Evaluating Approaches to and Benefits of Minimising the Formation of Acid Rock Drainage through Management of the Disposal of Sulphidic Waste Rock and Tailings

Report to the
Water Research Commission
by

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EXECUTIVE SUMMARY

The ideal approach to handling of sulphidic waste rock is to prevent the potential for generation of ARD through the removal of the sulphide phase before its disposal, thus avoiding the need for long-term mitigation strategies. In the best case, this processing of waste rock prior to disposal should result in an increase in the recovery of values from the starting material and the re-allocation of waste materials as feedstocks for other uses.

This report is focussed on the goal of establishing feasible approaches for the prevention of the formation of acid rock drainage (ARD) from mining wastes by the removal of the risk rather than its delay. Current rock drainage prevention strategies focus on covers and coatings. While these have been shown to be effective, the life span of their effectiveness remains in question, motivating the topic of this project. The potential for the removal of sulphides from tailings was demonstrated in WRC 1831/1/11, using tailings and waste rock from a base metal operation as a model system. Both the removal of sulphide by separation and by reaction was demonstrated for the tailings and waste rock respectively, with the former showing the most promise. In this report, the general application of sulphide removal by separation to reduce the risk of ARD generation is presented across tailings and finely divided mineral wastes from various sources, including a variety of coal fines and tailings from the gold industry. Demonstration of the removal of sulphide is presented with the associated reduction in potential for ARD generation. Further, the cost implications and disposal routes for the sulphide and benign fractions removed are considered. With respect to removal by reaction, accelerated bioleaching has, to date, shown limited value; however new approaches, using a broader spectrum of reaction systems, have been highlighted for further study. To extend this work, it is necessary to recognise the need for both acceleration of the reaction of sulphide under controlled conditions as well as deceleration or closing off of these reactions by restricting the supply of reactants through restricting access of water, oxygen, leach agents as well as microbial colonisation. The closing off of these reactions may be a treatment in itself or may follow the accelerated reaction to remove readily reactive sulphur. The role in waste rock dump characteristics, including permeability, as a means to manipulate this is addressed. In summary, this study encompassed the following investigations:

1. Review of current rock drainage prevention strategies
2. Review of ore bed permeability and its impact on ARD generation reactions
3. Experimental studies with respect to the effect of packing on bed permeability and leaching
4. Experimental studies on the effect of irrigation on colonization, moisture content and stagnant zones
5. Approaches to modelling and / or predicting bulk fluid flow in the rock bed
6. Further considerations of sulphide removal by reaction
7. Sulphide removal from tailings by separation across a variety of tailings materials, including a base mineral tailings (WRC 1831/1/11), coal fines and gold tailings, to establish the generic value of the approach
8. Potential uses for the streams generated by sulphide separation
9. Provision of a framework for costing of the sulphide separation, with preliminary insights.

Hydrology and mass transfer influence mineral bioleaching, and therefore impact ARD formation. Particularly, waste rock dumps are characterized by non-homogeneous flow and channelling. The impact of particle size distribution and irrigation rate on preferential flow patterns is described in the report. Further, their influence on gas and heat transport impacts ARD formation. Through review of the literature, it is clear that the hydrology studies available to provide useful insight into the interactions between flow patterns, microbial colonisation and clogging, whether with heterotrophic microbial populations in soils or precipitates in waste rock dumps, are limited. To date, most discussion of the hydrology of waste rock dumps and low grade mineral heaps for extraction is based on modelling studies. From the studies reported, the distribution of fluid in the heap between flowing liquid, stagnant liquid, particles and the gas phase is key. In this report, the research to date with respect to mineral leaching ore beds is reviewed, indicating that current modelling approaches are limited owing to inappropriate assumptions of the nature of fluid flow in the ore bed and the resultant poor representation of the non-uniform flow through the ore bed. Two independent studies have demonstrated rivulet flow. Recently, in associated collaborative projects of the UCT team, magnetic resonance imaging (MRI) and positron emission tomography (PET) have been used to investigate flow distribution in the ore bed to enhance the understanding of controlling factors.

Strategies for limiting the permeability of waste rock dumps to restrict access of reactants were reviewed and extended. Two predominant approaches were found: provision of borders or covers, and reduction of bed permeability through the co-mingling of waste rock with fine material. Discussion of the latter in the literature is limited to date and is of interest for further study. An experimental study was conducted to establish methodology and provide proof of concept of the 'mingling' approach through analysis of flow. Here, permeability decreased, residence time increased, and degree of saturation increased with decreasing particle size for uniform sized particles. Most importantly, the model system demonstrated that, by including a fraction of fine particles with the waste rock material in the dump, permeability can be manipulated and flow restricted, thereby restricting access of reactants to the reactive sulphide minerals present. A substantial reduction in permeability resulted on homogeneous mixing of large waste rock particles with fines; however, the layering of fines (<2 mm) and waste rock provided a greater reduction. Leaching of a low grade base metal ore in such layers was compared to standard leach conditions using agglomerated ore and illustrated that the leach rate, under forced leaching conditions, was slowed, but not eradicated. Investigation of the co-mingling of waste coal with a benign fine tailings sample is recommended; however it was not possible to source the appropriate inter-burden sample, with samples received being of inappropriate composition.

The impact of flow rate on colonisation and leaching was also studied experimentally. Here it was shown that rapid irrigation rates result in greater flow of micro-organisms through the bed while reduced irrigation rates encourage microbial colonisation of the waste rock bed. Preliminary data on associated leach rates of low grade ore with irrigation rate are available.

Further irrigation of the waste rock bed from a single point demonstrated that regions of differing moisture content develop. In 'drier' regions, with moisture content of around 7%, colonisation was not detected with methods used ($<10^3$ cells per kg), whereas in higher moisture zones, of around 10%, colonisation was significant (10^9-10^{11} cells per kg). This illustrates the importance of restricting moisture content for avoidance of ARD formation.

Recent studies on the removal of sulphide from tailings by separation were reviewed. This demonstrated that significant strides forward, independent of this study, have not been reported in the open literature since the completion of WRC K5/1831//3. In this study, we have extended the sulphide removal studies to a range of finely divided materials, including the tailings from the preparation of pyritic gold ore concentrate, the BIOX® tailings, and coal fines. In addition to demonstrating the preparation of the bulk of the material for disposal such that the ARD generation potential is small, potential uses for the residues are considered, as is the process costing.

Using a series of five samples of coal fines, the proof of concept was demonstrated of sulphide removal from the bulk of the waste tailings by separation, in this case flotation, in order to eliminate or decrease ARD generation potential. Further, it was demonstrated that biodegradable oleic acid was an excellent collector, yielding improved performance over dodecane. A similar study on tailings from the gold industry has illustrated mixed results. Using flotation to upgrade the tailings from the laboratory bioleaching of pyritic gold concentrates has been successful with decreased sulphide grades reporting to the bulk tailings. Here ARD generation potential was reduced but not eliminated as with other mineral systems. On treatment of the tailings (collected from the tailings dam) from the concentrator circuit by further flotation, no significant upgrading was achieved; however the sulphide associated with the solid tailings was already low. The study of gold tailings samples was limited by those samples attainable. It is recommended that further representative samples be sourced for study to further assess the generalised nature of the findings

Potential uses for both the sulphide-rich and sulphide lean tailings samples have been identified and illustrate a range of potential applications. For the use of the sulphide rich stream, consideration is required for the quality of material needed as well as the impact of associated gangue fractions. To address this, the development of flowsheets for handling these streams and a system for their rating in selection of use is underway and will contribute to the project emanating from WRC proposal 1003088.

In order to establish a framework for the economic costing of the sulphide removal from tailings and fine waste materials, a flotation desulphurisation flowsheet has been proposed to follow the traditional coal processing flowsheet. This has been used as the basis for an order of magnitude estimate of a new fine coal desulphurisation plant using flotation and the performance estimated in Section 5. Based on assumptions specified, this preliminary costing has suggested potential for economic viability. A sensitivity analysis is presented which targets, among others, value of the resource recovered, yield and reagent costs as key considerations for optimisation of the approach.

A survey was done of studies on the removal of sulphide by reaction. In particular, the limited work on accelerated bioleaching was reviewed. Most notably the use of potassium ferrate as an oxidizing agent and use of the Fenton reaction provide interesting approaches. The recent report on the Fenton reaction is confirmatory of work conducted at CeBER, UCT with respect to bioleaching and opens a new and potentially fruitful avenue for consideration.

In summary, the following insights have been gained or highlighted through this study:

1. In the absence of removal of the sulphide from waste rock and tailings, it is unlikely that ARD generation can be avoided in perpetuity.
2. The introduction of fines through co-mingling or establishment of layers within or on top of the waste rock dump reduces the permeability through the dump, but does not restrict leaching completely, under conditions of forced irrigation (worst case illustration) once microbial colonisation has been established. The rate of this leaching is affected by the ore packing.
3. The poor understanding of the fluid path through a heterogeneous bed under unsaturated conditions compromises the modelling approach on which most prediction of ARD formation from waste rock dumps has been based.
4. Where microbial colonisation of the waste rock dump occurs, the formation of ARD is continuous in time, de-coupled from the supply of irrigant. In this case, the irrigant serves to flush out the already formed ARD from the rock dump. The rate of flow of this irrigant (through dry and wet periods) influences both the flushing of ARD achieved and the colonisation of the rock surface.
5. With tailings or fine waste rock / coal, proof of concept has been shown across a variety of feed materials that removal of sulphide through separation using, for example, flotation may result in a bulk tailings sample which is benign with respect to ARD generation. The minority stream is enriched with the sulphide material and requires contained disposal or use.
6. A wide range of potential uses exist for both the sulphide rich stream and the sulphide lean stream resulting from the flotation separation. These include the generation of products such as sulphuric acid and cover materials, respectively, for which there is significant demand in South Africa, amongst others.
7. A framework has been established for the costing of the separation approach. Preliminary analysis under specified conditions suggests potential for viability. Further sensitivity analyses highlight the cost of resource recovered, yield and reagent costs as key variables to be studied further.
8. The limitation of the suite of characterisation methods for ARD is noted. Static tests lack a kinetic framework. Biokinetic tests require refinement to consider the flow through environment and reduction in labour intensity. Humidity cell tests are too time consuming, requiring data collection for over a year.

Key recommendations for further work include the following:

1. Refinement of the tests available for the characterisation ARD potential is required. It is proposed that refinement of the biokinetic test be undertaken in terms of data analysis, kinetic information attainable and the potential of a flow through system. Further, characterisation based on mineralogy should be considered.
2. Improved understanding of fluid flow and fluid exchange within the unsaturated heterogeneous heap is required to inform the meaningful implementation of modelling approaches.
3. Further testwork on co-mingling and layering of fines in the reduction of ARD generation from waste rock dumps is required. Specifically this testwork should consider the use of the fine benign fraction from the separation process. Further the work should be conducted on the 4 kg lab-scale as well as at the pilot scale on site. The latter will enable constraints to experimental interpretation of edge / wall effects to be removed.
4. Investigation of the use of chemical oxidants for the removal of sulphide in waste rock by reaction should be considered. Of specific interest here is the implementation of Fenton chemistry.
5. With respect to the sulphide separation from fine waste materials such as tailings and coal fines, the economic analysis needs to be rolled out to other systems to evaluate the generic value of this approach. Further, environmental assessment is critical. Further experimental work is required to investigate the key parameters highlighted by these studies, e.g. reagent costs and the potential environment footprint associated with reagents. The potential for use of bio-flotation agents that can be generated on site and have a low environmental footprint should be investigated. Further to this, a proof of concept study is required at a larger scale, on site.

6. Expanded analysis of the potential use of streams generated through the separation is required. Particularly, the match between material availability and potential product demand is required, as is perceived value, technology availability, etc.
7. The current study has been restricted by access to representative samples of the waste rock, tailings samples and fine coal samples of interest. The securing of appropriate and representative samples is a key requirement of further studies and it is recommended that these are secured with the help of industrial representatives. In addition, field sites should be sought for both the investigation of the use of fines in slowing ARD formation in waste rock dumps and for the demonstration scale proof of concept of the sulphide separation.

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ACRONYMS & ABBREVIATIONS

ABA	Acid base accounting
ANC	Acid neutralising capacity
ARD	Acid rock drainage
CeBER	Centre for Bioprocess Engineering Research, University of Cape Town
CPB	Cemented paste backfill
MIBC	Methyl iso-butyl carbinol
MPA	Maximum potential acidity
MRI	Magnetic Resonance Imaging
NAF	Not acid forming (ARD characterisation based on NAPP and NAG trests)
NAG	Net acid generation
NAPP	Net acid producing potential
PAF	Potentially acid forming (ARD characterisation based on NAPP and NAG trests)
PAX	Potassium amyl xanthate
PET	Positron emission tomography
RTD	Residence time distribution
SARChI	South Africa Research Chair Initiative
UC	Unclassified with respect to acid forming potential (ARD characterisation based on NAPP and NAG trests)
WRC	Water Research Commission of South Africa

NOMENCLATURE

A	Cross-sectional area	m^2
B	Permeability coefficient	
d	Particle diameter	m
d_s	Effective diameter of equivalent sphere	m
e	Fractional voidage	
K	Permeability coefficient	
K''	Kozeny constant	
l	Bed height	m
l'	Length of tortuous channels in bed	m
ΔP	Pressure drop	N/m^2
q_x	Flow rate	m^3/s
S	Specific surface area	1/m
u_c	Mean velocity	m/s
x_i	Mass fraction of component i	
μ_L	Fluid viscosity	NS/m^2

CHAPTER 1: BACKGROUND

1.1 PROBLEM STATEMENT

One of the major environmental issues in the mining industry is that of Acid Rock Drainage (ARD), caused by the disposal of voluminous sulphide-bearing wastes. The legacy of the ongoing generation of ARD from the disposal of low grade dump rock, tailings and from the mine site itself may continue for decades following active metal extraction. Changes in legislation have put the burden of responsibility for perpetuity on mining companies. This has led to a change in process thinking in order to reduce potentially harmful emissions from deposits. This will reduce long-term costs of tailings management and ARD remediation as well as the re-examination of the manner in which waste materials are disposed from the mineral processing and extraction stages of metal recovery in order to relieve the environmental burden created and reduce the time frame of risk. Particularly, it is well recognised that, rather than treat ARD subsequent to its formation, the prevention of ARD formation should be achieved for new waste dumps and, where possible, retrofitted. Further, prevention of ARD formation through the delay in the time of its formation is no longer acceptable and the need to remove the risk completely or to provide ongoing remediation of effluents created is accepted.

This has led to a substantial body of work on methods by which to prevent the ARD-forming reactions from taking place. Particularly, covers and coating have been reported, along with ARD treatment strategies and strategies to reverse ARD formation at point of formation. Limited research deals with risk removal.

In this project, the research reported in WRC 1831/1/11 is extended to address aspects of the disposal of dump rock and tailings from mining operations processing mineral sulphides (especially pyrite), specifically with the focus of reducing their capacity to form acid mine drainage (ARD) and thereby the ongoing risk associated with the disposal of sulphidic mineral ore wastes, through removal of the sulphidic component of the waste. The understanding of the factors governing ARD generation from dump rock and tailings (similar to those governing mineral bioleaching for value recovery) is used to improve the planned disposal of these waste materials to mitigate ARD generation. In WRC 1831/1/11 the components responsible for ARD generation and characteristics of the waste for disposal to ensure minimisation and control of this generation were identified. This report is focused on the methodologies used to minimise and control ARD formation and provide an approach to evaluate the relative cost of ARD prevention based on treatments up front of disposal.

1.2 SCOPE AND OVERVIEW

The project seeks to address the prevention of ARD formation through the utilisation of a deep understanding of the ARD generation reactions and associated mineralogy, and through its assessment in terms of realistic reaction environments. Specifically, the focus is on long-term solutions to ARD generation.

Through the use of the ‘sulphide-rich’ and ‘benign’ gangue characterisation, it has been shown in WRC 1831/1/11 at the proof of principle level that improvements in waste disposal can be achieved through the removal of sulphides prior to disposal, using base-metal-containing ores and non-selective flotation. Two tailings waste fractions are produced: a benign tailings stream with greatly reduced acid generation potential and a sulphide-rich tailings stream. In this project, the study is extended to assess general applicability across other mineral ore types, specifically relevance to coal materials and sulphidic tailings from gold-bearing ores. Further, a critical consideration is the potential disposal routes or uses for the sulphide-rich stream.

In the report 1831/1/11, acceleration of ARD formation was assessed as a method of reducing sulphidic content of waste under a defined time-scale and controlled conditions. In this study, we expand our work on accelerated oxidation to assess its feasibility, but also consider the opposite approach for handling of waste rock in which the permeability of the waste rock dump is reduced, thereby reducing permeation of O2 and water, and reducing or eliminating the acid forming leach reactions. Co-disposal of fines, potentially benign tailings, with waste rock is used to manipulate dump permeability. These studies are supported by related studies on ore bed permeability and operating conditions on mineral bioleaching.

In the integrating component of this report, a basic costing of such interventions has been sought. This takes into account approaches to costing of ongoing waste handling, previously considered by the group of

Cilliers at Imperial College London. This approach is used to assess the motivation for lessening of the risk of ARD generation prior to disposal relative to ongoing treatment. It is noted that methodologies to achieve this comparison are limited and their capability is still in need of refinement. This is a limitation of the study.

Further, the fate of each by-product or waste stream generated through the processing routes selected has been considered. Specifically, in this report, the requirements for contained disposal, treatment to benign status or use of concentrated sulphidic tailings and of high sulphate liquid effluents have been given consideration.

The objective of the study as a whole, consistent with global sustainability and the systematic approach of the Minerals-to-Metals Research Initiative, is to enhance the overall environmental performance of metal sulphide process operations by jointly maximising economic and environmental efficiency and minimising environmental burden.

The project is conducted collaboratively with the Centre for Bioprocess Engineering Research (CeBER) and the Minerals-to-Metals Research Initiative at UCT and receives extension funding through both the SARChI Research Chairs in Bioprocess Engineering and in Mineral Processing.

The report structure has been developed incrementally to form the final report. The context of ARD formation is reviewed in Chapter 2. In Chapter 3, the permeability of the ore bed is reviewed in the context of factors influencing the formation of ARD and those influencing the progression of the bioleach reactions and neutralising reactions. This sets the context for our experimental studies in which the effect of packing configuration on leaching is considered, comparing agglomeration, coarse particles only and layering of fines. Preliminary experimental studies of the blinding of the ore bed with fines are considered here. In Chapter 4, strategies for sulphide removal for risk removal are reviewed. This links the study to previous research reported in WRC 1831/1/11, reviews new literature currently available and provides a framework for the new experimental work being undertaken. Case studies on sulphide removal from fine waste coal and from tailings from refractory gold processing are presented in Chapters 5 and 6 respectively. In Chapter 7, potential uses for the fractions resulting from the sulphide separation are reviewed – these include both the sulphide enriched fraction and the benign non-ARD forming tailings prepared. Chapter 8 introduces our approach to costing of this separation process.

CHAPTER 2: THE GENERATION OF ACID ROCK DRAINAGE

In this chapter, it is not intended to review the generation of ARD comprehensively as this is a vast task. Rather, it is intended to ensure that the necessary fundamentals are summarised as a starting point from which to consider the mitigation of ARD formation through removal of sulphide by separation or reaction, or through the exclusion of micro-organisms and key reactants, specifically water and oxygen, from the reactive mineral ore surfaces.

2.1 THE CHEMISTRY OF THE FORMATION OF ACID ROCK DRAINAGE

Acid Rock Drainage (ARD) is formed primarily through the chemical leaching of sulphide minerals by ferric iron, protons or both. The regeneration of these leach agents is most rapid through their microbial formation. For example, the resultant ferrous iron is microbially oxidised to ferric iron in the presence of iron-oxidising bacteria or archaea. Similarly, sulphide and elemental sulphur undergo microbial oxidation to sulphate with the generation of protons. In combination, abiotic oxidation takes place at a slower rate under conditions of ambient temperature and pressure, using oxygen as the oxidant. The abiotic oxidation rates are enhanced by increasing temperature, but do not approach microbial rates.

Bioleaching of sulphidic minerals, implicated in ARD formation, proceeds by two different routes depending on the nature of the mineral, as shown in Figure 1. These are classified as acid insoluble minerals (e.g. FeS2, MoS2, WS2) and acid soluble minerals (e.g. FeAsS, PbS, ZnS, MnS2, CuFeS2). The acid insoluble minerals are solubilised by ferric iron through six one electron removal steps, leading to the release of thiosulphate according to reaction [2.1]. Thiosulphate is oxidised biologically to sulphate through reaction [2.2] or rearranges to elemental sulphur through reaction [2.3] (Rawlings et al., 2003).

$$FeS_2 + 6\ Fe^{3+} + 3H_2O \rightarrow\ S_2O_3^{2-} + 7Fe^{2+} + 6H^+ \qquad [2.1]$$

$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+ \qquad [2.2]$$

$$8S_2O_3^{2-} \rightarrow\ S_8 + 8SO_3^{2-} \qquad [2.3]$$

In the mineral leaching of acid soluble minerals, solubilisation occurs by combined action of ferric iron and protons, releasing H_2S through reaction [2.4] which rearranges spontaneously to polysulphide. This undergoes chemical oxidation to elemental sulphur, shown in reaction [2.5] and microbial oxidation to sulphate shown in reaction [2.6] (Rawlings *et al*., 2003).

$$ZnS + Fe^{3+} + H^+ \rightarrow\ Zn^{2+} + 0.5\ H_2S_n + 7Fe^{2+}\ (n \geq 2) \qquad [2.4]$$

$$H_2S_n + 2Fe^{3+} + 5H_2O \rightarrow 0.25S_8 + 2Fe^{2+} + 2H^+ \qquad [2.5]$$

$$0.25S_8 + 3\ O_2 + 2\ H_2O\ \ 2\ SO_4^{2-} + 4\ H^+ \qquad [2.6]$$

The chemistry of the re-generation of leach agents is given through reactions below (Rawlings *et al*., 2003). These are mediated abiotically, through iron oxidising micro-organisms (reaction [2.7]) or through sulphur oxidising organisms (reactions [2.2, 2.6]). The latter two occur as part of the respirometry cycle. Sulphur oxidation releases more energy than Fe^{2+} oxidation.

$$2Fe^{2+} + 0.5O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \qquad [2.7]$$

The mineral leaching reaction is influenced by system Eh, pH in the acid-soluble case and temperature (Arrhenius function). It is also affected by the supply of leach agent or the accessibility of mineral grains. Similarly, regeneration of co-factors is influenced by the microbial activity, temperature (Arrhenius function), pH, Eh and dissolved solutes.

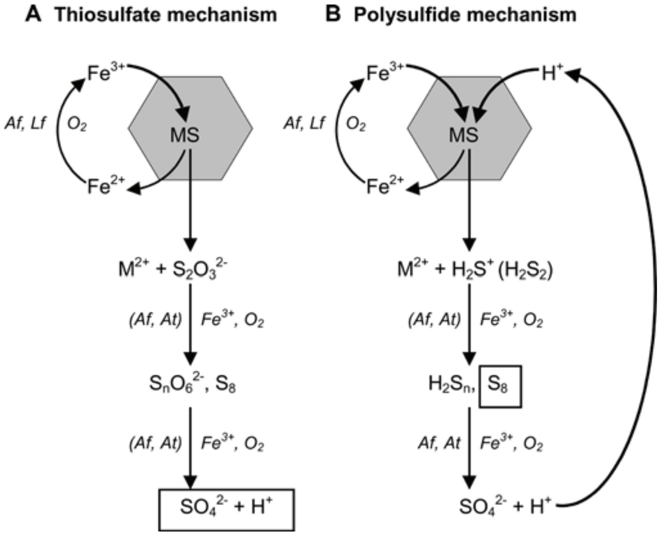


Figure 1: Schematic comparing the thiosulphate (A) and polysulphide (B) mechanisms in (bio)leaching of mineral sulphides as explained by Schippers and Sand (sourced from Rohwerder et al., 2003)

Acid leaching of non-sulphidic rock components is well-established. Mineral phases may be acid-consuming, thus neutralising acidity leached from the mineral sulphides, or acid generating. This implies that the mineralogy of the non-sulphidic components influences ARD generation capacity significantly, and also affects the deportment of metals not associated with sulphide minerals. The acidic environment created by sulphide oxidation promotes the deportment of acid soluble and ion exchangeable metals from the stable, solid phase of minerals also liberated through the mining process. Table 1 gives some of the elements found within a complex porphyry-type ore which could pose an environmental threat. These are grouped based on their typical natural abundance.

Table 1: Typical element distributions for a porphyry-type copper sulphide ore (after Broadhurst, 2007)

	Mineral association	**Elements**
Major elements	Lithophilic*	Al, Mg, Ca, Na, K
	Chalcophilic*	Cu, Fe, S
Minor elements	Lithophilic	Mn, Cr
	Chalcophilic	Zn, Ni, Pb, Cd, Se
Trace elements	Chalcophilic	Co, As, Mo, Ag

*Lithophilic – oxide forming elements; Chalcophilic – sulphide forming elements

2.2 PHYSICAL FACTORS OBSERVED TO INFLUENCE THE BIOLEACHING REACTIONS

It is well established that an effective heap bioleach process, the same process responsible for the generation of ARD, requires effective supply of reagents to the reactive sites in the ore and removal of dissolved solutes to these sites. Further, for the effective regeneration of leach agents, microbial activity is required. In WRC 1831/1/11, the role of oxygen, temperature, dissolved iron concentration, amongst others, was discussed (Harrison et al., 2010). Bryan et al. (2006) highlighted the key role of pH and aridity on microbial activity. Accessibility of the mineral grains to leaching is influenced strongly by both particle size and treatment of the ore influencing its porosity.

McGuire et al. (2001) confirmed that ferric iron is a more efficient oxidiser of metal sulphides than oxygen at low pHs. The regeneration of ferric iron from ferrous iron may be the rate limiting step of the oxidation of sulphide minerals under conditions of limited colonisation or microbial activity within the waste rock dump. On observing the surfaces of the minerals pyrite, arsenopyrite and marcasite, they showed that the leach rates are a function of the mineral to be leached. In their system, pyrite < marcasite < arsenopyrite with rates of 100-150, 20-320 and 380-980 µmol m-2 d-1 for fine material contacted efficiently with the leach solution in the presence of pure cultures. These rates increased to 230, 1000 and 1300 µmol m-2 d-1 respectively for enrichment cultures containing both iron and sulphur oxiders. Specifically, the build-up of sulphur rich deposits, primarily elemental sulphur and polysulphides was demonstrated using Raman spectroscopy in the absence of a sulphur oxidising organism such as Acidithiobacillus caldus. In the presence of iron oxidising micro-organisms, it is proposed that the type of species has little effect on the ferric iron regeneration rate (Norris, 1990). Analysing the relative kinetics of the process, sulphur passivation was not indicated, contrary to many bioleaching studies. This suggests that the intensity of the reaction may influence findings. McGuire et al. suggest that either the sulphur coverage is not complete or the sulphur layer is porous. This requires extended investigation to explain the results relative to both ARD prevention and metal recovery by heap bioleaching.

It must be noted that, even under conditions of low microbial activity and low mass transfer rates, ARD can be generated, albeit over a longer time scale. Hence complete exclusion of reactants is preferred.

2.3 CURRENT ACID ROCK DRAINAGE PREVENTION STRATEGIES

Several approaches have been evaluated for treatment and prevention of ARD. The treatment methods are directed towards remediation of the resulting drainage by pH adjustment and removal of dissolved metals ions by precipitation. While various treatment methods may be effective, the high cost involved and the open-ended nature of the operation, which can last for many years after the mining operation has stopped, make ARD mitigation by treatment a less attractive option (Nyavor and Egiebor, 1995). Methods directed towards prevention of ARD at source have been found to be more promising since they can provide permanent solutions to ARD problem and will therefore not require treatment facilities after mine closure. Prevention of ARD generation at source is also considered to be a more cost-effective management approach (Johnson and Hallberg, 2005).

The primary objective of ARD prevention methods is to inhibit the oxidation of sulphide minerals by limiting the influx of oxygen and contact with water (Romano et al., 2003). Johnson and Hallberg (2005) reviewed various methods for ARD prevention at source. The most commonly used ARD prevention strategies include underwater storage of mine tailings (Li et al., 1997), creation of fully anoxic environments using engineered covers such as low permeability benign materials (Woyshner and Yanful, 1995) and blending and layering of mine waste (Mehling et al., 1997; Delaney et al., 1997).

Vigneault et al. (2001) studied the effectiveness of an engineered shallow water cover and found that the superficial layer was altered over time. This stood in contrast to the previous studies which had shown that the submerged tailings were effectively inert (Pedersen et al., 1991). According to Johnson and Hallberg (2005), the effectiveness of shallow water covers may be improved by covering the tailings with a layer of sediment or organic material, which has the dual benefit of limiting oxygen ingress and re-suspension of the tailings due to the actions of wind and waves.

The use of other materials such as clay, fly ash, cement stabilized fly ash, bio-sludge, organic matter and coatings have also been investigated as cover materials for land-based mine waste (Nicholson et al., 1989; Broman et al., 1991; Evangelou and Zhang, 1995; Nyavor and Egiebor, 1995). Hallberg et al. (2005) investigated the use of fly ash and biosludge dry cover. The study found that the high levels of carbon released by the cover may accelerate bacterial sulphate reduction, producing sulphide that may precipitate metals but it can also accelerate the reductive dissolution of ferric iron. Peppas et al. (2000), on the other hand, evaluated the performance of the organic cover (i.e. sewage sludge) over reactive sulphide concentrates and tailings. It was found that the organic layer which is characterised by high alkalinity, cation exchange capacity and low permeability acts as both a physical and chemical barrier against oxygen diffusion into the underlying concentrates and tailings mass. However, the performance of the cover (in terms of efficiency and life span) was found to depend on the maintenance of favourable conditions (e.g. moisture and hydraulic permeability) within the organic mass. Nyavor and Egiebor (1995) investigated the application of low and high temperature phosphate coating of pyrite to control its rate of oxidation. The results showed that the phosphate coating reduces the rate of pyrite oxidation significantly. Thicker coatings were obtained at higher temperatures, but this did not improve the oxidation stability of pyrite by any significant amount. In a more recent study, Huminicki and Rimstidt (2009) investigated iron oxyhydroxide coating of pyrite for ARD control. The investigation showed that surface precipitation of iron oxyhydroxide reduced the diffusion coefficient of the oxidant by more than five orders of magnitude and this caused the pyrite oxidation rate to decline as the square root of time. However, extrapolation of the results to longer times showed that pyrite bearing materials needed to be treated with an extra source of alkalinity for several decades to produce coating that is thick enough to be sustained by alkalinity levels of typical groundwater. The use of bulk tailings which have been de-sulphurised to provide sufficient material with appropriate geotechnical and geochemical properties for a surface cover have also been considered (Aubertin et al., 1997; Hanton-Fong et al., 1997). Romano et al. (2003) investigated the potential performance of de-sulphurised tailings as a cover material for the reduction of acidic drainage from sulphidic tailings by considering de-sulphurised cover exposed to ambient climate conditions, a water cover and a combination of the two. Modelling results after a simulation period of 100 years indicated that a water cover alone or an exposed de-sulphurised cover alone are both less effective options than the combined cover type. The results, however, also indicated that the combined cover approach achieves only a minor improvement over the use of a water cover alone.

Although much work has been done on covers, and different types of covers have been applied successfully in different places, the design of most covers has focused mostly on permeability. The importance of biogeochemical processes in mine waste and tailings has received very little attention (Hallberg et al., 2005). Nyavor et al. (1996) showed the importance of biological and chemical processes involved in ARD formation by investigating the stability of fatty acid amine treated pyrite in the presence and absence of Acidithiobacillus ferrooxidans. The study found that fatty acid amine treatment reduced the rate of both chemical and biological oxidation of the pyrite. The study also showed that ferrous to ferric ion oxidation was the rate limiting step in the absence of bacteria while ferric oxidation was the rate limiting step in the presence of bacteria. These results show that the chemical and biological processes involved in ARD formation are very complex, highlighting the need for a more integrated approach for the development of more efficient ARD prevention strategies.

CHAPTER 3: ORE BED PERMEABILITY IN WASTE ROCK DUMPS AND THE GENERATION OF ACID ROCK DRAINAGE

3.1 KEY REACTANTS IN THE GENERATION OF ACID ROCK DRAINAGE

Some 70% of all material mined world-wide is waste rock (Younger et al., 2002). Much of this remains on the surface level post mining operation and thus has increased exposure to the atmosphere compared with in situ rock, aggravating oxidative reactions at the surface of the minerals present and resulting in vigorous ARD generation. The magnitude of such waste rock dumps is substantial, e.g. in the Ronnenberg district of Germany, the waste rock pile is some 27 000 000 m^3 (Lefebvre et al., 2001). To reduce the impact of these spoils, it is preferable to re-vegetate them with lasting vegetation and to prevent or mitigate the release of polluting leachates. Prevention is obviously the preferred path. The challenges to re-vegetation include the provision of viable soil covers, a tendency to settlement (Younger et al., 2002) and a need to minimise ingression of water and air (see Section 2.1).

Recent research has highlighted that the latter presents a key challenge, owing to the following factors (Younger et al., 2002):

(i) Waste rock dump materials host sub-surface flow systems of their own
(ii) The heterogeneous nature of the waste rock dump results in highly preferential sub-surface flow patterns
(iii) The physical instability of the waste rock dump leads to rapid changes in both the surface and sub-surface flows, allowing the exposure of new regions within the rock dump during the course of its life.

As an example of the point (ii), it has been estimated that some 55 to 70% of the total water content of the dumps at the Aitik copper mine in northern Sweden moves in preferential flow patterns (Stromberg and Banwart, 1999). It has been recognised that understanding and characterisation of these issues is critical for the appropriate treatment of waste rock materials.

The quality of the water leaching from these dumps has been proposed to improve only after some tens of years (Younger et al., 2002). Even then, the improvement that follows is asymptotic, again highlighting the importance of minimising potential for ARD generation.

