	0.78	33.0
0.22	23.54	14.6	0.46	76.46	35.9	0.79	33.1
0.28	24.37	14.0	0.45	75.63	36.9	0.84	33.0

**Figure 4.5:** Kinetic flotation results for different dosages of MIBC frother. Dodecane collector was kept constant at 1.86 kg/t.

Normally, as the dosage of frother increases, so also does the flotation of the undesired pyrite (Bonner and Aplan, 1993). However, in this study the increase of the MIBC concentration did not drastically affect the flotation of ash-forming and sulfur-bearing

minerals. This shows that the concentration of the frother varied below or around the most favourable level.

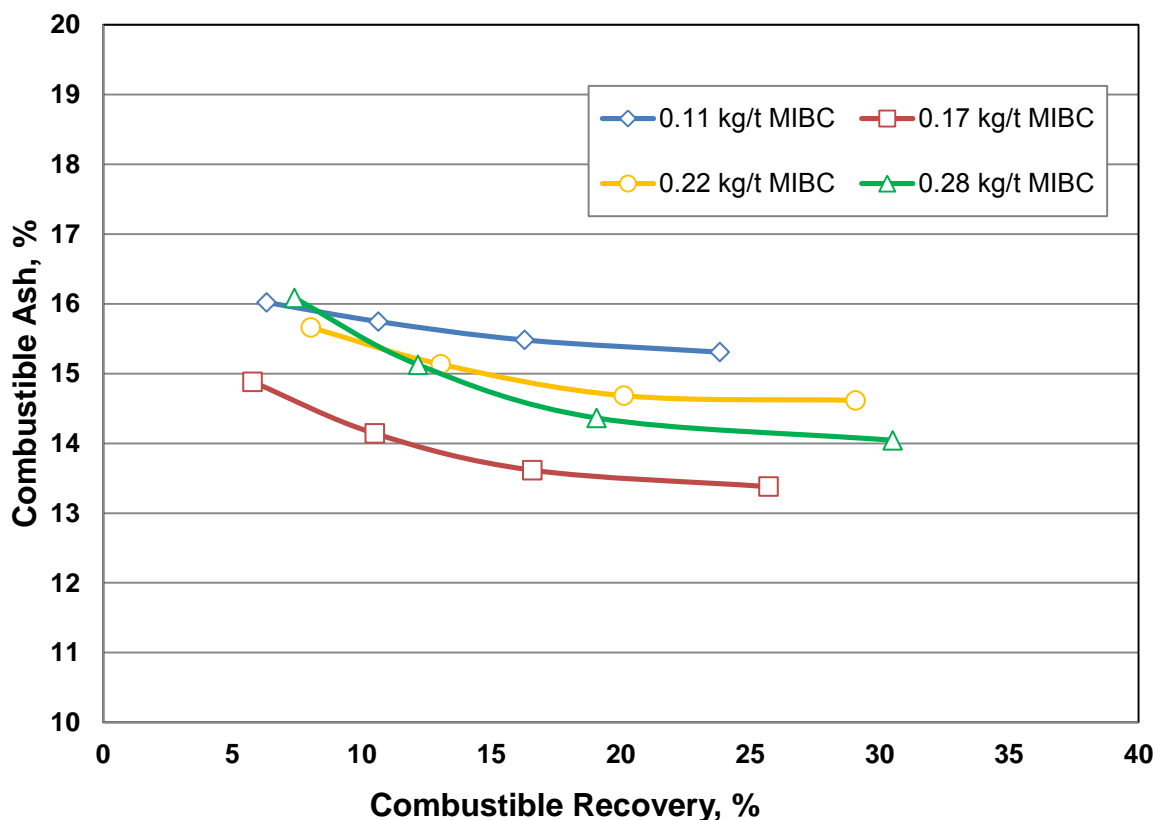


Figure 4.6: Combustible recoveries and ash contents of concentrates during flotation with dosages of MIBC frother. The dodecane collector dosage was kept constant at 1.85 kg/t.

4.3.3 Effect of various collectors

Initially, as reported in Section 4.3.1, the coal flotation tests were conducted with dodecane as the collecting agent. However, in an attempt to improve the yield and recovery of the clean coal, and to compare the performance of this standard reagent with other collectors, two other laboratory grade reagents, namely, kerosene and oleic acid were tested. The flotation tests were conducted under similar parametric conditions. The clean coal yield and ash content (Tables 4.9 and 4.10) and the combustible recovery (Figure 4.7) provide the basis for comparing the three collectors.

Although kerosene has been used extensively in the flotation of coal at the industrial scale because it has a low enough viscosity to disperse in the slurry and spreads over the coal particles easily, the results indicate that oleic acid was much more efficient in increasing both

the recovery and yield of clean coal. As can be seen from Figure 4.7, the coal ultrafine waste sample responded well to oleic acid as the collecting agent; significant yield was achieved compared to what was obtained in the presence of the aliphatic hydrocarbons. The most striking feature of the Figure below is the remarkable improvement in terms of combustibles recovery when using oleic acid as collector, reaching 35.83% at a dosage of only 0.7 kg/t of collector. This increased further, to 69.06 %, far above anything obtained with dodecane or kerosene, when the oleic acid dosage was increased to 2.79 kg/t.

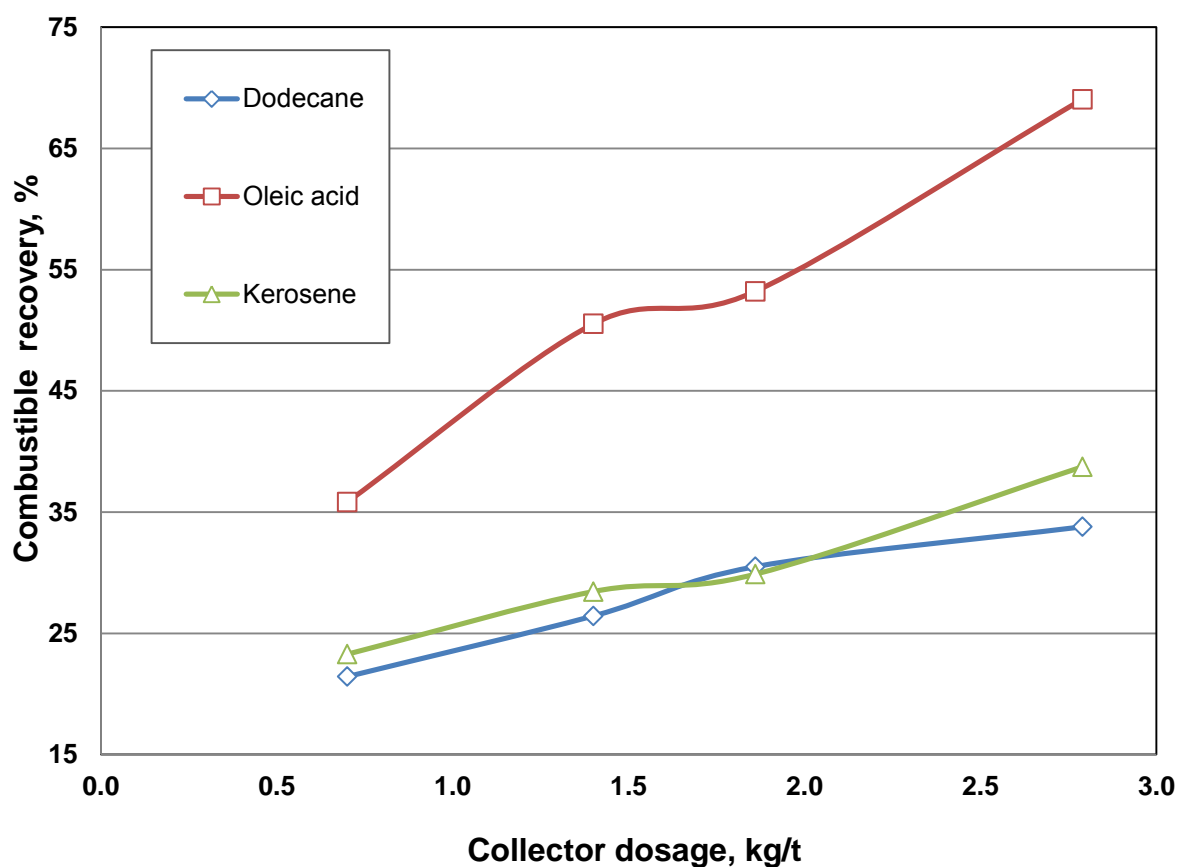


Figure 4.7: Comparison of the collecting ability of dodecane with that of kerosene and oleic acid at different dosages. The MIBC frother dosage was kept constant at 0.28 kg/t.

The results in Table 4.9 indicate that when the oleic acid dosage was 2.79 kg/t, the yield and ash content of the clean coal were 55.98% and 18.10%, respectively. At same dosage of kerosene and dodecane collectors, the yields were 31.44% and 27.37%, respectively, with corresponding ash contents of 15.4% and 15.5%, respectively (Table 4.11). These results suggest that there was a stronger interaction between the oleic acid molecule and the aromatic sites on the coal surface than between an aliphatic hydrocarbon chain and the coal

surface. This can be explained by the strong π -bonding that occurs between the hydrophobic component of the coal surface and the double-bond of oleic acid.

It has been shown previously (Section 4.3.1) that the coal under investigation might have been partly exposed to atmospheric oxygen, that could have resulted in the reduced floatability of coal in the presence of oily hydrocarbons. However, regardless of this behavior, oleic acid was more efficient in floating this difficult-to-float coal which could not be floated easily with conventional collectors such as dodecane and kerosene. These results confirm that lower-rank or oxidized coal can be floated if the collecting agent is properly selected.

Table 4.9: Coal flotation results (after 5min) with oleic acid collector and 0.28 kg/t MIBC frother

Oleic acid dosage (kg/t)	Clean coal			Tailing			Ash of raw coal (%)
	Yield (%)	Ash (%)	Sulfur (%)	Yield (%)	Ash (%)	Sulfur (%)	
0.7	29.73	17.0	0.49	70.27	37.1	0.80	33.9
1.4	43.03	18.7	0.54	56.97	39.9	0.81	32.9
1.86	44.37	17.7	0.49	55.63	42.3	0.87	33.7
2.79	55.98	18.1	0.50	44.02	51.8	0.95	33.0

At the same time, it is apparent that the selectivity of the aliphatic oils (kerosene and dodecane) for hydrophobic carbonaceous material was greater than that of oleic acid. However, the results also show that the presence of excess oil did not result in adsorption onto ash-forming gangue: i.e. the increased oleic acid dosage did not affect the clean coal grade beyond the increase which would be expected as a result of the greater mass of coal floated. Nevertheless, both dodecane and kerosene produced clean coal with low sulfur content, confirming that oleic acid was less selective. The comparative results of these three collectors confirm the finding of Erol *et al.* (2003) that the type and amount of reagent are the key factors in determining the performance parameters, the combustible recovery and the purity of the concentrate.

Table 4.10: Coal flotation results (after 5 min) with kerosene collector and 0.28 kg/t MIBC frother

kerosene dosage (kg/t)	Clean coal			Tailing			Ash of raw coal (%)
	Yield (%)	Ash (%)	Sulfur (%)	Yield (%)	Ash (%)	Sulfur (%)	
0.7	19.08	16.0	0.47	80.92	34.7	0.68	33.9
1.4	22.86	15.0	0.46	77.14	36.7	0.77	33.0
1.86	24.14	14.7	0.45	75.86	36.3	0.71	33.1
2.79	31.44	15.4	0.47	68.56	38.6	0.76	33.1

Table 4.11: Comparison of dodecane, kerosene and oleic acid at the dosage of 2.79 kg/t and 0.28 kg/t MIBC frother.

Collector	Yield	Recovery	Clean coal ash	Residual ash	Residual total sulfur
	%				
Dodecane	27.37	33.79	15.5	37.6	0.87
Kerosene	31.44	38.74	15.4	38.6	0.76
Oleic acid	55.98	69.06	18.1	51.8	0.95

In summary, a comparison of three collectors has shown that oleic acid was able to achieve a marked improvement in both the yield and recovery of the coal ultrafines, although the grade of clean coal was somewhat poorer compared to what was obtained with dodecane and kerosene.

Although the literature contains little concerning the use of oleic acid in coal flotation (De Jager, 2002; Denby *et al.*, 2002; Sis *et al.*, 2003), their use is widespread in the flotation of non-sulfide ores (Sis and Chander, 2003; Miller *et al.*, 2007). The findings from laboratory flotation investigations have demonstrated that oleic acid can substitute for some of the commercial reagents currently used. It is of particular interest that oleic acid use is environmentally safe and preferable given that it is biodegradable and can be of vegetable origin, and because of environmental concerns over the use of traditional reagents in coal flotation.

4.4 SULFIDE FLOTATION RESULTS

Coal desulfurization by flotation was studied to investigate the possibility of removing sulfur-bearing minerals[§] from the coal in one stage, and to compare the results with the separation performance achieved with the two-stage process. It is common practice to float coal material from associated mineral matter: several investigations have suggested the flotation of sulfur-bearing minerals, in particular pyrite, from coal with simultaneous depression of coal (Kawatra and Eisele, 2001; Laskowski, 2001). Sulfide flotation, in which bulk coal is left behind in the tailing, is sometimes referred to as reverse flotation.

The desulfurization of coal was investigated systematically through laboratory batch flotation tests under various conditions. All experiments were carried out according to the procedure outlined in Section 3.3.3.2. In all of the tests the impeller speed was 1200 rpm, the aeration rate was 6 L/min and the pulp pH that of Cape Town tap water (pH 7.6). Except in the preliminary study, the xanthate dosages were varied from 0.93 to 2.33 kg/t, the MIBC frother dosages from 0.06 to 0.11 kg/t and the yellow dextrin (coal depressant) dosages from 0.7 to 1.4 kg/t.

4.4.1 Effect of collector type

Preliminary tests were carried out to determine the most effective xanthate collector for floating pyrite from the coal ultrafine waste under investigation. Potassium amyl xanthate (PAX), sodium isobutyl xanthate (SIBX) and sodium ethyl xanthate (SEX) were tested under the same conditions. These xanthates, most commonly used in mineral flotation, are highly selective for sulfide minerals, as they react chemically with the sulfide surfaces and do not have any affinity for the hydrophilic non-sulfide minerals.

Figure 4.8 shows the kinetic results for the three xanthates; it is clear that PAX produced the best recovery of 26.27% after 20 min of collection time, while SIBX and SEX recovered 20.81% and 1.44%, respectively. This is as expected, as PAX is a stronger collector than the other xanthate homologues. As a consequence, PAX was used exclusively in all subsequent sulfide flotation tests described in this research. (It is worth noting that PAX is a very expensive collector in South Africa and the benefit of using PAX vs SIBX needs to be established in an economic analysis).

[§] which are potentially acid-generating

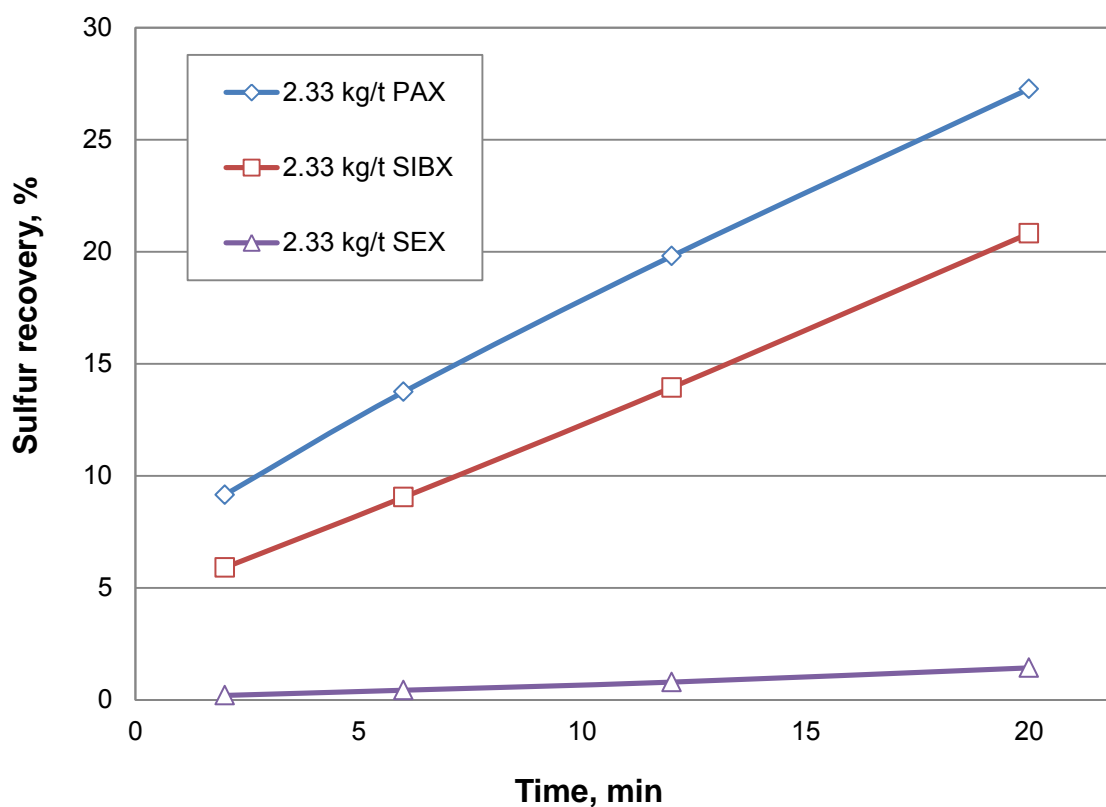


Figure 4.8: Kinetic flotation results of sulfide flotation for 2.33 kg/t of different xanthate collectors, 0.11 kg/t MIBC frother and 0.93 kg/t dextrin coal depressant.

4.4.2 Effect of collector dosage

On the basis of the above result, a series of tests was undertaken in which PAX collector dosage was varied from 0.93 kg/t to 2.33 kg/t. The MIBC frother and yellow dextrin (coal depressant) dosages were kept constant at 0.11 and 0.93 kg/t, respectively. It is interesting to observe the large amount of collector required in the flotation of sulfide from coal compared to that used to recover sulfide minerals from metallic ores (0.10 to 0.25 kg/t). This is in agreement with Miller and Deurbrouck (1982) who reported that coal-sourced pyrite differs significantly from ore-sourced pyrite due to surface heterogeneities in the sulfide component, such as clay inclusions, which contribute to the hydrophilic character of the coal-pyrite; as a result, xanthate consumption is about one order of magnitude greater for coal-pyrite than for ore-pyrite.

Figure 4.9 shows the effect of collector dosage on the recovery of sulfur over 20 min of flotation time. As expected, flotation recovery increased with an increase in the collector concentration. As can also be seen, the recovery of sulfur to the concentrate was still

occurring at a measurable rate after 20 minutes of collection. At 0.93 kg/t of PAX, the lowest dosage, only 4.87% of the total sulfur mass reported to the concentrate. The mass yield at this dosage was 7.40%. The increase of collector dosage to 2.33 kg/t increased both the mass yield and sulfur recovery to 14.12% and 27.26%, respectively.

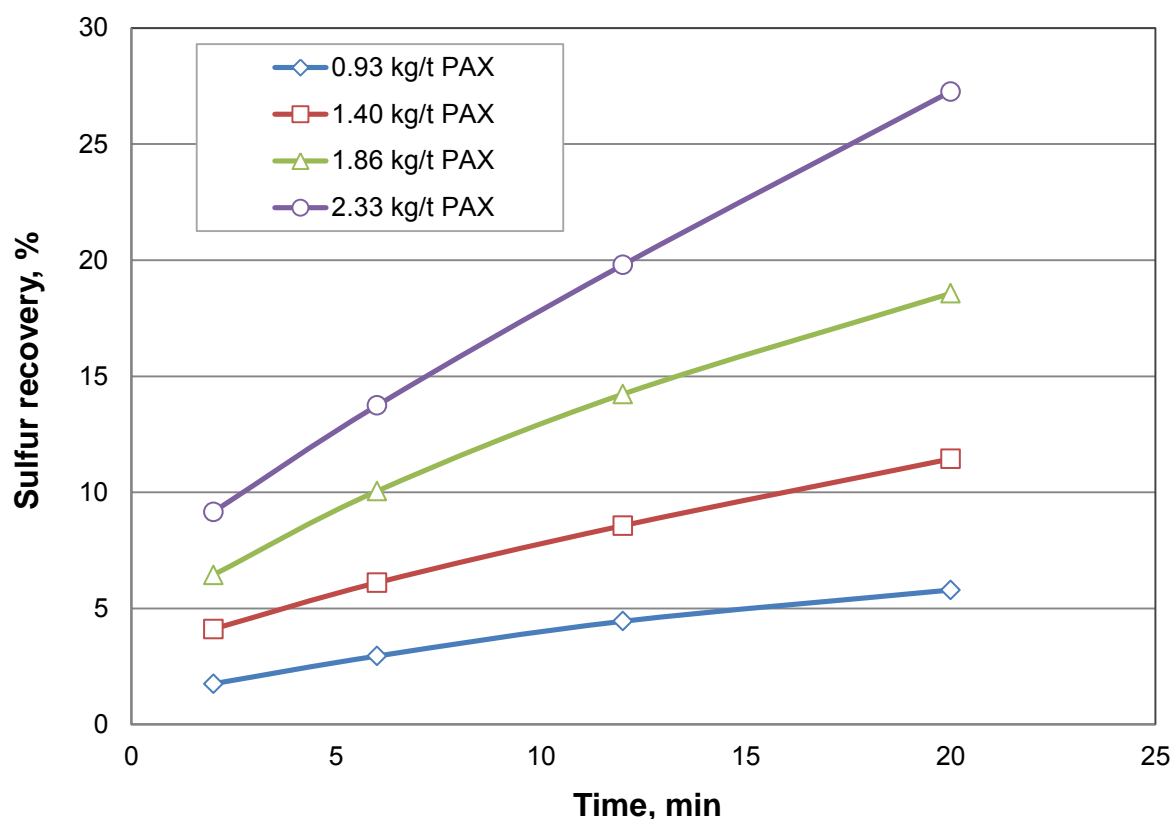


Figure 4.9: Kinetic flotation results for different dosages of potassium amyl xanthate (PAX) collector. MIBC frother and dextrin (coal depressant) were kept constant at 0.11 kg/t and 0.93 kg/t, respectively.

The grade of total sulfur increased as the collector dosage was increased, but at low dosage the grade of total sulfur was very low indicating that the coal was also floating, owing to its natural floatability. This also shows that the dextrin depressant was ineffective and inadequate as indicated by the poor ratio between sulfur and coal recovery, shown in Table 4.12. The poor depressant activity can be attributed to the oxidized nature of the coal. Dextrin is most strongly adsorbed on coals that are fresh, unoxidized and highly hydrophobic, and its adsorption by the coal surface decreases as the coal becomes more

oxidized (Miller *et al.*, 1984). To this end, a depression experiment carried out (section 4.4.5 below) provided more light on the response of coal toward sulfide flotation.

Table 4.12: Sulfide flotation results (after 20 min) with different dosages of PAX collector, 0.11 kg/t MIBC frother and 0.93 kg/t dextrin depressant

PAX dosage (kg/t)	Yield (%)	Concentrate sulfur (%)	Concentrate Ash (%)	Recovery ratio (sulfur: coal)
0.93	7.40	0.43	19.5	0.65
1.40	9.93	0.96	20.9	0.97
1.86	11.92	1.42	23.1	1.36
2.33	14.12	1.76	23.7	1.70

4.4.3 Stage-wise collector addition

In order to improve the sulfur recovery from the coal ultrafine waste, and thereby achieve a final tailing with as low a sulfur content as possible, sulfide flotation tests were performed with stage-wise addition of collector. This has been shown in the past to increase flotation yields and recoveries (Stonestreet, 1991; Wills, 1997). The conditions were similar to the previous single stage addition runs except that the total quantity of PAX was added in two or three stages. In addition, six concentrates, instead of four, were collected over 30 min for the 3-stage addition test. In practice, the collector was added incrementally and the pulp conditioned for 5 min after each addition. The frother MIBC and dextrin depressant were introduced into the pulp at the beginning in a single addition as described in Section 3.3.3.2. Table 4.13 summarizes the flotation results for 1-, 2- and 3-stage sulfide flotation runs in the presence of PAX as collector, dextrin as coal depressant and MIBC as frother.

As noted above (Table 4.12), addition of 2.33 kg/t PAX in one stage resulted in 27.26% sulfur recovery at 1.76% S. With a 2-stage addition, 38.30% (cumulative) sulfur recovery was obtained at 1.51% S grade, and with 3-stage addition, 42.13% (cumulative) sulfur recovery was obtained at 1.39% S. The mass yields obtained were 14.12%, 18.49% and 22.69%, respectively. The sulfur grade in the tailings was 0.56% S for both the 2-stage and 3-stage flotation, and 0.77% S for the 1-stage addition test. The corresponding coal recoveries were 23.10% at 23.7% ash in one stage; 21.69% at 22.6% ash and with 2 stages and 26.67% at 11.3% with 3 stages of collector addition. This provides the reason for the low sulfur content in the 3-stage addition test: the higher the coal content of the sulfide concentrate, the lower was the sulfur content. This suggests that the depression of coal was

reduced owing to longer collection time (30 min), resulting in greater recovery of coal into the concentrate. As a result, the ash content of the product was much lower in the 3-stage than in the 1-stage and 2-stage addition tests.