The reaction chemistry, reviewed in Section 2.1, highlights the influence of dissolved iron, dissolved oxygen and protons. Further the rate of regeneration of ferric iron is influenced by O2 availability and microbial activity. These reactions are also impacted by ionic strength and the availability of neutralising agents (Younger et al., 2002). The relative importance of these factors varies through the literature and depends on the environment developed within the waste rock dump, which is a function of the ore body and its disposal method. For example, McGuire et al. (2001) acknowledge that ferric iron is a more efficient oxidiser than oxygen. Further they acknowledge the role that micro-organisms play in regeneration of ferric iron. In contrast, Lefebvre et al. (2001) model ARD formation predominantly through reaction with oxygen. It is clear that the fluid flow through the heap, both in terms of liquid flow and air ingression, impact each of these factors. Thus fluid flow is a major focus of this review.

3.2 ORE BED PERMEABILITY AND THE GENERATION OF ACID ROCK DRAINAGE – A REVIEW

It is well recognised that adequate and uniform flow is critical for effective leaching of heaps for effective metal recovery (O'Kane et al., 2000). The corollary also holds; adequate flow aggravates the generation of acid rock drainage from waste and dump rock stocks. While the required well-defined flow is difficult to achieve in non-ideal porous heap bioleaching systems, it is equally difficult to preclude fluid flow from these heaps over an extended life cycle.

The liquid reaching the surface of the heap or dump as rain, irrigant or run-off percolates through the crushed ore in a downward direction (Petersen and Dixon, 2006). As the liquid flows, a portion is trapped in a stagnant network in the pores and interstitial spaces in the agglomerates and between the particles. Microbial and chemical species are then transported through the heap by diffusion through the spaces filled with solution. The flow of solution is a function of permeability and heap saturation (Ogbonna, 2006).

In establishing approaches for the control of ARD formation, an understanding of this fluid flow, its impact and the potential to control or manipulate it is essential. Current knowledge is thus reviewed.

3.2.1 Characteristics of solution flow

The rate at which fluid flows through an ideal saturated bed is defined by Darcy's Law (Coulson and Richardson, 1990):

$$q_x = \frac{K}{\mu_L}\frac{\Delta P}{l}A \qquad [3.1]$$

q_x is the flow rate [m^3/s], μ_L is the fluid viscosity [Ns/m^2], ΔP is the pressure drop across the bed [N/m^2], l is the bed height [m], A is the cross-sectional area [m^2] and K is the permeability coefficient.

It is often useful to express the pressure drop and mean velocity for flow through packed beds in terms of voidage and surface area as these quantities are readily measured. Carman-Kozeny equations can be developed to obtain general expressions of streamline flow through beds (Richardson et al., 2006). Assuming that the spaces in the bed consist of tortuous channels of length l' proportional to l, u1=uc/e and the permeability coefficient is related to the specific surface area S (1/m), the Kozeny constant K'' and voidage e, then the mean velocity uc is expressed as:

$$u_c = \frac{1}{K''}\frac{e^3}{S^2(1-e)^2 \frac{1}{\mu}\frac{(-\Delta P)}{l}} \qquad [3.2]$$

$$u_c = \frac{1}{180}\frac{e^3}{(1-e)^2}\frac{(-\Delta P)d^2}{\mu l} \qquad [3.3]$$

where *K''* is 5 and S = 6/d for a sphere and d is particle diameter. For non-spherical particles *d* is replaced by d_s which can be written as:

$$d_s = \frac{1}{\Sigma(\frac{x_i}{d_i})} \qquad [3.4]$$

where x_i is the mass fraction of solids of diameter d_i.

Waste rock dumps and heap systems both operate under low flow and so form unsaturated ore beds. Here the available void spaces are filled with a combination of air, water vapour and water. In unsaturated flow systems, the degree of bed wetness and hydraulic conductivity vary constantly, rendering unsaturated fluid flow complex and difficult to model. Further the unsaturated flow allows the ingress of air, assisting oxygen gas liquid mass transfer and providing an additional reagent to the leaching system.

Three flow regimes in the unsaturated bed are described by Bartlett (1992; 1997). These include:

(i) capillary drainage with no solution flow,
(ii) percolation and
(iii) solution flooding (no air flow).

The downward percolation of leach solution through unsaturated beds or heaps of waste rock is driven by gravity, and influenced by air flow driven by the buoyancy gradient induced by changes in air temperature and composition (Bartlett, 1992). Forces resist fluid movement through the heap, including gravity, surface tension and atmospheric pressure (Bartlett, 1992).

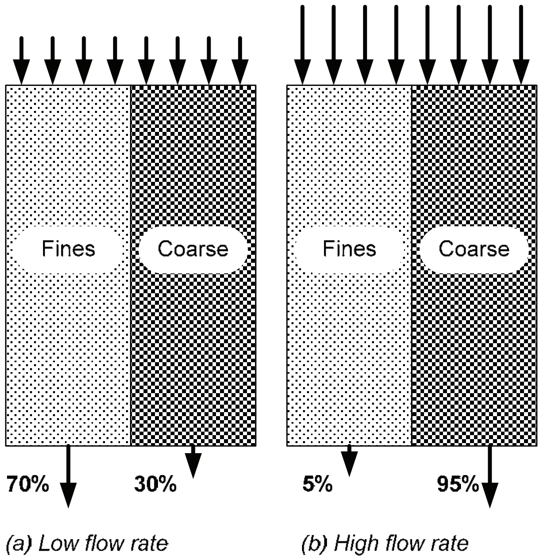
Decker and Tyler (1999) reported the existence of preferential pathways which permit much of the leach solution to migrate rapidly to the heap pad while contacting only a small fraction of the solid material (Rossi, 1990). Preferential flow exists in three forms: funnelling, short-circuiting and fingering (O'Kane et al., 2000), detailed in Table 2.

Table 2: Forms of preferential flow (O'Kane et al., 2000)

Type of flow	
Funnelling:	Solution flows preferentially through the layers easily permeated according to the texture of the material in the porous bed.
Short circuiting:	Flow occurs through the larger pores. High application rates cause high water-saturation leading to a significant amount of short-circuiting.
Fingering:	The development of an interface when the fluid infiltration of the porous bed displaces another fluid of different density or viscosity.

O'Kane et al. (2000) undertook a laboratory column study to characterise the nature of preferential flow within heap leach piles and its impact on mineral leaching. Preferential flow paths were dependent on the physical properties of layers, stress state and the degree of saturation, i.e. solution application rate. The study demonstrated the application of unsaturated zone hydrology to aspects of heap and dump leach hydraulic dynamics. The reported results suggested that where solution application rates were greater than the saturated hydraulic conductivity of the finer material, preferential flow in the coarser layer resulted. However, when the application rates were less than the saturated hydraulic conductivity of the fine material, the preferred path became the finer material. This is illustrated in Figure 2.

Wu et al. (2007, 2009), conducted research analysing the effect of preferential flow on copper recovery. Solution channelling and non-uniform flow was reported as a consequence of the heterogeneity of the material within the packed bed. The penetration of solution through the porous bed was attributed to the capillary action of micropores and crannies. The study reported that solution tends to move rapidly through a heap that is finely packed, whereas the solution seeps through a heap containing coarse particles, corresponding to observations in the study by O'Kane et al. (2000) for low flow.



(a) Low flow rate *(b) High flow rate*

Figure 2: Demonstration of preferential flow conditions within unsaturated porous media (adapted from O'Kane et al. (2000)).

Despite the known existence of preferential flow phenomenon (Lefebvre *et al*., 2001, Younger *et al*., 2002), comprehension on the extent of its impact on both heap leaching and ARD generation is poorly studied and has been cited as a key requirement for developing appropriate handling of waste rock (Younger *et al*., 2002). An understanding of leach solution flow paths through the ore bed following a variety of modes of irrigation is required. Analysis of the significance of preferential flow on the distribution of moisture, microbial communities catalysing ARD formation, and reaction zones within the ore bed will inform strategies both to maximise efficient metal recovery from commercial heap bioleaching of low grade ore and to minimise or prevent ARD formation from waste rock dumps.

3.2.2 Gas and heat flows

While liquid flows form the key focus of this review, it is important to note the interaction with gas and heat flows. Both gas and heat flows affect the reactions taking place; the former through the provision of oxygen and the latter through the temperature dependence of these reactions.

Gas flow is also a function of heap permeability, saturation and oxygen depletion. Insufficient gas flow compromises gas liquid mass transfer, implying O2 becomes a limiting oxidation reaction and CO2 limits the microbial growth and colonisation. While heaps are typically aerated (forced) from the bottom, in dump heaps air is drawn into the dump through the side slopes and top of the dump in response to convection.

Heat is generated in the heap as a result of the exothermic oxidation of sulphide minerals. Heat is transported through the heap by solution flow, conductive heating of the rock and stagnant liquid, and gas flow (Petersen, 2006). These are, in turn, affected by permeability.

3.2.3 Influence of irrigation rate on flow, colonisation and leaching

Rossi (1990) reported that the solution flow distribution through the heap is unpredictable when operating at flow rates lower than 3×10^{-4} $m^3/m^2/s$ (i.e. <1080 $L/m^2/h$). At higher flow rates the flow distribution pattern is not a function of the flow rate, as it is more stable (Rossi, 1990). Bioheaps are typically irrigated at an application rate which does not cause saturation (Brierley, 2001). Oxygen and carbon dioxide gas-liquid mass transfer to solution, reaction sites and micro-organisms is enhanced under unsaturated conditions. Industrial irrigation rates are usually low, falling in the range 5 to 10 $L/m^2/h$ (Petersen and Dixon, 2007a). For consideration of waste rock dumps, the hydrologically effective precipitation informs their irrigation rates. This hydrologically effective precipitation is the difference between the rainfall received and the combination of the losses to satisfy soil moisture deficit (affected by soil moisture content) and evapotranspiration (affected by solar radiation, wind speed and direction, and air temperature and humidity) (Younger *et al*., 2002).

Irrigation rates also influence the bio- and chemical leaching process through heat conservation (Du Plessis *et al*., 2007). Temperature affects the rate of reaction, both chemical and biological, and is influenced by the exothermic reactions and metabolic heat generated. Reduced irrigation rates cause increased temperature gradients. The extent of temperature increase is also affected by the heat conductivity of the waste rock. Further irrigation rates influence the accumulation of soluble salts and the development of high osmotic potential, both of which have a detrimental impact on microbial activity (Du Plessis *et al*., 2007). Lizama et al. (2005) studied the effect of irrigation rate and ore bed height on leaching of pyrite and sphalerite. Growth rates of key micro-organisms implicated in generation of ARD were reported to increase with increasing irrigation rate and decreasing bed height; however this was not a strong dependence.

Most discussion on the effect of irrigation rate in both heap leaching and the generation of ARD from the waste rock dumps is informed by the interpretation of results simulated by leaching models rather than actual experiments (Decker and Tyler, 1999; Bouffard and Dixon, 2001; Lefebvre *et al*., 2001; Cariaga *et al*., 2005; Lin *et al*., 2005; Cooper and Dixon, 2006; Dixon and Afewu, 2006; Dixon and Petersen, 2007; Bouffard and Dixon, 2009). Researchers have simulated the effects of irrigation rate on temperature in the heap, sulphide oxidation rates and metal recovery (Cooper and Dixon, 2006; Bouffard and Dixon, 2009), amongst others. Modelling codes and simulations available include OTIS and OTEQ (http://co.water.usgs.gov/otis), TOUGH ARD (Lefebvre *et al*., 2001) and HeapSim (Petersen and Dixon, 2007b). Only very limited experimental studies have been carried out to assess the leaching rates, ability of the bioleaching micro-organisms to colonise the ore and thrive under the different solution flow rates employed during heap and waste rock leaching operations.

Magnetic Resonance Imaging (MRI) techniques were used by Graf von der Schulenburg et al. (2007) to assess fluid velocities through porous media. MRI was also adopted in investigations related to biofilm growth to verify various model simulations (Graf von der Schulenburg *et al*., 2007; Graf von der Schulenburg *et al*., 2008; Pintelon *et al*., 2009). Sen et al. (2005) modelled the effect of solution velocity on microbial transport proposing significant effects which can be correlated to rates of colonisation and bio-oxidation. The model simulation showed faster bacterial transport rates with increasing flow velocity.

As previously mentioned, even a mild shear fluid force can cause detachment of microbes from the mineral surface, hence allowing them to be washed out of the heap. In continuous culture systems using planktonic cells, the growth of micro-organisms under conditions of increasing solution flow rate results in the enrichment of fast growing bacteria, while slow growing bacteria are washed out (Watling, 2006; Rawlings and Johnson, 2007). Micro-organisms attached firmly to the mineral surface are retained in the system. It has also been suggested (Petersen and Dixon, 2007b), and shown experimentally (Chiume et al., 2011, Govender et al., 2012) that the microbial cells populate the solution within the stagnant pore network. This partitioning of cells between the free flowing liquid phase, stagnant liquid phase and ore surface can be expected to influence microbial colonisation of ore beds subject to seasonal irrigation.

In addition to the partitioning of cells, the contacting of the reactants with the mineral phases to undergo dissolution is key. The dissolution of the mineral sulphides responsible for ARD formation requires accessibility of ferric iron, protons and oxygen to the mineral surface. Its rate is aided by accessibility to micro-organisms dependent on CO2 for growth. Similarly, the dissolution of acid-neutralising capacity from calcite, silicates, etc. is also dependent on effective contacting.

The fluid flow rate influences the residence time of the dissolved solutes in the ore bed. This is further affected by the partitioning of the fluid within the bed between the free flowing and stagnant fluid zones. The resultant residence times influence the potential for stoichiometric balance attainable between the generated acid, and that consumed by the component mineral fractions. Reaction times for each mineral fraction are different and are affected by the solution conditions, including pH and Eh, and surface exposure. Alkalinity is typically generated by the dissolution of calcite, the exchange of cations on the silicate surfaces and the dissolution of primary silicates. Acidity is typically the result of the dissolution of sulphide minerals. Metal deportment is a by-product of these reactions. As an example of the relative reaction times, calcite dissolution is typically four fold that of pyrite dissolution in the early stage of the leach process (Stromberg et al., 1999). The turnover time for reduced sulphur compounds is typically of the order of decades, whereas that of silicates is of the order of hundreds of years (Stromberg et al., 1999).

Owing to the dependency of reaction rates on proton availability and the need to neutralise protons and hydroxide ions released, pH is a master variable in the generation of ARD, or its prevention. Further, effective pH is impacted by the level of dilution achieved through fluid flow and is a function across the time course of the life of the waste rock dump, owing to differing solubilisation rates of the components of the waste ore and their relative stoichiometry.

3.2.4 Microbial colonisation of porous systems

Microbial colonisation and oxygenation of porous systems depend on solution flow and aeration. Typically, the different phases present in unsaturated porous media as described by Bartlett (1992; 1997) (Table 3) with emphasis on the: (i) *mobile phase:* leach liquid and gas filled voids (inter-rock void spaces) and (ii) *immobile phase:* solution filled ore pores (intra-rock porosity). This is further illustrated by Figure 3. More recently the role of the stagnant fluid zones between ore particles within the ore agglomerates has been recognised and highlighted (Chiume et al., 2011) as illustrated in Figure 4.

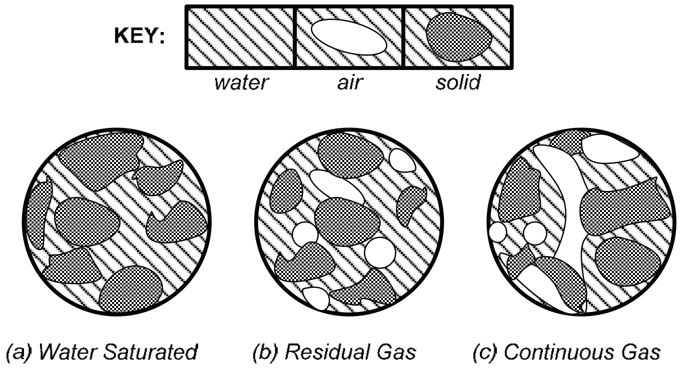


Figure 3: Cross-sectional sketch of three different degrees of saturation of porous media (extracted and adapted from Wan et al., 1994).

Table 3: Typical phase region in porous media (adapted from Bartlett, 1992)

Phase		**Stagnant/mobile**	**Typical volume (%)**
Solid rocks (includes closed pores)	- V_s	Stagnant (dead space)	59%
Open porosity within rocks	- ε	Stagnant (dead space)	2.40%
Solution void space between rocks	- V_l	Mobile (water flow)	19 to 21.5%
Air void space between rocks	- V_g	Mobile (airflow) + trapped air pockets	18.1 to19.6%

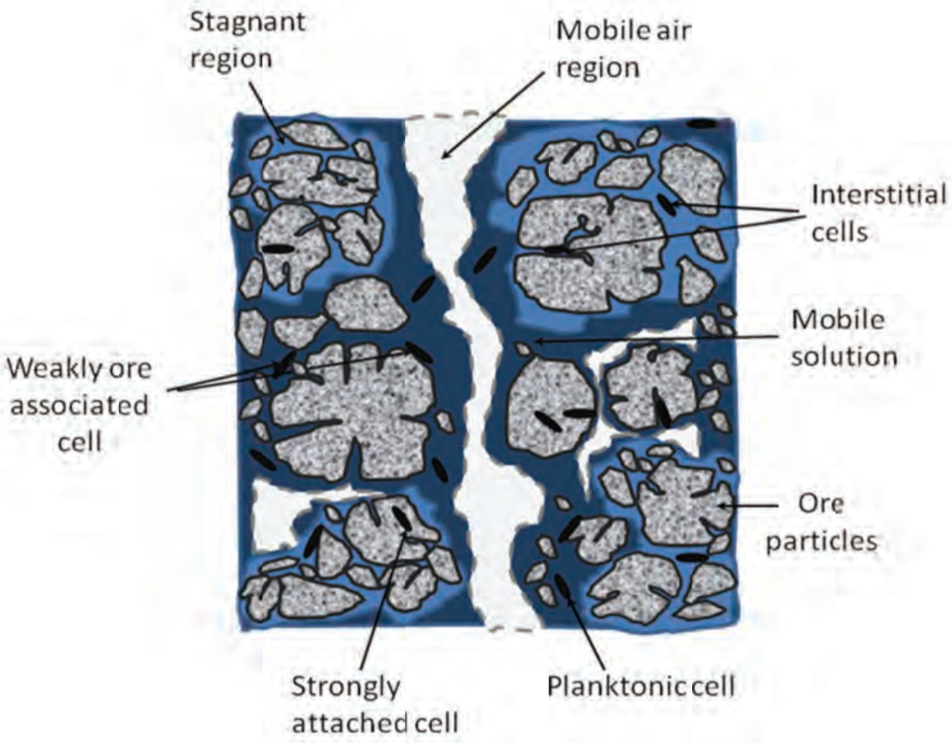


Figure 4: Schematic of the inside of the ore bed, showing the flowing mobile liquid phase, the porous ore phase, and the stagnant regions between the porous rocks (sourced from Chiume et al., 2012).

Wan et al. (1994) employed visualisation with quantification to determine the effect of cell surface hydrophobicity and gas saturation on microbial transport using two different bacterial strains, one hydrophilic and the other hydrophobic. The experiments were conducted in glass micro-models packed with quartz sand which simulated the complexities of natural porous media (Wan *et al.*, 1994). The cells were injected and the initial cell breakthrough was determined. Figure 3 illustrates the three different degrees of gas saturation used to test the effect of the gas-water interface on microbial retention. There was good reproducibility within and across experimental runs. Wan et al. (1994) reported that the retention rate of bacteria was proportional to the gas saturation in porous media. They attributed this to the observed preferential sorption of bacteria onto the gas-water interface over the solid-water interface. While this is an expected observation for the system used, it is not expected to be extrapolated to sulphidic mineral systems as sulphide minerals are recognised to have a much greater affinity for micro-organisms over quartz (Africa *et al.*, 2009, 2010; Bromfield *et al.*, 2010). Therefore, the gas-liquid and solid-liquid interfaces play a role in microbial transport and retention (Wan *et al.*, 1994). Rockhold et al. (2002) suggested that oxygen limitations could also propel the preferential growth of aerobic bacteria at the air-water interface, and oxygen gradients favour the migration of motile aerobic micro-organisms to this interface via chemotaxis (Rockhold *et al.*, 2002). Wan et al. (1994) showed that hydrophobic cells have a greater affinity for the gas-liquid and the solid-liquid interface, in comparison to the hydrophilic cells. Therefore, the hydrophobic bioleaching micro-organisms could have longer retention times within the ore bed, contributing to more bio-oxidation. The experiments also showed that, under slow-flow conditions, a static gas-water interface developed, consequently inhibiting microbial transport. Wan et al. (1994) noted that high solution velocities induced shear stress which could mobilise the gas-water interface, potentially enhancing microbial transport. However, the hydrodynamic stress caused by high solution velocities could have a negative effect on the leaching process caused by the detachment of active micro-organisms from the mineral surface and hence their potential to be transported to inoculate a remote region. Wan et al. (1994) established that the cell mass recovery in the effluent was inversely proportional to the gas saturation, confirming that water-saturated conditions are unfavourable for cell attachment to the solid phase and oxygen transport.

Studying heterotrophic microbial systems dependent on an organic carbon source, Thullner (2010) and Pintelon et al. (2009) described the ‘bioclogging’ effect as the accumulation of microbial cells leading to reduction in permeability due to plugging of pore space, with associated decreases in the hydraulic conductivity of the porous medium. Multiple factors control the bioclogging effect, including fluid shear, porous media particle size, substrate and nutrient supply, and EPS producing capacity (Vandevivere and Baveye, 1992; Thullner, 2010; Pintelon et al., 2009).

Yarwood et al. (2006) reviewed several studies on the transport of soil bacteria through both saturated and unsaturated porous media, noting the lack of definition on the impact of microbial growth on hydrological properties. Several investigators in other fields such as soil-groundwater engineering, agricultural engineering and contaminant hydrology have assessed this bioclogging phenomenon through laboratory and theoretical studies (Vandevivere and Baveye, 1992; Thullner et al., 2002; 2004; Rockhold et al., 2002; Yarwood et al., 2006; Rockhold et al., 2007; Seitert and Engesgaard, 2007; Thullner, 2010). The studies have focused on the dynamic interaction between microbial growth, fluid flow, solute transport and gas exchange through porous media. Extrapolation of their findings to the heap bioleaching space has not been implemented, largely because the formation of biofilms in bioleaching is restricted to thin films.

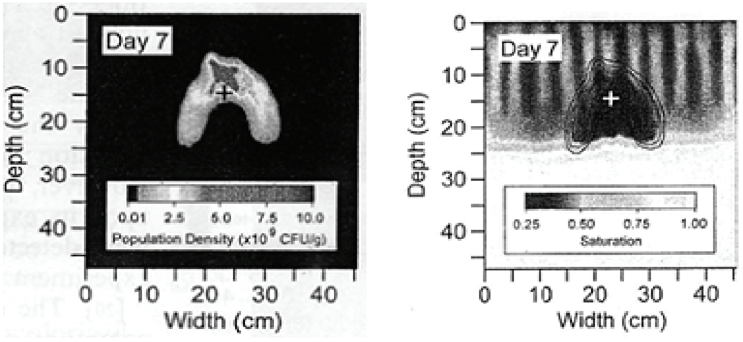
Most studies investigated the bioclogging effects using columns packed with either sand or glass beads. These systems differ from typical heap structures which have more random packing due to the variations in ore particle sizes, the pore network created during stacking, and the shrinking particle effect as a consequence of mineral leaching. Water containing nutrients for microbial growth is percolated through the system allowing investigators to assess 1-D or 2-D unsaturated flow. Column experiments operated as 1-D systems are under the assumption of evenly distributed flow (Thullner, 2010).

Pintelon et al. (2009) used a Lattice-Boltzmann simulation to illustrate the temporal distribution of microbial communities over time, verified by MRI data. The studies (Thullner et al., 2002; Yarwood et al., 2006; Seitert and Engesgaard, 2007) used tracer tests to investigate changes in flow and transport properties due to bioclogging of porous media. The columns were packed with porous media, such as sand or glass beads, operated under continuous flow conditions and fully saturated. Monitoring of the flow rate and changes in the hydraulic head, measured using pressure transducers located at different depths in the column, enabled changes in hydraulic conductivity to be determined from Darcy’s law (Seitert and Engesgaard, 2007).

Yarwood et al. (2006) and Rockhold et al. (2007) combined light transmission and bioluminescence for non-invasive monitoring of the interactions and evolving patterns of microbial growth, water flow and solute transport in unsaturated porous media. HK44 bacterium was genetically modified with a lux gene that resulted in bioluminescence on exposure to salicylate (Yarwood et al., 2006). Therefore, bioluminescence was used to quantify the sequential and spatial development of colonisation by relating it to cell population density measured by dilution plating. Hydraulic flow paths were determined by pulsing bromophenol blue dye (indicator) through the bed and water-saturation was measured by light transmission and gravimetric analysis.

Bioclogging of the pores by soil bacteria growing on organic compounds typically occurred within two to four weeks of inoculation (Thullner, 2010) and led to preferential flow paths (Yarwood et al., 2006; Thullner, 2010). Previous studies have shown that during microbial growth and colonisation, there are biomass-induced changes in pressure heads, water contents and permeability reduction (Rockhold et al., 2002; Yarwood et al., 2006; Seitert and Engesgaard, 2007).

The study by Seitert and Engesgaard (2007) reported decreased hydraulic conductivity of two to four orders of magnitude in their systems as a consequence of bioclogging. The hydraulic conductivity decreased by four orders of magnitude at the top of the column and 2 orders of magnitude throughout the whole column. This indicated that the initial microbial growth occurred near the point source of irrigation, consuming the majority of the substrate, depleting the supply to micro-organisms located at increasing depths causing them to either decay or migrate upstream by chemotaxis (Seitert and Engesgaard, 2007; Thullner, 2010). Seitert and Engesgaard (2007) also suggested that further changes in hydraulic conductivity could be attributed to detachment and migration of micro-organisms downstream. A regression analysis showed that solution velocity through colonised regions was significantly reduced during the initial days of the experiments (Yarwood et al., 2006).



(a) Bioluminescence projection of cell population density

(b) Saturation content from light transmission

Figure 5: Illustration of the development of colonisation and water content distribution (Extracted from Yarwood et al. (2006) by permission of John Wiley & Sons, Inc.).

Some studies indicated that the bioclogging effect was localised such that the hydraulic properties of the whole system remained constant (Thullner et al., 2002; Yarwood et al., 2006). This suggested that microbial growth and accumulation can manifest greater heterogeneity within a porous structure, or homogenise the effect (Rockhold et al., 2002), resulting in preferential flow paths and/or stabilised flow patterns (Thullner et al., 2002). Yarwood et al. (2006) noted that the expansion of microbial colonies was mainly lateral and downward, but upward expansion also occurred (Figure 5 (a)). Hence, cells can migrate upward against solution flow. Yarwood et al. (2006) attributed these observations to the physical clogging of ore pores due to accumulation of cells and microbially induced changes in the chemical properties of liquid and solid phases (Yarwood et al., 2006).

Yarwood et al. (2006) also implicated EPS formation in the bioclogging of localised pore networks. However, their study did not quantify or account for the presence of EPS. Vandevivere and Baveye (1992) compared an EPS-producing strain with a non-EPS producing mutant strain. They only observed the bioclogging effect in the system containing the heterotrophic EPS producing bacterial strain. Bioclogging induced by EPS formation was suggested to be stimulated by high nutrient loading (Thullner, 2010). Protocols for isolation and quantification of EPS in a batch (Gehrke et al., 1998; Kinzler et al., 2003) and continuous culture systems (Michel et al., 2009) have been developed.

The observations from the aforementioned studies have resulted in the modelling of the interactions between fluid flow and bioclogging attributed to microbial growth. These models only consider 1-D flow and ignore the multi-dimensional flow paths that would be accessible to percolating leach solution (Thullner, 2010). Further, the knowledge gained from the studies conducted in agricultural and soil engineering fields (Ginn et al., 2002; Rockhold, 2002; Sen et al., 2005; Yarwood et al., 2001; 2006; Chen, 2008; Thullner, 2010), has not been applied to the heap leaching systems. However, its application is limited because heap leaching systems are more complex structures than the porous media evaluated in the other studies (in terms of ore mineralogy, particles size distributions, microbial diversity and operating conditions). Further, similar to bio-clogging, clogging of the porous media by precipitation needs to be included in the analysis of waste rock dumps and bioheap leaching.

Several investigators have reported on their attempts to model heap hydrology (Decker and Tyler, 1999; Bouffard and Dixon, 2001; Cariaga et al., 2005; Lin et al., 2005; Dixon and Afewu, 2006; Dixon and Petersen, 2007b). Most heap leach models incorporate liquid dynamics, mass transport, heat transfer, and mineral leaching reactions. However, different approaches are used to account for the factors above in terms of the equations developed. In general, microbial propagation has not been considered explicitly. Therefore, current bioleaching models need to be extended. The models should be designed on a better understanding of the behaviour of micro-organisms within the heap in order to predict the rate and extent of microbial transport, colonisation and activity.

3.2.5 Bed structure of the waste rock dump and its permeability

The metal, sulphate and proton release on the leaching of mineral sulphides is a function of the waste rock characteristics, including mineralogy, chemical composition, particle size distribution (PSD), surface area, porosity, etc. Stromberg and Banwart (1999) estimate that 80% of the sulphide and silicate dissolution in the waste rock dump results from the leaching of material with a particle diameter below 0.25 mm. This dissolution is very rapid. Lefebvre et al. (2001) proposed a reaction core model for this leaching, suggesting that the mineral grains in the outer region are reacted away while the fresh mineral remains in the core. This partially explains the rapid initial leaching profiles of Al, Si, Mg, K, Na, Cu, Fe with a decreasing rate on extended leaching times. Stromberg and Banwart (1999) report that the initial leach rates are a function of particle diameter represented as d-0.3 to -0.6. The ongoing reaction is a function of d-0.2 to -0.5, whereas the relationship with respect to porosity measured by BET is d-0.1.

In a porous waste rock dump, air convection driven by temperature gradients provides the oxygen supply and mass transfer needed (Lefebvre et al., 2001). Water infiltration provides the required moist environment while the heterogeneous ore bed of coarse particles and low flow rates ensure unsaturated flow.

It is recognised that the particle size distribution and particle characteristics, including shape, compressibility and homogeneity of packing, may influence the pore network, permeability and subsequent fluid flow. Not all pores are conductive and blind pores may lead to stagnant zones while closed pores prevent access of leach agents.

Weathering of the rock material and its oxidation can lead to the breakdown of the rock structure (Lefebvre et al., 2001), causing instabilities in the bed and changes to the preferential flow paths. This results in the further exposure of new regions of the waste rock dump to leaching.

3.2.6 Strategies to slow or prevent ARD generation in waste rock dumps

A range of strategies to slow or prevent the generation of ARD have been reported. These are further discussed in Section 2.3. To date, those strategies associated with the waste rock dumps are largely associated with the prevention or delay of the oxidation reactions resulting in ARD through the exclusion of the necessary reactants (water, oxygen, iron, micro-organisms) from the reaction sites. The potential to remove the risk of ARD generation is discussed in terms of the removal of sulphide by separation in Section 4.1 and its removal by reaction in Section 4.2.

The provision of a border “membrane” in the form of a low permeability cover is the most common approach to the prevention of ARD formation. While technologies for the provision of such non-porous zones are well understood, the challenge exists in its long term integrity, despite the re-vegetation of the dump and the potential for settlement, etc. over the life of the dump. It is anticipated that the ingress of oxygen through the sides or slopes of the dump is critical in providing the reactants for the ARD generation. Lefebvre et al. (2001) assessed the relative benefit of providing the border membrane to the whole dump surface versus to the slopes only, the latter requiring less material. On providing covering of the slopes only, oxygen ingress was shifted to the top surface from the side surfaces owing to the convection patterns. However, oxygen ingress from the top was not predicted to reach the warmest zones of the dump as it was consumed en route, leading to the overall cooling of the dump and decreasing convection. Nicholson et al. (1989) calculated a theoretical reduction in acid generation rates of four orders of magnitude, based on the reduced oxygen diffusion coefficients through the fine-grained, non-reactive, moisture-holding tailings surface coat.

An alternative approach, highlighted for extension through this and subsequent projects, is the co-mingling of the waste rock with other materials in the dumping process to provide lower bulk permeability. This may take the form of mixed particle sizes or the formation of layers of finely divided materials as reported by Poulin et al. (1996). In both cases, access to the tailings material, its mechanical dewatering and transport to the waste rock dump assembly site is an additional burden which the benefits need to outweigh. Wickland et al. (2006) examined the mixture of tailings and waste rock in terms of tailings rheology, compressibility of the mixture and properties of both phases for the design of the geotechnical properties. They demonstrated homogeneous mixtures at the laboratory scale. Lamontagne et al. (2000) have presented simulations to predict the value of this approach at large scale. It is well recognised that additional laboratory data is essential to characterise these systems further to facilitate their simulation at a large scale. Experimental work is presented in Sections 3.3, 0 and 3.5.

As it is recognised that the rate of dissolution of the acid-generating and acid-consuming materials is not consistent (Stromberg and Banwart, 1999), it has been proposed that an acid-consuming material be added to the waste rock material to ensure that the acid generated is balanced stoichiometrically. Perez-Lopez et al. (2006) demonstrated this through the addition of the abundant fly-ash material to sulphide rich residues. The study was conducted in leach columns, comparing the leaching of pyrite with sand, pyrite with sand covered by a top layer of fly-ash (equivalent to 14% of the column material), and pyrite with sand mixed homogeneously with fly-ash (equivalent to 6% of the column material). While the control column was acid generating, the columns to which fly-ash was added delivered leachate at pH 10 that was low in sulphate and lacked dissolved iron and other metals. The results presented in our previous report (WRC 1831/1/11) indicate the importance of matching the potential rates of acid generation with the release of acid neutralisation capacity for this approach (Harrison et al., 2010).