Table 4.13: Sulfide flotation results of stage-wise addition tests

	1-stage	2-stage	3-stage
Flotation time (min)	20	20	30
PAX dosage (kg/t)	2.33	1.4 + 0.93	1.39 + 0.47+ 0.47
Yield (%)	14.12	18.49	22.69
Sulfur grade (%)	1.76	1.51	1.39
Sulfur recovery (%)	27.26	38.30	42.13
Coal recovery (%)	16.00	21.69	26.67
Ash recovery (%)	10.24	12.29	15.04
Ash product (%)	23.7	22.6	11.3
Sulfur tailings	0.77	0.56	0.56
Recovery ratio (Sulfur/coal)	1.70	1.77	1.58

Figure 4.10 shows the recovery/time profile for sulfur. It can be seen that adding the collector in stages substantially increased the total sulfur recovery, especially in the 3-stage addition test. However, the results indicate that 2-stage collector addition gave the best overall separation in terms of residual total sulfur in the tailings, low yield and shorter collection time as compared to the 1- and 3-stage flotation tests.

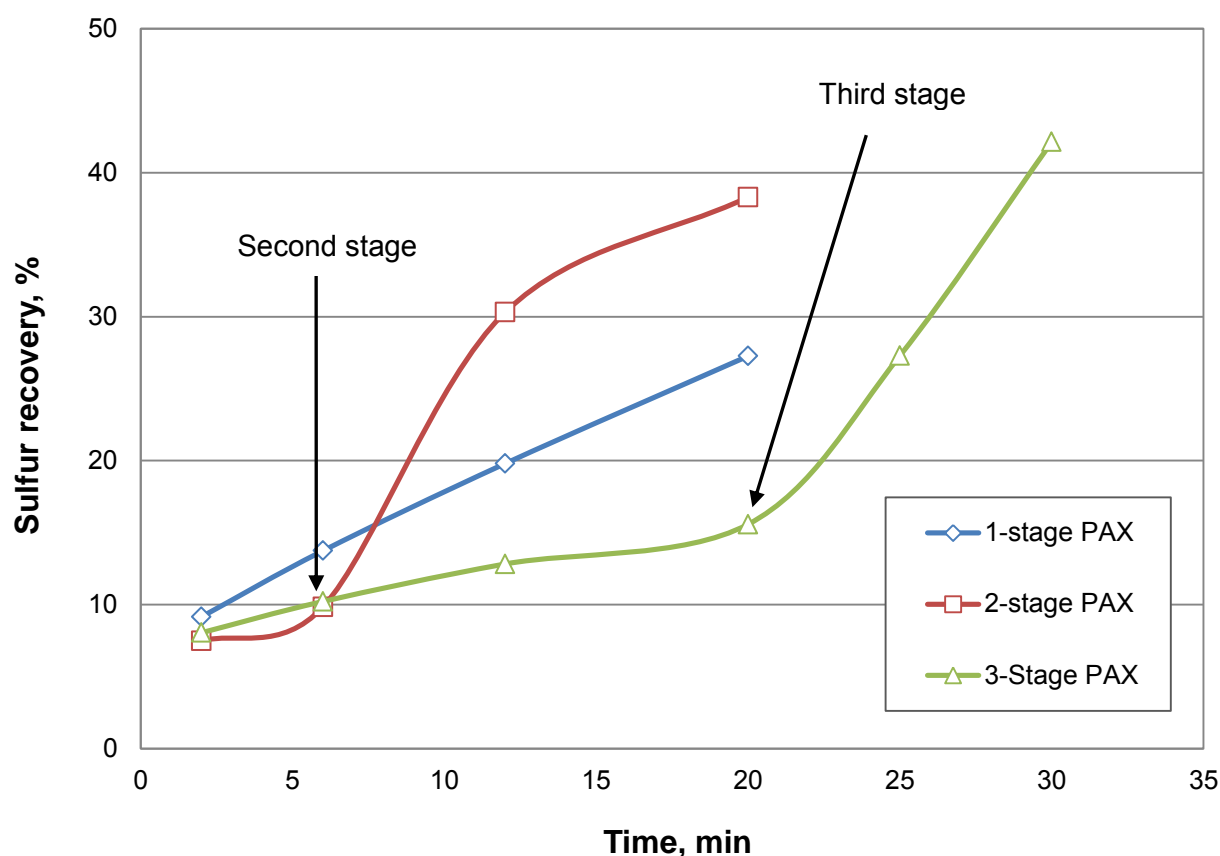


Figure 4.10: Sulfide flotation results for staged addition of collector PAX. MIBC frother and dextrin coal depressant were kept constant at 0.11 kg/t and 0.93 kg/t, respectively

4.4.4 Effect of frother addition

In this set of tests, the MIBC frother dosage was varied from 0.06 kg/t to 0.11 kg/t, while the PAX and dextrin dosages were kept constant at 2.33 and 1.4 kg/t. The influence of MIBC dosage on the sulfur recovery can be seen clearly in the Figure 4.11, which indicated that doubling the frother dosage did not have a considerable impact on the recovery of sulfur, which increased from 25.87 to 28.04% while the yield decreased from 15.23 to 13.71 %. As a result, the total sulfur grade increased from 1.01 to 1.34%.

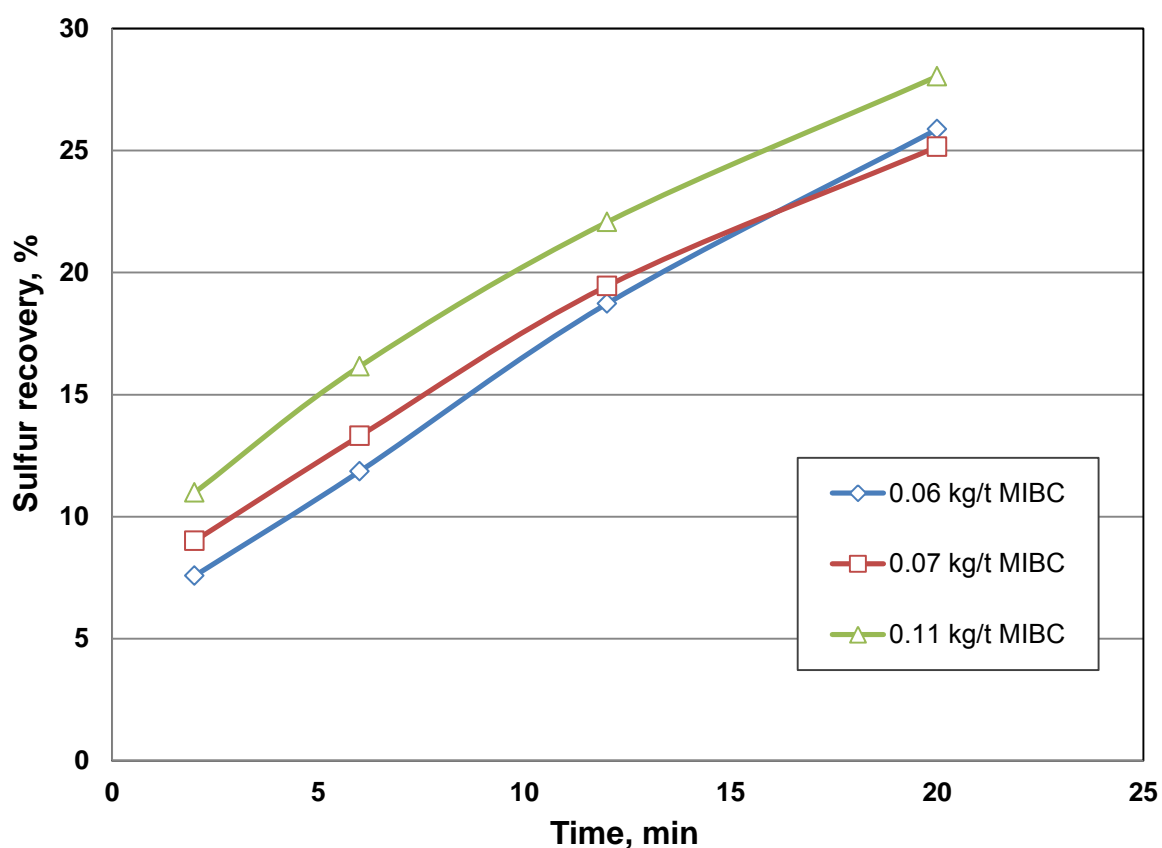


Figure 4.11: Kinetic flotation results of different dosages of MIBC frother. PAX collector and yellow dextrin (coal depressant) were kept constant at 2.33 and 1.4 kg/t, respectively.

4.4.5 Effect of depressant

In an attempt to reduce the deportment of coal into the sulfide concentrate and improve the recovery of sulfur, a set of flotation tests was carried out with different dosages of coal depressant. A depressant inhibits the flotation of a given mineral; its function is opposite to that of a collector. Any reagent which will oxidize the surface of coal, thus destroying its natural hydrophobicity, may be considered as a potential coal depressant. In this study, yellow dextrin was used as coal depressant, and its dosage was varied from 0.7 kg/t to 1.4 kg/t, while keeping the PAX collector and MIBC frother dosages constant at 1.4 and 0.11 kg/t, respectively. Figure 4.12 and Table 4.14 show that the addition of dextrin did not reduce the amount of floating coal substantially, but did reduce the recovery of total sulfur reporting to the concentrate. The recovery of coal at low dosage (0.7 kg/t) of dextrin was 13.13 %, and it dropped slightly to 11.71% when the dosage was doubled (1.4 kg/t). The increased level of dextrin had a negative impact on the froth structure and froth stability: each increase in the

dosage of the depressant was seen visually to decrease the stability of the froth and reduced the water recovery.

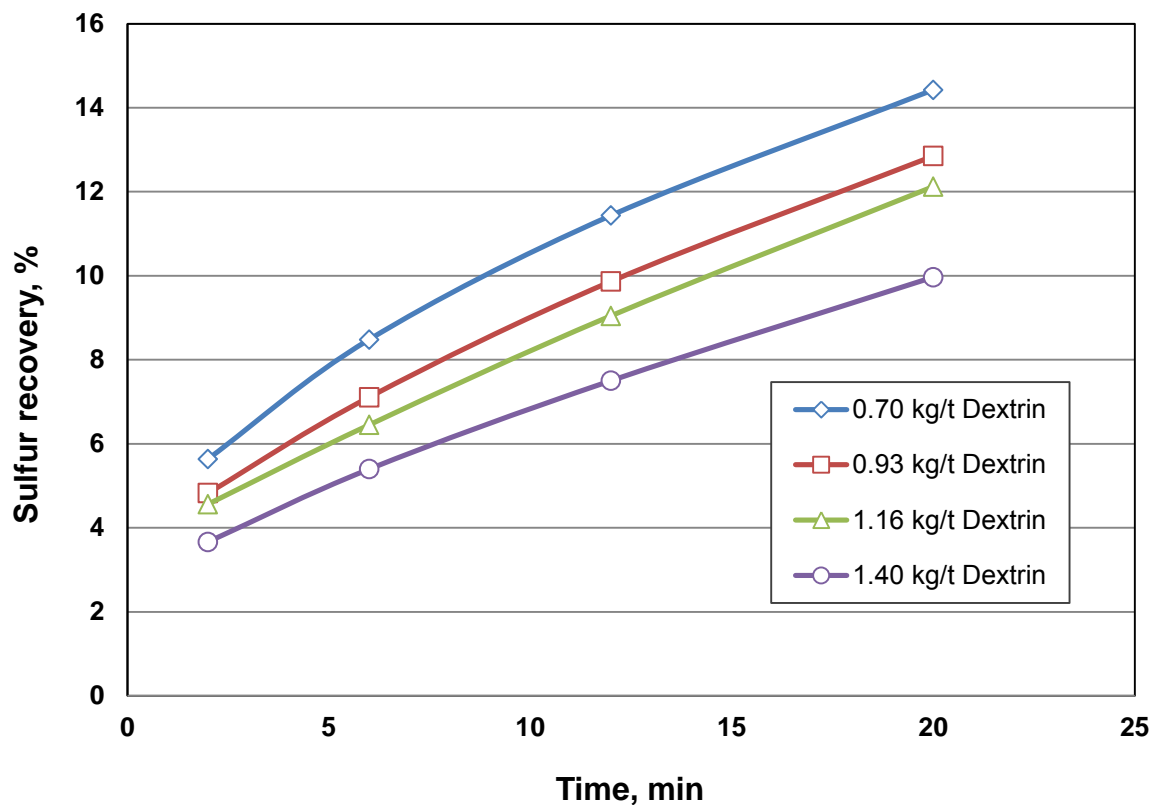


Figure 4.12: Kinetic flotation results for different dosages of yellow dextrin (coal depressant). PAX collector and MIBC frother were kept constant at 1.4 and 0.11 kg/t, respectively.

Table 4.14: Sulfide flotation results (after 20 min) with different dosages of dextrin depressant, 1.4 kg/t PAX collector 0.11 kg/t MIBC frother

Dextrin dosage (kg/t)	Yield (%)	Concentrate sulfur (%)	Concentrate Ash (%)	Residual ash (%)	Coal recovery (%)
0.70	11.28	1.07	21.8	34.2	13.13
0.93	9.93	1.11	20.9	34.5	11.74
1.16	10.11	1.00	21.9	34.2	11.78
1.40	10.19	0.75	22.8	34.0	11.71

The flotation performance clearly declined on increasing the dextrin dosage from 0.70 to 1.4 kg/t. This supports the earlier discussion that the coal under investigation may be oxidized. Fresh, unoxidized and highly hydrophobic coal strongly adsorbs dextrin, and its adsorption

by the coal surface decreases as the coal becomes more oxidized. Most coals are susceptible to oxidation by weathering, which begins as soon as the coal is mined and continues during transportation and storage. Oxidation processes result in the formation of oxygen functional groups, most commonly carboxyl, phenolic and carbonyl functionalities, on the coal surface, which reduce the hydrophobicity of the coal surface by increasing the number of sites that can hydrogen bond with water molecules. Increasing the dosage of dextrin affected not only the flotation of coal to the concentrate, but also inhibited the floatability of sulfide to some extent. This confirms the finding of Purcell and Aplan (1991) that most pyrite depressants are also coal depressants at a similar, though usually higher dosage. For example, many common starches are pyrite depressants at ≈ 0.1 kg/t but they are coal depressants at 0.3-1.0 kg/t (Purcell and Aplan, 1991).

4.5 SULFUR DEPARTMENT DURING FLOTATION

The results of the coal and pyrite flotation studies have highlighted the need for a more quantitative understanding of the department of the different sulfur species during flotation. This understanding was needed for a more accurate interpretation of both the two-stage flotation and ARD prediction tests. There are three forms of sulfur in coal: sulfide, organic and sulfate sulfur, which have different characteristics with regard to coal cleaning and in the release of pollution to the receiving environment.

The samples for sulfur speciation analysis were taken from the coal flotation test that was carried out using 2.79 kg/t of dodecane collector and 0.28 kg/t of MIBC frother; and the sulfide flotation experiment performed using 1.86 kg/t of PAX collector, 0.93 kg of dextrin coal depressant and 0.11 kg/t of MIBC frother. The sulfur speciation was carried out at ALS Laboratory according to ISO 157:1996, in which sulfate and sulfide sulfur content is determined, while the amount of organic sulfur is calculated by difference based on the total sulfur analysis determined according to the ASTM 4239:1997.

Table 4.15 shows the approximate proportion of the different sulfur forms in the feed, concentrates and tailings resulting from coal and pyrite flotation. The feed contained 1.08% total sulfur: 0.52% in the form of sulfide, 0.32% is in the form of sulfate and 0.25% in the form of organic sulfur. The XRD results indicated that the feed sample contained 1.52 % of gypsum, approximately 0.36% of sulfate sulfur. This shows that some of the pyrite present in the original coal underwent oxidation, because in unoxidized coal, sulfate salts such as

gypsum are present in small quantities, and are not a major source of sulfur. Oxidized coals, however frequently contain iron sulfates as a result of sulfide sulfur oxidation.

The amounts of sulfide, sulfate and organic sulfur in the tailings from coal flotation were 0.58% S, 0.01% S and 0.14% S, respectively, and 0.16%, 0.01% and 0.21%, respectively, in the clean coal. Since the sulfates are mostly soluble in water, the flotation process would have removed them almost completely; they should not be considered a serious source of sulfur in either the clean coal or the tailing, and would consequently have no appreciable impact in the generation of coalmine drainage. The organic sulfur is inherent to the coal structure and cannot be removed by flotation.

Table 4.15: Sulfur species department in selected coal and pyrite flotation products

	Sample	Total sulfur (%)	Forms of sulfur (wt %)		
			Sulfide	Sulfate	Organic
	Feed	1.08 ± 0.01	0.52 ± 0.01	0.32 ± 0.01	0.25 ± 0.02
Coal flotation; 2.79 kg/t dodecane, 0.28 kg/t MIBC, 5 min flotation time	Concentrate	0.37 ± 0.03	0.16 ± 0.01	0.01 ± 0	0.21 ± 0.04
	Tailings	0.73 ± 0.02	0.58 ± 0.01	0.01 ± 0	0.14 ± 0.03
Sulfide flotation; 1.86 kg/t PAX, 0.11 kg/t MIBC, 0.93 kg/t dextrin, 20 min flotation time	Concentrate	1.49 ± 0.01	1.12 ± 0	0.03 ± 0	0.34 ± 0.01
	Tailings	0.59 ± 0.02	0.42 ± 0.01	0.02 ± 0	0.15 ± 0.04

The speciation results from the sulfide flotation tests confirm that the sulfide sulfur can be removed by preparation means, such as flotation. However, if the pyrite is finely disseminated as in the case of South African coal (Gondwana coal), locking may restrict its removal. The concentrate contained 1.49% total sulfur: 1.12% in the form of sulfide and 0.34% in the form of organic sulfur, which was bound in the structure of coal, and floated along with the sulfide. The presence in the sulfide concentrate of organic sulfur, closely bound to/within the coal macromolecule structure appears to be largely due to inadequate depression of coal during desulfurization flotation.

The department of sulfur during sulfide flotation depended on the size distribution of the coal sample. Because sulfide was thought to be finely disseminated in the as-received coal, it was rod-milled prior to flotation. The influence of particle size distribution on the flotation response is given in Figure 4.13, which shows that rod-milling the coal for 20 minutes

improved the total sulfur recovery from 22.60 to 27.59 % and the sulfur grade from 1.52 to 1.76%. The yield decreased from 18.36 to 14.12 % due to reduction of entrainment of coal that reported to the concentrate. The increase of the total sulfur recovery can be attributed to the liberation of locked sulfide minerals and the fact that fine coal and pyrite particles float more readily than do the corresponding coarse particles. However, as Table 4.15 shows, even when the coal was ground to a finer size, there were still a substantial number of pyritic particles that were bound to coal macromolecules. These locked particles did not float and were left behind in the tailing sulfide flotation. These results suggest that only sulfide minerals that are liberated can be separated from coal.

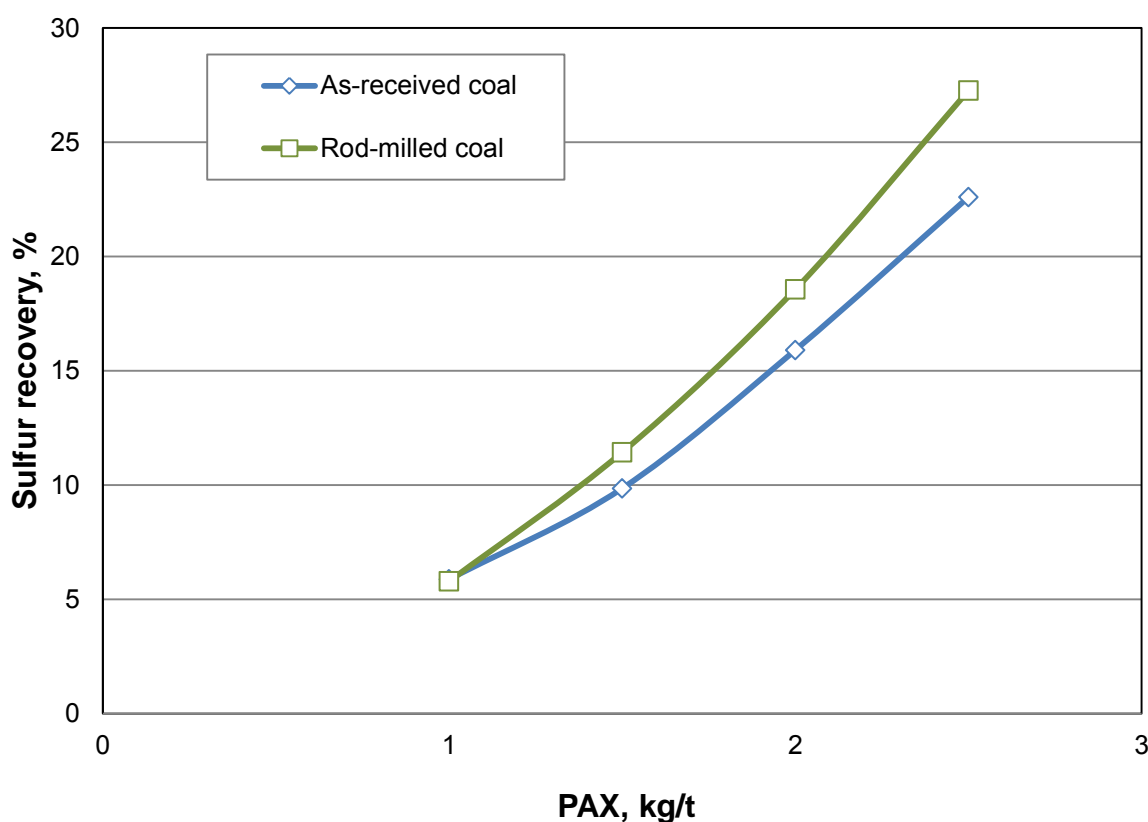


Figure 4.13: Effect of particle size distribution on the recovery of sulfur of as-received and rod-milled coal samples at different PAX collector dosages. Dextrin depressant and MIBC frother were kept constant at 0.93 kg/t and 0.11 kg//t, respectively.

4.6 TWO-STAGE FLOTATION

An experiment was carried out to test the feasibility of the concept outlined in Figure 1.2, in which coal flotation is followed by a sulfide flotation stage to enable recovery of a coal rich

stream (concentrate 1) and a benign tailings as the major stream (tailings 2). The experiment reported below aimed to show, at the laboratory scale, the technical feasibility of mitigating the generation of ARD in a two-stage flotation process. In the first stage valuable coal was recovered from the coal ultrafines in the froth; in the second stage the tailing was reprocessed to remove the sulfide minerals, in particular pyrite that may contribute to environmental damage, to produce a low-sulfur tailings that was not acid-generating.

This is different from the two-stage froth flotation process developed by Miller (1975), in which the first-stage clean coal froth concentrate is repulped in fresh water, and a pyrite collector, a frother and coal depressant added to float the remaining pyritic material in an attempt to reduce SO₂ pollution into the atmosphere. In the conceptual approach adopted in this research, the tailing from the first stage was re-floated using a coal depressant and pyrite collector with a view to mitigate the ARD risks to the receiving environment. Three fractions resulted from this two-stage flotation process: the valuable coal that can be converted into saleable products, an environmentally benign tailings that can be disposed of safely, and a small sulfide-rich fraction.

The first stage was performed following the procedure outlined in Section 3.3.2.2, using 1.86 kg/t dodecane as collector and 0.11 kg/t MIBC as frother, except that the pulp density was 10%. In the second stage, the first-stage tailings was conditioned with 1.93 kg/t PAX as collector, 0.93 kg/t dextrin as depressant and 0.11 kg/t MIBC as frother. The tailing from the coal flotation test was dried and weighed before being used as feed in the second-stage, which was conducted according to the procedure outline in Section 3.3.3.2. The detailed results of the two-stage flotation tests can be found in the Section D.1 of Appendix D.

Table 4.16 shows the feed compositions, reagent dosages and the mass balances for coal and total sulfur over the two stages, based on 100 units of feed. The clean coal yield of approximately 19.7% had a low ash content of 13.5% and a low sulfur content of 0.48% S; while the tailings of the first stage contained 0.92% S. The majority of the fresh feed material reported to the tailings of the second stage (67.2 %) and was characterized by a high ash (40%) and low total sulfur (0.38% S) content. The second stage recovered a low volume sulfide rich fraction (2.68% total sulfur) to the concentrate which may be amenable to bio-desulfurization. All products were assessed to ascertain their ARD generation potential as reported in the next Chapter.

The conceptual flow sheet of the overall process is described in the Figure 4.14, which demonstrates the impact of the concept outlined on Figure 1.3 by showing the proportional

mass balance for the material over the two-stage flotation process. The performance and selectivity of the process was clearly shown by the low sulfur content of the second-stage tailing (0.38%) and the low ash content of the clean coal product (13.5%).

Table 4.16: Two stage flotation results (first stage: coal flotation; second stage: sulfide flotation).

Product	Amount	Weight percent	
		Ash	Total Sulfur
<u>First Stage</u>			
Reagent addition:	1.86 kg/t Dodecane		
	0.11 kg/t MIBC		
Feed	100	34.4	1.08
Clean coal (concentrate)	19.7	13.5	0.48
Tailings	80.3	38.8	0.92
<u>Second Stage</u>			
Reagent addition:	2.33 kg/t PAX		
	0.11 kg/t MIBC		
	0.93 kg/t Dextrin		
Feed (tailings from stage 1)	80.3	38.8	0.92
Sulfide concentrate	13.1	28.9	2.68
“Benign” Tailings	67.2	40.8	0.38

According to the flow sheet, the amount of total sulfur was reduced by approximately 75% in the benign tailing; the majority of the sulfur in “the environmentally benign waste” was in the form of organic sulfur, as a result of the greater part of the pyrite having been removed in the second flotation stage. Even though, in this research, the process was not optimized, the clean coal yield was nearly 20 % of the total feed mass, with low sulfur content (0.48 %) and a saleable ash content (13.5%). The results obtained in Section 4.3.3 suggest that if the first stage flotation was conducted with oleic acid as collector, the clean coal yield could have been considerably higher, with a similar sulfur content. The reduction in the amount of coal in the second stage feed could play a key role in decreasing the large dosage of PAX collector and increasing the sulfur grade in the “sulfide-rich waste”, because of less interaction between the collector and the coal particles. As a result, the quantity of

“environmentally benign waste” for disposal might be even lower, possibly with lower sulfur content.