3.3 EXPERIMENTAL STUDIES – THE IMPACT OF FLUID FLOW ON THE GENERATION OF ACID MINE DRAINAGE

3.3.1 Introduction

Preliminary research on microbial propagation and colonisation in ore beds has been conducted in the Centre of Bioprocess Engineering Research (CeBER), at the University of Cape Town. Van Hille et al. (2010) used a bucket reactor (320 mm diameter, 400 mm high) to observe the radial distribution of leach solution and microbial populations (Figure 6). The bucket was packed with agglomerated ore divided into three concentric annuli and two layers separated by stitched shade cloth made from high density polyethylene. The system was irrigated from a single central point and solution was collected from nine outlets, corresponding to the annuli. Van Hille et al. (2010) found that high feed rates resulted in preferential flow paths, as expected. In an attempt to rectify the preferential flow effects, reduced flow velocities were employed in later experiments; however reduced liquid feed rates did not result in greater radial diffusion of microbes. The study concluded that liquid flow affected the distribution of attached micro-organisms. It showed that leaching efficiency was a function of liquid flow and microbial colonisation. It was recommended that more detailed investigations of fluid flow in conjunction with microbial colonisation would contribute to increased understanding of microbially operated heaps.

In extending these studies, the research team has considered the impact of irrigation rate on colonisation, and thereby subsequent capacity for regeneration of leaching agents, as well as the distribution of liquid and microbial cells across the ore bed, experimentally.

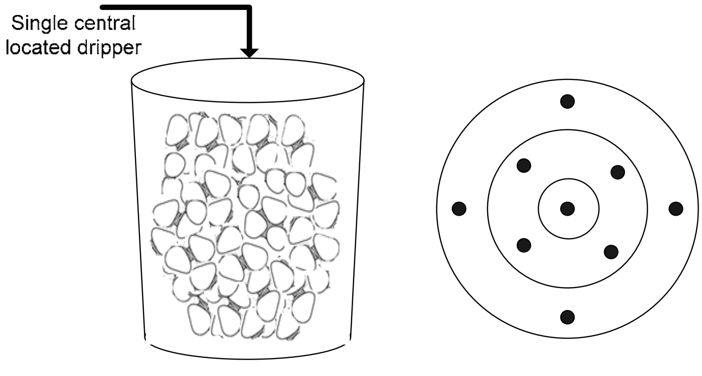


Figure 6: Bucket reactor set up with three concentric layers: dots represent solution collection points from nine different zones (Van Hille et al. (2010) experimental setup)

3.3.2 Effect of irrigation rate on microbial colonisation

3.3.2.1 Experimental method

Ore, Microbial Cultures and Growth Media

Low grade copper-bearing ore, containing 0.69% copper, 2.95% iron and 2.02% sulphur was utilised. The crushed ore (80% of the material passing 12.7 mm) was agglomerated using 50 ml deionised H_2O and 3.7 ml conc. H_2SO_4 / kg ore to secure the fines fraction.

A mixed mesophilic stock culture containing At. ferrooxidans, At. caldus, and predominantly L. ferriphilum, grown on pyrite concentrate in a batch stirred tank reactor at 30°C and sub-cultured weekly, was used. A preliminary study was conducted to determine the inoculum concentration at which the concentration of the cells eluting without attachment was within the detection limit of the total microscopic cell count (3×105 cells/ml). The range 108 to 1013 cells/ton of ore was considered and 1012 cells/ton of ore chosen for this investigation (data not shown).

The irrigation feed composition was: 0.5 g/l $FeSO_4.7H_2O$, 183.3 mg/l $(NH_4)_2SO_4$, 60.5 mg/l $NH_4H_2PO_4$, and 111.2 mg/l K_2SO_4 in deionised water. The pH was adjusted to pH 1.15 using 96-98% concentrated sulphuric acid (H_2SO_4). All reagents used were of analytical grade.

Column Operation

The experiments were conducted in small scale heap leach columns of 100 mm diameter and 360 mm height. The columns were packed with approximately 4 kg acid agglomerated ore as described by van Hille et al. (2010). Liquid irrigation rates of 2, 6 and 18 $l/m^2/h$ were used. Prior to inoculation, the systems were acid washed at the same rate (6 $l/m^2/h$) for 1 day to remove readily leachable materials and create an environment conducive to microbial attachment to the ore surface. The columns were operated under ambient temperature conditions and a feed pH of 1.15. The columns were aerated from the base at 200 ml/min and drip irrigated from above with acidic feed solution resulting in counter-current flow systems. The experiments ran for 32 days. In each experimental run, one column was run for each operating condition. The experiment was repeated three times.

Analytical procedures

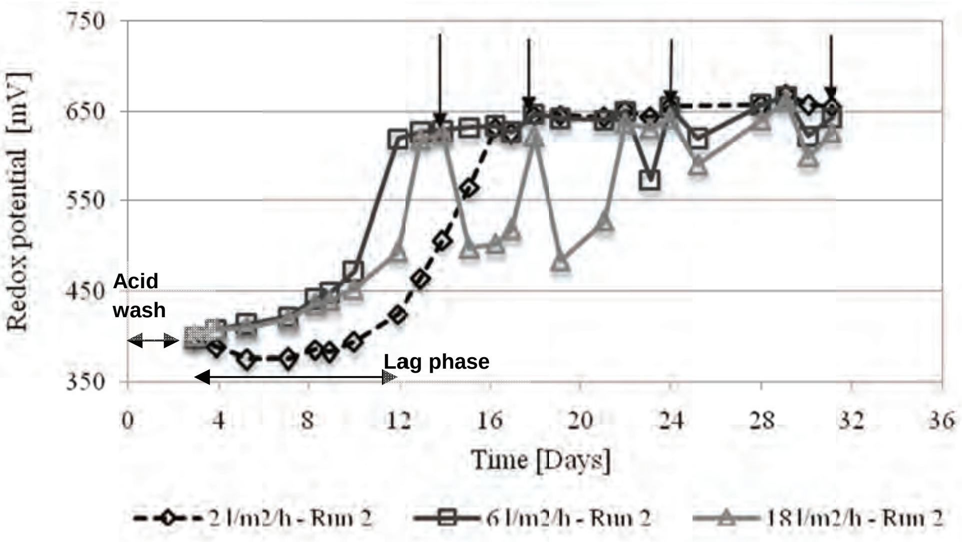
Variation in pH was measured using a Metrohm 691 pH meter. The redox potential was measured with a Crison GLP 21 Redox meter, relative to a silver-silver chloride reference system at 25°C. The ferrous iron concentration was measured spectrophotometrically, using the colorimetric 1-10 phenanthroline method described by Komadel and Stucki (1988). Total iron in solution was determined using both atomic absorption spectroscopy (AAS) and the spectrophotometric method following conversion of all iron to the ferrous form in the presence of stannous chloride. Copper concentration in solution was also obtained from AAS. The analytical measurements were performed in triplicate. Microbial cell counts were determined using a Thoma counting chamber and an Olympus BX40 Microscope at 1500 fold magnification (oil phase, phase contrast optics, 15× magnification eyepiece, 100× magnification objective, detection limit of direct counting method of 3×10^5cells/ml, inherent 30% error margin (Bryan *et al.,* submitted for publication). Cell counts were performed on the eluted PLS as well as the samples obtained following mechanical detachment from the ore (Chiume et al., 2012).

3.3.2.2 Results and discussion

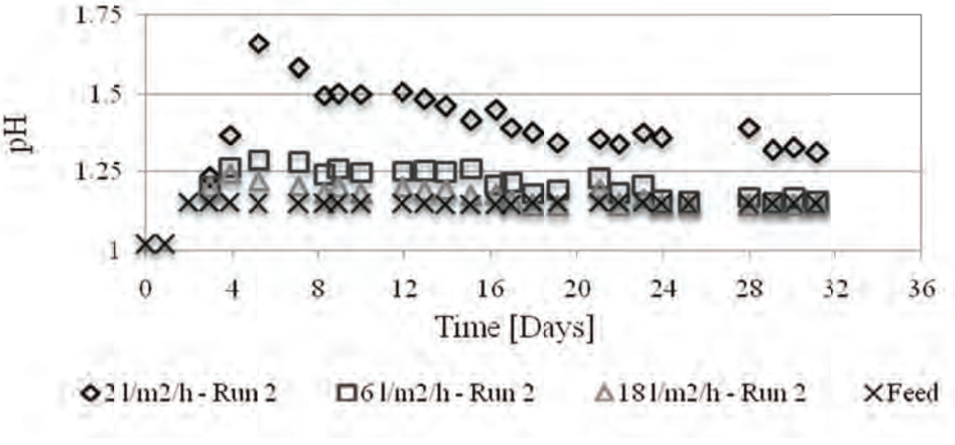
A comparison of data generated at irrigation rates of 2, 6 and 18 $l/m^2/h$ is presented in Figure 7 to Figure 10. Figure 7 shows the trend in redox and pH profiles of the eluted leachate. The fluctuations in the redox potential at 18 $l/m^2/h$ correspond to the days immediately after each in-bed sampling point, indicating greater susceptibility of the high flow system to changes in the leaching environment caused by the in-bed sampling procedure technique. However, in later runs such fluctuation was not observed. The redox potential of the leachate increased slowly from 400 to 470 mV during the 10 day lag phase at irrigation rates 6 and 18 $l/m^2/h$. From day 10 to 12, there was a significant increase in redox potential from about 450 to 650 mV, indicating the rate of microbial oxidation of ferrous iron was greater than ferric leaching of the sulphide minerals present. Under low flow conditions (2 $l/m^2/h$), the redox potential took longer to climb to 600 mV (16 days) than the other flow conditions, before stabilising at 650 mV. This occurrence can be attributed to slower transport of microorganisms into the ore bed. Additionally, the slower rise in redox potential could be a result of mass transfer limitation within the low flow system.

The pH of the leachate fluctuated between pH 1 and 1.5 for the duration of the leach run (Figure 7b). There was no significant difference between the pH at the different flow rates 6 l/m^{2}/h and 18 l/m^{2}/h. The profile indicated that the pH was higher at 2 l/m^{2}/h than for the other irrigation conditions. This could be due to acid consumption via gangue dissolution occurring at a faster rate than the delivery of acid to the leaching environment at low flow conditions and the microbially assisted acid regeneration.

Figure 8 shows the cumulative planktonic cells observed in the leachate over time, at irrigation rates of 2, 6 and 18 l/m^{2}/h, during run 2. No cells were detectable in the effluent during the first 8 days of leaching. Thereafter, the removal of cells through the PLS was observed indicating microbial growth. The microbial cell concentrations in the PLS from all three columns fluctuated, with cell concentrations reaching as high as 6.0×106 cells/ml (2 l/m^{2}/h) and 3×106 cells/ml (18 l/m^{2}/h) (data not shown). After 32 days of leaching, high cell exportation from the column was observed for 6 and 18 l/m^{2}/h removing approximately 6.5×1010 and 7.0×1010 cells respectively, compared to 2.2×1010 cells at 2 l/m^{2}/h, with the propagated cumulative error being < 25%. The larger cell removal at the higher flow conditions could be attributed to the detachment of cells as a consequence of the greater shear stress induced, suggesting a lower colonisation of the heap at higher irrigation rates. In this data, there was little variation between the planktonic cell data for irrigation rates of 6 and 18 l/m^{2}/h. However, one of the three repeat runs showed higher cell removal from the column for high flow (18 l/m^{2}/h) with a total of 2.2×1011 cells exported after 32 days leaching, compared to 1.1×1010 and 5.7×1010 cells for 2 and 6 l/m^{2}/hr respectively (Table 4).



(a)



(b)

Figure 7: Trend in (a) the redox potential and (b) the pH, of the eluted solution passing through the column heap given for different irrigation rates ◊ – 2 l/m^{2}/h, □ – 6 l/m^{2}/h and ∆ – 18 l/m^{2}/h, during run 2. Arrows are indicative of in-bed sampling days.

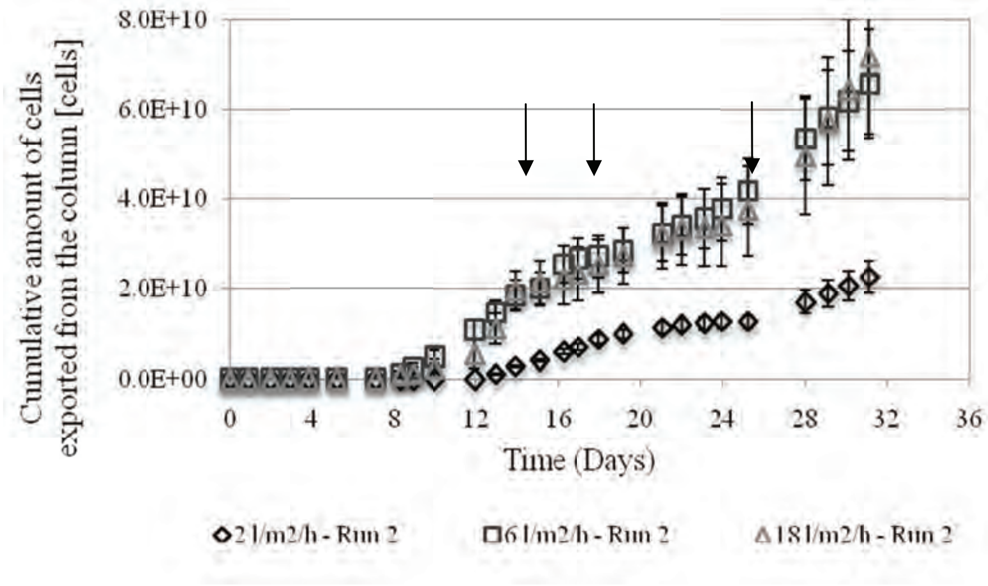


Figure 8: Cumulative removal of microbial cells in column effluent at irrigation rates ◊ – 2 l/m^2/h, □ – 6 l/m^2/h and Δ – 18 l/m^2/h, during run 2. Error bars represent the propagated error determined from the standard deviation of the mean cell count within each experimental run (n=2). Arrows are indicative of in-bed sampling days.

Table 4: Total cumulative exported cells after 32 days leaching for runs 2 and 3, and the preliminary run 1.

	Cells (x10^{10})		
Irrigation rate (l/m^2/h)	2	6	18
Run 1	1.1	5.7	22
Run 2	2.2	6.5	7.0
Run 3	1.2	4.2	5.9

Figure 9 shows the growth curve of the combined interstitial and attached cells at irrigation rates of 2, 6 and 18 l/m^2/h, during run 2. Increased accumulation of microbes within the systems was observed under all flow conditions resulting in final concentrations of ore associated cells of 4.3×10^{13} (2 l/m^2/h), 3.0×10^{13} (6 l/m^2/h) and 2.0×10^{13} (18 l/m^2/h) cells/ton ore remained in the columns after 32 days. A greater number of ore associated bacteria accumulated in the systems under low flow conditions (2 and 6 l/m^2/h).

Figure 10 shows the progression of the microbial growth and the relative proportions of exported planktonic cells, interstitial and attached cells at the three irrigation rates, during run 2. Increasing bacterial association with the ore was observed over the 32 day leaching period across all conditions. A greater number of micro-organisms adhere to ore under low flow conditions (2 and 6 l/m^2/h), due to the reduced detachment of microorganisms by the fluid shear and slower exportation of microorganisms from the systems. Higher attachment of microorganisms to the ore at low flow rates could also be a response to nutrient and ferrous iron limitations, due to the low availability as a consequence of slower supply to the system. Additionally, the higher surface attachment and colonisation observed for lower flow rates can be attributed to the control of the available void space by the irrigation rate (Bouffard and West-Sells, 2009) and gas saturation of the system allowing for higher microbial retention within the system (Wan et al., 1994). Under low flow conditions, microorganism-ore contact time increased within the leaching system, allowing the cells to form stronger surfaces bonds and remain attached for longer periods.

Increased cell numbers in stagnant fluid were also observed. A cell balance over the system is shown in Table 5. For all conditions, the interstitial cells were the most dominant form of cells accumulated within the heap systems. The total quantity of cells retained in the ore bed for an irrigation rate of 18 l/m^2/h was much lower than for the other flows, inferring that under higher flow conditions the detachment and transport of microbial species out of the column affected the microbial growth.

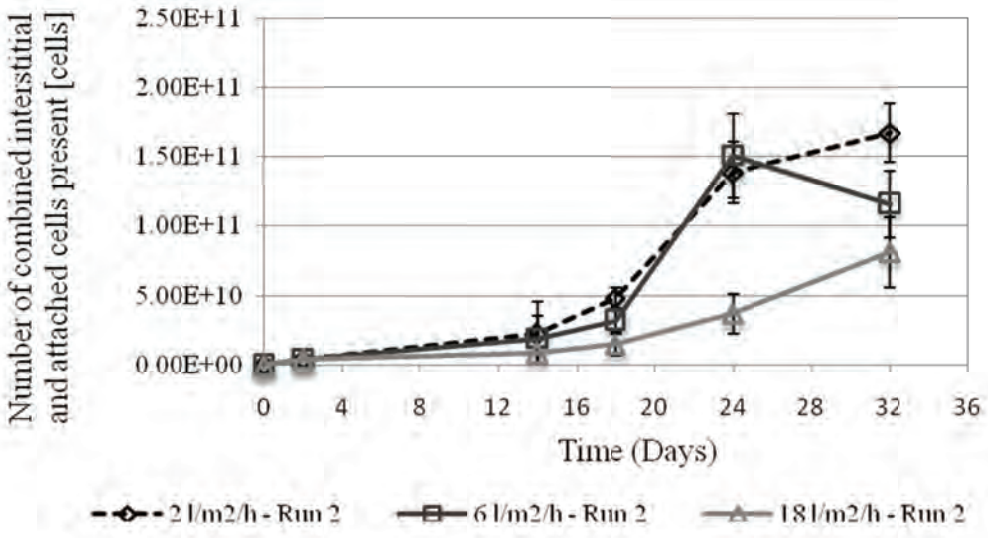


Figure 9: Microbial growth curve obtained by combining the interstitial and attached cells accumulated in the ore bodies, determined from the mechanical detachment of cells from the ore samples periodically removed from the heap systems using the in-bed sampling technique, given for different irrigation rates ◊ – 2 l/m^2/h, □ – 6 l/m^2/h and Δ – 18 l/m^2/h, during run 2. Error bars represent the standard deviation of the combined interstitial and attached cell counts (n=2).

Table 5: Cell balance over the three flow systems during leaching run

	Irrigation rate (l/m^2/h)		
	2	6	18
Inoculated (cells)	4.00E+09	4.00E+09	4.00E+09
Total planktonic (cells)	1.18E+10	4.50E+10	5.88E+10
Total interstitial (cells)	1.13E+11	1.28E+11	7.29E+10
Total attached (cells)	6.02E+10	6.35E+10	2.32E+10
Total cells (cells)	1.85E+11	2.36E+11	1.55E+11
% planktonic	**6.4**	**19.0**	**38.0**
% interstitial	**61.0**	**54.1**	**47.0**
% attached	**32.6**	**26.9**	**15.0**

3.3.2.3 Conclusions

The enhancement of microbial surface colonisation at lower irrigation rates was observed, as illustrated by the increase in attached and interstitial cell numbers with time and with respect to similar experiments. There was preferential accumulation of the microbes in the stagnant regions over those in the PLS and those on the ore surfaces, as illustrated by the dominant interstitial population.

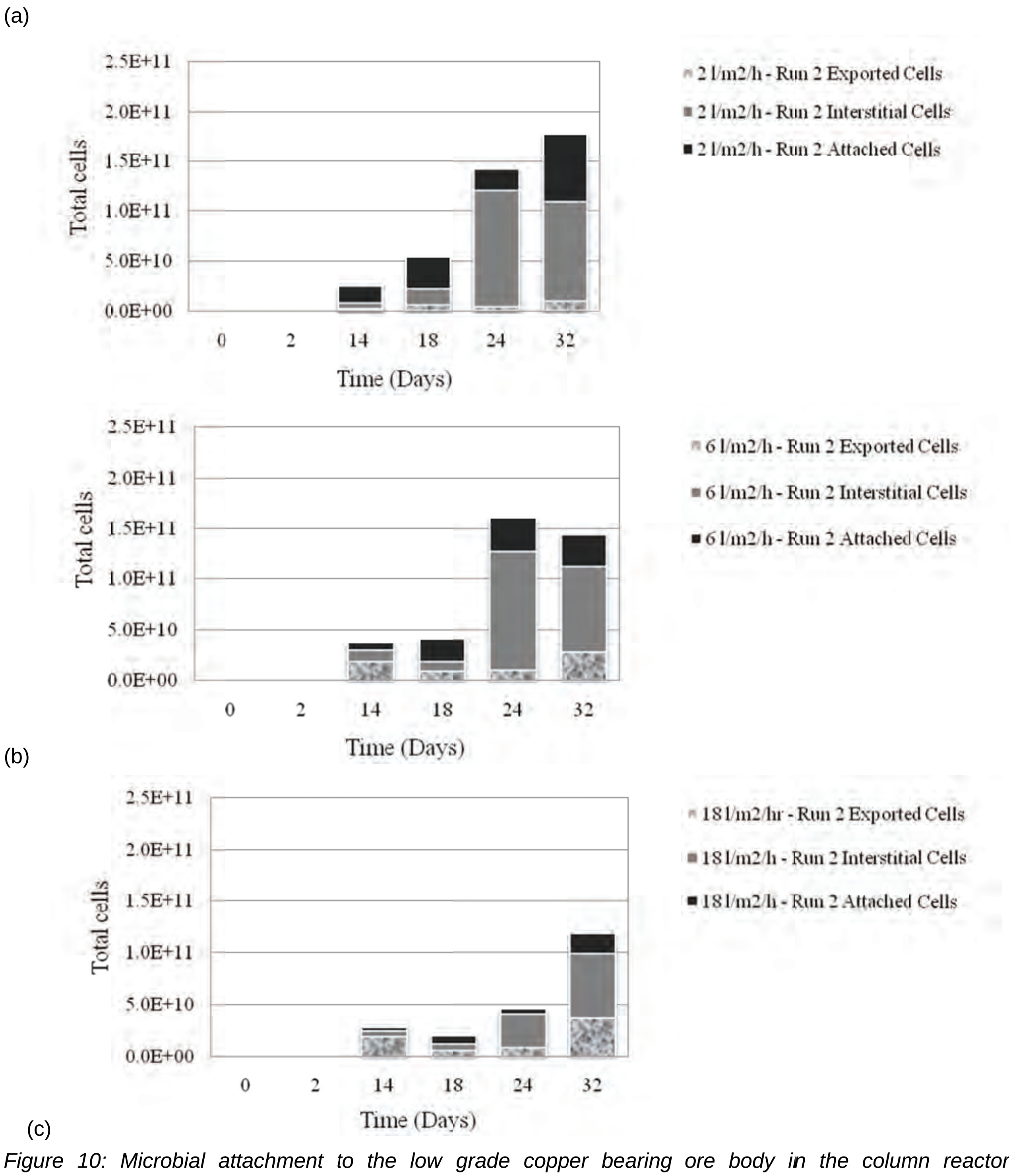


Figure 10: Microbial attachment to the low grade copper bearing ore body in the column reactors, determined from the mechanical detachment of cells from the ore samples periodically removed from the heap systems using the in-bed sampling technique, given for different irrigation rates for run 2.

3.4 EXPERIMENTAL STUDIES – PARTICLE SIZE AND ITS INFLUENCE ON ORE BED CHARACTERISTICS AND PERMEABILITY

3.4.1 Introduction

The focus of this study is limited to the effect that the particle size distribution of the packed bed has on the fluid flow through it, and therefore the bed conditions and reactions that occur within the bed. The study is conducted using a model system of glass marbles, ballotini and sand. Comparison is made to a real low grade ore system.

3.4.2 Experimental method

3.4.2.1 Materials

Bed packing

A model system approach was taken in this initial stage of the research project. The materials used to pack the bed were 24 mm diameter glass marbles, 15 mm marbles, 5 mm glass beads, 2 mm glass beads, +1000 µm sand, -1000+500 µm sand and -500 µm sand. The diameters given above for the marbles and beads were measured with a vernier calliper over multiple particles. The sand particles were prepared by wet sieving. Uniform particle size distributions of the following diameters were studied: 24 mm marbles, 15 mm marbles, 5 mm ballotini, 2 mm ballotini, +1000 µm sand, -1000+500 µm sand, and -500 µm sand.

Table 6 shows a listing of the mixed size packing used in this study. The columns were packed to the 93 mm mark and the mass of each particle was measured after each run. The particle size distributions are shown in Figure 11 for each packing.

Escondida simulation bed

The particle size distribution of a typical ore sample for bioleaching (Escondida) was estimated in this bed by empirically fitting the experimental material masses to the cumulative particle size curve for the ore sample. The Escondida and experimental simulation particle size distributions are shown in Figure 11 and compared with other packing used in Figure 12.

Water was pumped into the column as the liquid phase and its flow through the column was studied. Aqueous sodium chloride was used as the tracer. The properties of sodium chloride solution used are similar to that of water.

Table 6: Listing of bed packing used in study

Particles	**Mass (g)**				
	Big to small	**Small to big**	**Randomly mixed**	**Marbles and sand layered**	**Marbles and sand mixture**
24 mm marbles	483	1315	780	1609	3368
15 mm marbles	748	498	830	1531	0
5 mm glass beads	833	888	796	0	0
2 mm glass beads	470	888	688	0	0
+1 mm sand	188	156	100	0	0
-1 mm +0.5 mm sand	380	700	125	3071	2405
-0.5 mm sand	292	0	139	0	0
Arrangement	Layers of descending particle size	Layers of ascending particle size	Particle sizes mixed prior to packing column	Sand placed in discrete layers between large particles	Homogeneous mixture

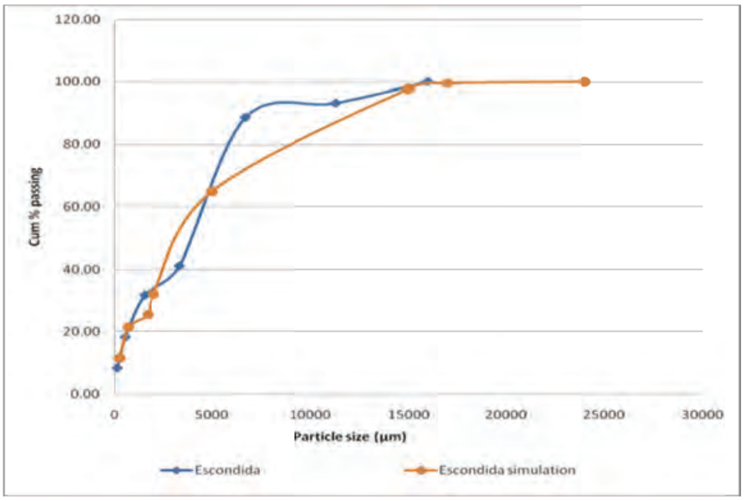


Figure 11: Particle size distribution for Escondida ore and the simulated bed packing

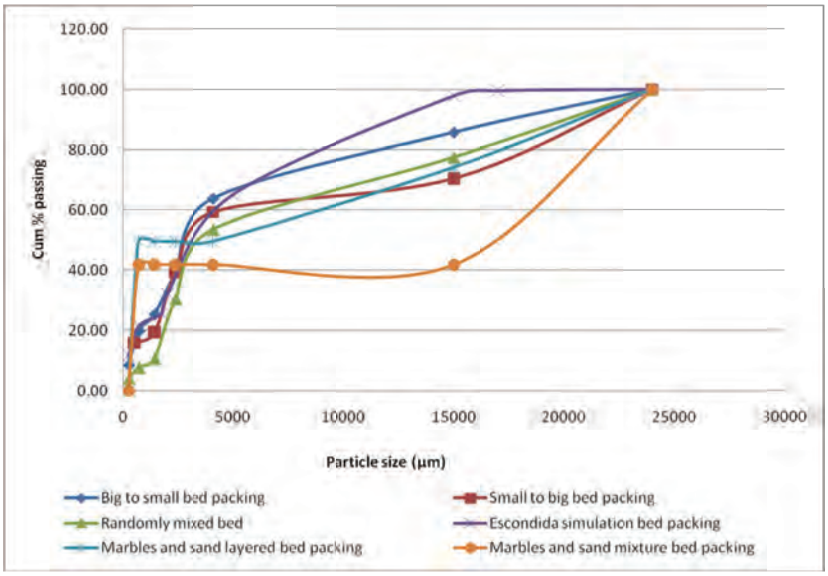


Figure 12: Particle size distributions of bed packing

3.4.2.2 Experimental apparatus

The experiments were carried out in three vertical columns of 100 mm diameter and 470 mm length, at ambient temperature and pressure. The experimental apparatus is shown in Figure 13. The AZ 86555 pH/Mv/Cand./TDS/ emp. conductivity meter was used to measure the conductivities. The MasterFlex console drive pump was used to pump the water into the column.

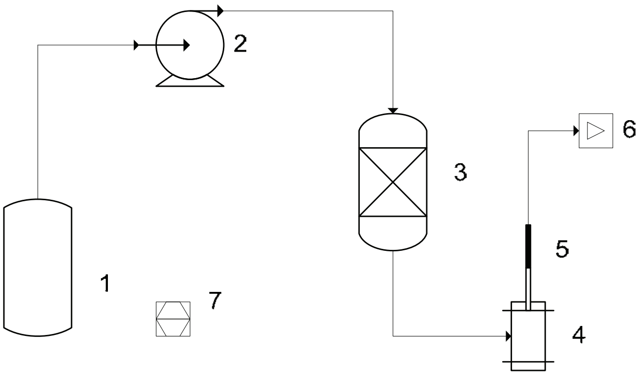


Figure 13: Experimental apparatus 1 solution vessel, 2 pump, 3 packed bed column, 4 sampling cup, 5 conductivity electrode, 6 conductivity meter and 7 stop watch

3.4.2.3 Experimental procedure

Voidage and permeability determination

The volume of water required to fill the column was recorded. The bed was then packed. Water was added to the packed column, to the volume indicator at the top of the column; the volume of water required to cover the level of the packing was recorded. The bottom of the column was then opened to drain the water; the volume of the water that drains from the column was recorded. The volume of water retained in the bed was estimated as the difference between the water added and the water drained. This was repeated six times for reproducibility.

Degree of saturation determination

The bed was packed with the solids fraction. The pump was used to pump water into the column at a feet rate of 4 ml/min, and the stop watch started simultaneously. Effluent samples were taken every twenty minutes to check if the column had reached steady state; the time required to reach steady was then recorded. The volume of the water collected was also measured.

Tracer studies

The two commonly used methods of injection of tracer pulse input and step input were compared by determining the RTD for a uniform bed, packed with 24 mm marbles. In a pulse input, 30 ml of sodium chloride solution (conductivity 10.5 mS) was injected in one shot at the top of the bed.

The bed was packed and the pump started to pump water into the column at a feed rate of 4 ml/min. Samples were taken at the effluent of the column every twenty minutes to check for steady state; that is the inlet and outlet flow rates being at 4 ml/min. Once the column had reached steady state, the background conductivity in the liquid phase of the column was measured. The tracer was then injected, and the stop watch started. Samples were taken at the effluent of the column every four minutes until the base conductivity of the column was restored.

3.4.3 Results

3.4.3.1 Voidage and intrinsic permeability

The relationship between the bed voidage (e) and particle diameter as well as permeability coefficient and particle diameter was determined using six measurements for each bed. The relationship is shown in Figure 14. The mean voidage of a packed bed was defined as the ratio of the void volume to the total volume of the bed. It is dependent on the particle diameter, tube diameter, packing method and the size distribution through the bed (Ismail *et al*., 2002). The permeability coefficient B was calculated from the measured voidage values using Equation 3.5.

$$B = \frac{1}{K''}\frac{e^3}{S^2(1-e)^2} \qquad [3.5]$$

From Figure 14, it can be seen that when the column was packed with particles of a diameter 5000 µm or higher, a voidage fraction between 0.33 ± 0.01 and 0.42 ± 0.01 was obtained. This result is expected, since the average voidage fraction for spherical particles is about 0.4. The lowest voidage fraction measured for uniform packs of 0.16 ± 0.01 was obtained when sand with a size distribution between 1000 µm and 500 µm was used. Voidage is recognised to decrease with increasing breadth of the particle size distribution.

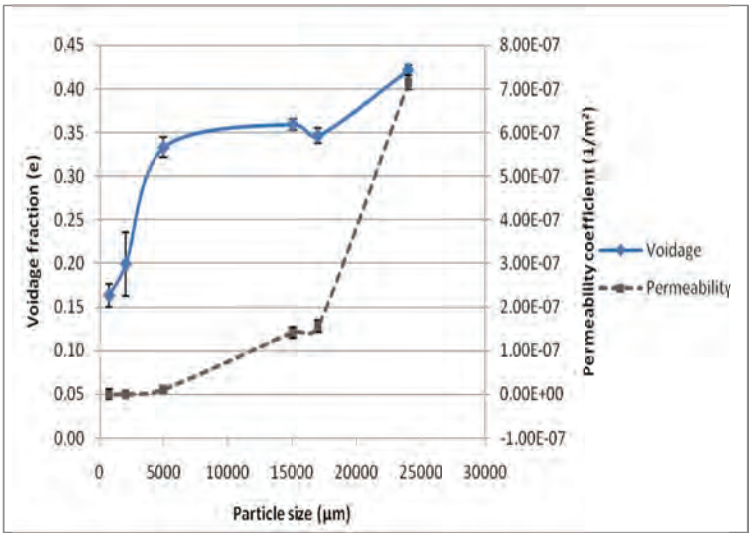


Figure 14: Relation between particle size and permeability coefficient and that between voidage fraction and bed packing in a uniform packed column.

The permeability coefficient gives an indication of the ease at which fluid flows through a packed bed. From Figure 14, the permeability coefficient was lowest for diameters 707 µm, 2000 µm and 5000 µm. On increasing the diameter of uniform size particles from 5000 µm to 24 000 µm, the permeability coefficient increased with particle size. Consistent with Equation 3.5, the permeability coefficient increases with decreasing specific surface area and increasing voidage. Therefore the permeability is expected to increase with increasing particle size.

3.4.3.2 Degree of saturation

The degree of saturation is the percentage of the void volume that is filled with water at steady state, given by the ratio of the volume of liquid held up in the bed to the void volume. The volume of the liquid holdup in each bed was measured and used to estimate the degree of saturation shown in Figure 15.

The liquid holdup in the bed gives an indication of portion of bed available to flow. The degree of saturation for beds packed with large particles (2000-24 000 µm) is low, compared to those with sand. The 24 mm marbles bed has the lowest degree of saturation of 0.86% followed by 5 mm beads (1.28%) and 2 mm beads (5.91%) packs. The low degree of saturation is a result of low liquid holdup in the bed.

The low grade ore sample from Escondida, which was used to represent waste rock, consisted mostly of finer particles, as shown in the particle size distribution in Figure 11. Here, 74% of void volume remained available to fluid flow. The portion of the bed available to flow decreased as more fine sand was added. This can also be seen by comparing the degree of saturation for beds packed with 24 mm marbles, marbles mixed homogeneously with 500 µm sand (small-big), marbles layered with 500 µm sand (marbles and sand) and 500 µm sand only.

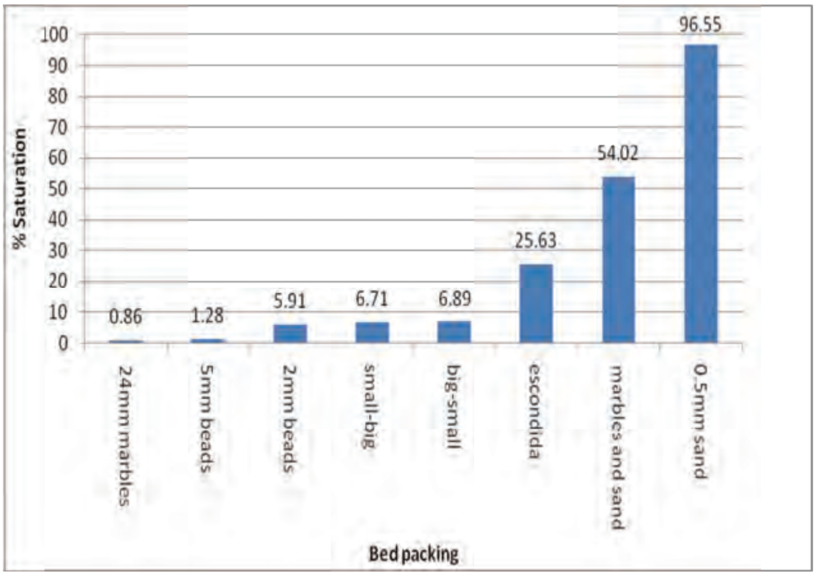


Figure 15: Degree of saturation of different packed bed

3.4.3.3 Tracer studies

Residence time distribution in uniform packed bed

The residence time distribution (RTD) in uniform packed beds was investigated by comparing beds packed with 24 mm marbles and 2 mm beads. The bed with the smallest particle size was expected to have the highest mean residence time. The mean residence times for the 24 mm marbles and 2 mm beads were 35.53 ± 4.13 and 63.13 ± 8.67 minutes respectively. The longer time required for the tracer to leave the bed packed with the smaller particles is consistent with increased stagnant zones or holdup. The small peak at the beginning of both graphs indicates short-circuiting of liquid as a result of channelling, aggravated by increased flow rate, due to the pulsing of the tracer.

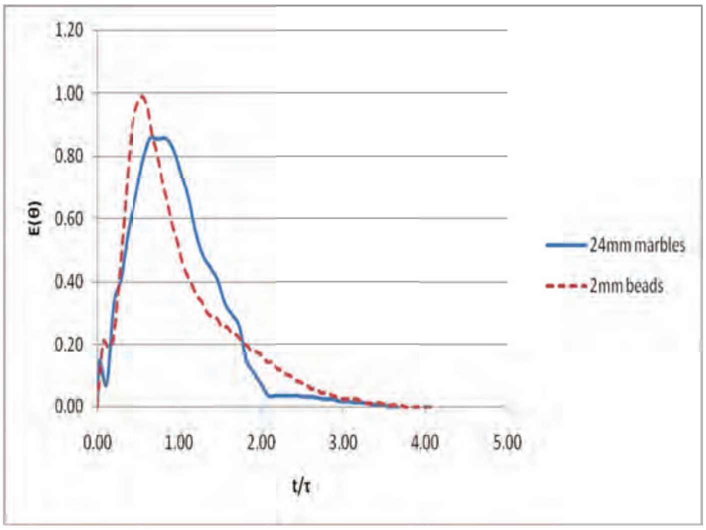


Figure 16: Exit age distribution for 24 mm marbles and 2 mm beads

Flow through mixtures of marbles and sand

In Figure 17, four different types of packing are reported: uniform 24 mm marbles, layered marbles and sand, a homogeneous mixture of marbles and sand, and fine sand (<500 µm). The mean residence times of the 24 mm marbles, layered marbles and sand, mixed marbles and sand and <500 µm sand were 35.53 ± 4.13, 203.89 ± 28.26, 162.80 ± 24.04 and 276.47 ± 29.78 minutes. Placing layers of fine sand over the marbles increased the mean residence time more than creating a homogeneous mixture of large particles and sand because the uniform sand bed within each of the layers was less permeable and restricted liquid from flowing.

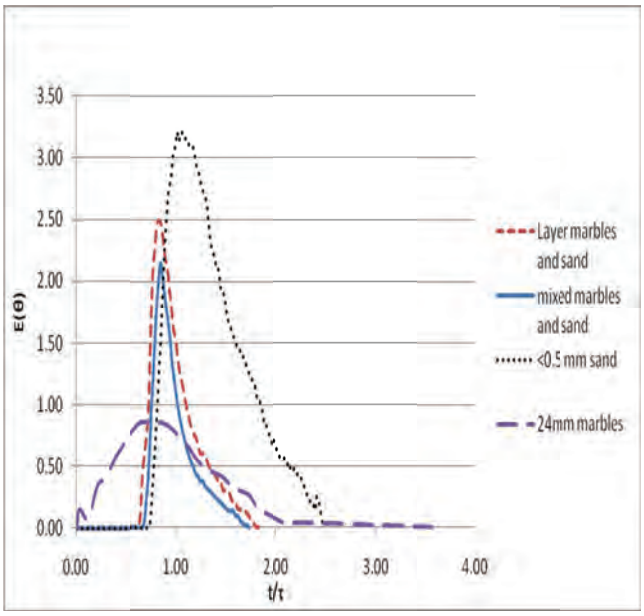


Figure 17: Exit age distribution of packed beds with mixed size distributions

Residence time distribution for mixed beds

The RTD for the flow through beds packed with a blend of particles is shown in Figure 18. Marbles, beads and sand of differing sizes were used to model a mixture of particles with the same particle size distribution as the low grade whole ore from Escondida as a random packing. The results from these two columns are compared to the RTD curve for sand with a size distribution between 1000 µm and 500 µm.

There was a short time delay in the elution of tracer for the Escondida and sand packing of 9 minutes and 17 minutes respectively. The RTD for these two packs showed a normal distribution indicating good flow through the bed with an elongated tail suggesting some stagnant zones. This indicated that where fines were not agglomerated onto large particles within the packing, as is the custom in heap leaching, the fines may control the fluid flow observed. The random packing showed evidence of channelling of fluid.

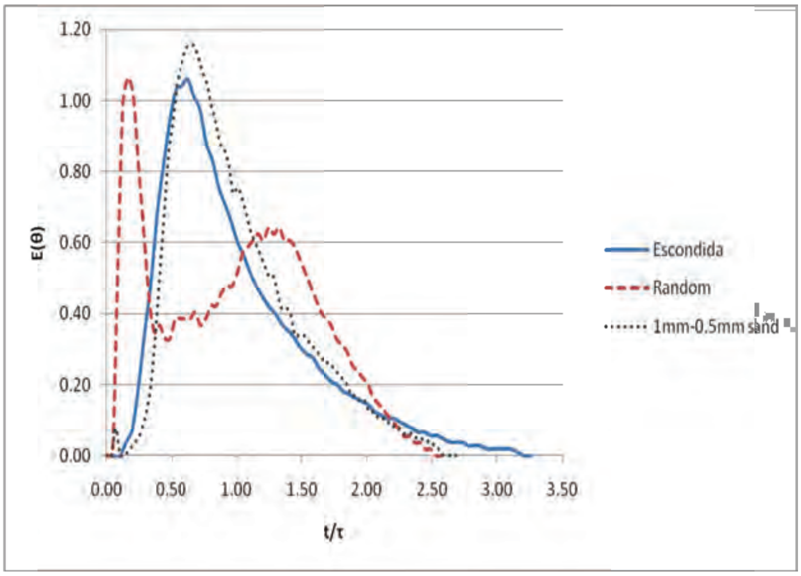


Figure 18: Exit age distribution of fine sand, modelled Escondida ore and a random mixture

3.4.4 Comparison of mean residence time

The mean residence time across all the packings studied is shown in Figure 19. The highest mean residence time of 276 minutes was obtained with the fine sand packing with a maximum size of 500 µm, as expected since this bed has the highest liquid holdup and only 3.45% of the void is available to flow. The second highest mean residence time of 204 minutes was obtained where layers of sand were placed between the large particles, simulated by marbles. This type of packing can be achieved on an industrial scale by layering waste rock and fine inert tailings.

The bed with the lowest mean residence time was that one of 24 mm marbles. This is expected since this bed has the lowest liquid holdup and 99.14% of the bed is available to fluid flow. The mean residence time increases as the resistance to flow increases. Beds containing packings of mixed sizes were characterised by higher mean residence times than those packed uniformly, owing to their decreased voidage, i.e. the fine particles fill the spaces between the bigger ones.

3.4.5 Relation between particle size and mean residence time

The relationship between the mean residence time and particle size in a uniform packed bed is shown in Figure 20. The highest mean residence time observed in this curve is for sand packing with a size distribution less than 500 µm. The mean residence time decreases as the diameter of the particles increases. While a large difference is seen with increasing particle size in the range 500 µm to 5 mm, there is little change between 5 mm and 24 mm.

In a uniform packed bed, it has been shown that the permeability coefficient increases with increasing particle size and the mean residence time increases as the flow resistance increases. Therefore, the mean residence time can be expected to decrease with increasing particle size.

There is a relation between the degree of saturation, voidage, mean residence time and the permeability of a bed. A bed with a large void space offers less resistance for fluid to flow and thus a high permeability coefficient. As the liquid flow through this bed is not hindered, there will be low liquid holdup resulting in a low degree of saturation and a low mean residence time. The 24 mm marble bed has a high voidage, high permeability coefficient, low saturation and low mean residence time.

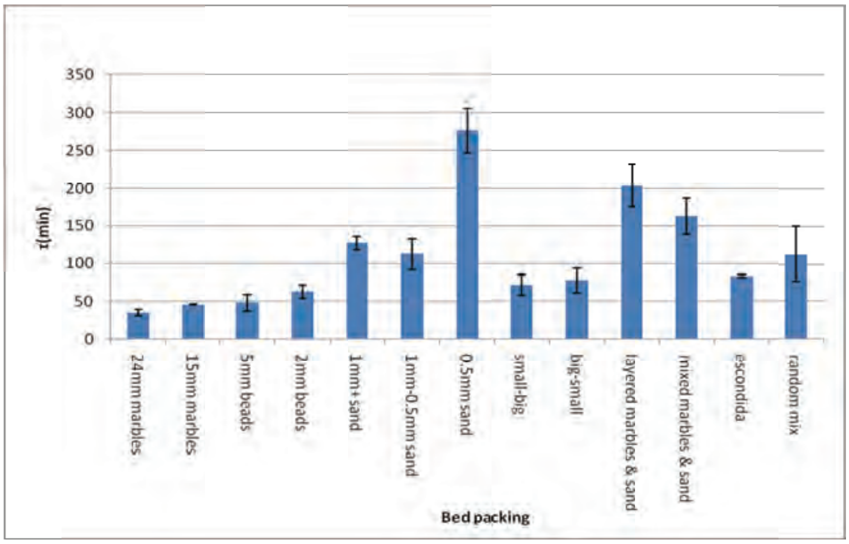


Figure 19: Mean residence time as a function of particle diameter with uniform packing

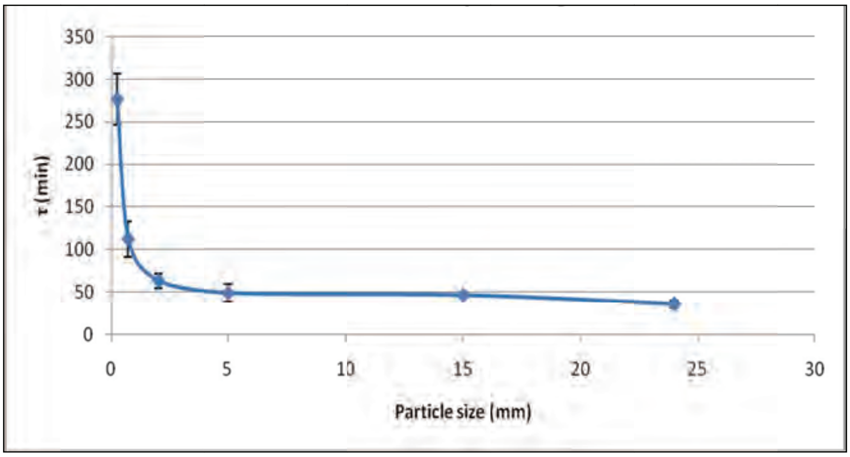


Figure 20: Mean residence time as a function of particle size

3.4.6 Discussion and Conclusions

The preliminary study using model particle systems has established a set of basic parameters for quantification of flow factors. More importantly, the model study has demonstrated that, by including a fraction of fine particles with the waste ore dump, the permeability of this bed can be manipulated to reduce fluid flow. Thus the supply of reactants to the reactive sulphide mineral sites is decreased. This is of particular interest where fines deplete of sulphide minerals are available for addition to the waste rock dump (see Sections 5.4.5 and 7.5.3). While a substantial reduction in permeability was achieved with a uniformly mixed system, the greatest impact was found on using layers of fine particles to reduce bed permeability. These studies inform the starting point for the studies with whole ore; however, it is imperative that the fluid flow studies are integrated with reaction studies. This is reported in Section 3.5.

3.5 EFFECT OF PACKING CONFIGURATION ON THE LEACHING OF SULPHIDE MINERALS FROM LOW GRADE ORE, SIMULATING WASTE ROCK

3.5.1 Introduction

The rate and extent of leaching of residual mineral sulphides in low grade ore or waste rock is influenced by physical and chemical parameters, biological factors, ore characteristics and heap geometry (Pradhan et al., 2008). The nature of the packing is expected to influence the leaching rate through its impact on permeability and residence time of the fluid phase discussed in Section 3.4, its effect on the ingress of oxygen and water (essential for the leaching reactions as well as microbial growth, ferrous and sulphur oxidation) and through its impact on microbial colonisation. Covers are used to minimise the supply of oxygen and moisture to the sites of potential reaction. Similarly, it has been demonstrated that the use of layers of fines reduce permeability of the ore bed and increase the residence time. In this study, a low grade chalcopyrite material was leached under optimum physicochemical conditions using three different packings: agglomeration to maximise permeability and colonisation, coarse particles only to simulate waste rock, and coarse particles layered with fine particles to study the effect of reduced permeability on the leach reactions. In addition to bioleaching with both continuous and intermittent feeds, abiotic leaching was also considered for the agglomerate material. An accelerated leaching system was used to enable data to be collected over a reasonable time frame (114 days).

To date, only three experimental studies (1970, 1983 and 2010) on understanding the effects of irrigation frequencies have been reported. These papers suggested that daily irrigation results in more rapid leaching than weekly irrigation (Aslam & Aslam, 1970); the irrigation frequency (cycle) is determined by the rate of evaporation and metal concentration in the effluent (Bruynesteyn, 1983) and Saririchi et al. (2012) postulated that intermittent irrigation is more efficient for metal recovery. Super-imposed on this study of packing regime, the effect of intermittent irrigation was investigated. While some data on irrigation regime are reported here, the comprehensive discussion of this study is provided by Vries (2013).

3.5.2 Experimental method

3.5.2.1 Ore mineralogy and preparation

The low grade chalcopyrite ($CuFeS_2$) ore used in this study was sourced from Arizona (USA) (Table 7). The size distribution of the sample, typical of heap bioleaching (Govender et al., 2012; Dew et al., 2011), is given in Table 8.

Table 7: Mineralogy of low grade ore used

Elements	**Analysis (%)**
Cu	0.587
Fe	2.629
S	1.070

Minerals	**Analysis (%)**
$CuFeS_2$	0.5 to 0.7
FeS_2	1.3 to 1.6
Other sulphides	< 0.1

Table 8: Particle size distribution of low grade ore used

All sizes		Coarse	
Size (µm)	Fraction	Size (µm)	Fraction
- 20 000 + 16 000	0.162	- 20 000 + 16 000	0.216
-16 000 + 8 000	0.293	- 16 000 + 8 000	0.391
- 8 000 + 5 600	0.147	- 8 000 + 5 600	0.196
- 5 600 + 2 000	0.147	- 5 600 + 2 000	0.196
- 2 000 + 1 000	0.074	- 2 000 + 1 000	0.000
- 1 000 + 250	0.074	- 1 000 + 250	0.000
- 250	0.103	- 250	0.000

An acid water solution was prepared at a ratio of 50 mL H_2O and 3.7 mL H_2SO_4 per kg of ore, which corresponds to 2 kg acid/ton ore and 5.5% moisture, where 0.5% comes from the ore (Tupikina et al., 2011). This acid solution was thoroughly mixed with 4kg ore before charged into the column. Through the provision of this acid (determined as a function of the ore type) the initial slowing of acid generation through reaction with the acid neutralisation capacity of the ore was avoided to allow an accelerated observation of packing effects.

3.5.2.2 Microbial cultures

In order to allow the accelerated observation of packing effects, forced inoculation with an appropriate microbial culture was used for the bioleaching studies. These were compared to abiotic treatment for the agglomerated ore configuration. Owing to chalcopyrite being the dominant copper sulphide mineral present in the low grade ore, the bioleaching experiments were run at 65°C to accelerate the reaction rate. The mixed thermophilic inoculum containing (>1%) *Sulfolobus metallicus*, *Acidianus* sp, *Acidiplasma cupricumulans*, *Acidothiobacillus caldus*, *Metallosphaera hakonensis* and the mixed mesophilic inoculum containing (>1%) *Leptospirillum ferriphilum*, *Acidithiobacillus ferrooxidans*, *Acidi(thio)microbium ferrooxidans* and *Acidithiobacillus thiooxidans* were combined. Each column was inoculated with 10^8 cells per kg ore.

3.5.2.3 Column operation

The leach experiments were carried out in PVC columns of 100 mm in diameter and 360 mm in height, previously described (Section 3.3.2.1, Figure 21). Each column was heated with an electrical heating coil, wrapped around the column and insulated with aluminium tape to control the temperature at 65°C. Humidified air was introduced from the base of the column at 200 ml/min. Drip irrigation occurred from above as specified.

Fourteen columns with different flow rates, intermittent irrigation types, packing types (agglomerated, coarse agglomerated and layered) and feed type (abiotic and biotic) were operated, as specified in Table 9. Three kinds of packing arrangements were used:

- Agglomerated packing: all size ranges
- Coarse packing (-20 +2 mm) where the fines were removed.
- Layered packing of coarse ore (-20 +2 mm) layered between -2 mm fines.

The agglomerated ore was exposed to both bioleaching and abiotic leaching. Four different types of irrigation methods were used – continuous and three intermittent irrigation regimes: continuous irrigation at 1 L/day (3 litres in 3 days); intermittent irrigation 1 irrigated for 2 days at 1 L/day followed by a one day rest (2 litres in 3 days); intermittent irrigation 2 irrigated for 1 day at 1 L/day followed by a 2 day rest (1 litre in 3 days); and intermittent irrigation 3 irrigated for 2 days at 1.5 L/day followed by a 1 day rest (3 litres in 3 days).

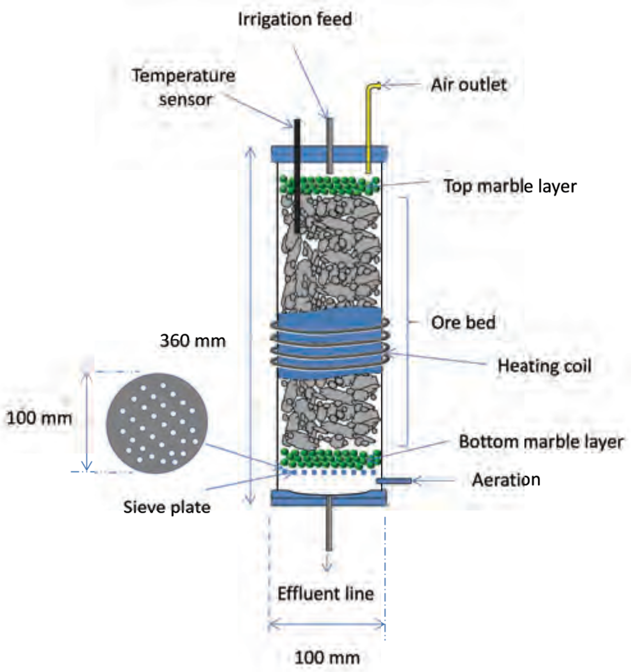


Figure 21: Schematic of heap leach column (adapted from van Hille et al., 2010)

3.5.2.4 Sampling and analytical procedures

Sampling was conducted every 3 days when the intermittent irrigation pumps were switched off. The following measurements were performed:

- Effluent volume measurement
- pH measured using a Metrohm 713 pH meter and AG 9101 Hersisau glass probe
- Redox potential measured with a Metrohm 704 equipped with a Pt.Ag/AgCl electrode
- Ferrous (Fe^{2+}), Ferric (Fe^{3+}) and total Fe (Fe^{tot}) determined spectrophotometrically using the phenanthroline method, pre- and post oxidation
- Total Cu and total Fe analysis by atomic absorption spectroscopy (AAS)
- Acid digestion was done on to analyse the Cu and Fe on the post and pre-leached ore by AAS
- The leached ore was acid washed with oxalic acid to remove all precipitates on the leached ore to determine the amount of Fe and Cu precipitated on the ore.

Table 9 Packing and irrigation regimes under which leach experiments were run

Column	Feed arrangement	Intermittent type	Flow rate (L/day)	Sample (L)	Packing	Leaching type
1	Continuous	n/a	1	3	Agglomerate	Acid
2	Continuous	n/a	1	3	Agglomerate	Bio
3	Continuous	n/a	1	3	Layered	Bio
4	Intermittent 1	2 days on 1 day off	1	2	Agglomerate	Acid
5	Intermittent 1	2 days on 1 day off	1	2	Agglomerate	Bio
6	Intermittent 1	2 days on 1 day off	1	2	Layered	Bio
7	Intermittent 2	1 day on 2 days off	1	1	Agglomerate	Acid
8	Intermittent 2	1 day on 2 days off	1	1	Agglomerate	Bio
9	Intermittent 2	1 day on 2 days off	1	1	Layered	Bio
10	Intermittent 3	2 days on 1 day off	1.5	3	Agglomerate	Acid
11	Intermittent 3	2 days on 1 day off	1.5	3	Agglomerate	Bio
12	Intermittent 3	2 days on 1 day off	1.5	3	Layered	Bio
13	Continuous	2 days on 1 day off	1	3	Coarse	Bio
14	Intermittent 4	2 days on 1 day off	1	2	Coarse	Bio

3.5.3 Results and Discussion

The progress of the accelerated leaching of the residual sulphidic mineral as a function of different packing regimes is illustrated through the profiles of pH in the PLS and H^+ consumption (Figure 22), redox potential of the PLS indicating the ratio of Fe^{3+}:Fe^{2+} (Figure 23), iron in solution (Figure 24) and cumulative copper release (Figure 25) over 114 days. These data are extended by illustrating each of these across both continuous and intermittent irrigation profiles.

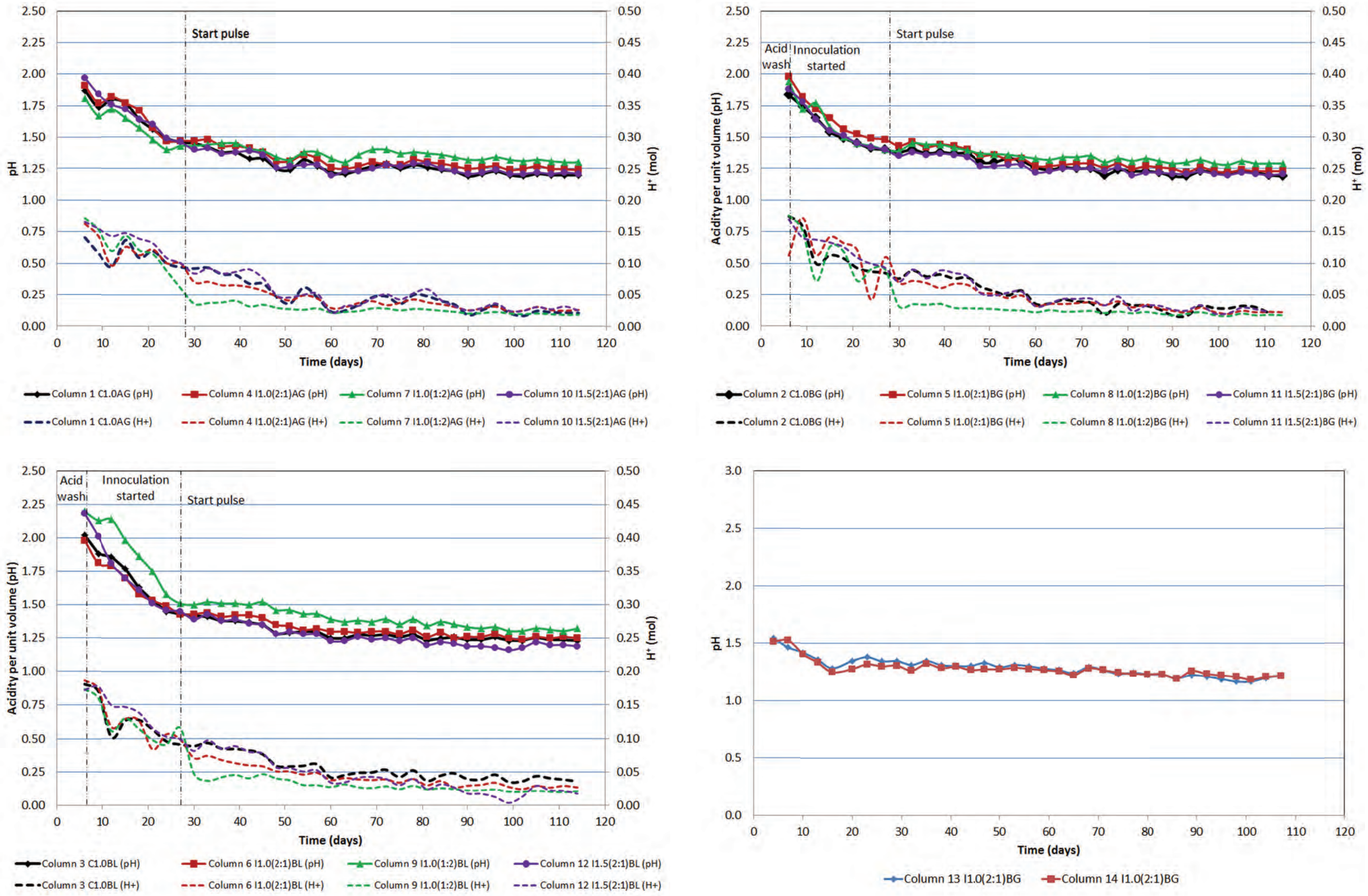


Figure 22: Daily pH of the PLS and H^+ consumption of A.) abiotic agglomerated columns 1, 4, 7 and 10; B.) agglomerated bioleaching columns 2, 5, 8 and 11; C.) layered bioleaching columns 3, 6, 9 and 12; and D.) coarse bioleaching columns 13 and 14.

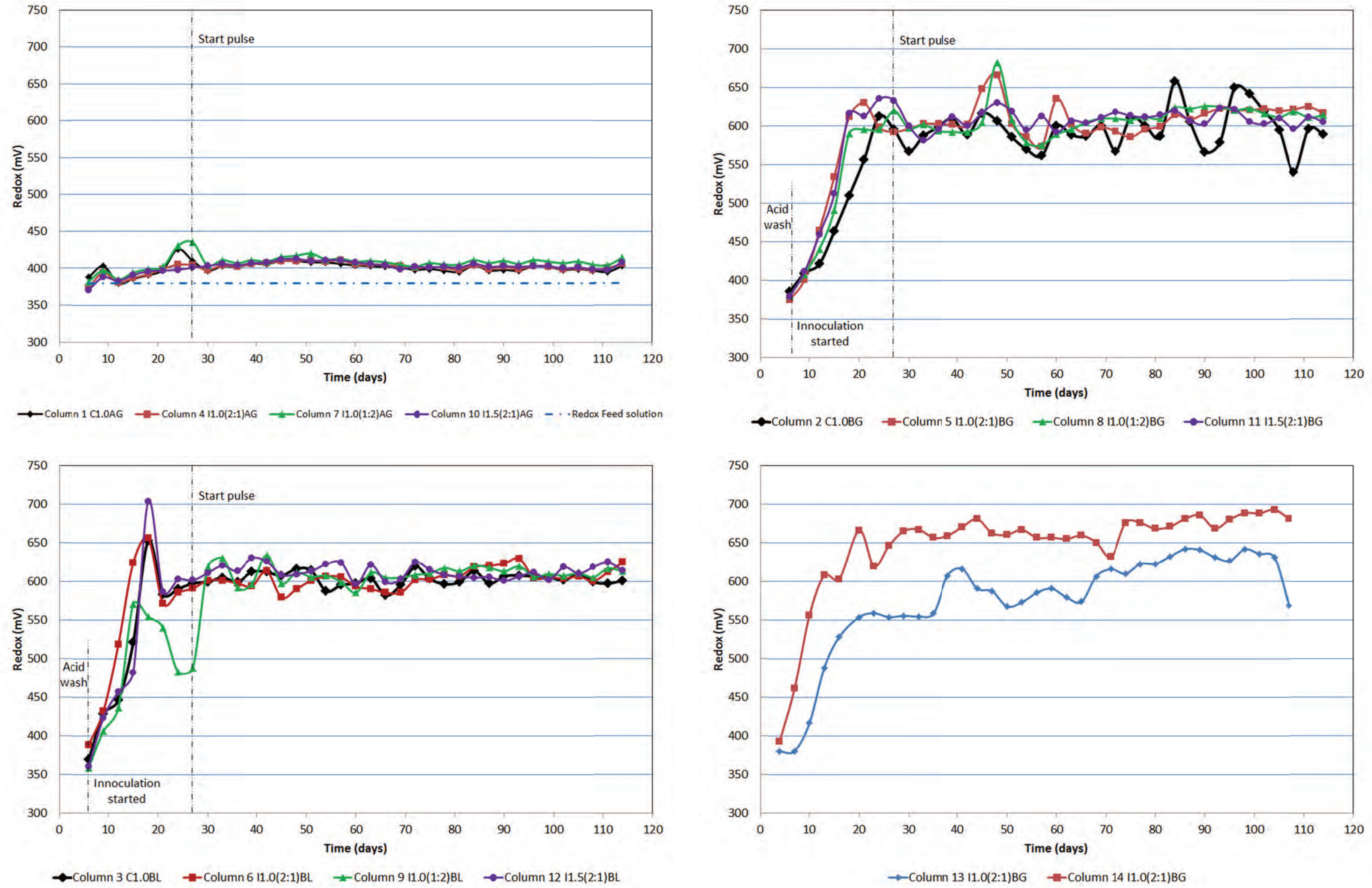


Figure 23: Redox potential of the PLS of A.) abiotic agglomerated columns 1, 4, 7 and 10; B.) agglomerated bioleaching columns 2, 5, 8 and 11; C.) layered bioleaching columns 3, 6, 9 and 12; and D.) coarse bioleaching columns 13 and 14.