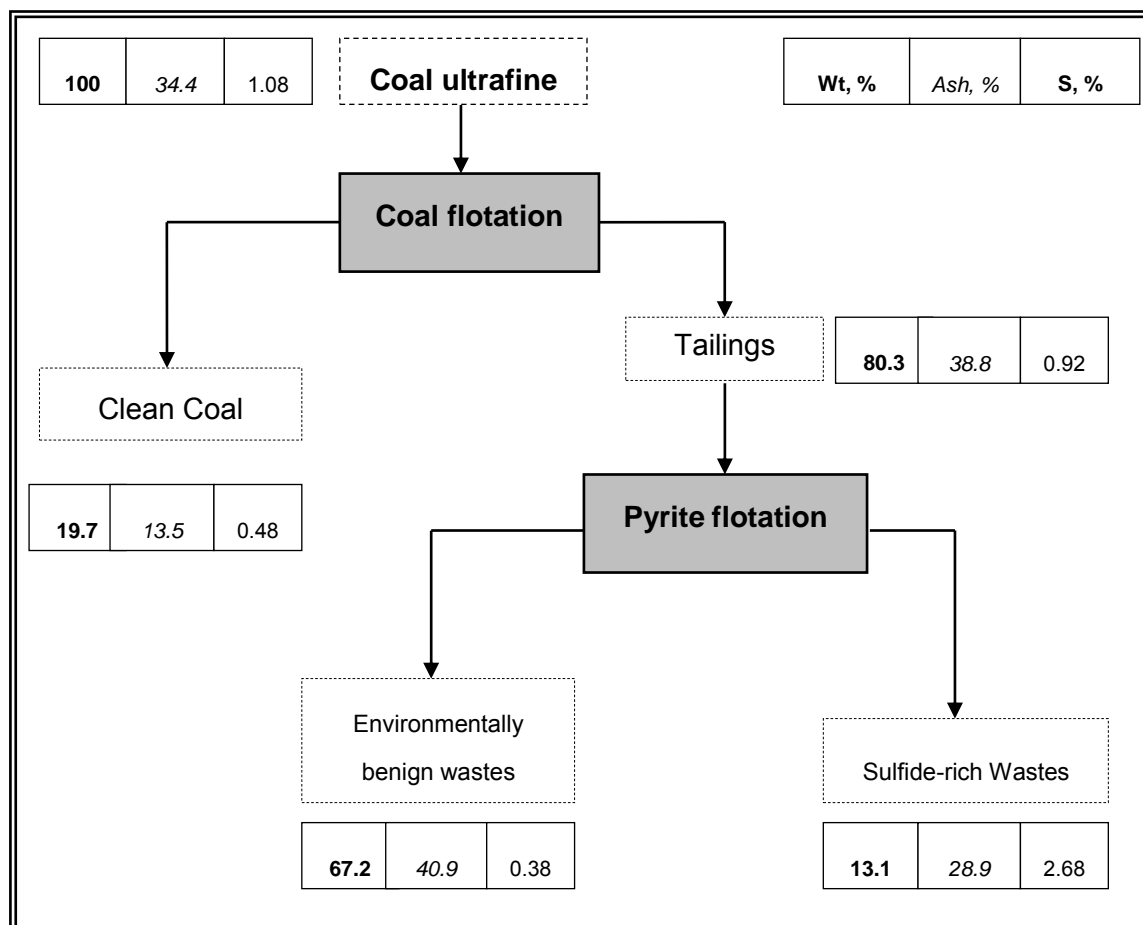


Figure 4.14: Conceptual flow sheet for coal ultrafine in two stage flotation process including coal and pyrite flotation

It should be noted that the sulfur content of both the tailings and concentrate of stage 1 are lower than in the feed. The original feed sample contained sulfide, organic sulfur and sulfate sulfur, the latter resulting possibly from the oxidation of sulfide minerals. The sulfates are mostly soluble in water and, therefore would not be present in either the tailings or clean coal. This accounts for the incomplete mass balance of sulfur in the solid phase across the first stage as indicated in Table 4.17. The overall difference Δ across the two stage-stage process is 0.36 units, a little bit higher to 0.32 units of sulfate in the sulfur speciation analysis (Table 4.3).

Table 4.17: Mass balance across all ash and total sulfur for the first and second stages

Flotation process	Stream	Mass (units)	Ash (units)	Total sulfur (units)
First stage	Feed	100	34.4	1.08
	Clean coal	19.7	2.66	0.09
	Tailings	80.3	31.16	0.75
	Δ	0	0.58	0.24
Second stage	Feed	80.3	31.16	0.75
	Sulfide concentrate	13.1	3.79	0.35
	“Benign” Tailings	67.2	27.43	0.26
	Δ	0	-0.06	0.14

4.7 CHAPTER SUMMARY

In this chapter of the dissertation, the recovery and desulfurization of coal through the application of froth flotation techniques were investigated systematically through laboratory batch flotation tests under various conditions in order to determine the technical feasibility of reclaiming valuable coal and selectively removing the acid-generating materials from coal ultrafines. The effects of key parameters, in particular reagents addition, and the extent of both coal yield and recovery in a direct coal float, and sulfide sulfur removal from the tailing, were investigated.

The experimental work was carried out using a thickener underflow (roughly 98.4% passing 850 μm) sample from a processing coal plant in the Middleburg area, South Africa; the sample was rod-milled to 75% passing – 150 μm to produce material suitable for flotation work. The petrographic analysis showed that the sample was a low medium bituminous coal with a high inertinite content, which predisposes the coal to respond poorly to froth flotation. Sulfur speciation analysis indicated that half of the total sulfur content was in the form of sulfide sulfur, while approximately 30% was sulfate sulfur resulting from the oxidation of sulfides.

Initial coal flotation experiments using dodecane collector and MIBC frother to investigate the extent of coal recovery, confirmed that the coal was difficult to float. The petrographic composition of the coal combined with the high ash content in the feed coal and oxidation due to weathering all resulted in poor flotation performance even in the presence of high concentration of reagents. Nevertheless, the concentrates were of high grade (low ash content), indicating that the affinity of dodecane in the presence of MIBC was good. Further

coal flotation experiments using oleic acid as collector gave much better results in terms of yield and recovery, owing to the collecting mechanism of this unsaturated fatty acid.

Sulfide flotation tests were carried out to investigate the possibility of removing sulfur-bearing minerals from coal in one or more stages. Staged addition of PAX collector provided enhanced total sulfur recovery and low sulfur content in the tailing, but a substantial amount of coal reported also reported to the concentrate, indicating inadequate depression.

The two-stage flotation process proposed in Figure 1.2 of this dissertation was also investigated in laboratory batch flotation tests, with no attempt to optimize the process at this point. Three fractions were produced: 19.7% of the fresh feed was recovered as clean coal product, containing 13.5% ash and 0.48% S; 67.2% was recovered with a high ash (40.9%) and low sulfur (0.40%) content; and 13.1% was recovered as a sulfur with concentrate containing 2.68% S. The performance and selectivity of the process were clearly shown by the high sulfur content of the second-stage concentrate and the low ash and sulfur content of the clean coal product. The first stage showed low recovery or yield, the coal recovery had a good grade (13.5%) with low content of sulfur (0.48%). The second stage demonstrated the recovery of a low volume sulfide rich fraction (2.68% total sulfur). All three fractions were subjected to ARD prediction tests to determine their acid-generating potential, as presented and discussed in the next Chapter.

CHAPTER 5

RESULTS AND DISCUSSION: ARD PREDICTION TESTS

5.1 INTRODUCTION

The previous chapter presented the investigation into the beneficiation of coal ultrafine wastes by froth flotation techniques to determine the extent of coal recovery and tailings desulfurization. The main objective of the two-stage flotation process investigated was to produce a saleable clean coal fraction, a sulfide-rich concentrate from which sulfur might eventually be recovered, and a sulfide-lean fraction with enough acid neutralizing capacity to safely compensate for its acid potential, to allow it to be discarded. Since this project seeks to reduce the adverse impacts on the environment in terms of the generation of acid rock drainage (ARD), it was considered imperative to evaluate the acid generating potential of the flotation input and outputs to be able to say that the high-volume wastes produced from the two-stage flotation process are benign. The prediction of ARD risks would provide evidence that the tailings can be disposed of under environmentally safe conditions, and ensure that the main objective of this study has been achieved.

Consequently, in order to establish the technical feasibility of the two-stage flotation process with regard to mitigation of long-term risks associated with coal, the feed, concentrate and tailing samples from both coal and sulfide flotation were evaluated in terms of their acid generating potential. This chapter presents the results of acid base accounting (ABA) and net acid generation (NAG) tests, and the biological kinetic flask test, on these samples. Three samples from direct sulfide flotation were also evaluated in terms of their potential to generate ARD: direct sulfide flotation might be used in cases of coal processing wastes with little or no economical value, but which nevertheless represent a risk of perpetual pollution to the environment.

Table 5.1a gives the sulfur content of the feed and four products from the two-stage flotation test (Section 4.6). The samples are designated by their acronyms, defined as follows: 1T and 1C are tailings and concentrate, respectively, from coal flotation; 2T and 2C are

generated from the second stage sulfide flotation. Table 5.1b shows the sulfur content of the products generated from sulfide flotation with 1-stage, 2-stage and 3-stage addition of amyl xanthate collector, respectively (Section 4.4.3).

Table 5.1a: Sulfur content of the samples used in ARD prediction tests for the feed and two-stage flotation outputs.

Legend	Samples	Sulfur content (%)
F	Feed	1.08
1T	First stage tailing	0.92
1C	Clean coal	0.48
2T	Second stage tailing	0.38
2C	Sulfide-rich fraction	2.68

Table 5.1b: Sulfur content of the samples used in ARD prediction tests for the tailings from sulfide flotation tests.

Legend	Samples	Sulfur content (%)
3T	1-stage (collector addition) tailing	0.73
4T	2-stage (collector addition) tailing	0.55
5T	3-stage (collector addition) tailing	0.56

Appendix C outlines the details of the standard ARD prediction methods, which included ABA, single NAG, sequential NAG, and biokinetic tests. The static test criteria outlined in Table 3.2, re-inserted below for ease of reference, were used in order to determine if the samples are acid or non-acid generating. Net acid production potential (NAPP) and net acid generation (NAG) test results were used in combination to provide a more reliable classification of acid potential.

Table 3.2: Classification for results of static tests (Stewart et. al., 2006; Hesketh et. al., 2010a)

ARD prediction tests	Result	Units	Classification guideline
Acid Base Accounting (ANC)	NAPP > 20 -20 < NAPP < 20 NAPP < -20	kg H ₂ SO ₄ /t kg H ₂ SO ₄ /t kg H ₂ SO ₄ /t	Acid forming Potentially acid forming (PAF) Non acid forming (NAF)
Net Acid Generation (NAG)	NAG pH < 4 & NAG _{pH7} > 10 NAG pH > 4 & NAG _{pH7} = 5-10 NAG pH > 4	kg H ₂ SO ₄ /t kg H ₂ SO ₄ /t pH	Acid Forming Potentially acid forming (PAF) Non acid forming (NAF)
Combined static tests	NAG pH < 4.5 and NAPP > 0 NAG pH > 4.5 and NAPP < 0		Potentially acid forming (PAF) Non acid forming (NAF)

If these criteria fail, the results are considered uncertain and further testing is required for classification.

5.2 STATIC TEST RESULTS

5.2.1 Acid base accounting (ABA) test

The results of ABA tests are expressed as net acid producing potential (NAPP) which gives the balance between the acid forming capacity (maximum potential acidity, MPA) and the acid neutralization capacity (ANC), in terms of kg H₂SO₄/t. The NAPP gives the theoretically determined amount of acid that a sample can produce. The results of the acid base accounting (ABA) tests, given in Table 5.2a, show that the feed coal had a positive NAPP; therefore it was potentially[‡] acid-generating according to the classification outlined in Table 3.2. This is as expected: the feed sample was selected on the basis that it exhibited acid generating potential, otherwise it was not going to reflect the objective of this study.

Outputs from the first stage of flotation were potentially acid-generating: the tailing and concentrate streams had NAPP values of -8.27 kg H₂SO₄/t and -6.24 kg H₂SO₄/t, respectively. This result indicates that the first stage flotation tailings were more acid-neutralizing, as a result of ash-forming minerals, including carbonates, being wetted and

[‡] The NAPP value of the feed is quite low, indicating a slight acid-generating potential.

reporting to the tailings. The NAPP values of the tailings and concentrate from the second stage flotation were $-45.17 \text{ kg H}_2\text{SO}_4/\text{t}$ and $64.78 \text{ kg H}_2\text{SO}_4/\text{t}$, respectively. This suggests that most of the sulfide minerals reported to the concentrate. As expected, the final tailing was non-acid forming (NAF) and the sulfide-rich fraction was strongly acid-forming as a result of selective separation during the second stage flotation. This indicates that the benign residue from the two-stage flotation process has enough neutralizing potential necessary to safely compensate for its acidity. As the total sulfur decreased down to 0.38% from a feed of 1.08%, the acid generating potential decreased to an acceptable level as far as mitigation measures are concerned. The acid generating potential of a sample is directly proportional to the amount of sulfide it contains and its acid neutralization potential.

Table 5.2a: Acid base accounting results for feed, tailings and concentrates from two-stage flotation

Sample	S grade (%)	MPA ($\text{H}_2\text{SO}_4 \text{ kg/t}$)	Fizz Rating	ANC ($\text{H}_2\text{SO}_4 \text{ kg/t}$)	NAPP ($\text{H}_2\text{SO}_4 \text{ kg/t}$)	Classification
F	1.08	33.05	1	29.86 ± 0.72	3.19	PAF
1T	0.92	27.85	1	36.11 ± 0.90	-8.27	PAF
1C	0.48	14.69	1	20.93 ± 1.08	-6.24	PAF
2T	0.38	11.32	2	56.49 ± 0.84	-45.17	NAF
2C	2.67	81.70	1	17.23 ± 1.62	64.48	Acid forming

Table 5.2b shows the NAPP results of the three tailings generated when floating sulfide directly from the feed sample (i.e without recovering coal in a previous stage). The 3T sample resulting from a single addition of xanthate was potentially acid-forming, whereas 4T and 5T, resulting from 2 stage- and 3 stage-addition of xanthate, respectively, were both non-acid forming. This indicates that more sulfide sulfur reported to the concentrate when the amyl xanthate collector was added incrementally to the flotation cell, increasing the amount of acid buffering material in the tailings as a result. Thus stage-wise addition of the collector has produced a sulfide-lean fraction with high acid neutralizing capacity, which can be disposed of safely without risk of harming the receiving environment. This is a useful finding: this scenario may be necessary and applicable in the case of coal processing wastes with little economical value that nevertheless present a risk of ARD pollution.

Table 5.2b: Acid base accounting test results for tailings from sulfide flotation experiments

Sample	S grade (%)	MPA (H ₂ SO ₄ kg/t)	Fizz Rating	ANC (H ₂ SO ₄ kg/t)	NAPP (H ₂ SO ₄ kg/t)	Classification
3T	0.73	22.34	1	33.82 ± 0.18	-11.48	PAF
4T	0.55	16.83	2	52.92 ± 0.84	-36.09	NAF
5T	0.56	17.14	2	46.98 ± 12.6	-29.84	NAF

5.2.2 Net acid generation (NAG) test

The NAG test measures the overall acid forming potential of a sample by allowing both the acid forming and acid neutralizing reactions to occur simultaneously, using H₂O₂ as oxidant. The final solution after complete reaction is a direct measure of the net acid generated by the sample. Tables 5.3a and 5.3b summarize the results of the net acid generation (NAG) tests, displaying the pH of leachate produced and the equivalent acid produced per ton, for pH 4.5 and 7. Samples were classified according to the criteria outlined in Table 3.2.

Table 5.3a: Net acid generation (NAG) test results for feed, tailings and concentrates from two-stage flotation process

Sample	S grade (%)	NAG pH	NAG pH 4.5 (kg H ₂ SO ₄ /t)	NAG pH7 (kg H ₂ SO ₄ /t)	Classification
F	1.08	3.97 ± 0.02	4.51 ± 0.55	26.26 ± 1.11	Acid forming
1T	0.92	4.28 ± 0.04	1.76 ± 0.28	22.83 ± 0.14	Acid forming
1C	0.48	3.24 ± 0.06	26.36 ± 2.08	43.51 ± 0.83	Acid forming
2T	0.38	5.39 ± 0.11	0	6.86 ± 1.11	NAF
2C	2.67	2.13 ± 0.01	60.66 ± 1.80	14.80 ± 2.91	Acid forming

Table 5.3b: Net acid generation (NAG) test results for tailings from sulfide flotation runs

Sample	S grade (%)	NAG pH	NAG pH 4.5 (kg H ₂ SO ₄ /t)	NAG pH7 (kg H ₂ SO ₄ /t)	Classification
3T	0.73	4.36 ± 0.04	1.18 ± 0.28	25.8 ± 0.42	Acid forming
4T	0.55	4.62 ± 0.12	0	23.4 ± 3.19	NAF
5T	0.56	5.33 ± 0	0	7.15 ± 0.14	NAF

In accordance with the NAG test results, the feed sample (F) had a NAGpH < 4, and was thus classified as acid generating. The concentrate from the coal flotation stage (1C) also had NAGpH < 4, showing that it was also acid generating, even though the total sulfur grade was lower than in the tailings sample, which had a NAGpH > 4. This results from the considerable ANC present in the tailings (i.e. carbonates, silicates and clays). Furthermore, the NAG value at pH 4.5, evaluating the amount of sulfide minerals, is higher in the concentrate (1C) than in the tailings (1T). This confirms that a considerable amount of sulfide reported to the concentrate at the same time as the clean coal. This is in agreement with the tendency of coal-sourced pyrite to float more rapidly than ore-sourced pyrite during coal flotation (Hirt and Aplan, 1991).[§]

As expected, the sulfide-rich concentrate resulting from the second stage flotation (2C) was acid-forming with a NAGpH of 2.13 and NAG value of 60.7 kg H₂SO₄/t at pH 4.5. The tailings generated from the second stage flotation (2T) were non-acid generating as conceptualized. This result shows that sulfide minerals reported to the concentrate during sulfide flotation, reducing the acid generating potential of the tailings.

Based on the deportment of sulfur during flotation reported in Table 4.11, another possible explanation of sample 1C exhibiting acid generating characteristics could be the formation of organic acid during digestion. The sample is carbonaceous (coal) and has low S (0.48% S), and the low NAGpH value measured may be attributable to the presence of organic acids. This would confirm the finding of Stewart *et al.* (2003), who indicated that the effects of organic acid are only a significant issue in carbonaceous (>5% organic C) samples with low S (0.7%). The combination of NAG and NAPP provides a better assessment of this sample in terms of classification (see Section 5.2.3 below).

As seen in Table 5.3b, the NAG results of the tailing samples produced from sulfide flotation confirm the ABA results: stage-wise addition of the collector has produced sulfide-lean tailings. One stage collector addition generated a tailing that exhibited acid forming

[§] This does not contradict the statement on sulfide flotation (*cf* page 73) that coal-sourced pyrite differs significantly from ore-sourced pyrite due to surface heterogeneities in the sulfide component, such as clay inclusions, which contribute to the hydrophilic character of the coal-pyrite; as a result, xanthate consumption is about one order of magnitude greater for coal-pyrite than for ore-pyrite (Miller and Deurbrouck, 1982).

characteristics, showing that the influence of the collector on sulfide deportment to the concentrate was low.

During NAG testing, the sulfide-rich concentrate (2C) sample caused excessive temperature rise, indicating decomposition of the hydrogen peroxide (H_2O_2) before the completion of the oxidation reaction of pyrite during digestion. Stewart *et al.* (2006) highlighted that a sequential NAG test is normally used to provide a total acid producing potential for samples with pyritic sulfur greater than 0.7 to 1%S. For this reason, it was necessary to carry out a sequential NAG test of four stages on the sample (2C) to produce a total acid potential. Table 5.4 shows the results of the sequential NAG testing performed on this sample.

Table 5.4: Sequential NAG stage for sample 2C with high content of total sulfur

Stage	S grade (%)	NAG pH	NAG pH 4.5 (kg H_2SO_4/t)	NAG pH7 (kg H_2SO_4/t)	Classification
1	2.67	2.13 ± 0.01	60.66 ± 1.8	14.80 ± 2.91	Acid forming
2	-	3.02 ± 0.01	13.23 ± 0.01	27.95 ± 0.02	Acid forming
3	-	3.72 ± 0.04	5.22 ± 1.30	16.51 ± 2.68	Acid forming
4	-	4.63 ± 0.08	0	6.29 ± 1.89	NAF

According to the sequential NAG test results, sample 2C was acid generating until the fourth stage, which produced a NAG solution with a pH greater than 4.5. The total acid potential generated at pH 4.5 and pH 7 were 77.11 and 65.55 kg H_2SO_4/t , respectively. The results confirm that the sulfide concentrate from the second stage flotation was chemically reactive (acid-generating), which is consistent with the single addition NAG result. However, although this sulfide-rich fraction is acid forming, it can be managed more safely and easily due to its reduced volume; it may also be amenable to bio-desulfurization.

5.2.3 Comparison between ABA and NAG results

Table 5.5 shows the ABA and NAG test results for the feed, concentrates and tailings resulting from coal and sulfide flotation. As indicated in Table 3.2, a sample is classified PAF when it has a NAGpH < 4.5 and NAPP > 0, and NAF when NAGpH ≥ 4.5 and NAPP < 0. Samples are classified UC when there is an apparent conflict between the NAGpH and NAPP results.

Table 5.5: NAPP and NAG test results for the feed, concentrates and tailings from flotation

Sample	Total S	MPA	ANC	NAPP	NAGpH	NAGpH4.5	NAGpH7	ARD Classification
	%	kg H ₂ SO ₄ /t				kg H ₂ SO ₄ /t		
Feed	1.08	33.05	29.86	3.19	3.97	4.51	26.26	PAF
1T	0.92	27.85	36.11	-8.27	4.28	1.76	22.83	UC
1C	0.48	14.69	20.93	-6.24	3.24	26.36	43.51	UC
2T	0.38	11.32	56.49	-45.17	5.39	0	6.86	NAF
2C	2.68	81.70	17.23	64.48	2.13	60.66	14.80	PAF
3T	0.71	22.34	33.82	-11.48	4.36	1.18	25.77	UC
4T	0.55	16.83	52.92	-36.09	4.62	0	23.42	NAF
5T	0.55	17.14	46.98	-29.84	5.33	0	7.15	NAF

Figure 5.1 plots the results of single addition NAG tests in conjunction with NAPP values to classify samples according to their acid forming potential. Three different classifications are indicated: potentially acid forming (PAF), non-acid forming (NAF) and uncertain (UC). The final tailings resulting from desulfurizing flotation (2T), representing some 67% of the starting material by mass, appears in the upper left hand domain with a negative NAPP value and NAGpH value over 4.5, therefore it is classified non acid-forming and can be considered environmentally benign. The feed (F) and the sulfide-rich fraction (2C) had positive NAPP values and NAGpH values below 4.5, and hence were potentially acid generating. The tailing (1T) and concentrate (1C) samples from coal flotation were situated in the uncertain zone.