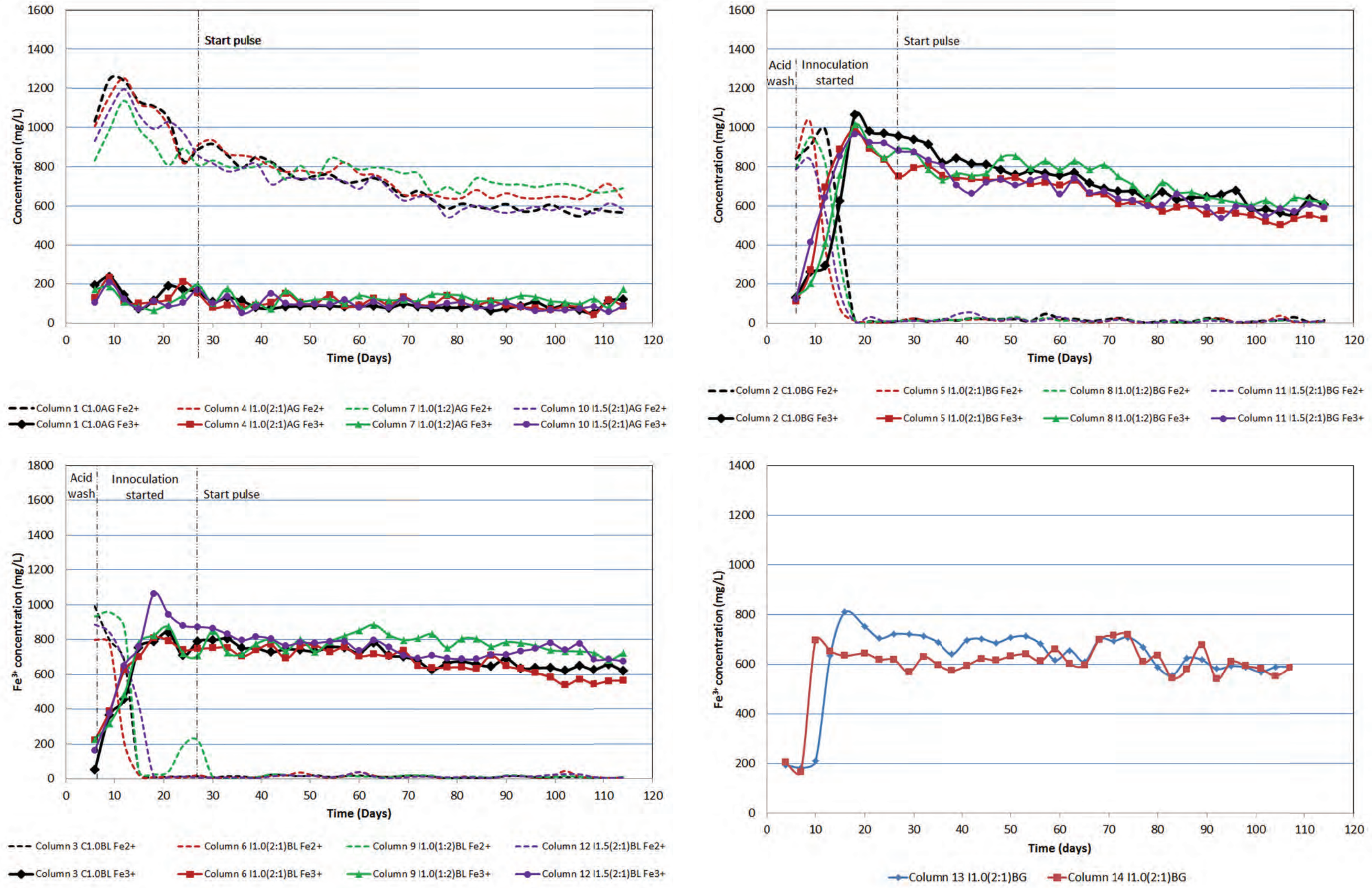


Figure 24: Daily Fe^{2+} and Fe^{3+} concentration in the PLS of A.) abiotic agglomerated columns 1, 4, 7 and 10; B.) agglomerated bioleaching columns 2, 5, 8 and 11; C.) layered bioleaching columns 3, 6, 9 and 12; and D.) coarse bioleaching columns 13 and 14.

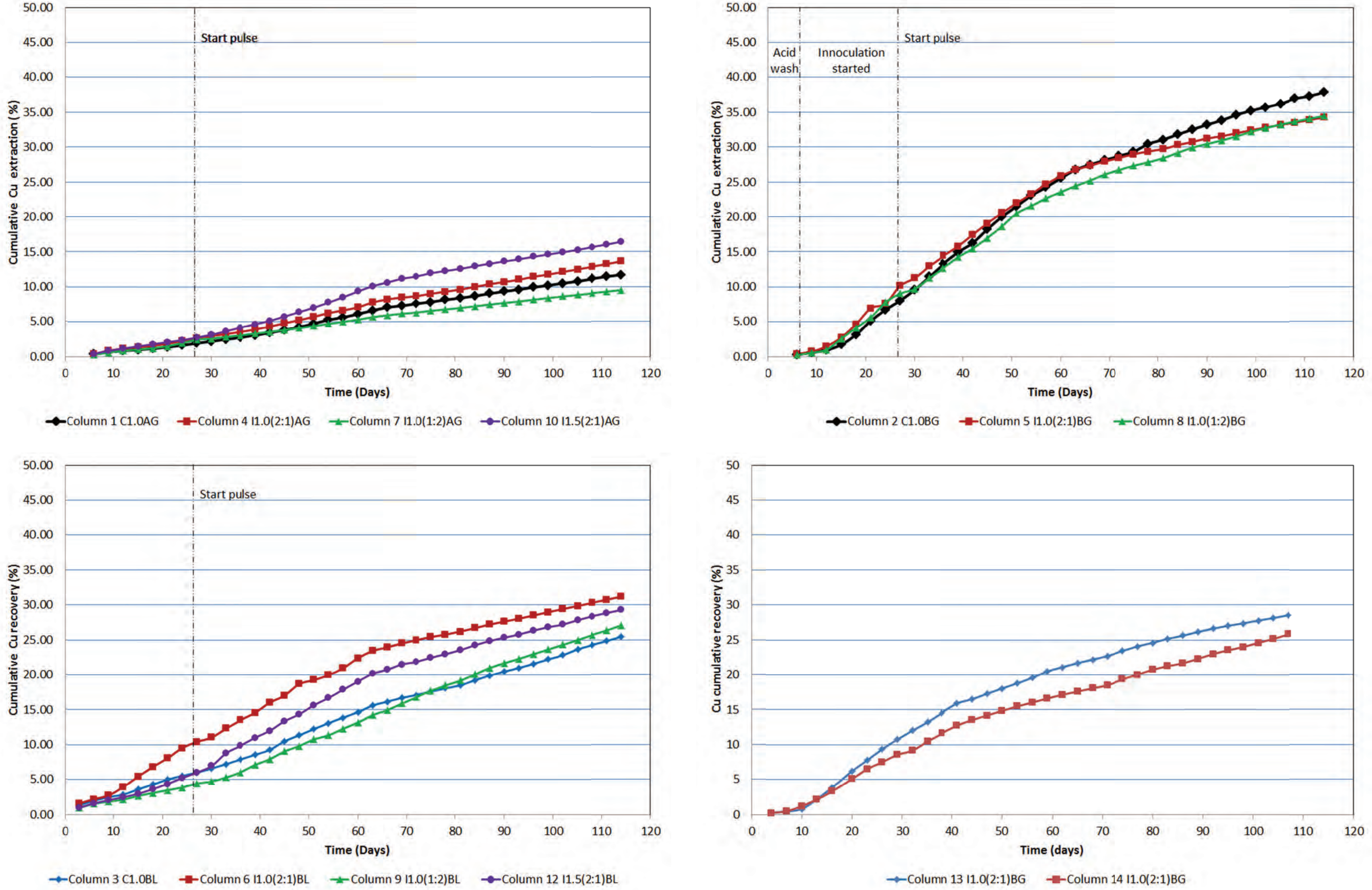


Figure 25: Cumulative copper extraction from A.) abiotic agglomerated columns 1, 4, 7 and 10; B.) agglomerated bioleaching columns 2, 5, 8 and 11; C.) layered bioleaching columns 3, 6, 9 and 12; and D.) coarse bioleaching columns 13 and 14.

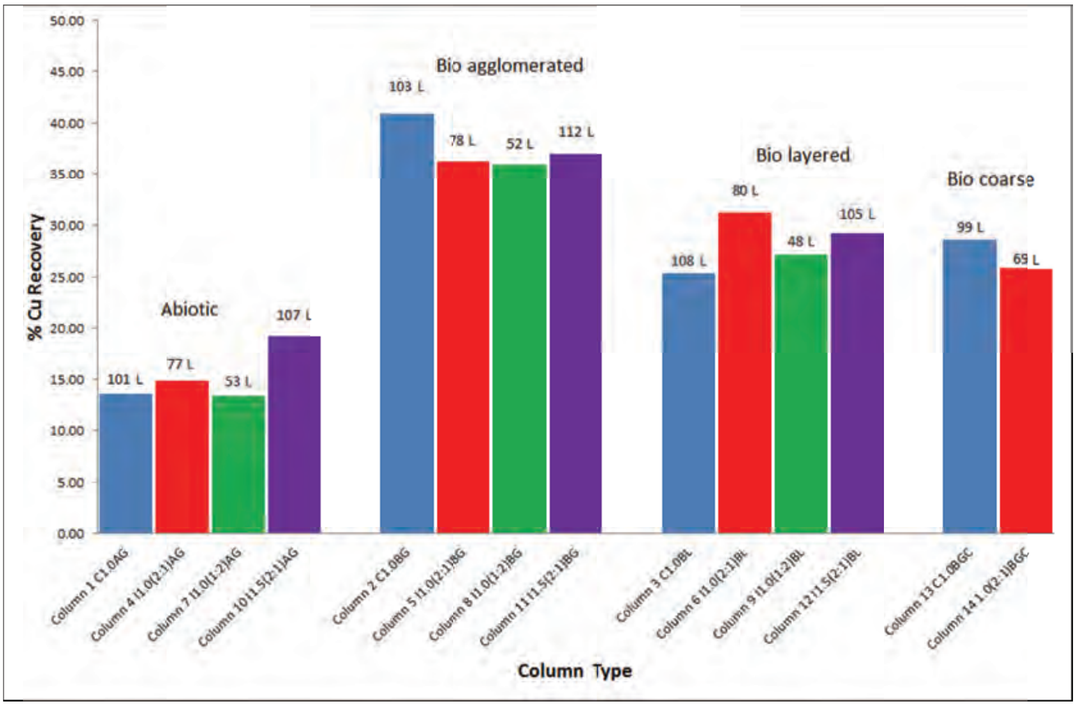


Figure 26: Total Cu recovery to the PLS after leaching for 114 days

While the detailed results are reported and discussed further in Vries (2013), these are readily summarised by comparing the extent of copper release as a function of packing configuration, irrigation type and biological activity in Figure 26. Further the material balance of the copper phase is given in Table 10, detailing the fate of the leached copper.

The role of the established microbial culture on ARD formation is demonstrated by comparing the abiotic and biotic conditions in the agglomerated ore columns. The total Cu recovery for the bio agglomerated columns 2 (41%), 5 (36%), 8(36%) and 11 (37%) in each flow type (intermittent or continuous irrigation), shown in Figure 26, was higher than its corresponding abiotic agglomerated columns 1 (14%), 4 (15%), 7 (13%) and 11 (19%). The low leaching rate in the abiotic columns results from the absence of microbial oxidation of ferrous iron to the powerful oxidising agent ferric iron which, in turn, causes dissolution of the Cu sulphide minerals (Pradhan et al., 2008). Dissolution of chalcopyrite in an acid ferric medium can be described in Reactions 3.6 and 3.7, illustrating that adequate provision of the ferric ion is crucial for chalcopyrite leaching (Lizama et al., 2003). The rate of chalcopyrite leaching is strongly affected by low ferric concentration (Kametani & Aoki, 1985).

$$\mathrm{CuFeS_2 + O_2 \rightarrow Cu^{2+} + 5Fe^{2+} + S^0} \qquad [3.6]$$

$$\mathrm{CuFeS_2 + 4Fe^{3+} + 3O_2 + 2H_2O \rightarrow Cu^{2+} + 5Fe^{2+} + S^0} \qquad [3.7]$$

The effect of ore packing is demonstrated by comparing the bioleaching of the agglomerated ore, layered coarse and fine ore, and the coarse ore packings. The total Cu recovery from the coarse agglomerated columns 13 (29%) and 14 (26%) for each flow type (intermittent or continuous) was lower than its corresponding recovery from the bio agglomerated columns 2 (41%) and 5 (36%). The rate limiting step is postulated to be caused by the increased permeability of the coarse ore, which allowed insufficient contact time between the leaching agent and the mineral surface.

The total Cu recovery for the bio agglomerated columns 2 (41%), 5 (36%), 8 (36%) and 11 (37%) in each flow type (intermittent or continuous) was higher than its corresponding layered agglomerated columns 3 (25%), 6 (27%), 9 (33%) and 12 (29%). This supports the finding of Miller et al. (2003) who demonstrated that uniform permeability is an important factor in effective leaching in a heap. The lower leaching rate that occurred in the bio layered columns is postulated to be caused by the low contact time of reactants with the mineral surface in the coarse material layer as well as the reduced permeability of the layers of fine material that decreased the oxygen distribution in the leaching medium, typically associated with slower chalcopyrite dissolution. Oxygen plays a key role in the regeneration of ferric ion as the oxidizing agent of the sulphide mineral (Cordoba et al., 2009).

In both cases the rate of chalcopyrite leaching was strongly affected by the packing types in heap bioleaching. It is, however, noted that in all cases studied, leaching under these active, irrigated leaching conditions was not arrested completely, but merely slowed. While this may reduce the environmental impact in the immediate future, it does not eradicate the long term risks and must be assessed in this light. A long term study under conditions more typical of waste rock dumps would shed further light onto this.

Table 10: Total Cu recovery (114 days) mass balance

Column No	Cu Pre-leached ore(g)	Cu Feed (g)	Cu post leached ore (g)	Cu in effluent (g)	Cu Precipitated (g)	Cu Leached (%)
1	105	50	81	71	3	23
4	105	39	82	59	3	22
7	105	27	84	43	5	20
10	105	54	80	76	3	24
2	105	53	65	70	23	39
5	105	40	61	48	36	42
8	105	26	64	36	32	40
11	105	59	66	74	25	38
3	105	69	69	84	21	34
6	105	43	69	50	29	34
9	105	26	71	34	25	33
66	105	66	67	86	19	36

3.5.4 Conclusions

It is evident from the study of packing configurations that the agglomeration of fine material onto coarse particles provides both enhanced permeability of the ore bed as well as a niche environment for microbial colonisation (Govender et al. in press). The absence of the agglomerated fine material reduced the residence time in the ore bed and slowed the leach rate and thereby ARD generation rate. In addition, the introduction of layers of fine material further slowed the leach rate through decreased permeability. It is noted, however, that in all cases following the establishment of leaching conditions, ARD generation will occur. The selection of packing arrangement simply defines the time period prior to the onset of leaching, as well as its rate and, thereby, duration. Our ongoing research seeks to provide tools by which to estimate these time scales.

3.6 PREDICTING SOLUTION CONTACTING AND FLOW THROUGH THE ORE BED

The roles of fluid flow, ore bed permeability and solid-liquid-gas contacting are well recognised as key challenges in heap construction and operation (Petersen and Dixon, 2007; Dixon and Afewu, 2011), hence equally in the construction of waste rock dumps to prevent leaching and the associated ARD. The transport phenomena are interlinked and interact with chemical reactions occurring in the rock bed. Furthermore, they depend directly or indirectly on the properties and mineralogy of the bed. Over the last forty years, many studies have been conducted to investigate these transport phenomena and their interactions in packed ore beds, starting from Roman et al. (1974), and have recently been summarised by Dixon (2003) and Petersen and Dixon (2007a). The ore bed is a heterogeneous environment, yielding differing levels of moisture penetration and holdup, mass and heat transfer with spatial position and dynamic changes in these properties with time. This inhomogeneity is accentuated in waste rock dumps and tailing impoundments over that experienced in ore beds for heap leaching. Much of the understanding of these challenges has been gleaned from the soil science literature and from model predictions of the heap system, owing to the challenge of gathering data on the large scale and of achieving representative small scale systems.

Recently, research into the influence of solid-liquid-gas contacting at the scale of the agglomerate have been conducted to consider the impact of these heterogeneities on performance, prior to further addressing contacting at the bulk scale. Using an experimental design allowing irrigation of an “ore slice” 10 cm in breadth, 60 cm in width and 1 m high, the irregularity of moisture penetration from a single dripper was demonstrated (Chiume, 2011), building on the study of Dixon and Afewu (2010) in their 6 m column. Colonisation was hampered by low moisture content.

There have been many attempts to describe solution flow phenomena in packed rock beds with mathematical models (Sheikhzadeh et al., 2005; Bennett et al., 2006; Cariaga et al., 2005; Ogbonna et al., 2006; Petersen and Dixon, 2007; Dixon and Afewu, 2010). However, this approach faces many problems such as poor correlation between measured and modelled data. This is partially due to the fact that most of these models are based on a conceptual picture of Darcian flow through porous media, with many assumptions not based on actual observations. This may be because historically the general approach was formulated for ground water flow through saturated soils, which was then adapted to describe unsaturated flow through coarse-grained packings of rocks (typically 1-100 mm) commonly found in the coarse ore packed beds under consideration here. The challenge of the study of the fluid distribution and permeability in the ore bed has led to the desire to validate the modelling approaches presented to date. This has been initiated through the setting up of three further studies, two of which were instigated by CeBER UCT and the third by the Royal School of Mines at Imperial College London. These studies inform the approach of this project.

Fagan et al. (2012a, b), working at the MRII at Cambridge University as part of a collaborative project with CeBER UCT, have developed a new MRI data acquisition technique to allow data capture in the presence of iron-containing ores. Using this, they have tracked the flow of liquid at the agglomerate scale, demonstrating liquid and gas holdups consistent with the residence time studies of Bouffard (2009). Most interestingly, this tool allows us to identify the liquid film thickness typical in the system, informing the modelling approach. Tracer studies at a variety of scales have enabled estimates of the stagnant liquid component of the ore bed to be established. Typical values of stagnant liquid in an agglomerated ore bed lie in the range 18 to 45% of the liquid present (Bouffard, 2009; Govender et al., 2012); however the relative mobility of this liquid is not yet known. Associated work using X-ray tomography has allowed the study of accessibility of mineral grains to leach agents in both large ore particles and agglomerated systems, again informing the modelling approach. Most interesting, the flow patterns developed in the bed have been shown to be characterised by rivulet flow, rather than as a uniform liquid front progressing through the bed. The liquid flow patterns are largely maintained following their establishment in the bed, although additional rivulets may form at increased irrigation rates.

In an independent study, Ilankoon et al. working at ICL (UK) demonstrated similar rivulet flow across a non-porous glass ballotini model system and a low grade copper ore, using photography, liquid holdup studies and associated modelling. They showed that this rivulet flow behaviour is the major flow feature through the packed bed and related the average flow rate of the rivulet to the liquid holdup of the bed. The importance of working with the real ore system, in addition to using the model system, was shown to be imperative (Ilankoon, 2012; Ilankoon et al., 2012a, b).

Through reviewing the literature relevant to the flow of liquid through the heterogeneous ore bed, it is demonstrated that the consistency between the flow distributions estimated through model approaches (such as that of Dixon and Afewu (2011)) are not consistent with experimental observation (such as that presented by Orr and Vesselinov (2002)), as illustrated in Figure 27.

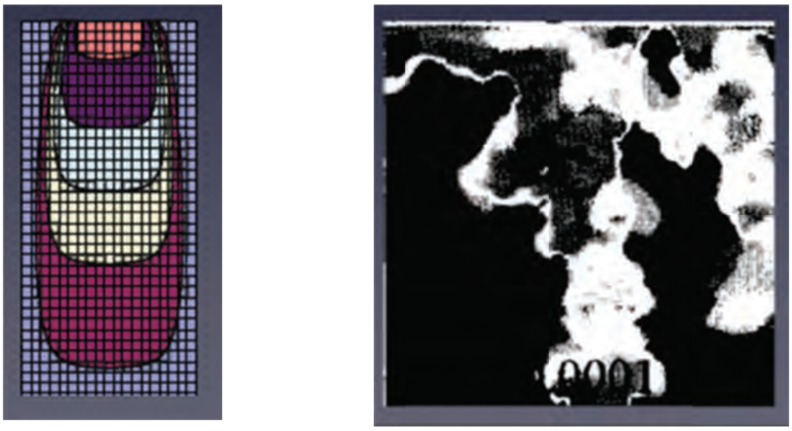


Figure 27. Variation of the water content in the space obtained from Darcian-type models: (a) with the uniform saturated intrinsic permeability (Dixon and Afewu, 2011) and (b) with the uneven permeability (Orr and Vesselinov, 2002)

Since it is not possible to achieve absolutely uniform saturated intrinsic permeability in packed beds, the instabilities of the flow suggested by the simulations of Orr and Vesselinov (2002) are likely to be always present to some degree. These instabilities make it impractical to apply the Darcian approach directly, as any small variation in the permeability would change the flow pattern. Further, some liquid at the micro-scale is immobile due to viscous interaction with the porous matrix and dead-end pores (Bear, 1972). Darcian models do not predict the occurrence of stagnant liquid in a porous medium.

To gain a better understanding of the liquid flow, we are using positron emission tomography (PET) to track the flow of liquid through the packed bed. A similar approach has been validated in other applications, e.g. to track solid movements in fluidised beds (van de Velden et al., 2008) and to study solid particle attachment in a flotation froth (Waters et al., 2008; Cole et al., 2010).

The PET scanner at iThemba LABS, Faure, Western Cape, was used for the preliminary tests, using a Gallium-68 tracer (as it is one of the most commonly used tracers in medical studies (Khan et al., 2009). A small column (20 cm tall and 10 cm in diameter), packed with a typical heap leach ore and initially wetted, was placed inside the camera. The experimental setup is shown in Figure 28A. Solution with the radioactive Gallium-68 tracer was fed to the top of the column and drained from the bottom to avoid tracer accumulation. Results of the preliminary tests are shown in Figure 28B. By comparing with the result of a Darcian-type model of a similar set-up (Dixon and Afewu, 2011) given in Figure 27, it was obvious that the model could not adequately describe the observed solute transport through a packed bed at this scale.

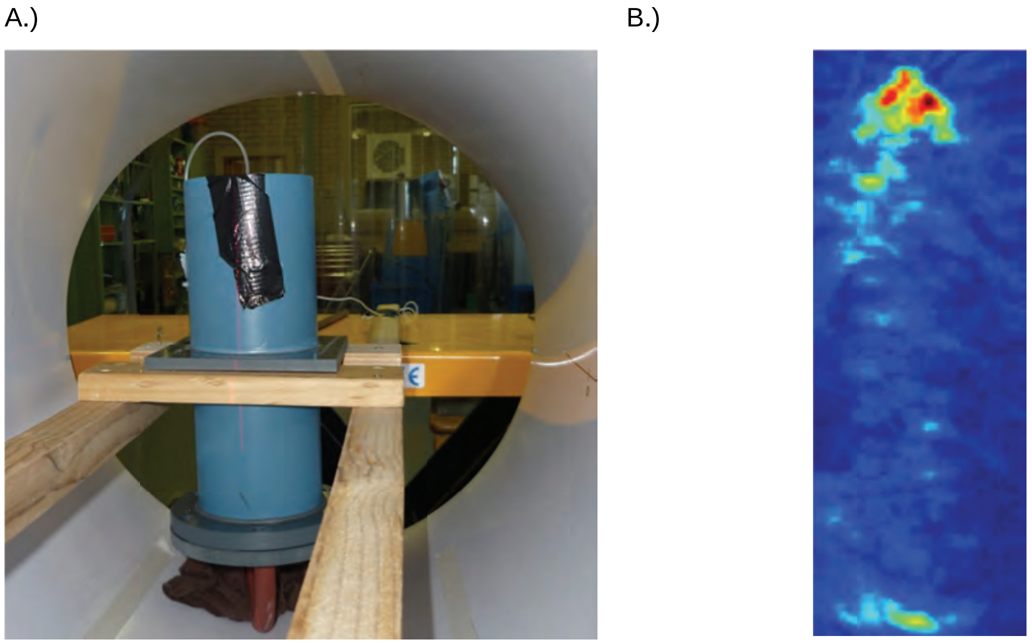


Figure 28. A.) The PET scanner used to follow liquid flow in the PVC column packed with ore shown positioned in the camera. B.) The preliminary result illustrating liquid movement through the ore column. The progression from dark blue (no moisture bearing tracer) to red (high liquid content) demonstrates the non-uniform distribution of the liquid.

Based on these findings, it is clearly of limited value to conduct the modelling of liquid and gas distribution in the ore bed using standard Darcian approaches in the main. Further, the HeapSim-based approach of the simulation model, using a known simple pattern of downward bulk flow modelled using the advection-diffusion equation, does not have sufficient power to handle changes in permeability actively. To this end, it has been considered inappropriate to continue with the paper study component originally proposed. As an alternative, two approaches have been taken. Firstly, the experimental impacts of packing and irrigation effects have been studied practically as reported in Sections 3.3, 0 and 3.5. Secondly, the basis has been established for the more rigorous understanding of fluid contacting in the ore bed, as described above. These detailed studies exceed the scope of the current project, but have been initiated through related projects and may be expected to inform an extension of this study.

CHAPTER 4: THE POTENTIAL FOR IMPLEMENTATION OF SULPHIDIC PHASE REMOVAL BY SEPARATION OR REACTION

4.1 STRATEGIES FOR SULPHIDE REMOVAL BY SEPARATION

4.1.1 Previous studies

Selective and non-selective sulphide separation techniques have traditionally been used to optimise value recovery in mineral processing (Fornasiero et al., 2001; Clarke et al., 1995). However, these techniques have now been proposed and adopted for desulphurization of acid generating mine waste and tailings (McLaughlin and Robertson, 1994; Humber, 1995; Leppinen et al., 1997; Stuparyk et al., 1995). The desulphurization process is based on separation of a sufficient quantity of sulphides from the tailings. This may be achieved through integration with the flotation steps for metal recovery, through the combined optimisation of recovery of the metal value to the product stream and the remaining sulphide components to the by-product stream, leaving an inert, benign tailings. More commonly, this desulphurisation is considered as a waste treatment add-on, using bulk sulphide flotation processes.

The biggest challenge with desulphurization of the tailings using a bulk sulphide float following recovery of values, however, is selective flotation of sulphides from an already treated pulp which contains various chemicals and ions that interfere with the flotation process (Benzaazou et al., 2008). Benzaazou et al. (2000) investigated the feasibility of non-selective froth flotation of sulphide tailings to produce low sulphur fraction and a low volume sulphide concentrate fraction using tailings from four different mines. Amyl xanthate was used as a collector. The study showed that cyanide-free pulps can be effectively desulphurised by froth flotation with amyl xanthate while the pulp containing cyanide requires the use of more expansive collectors such as amine acetate without pre-treatment. Kongolo et al. (2004) conducted a comparative study on the adsorption of amine thioacetate and amyl xanthate collectors on pyrite for flotation of sulphidic tailings. The study showed that amine thioacetate was adsorbed better in alkaline environments but the use of this collector can be limited due to cost implications. According to the results of Benzaazou and Kongolo (2003), pH, redox potential, collector and frother concentrations are the most important parameters affecting flotation of sulphidic tailings. If these are well optimised, the flotation kinetics of the process can be well optimised.

Hesketh et al. (2010) proposed and explored a conceptual integrated approach whereby conventional tailings are separated into a largely benign tailings stream from which sulphide is predominantly removed and a sulphide rich product, using flotation. The feasibility of using such an approach was demonstrated by desulphurisation of a typical porphyry-type copper sulphide tailing. It was shown that through manipulation of collector dosage, the sulphur content in the benign tailings can be reduced to 0.2% which were classified as non-acid forming using static ABA tests. The benign tailings represented 88% of the original tailings. Further to this, Hesketh et al. (2010) expanded approaches to testing ARD generation potential to include exposure to an active bioleaching environment and to explore the differing time scales of acid consumption and generation. Benzaazou et al. (2008) conducted a similar integrated sulphide removal study to investigate the conditions that allow for good recovery of sulphide minerals using flotation test at laboratory scale and intermediate scales. The study also investigated the acid generating potential of the desulphurised tailings using a kinetic test. The sulphur content in the desulphurised tailings, which represented 85% of the total tailings, was found to be less than 0.3 wt% and not acid generating; but high entrainment, which resulted in the dilution of the sulphide concentrate, was observed.

The concept of sulphide separation was previously explored in WRC 1831/1/11, through the work of Hesketh et al. (2009, 2010) and reported in Harrison et al. (2010). Further studies have not been reported in the literature since then. In this project, we seek to explore its potential further through conducting two further case studies on coal and gold-bearing ore tailings.

4.1.2 Requirements to determine feasibility

Desulphurisation of mine waste and tailings using flotation can be considered the most promising technology to limit the production of ARD in a manner that reduces risk and provides long term certainty of its prevention. Many current mining operations already use flotation for mineral separation and concentration. By implementing additional flotation circuits integrated within the current operations for desulphurization, as proposed by Hesketh et al. (2010), or using multiple criteria in the selection of operating conditions, i.e. both recovery of metal values and removal of sulphide, the long term benefits may be significant relative to the long-term management of acid generating sulphidic waste and/or treatment of ARD. To explore these benefits fully, both a cost and environmental risk analysis are required for the feasibility studies.

Benzaazou and Kongolo (2003) developed a model which estimates the cost of desulphurization. After optimizing the important operational parameters for the flotation process (i.e. collector dosage and flotation time), the desulphurization cost (i.e. a combination of capital costs and operational costs) was found to be CND$0.35 per ton (dry tailings). This was considered to be comparable and competitive with the existing methods for tailings management.

Although various options exist for the safe disposal of desulphurised fraction of the tailings, the sulphide concentrated fraction would still require proper management. Benzaazou et al. (2008) investigated the feasibility of using the concentrated fraction as a cement paste backfill and showed that this was achievable if used in combination with the currently used binders. However, the long term implications of using cement paste backfill with such highly reactive component are still unknown.

The limited studies on both the economics of desulphurisation by sulphide separation and disposal or use strategies for the separated sulphide highlight the importance of these for further study. In this project, these are considered in Sections 7 and 8.

4.2 STRATEGIES FOR SULPHIDE REMOVAL BY REACTION

A number of studies have been conducted on accelerated oxidation of sulphide minerals waste and tailings. The effectiveness of mineral oxidation is highly dependent on the physical, chemical and biological factors in the system (Chen and Lin, 2000) as well as the nature of the mineral and its accessibility. Several studies have shown that the oxidation process can be accelerated by addition of strong oxidising agents, modification of mineral surfaces by addition of surface active agents and supplementation of the nutrients.

Murshed et al. (2003) investigated the use of potassium ferrate as an oxidising agent for accelerated oxidation of sulphide mine tailings. The study showed that the potassium salt of ferrate ions (FeO_{42-}) is a strong oxidizing agent which rapidly oxidises sulphides into sulphates while enhancing metal extraction by liberating sulphide-bound metals. The interaction between ferrate ions (FeO_{42-}) and sulphide minerals was found to be comparable to a system of geochemical oxidation reactions and the sulphide concentration in the tailings was reduced by more than an order of magnitude at a rate of two to three orders of magnitude faster than the natural process. However, the observed reactions were found to occur in a mass transfer-limited regime with a rate on the same order as the reduction of ferrate by oxidation of water. In another study, Silva and co-workers (2011) investigated accelerated oxidation of sulphides associated with the coal mining residues by Fenton's reaction using hydrogen peroxide (H_2O_2) as the oxidising agent. According to the results of this study, effective oxidation of pyrite by H_2O_2 appears to occur within a short period of time, complete after 72 hrs. This was attributed to a direct reaction of the hydroxyl radical (HO•) and the disulphide group on the pyrite surface. Other studies have shown that HO• affects oxidation kinetics of intermediate sulphur species (Ermakov et al., 1997; Druschel et al., 2004) and the presence of HO• in solution also initiates a series of free radical chain reactions with the production of Fe_3+, H+ and H_2O (Silva et al., 2011). Within the CeBER research centre at UCT, Jones et al. (2011, 2012a,b) have demonstrated the key role of the Fenton reaction in mineral bioleaching, both in terms of mineral reactivity and impact on the biological catalyst for leach agent regeneration, as well as the variation in accessibility of minerals to the reaction.

The effect of biochemical additives and nutrient supplement on the bioleaching kinetics of sulphidic mine tailings has also been reported. Rojas-Chapana and Tributsch (2000) studied the effect of thiol compounds on the dissolution kinetics of pyrite in sterile culture solutions using amino acid cysteine as a biochemical additive. The results of the study showed that the activity of Acidithiobacillus ferroxidans is enhanced and the leaching rate of the sulphide is increased three times compared to the normal process without biochemical additives. The investigation also found that the leaching kinetics of pyrite in the presence of cysteine without bacteria were comparable to those attained by bacteria under normal leaching conditions. These results were attributed to the interaction between sulphydril group of the cysteine and the pyrite surface through a thiol-disulphide reaction which releases iron-sulphur species. The bacteria would take advantage of this biochemical corrosion process, which is promoted by acidic conditions, by uptake and oxidation of the released species. Van Hille et al. (2009) demonstrated the improved colonization of the ore surface through nitrogen supplementation, aiding accelerated leaching of low grade whole ores. Further, van Hille et al. (2010) demonstrated the minimum soluble iron concentration for effective leaching of low grade ores, again supporting approaches for accelerated oxidation. Building on this, the preliminary work of Opitz and co-workers, reported in Harrison et al. (2010), illustrated the benefit of seeding low grade ore beds with finely milled pyrite to enhanced available soluble iron levels, colonization and temperature within the bed to assist in the acceleration of the natural bioleaching process. Liu et al. (2008) investigated the effect of substrate (elemental sulphur) concentration on remobilization of heavy metals from mine tailings by Acidothiobacillus thiooxidans. According to the results of the study, the substrate concentration strongly affects the solubilisation of heavy metals during the bioleaching process. The results also indicated that the difference in heavy metal binding before and after bioleaching were significant. After bioleaching, metals remaining in the mine tailings were mainly found in the stable fractions and were stable to the surrounding environment.

CHAPTER 5: SULPHIDE SEPARATION FOR BENIGN BULK TAILINGS – CASE STUDY ON COAL FINES

5.1 INTRODUCTION

Beneficiation of coal using conventional methods 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 is both difficult and expensive, due to the requirement of dewatering to dry the product. This occurs despite the quality of the ultrafines generally being 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 sulphur content is typically 0.6-2.2%. It is this sulphur in the ultrafine coals that contributes to the environmental problems of ARD, once these coals are discarded. The impact of dry washing methods on the discard fractions has yet to be defined as these methods have not yet found broad implementation.

Coal ultrafines are likely to generate acid rock drainage (ARD) due to their size, their large surface area and the liberated state of the sulphur-bearing minerals. The same is true for coarse coal discards, with increased permeability of dumps aggravating ARD generation while reduced sulphide liberation with increasing coarseness may slow ARD generation relative to fines. Typically fines account for some 6 to 10% of run-of-mine (ROM) coal while coarse discards account for 25 to 50% of ROM (Cogho, personal communication), making the handling of these streams very important in ARD prevention.

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, frequently leading to a contribution to ARD generation. 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 emanated from old opencast workings which had been backfilled.

It is important to clarify that coal is central to the economy of South Africa. It is the primary source of energy (88%), and will remain so 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 ensure that the maximum achievable combustibles are recovered from the coal in line with responsible maximisation of resource productivity. At the same time, it is important to improve the way in which the processing wastes are discarded to avoid their potential for environmental degradation in the future. In particular, the prevention of ARD generation from coal waste products is critically important in South Africa (Geldenhuis and Bell, 1998; Bell et al., 2001) to prevent the need for ongoing water treatment systems beyond the life-time of the mine, hence it is desirable to consider the desulphurisation of these ultrafines before disposal.

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. It would also provide economic benefit and improved resource utilisation, as a result of the recovery of valuable coals from these wastes. This development could be incorporated into an integrated coal handling and waste management scheme to ensure both the efficient recovery of valuable coal from the ultrafines and the production of a bulk low sulphur tailings for disposal without environmental harm, while the sulphur-containing material is concentrated into a low volume for further processing or contained disposal.

Flotation is 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 desulphurization of coal processing wastes by flotation. Desulphurization of coal can take place by depressing the sulphide minerals or pyrite, and floating coal, or by depressing coal and floating pyrite.

To date, no in-depth research on the recovery of coal ultrafines for the mitigation of ARD risks is reported in South Africa and limited research is presented globally. In an attempt to fill the gap, some preliminary studies on desulphurization 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 (Harrison et al., 2010). The feed coal used in this investigation did not exhibit acid-generating characteristics, and no significant total sulphur removal took place through reverse flotation. However, the overall results of this earlier work provided a basis for a more rigorous investigation into the technical feasibility of desulphurization of coal with environmental benefits, and the development of appropriate conceptual process routes for minimizing the risks of ARD generation over the long-term, through the production of a coal tailings waste which is depleted in sulphide-bearing minerals. This approach was built on a similar approach used by Hesketh et al. (2010a) for the desulphurisation of base-metal tailings for the prevention of ARD formation following disposal, presented by Harrison et al. (2010).

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 ensures that resource productivity is maximised and 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 in terms of ARD, recover substantial amounts of energy currently wasted and reduce the amount of ultrafine wastes for disposal. Section 5.2 addresses in more detail the development of a conceptual approach to the desulphurisation of coal ultrafines to reduce ARD and maximise resource productivity.

5.2 COMBINED APPROACH FOR COAL RECOVERY AND ARD MITIGATION

Coal is inherently floatable. Further, reagents can be used to promote flotation. The petrographic composition of South African coals, referred to as Gondwana coals, is generally more difficult to float than Northern Hemisphere coals. Coal beneficiation in South Africa is made more difficult by the large quantity of mineral matter, finely disseminated in these coals. Yet, 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 desulphurising flotation focuses on selective removal of sulphide minerals, especially pyrite, the source of ARD generation.

The investigation considered two process routes for the selective removal of sulphide minerals and the recovery of valuable coal. As described in Figure 29, each option or process route is a two-stage flotation process aimed at the optimum removal of the sulphide-bearing minerals that are present in coal ultrafines.

During the course of this work, it became increasingly apparent that the first process route involving the selective removal of sulphide minerals in the first stage was not a viable method due to the difficulty of subsequently floating coal that had been depressed by dextrin. As a result, the conceptual approach, adopted after the preliminary experiments, entailed coal flotation in the first stage (Figure 30). This takes advantage of coal’s natural hydrophobicity while hydrophilic gangue material reports to the tailings. The recovered clean coal can be converted into saleable product through dewatering; blended into a middlings coal and sold via the already established export market (Reddick et al., 2007; 2008), or used locally.

In the second stage of the proposed approach, sulphides remaining in the first stage tailing were removed selectively, also by flotation. A small stream of sulphide-rich acid-generating material was collected 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 sulphide-rich concentrate may be reduced through its subsequent bio-desulphurization or contained disposal of the reduced volume. It should be pointed out that this flowsheet differs from the previous two-stage flotation process (Miller, 1975), in which sulphides were floated from the coal concentrate rather than the tailing. The modification is motivated by decision-making being driven by the combination of efficient value recovery, maximising resource productivity and tailoring wastes for benign disposal.

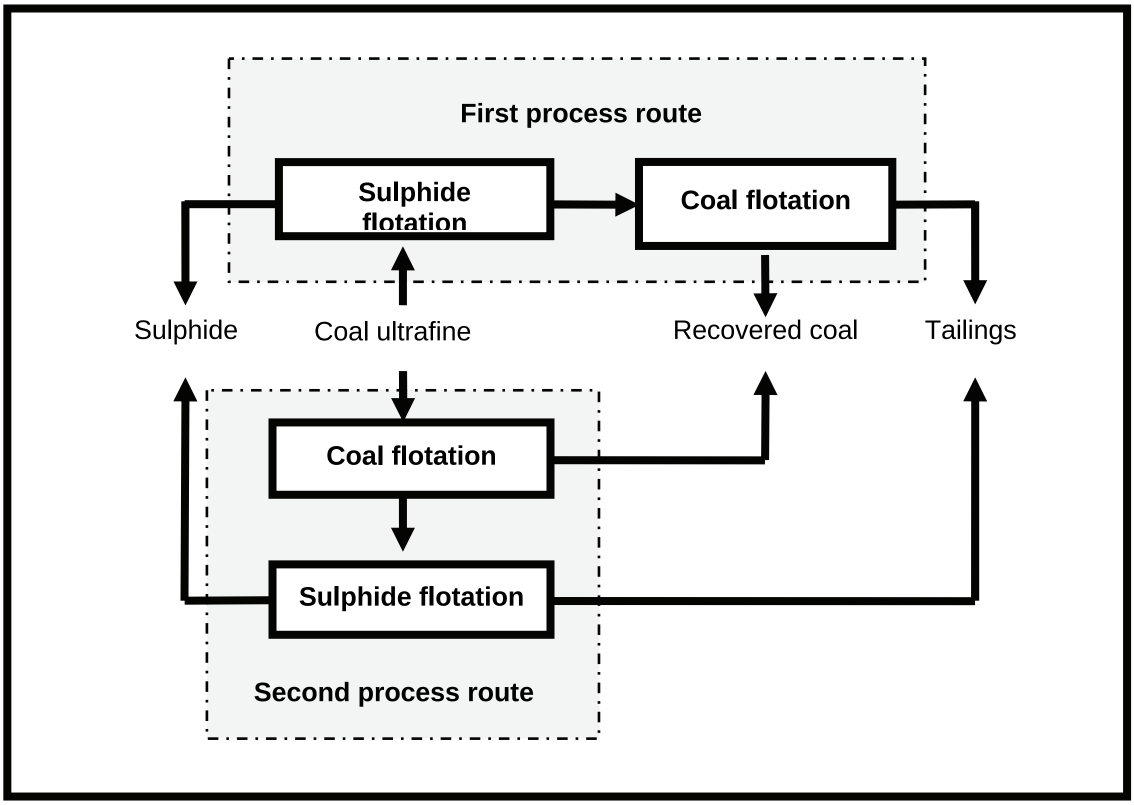


Figure 29: Process routes for reclaiming coal ultrafines and mitigating associated environmental impacts in two-stage processes

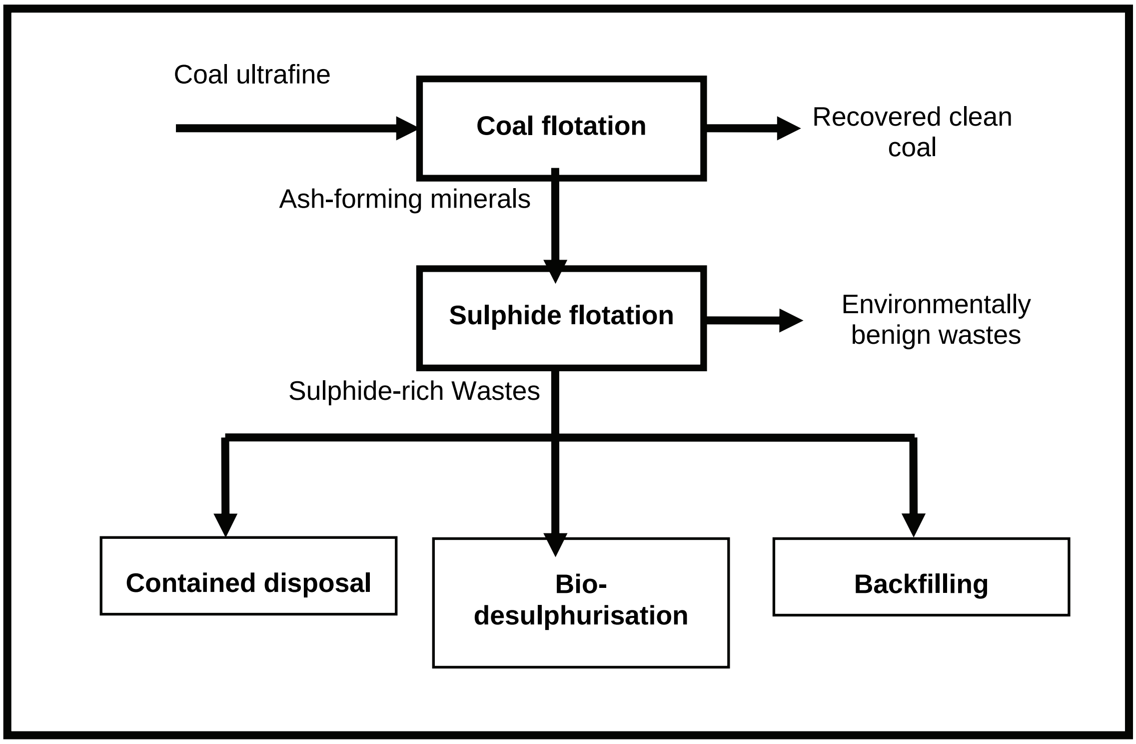


Figure 30: Adopted conceptual approach aimed at recovering coal and mitigating ARD risks in a two-stage process

5.3 MATERIALS AND METHODS

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. The experimental work included the coal sample characterization, the flotation procedures and the ARD prediction tests. Flotation experiments included both coal and sulphide flotation tests; while the acid prediction tests included the acid base accounting (ABA), net acid generation (NAG) and the newly developed biokinetic tests.

5.3.1 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 sulphide minerals.

The ultrafine coal slimes sample which was received was thoroughly mixed using a riffler; a manually operated device that divides a sample into halves to allow representative preparation of test material. The whole sample was passed through the riffler 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 which was 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 a pulp density of 10%, 0.3 kg was used. The weighed milled samples were sealed in plastic bags.

All of the research work described in this work 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 to other coal ultrafines from different South African coalfields.

5.3.2 Coal Characterisation

The characterisation of the coal ultrafine slurry sample under investigation, taken from the thickener underflow of the washing plant, included particle size and ash-by-size determination of the as-received and rod-milled coal waste sample, flotation release analysis, petrographic analysis, sulphur speciation analysis, ultimate and proximate analyses as well as X-ray diffraction (XRD) analysis.

5.3.2.1 Size analysis distribution

The size and ash-by-size distributions of the as-received coal are given in Table 11. The as-received sample contained a significant amount of ultrafine material (23.64% passing 106 µm) and a substantial amount of coarser material (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 150 µm prior to flotation such that the ash content of the milled -75 µm fraction dropped to 38.6%.

5.3.2.2 Proximate and ultimate analyses

The proximate and ultimate analyses and the calorific value (CV) for the feed coal sample are shown in Table 12. The coal sample used in this study was characterized by a high ash content of approximately 34.4% (dry basis) with a gross CV of 19 kJ/kg. The total sulphur content, determined according to ASTM D4239:1997 at ALS Laboratory, was approximately 1.08%.

5.3.2.3 Sulphur speciation

Sulphur speciation analysis was performed at the ALS Laboratory in Witbank on rod-milled coal samples according to ISO 157:1996 and is shown in Table 13. The coal sample contained approximately 0.52% of sulphidic sulphur and 0.32% of sulphate sulphur. The amount of organic sulphur, calculated by difference based on the total sulphur (1.08%), was 0.24%. The proportion of sulphate sulphur indicated that the sample was oxidized: pristine coal contains negligible sulphate sulphur.

Table 11: 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	8.05	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

Table 12: 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 mater	19.3 ± 0.00
Moisture	3.8 ± 0.07
Fixed Carbon	42.5 ± 0.07
b) Ultimate analysis % (air-dry basis)	
Total Sulphur	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

Table 13: Sulphur speciation of coal sample (ALS Laboratory, Witbank)

Forms of sulphur	Average amount (%)
Sulphide	0.52 ± 0.01
Sulphate	0.32 ± 0.01
Organic	0.25 ± 0.02
TOTAL	1.08 ± 0.04

5.3.2.4 X-ray Diffraction

X-ray Diffraction (XRD) analysis was performed on the rod-milled coal sample in the Centre for Catalysis Research in the Department of Chemical Engineering at the University of Cape Town to determine the minerals associated with the coal ultrafines. Powder XRD spectra were obtained by using a Bruker D8 Advance powder diffractometer with Vantec detector and fixed divergence and receiving slits with Co-Kα radiation. The phases were identified using Bruker Topas 4.1 software and the relative phase amounts (weight %) were estimated using the Rietveld method.

Table 14 shows the mineralogical composition of the ultrafine coal waste sample determined by XRD. Pyrite was the only sulphide mineral present in the coal, present at about 1.13 wt%. The most common carbonate minerals which were present were calcite ($CaCO_3$, 2.99 wt%), siderite ($FeCO_3$, 0.55 wt%) and dolomite ($CaMg(CO_3)2$, 0.33 wt%). The gangue minerals kaolinite ($Al2Si2O_5(OH)4$, 59.16%) and quartz (SiO_2, 29.4%) were the most abundant. The sulphate minerals included gypsum ($CaSO_4.2H_2O$) and epsomite ($MgSO_4 \bullet 7(H_2O)$), accounting for 4.03 and 1.65 wt%, respectively. Based on the amount of pyrite in the sample, the proportion of sulphide sulphur is 0.6 wt%, in approximate agreement with the 0.52 wt% found in the sulphur speciation analysis (cf Table 13).

Table 14: Mineralogical characterization of the coal ultrafine waste

Mineral	**Chemical composition**	**Concentration (wt %)**
Quartz	SiO_2	29.40
Pyrite	FeS_2	1.13
Siderite	$FeCO_3$	0.55
Calcite	$CaCO_3$	2.99
Dolomite	$CaMg(CO_3)_2$	0.33
Gypsum	$CaSO_4 \cdot 2H_2O$	4.03
Kaolinite	$Al_2Si_2O_5(OH)_4$	59.16
Epsomite	$MgSO_4 \bullet 7(H_2O)$	1.65
Jarosite	$KFe^{3+}{}_3(OH)_6(SO_4)_2$	0.76

5.3.2.5 Petrographic analysis

Petrographic analysis was carried out on the as-received coal by Petrographics SA in Pretoria. Table 15 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. It was suggested that some cracking probably occurred 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 15: Summary of the major petrographic properties of the coal feed

Petrographic properties	Feed coal
1. Rank (degree of maturity)	Bituminous
ISO 11760-2005 Classification of Coals	Medium Rank C
2. Mean maximum reflectance %	0.83
Vitrinite-class distribution	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

5.3.3 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 sulphide flotation processes. A consistent flotation protocol was maintained to ensure reproducibility.

5.3.3.1 Coal flotation procedure

The standard collector used in the coal flotation tests was laboratory grade dodecane (Merck), at a dosage varying from 0.70 to 3.72 kg/t. In order to compare the results obtained with dodecane, kerosene (Sigma-Aldrich) and oleic acid (May & Baker LTD Dagenham England) were used in a selection of flotation coal tests. Methyl iso-butyl carbinol (MIBC), supplied by Sigma-Aldrich, was used as frother. It is the most common frother for coal flotation.

The coal flotation tests were carried out at room temperature in the 3 L modified Leeds batch flotation cell, shown in Figure 31. The cell is equipped with electronic impeller speed and air flow rate regulators. Approximately 1 L of tap water was introduced into the cell and 200 g of coal solids (dry basis) added. The impeller speed was set to 1200 rpm; and the cell 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 air was supplied to the flotation cell 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%. Experiments within each subset were performed on the same day to maintain similar conditions.

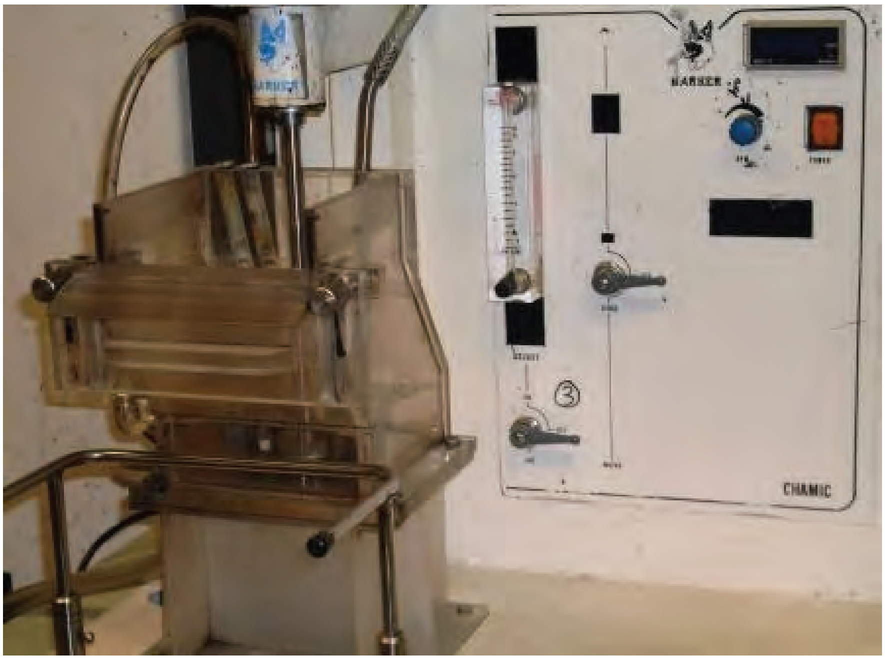


Figure 31: Picture of the laboratory batch Leeds-type cell used for coal and sulphide flotation

5.3.3.2 Sulphide flotation procedure

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

The sulphide flotation procedure mimicked that for coal flotation with the following exceptions: After the pulp had been conditioned with the collector (standard collector used: 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 starting 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.

5.3.3.3 Analysis of Flotation Samples

Feed, concentrate and tailings samples from each flotation experiment were filtered, oven dried overnight and weighed before analysis. Sulphur analysis was carried out using a LECO sulphur 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.

5.3.3.4 Double-stage flotation

Since the objective of this research was to develop a two-stage process aimed at coal recovery and the mitigation of acid generation risks associated with ultrafine coal waste, a double-stage flotation test was performed to demonstrate the conceptual approach described in Section 5.2. 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 5.3.3.1; pyrite and non-sulphide minerals were left behind in the tailings. The residue from the coal flotation test was dried and weighed before being used as feed in the subsequent stage. While the drying was introduced to allow upgrading per stage to be quantified, it has potential to introduce oxidation; hence is not ideal. The second stage involved a conventional flotation of pyrite and depression of non-sulphide minerals, described Section 5.3.3.2. The operating conditions for the second-stage test were selected from the single-stage test to maximise the grade of sulphide in the concentrate and keep the yield of concentrate as low as possible. Analysis of the flotation performance was carried out as described in

Section 5.3.3.3, while the solid fractions collected and feed solids were further categorised in terms of the ARD generation capacity, as described in Section 5.3.4.

5.3.4 Acid Rock Drainage (ARD) prediction tests

5.3.4.1 Acid-base accounting

Acid-base accounting involved the estimation of the capacity of each sample for both acid formation, in terms of the maximum potential acidity (MPA), and acid neutralization capacity (ANC). These were then combined to give the net acid production potential (NAPP).

The *maximum potential acidity (MPA)* generated by a sample was determined from its total sulphur content, determined using the high temperature combustion LECO test. It was assumed that all the sulphur measured in the sample reacts under oxidizing conditions to generate acid, as would be found where this sulphur was present as pyrite (FeS2).

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 study, the ANC of each sample was determined by the incremental H_2O_2 addition method, modified from the standard method of Skousen et al. (1998) 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 approach of Skousen et al. (1997) was included 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 flask, containing no solid sample, serving as the control (blank). The amount and strength of the HCl which was added to all the beakers were determined according to the fizz rating as outlined in Table 16. The sample was boiled for 5 min, cooled and filtered to eliminate the possibility of pyrite oxidation associated with H_2O_2 addition. The solution was back-titrated to pH 4.5, and treated with 5 mL of 30% peroxide to enhance the oxidation of dissolved Fe (II) and the precipitation of Fe(OH)3. 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 pH 7 if required and a further 5 mL of H_2O_2 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 H_2SO_4/t.

The ANC method was conditional upon performing a fizz test to determine the appropriate amount and strength of acid needed 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 16. The presence of CaCO3 was indicated by bubbling or audible effervescence.

Table 16: 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

The *Net Acid Producing Potential (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 H_2SO_4/t and is calculated as follows:

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

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).

5.3.4.2 Net acid generation (NAG)

Net acid generation (NAG) 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 accelerate the oxidation of any sulphide minerals which the sample may contain. During the NAG test, acid generation and acid neutralization reactions occur simultaneously, leading to a direct measurement of the net acid generated by the sample. The NAG capacity is expressed in the same units as NAPP. The NAG test was carried out in two ways, as was the single addition test and the sequential addition test, which are described below.

In the single addition NAG test, 250 ml 15% H_2O_2 was added to 2.5 g pulverised sample. The solution was allowed to react overnight, and then heated until gently bubbling for approximately 2 hours, in order to remove excess H_2O_2 and encourage the release of inherent neutralizing capacity. Once the sample had cooled to room temperature, the pH and the titrated acidity (to pH 4.5 and 7) of the mixture were determined in kg H_2SO_4/t (Stewart et al., 2006).

The sequential addition method was used to overcome the effect of H_2O_2 decomposition, found with high sulphide content. The sequential NAG test involved multi-stage addition of H_2O_2, representing a series of single addition NAG tests on the one sample. At the end of each stage, the sample was filtered and the filtrate was used to determine the NAG pH and titrated pH at 4.5 and 7. The cycle was repeated until the NAG pH was greater than 4.5, or until the catalytic decomposition of peroxide did not occur. The overall sequential NAG capacity in kg H_2SO_4/t of the sample was then determined by the summation of the individual generated acidity obtained at each stage.

5.3.4.3 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 NAG pH < 4.5
4. Uncertain (UC): positive NAPP and NAG pH > 4.5, or negative NAPP and NAG pH ≤ 4.5.

The classification of samples as acid forming, non-acid forming or non-conclusive is described in Table 17 for both the NAPP and NAG assays and their combination. This classification is based on the work of Stewart et al. (2006).

Table 17: *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	kg H_2SO_4/t	Acid forming
	-20< NAPP<20	kg H_2SO_4/t	Potentially acid forming (PAF)
	NAPP < -20	kg H_2SO_4/t	Non-acid forming (NAF)
Net Acid Generation (NAG)	NAG pH < 4 & NAG pH_7>10	kg H_2SO_4/t	Acid Forming
	NAG pH > 4 & NAG pH_7=5-10	kg H_2SO_4/t	Potentially acid forming (PAF)
	NAG pH > 4	pH	Non-acid forming (NAF)
Combined static tests	NAG pH < 4.5 and NAPP > 0		Potentially acid forming (PAF)
	NAG pH > 4.5 and NAPP < 0		Non-acid forming (NAF)

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

5.3.4.4 Biokinetic flask test

The biokinetic test is an emerging protocol under development at the University of Cape Town (Hesketh et al., 2010b). It is 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 micro-organisms 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 37oC on an orbital shaker at 150 rpm for 75 days. Distilled water was added to maintain constant weight during the experiment.

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 (Fe2+ and total) 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.

5.4 RESULTS AND DISCUSSION

5.4.1 Coal flotation test work

The objective of coal flotation is to recover a coal product of high-calorific value and low-ash content from the coal ultrafine wastes by means of froth flotation. While this is not essential to reduce ARD potential, it has potential to decrease the volume of the discards in the slimes dams and to derive some economic value to offset additional processing costs associated with disposal for low ARD generation. To this end, laboratory batch flotation experiments were carried out on subsamples of the ultrafine coal suspension from the thickener underflow of the washing plant according to the procedure outlined in Section 5.3.3.1. 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, recovery of combustibles and ash content of the concentrate. The term “combustibles” refers to the fraction of the sample that was consumed when the material was placed in a muffle furnace, on a mass basis. The ash percentage was calculated on a moisture-free basis.

5.4.1.1 Effect of collector addition

Collector addition is a pre-requisite for the effective flotation of most South African coals. Collector concentration was therefore a key variable, studied to determine its effect on the extent of coal recovery and the quality of the coal product obtained.

Initial laboratory batch flotation tests were carried out using dodecane collector concentrations in the range 0.70 to 3.72 kg/t to optimize the process. Figure 32 shows the cumulative recovery of combustibles over 5 min of flotation time as a function of collector dosage and an MIBC frother concentration of 0.11 kg/t. After 5 min flotation, the flotation yield (mass product / mass feed) and recovery (combustible in product / combustible in feed) were 19.0% and 23.8%, 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 8.7% to 15.5% as shown in Table 18.

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 2.79 kg/t. A float test was also carried out, in the absence of dodecane collector, using 0.28 kg/t MIBC frother only. The data are presented in Table 19 and Figure 33.

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 increased from 23.8% at 0.11 kg/t MIBC to 30.5% at 0.28 kg/t MIBC, an increase of 6.67%. In the complete absence of collector, the combustible yield was 7.1% 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.

Under the new reagent conditions, flotation performance increased upon increasing collector concentration. The recovery and yield at the highest dosage of dodecane were 33.8% and 27.4%, 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 7.4% and the yield by 6.2%. 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 18: Coal flotation results (after 5 min) with dodecane collector and 0.11 kg/t MIBC frother

Dodecane dosage (kg/t)	**Yield (%)**	**Product sulphur (%)**	**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

Table 19: 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 (%)**	**Sulphur (%)**	**Yield (%)**	**Ash (%)**	**Sulphur (%)**	
0.0	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

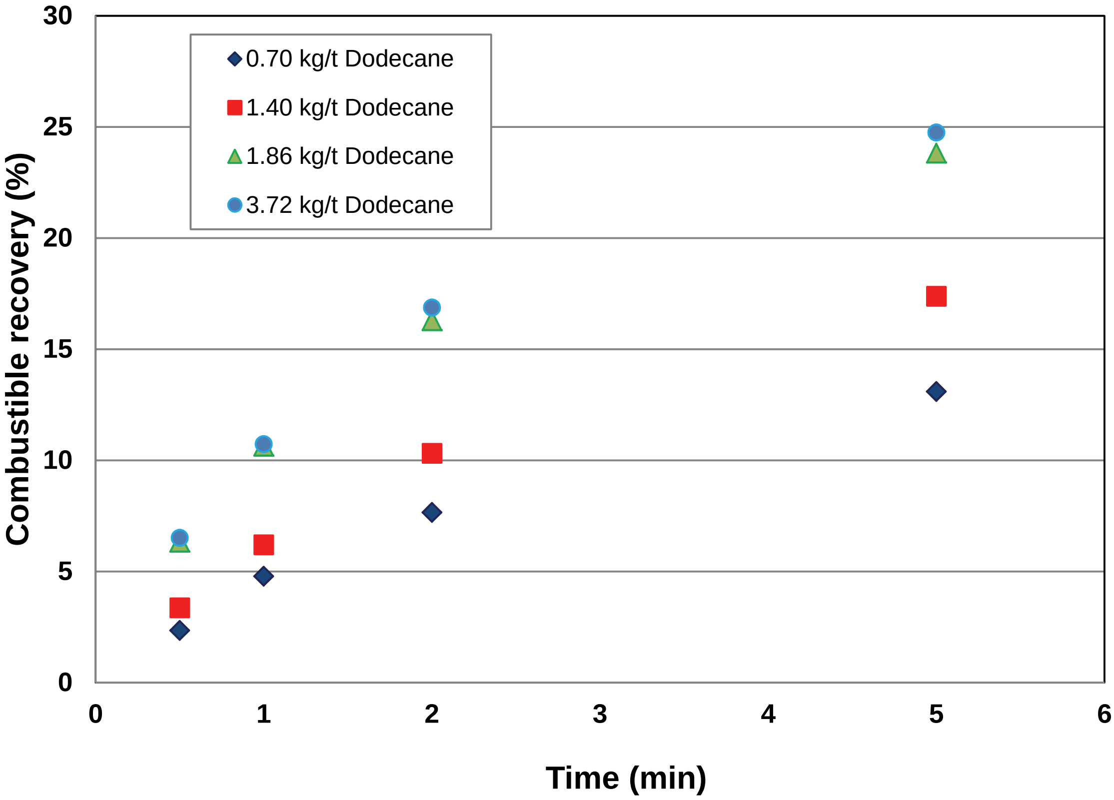


Figure 32: Kinetic flotation results for different dosages of dodecane collector. MIBC frother was kept constant at 0.11 kg/t.

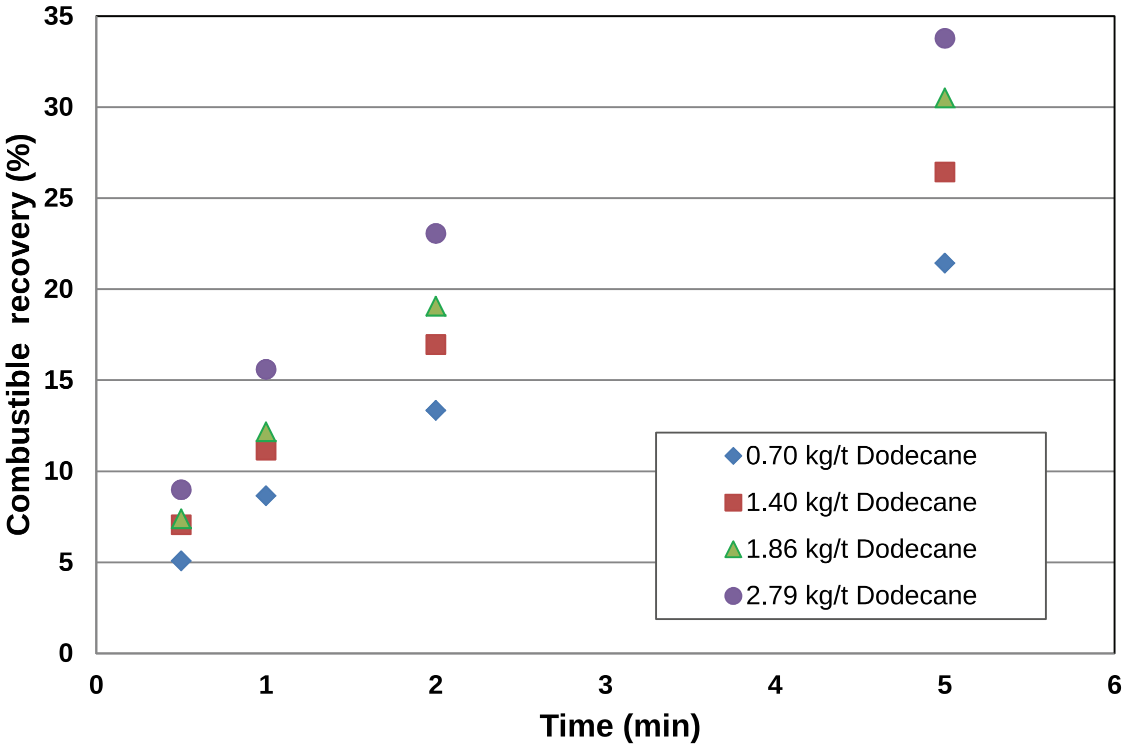


Figure 33: Kinetic flotation results for different dosages of dodecane collector. MIBC frother was kept constant at 0.28 kg/t.

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 a high concentration of dodecane may be explained by the petrographic composition of the coal (see Table 15, p 62), 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 to flotation 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). Petrographic analysis (Table 15, p 62) indicated that at least 11% of the coal was oxidized.

Additionally, the limited recovery may be due to the high-ash content of 34% of the coal sample. 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).

Regardless of the poor recovery and yield, the concentrate grade was good (low ash content), ranging from 15.5% to 18.1%, as indicated in Figure 34. 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.

The addition of dodecane did not prevent some sulphur-bearing minerals from floating with the coal. Table 19 shows that the sulphur content of the clean coal was about 0.46% compared to 1.08% in the feed. It may be assumed that the sulphur that reported to the concentrate was in the form of organic and sulphide sulphur (sulphate sulphur would be expected to dissolve in the slurry; hence the poor sulphur mass balance). This unintentional flotation of sulphide mineral during flotation may have been caused by locked particles, excessive collector or conditioning promoting the natural floatability of pyrite particles (Aplan, 1993). This study did not attempt to depress pyrite during coal flotation, owing to similarity between pyrite and coal depressants (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 sulphur content of the floated coal.