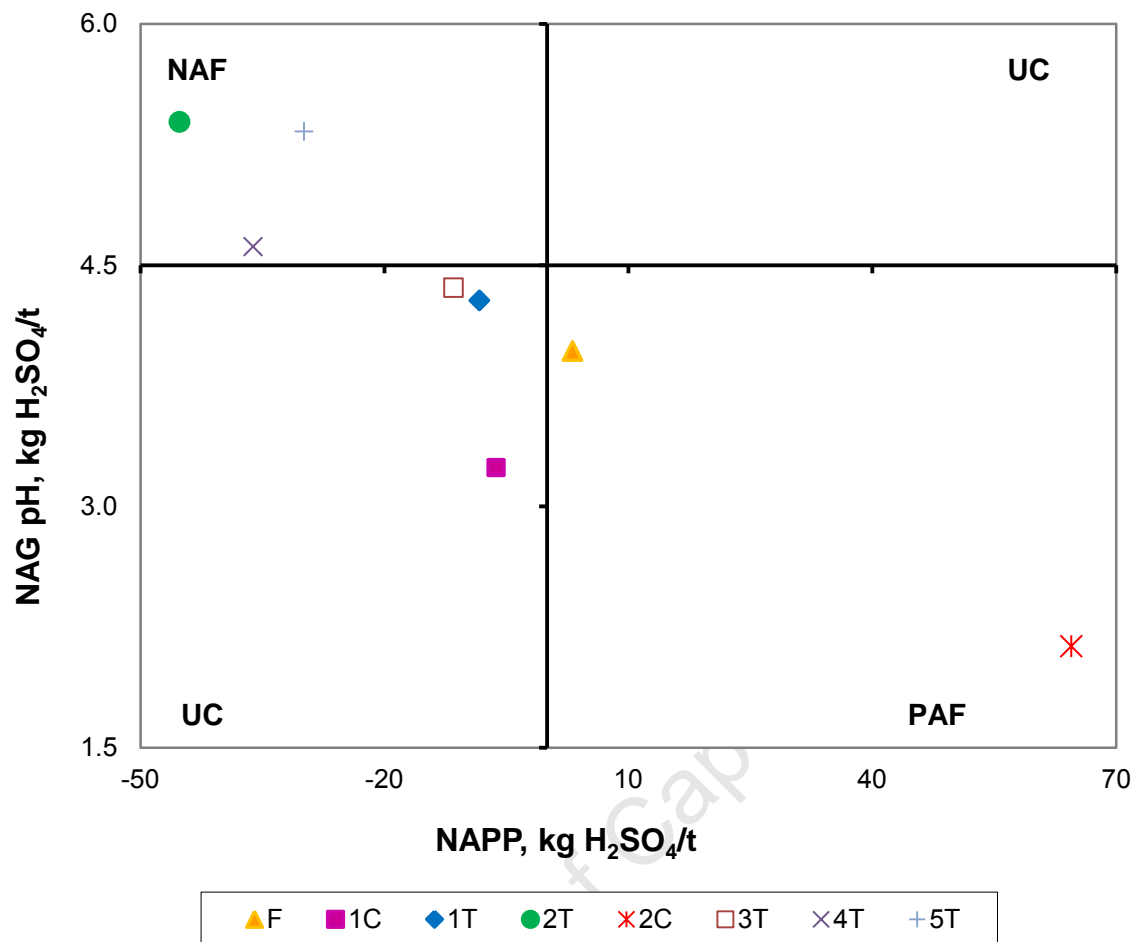


Figure 5.1: ARD classification plot showing NAGpH versus NAPP for flotation outputs and feed

5.3 BIOKINETIC TEST RESULTS

The biokinetic shake-flask test described in Section 3.4.4 was used to confirm the results of the ABA and NAG tests, to classify these samples with respect to their leachability in the presence of micro-organisms and to provide information on the relative timing of liberation of acid neutralising capacity and acid generation. Hesketh *et al.* (2010b) recommended the addition of the biokinetic test to the suite of tests used to evaluate the acid-generating potential of materials. To this end, the five samples from the two-stage flotation tests (namely F, 1T, 1C, 2T, and 2C) were selected for biokinetic testing and are reported in this section.

Each inoculated experiment was carried out in triplicate under non-sterile and controlled temperature conditions. The influence of microorganisms on the process and associated leaching of sulfide minerals was estimated by the pH, redox potential (Eh) (against a Ag/AgCl reference electrode) and the concentration of dissolved ferric iron in solution over a period of 76 days. At the beginning of the test, after determination of the pH of the pulp, the flasks were weighed and the weight was recorded. The flasks were then clamped to the shaker platform and the apparatus was started up. Agitation was interrupted at fixed time intervals and the weight of the flasks recorded. The initial weight was restored by adding distilled water to compensate for evaporation.

The pH profiles are represented in Figure 5.2. The initial pH for all the samples was set at pH 2 and not adjusted during the leaching process. The initial acidic pH is advantageous in accelerating microbial leaching (Acharya *et al.*, 2001) and can reduce the lag-phase of the bacteria and prevent the precipitation of jarosites and other ferric salts on the coal surface which may inhibit the oxidation of pyrite within the coal grain.

At the start of each biokinetic test, the pH increased as a result of carbonate dissolution. This initial increase in pH can be related to the period during which the metabolism of the microorganisms adjusted to the environmental conditions, and is consistent with the acid neutralizing capacity of the same materials presented in Table 5.2a. Accordingly, the pH profiles of the samples in the biokinetic assays on days 4 to 7 correlate with the ANC values, with the sample with the highest ANC value yielding the highest pH value between days 4 and 7.

Following the attainment of redox values of 600 mV or greater by day 4, sulfide leaching by the ferric ions and protons took place, with acid generation and neutralization occurring simultaneously. This led to a decrease or stabilization of the pH, depending on the availability of acid generating capacity. The pH decreased in all the samples from day 4, except for the low sulfur final tailings sample (2T). In this tailings sample, the pH increased gradually to around pH 2.60 by day 16 whereafter it remained constant. For all other samples, the rate of decrease of the pH from day 4, better considered in terms of release of protons, was influenced by the combination of ANC and the sulfur content of the sample. The pH of the biokinetic test of the feed sample decreased from pH 2.4 on day 4 to pH 2.2 some 20 days later, at which point it stabilized. The pH of the sulfur-rich concentrate sample (2C) decreased from pH 2.1 to pH 1.9 over a 20 day period, continuing to decrease until the

49th day, when it stabilized around pH 1.75 for the remainder of the biokinetic test. Although the sulfur content of the clean coal is close to the sulfur content of the final tailing, their pH graphs present different behaviors. This may be related to the forms of sulfur and ash in each sample.

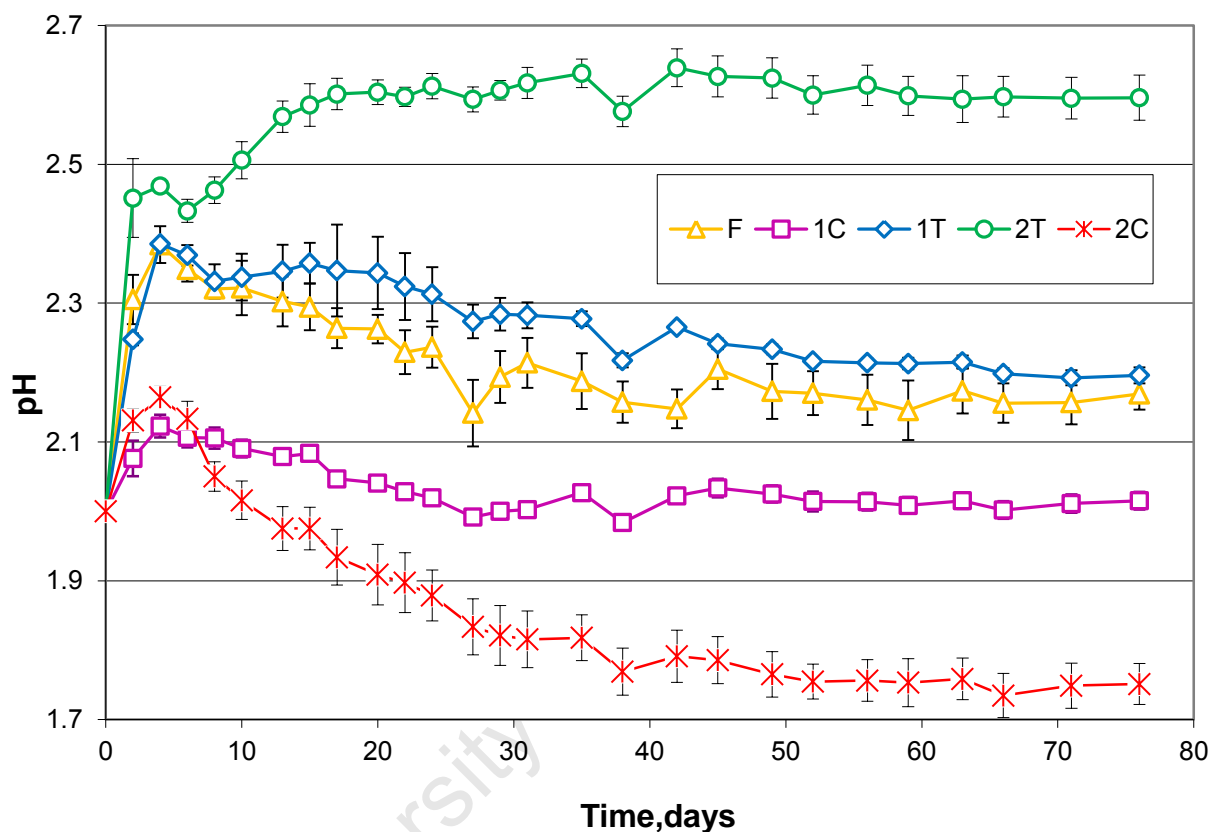


Figure 5.2: Average pH with time during the shake flask biokinetic tests performed on feed (F) flotation and products (1C, 1T, 2T, 2C).

Figure 5.3 shows the pH profiles of the feed and final tailing, and of the final tailings sample controlled at pH 2 and in the absence of bacteria (abiotic). In the constant pH test, drops of sulfuric acid were added from a burette to maintain the pH steady at pH 2. After 20 days, the pH remained steady or varied by a few decimal points until the end of the biokinetic process, and the amount of sulfuric acid added was a reliable estimate of acid consumption by the sample. A total of approximately 19 kg H₂SO₄/t was consumed by the sample over the first 20 days, indicating that the majority of the acid-consuming material had been depleted within this time. According to this biokinetic leach test, the condition of oxidation was optimal at pH 2, while the leach test in the absence of microorganism indicated pH values ranging between

5.8 and 6.3: this shows that the oxidation of ferrous iron was limited under abiotic conditions. The results of the test controlled at pH 2 suggest that the maintenance of the pH in the preferred range for microbial iron and sulfur oxidation was also important for ferric ion and acid regeneration by the microbial regeneration.

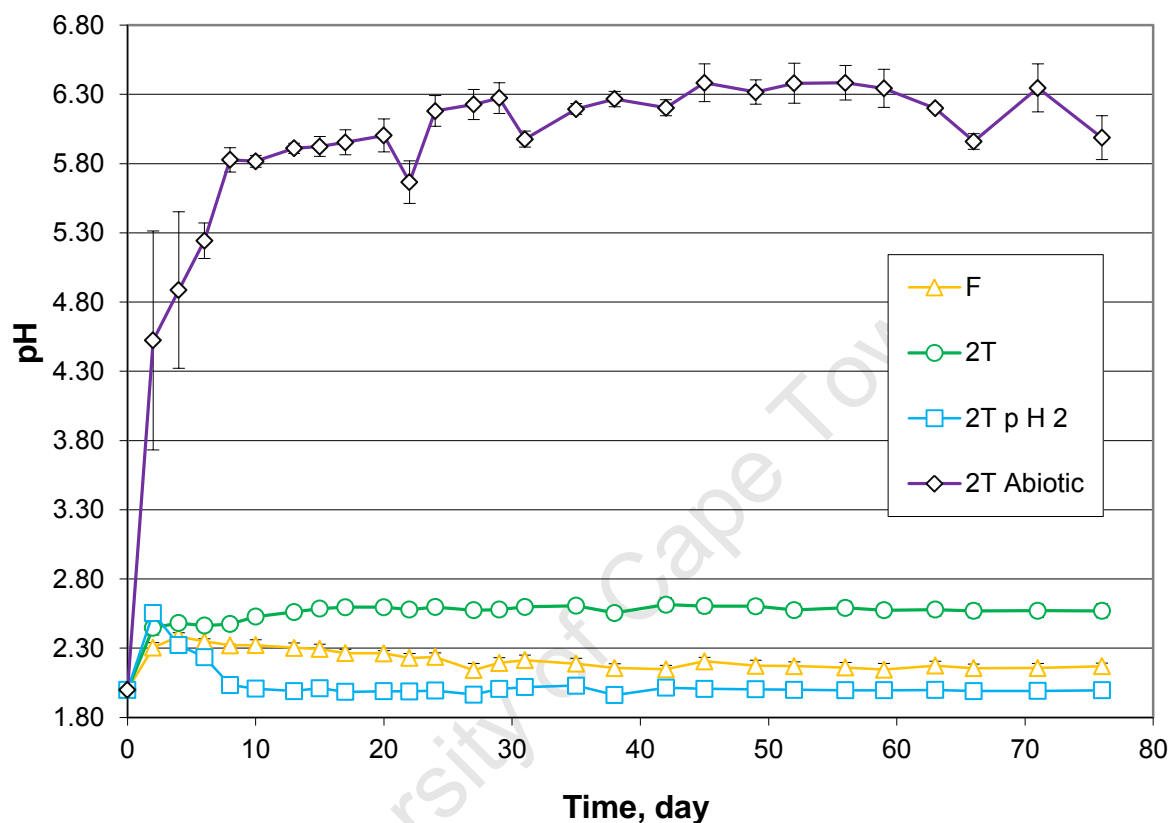


Figure 5.3: Average pH with time during the shake flask biokinetic tests performed on the feed (F) and the final tailing (2T), and the final tailings sample controlled at pH 2 and in the absence of bacteria (abiotic).

Figure 5.4 presents the behavior of the redox potential during the biokinetic test relative to the Ag/AgCl reference electrode. The redox potential gives an indication of the oxidizing conditions being maintained throughout the experiment in terms of the relative ratio of ferrous to ferric iron, through the Nernst equation. In all cases the microbial activity was evident by the increase of the redox potential, with values above 670 mV attained in the inoculated samples indicating efficient microbial ferrous iron oxidation, ensuring the ferric iron speciation was dominant thereby providing favorable conditions for pyrite leaching. A high redox potential of around 720 mV in the case of sample 2C, which contained large

amount of sulfur, suggests that the cultures had grown faster, resulting in sulfide oxidation. The redox potential increased to 680 mV for both the feed (F) and the tailing (1T) resulting from coal flotation, providing an oxidative environment for the reaction to occur. Although the redox potential of the clean coal sample (1C) increased to the same values, the dissolution of the sulfur-bearing minerals seemed to be low. It is unclear why this should be so.

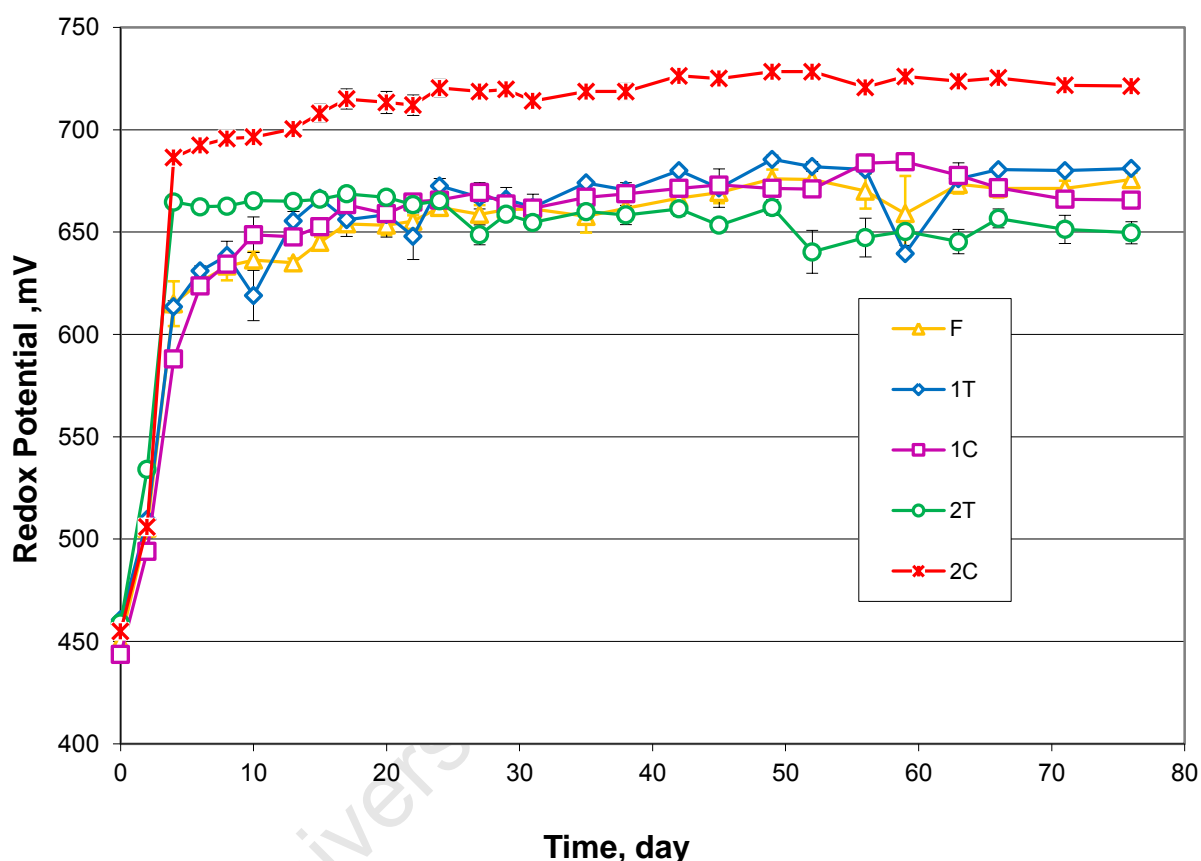


Figure 5.4: Eh evolution graphs for the shake flask biokinetic tests performed on the flotation feed (F) and products (1C, 1T, 2T, 2C).

Figure 5.5 shows the evolution of the redox potential in the biokinetic tests carried out on the feed and final tailings, and on the final tailings sample controlled sample at pH 2 and under abiotic conditions (cf Figure 5.3). As long as the solution pH remained stabilized in the range suitable for microbial oxidation, the controlled pH sample (2T pH 2) showed redox potential greater than the final tailings sample (2T). This shows that a pH of around 2 was suitable for microbial growth and activity. The results also indicate that more sulfide leaching could be achieved when the sample is co-disposed in acidic environment, even though the sulfur

content of the sample was low. It should be pointed out, however, that although the controlled pH sample was active, no significant potential redox was observed with the abiotic sample, in the absence of the sulfur- and iron-oxidizing bacteria.

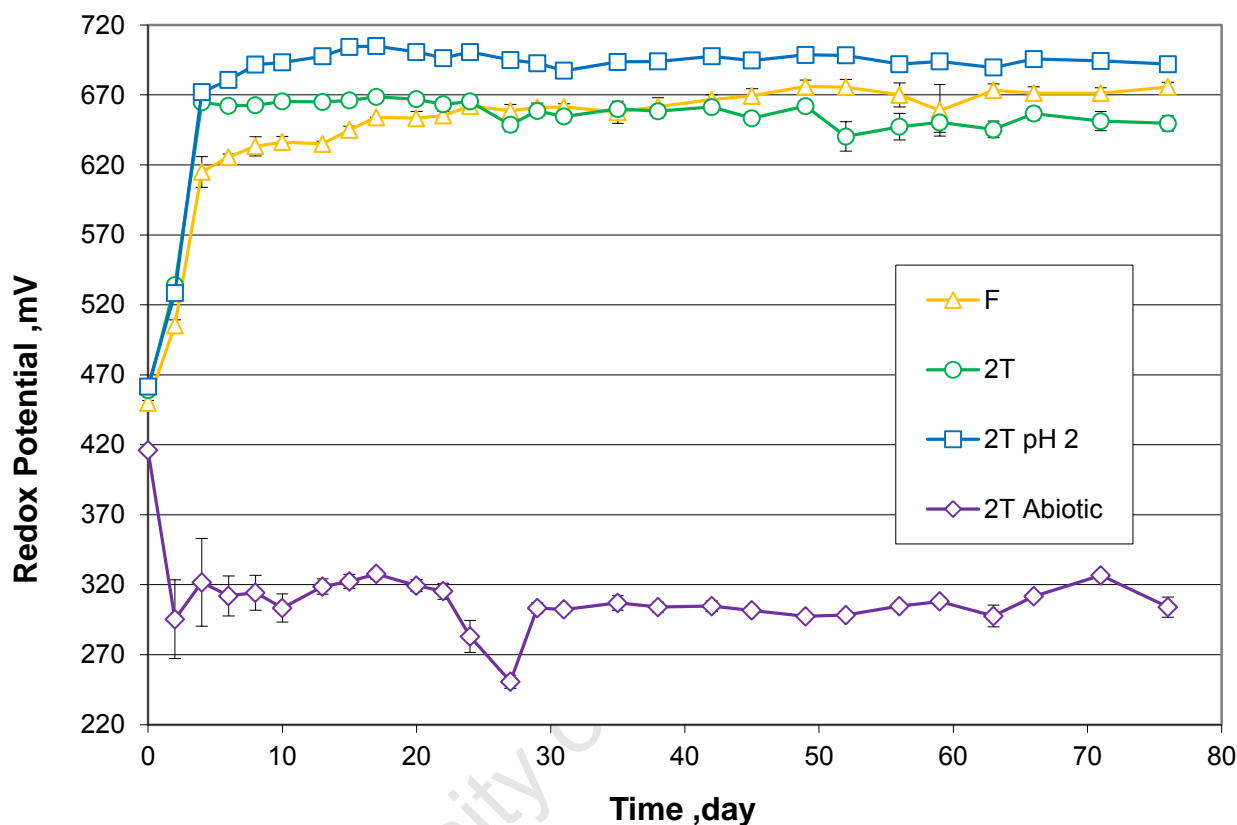


Figure 5.5: Eh evolution graphs for the shake flask biokinetic tests performed on the feed (F) and the final tailing (2T), and the final tailings sample controlled at pH 2 and in the absence of bacteria (abiotic).

The high redox potential indicates that iron in solution was predominantly present as ferric iron. The profile of ferric iron concentration with time is shown in Figure 5.6. Despite the high Eh values suggesting a suitable oxidizing environment in all biokinetic tests, there was no significant release of ferric iron into solution for all samples, except for the concentrate product (2C) with the highest content of sulfur. This sample showed dissolution of 1155 mg iron /L by day 52 as a result of high pyrite oxidation and total sulfur removal. This release of iron and its subsequent oxidation to ferric iron augments pyrite leaching. The slight decrease in ferric iron concentration after day 54 for sample 2C and between day 4 and 15 for the remaining samples (F, 1C, 1T, 2T) can be explained either by the depletion of sulfur-bearing

minerals corresponding to slow microbial growth or by the precipitation of iron as jarosite, particularly with increasing pH. As the literature suggests, the occurrence of jarosite is due to the solubility limit of iron and sulfates, leading to the formation of layers on the coal surface acting as a barrier for chemical reactions (Cardona and Márquez, 2009).** Even though the redox potential of the final tailings sample 2T increased considerably until day 4, the concentration of ferric iron in solution decreased from 217 mg/L on day 2 to 62 mg/L at the end of the process.

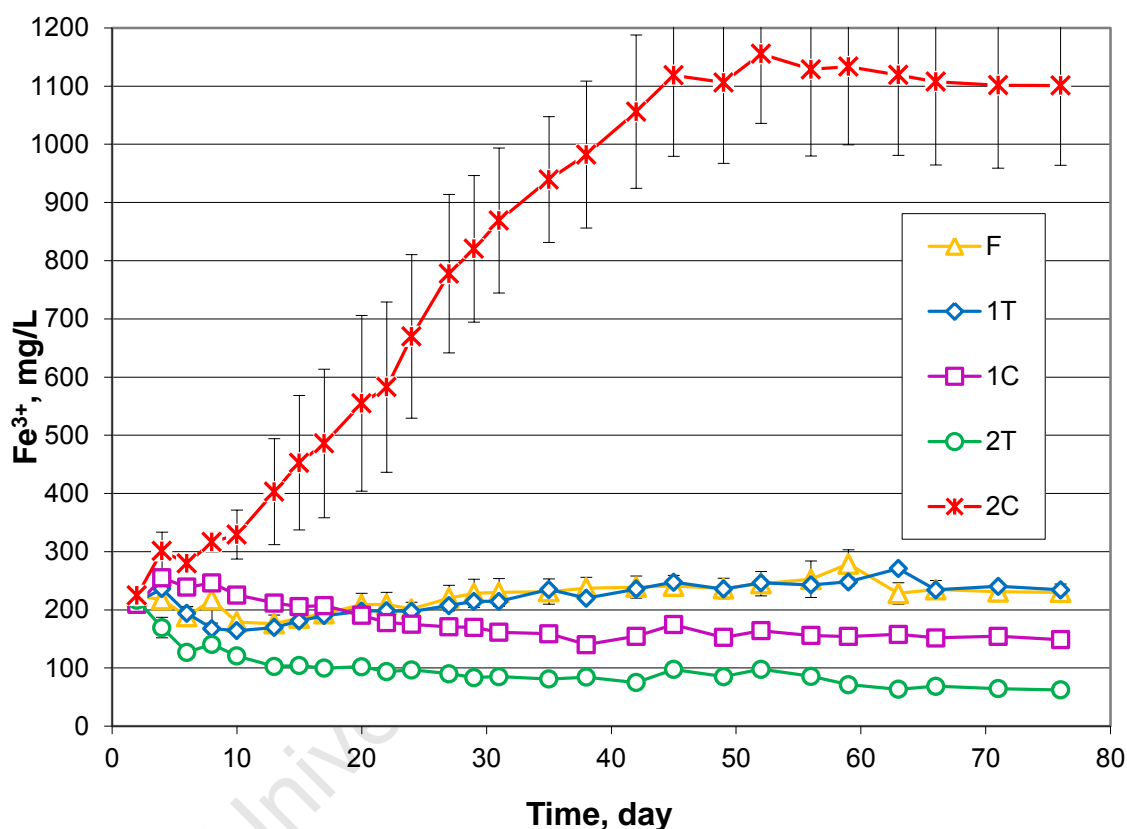


Figure 5.6: Ferric iron evolution graphs for the shake flask biokinetic tests performed on the flotation feed (F) and products (1C, 1T, 2T, 2C).

The profile of ferric iron concentration with time for the controlled experiments is shown in Figure 5.7. Evidence of microbial activity under the controlled pH conditions is provided by the behavior of soluble ferric iron, which increased to a concentration of approximately 370

** Alternatively the observed decrease may be the result of experimental error.

mg/L in the first 20 days, whereafter a gradual decrease was observed, due likely to the formation and precipitation of jarosite. In the sample without pH control the ferric concentration was approximately 90 mg/L after 20 days. Due to the absence of microorganisms, the abiotic experiment did not show appreciable concentration of ferric iron greater than 50 mg/L.