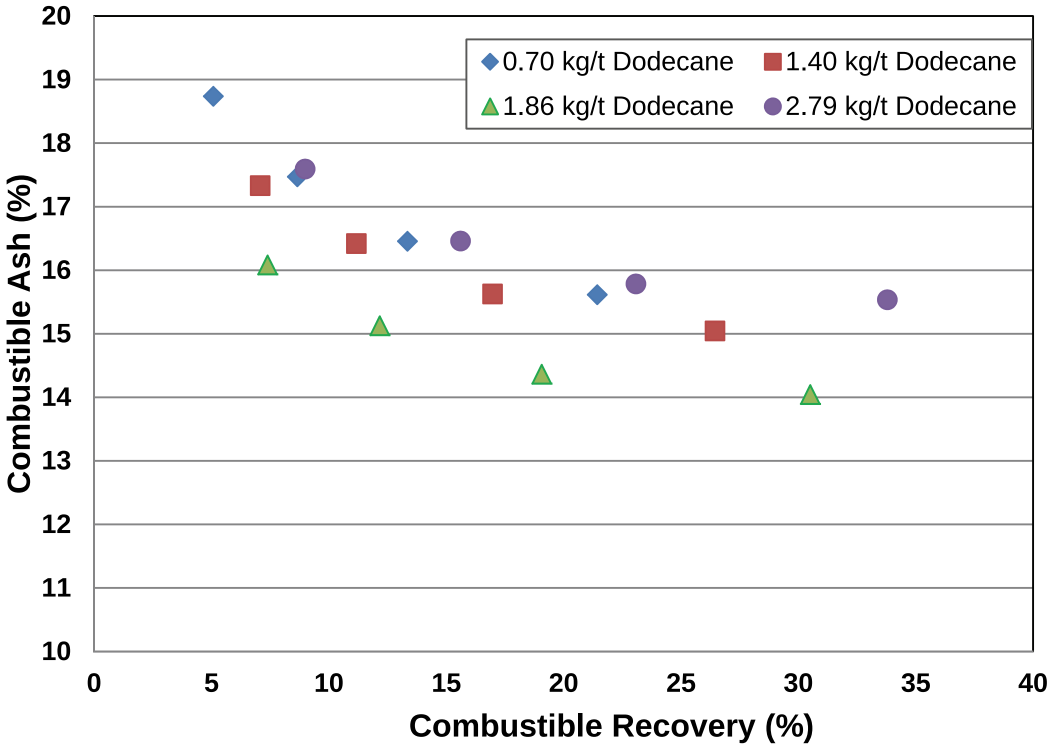


Figure 34: Combustible recoveries and ash contents of concentrates during flotation with different dosages of dodecane collector. The MIBC dosage was kept constant at 0.28 kg/t.

5.4.1.2 *Effect of various collectors*

Initially, the coal flotation tests were conducted with dodecane as a collector. 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, ash content (Table 20) and the combustible recovery (Figure 35) provide the basis for comparing the three collectors.

Although kerosene has been used extensively in the flotation of coal on an industrial scale, because its lower viscosity allows it to disperse in the slurry and coat the coal particles easily, the results indicate that oleic acid was more efficient in increasing both the recovery and yield of clean coal. As can be seen from Figure 35, the ultrafine coal waste sample responded well to oleic acid as the collecting agent; significant yield was achieved compared to that obtained with aliphatic hydrocarbons. The improvement in combustibles recovery when using oleic acid as collector was substantial. The recovery of combustibles reached 35.8% at a dosage of only 0.7 kg/t of collector, increasing further to 69.1% when the oleic acid dosage was increased to 2.79 kg/t. This can be compared to a maximum combustibles recovery of 34 and 39% for dodecane and kerosene respectively at 2.79 kg/t.

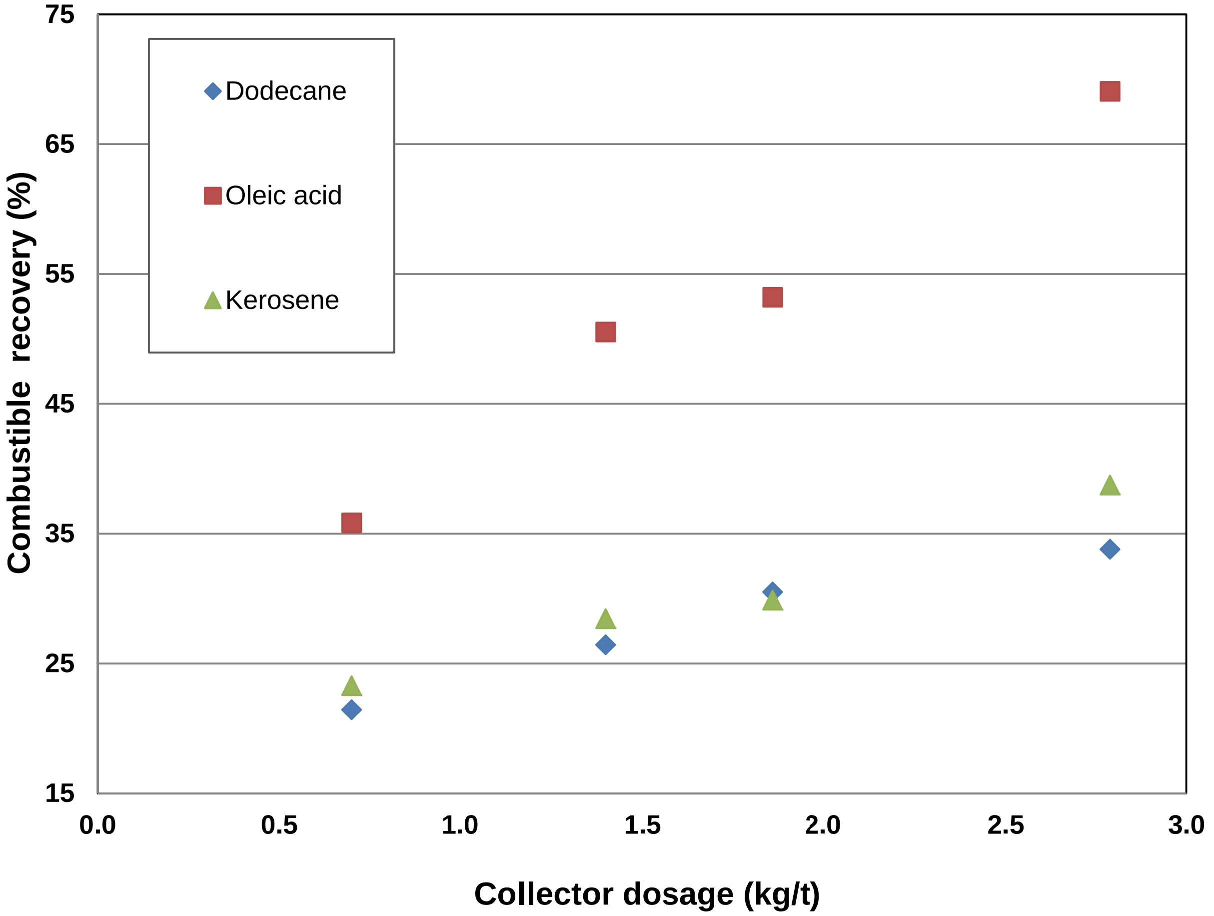


Figure 35: Comparison of the collecting ability of dodecane with that of kerosene and oleic acid at different dosages. The MIBC frother dosage was kept constant at 0.28 kg/t.

The results in Table 20 indicate that when the oleic acid dosage was 2.79 kg/t, the yield and ash content of the clean coal were 56.0% and 18.1%, respectively. At the same dosage of kerosene and dodecane collectors, the yields were 31.4% and 27.4%, respectively, with corresponding ash contents of 15.4% and 15.5%. 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 suggested (Table 15, p 62) that the coal under investigation might have been partly exposed to atmospheric oxygen, which could have resulted in the reduced floatability of coal in the presence of oily hydrocarbons. However, regardless of this behaviour, 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 20: 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 sulphur
	%				
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

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 sulphur 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.

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), its use is widespread in the flotation of non-sulphide ores (Sis and Chander, 2003; Miller et al., 2007). The findings of laboratory flotation investigations have demonstrated that oleic acid can substitute for some of the commercial reagents which are currently used. Oleic acid is environmentally safe, biodegradable and can be of vegetable origin. It has the potential to address environmental concerns over the use of traditional reagents in coal flotation.

5.4.2 Sulphide flotation results

Coal desulphurization was studied to investigate the possibility of removing sulphur-bearing minerals from the waste coal in one stage flotation, compared with the separation performance of the two-stage process. It is common practice to float coal material from associated mineral matter; several investigations have suggested the flotation of sulphur-bearing minerals, in particular pyrite, from coal with simultaneous depression of coal (Kawatra and Eisele, 2001; Laskowski, 2001). Sulphide flotation, in which bulk coal is left behind in the tailing, is sometimes referred to as reverse flotation.

All desulphurization flotation experiments were carried out according to the procedure outlined in Section 5.3.3.3. In all of the tests the impeller speed was 1200 rpm, the aeration rate was 6 L/min and the pulp 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.

5.4.2.1 Effect of collector type

Preliminary tests were done 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, commonly used in mineral flotation, are highly selective for sulphide minerals. They react chemically with the sulphide surfaces and have no affinity for the hydrophilic non-sulphide minerals.

The kinetic results for the three xanthates in Figure 36 show that PAX produced the best recovery, characterized by 26.3% after 20 min collection time, compared with SIBX and SEX recoveries of 20.8% and 1.4%, respectively. This is as expected, as PAX is a stronger collector than the other xanthate homologues. PAX was used exclusively in the subsequent sulphide flotation tests reported.

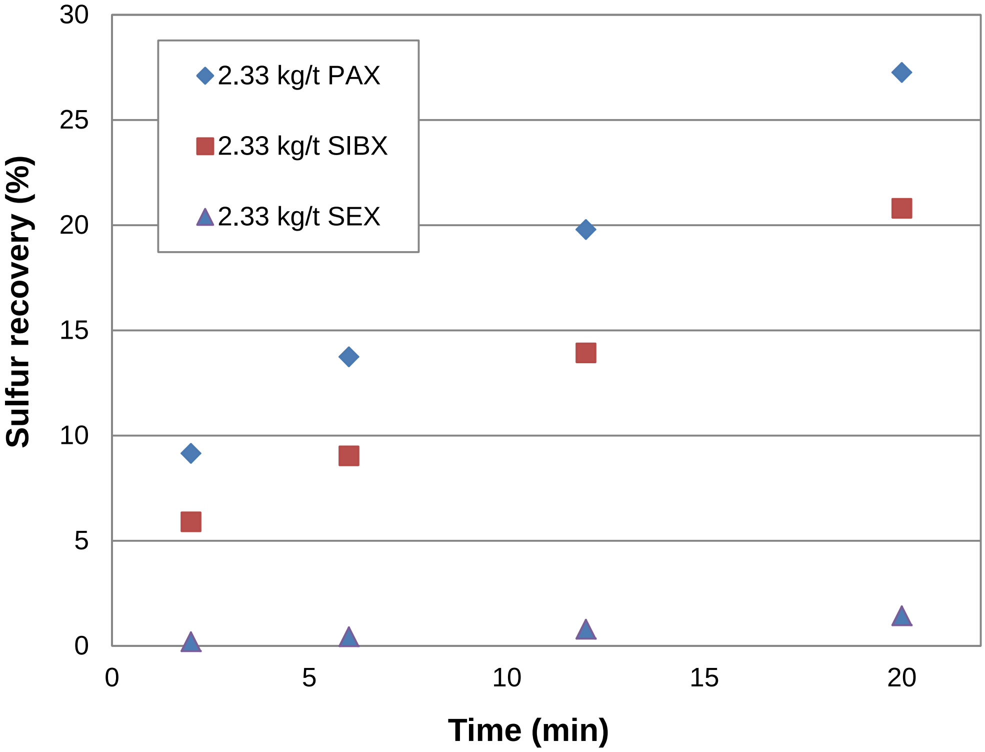


Figure 36: Kinetic flotation results of sulphide flotation for 2.33 kg/t of different xanthate collectors, 0.11 kg/t MIBC frother and 0.93 kg/t dextrin coal depressant.

5.4.2.2 Effect of collector dosage

The 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. Figure 37 shows the effect of collector dosage on the recovery of sulphur over 20 min flotation. Flotation recovery increased with an increase in the collector concentration. The recovery of sulphur 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 sulphur 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 sulphur recovery to 14.12% and 27.3%, respectively.

It is interesting to observe the large amount of collector required in the flotation of sulphide from coal, compared to that which was used to recover sulphide 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 sulphide 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.

The grade of total sulphur increased as the collector dosage was increased. At a low dosage, the grade of total sulphur was very low, indicating that the coal was also floating, owing to its natural floatability. The dextrin depressant was ineffective and inadequate, as indicated by the poor ratio between sulphur and coal recovery, shown in Table 21. 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).

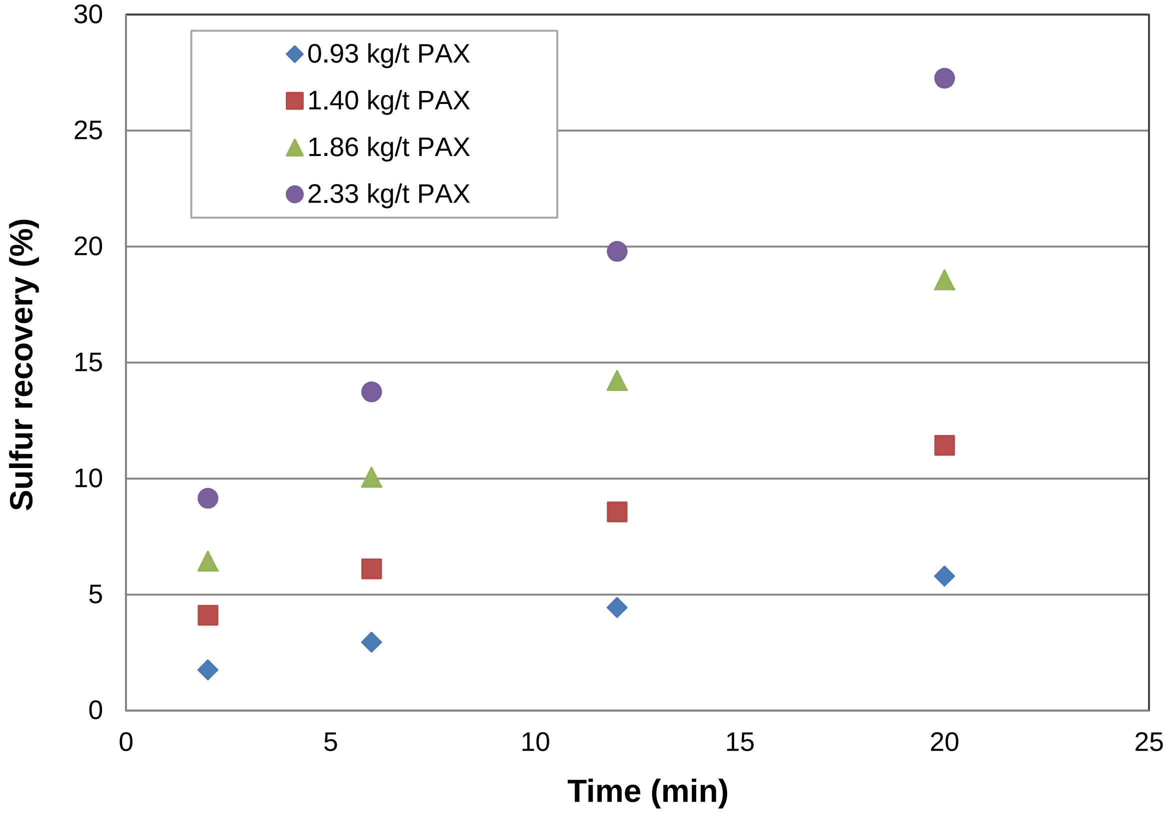


Figure 37: Kinetic flotation results for different dosages of potassium amyl xanthate (PAX) collector. MIBC frother and dextrin (coal depressant) were kept constant at 0.11 kg/t and 0.93 kg/t, respectively.

Table 21: Sulphide 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 sulphur (%)	Concentrate Ash (%)	Concentrate coal (%)	Recovery ratio (sulphur: coal)
0.93	7.40	0.43	19.5	80.53	0.65
1.40	9.93	0.96	20.9	79.08	0.97
1.86	11.92	1.42	23.1	76.86	1.36
2.33	14.12	1.76	23.7	76.27	1.70

5.4.2.3 Stage-wise collector addition

In order to improve the sulphur recovery from the coal ultrafine waste, and thereby achieve a final tailing with as low a sulphur content as possible, sulphide flotation tests were performed with stage-wise addition of collector, previously shown 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 5.3.3.3. Table 22 summarizes the flotation results for 1-, 2- and 3-stage sulphide flotation runs in the presence of PAX as collector, dextrin as coal depressant and MIBC as frother.

As noted in Table 21 and Table 22, the addition of 2.33 kg/t PAX in one stage resulted in 27.3% sulphur recovery at a sulphur concentration of 1.76% in the concentrate. With a 2-stage addition, 38.3% (cumulative) sulphur recovery was obtained at 1.51% S grade (Table 22), and with 3-stage addition, 42.1% (cumulative) sulphur recovery was obtained at 1.39% S in the concentrate (Table 22). The mass yields obtained were

14.1%, 18.5% and 22.7%, respectively. The sulphur 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 23.1% at 23.7% ash in one stage; 21.7% at 22.6% ash with 2 stages and 26.7% at 11.3% ash with 3 stages of collector addition. This provides the reason for the low sulphur content in the 3-stage addition test: the higher the coal content of the sulphide concentrate, the lower was the sulphur 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 22: Sulphide 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
Sulphur grade (%)	1.76	1.51	1.39
Sulphur 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
Sulphur tailings	0.77	0.56	0.56
Recovery ratio (Sulphur/coal)	1.70	1.77	1.58

Figure 38 shows the profile of recovery as a function of time for sulphur. Adding the collector in stages substantially increased the total sulphur 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 sulphur in the tailings, low yield and shorter collection time, as compared to the 1- and 3-stage flotation tests.

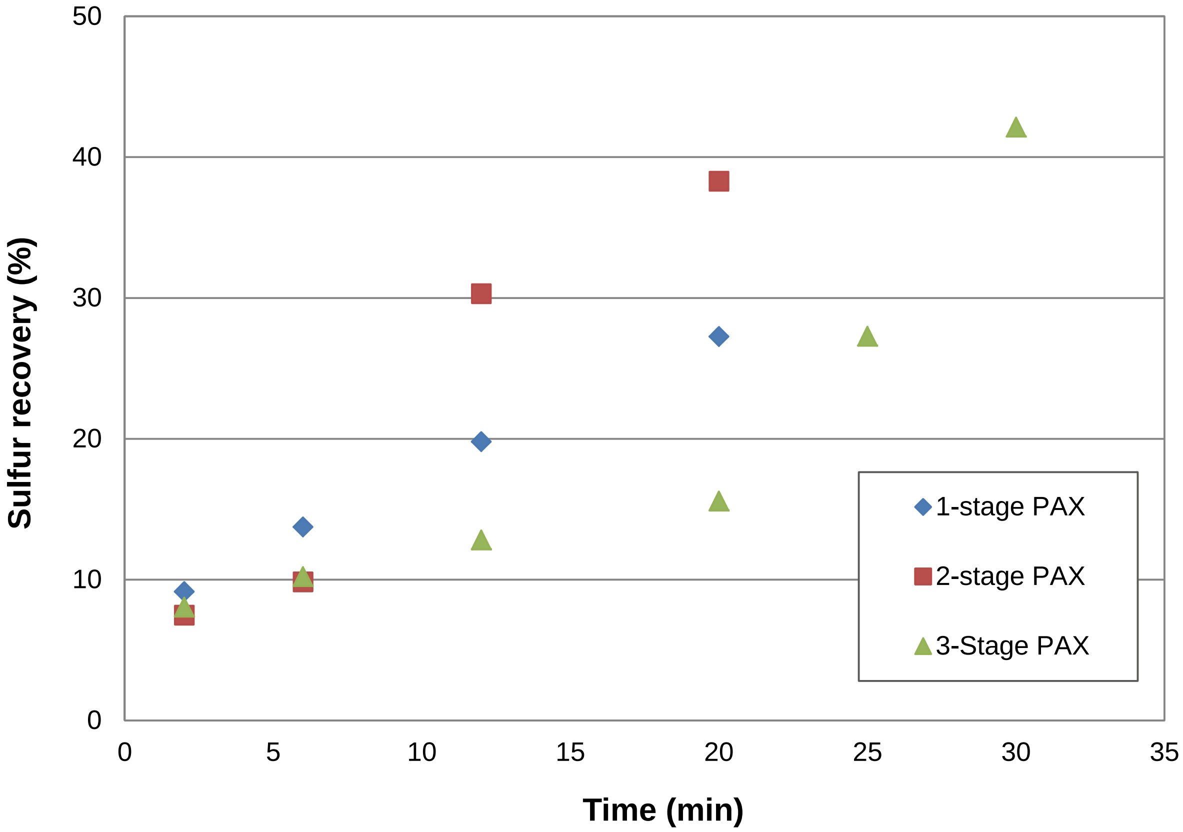


Figure 38: Sulphide flotation results for staged addition of collector PAX. MIBC frother and dextrin coal depressant were kept constant at 0.11 kg/t and 0.93 kg/t, respectively

5.4.3 Sulphur deportment during flotation

The results of the coal and pyrite flotation studies have highlighted the need for a more quantitative understanding of the deportment of the different sulphur 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 sulphur in coal: sulphide, organic and sulphate sulphur. These have different characteristics with regard to coal cleaning and the release of pollution to the receiving environment.

The samples for sulphur speciation analysis were taken from the coal flotation test carried out using 2.79 kg/t of dodecane collector and 0.28 kg/t of MIBC frother; and the sulphide 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 sulphur speciation was carried out at ALS Laboratory according to ISO 157:1996. The sulphate and sulphide sulphur content was determined, while the amount of organic sulphur was calculated by difference, based on the total sulphur analysis determined according to the ASTM 4239:1997. Table 23 shows the approximate sulphur speciation in the feed, concentrates and tailings of coal and pyrite flotation. The feed contained 1.08% total sulphur: 0.52% in the form of sulphide, 0.32% is in the form of sulphate and 0.25% in the form of organic sulphur. The XRD results indicated that the feed sample contained 4.03% of gypsum, approximately 0.95% of sulphate sulphur. This suggests that some of the pyrite present in the original coal underwent oxidation.

The amounts of sulphide, sulphate and organic sulphur 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 sulphates are mostly soluble in water, these are removed in the flotation process. The organic sulphur is inherent to the coal structure and cannot be removed by flotation.

Table 23: Sulphur species deportment in selected coal and pyrite flotation products

	Sample	**Total sulphur (%)**	**Forms of sulphur (wt %)**		
			Sulphide	**Sulphate**	**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	Clean Coal Concentrate	0.37 ± 0.03	0.16 ± 0.01	0.01 ± 0.00	0.21 ± 0.04
	Tailings	0.73 ± 0.02	0.58 ± 0.01	0.01 ± 0.00	0.14 ± 0.03
Sulphide 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 ± 0.00	0.03 ± 0.00	0.34 ± 0.01
	Tailings	0.59 ± 0.02	0.42 ± 0.01	0.02 ± 0.00	0.15 ± 0.04

The speciation results from the sulphide flotation tests confirmed that the sulphide sulphur 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 sulphur: 1.12% in the form of sulphide and 0.34% in the form of organic sulphur, which was bound in the structure of coal and floated along with the sulphide.

The deportment of sulphur during sulphide flotation depended on the size distribution of the coal sample because the sulphide is finely disseminated in the as-received coal. To demonstrate, the effect of particle size and liberation, it was rod-milled prior to flotation. The influence of particle size on the flotation response is given in Figure 39. This shows that rod-milling the coal for 20 minutes improved the total sulphur recovery from 22.6 to 27.6%, the sulphur recovery from 22.6 to 27.6% and the sulphur grade from 1.52 to 1.76%. The yield decreased from 18.4 to 14.1% due to reduction of entrainment of coal that reported to the concentrate. The increase of the total sulphur recovery can be attributed to the liberation of locked sulphide minerals and the fact that fine coal and pyrite particles float more readily than do the corresponding coarse particles. However, as Table 23 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 sulphide flotation. These results suggest that only sulphide minerals that are liberated can be separated from coal. Further, while the milling did assist S recovery, this increase was limited.

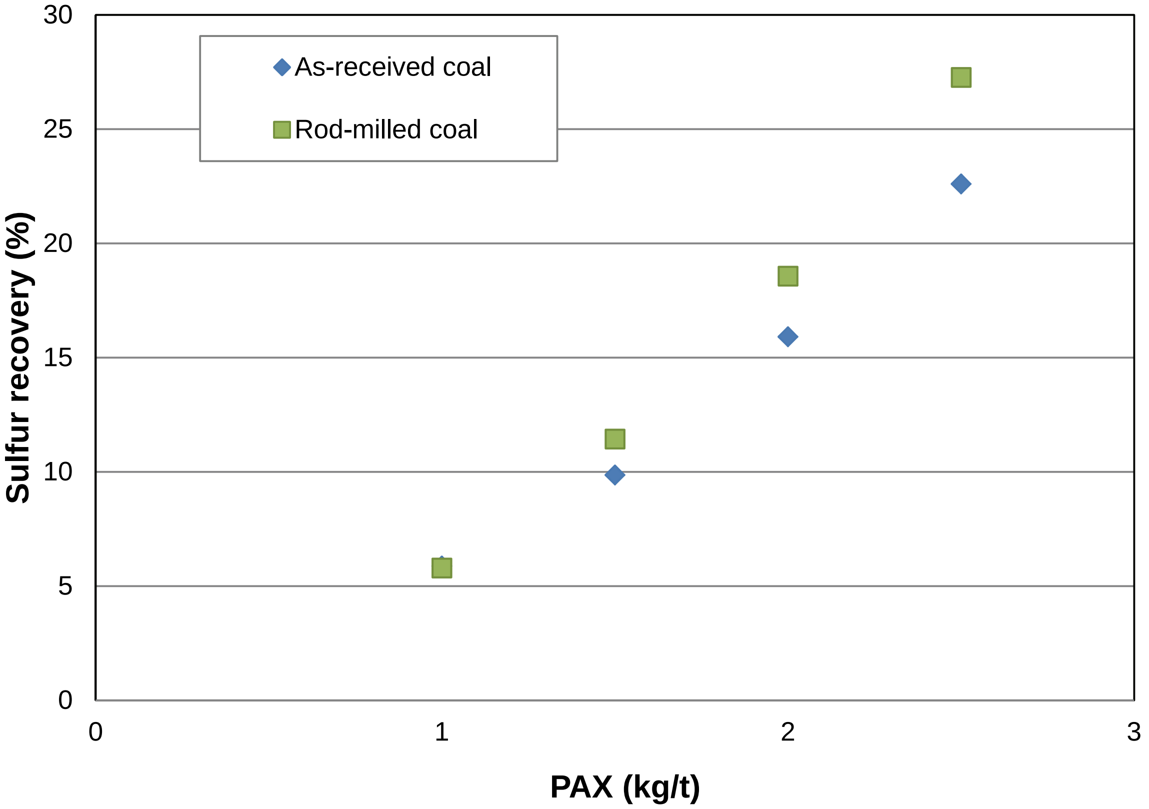


Figure 39: Effect of size fraction on the recovery of sulphur of as-received and rod-milled coal samples at different PAX collector dosages. Dextrin depressant and MIBC frother were kept constant at 0.93 kg/t and 0.11 kg//t, respectively.

5.4.4 Two-stage flotation

An experiment was carried out to test the feasibility of the concept outlined in Figure 29, in which coal flotation is followed by a sulphide flotation stage to enable recovery of a coal rich stream (concentrate 1) and a benign tailings as the major stream (tailings 2). In the first stage, valuable coal was recovered from the coal ultrafines in the froth. In the second stage, the tailings were re-processed to remove the sulphide minerals, in particular pyrite, to produce a low-sulphur tailings that was not acid-generating, preventing environmental damage. 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 sulphide-rich fraction.

The first stage was performed following the procedure outlined in Section 5.3.3.1, 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 (to allow analysis at the intermittent stage), forming feed to the second-stage, which was conducted according to the procedure outline in Section 5.3.3.4.

Table 24 shows the feed compositions, reagent dosages and the mass balances for coal and total sulphur 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 sulphur content of 0.48% S. 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 sulphur (0.38% S) content. The second stage recovered a low volume sulphide rich fraction (2.68% total sulphur) to the concentrate which may be amenable to bio-desulphurisation. All products were assessed to ascertain their ARD generation potential, reported in Section 0 .

The conceptual flow sheet of the overall process is shown with the proportional mass balance achieved under standard conditions in Figure 40. The performance and selectivity of the process was clearly shown by the low sulphur content of the second-stage tailing (0.38%) and the low ash content of the clean coal product (13.5%).

Table 24: Two stage flotation results (first stage: coal flotation; second stage: sulphide flotation).

		Weight percent		
Product		**Amount**	**Ash**	**Total Sulphur**
First Stage				
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
Second Stage				
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
Sulphide concentrate		13.1	28.9	2.68
"Benign" Tailings		67.2	40.8	0.38

The amount of total sulphur was reduced by approximately 75% in the benign tailings (Figure 40). A significant proportion of the sulphur in "the environmentally benign waste" was in the form of organic sulphur, as a result of the greater part of the pyrite having been removed in the second flotation stage. Even though this process was not optimized, the clean coal yield was nearly 20% of the total feed mass, with low sulphur content (0.48%) and a saleable ash content (13.5%). The results obtained in Section 5.4.1.2 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 sulphur content. The reduction in the amount of coal in the second stage feed may be expected to reduce the large dosage of PAX collector and increase the sulphur grade in the "sulphide-rich waste", because of less interaction between the collector and the coal particles.

The sulphur content of both the tailings and concentrate of stage 1 are lower than in the feed. The feed sample contained sulphide, organic sulphur and sulphate sulphur, the latter resulting possibly from the oxidation of sulphide minerals. The soluble sulphates were absent from the tailings or clean coal, accounting for the incomplete mass balance of sulphur in the solid phase across the first stage (Table 25). The sulphur un-accounted in the solid phase across the two stage-stage process was 0.36 units, compared with 0.32 units of sulphate in the sulphur speciation analysis (Table 13, p 61).

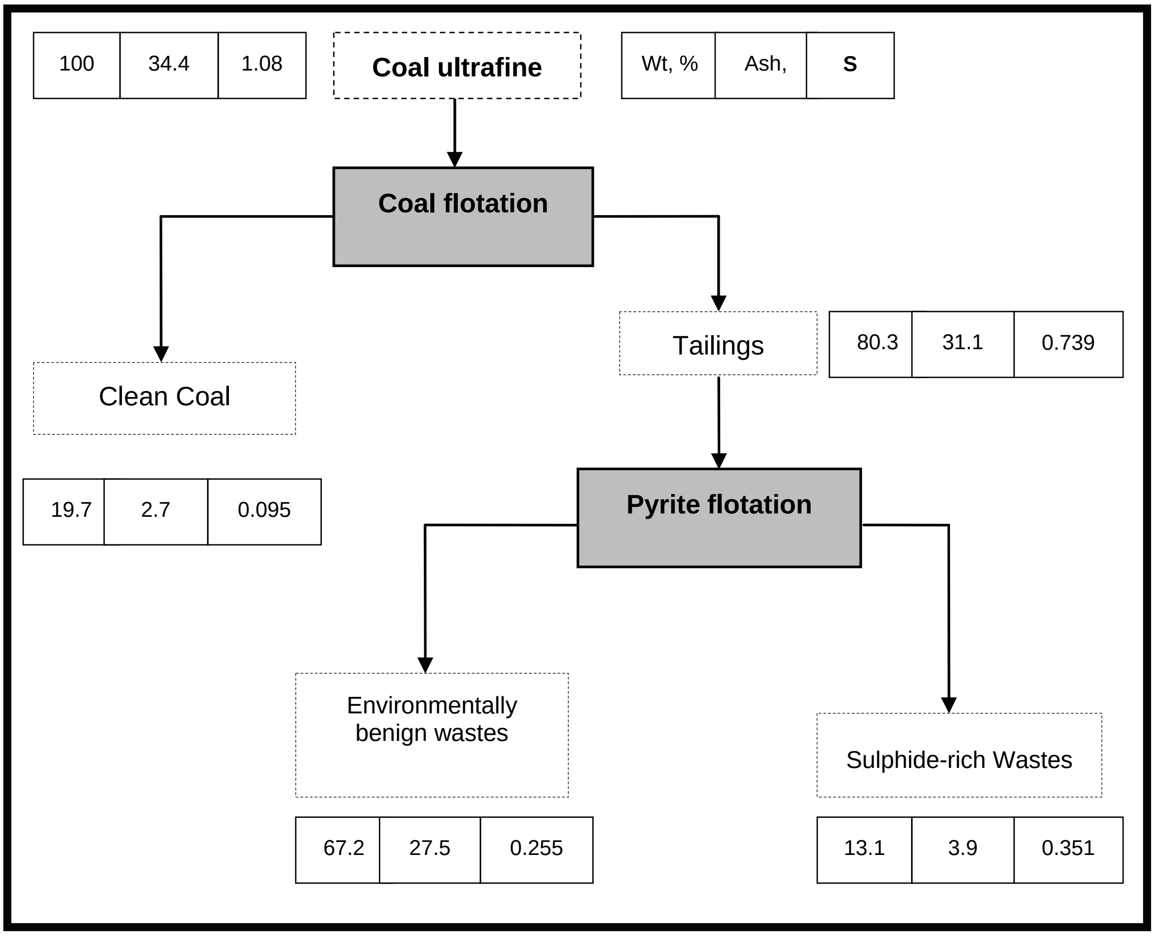


Figure 40: Performance flow sheet for coal ultrafine in two stage flotation process including coal and pyrite flotation, indicating mass recovery (as wt%), ash recovery and S recovery as units per 100 units total fresh feed (34.4 unit ash and 1.08 unit S respectively).

*The incomplete closure of the S balance resulted from the dissolution of sulphate sulphur.

Table 25: Mass balance across all ash and total sulphur for the first and second stages

Flotation process	**Stream**	**Mass (units)**	**Ash (units)**	**Total sulphur (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
	Sulphide concentrate	13.1	3.79	0.35
	“Benign” Tailings	67.2	27.43	0.26
	Δ	0	-0.06	0.14

*The incomplete closure of the S balance resulted from the dissolution of sulphate sulphur.

5.4.5 Acid Rock Drainage Prediction Tests

The primary focus of this study is to reduce potential for the generation of acid rock drainage (ARD), hence it was imperative to evaluate the acid generating potential of the flotation streams. The categorisation of ARD risks associated with these solid materials allows decision making on which tailings can be disposed of without threat to the environment and which require further treatment or containment. Consequently, the feed, concentrate and tailing samples from both coal and sulphide flotation were evaluated in terms of their acid generating potential using acid base accounting (ABA), net acid generation (NAG) tests and the biokinetic flask test, currently under development.