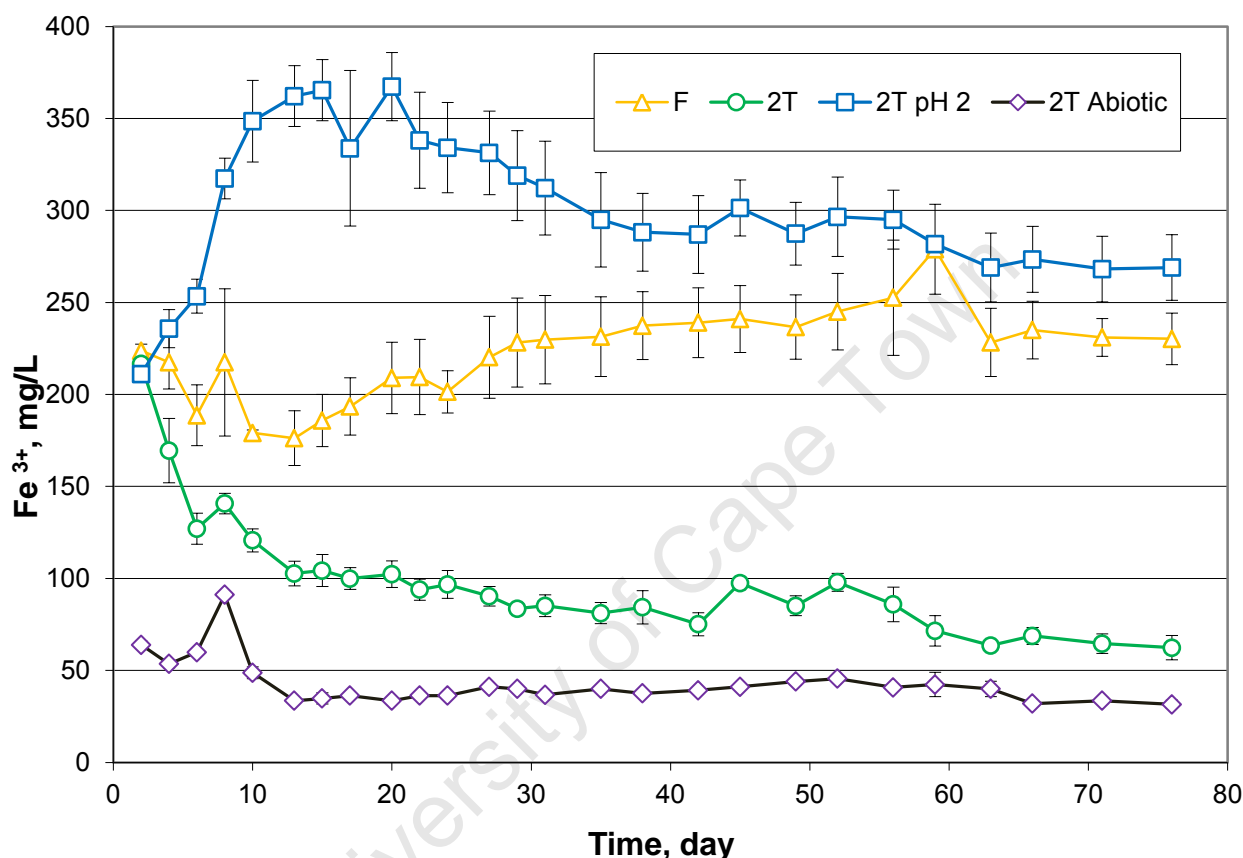


Figure 5.7: Ferric iron evolution graphs for the shake flask biokinetic tests performed on the feed (F) and the final tailing (2T), and the final tailings sample controlled at pH 2 and in the absence of bacteria (abiotic).

Biokinetic tests were followed by sulfur and ash analyses carried out on the residues. Table 5.6 shows the sulfur reduction, which is defined as the percentage change in the amount of sulfur in the residue after the biokinetic test. The chemical analysis performed on the residue indicated a total sulfur composition of 0.40% in the sulfide-rich concentrate sample (2C) from a feed of 2.68% S. The sulfur reduction was approximately 85%, indicating high microbial activity and the oxidation of sulfide sulfur during the process. This result suggests that this concentrate is indeed amenable to bio-desulfurization due to the high content of pyritic sulfur

providing a suitable environment for the culture of microorganisms to thrive. It is important to note that the biokinetic experimental methodology is the same as that used in the bio-desulfurization of coal in terms of physical, chemical and biological factors influencing pyrite removal (Zhang *et al.*, 2008).

The ash level in all the biokinetic residues was reduced owing to dissolution of various minerals from the samples. The ash reduction of the sulfide-rich sample was the highest, approximately 20 wt%; this was probably due to the extremely acidic conditions imposed by the experimental process.

Table 5.6: Total sulfur reduction of residues from biokinetic tests

Sample	Total sulfur (%)			Ash (%)		
	Before	Residue	reduction	Before	Residue	reduction
F	1.08	0.55	48.8	34.4	31.5	8.5
1 T	0.92	0.52	42.7	39.0	36.5	6.3
1 C	0.48	0.40	16.9	13.5	13.2	2.4
2T	0.40	0.38	6.0	40.9	38.6	5.6
2 T pH 2	0.40	0.32	20.3	40.9	37.8	7.5
2 C	2.68	0.40	85.3	28.6	22.9	20.1
2 T Abiotic	0.40	0.40	0.0	40.9	38.6	5.5

5.4 COMPARISON OF STATIC AND BIO-KINETIC TESTS

Biokinetic tests were carried out in an attempt to validate the results of the static tests carried out on the coal flotation products to characterize their ARD generation potential. Table 5.7 summarizes the key findings of the biokinetic tests over 76 days in terms of pH, and provides a comparison with the static ARD prediction test results. There is a consistency between the trends in the ANC results (both as pH and acid generation) and the pH profiles of the biokinetic tests. For example, the final tailings (2T) with a high ANC and low S content, hence MPA (see Table 5.2a above), showed a corresponding high pH in the biokinetic experiment with no subsequent acidification, while the final concentrate sample (2C), with

the lowest ANC value and high S content, showed the lowest pH with substantial acidification observed following the initial release of neutralizing capacity.

Table 5.7: Comparison of static and biokinetic ARD test results

Sample	Static test				Biokinetic test				
	S %	ANC	NAGpH	Classification	pH, day 7	pH, day 22	pH, day 38	pH, day 76	Classification
Feed	1.08	29.86	3.97	Acid forming	2.32	2.26	2.16	2.17	Acid forming
1T	0.92	36.11	4.28	Acid forming	2.33	2.34	2.22	2.20	Acid forming
1C	0.48	20.93	3.24	Acid forming	2.11	2.04	1.98	2.02	Acid forming
2T	0.38	56.49	5.39	NAF	2.48	2.60	2.62	2.57	NAF
2C	2.68	17.23	2.13	Acid forming	2.05	1.91	1.77	1.75	Acid forming

In the classification of samples based on the biokinetic test, samples in which the liberation of neutralizing capacity resulted in an increased pH with no subsequent decrease due to acid formation were classified as non-acid forming. Where the initial neutralization was followed by acidification such that the pH decreased below pH 2.5, samples were classified as acid forming. The biokinetic test provides extended data over the static tests, particularly in terms of the rate of release of neutralization capacity and of acidification, as well as the potential for the sample to acidify. These are critical data for prediction of behavior in the field.

5.5 CHAPTER SUMMARY

Static and biokinetic tests were performed to study the acid-generating behavior of the feed and outputs from different flotation runs, in particular the two-stage flotation process. The results showed that the final tailings resulting from the second stage flotation test were non-acid generating according to the ABA test, while the two other products of the process were acid generating. The feed sample also exhibited acid-generating properties. These results were confirmed and validated by the net acid generation (NAG) test. In accordance with NAG test results, the feed sample was classified as acid generating, while the benign tailings

was not acid generating, as a result of sulfide mineral reporting to the concentrate during the second stage (sulfide) flotation thereby reducing the acid-generating potential.

The combination of net acid generation (NAG) and acid base accounting (ABA) tests show that the final tailing was non acid-forming, while the feed and the sulfide-rich fraction, with positive NAPP values and NAGpH values below 4.5, were potentially acid generating. According to this classification, the final tailing (2T) sample resulting from desulfurizing flotation was non-acid-forming, and thus considered environmentally benign.

As expected the pH values showed a typical behavior during the biokinetic tests, where at the start there was a pH increase as a result of carbonates dissolution, during which the metabolism of microorganisms readjusted to the environmental conditions. The sulfur-rich concentrate from the second stage flotation tests showed a larger sulfide oxidation rate, as demonstrated by the lowest pH values during the leaching process. These were consistent with the ANC values of the same materials: when plotted, the pH profile of the samples were in order of decreasing ANC values, with the sample with highest ANC value on top and the one with lowest value at the bottom. The pH profile of the feed sample, with an in-between ANC value, appears between the high and low acidic samples.

Despite the fact that high Eh values suggested suitable oxidizing environments throughout the experiments, there was no significant change in the profile of the ferric iron concentration for all samples, except for the sample with the highest content of sulfur (2C), which showed greater dissolution of iron. The considerably higher ferric iron concentration was likely to be the major factor responsible for the high oxidation. Although the Eh profile of the final tailing (2T) increased considerably at the start of the biokinetic test, the concentration of ferric iron in solution was the lowest and decreased from 216 mg/L on the second day to 62 mg/L at the end of the process. From these results, it can be concluded that the desulfurized fraction would not be non-problematic in terms of acid-generating behavior and would be able to be disposed of safely in slimes dams.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This chapter consolidates the findings of this exploratory study into mitigating the ARD risks associated with coal ultrafines. The main objective of this research was to develop, in concept, a two-stage flotation process that will mitigate the generation of acid rock drainage (ARD) from South African coal ultrafines, and simultaneously recover valuable coal from these wastes. The goal was to identify a technological ARD pollution reduction strategy which is not based solely on the application of end-of-pipe abatement strategies.

The proposed approach entails a two-stage flotation process in which the valuable coal is floated in the first stage, by taking advantage of its natural hydrophobicity, while sulfide minerals, in particular pyrite, and other ash-forming minerals reports to the tailings. In a second flotation step, a small amount of acid generating material, in particular pyrite, is selectively removed from the first stage tailings to produce a benign tailings fraction with reduced long term ARD risks. The low-volume sulfide-rich fraction from the second flotation step would go to a further treatment approach, which is beyond the scope of this research.

The technical feasibility of the conceptual approach has been demonstrated by means of a case study relating to the coal processing sector. The recovery of valuable coal was investigated systematically through laboratory-scale flotation tests using different collectors (dodecane, kerosene and oleic acid) while xanthates were investigated as sulfide collectors. The effects of key parameters, in particular reagent addition, and the extent of both coal recovery, and sulfide sulfur removal were investigated. Concentrates and tailings from flotation tests were subjected to ARD prediction tests to determine their acid generating potential.

This chapter presents the key findings of the laboratory flotation tests, the proof of the concept based on the two-stage flotation study, and the recommendations for further work in this area.

6.1 KEY FINDINGS

This section presents a summary of the main findings of the coal and sulfide flotation tests and the key aspects of the ARD characterisation tests carried out on the coal sample and on the concentrates and tailings arising from those flotation tests.

6.1.1 Coal flotation tests

Laboratory batch flotation tests using unoptimized dosages of aliphatic collector oils, dodecane and kerosene, showed that the coal under investigation was difficult to float. The poor recovery of combustibles even in the presence of high concentrations of dodecane and kerosene was probably due to the petrographic composition of the coal (low rank, inertinite-rich and low in vitrinite content), the high-ash content (about 34.4%), and the long exposure of the coal to atmospheric oxygen, which would result in the formation of hydrophilic oxygen functional groups on the surface of coal (petrographic analysis indicated that at least 11% of the coal was oxidized). Nevertheless, the concentrates recovered using aliphatic collectors had high grade (low ash content), indicating that the affinity of coal for dodecane and kerosene in the presence of MIBC was fairly good. As an illustration, at a dosage of 2.89 kg/t of dodecane, the yield, recovery and the ash content of clean coal were 27.37%, 33.79% and 15.54%, respectively; at the same dosage of kerosene collector, the yield, recovery and the ash content of clean coal were 31.44%, 38.74% and 15.37%, respectively.

Additional tests employing oleic acid as collector improved the recovery and yield of clean coal significantly, suggesting that there was a stronger interaction between the oleic acid molecule and the aromatic sites on the coal surface than between aliphatic hydrocarbon chains and the coal surface. This was probably due to strong π -bonding that occurs between the hydrophobic component of the coal surface and the double-bond of oleic acid. At a dosage of 2.89 kg/t of oleic acid, the yield, recovery and the ash content of clean coal were 55.98%, 69.06% and 18.10%, respectively.

It may be concluded that froth flotation techniques are a viable (technical) method for reclaiming a large amount of coal ultrafines that are currently wasted in slimes dams.

6.1.2 Sulfide flotation tests

Potassium amyl xanthate (PAX) was chosen as the sulfide collector in this study, because of its collecting strength compared to other xanthate homologues. Laboratory batch flotation

tests showed that a much larger amount of the collector (about one order of magnitude greater) was required to float sulfide from coal in comparison to sulfide flotation from mineral ores. This is in agreement with previous work showing that coal-pyrite differs significantly from ore-pyrite due to surface heterogeneities, such as clay inclusions in the sulfide component, which contribute to the hydrophilic character of the coal-pyrite.

Consequently, to improve the overall sulfide recovery and obtain a tailing with low sulfur content, stage-wise flotation tests were conducted. The results showed that the addition of 2.33 kg/t PAX in one stage resulted in 27.26% sulfur recovery at 1.76% total sulfur in one stage; with a 2-stage addition, 38.30% sulfur recovery was obtained at 1.51% grade, and with 3-stage addition, 42.13% sulfur recovery was obtained at 1.39% grade. The mass yields obtained were 14.12%, 18.49% and 22.69%, respectively. The total sulfur remaining in the tailings was 0.56% for both the 2-stage and 3-stage collector addition tests, compared with 0.77% in the tailing from the 1-stage test.

The overall results of the sulfide flotation tests also indicated that the adsorption of dextrin depressant by the coal surface was not strong enough. Increasing the dosage of dextrin decreased the recovery of coal to the concentrate but also inhibited the floatability of sulfide to some extent. The inadequate depression of coal indicated that the coal under investigation was oxidized, because dextrin is well absorbed by fresh coal.

6.1.3 ARD characterisation tests

The feed, concentrate and tailing samples from both coal and sulfide flotation were evaluated in terms of their acid generating potential using acid base accounting (ABA) and net acid generation (NAG) tests, and the biokinetic flask test. The overall results of ARD prediction tests showed that static ABA and NAG tests can adequately classify a sample when used in combination. The ABA and NAG tests indicated that the feed was potentially acid-generating, as expected: the feed sample was selected on the basis that it exhibited acid generating potential, otherwise it was not going to reflect the objective of this study. Both concentrate and tailings from coal flotation were potentially acid-generating, but the tailings were more acid-neutralizing, as a result of ash-forming minerals, including carbonates, being wetted and reporting to the tailings.

The tailings generated by floating pyrite with a single addition of xanthate were potentially acid-forming. However, the tailings resulting from 2 stage- and 3 stage-addition of xanthate were both non-acid forming, showing that more sulfide sulfur reported to the concentrate

when the amyl xanthate collector was added incrementally to the flotation cell. This increased the amount of acid buffering material in the tailings as a result. Thus, stage-wise addition of the collector produced a sulfide-lean fraction with high acid neutralizing capacity, which can be disposed of safely without harming the receiving environment: thus, a scenario that would be useful in the case of coal processing wastes with no economical value that present a risk of ARD pollution.

Biokinetic tests were carried out to characterize the ARD generation potential of the same samples and the results were compared to those of the static tests. The pH profiles of the biokinetic tests over a period of 76 days were consistent with the trends in the ANC results. However, the biokinetic tests provided extended data over the static tests, particularly in terms of the rate of release of neutralization capacity and of acidification as well as the potential for the sample to acidify. These are critical data for prediction of behavior in the field.

6.2 PROOF OF THE CONCEPT

The results of laboratory batch flotation tests to investigate the two-stage flotation process showed that a low-sulfur tailings with low ARD potential can be produced, together with a clean coal stream with a low ash content. The performance and selectivity of the process was clearly indicated by the low sulfur content of the second-stage tailing (0.38%) and the low ash content of the clean coal product (13.5%). The second stage recovered a low volume sulfide-rich fraction (2.68% total sulfur). The majority of the original feed reported to the tailings of the second stage (67.2%) and was characterized by a high ash (40%) and low total sulfur (0.38% S) content. This product was assessed to be benign with respect to ARD generation, which was the objective of the study. The clean coal had a low sulfur content of 0.48% S. Although only low yield and recovery were achieved with dodecane as collector, the use of oleic acid would probably have presented a better scenario. Oleic acid was found in one stage flotation to improve the yield and recovery of clean coal considerably reaching 55.98% and 69.06%, respectively, with low ash content. No attempt was made in this research to optimize the reagents.

The results of the biokinetic tests demonstrated that the high-sulfur content of the second stage concentrate was the most amenable to microbial desulfurization due to the high content of pyritic sulfur, which provides a suitable environment for the culture of microorganisms to thrive. This suggests that the bioleaching of the second stage flotation

concentrate can be integrated into the two-stage flotation process to produce holistic environmental management scheme for coal thickener underflow coal wastes.

6.3 RECOMMENDATIONS FOR FURTHER WORK

The results obtained in this research suggest that the application of froth flotation to ultrafine coal wastes will allow the recovery of substantial amounts of valuable coal that are currently disposed of in slimes dams. Furthermore, the risk of ARD pollution in the receiving environment would be reduced considerably to acceptable levels by the selective removal of acid generating materials from these wastes. It has been shown, from a scientific standpoint, that it is possible to address simultaneously the value recovery and pollution concerns associated with coal ultrafines.

The findings of this research have confirmed the hypothesis stated in Section 1.2.3 in the introduction, that “a two-stage flotation process can effectively eliminate the major environmental risks of ARD associated with the disposal of coal ultrafines, as well as provide economic benefit as a result of recovering valuable coals from these wastes”.

The summary of the key findings of this exploratory study has highlighted a number of areas which require a more in-depth investigation:

All of the research work described in this dissertation was conducted on only one thickener underflow coal sample: it was felt that once the process had been proven for one coal, the same procedures could be extended to coal ultrafines from other South African coalfields. It is necessary to confirm the results on samples from different coalfields because coal does not have a fixed composition and varies a good deal in its properties and the amount and the liberation of pyrite will be different from coal to coal. Consequently, investigations using laboratory batch flotation tests should be carried out using coal ultrafine samples from different coalfields with proven acid generating characteristics to establish to what extent the valuable coal can be recovered and ARD pollution eliminated at source.

Work should also be carried out to optimize the flowsheet in terms of reagents and operating conditions. The recovery of clean coal from the first stage of the process, aimed at reclaiming valuable product from the ultrafine wastes needs to be improved significantly. In this regards, further test work to investigate the effects of optimizing the type and dosage of reagents, in particular collectors, is recommended. For example, oleic acid was shown to

enhance the recovery and the yield of clean coal: it is recommended that the two-stage flowsheet be investigated using this unsaturated fatty acid collector. An assessment of cost should also be investigated particularly with respect to the inclusion of reagent costs.

There is also a need to improve the selectivity of sulfur removal to increase the amount of sulfide reporting to the concentrate, while simultaneously reducing the volume requiring bio-desulfurization. In the same framework, the potential to upgrade the high sulfur coal stream through bio-desulfurization under optimum pH and temperature conditions using coal-derived inoculums, also needs to be explored in-depth.

There is scope to refine the biokinetic test for coal samples. It is recommended that the use of mixed cultures of acidophilic bacteria isolated from the drainage of a coal mine be studied so as to optimise the sulfide oxidation during the leaching process.

Although the proposed two-stage flotation process has demonstrated the potential for reducing ARD risk from ultrafine coal tailings, of equal importance is the possible mobilization of toxic metals, associated with sulfur bearing minerals, in the desulfurization process. The deportment and associated environmental risks of the co-elements should be evaluated on the sulfide-lean fraction resulting from the second stage flotation, the high-sulfur concentrate and on the biokinetic leachates.

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APPENDICES

APPENDIX A COAL CHARACTERISATION

A.1 Analysis methods

A.1.1 Ash analysis

The ash contents of the concentrate and tails samples were used to determine the concentrate recovery. The ash analysis of each sample was performed according to the following procedure based on the Standard Method SANS 131:1997:

- i. Weigh the crucible to be used for a particular sample. Heat the crucible to 815 ± 15 °C and maintain at this temperature for 15 min and then cool down.
- ii. Place a representative sample of about 0.7 to 1 g in the crucible, and determine the mass of the coal and crucible.
- iii. Place the crucible containing the coal in a furnace and raise the temperature evenly to 500 °C over a period of 60 min and hold at this temperature for 1 hour.
- iv. Continue heating to 815 ± 10 °C in the same furnace. Maintain this temperature for at least one hour.
- v. Removed the crucible from the furnace when the incineration period is complete. Transfer it to a dessicator and allow it to cool to room temperature. Once the crucible cools to room temperature obtain the mass of the content by weighing. This will enable the ash content of the sample to be calculated.

A.1.2 Sulfur analysis using Leco S 632

- i. Open medical oxygen and synthetic air cylinders.
- ii. Open Leco programme:
 - Instrument will perform an automatic loader check,
 - Click on Diagnostics – Perform a System check.
- iii. Load 3 x Conditioning Samples of about 0.3 g.
- iv. Load 3 x Blank crucibles from Sample Login Screen.
- v. Load 3 x Drift Samples from specific calibration.

-
- vi. Configuration – Blank first (Highlight results & click):
 - Drift samples – Do Low & High separately.
 - vii. Load samples either using Login or manually – check method & calibration.
 - viii. Drift correction needs to be done for each calibration before analysing samples.
 - ix. Try to use a calibration method as close to expected results as possible. Decrease or increase sample mass to fit “Calibration Area”.
 - x. Results are saved automatically.
 - xi. Print preview - add person’s name, check fields –Print.
 - xii. Gas off, close program.
 - xiii. Always close Oxygen & Syn Air at cylinders.
 - xiv. Empty bucket and clean boats once cool.

A.2 Release flotation

The release flotation test was carried out in a batch flotation cell, according to the method outlined in Section 3.2.3. The method involves using starvation quantities of reagents; concentrates are collected in small quantities over long period of time. The conditions used were as follows:

Aeration rate:	5 L/min
Impeller speed:	1200 rpm
Froth height:	2.5 cm
Collector dosage:	starvation amounts of dodecane
Frother dosage:	starvation amounts of MIBC

The results are presented in Table A.1

Table A.1: Release analysis results for the coal ultrafine sample

Fraction	Mass (g)	Cum mass (g)	Mass (%)	Cum Mass %	Ash (%)	Cum Ash (%)
FINAL CONC	21.43	21.43	15.3	15.3	10.2	10.2
T12	3.49	24.92	2.49	17.79	10.7	10.3
T11	2.22	27.14	1.58	19.37	11	10.3
T10	1.33	28.47	0.95	20.32	11.4	10.4
T9	1.91	30.38	1.36	21.68	12.2	10.5
T8	2.1	32.48	1.5	23.18	14.2	10.7
T7	1.95	34.43	1.39	24.58	14.1	10.9
T6	2.25	36.68	1.61	26.18	15	11.2
T5	3.54	40.22	2.53	28.71	17.2	11.7
T4	7.04	47.26	5.02	33.73	18.6	12.7
T3	7.54	54.8	5.38	39.11	19.3	13.6
T2	13.9	68.7	9.92	49.04	27.1	16.4
T1	71.4	140	50.96	100	53.2	35.2

APPENDIX B: BATCH FLOTATION EXPERIMENTS

The batch flotation procedures are outlined below

B.1 Coal flotation procedure

- i. Fill the 3 L Leeds cell to a volume of 2 L with water.
- ii. Set the impeller speed to 1200 rpm.
- iii. Add 200 g of coal solids (dry basis).
- iv. Fill the cell to 3 L with additional water. This gives a froth height of 3 cm.
- v. Allow the pulp to condition for 5 minutes.
- vi. Add the desired quantity of oily collector to the suspended pulp using a microsyringe, below the pulp surface and condition the pulp for 5 min.
- vii. Add the required quantity of frother, using a microsyringe, below the pulp surface.
- viii. Allow 60 s for frother dispersion before turning on the air to a flow rate of 5 L/min.
- ix. Let $t=0$ be 60 s after the time at which the frother was added.
- x. Scrape the froth manually every 5 seconds. Collect the cumulative concentrates after total flotation times of 0.5 min, 1 min, 2 min and 5 min.
- xi. Once the final concentrate has been collected turn the air and the impeller off.
- xii. Drain the cell. The remaining pulp is the tails sample.
- xiii. filter, dry in the oven over night at 105 °C, weigh and then analyze the concentrate and tails samples.
- xiv. Calculate the yield of clean coal as shown below:

$$\text{Yield} = \frac{\text{mass of concentrate}}{\text{mass of feed}} \times 100 \quad (\text{B.1})$$

- xv. Calculate coal recovery to the concentrate as shown below:

$$\text{Recovery} = \frac{(1 - \text{ash content of concentrate}) \times \text{mass of concentrate}}{(1 - \text{ash content of feed}) \times \text{mass of feed}} \times 100 \quad (\text{B.2})$$

B.2 Sulfide flotation procedure

- i. Fill the 3 L Leeds cell to a volume of 2 L with water.
- ii. Set the impeller speed to 1200 rpm.

- iii. Add 200 g of coal solids (dry basis).
- iv. Fill the cell to 3 L with additional water. This gives a froth height of 3 cm.
- v. Allow the pulp to condition for 5 minutes.
- vi. Add the desired quantity of collector to the suspended pulp using a syringe, below the pulp surface and condition the pulp for 5 min.
- vii. Add the required quantity of depressant using a syringe, below the pulp surface and condition for 5 minute.
- viii. Add the required quantity of frother, using a microsyringe, below the pulp surface.
- ix. Allow 60 s for frother dispersion before turning on the air to a flow rate of 6 L/min.
- x. Let $t=0$ be 60 s after the time at which the frother was added.
- xi. Scrape the froth manually every 15 seconds. Collect the cumulative concentrates after total flotation times of 2 min, 6 min, 12 min and 20 min.
- xii. Once the final concentrate has been collected turn the air and the impeller off.
- xiii. Drain the cell. The remaining pulp is the tails sample.
- xiv. Filter, dry in the oven over night at 105 °C, weigh and analyze the concentrate and tails samples
- xv. Calculate the yield as shown below:

$$\text{Yield} = \frac{\text{mass of concentrate}}{\text{mass of feed}} \times 100 \quad (\text{B.3})$$

- xvi. Calculate coal recovery to the concentrate as shown below:

$$\text{Recovery} = \frac{(\text{sulfur content of concentrate}) \times \text{mass of concentrate}}{(\text{sulfur content of feed}) \times \text{mass of feed}} \times 100 \quad (\text{B.4})$$

APPENDIX C: ARD PREDICTION TESTS

C.1 Acid-base accounting

The acid-base accounting experiments involve static tests that evaluated the balance between acid generation processes and acid neutralizing processes.

C.1.1 Maximum potential acidity

The maximum potential acidity (MPA) of a sample was determined from the sample sulfur content. The total sulfur was determined using the LECO sulfur analyser. It is assumed that all the sulfur measured in the sample occurs as pyrite (FeS_2) and that the pyrite reacts under oxidizing conditions to generate acid as follows.



The MPA of a sample was calculated from the total sulfur content using the following formula:

$$\text{MPA (kg H}_2\text{SO}_4/\text{t)} = (\text{Total \%S}) \times 30.6 \quad (\text{C.2})$$

C.1.2 Acid neutralizing capacity

C.1.2.1 H_2O_2 siderite correction ANC test method

- i. Weight 2 g of coal ultrafine into 250 ml Erlenmeyer flasks.
- ii. Add HCl to the sample at concentration and volume as determined by fizz rating.
- iii. Boil the mixture for 5 minutes .
- iv. Allow to cool and filter solution.
- v. Back-titrate solution with NaOH to pH 4.5 with constant mixing.
- vi. Add 5 ml 30 % H_2O_2 and allow it to stand for an hour.
- vii. Back-titrate solution with NaOH to pH 7 over 1-2 hours or until stable (no pH change in two decimal place in 10 minutes)
- viii. Let solution stand overnight
- ix. Check pH and adjust with further back-titrate to pH 7 if required
- x. Add 8 drops of 30% H_2O_2 , boil for 5 minutes
- xi. Check pH and adjust with further back-titrate to pH 7 if required

- xii. Repeat step vii to xi.
 xiii. Sum the total volume NaOH added to calculate the final ANC as follows

$$\text{ANC} = \frac{[(V_{\text{HCl}} \times M_a) - V_{\text{NaOH}} \times C]}{W} \times 49 \quad (\text{C.3})$$

$$C = \frac{(M_a \times V_{\text{HCl}} \text{ in blank})}{\text{Vol}_{\text{NaOH}} \text{ titrated in blank}} \quad (\text{C.4})$$

where M_a = the molarity of HCl, W is weight of sample (g) and C is required to account the differences in stoichiometry in the acid and base solutions.

NB: filtering the ANC digestion solution before titration is essential, because the H_2O_2 added coal oxidize the pyrite in the solid residue, releasing acid and causing underestimation of the ANC.

C.1.2.2 Fizz rating

The method used for the fizz rating determines the presence of CaCO_3 which is indicated by bubbling or audible “fizz” (effervescence).

Fizz rating method

- Weight 0.5 g of pulverized sample.
- Place sample on a ceramic plate and add two to three drops of 25% HCl.
- Give the audible “fizz” a rating using the scale as indicated in Table C.1.

Table C.1: Fizz rating and associated HCl volume, HCl and NaOH concentration to be used in ANC test

Reaction Scale	Fizz rating	HCl Molarity (M)	Volume (ml)	NaOH Molarity (M)
None	0	0.5	4	0.1
Slight	1	0.5	8	0.1
Moderate	2	0.5	20	0.5
Strong	3	0.5	40	0.5
Very Strong	4	1.0	40	0.5
Carbonate	5	1.0	60	0.5

C.1.3 Net acid producing potential

The NAPP represents the balance between the capacity of a sample to generate acid (MPA) and its capacity to neutralize acid (ANC). The NAPP is expressed in units of kg H₂SO₄/t and was calculated as follows:

$$\text{NAPP} = \text{MPA} - \text{ANC} \quad (\text{C.5})$$

If the MPA is smaller than the ANC, this indicates that the sample has sufficient ANC to neutralize the acid. Conversely, if the MPA exceeds the ANC then the NAPP has a positive value, which gives an indication that the sample may be acid generating.

C.2 Net acid generating test

The NAG test was used in association with the NAPP to classify the acid generating potential of a sample. The NAG test involves reaction of a sample with hydrogen peroxide to rapidly oxidize any sulfide minerals contained within a sample. During the NAG test both acid generation and acid neutralization reactions can occur simultaneously. Therefore, the end result represents a direct measurement of the net amount of acid generated by the sample. This value is commonly referred to as the NAG capacity and is expressed in the same units as NAPP.

Reagents:

- Sodium Hydroxide (NaOH) – 0.10 M and 0.50 M
- 15 % v/v H₂O₂

C.2.1 Single addition NAG Test

H₂O₂ should be at room temperature before starting the test and its pH should be greater than or equal to pH 4.5.

- i. Weigh approximately 2.5 g of coal ultra-fine sample into a 500 mL Erlenmeyer flask.
- ii. Add 250 mL of 15 % hydrogen peroxide (H₂O₂ should be room temperature before it is used in the test).
- iii. Cover with a watch glass and place the Erlenmeyer flask containing the solution in a fume-hood for 24 hours.
- iv. Measure the pH before boiling the digested mixture.

- v. Place the Erlenmeyer flask on a hot plate and gently heat until effervescence stops or for a minimum of 2 hours. The sample must not boil dry. Add deionised water as required to maintain the volume approximately constant.
- vi. Measure the pH and acidity of the NAG liquor when it is cool. The acidity of the liquor is then used to estimate the net amount of acidity produced per unit weight of sample
- vii. Filter the NAG solution and rinse down solid that has adhered to the sides of the flask into the solution using de-ionized water, to give a final volume of 250 mL. (Solids are retained for further analysis).
- viii. Record the final pH of the solution (after-boil NAGpH).
- ix. Titrate the NAG liquor to pH 4.5, and then titrate to pH 7.

When NAGpH>2 titrate with 0.1 NaOH

When NAGpH=2 titrate with 0.5 NaOH

- x. Use the volume of NaOH added to calculate NAG in units of kg H₂SO₄/t, using the following equation:

$$\text{NAG} = \frac{V \times M}{W} \times 49 \quad (\text{C.5})$$

Where V = volume of NaOH used in titration (mL); M = molarity of NaOH used in titration (mol/L); W = weight of sample (g).

C.2.2 Sequential NAG test

- i. Steps i to x of the single addition NAG test form the first stage of the sequential NAG test procedure.
- ii. Repeat the single addition NAG tests using the solid residue from first stage.
- iii. Repeat steps ii to x until such a time no further reaction is observed and the filtered NAG liquor has a pH ≥ 4.5.

C.3 Classification of sample

The acid forming potential of a sample is classified on the basis of the acid-base and NAG test results as follows:

-
- i. Barren: essentially as no acid generating capacity and no acid buffering capacity.
 - ii. Non-acid forming (NAF): has negative NAPP and the final NAG pH ≥ 4.5 .
 - iii. Potentially acid forming (PAF): positive NAPP and a final NAGpH < 4.5 .
 - iv. Uncertain (UC): when the NAPP is positive and NAGpH > 4.5 , or when the NAPP is negative and NAGpH ≤ 4.5 .

C.4 Biokinetic test methods

- i. Add 150 mL autotrophic basal salts (ABS) solution to 250 ml Erlenmeyer flask.
- ii. Autoclave to sterilise the ABS solution.
- iii. After cooling, weigh in 7.5 g feed, concentrate or tailings sample to each flask.
- iv. Inoculate with 7.5 mL mixed culture of iron and sulfur oxidising microorganisms.
- v. Measure Redox potential and ensure pH is at 2.0; adjust with H₂SO₄ if necessary.
- vi. weigh each flask, fit a cotton wool bung, cover with foil and place in shaking incubator at 150 rpm at 37°C.
- vii. Before sampling, weigh flask. Top up with de-ionised water to account for water loss due to evaporation.
- viii. Record pH, redox, ferrous and total iron concentrations every 2-4 days.

Note. For the controlled pH test, at each pH measurement, if the pH has increased, titrate with H₂SO₄ back to pH 2, recording the volume and molarity of acid added. Ferrous assay is conducted following the 1-10 phenanthroline method (Komadel and Stucki 1988).

APPENDIX D EXPERIMENTAL RESULTS

D.1 Flotation results

University of Cape Town

Table D.1 Coal flotation results using dodecane collector and MIBC frother

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass, g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
1	MIBC = 0.11 kg/t Dodecane = 0.7 kg/t Feed = 200 g Feed ash = 34.04% Feed T sulfur = 0.81%	C1	0.5	3.64	14.74	0.33	3.64	14.74	0.33	0.80	0.86	2.40	
		C2	1	4.12	14.25	0.32	7.76	14.48	0.33	1.69	1.79	5.13	
		C3	2	4.39	14.24	0.33	12.15	14.39	0.33	2.65	2.79	8.04	
		C4	5	8.52	14.36	0.34	20.67	14.38	0.33	4.59	4.74	13.67	
		T		185.37	34.85	0.83							
		Recons. feed						192.17	32.646	0.78			
2	MIBC = 0.11 kg/t Dodecane = 0.7 kg/t Feed = 200 g Feed ash = 33.76% Feed T sulfur = 0.62%	C1	0.5	3.47	13.98	0.36	3.47	13.98	0.36	1.07	0.78	2.31	
		C2	1	3.19	13.31	0.27	6.66	13.66	0.31	1.81	1.46	4.44	
		C3	2	4.24	13.36	0.28	10.90	13.54	0.30	2.82	2.36	7.28	
		C4	5	7.83	13.43	0.30	18.73	13.49	0.30	4.88	4.04	12.52	
		T		169.35	34.63	0.63							
		Recons. feed						191.87	32.57	0.60			
3	MIBC = 0.11Kg/t Dodecane = 1.4 kg/t Feed = 200 g Feed ash = 34.12% Feed T sulfur = 0.55%	C1	0.5	5.07	14.46	0.34	5.07	14.46	0.34	1.76	1.17	3.33	
		C2	1	4.63	13.96	0.35	9.70	14.22	0.34	3.43	2.20	6.39	
		C3	2	6.38	13.76	0.27	16.08	14.04	0.31	5.20	3.60	10.62	
		C4	5	10.81	14.23	0.39	26.89	14.12	0.35	9.59	6.05	17.74	
		T		162.64	35.49	0.53							
		Recons. feed						192.88	32.51	0.50			
4	MIBC = 0.11 kg/t Dodecane = 1.4 kg/t Feed = 200 g Feed ash = 33.95% Feed T sulfur = 0.78%	C1	0.5	5.31	15.02	0.32	5.31	15.02	0.32	1.57	1.24	3.41	
		C2	1	4.04	14.64	0.37	9.35	14.85	0.34	2.94	2.16	6.01	
		C3	2	6.20	14.30	0.18	15.55	14.63	0.28	3.96	3.55	10.02	
		C4	5	10.81	14.25	0.37	26.36	14.48	0.32	7.61	5.95	17.03	
		T		166.66	35.45	0.60							
		Recons. feed						196.57	32.64	0.56			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass, g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %
5	MIBC = 0.11 kg/t	C1	0.5	9.47	15.70	0.40	9.47	15.70	0.40	2.88	2.38	6.15
	Dodecane = 1.86 kg/t	C2	1	6.48	14.88	0.39	15.95	15.36	0.40	4.81	3.92	10.39
	Feed = 200 g	C3	2	8.54	14.47	0.41	24.49	15.05	0.40	7.45	5.89	16.02
	Feed ash = 33.57%	C4	5	11.99	14.20	0.42	36.48	14.77	0.41	11.31	8.61	23.94
	Feed T sulfur = 0.79%	T		152.75	36.67	0.75						
		Recons. feed					192.45	32.52	0.68			
6	MIBC = 0.11 kg/t	C1	0.5	10.28	16.34	0.41	10.28	16.34	0.41	2.98	2.61	6.49
	Dodecane = 1.86 kg/t	C2	1	6.91	15.81	0.38	17.19	16.13	0.40	4.82	4.31	10.88
	Feed = 200 g	C3	2	8.90	15.49	0.42	26.09	15.91	0.40	7.44	6.45	16.55
	Feed ash = 33.61%	C4	5	11.26	15.68	0.40	37.35	15.84	0.40	10.62	9.20	23.71
	Feed T sulfur = 0.78%	T		156.19	36.62	0.79						
		Recons. feed					196.92	32.68	0.72			
7	MIBC = 0.11 kg/t	C1	0.5	8.99	15.52	0.41	8.99	15.52	0.41	2.35	2.24	5.88
	Dodecane = 3.72 kg/t	C2	1	6.48	14.81	0.42	15.47	15.22	0.41	4.10	3.78	10.15
	Feed = 200 g	C3	2	8.60	14.72	0.48	24.07	15.04	0.44	6.78	5.82	15.82
	Feed ash = 33.39%	C4	5	12.06	15.42	0.45	36.13	15.17	0.44	10.25	8.81	23.71
	Feed T sulfur = 0.73%	T		152.12	36.53	0.90						
		Recons. feed					191.49	32.50	0.81			
8	MIBC = 0.11 kg/t	C1	0.5	11.01	15.45	0.40	11.01	15.45	0.40	3.63	2.74	7.16
	Dodecane = 3.72 kg/t	C2	1	6.35	14.85	0.36	17.36	15.23	0.38	5.50	4.26	11.32
	Feed = 200 g	C3	2	10.07	14.58	0.35	27.43	14.99	0.37	8.41	6.63	17.93
	Feed ash = 33.04%	C4	5	12.09	15.33	0.31	39.52	15.10	0.35	11.55	9.62	25.80
	Feed T sulfur = 0.73%	T		152.53	36.74	0.70						
		Recons. feed					192.05	32.29	0.63			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
9	MIBC = 0.28 kg/t	C1	0.5	4.12	20.92	0.51	4.12	20.92	0.51	1.69	1.40	2.44	
	Dodecane = 0 kg/t	C2	1	2.61	17.86	0.49	6.73	19.73	0.50	2.72	2.16	4.05	
	Feed = 200 g	C3	2	3.05	16.64	0.46	9.78	18.77	0.49	3.86	2.99	5.96	
	Feed ash = 33.61%	C4	5	5.01	16.74	0.46	14.79	18.08	0.48	5.72	4.36	9.09	
	Feed T sulfur = 0.80%	T		179.88	32.63	0.65							
		Recons. feed						194.67	31.53	0.63			
10	MIBC = 0.28 kg/t	C1	0.5	8.85	18.91	0.48	8.85	18.91	0.48	2.62	2.83	5.41	
	Dodecane = 0.70 kg/t	C2	1	6.05	15.64	0.47	14.90	17.58	0.48	4.10	4.70	9.26	
	Feed = 200 g	C3	2	7.91	14.82	0.46	22.81	16.62	0.47	5.93	7.08	14.34	
	Feed ash = 33.64%	C4	5	12.83	14.43	0.46	35.64	15.83	0.47	8.82	10.97	22.61	
	Feed T sulfur = 0.80%	T		160.96	36.22	0.84							
		Recons. feed						196.60	32.53	0.77			
11	MIBC = 0.28 kg/t	C1	0.5	7.76	18.57	0.49	7.76	18.57	0.49	2.28	2.52	4.75	
	Dodecane = 0.70 kg/t	C2		5.22	15.57	0.46	12.98	17.36	0.48	3.56	4.13	8.06	
	Feed = 200 g	C3		1	6.66	14.20	0.46	19.64	16.29	0.47	5.06	6.19	12.35
	Feed ash = 33.15%	C4		2	12.21	13.96	0.44	31.85	15.40	0.46	7.75	9.76	20.25
	Feed T sulfur = 0.74%	T		5	164.52	35.49	0.82						
		Recons. feed							196.37	32.23	0.76		
12	MIBC = 0.28 kg/t	C1	0.5	11.35	17.01	0.46	11.35	17.01	0.46	3.09	3.66	7.05	
	Dodecane = 1.4 kg/t	C2	1	6.20	14.65	0.46	17.55	16.18	0.46	4.55	5.62	11.00	
	Feed = 200 g	C3	2	8.77	14.04	0.45	26.32	15.46	0.46	6.52	8.37	16.64	
	Feed ash = 33.78%	C4	5	14.13	13.87	0.45	40.45	14.91	0.45	9.65	12.77	25.75	
	Feed T sulfur = 0.74%	T		155.69	36.25	0.81							
		Recons. feed						196.14	31.85	0.73			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %
13	MIBC = 0.28 kg/t	C1	0.5	11.54	17.65	0.47	11.54	17.65	0.47	3.23	3.66	7.09
	Dodecane = 1.4 kg/t	C2	1	6.68	14.96	0.45	18.22	16.67	0.46	4.82	5.70	11.33
	Feed = 200 g	C3	2	9.29	14.08	0.45	27.51	15.79	0.46	6.89	8.53	17.29
	Feed ash = 33.08%	C4	5	15.37	14.10	0.43	42.88	15.19	0.45	10.33	12.96	27.14
	Feed T sulfur = 0.72%	T		154.17	36.67	0.84						
		Recons. feed						197.05	32.00	0.75		
14	MIBC = 0.28 kg/t	C1	0.5	11.90	16.06	0.47	11.90	16.06	0.47	3.07	3.77	7.31
	Dodecane = 1.86 kg/t	C2	1	6.93	13.54	0.46	18.83	15.13	0.47	4.58	5.89	11.70
	Feed = 200 g	C3	2	10.56	12.85	0.43	29.39	14.31	0.45	6.76	8.94	18.44
	Feed ash = 33.02%	C4	5	17.88	13.08	0.45	47.27	13.84	0.45	10.52	14.32	29.82
	Feed T sulfur = 0.73%	T		151.52	36.75	0.84						
		Recons. feed						198.79	31.30	0.75		
15	MIBC = 0.28 kg/t	C1	0.5	12.00	16.11	0.47	12.00	16.11	0.47	3.14	3.88	7.46
	Dodecane = 1.86 kg/t	C2	1	8.07	13.65	0.46	20.07	15.12	0.46	4.93	6.42	12.63
	Feed = 200 g	C3	2	10.97	13.13	0.44	31.04	14.42	0.45	7.26	9.75	19.70
	Feed ash = 32.98%	C4	5	18.00	13.95	0.45	49.04	14.25	0.45	11.34	15.32	31.18
	Feed T sulfur = 0.72%	T		147.45	37.05	0.83						
		Recons. feed						196.49	31.36	0.74		
16	MIBC = 0.28 kg/t	C1	0.5	14.48	16.40	0.47	14.48	16.40	0.47	3.81	4.52	9.01
	Dodecane = 2.79 kg/t	C2	1	10.63	14.30	0.45	25.11	15.51	0.46	6.24	7.70	15.78
	Feed = 200 g	C3	2	11.87	13.78	0.45	36.98	14.96	0.46	8.86	11.26	23.40
	Feed ash = 33.49%	C4	5	17.20	14.40	0.47	54.18	14.78	0.46	12.83	16.57	34.35
	Feed T sulfur = 0.71%	T		142.63	38.14	0.88						
		Recons. feed						196.81	31.71	0.77		

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %
17	MIBC = 0.28 kg/t	C1	0.5	14.93	18.79	0.50	14.93	18.79	0.50	4.53	4.95	8.97
	Dodecane = 2.79 kg/t	C2	1	10.32	15.41	0.47	25.25	17.41	0.48	7.10	8.17	15.43
	Feed = 200 g	C3	2	11.62	14.90	0.46	36.87	16.62	0.48	9.89	11.78	22.75
	Feed ash = 33.13%	C4	5	16.77	15.58	0.46	53.64	16.29	0.47	14.11	16.89	33.22
	Feed T sulfur = 0.71%	T Recons. feed			143.47	37.09	0.87	197.11	31.43	0.76		
18	MIBC = 0.11 kg/t	C1	0.5	9.47	15.70	0.33	9.47	15.70	0.33	2.38	2.20	6.15
	Dodecane = 1.86 kg/t	C2	1	6.48	14.88	0.32	15.95	15.36	0.33	3.92	3.68	10.39
	Feed = 200 g	C3	2	8.54	14.47	0.33	24.49	15.05	0.33	5.89	5.64	16.02
	Feed ash = 33.57%	C4	5	11.99	14.20	0.34	36.48	14.77	0.33	8.61	8.52	23.94
	Feed T sulfur = 0.81%	T Recons. feed			155.97	36.67	0.83	192.45	32.52	0.73		
19	MIBC = 0.11 kg/t	C1	0.5	10.28	16.34	0.36	10.28	16.34	0.36	2.61	3.26	6.49
	Dodecane = 1.86 kg/t	C2	1	6.91	15.81	0.27	17.19	16.13	0.32	4.31	4.88	10.88
	Feed = 200 g	C3	2	8.90	15.49	0.28	26.09	15.91	0.31	6.45	7.08	16.55
	Feed ash = 33.61%	C4	5	11.26	15.68	0.30	37.35	15.84	0.31	9.20	10.11	23.71
	Feed T sulfur = 0.62%	T Recons. feed			159.57	36.62	0.63	196.92	32.68	0.57		
20	MIBC = 0.17 kg/t	C1	0.5	9.60	15.87	0.44	9.60	15.87	0.44	2.48	2.96	5.94
	Dodecane = 1.86 kg/t	C2	1	7.32	13.31	0.45	16.92	14.76	0.45	4.07	5.26	10.61
	Feed = 200 g	C3	2	9.85	12.59	0.44	26.77	13.97	0.44	6.09	8.27	16.94
	Feed ash = 33.03%	C4	5	13.91	12.72	0.45	40.68	13.54	0.45	8.97	12.63	25.87
	Feed T sulfur = 0.75%	T Recons. feed			156.71	35.68	0.80	197.39	31.12	0.73		

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %
21	MIBC = 0.17 kg/t	C1	0.5	8.91	13.89	0.46	8.91	13.89	0.46	2.01	3.01	5.61
	Dodecane = 1.86 kg/t	C2	1	7.52	13.08	0.45	16.43	13.52	0.46	3.61	5.45	10.40
	Feed = 200 g	C3	2	9.14	12.81	0.44	25.57	13.27	0.45	5.51	8.34	16.23
	Feed ash = 32.17%	C4	5	14.65	13.14	0.45	40.22	13.22	0.45	8.64	13.09	25.54
	Feed T sulfur = 0.73%	T		158.00	35.60	0.76						
		Recons. feed						198.22	31.06	0.69		
22	MIBC = 0.22 kg/t	C1	0.5	13.27	15.93	0.48	13.27	15.93	0.48	3.49	4.64	8.11
	Dodecane = 1.86 kg/t	C2	1	8.49	14.48	0.46	21.76	15.37	0.47	5.51	7.51	13.39
	Feed = 200 g	C3	2	11.14	14.09	0.45	32.90	14.94	0.46	8.10	11.23	20.35
	Feed ash = 0.73%	C4	5	14.11	14.73	0.46	47.01	14.87	0.46	11.53	15.96	29.10
	Feed T sulfur = 33.35%	T		151.15	35.5	0.76						
		Recons. feed						198.16	30.61	0.69		
23	MIBC = 0.22 kg/t	C1	0.5	12.77	15.40	0.47	12.77	15.40	0.47	3.20	4.06	7.93
	Dodecane = 1.86 kg/t	C2	1	7.53	14.07	0.45	20.30	14.90	0.46	4.92	6.37	12.69
	Feed = 200 g	C3	2	11.34	13.59	0.45	31.64	14.43	0.46	7.43	9.83	19.88
	Feed ash = 32.81%	C4	5	14.53	14.21	0.47	46.17	14.36	0.46	10.79	14.46	29.04
	Feed T sulfur = 0.75%	T		151.44	36.20	0.83						
		Recons. feed						197.61	31.09	0.74		

Table D.2: Coal flotation results using oleic acid collector and MIBC frother

Run no.	Reagents	Sample	Time min	Mass g	Ash%	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
24	MIBC = 0.28 kg/t Oleic acid = 0.70 kg/t Feed = 200 g Feed ash = 33.96% Feed T sulfur = 0.75%	C1	0.5	16.24	18.79	0.47	16.24	18.79	0.47	5.49	5.06	9.89	
		C2	1	7.10	16.12	0.48	23.34	17.97	0.47	7.97	6.96	14.35	
		C3	2	9.85	15.45	0.48	33.19	17.23	0.47	11.39	9.49	20.59	
		C4	5	24.40	16.69	0.51	57.59	17.00	0.49	20.37	16.24	35.83	
		T		136.11	37.09	0.80							
		Recons. feed						193.70	31.12	0.71			
25	MIBC = 0.28 kg/t Oleic acid = 1.4 kg/t Feed = 200 g Feed ash = 32.91% Feed T sulfur = 0.71%	C1	0.5	38.24	19.57	0.56	38.24	19.57	0.56	15.87	12.53	22.90	
		C2	1	12.12	17.57	0.51	50.36	19.09	0.55	20.45	16.10	30.34	
		C3	2	10.19	16.96	0.50	60.55	18.73	0.54	24.25	18.99	36.64	
		C4	5	22.94	18.69	0.54	83.49	18.72	0.54	33.53	26.17	50.53	
		T		110.53	39.89	0.81							
		Recons. feed			194.02	32.91	0.71	194.02	30.78	0.69			
26	MIBC = 0.28 kg/t Oleic acid = 1.86 kg/t Feed = 200 g Feed ash = 33.69% Feed T sulfur = 0.78%	C1	0.5	27.74	18.15	0.49	27.74	18.15	0.49	9.95	8.25	17.01	
		C2	1	9.89	16.61	0.47	37.63	17.74	0.49	13.37	10.94	23.18	
		C3	2	12.34	16.66	0.49	49.97	17.47	0.49	17.75	14.31	30.89	
		C4	5	36.34	17.98	0.50	86.31	17.68	0.49	30.97	25.01	53.21	
		T		108.23	42.28	0.87							
		Recons. feed			194.54	33.69	0.78	194.54	31.37	0.70			
27	MIBC = 0.28 kg/t Oleic acid = 2.79 kg/t Feed = 200 g Feed ash = 33.02% Feed T sulfur = 0.76%	C1	0.5	47.57	18.67	0.50	47.57	18.67	0.50	17.29	13.61	29.13	
		C2	1	13.01	16.44	0.48	60.58	18.19	0.50	21.81	16.89	37.32	
		C3	2	13.49	16.90	0.50	74.07	17.96	0.50	26.65	20.38	45.76	
		C4	3	36.79	18.41	0.51	110.86	18.10	0.50	40.15	30.76	68.37	
		T		87.18	51.82	0.95							
		Recons. feed			198.04	33.02	0.76	198.04	32.95	0.70			

Run no.	Reagents	Sample	Time min	Mass g	Ash%	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
28	MIBC = 0.28 kg/t Oleic acid = 2.79 kg/t Feed = 200 g Feed ash = 33.32% Feed T sulfur = 0.785	C1	0.5	55.89	20.42	0.61	55.89	20.42	0.61	22.72	17.30	33.37	
		C2	1	17.74	18.16	0.52	73.63	19.88	0.59	28.89	22.18	44.26	
		C3	2	12.16	18.42	0.52	85.79	19.67	0.58	33.12	25.57	51.71	
		C4	5	29.07	20.46	0.56	114.86	19.87	0.57	44.06	34.59	69.06	
		T		84.41	51.14	0.99							
		Recons. feed		199.27	33.32	0.78	199.27	33.12	0.75				

Table D.3: Coal flotation results using kerosene collector and MIBC frother

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
29	MIBC = 0.28 kg/t Kerosene = 0.70 kg/t Feed = 200 g Feed ash = 33.98% Feed T sulfur = 0.75%	C1	0.5	10.19	18.46	0.49	10.19	18.46	0.49	4.05	3.12	6.23	
		C2	1	6.31	15.63	0.48	16.50	17.38	0.49	6.48	4.75	10.22	
		C3	2	8.77	14.55	0.46	25.27	16.40	0.48	9.74	6.87	15.85	
		C4	5	11.68	15.10	0.46	36.95	15.99	0.47	14.08	9.79	23.28	
		T		156.70	34.73	0.68							
		Recons. feed		193.65	33.98	0.75	193.65	31.15	0.64				
30	MIBC = 0.28 kg/t Kerosene = 1.4 kg/t Feed = 200 g Feed ash = 0.76% Feed T sulfur = 33.01%	C1	0.5	10.77	16.89	0.47	10.77	16.89	0.47	3.71	2.93	6.70	
		C2	1	7.14	14.84	0.46	17.91	16.07	0.47	6.12	4.64	11.25	
		C3	2	10.73	14.06	0.45	28.64	15.32	0.46	9.67	7.07	18.15	
		C4	5	16.09	14.46	0.46	44.73	15.01	0.46	15.06	10.82	28.45	
		T		150.95	36.67	0.77							
		Recons. feed		195.68	33.01	0.76	195.68	31.72	0.70				
31	MIBC = 0.28 kg/t Kerosene = 1.86 kg/t Feed = 200 g Feed ash = 33.05% Feed T sulfur = 0.75%	C1	0.5	11.40	16.52	0.48	11.40	16.52	0.48	4.35	3.13	7.12	
		C2	1	7.17	14.70	0.46	18.57	15.82	0.47	6.96	4.88	11.70	
		C3	2	12.02	13.90	0.44	30.59	15.06	0.46	11.21	7.65	19.45	
		C4	5	16.20	14.01	0.45	46.79	14.70	0.45	17.00	11.41	29.88	
		T		147.03	36.30	0.71							
		Recons. feed		193.82	33.05	0.75	193.82	31.09	0.65				
32	MIBC = 0.28 kg/t Kerosene = 2.79 kg/t Feed = 200 g Feed ash = 33.14% Feed T sulfur = 0.68%	C1	0.5	19.56	16.46	0.49	19.56	16.46	0.49	7.36	5.27	12.20	
		C2	1	11.47	14.59	0.46	31.03	15.77	0.48	11.42	8.01	19.51	
		C3	2	14.88	14.43	0.46	45.91	15.34	0.47	16.67	11.52	29.01	
		C4	5	15.42	15.49	0.46	61.33	15.37	0.47	22.11	15.43	38.74	
		T		133.74	38.63	0.76							
		Recons. feed		195.07	33.14	0.68	195.07	31.32	0.67				

Table D.4: Sulfide flotation results (as-received coal)

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %
33	MIBC = 0.11 kg/t	C1	2	3.36	26.80	0.66	3.36	26.80	0.66	1.42	1.60	1.94
	PAX = 0.93 kg/t	C2	6	2.99	17.04	0.48	6.35	22.20	0.58	2.23	2.63	3.89
	Dextrin = 0.93 kg/t	C3	12	3.55	15.98	0.41	9.90	19.97	0.52	3.13	3.68	6.24
	Feed = 200 g	C4	20	7.84	15.48	0.37	17.74	17.99	0.45	5.05	5.77	11.47
	Feed ash = 33.81%	T		172.38	34.84	0.76						
	Feed T sulfur = 0.76%	Recons. feed					190.12	33.27	0.73			
34	MIBC = 0.11 kg/t	C1	2	2.85	27.89	0.57	2.85	27.89	0.57	1.27	1.19	1.62
	PAX = 0.93 kg/t	C2	6	2.41	16.69	0.50	5.26	22.76	0.53	1.91	2.07	3.19
	Dextrin = 0.93 kg/t	C3	12	4.35	15.06	0.50	9.61	19.28	0.52	2.95	3.69	6.10
	Feed = 200 g	C4	20	7.59	14.11	0.41	17.20	17.00	0.47	4.66	5.98	11.22
	Feed ash = 32.29%	T		172.75	34.62	0.74						
	Feed T sulfur = 0.67 %	Recons. feed					189.95	33.03	0.71			
35	MIBC = 0.11 kg/t	C1	2	3.69	29.65	1.04	3.69	29.65	1.04	1.79	2.66	2.05
	PAX = 1.4 kg/t	C2	6	3.02	17.57	0.74	6.71	24.21	0.90	2.66	4.20	4.01
	Dextrin = 0.93 kg/t	C3	12	4.21	17.42	0.84	10.92	21.59	0.88	3.86	6.64	6.75
	Feed = 200 g	C4	20	6.82	17.79	0.67	17.74	20.13	0.80	5.85	9.79	11.17
	Feed ash = 33.74%	T		170.14	33.78	0.77						
	Feed T sulfur = 0.78%	Recons. feed					187.88	32.50	0.77			
36	MIBC = 0.11 kg/t	C1	2	3.52	29.51	0.86	3.52	29.51	0.86	1.69	2.17	1.93
	PAX = 1.4 kg/t	C2	6	2.97	17.94	0.90	6.49	24.21	0.88	2.56	4.06	3.83
	Dextrin = 0.93 kg/t	C3	12	4.49	18.35	0.70	10.98	21.82	0.80	3.90	6.30	6.69
	Feed = 200 g	C4	20	6.47	17.27	0.79	17.45	20.13	0.80	5.71	9.93	10.87
	Feed ash = 32.19%	T		172.29	33.64	0.73						
	Feed T sulfur = 0.72%	Recons. feed					189.74	32.40	0.74			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
37	MIBC = 0.11 kg/t PAX = 1.86 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash =33.68 % Feed T sulfur = 0.75%	C1	2	4.75	28.43	1.33	4.75	28.43	1.33	1.84	3.69	2.94	
		C2	6	3.47	17.22	1.12	8.22	23.69	1.24	2.65	5.97	5.43	
		C3	12	4.84	17.44	1.41	13.06	21.38	1.30	3.80	9.97	8.88	
		C4	20	6.26	17.95	1.13	19.32	20.27	1.25	5.34	14.12	13.33	
		T		169.66	40.94	0.86							
		Recons. feed						188.98	38.83	0.90			
38	MIBC = 0.11 kg/t PAX = 1.86 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 32.82% Feed T sulfur =0.85 %	C1	2	4.84	30.39	1.28	4.84	30.39	1.28	2.40	4.78	2.75	
		C2	6	3.71	19.63	1.03	8.55	25.72	1.17	3.58	7.73	5.19	
		C3	12	4.71	17.51	1.10	13.26	22.81	1.15	4.93	11.73	8.37	
		C4	20	6.56	17.92	1.18	19.82	21.19	1.16	6.84	17.70	12.77	
		T		163.86	34.89	0.65							
		Recons. feed						183.68	33.41	0.71			
39	MIBC = 0.11 kg/t PAX = 2.33 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.17% Feed T sulfur =0.77 %	C1	2	6.47	30.97	1.40	6.47	30.97	1.40	3.17	5.90	3.49	
		C2	6	4.31	18.08	1.22	10.78	25.81	1.33	4.40	9.34	6.26	
		C3	12	5.71	18.60	1.63	16.49	23.32	1.43	6.08	15.43	9.89	
		C4	20	7.24	19.16	1.57	23.73	22.05	1.47	8.28	22.87	14.47	
		T		167.29	34.66	0.70							
		Recons. feed						191.02	33.09	0.80			
40	MIBC = 0.11 kg/t PAX = 2.33 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 34.44% Feed T sulfur = 32.96%	C1	2	6.17	30.22	1.23	6.17	30.22	1.23	2.98	4.79	3.38	
		C2	6	3.92	17.27	1.26	10.09	25.19	1.24	4.06	7.90	5.93	
		C3	12	5.71	18.35	2.01	15.80	22.72	1.52	5.74	15.14	9.59	
		C4	20	6.79	18.82	1.68	22.59	21.54	1.57	7.78	22.34	13.92	
		T		167.29	34.50	0.74							
		Recons. feed						189.88	32.96	0.83			

Table D.5: Sulfide flotation results (rod-milled coal)

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %
41	MIBC = 0.11 kg/t PAX = 0.93 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.72% Feed T sulfur = 0.66%	C1	2	3.06	26.46	0.72	3.06	26.46	0.72	1.25	2.05	1.73
		C2	6	2.99	17.49	0.39	6.05	22.03	0.56	2.06	3.15	3.62
		C3	12	4.09	16.53	0.37	10.14	19.81	0.48	3.11	4.55	6.23
		C4	20	3.43	19.33	0.42	13.57	19.69	0.46	4.13	5.90	8.36
		T		181.46	34.13	0.55						
		Recons. feed					195.03	33.13	0.55			
42	MIBC = 0.11 kg/t PAX = 0.93 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.67% Feed T sulfur = 0.53%	C1	2	2.71	26.11	0.57	2.71	26.11	0.57	1.10	1.46	1.56
		C2	6	3.70	18.01	0.37	6.41	21.43	0.45	2.14	2.75	3.93
		C3	12	4.55	17.33	0.37	10.96	19.73	0.42	3.37	4.35	6.87
		C4	20	4.14	18.01	0.34	15.10	19.26	0.40	4.53	5.69	9.52
		T		177.14	34.62	0.56						
		Recons. feed					192.24	33.41	0.55			
43	MIBC = 0.11 kg/t PAX = 1.4 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.72% Feed T sulfur = 0.99%	C1	2	4.19	30.22	1.97	4.19	30.22	1.97	2.01	4.95	2.29
		C2	6	3.16	20.13	1.22	7.35	25.88	1.65	3.02	7.27	4.27
		C3	12	4.71	18.19	0.92	12.06	22.88	1.36	4.37	9.86	7.28
		C4	20	6.51	17.35	0.71	18.57	20.94	1.13	6.16	12.64	11.50
		T		172.23	34.38	0.85						
		Recons. feed					190.80	33.07	0.87			
44	MIBC = 0.11 kg/t PAX = 1.4 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.28% Feed T sulfur = 0.93%	C1	2	4.43	30.32	1.75	4.43	30.32	1.75	2.07	4.70	2.36
		C2	6	3.27	19.18	1.14	7.70	25.59	1.49	3.03	6.96	4.38
		C3	12	4.89	17.80	0.98	12.59	22.56	1.29	4.37	9.87	7.46
		C4	20	7.22	18.02	0.73	19.81	20.90	1.09	6.38	13.06	11.99
		T		175.85	34.57	0.82						
		Recons. feed					195.66	33.19	0.84			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
45	MIBC = 0.11 kg/t PAX = 1.86 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.01% Feed T sulfur = 0.89%	C1	2	5.66	32.44	2.18	5.66	32.44	2.18	2.81	7.22	2.94	
		C2	6	3.77	24.50	1.58	9.43	29.27	1.94	4.23	10.71	5.12	
		C3	12	5.65	20.69	1.32	15.08	26.05	1.71	6.02	15.09	8.57	
		C4	20	7.94	18.75	0.97	23.02	23.54	1.45	8.31	19.60	13.52	
		T		172.38	34.70	0.80							
		Recons. feed						195.40	33.38	0.87			
46	MIBC = 0.11 kg/t PAX = 1.86 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.66% Feed T sulfur = 0.93%	C1	2	5.78	31.61	1.82	5.78	31.61	1.82	2.84	5.67	3.02	
		C2	6	3.91	21.14	1.77	9.69	27.39	1.80	4.13	9.40	5.37	
		C3	12	5.95	20.28	1.24	15.64	24.68	1.59	6.01	13.37	8.99	
		C4	20	7.90	18.93	0.98	23.54	22.75	1.38	8.33	17.53	13.87	
		T		171.80	34.30	0.89							
		Recons. feed						195.34	32.91	0.95			
47	MIBC = 0.11 kg/t PAX = 2.33 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.54% Feed T sulfur = 0.80%	C1	2	6.83	31.74	2.17	6.83	31.74	2.17	3.41	8.59	3.55	
		C2	6	4.67	21.79	1.76	11.50	27.70	2.00	5.01	13.35	6.34	
		C3	12	7.05	20.87	1.68	18.55	25.10	1.88	7.32	20.19	10.59	
		C4	20	9.37	20.79	1.41	27.92	23.66	1.72	10.38	27.82	16.24	
		T		166.95	34.16	0.75							
		Recons. feed						194.87	32.65	0.89			
48	MIBC = 0.11 kg/t PAX = 2.33 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.63% Feed T sulfur = 0.87%	C1	2	7.91	32.36	2.25	7.91	32.36	2.25	3.99	9.73	4.06	
		C2	6	4.51	21.81	1.79	12.42	28.53	2.08	5.52	14.14	6.73	
		C3	12	6.22	19.94	1.55	18.64	25.66	1.91	7.45	19.41	10.51	
		C4	20	8.62	19.76	1.55	27.26	23.79	1.79	10.10	26.71	15.76	
		T		168.75	34.20	0.79							
		Recons. feed						196.01	32.76	0.93			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
49	MIBC = 0.11 kg/t PAX = 1.4 kg/t Dextrin = 0.70 kg/t Feed = 200 g Feed ash = 33.67% Feed T sulfur = 0.91%	C1	2	4.94	30.65	1.92	4.94	30.65	1.92	2.38	5.74	2.60	
		C2	6	3.54	20.62	1.26	8.48	26.46	1.64	3.53	8.44	4.73	
		C3	12	5.52	18.85	0.91	14.00	23.46	1.35	5.16	11.48	8.12	
		C4	20	7.63	19.85	0.66	21.63	22.19	1.11	7.54	14.55	12.76	
		T		173.93	33.82	0.81							
		Recons. feed						195.56	32.53	0.84			
50	MIBC = 0.11 kg/t PAX = 1.4 kg/t Dextrin = 0.70 kg/t Feed = 200 g Feed ash = 35.73% Feed T sulfur = 0.84%	C1	2	4.50	29.35	2.01	4.50	29.35	2.01	2.02	5.53	2.40	
		C2	6	4.32	20.99	1.13	8.82	25.26	1.58	3.41	8.52	4.99	
		C3	12	6.00	19.20	0.78	14.82	22.80	1.26	5.17	11.39	8.65	
		C4	20	7.89	18.69	0.60	22.71	21.37	1.03	7.43	14.31	13.51	
		T		174.83	34.59	0.80							
		Recons. feed						197.54	33.07	0.83			
51	MIBC = 0.11 kg/t PAX = 1.4 kg/t Dextrin = 1.16 kg/t Feed = 200 g Feed ash = 33.09% Feed T sulfur = 0.85%	C1	2	4.27	31.20	1.91	4.27	31.20	1.91	2.11	5.13	2.27	
		C2	6	2.85	19.79	0.99	7.12	26.63	1.54	3.00	6.90	4.03	
		C3	12	5.05	18.40	0.79	12.17	23.22	1.23	4.48	9.40	7.21	
		C4	20	6.83	18.39	0.65	19.00	21.48	1.02	6.47	12.20	11.51	
		T		173.71	33.98	0.80							
		Recons. feed						192.71	32.74	0.82			
52	MIBC = 0.11 kg/t PAX = 1.4 kg/t Dextrin = 1.16 kg/t Feed = 200 g Feed ash = 33.89% Feed T sulfur = 0.91%	C1	2	4.61	31.87	1.40	4.61	31.87	1.40	2.30	3.99	2.44	
		C2	6	2.78	20.57	1.17	7.39	27.62	1.31	3.19	6.00	4.16	
		C3	12	4.92	18.71	0.88	12.31	24.06	1.14	4.63	8.69	7.27	
		C4	20	7.62	19.34	0.71	19.93	22.25	0.98	6.93	12.04	12.05	
		T		172.57	34.49	0.82							
		Recons. feed						192.50	33.23	0.84			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
53	MIBC = 0.11 kg/t PAX = 1.4 kg/t Dextrin = 1.4 kg/t Feed = 200 g Feed ash = 33.66% Feed T sulfur = 0.89%	C1	2	4.64	32.20	1.27	4.64	32.20	1.27	2.34	3.85	2.42	
		C2	6	2.96	21.77	1.07	7.60	28.14	1.19	3.35	5.93	4.20	
		C3	12	4.77	19.75	0.70	12.37	24.90	1.00	4.82	8.13	7.15	
		C4	20	6.88	18.84	0.63	19.25	22.74	0.87	6.85	10.96	11.44	
		T		174.59	34.07	0.78							
		Recons. feed						193.84	32.94	0.79			
54	MIBC = 0.11 kg/t PAX = 1.4 kg/t Dextrin = 1.4 kg/t Feed = 200 g Feed ash = 33.04 Feed T sulfur = 0.66%	C1	2	5.07	32.72	0.97	5.07	32.72	0.97	2.63	3.48	2.62	
		C2	6	2.55	20.60	0.77	7.62	28.67	0.90	3.46	4.86	4.18	
		C3	12	5.43	20.05	0.53	13.05	25.08	0.75	5.18	6.88	7.51	
		C4	20	7.15	18.74	0.42	20.20	22.84	0.63	7.30	8.98	11.98	
		T		173.15	33.83	0.74							
		Recons. feed						193.35	32.68	0.73			
55	MIBC = 0.057 kg/t PAX = 2.33 kg/t Dextrin = 1.4 kg/t Feed = 200 g Feed ash = 33.40% Feed T sulfur = 0.52%	C1	2	7.35	32.46	0.95	7.35	32.46	0.95	3.52	6.47	3.96	
		C2	6	4.94	22.62	0.79	12.29	28.50	0.89	5.18	10.10	7.01	
		C3	12	7.16	20.95	0.90	19.45	25.72	0.89	7.39	16.04	11.52	
		C4	20	10.12	54.05	0.83	29.57	35.42	0.87	15.47	23.83	15.23	
		T		163.52	34.99	0.50							
		Recons. feed						193.09	35.06	0.56			
56	MIBC = 0.057 kg/t PAX = 2.33 kg/t Dextrin = 1.4 kg/t Feed = 200 g Feed ash = 33.39% Feed T sulfur = 0.69%	C1	2	8.20	32.30	1.29	8.20	32.30	1.29	4.20	8.68	4.26	
		C2	6	4.80	22.17	1.25	13.00	28.56	1.28	5.88	13.60	7.12	
		C3	12	6.80	20.91	1.40	19.80	25.93	1.32	8.14	21.41	11.24	
		C4	20	9.53	19.69	0.83	29.33	23.90	1.16	11.11	27.91	17.11	
		T		164.21	34.16	0.54							
		Recons. feed						193.54	32.60	0.63			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
57	MIBC = 0.075 kg/t PAX = 2.33 kg/t Dextrin = 1.4 kg/t Feed = 200 g Feed ash = 33.60% Feed T sulfur = 0.77%	C1	2	7.86	32.15	1.78	7.86	32.15	1.78	4.05	10.32	4.17	
		C2	6	5.14	22.68	0.95	13.00	28.41	1.45	5.91	13.93	7.29	
		C3	12	7.22	21.60	1.10	20.22	25.98	1.32	8.41	19.81	11.72	
		C4	20	9.23	19.42	1.00	29.45	23.92	1.22	11.28	26.63	17.54	
		T		160.74	34.47	0.62							
		Recons. feed						190.19	32.83	0.71			
58	MIBC = 0.075 kg/t PAX = 2.33 kg/t Dextrin = 1.4 kg/t Feed = 200 g Feed ash = 33.53% Feed T sulfur = 0.77%	C1	2	7.60	32.47	1.29	7.60	32.47	1.29	3.90	7.69	4.01	
		C2	6	4.68	22.64	1.36	12.28	28.72	1.32	5.57	12.68	6.84	
		C3	12	6.84	21.81	1.20	19.12	26.25	1.27	7.93	19.09	11.03	
		C4	20	9.10	32.79	0.64	28.22	28.36	1.07	12.65	23.67	15.81	
		T		162.93	33.92	0.60							
		Recons. feed						191.15	33.10	0.67			
59	MIBC = 0.11 kg/t PAX = 2.33 kg/t Dextrin = 1.4 kg/t Feed = 200 g Feed ash = 33.93% Feed T sulfur = 0.68%	C1	2	8.49	32.99	1.46	8.49	32.99	1.46	4.45	11.79	4.41	
		C2	6	4.40	23.24	1.31	12.89	29.66	1.40	6.07	17.27	7.03	
		C3	12	6.07	21.41	1.10	18.96	27.02	1.30	8.13	23.62	10.73	
		C4	20	7.62	19.62	0.88	26.58	24.90	1.18	10.50	30.03	15.48	
		T		165.38	34.10	0.44							
		Recons. feed						191.96	32.82	0.55			
60	MIBC = 0.11 kg/t PAX = 2.33 kg/t Dextrin = 1.4 kg/t Feed = 200 g Feed ash = 33.18% Feed T sulfur = 0.81%	C1	2	8.62	33.54	1.80	8.62	33.54	1.80	4.54	10.18	4.39	
		C2	6	4.20	24.04	1.76	12.82	30.43	1.78	6.13	15.03	6.84	
		C3	12	5.84	21.59	1.43	18.66	27.66	1.67	8.11	20.52	10.36	
		C4	20	7.68	19.79	1.10	26.34	25.37	1.50	10.50	26.05	15.08	
		T		167.66	33.98	0.67							
		Recons. feed						194.00	32.81	0.78			

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
61	MIBC = 0.11 kg/t SIBX= 2.33 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 32.92% Feed T sulfur = 0.81%	C1	2	7.07	28.76	1.57	7.07	28.76	1.57	6.63	2.99	3.79	
		C2	6	5.35	17.46	1.10	12.42	23.89	1.37	10.14	4.36	7.11	
		C3	12	8.96	17.20	0.97	21.38	21.09	1.20	15.34	6.62	12.70	
		C4	20	12.06	17.13	0.95	33.44	19.66	1.11	22.17	9.66	20.22	
		T		167.53	36.72	0.78							
		Recons. feed						200.97	33.88	0.83			
62	MIBC = 0.11 kg/t SIBX = 2.33 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.45% Feed T sulfur = 0.84%	C1	2	6.41	29.49	1.32	6.41	29.49	1.32	5.19	2.79	3.41	
		C2	6	4.52	18.45	1.00	10.93	24.93	1.19	7.95	4.02	6.18	
		C3	12	7.45	17.63	1.01	18.38	21.97	1.11	12.54	5.96	10.81	
		C4	20	11.06	17.52	1.02	29.44	20.30	1.08	19.46	8.81	17.68	
		T		171.04	36.14	0.77							
		Recons. feed						200.48	33.82	0.81			
63	MIBC = 0.11 kg/t SEX = 2.33 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed T sulfur = 0.85%	C1	2	0.79		0.51	0.79		0.51	0.26			
		C2	6	0.82		0.55	1.61		0.53	0.54			
		C3	12	0.94		0.59	2.55		0.55	0.89			
		C4	20	1.78		0.64	4.33		0.59	1.61			
		T		197.26		0.79							
		Recons. feed						201.59		0.78			
64	MIBC = 0.11 kg/t SEX = 2.33 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed T sulfur = 0.65%	C1	2	0.44		0.47	0.44		0.47	0.16			
		C2	6	0.53		0.46	0.97		0.46	0.34			
		C3	12	0.99		0.50	1.96		0.48	0.71			
		C4	20	1.32		0.56	3.28		0.51	1.26			
		T		197.32		0.67							
		Recons. feed						200.60		0.67			

Table D.6: Two-stage flotation results

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %
65	MIBC = 0.11 kg/t	C1	0.5	12.20	15.07	0.49	12.20	15.07	0.49	2.44	1.84	5.30
	Dodecane = 1.86 kg/t	C2	1	8.61	13.66	0.47	20.81	14.49	0.48	4.11	3.02	9.10
	Feed = 300 g	C3	2	12.97	12.98	0.48	33.78	13.91	0.48	6.67	4.70	14.87
	Feed ash = 34.35%	C4	5	24.28	13.16	0.48	58.06	13.60	0.48	11.49	7.90	25.66
	Feed T sulfur = 1.10%	T		237.32	38.75	0.91						
	FIRST STAGE	Recons. feed					295.38	33.81	0.82			
66	MIBC = 0.11 kg/t	C1	0.5	11.34	15.56	0.49	11.34	15.56	0.49	2.21	1.74	4.94
	Dodecane = 1.86 kg/t	C2	1	8.17	13.56	0.49	19.51	14.72	0.49	3.82	2.83	8.58
	Feed = 300 g	C3	2	11.51	12.76	0.48	31.02	14.00	0.48	6.02	4.28	13.76
	Feed ash = 34.43%	C4	5	24.83	12.86	0.48	55.85	13.49	0.48	10.81	7.43	24.91
	Feed T sulfur = 1.06%	T		239.53	39.20	0.93						
	FIRST STAGE	Recons. feed					295.38	34.34	0.84			
67	MIBC = 0.11 kg/t	C1	2	13.11	40.96	5.01	13.11	40.96	5.01	41.34	6.92	6.34
	PAX = 2.33 kg/t	C2	6	5.86	23.78	2.04	18.97	35.65	4.09	48.85	8.72	9.99
	Dextrin = 0.93 kg/t	C3	12	6.93	20.53	1.13	25.90	31.61	3.29	53.77	10.56	14.50
	Feed = 200 g	C4	20	8.75	20.88	0.85	34.65	28.90	2.68	58.46	12.91	20.17
	Feed ash = 38.75%	T		165.05	40.92	0.40						
	Feed T sulfur = 0.91%	Recons. feed					199.70	38.83	0.79			
SECOND STAGE (65)												
68	MIBC = 0.11 kg/t	C1	2	14.27	38.99	5.06	14.27	38.99	5.06	45.63	7.19	7.06
	PAX = 2.33 kg/t	C2	6	6.03	21.98	1.84	20.30	33.94	4.10	52.62	8.91	10.88
	Dextrin = 0.93 kg/t	C3	12	7.39	20.82	1.01	27.69	30.44	3.28	57.31	10.90	15.63
	Feed = 200 g	C4	20	8.77	21.63	0.78	36.46	28.32	2.67	61.62	13.35	21.20
	Feed ash = 39.20%	T		164.16	40.83	0.37						
	Feed T sulfur = 0.93%	Recons. feed					200.62	38.56	0.79			
SECOND STAGE (66)												

Table D.7: Stage-wise addition sulfide flotation results

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %	
69	MIBC = 0.11 kg/t PAX = 1.4 kg/t PAX = 0.93 kg/t Dextrin = 0.93 kg/t Feed = 200 g Feed ash = 33.37% Feed T sulfur = 0.69%	C1	2	4.75	29.27	2.27	4.75	29.27	2.27	7.29	2.01	2.52	
		C2	6	4.01	19.29	0.81	8.76	24.70	1.60	9.47	3.14	4.94	
		C3	12	15.41	23.68	1.95	24.17	24.05	1.82	29.78	8.42	13.76	
		C4	20	13.75	18.92	0.90	37.92	22.19	1.49	38.15	12.19	22.11	
		T		164.55	36.83	0.56							
		Recons. feed						202.47	34.09	0.73			
71	MIBC = 0.11 kg/t PAX = 1.4 kg/t PAX = 0.93 kg/t Dextrin = 0.98 kg/t Feed = 200 g Feed ash = 33.82% Feed T sulfur = 0.69%	C1	2	5.64	30.41	2.00	5.64	30.41	2.00	7.67	2.49	2.93	
		C2	6	4.24	20.55	0.88	9.88	26.18	1.52	10.22	3.75	5.44	
		C3	12	14.26	24.57	2.13	24.14	25.23	1.88	30.83	8.83	13.47	
		C4	20	12.91	18.99	0.87	37.05	23.06	1.53	38.45	12.38	21.28	
		T		165.92	36.42	0.55							
		Recons. feed						202.97	33.98	0.72			
71	MIBC = 0.11 kg/t PAX = 1.4 kg/t PAX = 0.5 kg/t PAX = 0.5 kg/t Dextrin = 0.98 kg/t Feed = 200 g Feed ash = 33.74% Feed T sulfur = 0.71%	C1	2	5.66	30.03	2.07	5.66	30.03	2.07	7.71	2.45	2.94	
		C2	6	4.02	18.97	0.88	9.68	25.44	1.57	10.02	3.54	5.36	
		C3	12	6.53	19.04	0.61	16.21	22.86	1.19	12.65	5.33	9.29	
		C4	20	7.21	20.56	0.57	23.42	22.15	1.00	15.36	7.46	13.54	
		C5	25	8.37	24.91	2.17	31.79	22.88	1.31	27.31	10.46	18.21	
		C6	30	15.28	22.17	1.52	47.07	22.65	1.37	42.54	15.34	27.04	
		T		157.06	37.46	0.56							
Recons. feed						204.13	34.05	0.74					

Run no.	Reagents	Sample	Time min	Mass g	Ash %	Total S %	Cum Mass g	Cum Ash %	Cum S %	Total S Rec. %	Ash Rec. %	Coal Rec. %
72	MIBC = 0.11 kg/t	C1	2	6.08	30.65	2.09	6.08	30.65	2.09	8.40	2.69	3.65
	PAX = 1.4 kg/t	C2	6	3.69	18.92	0.83	9.77	26.22	1.61	10.42	3.70	6.23
	PAX = 0.5 kg/t	C3	12	6.09	18.53	0.64	15.86	23.27	1.24	13.00	5.33	10.52
	PAX = 0.5 kg/t	C4	20	7.40	20.21	0.57	23.26	22.30	1.03	15.80	7.49	15.63
	Dextrin =1 kg/t	C5	25	7.87	24.19	2.21	31.13	22.77	1.33	27.27	10.23	15.63
	Feed = 200 g	C6	30	13.89	22.49	1.58	45.02	22.69	1.40	41.73	14.74	15.63
	Feed ash = 33.46% Feed T sulfur = 0.67%	T			156.63	37.71	0.56					
	Recons. feed						201.65	34.36	0.75			

D.2 Acid prediction test results

Table D.8: Characteristics of samples used in ARD prediction tests

Legend	Samples	Sulfur content (%)
F	Feed	1.08
1T	First stage tailing	0.92
1C	Clean coal	0.48
2T	Second stage tailing	0.38
2C	Sulfide-rich fraction	2.68
3T	1-stage tailing from sulfide flotation	0.73
4T	2-stage tailing (2 stage PAX addition)	0.55
5T	3-stage tailing (3 stage PAX addition)	0.56

Table D.9: Acid base accounting results

Float No	% S	MPA (kg H ₂ SO ₄)	Fizz Rating	Vol NaOH (mL)	ANC (H ₂ SO ₄ kg/t)	NAPP (H ₂ SO ₄ kg/t)
F	1.08	33.05	1	26.7 ± 0.28	29.86 ± 0.72	3.19
1T	0.92	27.85	1	24.3 ± 0.35	36.11 ± 0.9	-8.27
1C	0.48	14.69	1	30.2 ± 0.42	20.93 ± 1.08	-6.24
2T	0.38	11.32	2	15.9 ± 0.07	56.49 ± 0.84	-45.17
2C	2.67	81.7	1	31.7 ± 0.64	17.23 ± 1.62	64.48
3T	0.73	22.34	1	25.2 ± 0.07	33.82 ± 0.18	-11.48
4T	0.55	16.83	2	16.2 ± 0.07	52.92 ± 0.84	-36.09
5T	0.56	17.14	2	16.7 ± 1.06	46.98 ± 12.61	-29.84

D.2.1 Net acid generation results

Table D.10: Single addition NAG test

Float No	S grade %	Before boil pH	After boil pH	NAG pH	Volume 1 mL	Volume 2 mL	NAG pH 4.5	NAG pH7
F	0.86	4.04 ± 0.27	3.53 ± 0.32	3.97 ± 0.02	2.3 ± 0.28	15.7 ± 0.85	4.51 ± 0.55	26.26 ± 1.11
1T	0.92	4.57 ± 0.25	3.85 ± 0.21	4.28 ± 0.04	0.9 ± 0.14	12.55 ± 0.21	1.76 ± 0.28	22.83 ± 0.14
1C	0.48	4.32 ± 0.01	3.04 ± 0.03	3.24 ± 0.06	13.45 ± 1.06	35.65 ± 1.48	26.36 ± 2.08	43.51 ± 0.83
2T	0.38	5.48 ± 0.03	5.23 ± 0.11	5.39 ± 0.11	0 ± 0	3.5 ± 0.57	0 ± 0	6.86 ± 1.11
2C	2.67	2.14 ± 0.01	1.87 ± 0.04	2.13 ± 0.01	30.95 ± 0.92	38.5 ± 2.4	60.66 ± 1.8	14.80 ± 2.91
3T	0.73	4.82 ± 0.25	3.86 ± 0.29	4.36 ± 0.04	0.6 ± 0.14	13.75 ± 0.35	1.18 ± 0.28	25.77 ± 0.42
4T	0.55	5.12 ± 0.01	4.33 ± 0.16	4.62 ± 0.12	0 ± 0	11.95 ± 1.63	0 ± 0	23.42 ± 3.19
5T	0.56	5.17 ± 0.01	5.08 ± 0.01	5.33 ± 0	0 ± 0	3.65 ± 0.07	0 ± 0	7.15 ± 0.14

Table D.11: Sequential NAG test

	S grade %	Before boil pH	After boil pH	NAG pH	Volume 1 mL	Volume 2 mL	NAG pH 4.5	NAG pH7
Stage 1	2.67	2.14 ± 0.01	1.87 ± 0.04	2.13 ± 0.01	30.95 ± 0.92	38.50 ± 2.4	60.66 ± 1.8	14.8 ± 2.91
Stage 2	-	2.61 ± 0.06	2.71 ± 0.01	3.02 ± 0.01	6.20 ± 0	19.3 ± 0	13.23 ± 0.01	27.95 ± 0.02
Stage 3	-	3.27 ± 0.03	3.64 ± 0.13	3.72 ± 0.04	1.15 ± 0.21	4.8 ± 0.57	5.22 ± 1.3	16.51 ± 2.68
Stage 4	-	4.20 ± 0.28	4.63 ± 0.08	4.63 ± 0.08	0 ± 0	0.50 ± 0.14	0 ± 0	6.29 ± 1.89

D.2.2 Biokinetic test results

Table D.12: Ferric concentration

Sample No.	Days	Ferric iron concentration (mg/L)						
		F	1 T	1 C	2 T	2 T pH 2	2 C	2 T Abiotic
1	2	224 ± 6	213 ± 6.8	209 ± 6	217 ± 7.7	211 ± 4.8	225 ± 3.7	64 ± 3.7
2	4	217 ± 25	236 ± 8.5	255 ± 3.7	169 ± 30	236 ± 18	301 ± 55	53.6 ± 3.7
3	6	189 ± 27	194 ± 20	239 ± 5	127 ± 15	253 ± 16	280 ± 22	60 ± 2.4
4	8	217 ± 69	168 ± 0	246 ± 15	141 ± 9.7	317 ± 19	317 ± 30	91.1 ± 2.4
5	10	179 ± 2.8	164 ± 8.5	225 ± 17	121 ± 11	349 ± 30	329 ± 73	48.8 ± 5.5
6	13	176 ± 26	170 ± 4.2	212 ± 18	103 ± 12	362 ± 29	403 ± 158	33.6 ± 2.1
7	15	186 ± 25	181 ± 3.4	205 ± 22	104 ± 15	365 ± 29	453 ± 200	34.8 ± 5.2
8	17	193 ± 27	190 ± 5.9	207 ± 22	100 ± 10	334 ± 73	486 ± 221	36.4 ± 2.5
9	20	209 ± 34	198 ± 6.8	191 ± 22	102 ± 13	367 ± 32	555 ± 261	33.6 ± 3.2
10	22	209 ± 35	198 ± 4.2	178 ± 21	93.9 ± 10	338 ± 45	583 ± 253	36.4 ± 1.8
11	24	201 ± 20	197 ± 4.2	175 ± 19	96.7 ± 13	334 ± 42	670 ± 244	36.4 ± 1.4
12	27	220 ± 39	207 ± 6.8	171 ± 13	90.3 ± 9.3	331 ± 39	778 ± 236	41.2 ± 3
13	29	228 ± 42	215 ± 3.4	170 ± 18	83.5 ± 5.9	319 ± 42	821 ± 218	40 ± 1.8
14	31	230 ± 42	215 ± 12	161 ± 19	85.1 ± 10	312 ± 44	869 ± 216	36.8 ± 1.4
15	35	231 ± 37	235 ± 10	159 ± 18	81.1 ± 10	295 ± 44	940 ± 187	40.0 ± 1.8
16	38	237 ± 32	220 ± 4.2	140 ± 5.2	84.3 ± 16	288 ± 36	982 ± 219	37.6 ± 1.8
17	42	239 ± 33	236 ± 2.5	155 ± 14	75.1 ± 11	287 ± 36	1056 ± 228	39.2 ± 1.4
18	45	241 ± 31	248 ± 5.9	175 ± 0.7	97.5 ± 6.2	301 ± 26	1119 ± 241	41.2 ± 1.4
19	49	237 ± 30	236 ± 5.9	153 ± 11	85.1 ± 9.4	287 ± 29	1106 ± 241	44 ± 3.7
20	52	245 ± 36	246 ± 9.3	164 ± 11	97.9 ± 8.4	297 ± 37	1155 ± 207	45.6 ± 1.2
21	56	253 ± 54	243 ± 2.5	156 ± 8.3	85.9 ± 16	295 ± 28	1129 ± 258	40.8 ± 2.1
22	59	279 ± 42	248 ± 14	154 ± 13	71.5 ± 14	282 ± 7.3	1133 ± 238	42.4 ± 11
23	63	228 ± 32	271 ± 8.5	158 ± 18	63.6 ± 3.2	269 ± 33	1119 ± 239	40 ± 7.3
24	66	235 ± 27	234 ± 2.5	152 ± 10	68.8 ± 8	273 ± 31	1108 ± 248	32 ± 0.7
25	71	231 ± 18	240 ± 5.9	155 ± 18	64.6 ± 9.1	268 ± 31	1102 ± 247	33.6 ± 3.2
26	76	230 ± 24	234 ± 2.5	149 ± 16	62.4 ± 11	269 ± 31	1101 ± 237	31.6 ± 3.9

Table D.13: pH

Sample No.	Days	pH						
		Feed	1 T	1 C	2 T	2 T p H 2	2 C	2 T abiotic
1	0	2 ± 0	2 ± 0	2 ± 0	2 ± 0	2 ± 0	2 ± 0	2 ± 0
2	2	2.31 ± 0.06	2.25 ± 0.01	2.08 ± 0.04	2.45 ± 0.09	2.55 ± 0.18	2.13 ± 0.03	4.52 ± 1.37
3	4	2.38 ± 0.05	2.39 ± 0.01	2.12 ± 0.03	2.48 ± 0.03	2.32 ± 0.02	2.16 ± 0.03	4.89 ± 0.98
4	6	2.35 ± 0.03	2.37 ± 0.02	2.11 ± 0.03	2.46 ± 0.05	2.24 ± 0.03	2.13 ± 0.04	5.24 ± 0.22
5	8	2.32 ± 0.01	2.33 ± 0.01	2.11 ± 0.03	2.48 ± 0.04	2.03 ± 0.01	2.05 ± 0.04	5.83 ± 0.15
6	10	2.32 ± 0.07	2.34 ± 0.01	2.09 ± 0.02	2.53 ± 0.03	2.01 ± 0.01	2.02 ± 0.05	5.82 ± 0.08
7	13	2.3 ± 0.06	2.35 ± 0.03	2.08 ± 0.01	2.56 ± 0.05	1.99 ± 0.01	1.98 ± 0.05	5.91 ± 0.07
8	15	2.29 ± 0.06	2.36 ± 0.01	2.08 ± 0.02	2.59 ± 0.05	2.01 ± 0.01	1.98 ± 0.05	5.92 ± 0.12
9	17	2.26 ± 0.05	2.35 ± 0.02	2.05 ± 0.01	2.6 ± 0.05	1.98 ± 0.02	1.93 ± 0.07	5.95 ± 0.16
10	20	2.26 ± 0.04	2.34 ± 0.02	2.04 ± 0.02	2.6 ± 0.04	1.99 ± 0.01	1.91 ± 0.08	6 ± 0.21
11	22	2.23 ± 0.05	2.32 ± 0.01	2.03 ± 0.01	2.58 ± 0.05	1.99 ± 0.01	1.9 ± 0.07	5.67 ± 0.27
12	24	2.24 ± 0.05	2.31 ± 0.01	2.02 ± 0.02	2.6 ± 0.06	1.99 ± 0	1.88 ± 0.06	6.18 ± 0.19
13	27	2.14 ± 0.08	2.27 ± 0	1.99 ± 0.01	2.57 ± 0.06	1.96 ± 0	1.83 ± 0.07	6.23 ± 0.19
14	29	2.19 ± 0.07	2.28 ± 0	2 ± 0.02	2.58 ± 0.07	2.01 ± 0	1.82 ± 0.07	6.27 ± 0.19
15	31	2.21 ± 0.06	2.28 ± 0.01	2 ± 0.01	2.6 ± 0.07	2.02 ± 0	1.82 ± 0.07	5.98 ± 0.1
16	35	2.19 ± 0.07	2.28 ± 0	2.03 ± 0.01	2.61 ± 0.07	2.03 ± 0.01	1.82 ± 0.06	6.19 ± 0.07
17	38	2.16 ± 0.05	2.22 ± 0	1.98 ± 0.02	2.55 ± 0.07	1.96 ± 0	1.77 ± 0.06	6.27 ± 0.1
18	42	2.15 ± 0.05	2.27 ± 0	2.02 ± 0.01	2.62 ± 0.08	2.01 ± 0.01	1.79 ± 0.06	6.20 ± 0.1
19	45	2.21 ± 0.05	2.24 ± 0	2.03 ± 0.02	2.6 ± 0.08	2.01 ± 0.01	1.79 ± 0.06	6.38 ± 0.24
20	49	2.17 ± 0.07	2.23 ± 0	2.03 ± 0.02	2.6 ± 0.08	2 ± 0	1.77 ± 0.06	6.32 ± 0.15
21	52	2.17 ± 0.05	2.22 ± 0	2.01 ± 0.02	2.58 ± 0.08	2 ± 0	1.75 ± 0.04	6.38 ± 0.25
22	56	2.16 ± 0.06	2.21 ± 0	2.01 ± 0.02	2.59 ± 0.08	2 ± 0.01	1.76 ± 0.05	6.38 ± 0.22
23	59	2.15 ± 0.07	2.21 ± 0.01	2.01 ± 0.02	2.57 ± 0.08	2 ± 0.01	1.75 ± 0.06	6.34 ± 0.24
24	63	2.17 ± 0.06	2.22 ± 0.02	2.02 ± 0.02	2.58 ± 0.08	2 ± 0.01	1.76 ± 0.05	6.2 ± 0.04
25	66	2.16 ± 0.05	2.20 ± 0.01	2 ± 0.02	2.57 ± 0.09	1.99 ± 0.01	1.73 ± 0.06	5.96 ± 0.1
26	71	2.16 ± 0.05	2.19 ± 0.01	2.01 ± 0.02	2.57 ± 0.08	1.99 ± 0.01	1.75 ± 0.06	6.35 ± 0.3
27	76	2.17 ± 0.04	2.20 ± 0	2.02 ± 0.02	2.57 ± 0.09	2 ± 0.01	1.75 ± 0.05	5.99 ± 0.28

Table D.14: Redox potential

Sample No.	Days	Redox Potential						
		Feed	1 T	1 C	2 T	2 T p H 2	2 C	2 T Abiotic
1	0	450 ± 2.7	461 ± 0.7	444 ± 2.1	459 ± 1.7	462 ± 3.1	455 ± 4.4	416 ± 4.4
2	2	505 ± 7	510 ± 3.5	494 ± 1.7	534 ± 1	528 ± 8.3	506 ± 9.2	295 ± 49
3	4	615 ± 19	614 ± 5	588 ± 7	665 ± 1.5	672 ± 7.2	686 ± 1.5	322 ± 54
4	6	626 ± 3.8	631 ± 4.2	624 ± 4.2	662 ± 2.1	681 ± 2.1	692 ± 2.5	312 ± 25
5	8	633 ± 12	639 ± 12	634 ± 5.5	663 ± 3.2	692 ± 3.1	696 ± 3.1	314 ± 22
6	10	636 ± 7	619 ± 21	649 ± 15	665 ± 2.1	693 ± 2.1	696 ± 4.9	303 ± 17
7	13	635 ± 3.5	656 ± 7.8	648 ± 2.9	665 ± 5	698 ± 1.5	700 ± 5.1	319 ± 9.5
8	15	645 ± 4.6	667 ± 3.5	653 ± 2.1	666 ± 6.1	704 ± 2.1	708 ± 7.6	322 ± 8.6
9	17	654 ± 0	656 ± 14	663 ± 4	669 ± 4.6	705 ± 3.6	715 ± 8.5	328 ± 5.9
10	20	653 ± 8.4	659 ± 19	659 ± 7.9	667 ± 3.5	701 ± 1.2	713 ± 9.3	319 ± 7.5
11	22	655 ± 4.9	648 ± 19	665 ± 2.5	663 ± 4.9	696 ± 2.3	712 ± 8.7	315 ± 9.9
12	24	662 ± 5.6	673 ± 6.4	666 ± 2.1	665 ± 5.8	701 ± 3.2	720 ± 7.5	283 ± 20
13	27	659 ± 7.8	667 ± 9.9	669 ± 8.3	649 ± 8.4	695 ± 1	719 ± 6.5	251 ± 8.1
14	29	661 ± 5.3	666 ± 9.9	664 ± 2.1	659 ± 5.5	693 ± 1.5	720 ± 6.1	303 ± 6.4
15	31	661 ± 4	662 ± 11.3	662 ± 2.1	655 ± 5	687 ± 4	714 ± 6.2	302 ± 4.7
16	35	658 ± 14	674 ± 1.4	667 ± 1	660 ± 5.6	694 ± 1.5	719 ± 4	307 ± 9.2
17	38	662 ± 11	671 ± 6.4	669 ± 2.1	658 ± 8.1	694 ± 4.4	719 ± 7.1	304 ± 6.1
18	42	667 ± 5.7	680 ± 1.4	671 ± 2.3	661 ± 6	698 ± 3.8	726 ± 5.7	305 ± 6.7
19	45	669 ± 9	672 ± 16.2	673 ± 5.6	653 ± 5	695 ± 1.5	725 ± 6.6	302 ± 2.3
20	49	676 ± 7.9	686 ± 3.5	671 ± 2.3	662 ± 6.6	699 ± 4.9	728 ± 4.2	297 ± 4.2
21	52	676 ± 9.5	682 ± 4.2	671 ± 2.7	640 ± 18	698 ± 2.9	728 ± 1.5	298 ± 2.1
22	56	670 ± 15	681 ± 3.5	684 ± 7.6	647 ± 16	692 ± 4.4	721 ± 6.1	305 ± 0.6
23	59	659 ± 32	640 ± 3.5	684 ± 5.7	650 ± 12	694 ± 2.7	726 ± 3.6	308 ± 5.2
24	63	673 ± 7.8	676 ± 1.4	678 ± 11	645 ± 10	690 ± 5.8	724 ± 5	298 ± 14
25	66	671 ± 7.6	681 ± 2.1	672 ± 6	657 ± 8.1	696 ± 4.9	725 ± 4.2	312 ± 0.6
26	71	671 ± 6.4	680 ± 2.8	666 ± 2.7	651 ± 12	694 ± 4.2	722 ± 1.2	327 ± 2.5
27	76	676 ± 5.8	681 ± 0	666 ± 1.53	650 ± 9.3	692 ± 1	721 ± 4.2	304 ± 13