5.4.5.1 Acid base accounting (ABA) test

Table 26 gives the sulphur content of the feed and four products from the two-stage flotation test (Section 5.4.4). The samples are designated by their acronyms: 1T and 1C are tailings and concentrate, respectively, from coal flotation; 2T and 2C are generated from the second stage sulphide flotation. In Table 27, the sulphur content is shown of the products generated from sulphide flotation with 1-stage, 2-stage and 3-stage addition of amyl xanthate collector, respectively (Section 5.4.2.3).

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 H_2SO_4/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 28, show that the feed coal had a positive NAPP; therefore it was potentially[1] acid-generating according to the classification outlined in Table 17. This is as expected; the feed sample was selected on the basis that it exhibited acid generating potential.

Table 26: Sulphur content of the samples used in ARD prediction tests for the feed and two-stage flotation outputs.

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

Table 27: Sulphur content of the samples used in ARD prediction tests for the tailings from sulphide flotation tests.

Legend	Samples	Sulphur 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

Outputs from the first stage of flotation were potentially acid-generating: the tailing and concentrate streams had NAPP values of -8.27 kg H_2SO_4/t and -6.24 kg H_2SO_4/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 reporting to the tailings. The NAPP values of the tailings and concentrate from the second stage flotation were -45.17 kg H_2SO_4/t and 64.78 kg H_2SO_4/t, respectively. This suggests that most of the

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

sulphide minerals reported to the concentrate. The final tailing was non-acid forming (NAF) and the sulphide-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 sulphur was decreased 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 sulphide it contains and its acid neutralization potential.

Table 28: Acid base accounting results for feed, tailings and concentrates from two-stage flotation

Sample	**S grade (%)**	**MPA (H_2SO_4 kg/t)**	**Fizz Rating**	**ANC (H_2SO_4 kg/t)**	**NAPP (H_2SO_4 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

PAF = potentially acid forming; NAF = non-acid forming

Table 29 shows the NAPP results of the three tailings generated when floating sulphide 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 non-acid forming. This indicates that more sulphide sulphur 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 sulphide-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 economic value that nevertheless present a risk of ARD pollution.

Table 29: Acid base accounting test results for tailings from sulphide flotation experiments

Sample	**S grade (%)**	**MPA (H_2SO_4 kg/t)**	**Fizz Rating**	**ANC (H_2SO_4 kg/t)**	**NAPP (H_2SO_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

5.4.5.2 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 H_2O_2 as oxidant. Table 30 and Table 31 summarises the results of the net acid generation (NAG) tests, displaying the pH of leachate produced and the equivalent acid produced per ton, relative to the pH 4.5 and 7 environments. Samples were classified according to the criteria outlined in Table 23.

Table 30: 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_2SO_4/t)**	**NAG pH7 (kg H_2SO_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	0.00 ± 0.00	6.86 ± 1.11	NAF
2C	2.67	2.13 ± 0.01	60.66 ± 1.80	14.80 ± 2.91	Acid forming

Table 31: Net acid generation (NAG) test results for tailings from sulphide flotation runs

Sample	**S grade (%)**	**NAG pH**	**NAG pH 4.5 (kg H_2SO_4/t)**	**NAG pH7 (kg H_2SO_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	0.00 ± 0.00	23.4 ± 3.19	NAF
5T	0.56	5.33 ± 0.00	0.00 ± 0.00	7.15 ± 0.14	NAF

In accordance with the NAG test results, the feed sample (F) had a NAG pH < 4, and was thus classified as acid generating. The concentrate from the coal flotation stage (1C) also had NAG pH < 4, showing that it was also acid generating, even though the total sulphur grade was lower than in the tailings sample, which had a NAG pH > 4. This results from the considerable ANC present in the tailings. Furthermore, the NAG value at pH 4.5, evaluating the amount of sulphide minerals, is higher in the concentrate (1C) than in the tailings (1T). This confirms that a considerable amount of sulphide 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 sulphide-rich concentrate resulting from the second stage flotation (2C) was acid-forming with a NAG pH of 2.13 and NAG value of 60.7 kg H_2SO_4/t at pH 4.5. The tailings generated from the second stage flotation (2T) were non-acid generating as conceptualized. This result shows that sulphide minerals reported to the concentrate during sulphide flotation, reducing the acid generating potential of the tailings.

Based on the deportment of sulphur during flotation reported in Table 23, 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 NAG pH 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.

As seen in Table 31, the NAG results of the tailing samples produced from sulphide flotation confirm the ABA results: stage-wise addition of the collector has produced sulphide-lean tailings. One stage collector addition generated a tailing that exhibited acid forming characteristics, showing that the influence of the collector on sulphide deportment to the concentrate was low.

During NAG testing, the sulphide-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 sulphur 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 32 shows the results of the sequential NAG testing performed on this sample.

Table 32: Sequential NAG stage for sample 2C with high content of total sulphur

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	0.00 ± 0.00	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 was 77.11 and 65.55 kg H_2SO_4/t, respectively. The results confirm that the sulphide concentrate from the second stage flotation was chemically reactive (acid-generating), which is consistent with the single addition NAG result. Although this sulphide-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-desulphurization.

5.4.5.3 Comparison between ABA and NAG results

Table 33 shows the ABA and NAG test results for the feed, concentrates and tailings resulting from the two-stage coal and sulphide flotation. As indicated in Table 17, a sample is classified PAF when it has a NAG pH < 4.5 and NAPP > 0, and NAF when NAG pH ≥ 4.5 and NAPP < 0. Samples are un-classified (UC) when there is an apparent conflict between the NAG pH and NAPP results.

Figure 41 plots the results of single addition NAG tests in conjunction with NAPP values to classify samples according to their acid forming potential. The final tailings resulting from desulphurizing flotation (2T), representing some 67% of the starting material by mass, appear in the upper left hand domain with a negative NAPP value and NAG pH value over 4.5, therefore it is classified non-acid-forming (NAF) and can be considered environmentally benign. The feed (F) and the sulphide-rich fraction (2C) had positive NAPP values and NAG pH values below 4.5, and hence were potentially acid generating (PAF). The tailing (1T) and concentrate (1C) samples from coal flotation were situated in the uncertain zone (UC).

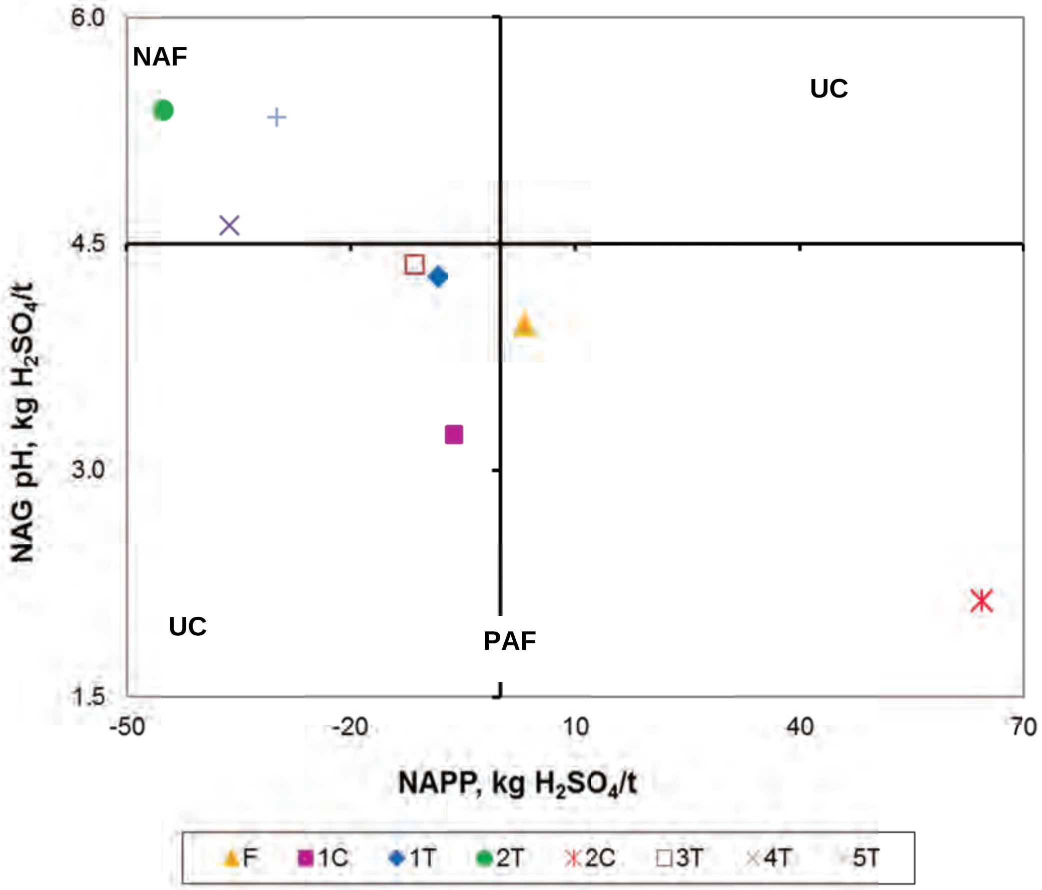

Figure 41: Acid Rock Drainage classification plot showing NAG pH versus NAPP for flotation outputs and feed

Table 33: NAPP and NAG test results for the feed, concentrates and tailings from flotation

Sample	Total S	MPA	ANC	NAPP	NAG pH	NAG pH4.5	NAG pH7	ARD Classification
	%	kg H_2SO_4 /t				kg H_2SO_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	0.00	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	0.00	23.42	NAF
5T	0.55	17.14	46.98	-29.84	5.33	0.00	7.15	NAF

5.4.5.4 *Biokinetic test results*

The biokinetic shake-flask test described in Section 5.3.4.4 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 testing2.

Each biokinetic test was carried out in triplicate under non-sterile and controlled temperature conditions. The influence of microorganisms on the process and associated leaching of sulphide minerals was estimated by the pH, redox potential (Eh) (against an Ag/AgCl reference electrode) and the concentration of dissolved ferric iron in solution over a period of 76 days.

The pH profiles are represented in Figure 42. 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), reducing the lag-phase of the bacteria and preventing 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 25. 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.

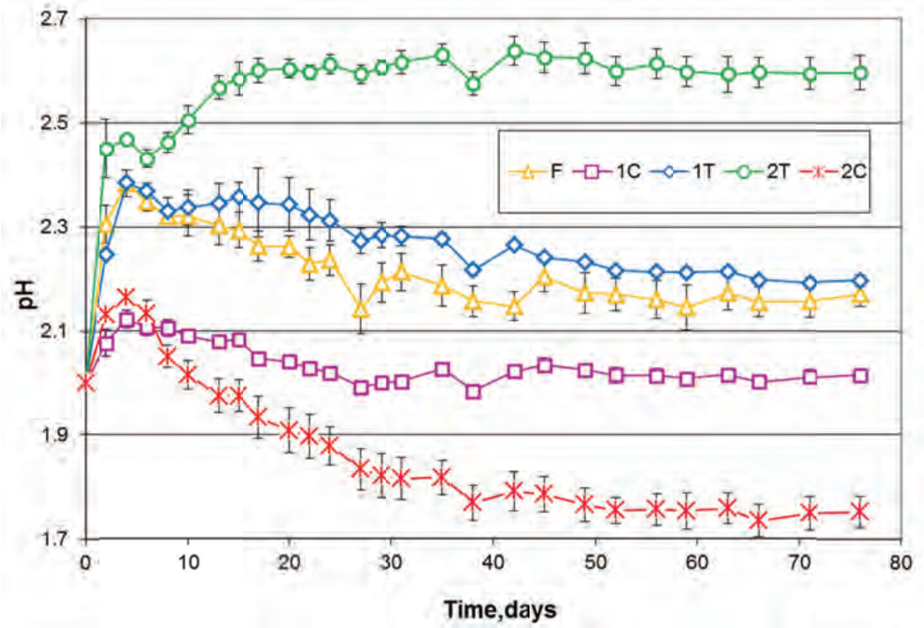

Figure 42: Average pH with time during the shake flask biokinetic tests performed on feed (F) flotation and products (1C, 1T, 2T, 2C).

Following the attainment of redox values of 600 mV or greater by day 4, sulphide 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 sulphur final tailings sample (2T). In this tailings sample, the pH increased gradually to around pH 2.60 by day 16; thereafter 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,

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[2] The biokinetic graphs of tailings from direct sulphide flotation presented similar profiles; for example sample 3T behaved like the feed sample (F), while samples 4T and 5T were similar to the second stage tailing (2T)

was influenced by the combination of ANC and the sulphur 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 sulphur-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 sulphur content of the clean coal is close to the sulphur content of the final tailing, their pH graphs present different behaviours. This may be related to the forms of sulphur and ash in each sample.

Figure 35 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, sulphuric acid was titrated 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. The amount of sulphuric acid added was a reliable estimate of acid consumption by the sample. A total of approximately 19 kg H_2SO_4/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. The conditions for microbial oxidation were optimal at pH 2 and below. In the absence of microorganisms, the pH tended to higher values, ranging between 5.8 and 6.3, which were less favourable for the acceleration of the microbial oxidation. The results of the test controlled at pH 2 suggest that the maintenance of the pH in the preferred range for microbial iron and sulphur oxidation was also important for accelerated microbial ferric ion and acid regeneration.

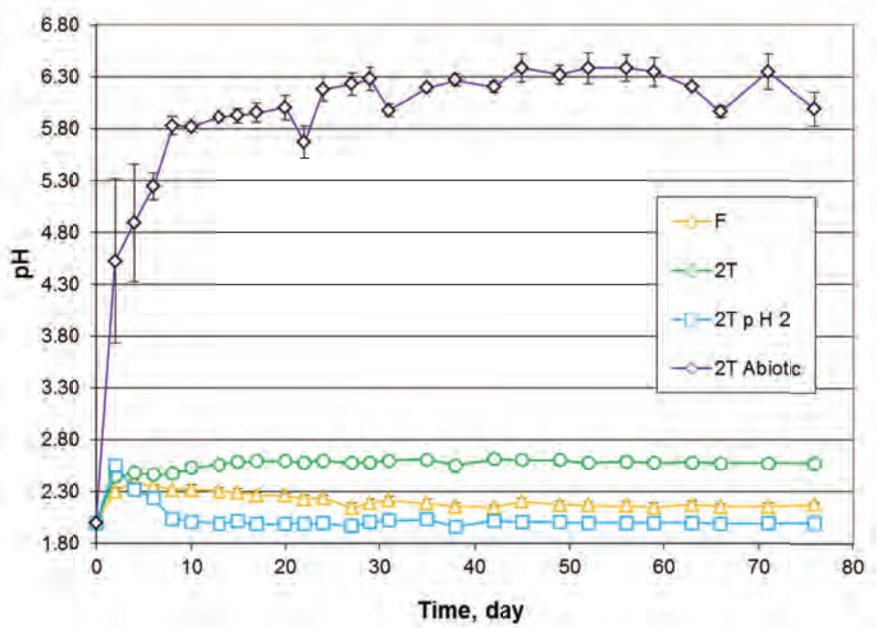


Figure 43: Average pH with time during the shake flask biokinetic tests performed on the feed (F) and the final tailing (2T), and the final tailings sample controlled at pH 2 and in the absence of bacteria (abiotic).

Figure 44 presents the behaviour 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 and ensuring the ferric iron speciation was dominant for favourable conditions for pyrite leaching. The attainment of a redox potential great than 650 mV with all species indicated that where acid conditions are present and micro-organisms colonise the solid phase, the iron present will be maintained as Fe3+ and contribute to leaching of any sulphide minerals available.

Figure 44 shows the redox potential profile for 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. 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. Sulphide leaching can be achieved when the sample is co-disposed in an acidic environment, even though the sulphur content of the sample was low. The redox did not increase into the range indicating the Fe3+ dominance with the abiotic sample, in the absence of the sulphur- and iron-oxidizing bacteria.

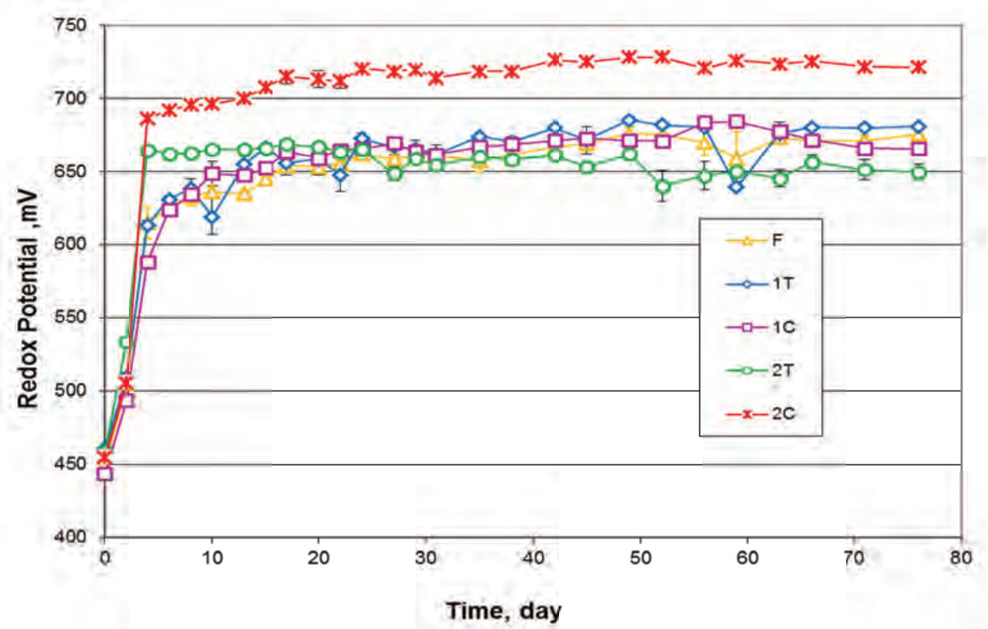


Figure 44: Redox profiles for the biokinetic tests performed on the flotation feed (F) and products (1C, 1T, 2T, 2C).

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 46. 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 sulphur. This sample showed dissolution of 1155 mg iron /L by day 52, as a result of high pyrite oxidation and total sulphur 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 sulphur-bearing minerals corresponding to slow microbial growth or by the precipitation of iron as jarosite, particularly with increasing pH. The occurrence of jarosite is due to the solubility limit of iron and sulphates, 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.

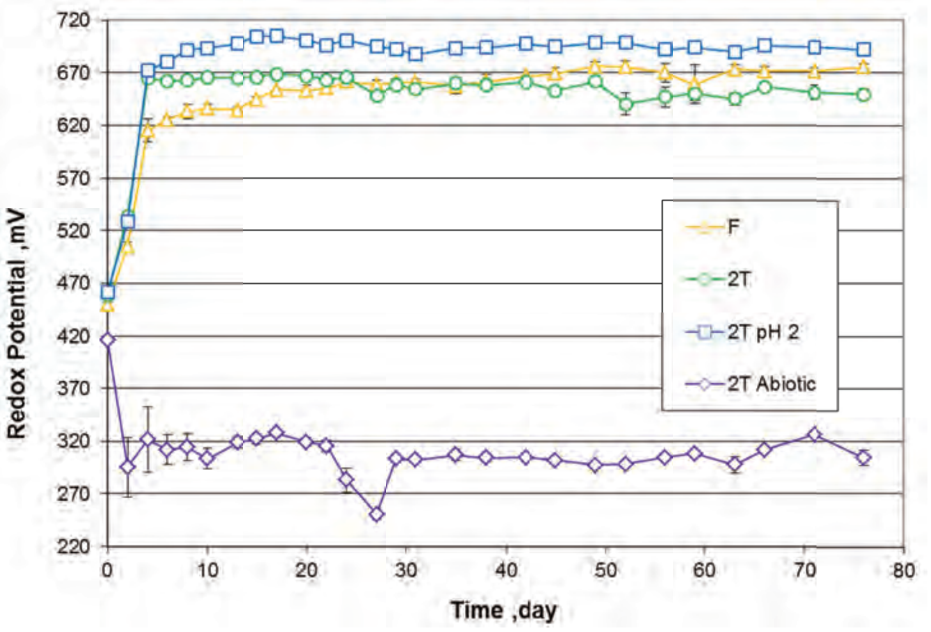


Figure 45: Redox potential of biokinetic tests performed on the feed (F) and the final tailing (2T), and the final tailings sample controlled at pH 2 and in the absence of bacteria (abiotic).

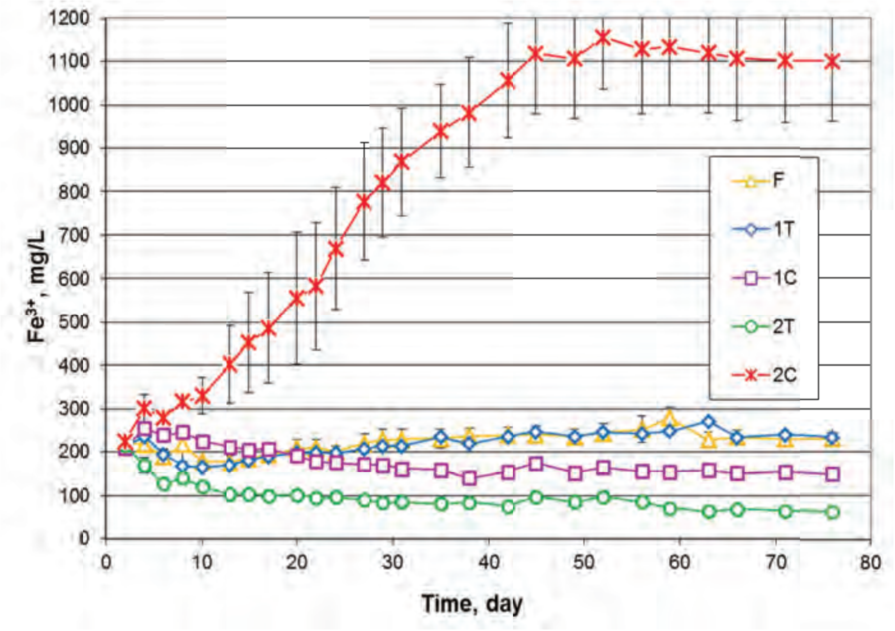


Figure 46: Fe^{3+} profiles for the biokinetic tests performed on the feed (F) and the final tailing (2T), and the final tailings sample controlled at pH 2 and in the absence of bacteria (abiotic).

The profile of ferric iron concentration with time for the controlled experiments is shown in Figure 47. Evidence of microbial activity under the controlled pH conditions is provided by the behaviour of soluble ferric iron, which increased to a concentration of approximately 370 mg/L in the first 20 days; thereafter a gradual decrease was observed. It is likely that this was due 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.

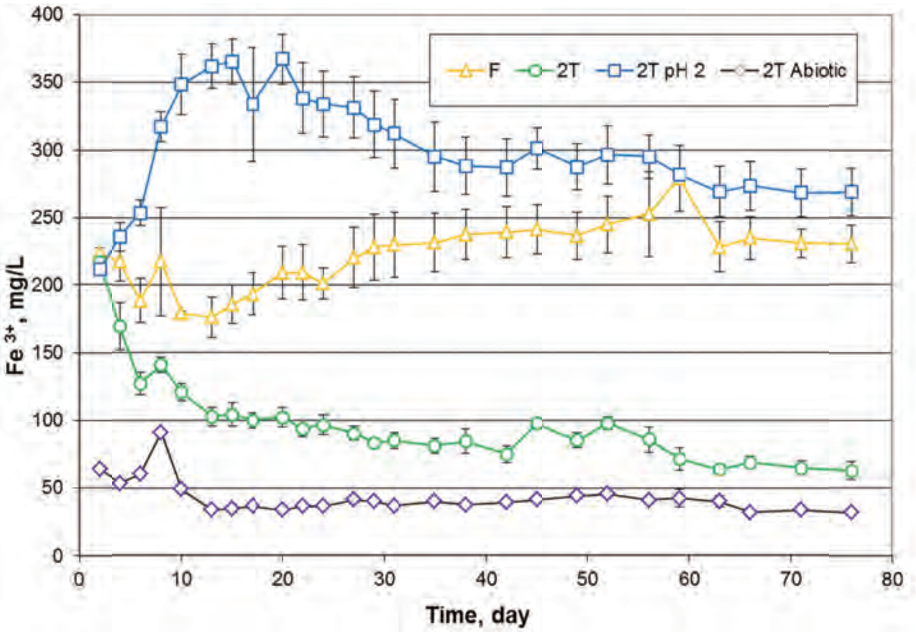


Figure 47: Ferric iron profiles for biokinetic tests performed on the feed (F) and the final tailing (2T), and the final tailings sample controlled at pH 2 and in the absence of bacteria (abiotic).

Biokinetic tests were followed by sulphur and ash analyses carried out on the residues. Table 34 shows the sulphur reduction, which is defined as the percentage change in the amount of sulphur in the residue after the biokinetic test. The chemical analysis performed on the residue indicated a total sulphur composition of 0.40% in the sulphide-rich concentrate sample (2C) from a feed of 2.68% S. The sulphur reduction was approximately 85%, indicating high microbial activity and the oxidation of sulphide sulphur during the process. This result suggests that this concentrate is indeed amenable to bio-desulphurization due to the high content of pyritic sulphur 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-desulphurization 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 sulphide-rich sample was the highest, approximately 20 wt%; this was probably due to the extremely acidic conditions imposed by the experimental process.

Table 34: Total sulphur reduction of residues from biokinetic tests

Sample	**Total sulphur (%)**			**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

5.4.5.5 Comparison of static and bio-kinetic tests

Biokinetic tests were carried out to ascertain the bioavailability of the acid-forming materials (owing to this being the major catalyst for acid formation in the field), to provide data on the relative kinetics of acid neutralization and acid generation, and to validate the results of the static tests carried out on the coal flotation products to characterize their ARD generation potential. Table 35 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 a low sulphur content, hence MPA (see Table 28, p 84) 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 a high sulphur content, showed the lowest pH with substantial acidification observed following the initial release of neutralizing capacity.

Table 35: Comparison of static and biokinetic ARD test results

Sample	Static test				Biokinetic test				
	S %	ANC	NAG pH	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. It must be noted that the criteria for this categorization with the biokinetic test are still under development as the datasets available for the biokinetic test remain limited. 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 the prediction of behaviour in the field.

5.5 CONCLUSION AND RECOMMENDATIONS

The results obtained in this work suggest that the application of froth flotation to ultrafine coal wastes allows 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 more acceptable levels by the selective removal of acid generating materials from these wastes. This reduction in risk is also an absolute reduction, rather than a delay in its onset. 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. It may be concluded that froth flotation techniques are a viable (technical) method for reclaiming large amounts of coal ultrafines that are currently wasted in slimes dams.

The results of laboratory batch flotation tests to investigate the two-stage flotation process showed that a low-sulphur 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 sulphur content of the second-stage tailing (0.38%) and the low ash content of the clean coal product (13.54%). The second stage recovered a low volume sulphide-rich fraction (2.68% total sulphur). 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 sulphur (0.38% S) content. This product was assessed to be benign with respect to ARD generation, which was the objective of the thesis. The clean coal had a low sulphur content of 0.48% S. Although only low yield and recovery were achieved with dodecane as a collector, the use of oleic acid showed evidence to suggest a better recovery and yield. 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. In this work, no attempt was made to optimize the reagents.

The results of the biokinetic tests demonstrated that the high-sulphur content of the second stage concentrate was the most amenable to microbial desulphurization, due to the high content of pyritic sulphur, 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 schemes for coal thickener underflow coal wastes.

All of the research work described in Section 5 was conducted on one thickener underflow coal sample only. It was necessary to confirm the results on samples from different coalfields, because coal does not have a fixed composition or fixed properties. Similar data (not shown) have been collected across two samples of coal ultrafines from other South African coalfields and a coarse coal discard, and confirms the demonstration of the proposed conceptual approach.

To take this conceptual flowsheet further, research is required to optimize the separations in terms of reagents and operating conditions. Further, the general operating conditions should be identified separately from the sample-specific requirements. The recovery of clean coal from the first stage of the process, aimed at reclaiming valuable product from the ultrafine wastes, requires substantial improvement.

CHAPTER 6: SULPHIDE SEPARATION FOR BENIGN BULK TAILINGS – CASE STUDY ON GOLD TAILINGS

6.1 INTRODUCTION

Laboratory scale experiments were conducted to determine the viability of separating the acid rock drainage forming components, notably sulphur, from a gold tailings sample. Froth flotation was used as an illustrative method for separation. The ARD generation potential of the feed and product streams were characterised through the use of standard acid-base accounting and net acid generation tests to ascertain that the low sulphide tailings generation were, indeed, not acid forming.

Four gold tailings samples have been considered for this study:

1. Gold tailing collected from Evander through Danie Vermeulen: These tailings were not acid generating
2. BIOX leach residue collected from the leaching experiments on the Fairview concentrate conducted in the CeBER laboratories
3. Flotation tailings from the concentration circuit at Fairview Mine, Barberton, S.A.
4. Tailings from the BIOX and CIP process for gold recovery at Fairview Mine, Barberton, S.A.

6.2 MATERIALS AND METHODS ‑ GOLD DESULPHURISATION

6.2.1 Sample Preparation

Preliminary proof of concept experiments and an investigation into the effect of frother dosage on sulphur recovery from a Fairview arsenopyrite concentrate leached in a simulated BIOX reactor were performed in the CeBER laboratories.

For the main study, two gold tailings samples were obtained from the Fairview plant. A 10 kg sample was obtained from the tailings stream off the concentration circuit (Fairview Tailings). A second sample of similar mass was obtained from the waste stream exiting the bioleaching reactor and CIP circuit (BIOX and CIP waste). The samples were dried at 37°C before being screened through a 250 µm screen and statistically split into approximate 200 g samples.

6.2.2 Flotation Methodology

Laboratory scale froth flotation was conducted using the equipment and methodology specified in Section 5.3.3 and Figure 31. As before, methyl iso-butyl carbinol (MIBC) was used as the frother agent with potassium amyl xanthate (PAX) used as the sulphide collector. Frother and collector dosages were varied during the course of the experiments.

6.2.2.1 Flotation sample analysis

Filtered solid samples were oven-dried at 78°C before analysis. Total sulphur analysis was conducted using a LECO sulphur analyser in the analytical laboratory in the Department of Chemical Engineering at the University of Cape Town. For experiments involving a second flotation stage, the appropriate product stream was dried at 37°C to limit sulphide oxidation before the additional flotation experiments were performed.

6.2.3 ARD Prediction tests

The ARD potentials of the feed, concentrate and tailings product streams were analysed using acid-base accounting and net acid generation tests. ARD potential test-work and sample classification was conducted as outlined in Section 5.3.4.

6.2.4 Liquid sulphate concentration measurements

Sulphate concentration was measured turbimetrically using the method outlined by the American Public Health Association (APHA, 1975). Measurements were conducted using a Helios α UV-Vis spectrophotometer at 420 nm. Concentrations were quantified against a constructed standard curve.

6.3 RESULTS AND DISCUSSION

6.3.1 ARD classification of the four gold tailings samples using ABA and NAG$_{pH}$ results

Characterization of the ARD potentials of the four tailings samples was conducted using a combination of the ABA results and the NAG$_{pH}$ and are presented in Figure 48. The CeBER BIOX leach residue was classified as potentially acid forming, the Concentration Circuit Tailings within the “Uncertain” region and the Evander and BIOX & CIP tailings as non acid forming. From these results therefore, the investigation into the potential for sulphide removal using froth flotation was conducted on the potentially acid forming and “uncertain” samples, CeBER BIOX leach residue and Concentration Circuit tailings respectively, with the others discarded.

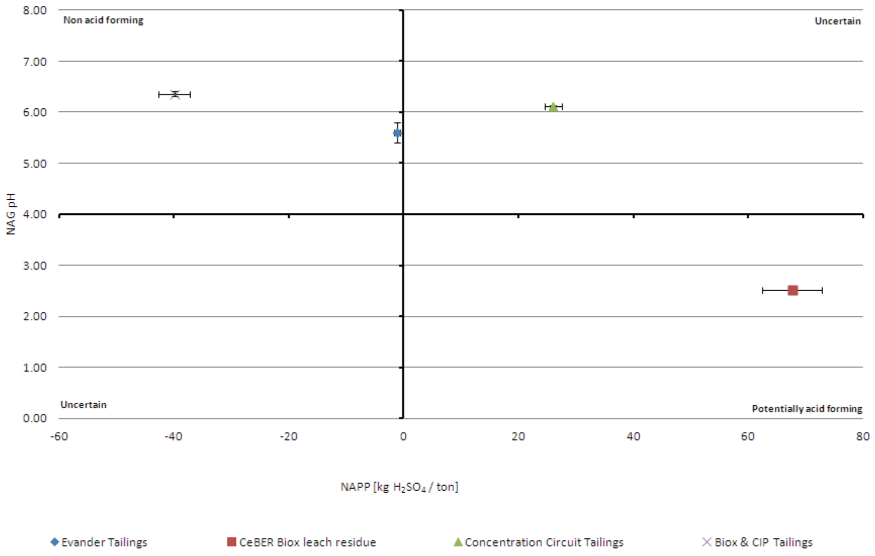


Figure 48: ARD classification of the four gold tailings samples showing that only the CeBER Biox leach residue and the Concentration Circuit Tailings are potentially acid forming

6.3.2 Preliminary investigation of sulphide removal using CeBER leached, Fairview arsenopyrite concentrate

The aim of the preliminary test work was to provide proof of concept for the use of froth flotation for the physical separation of sulphide minerals, resulting in a sulphide-rich and benign sulphide-lean product streams. For this investigation, a Fairview arsenopyrite concentrate was leached in a simulated BIOX reactor system in the CeBER laboratories, with the resulting solid phase used as the feed stream for the froth flotation test-work. The dosages of the MIBC frother were varied while the PAX collector dosage was kept constant at 1.8 kg/ton. Likewise, the agitation speed and aeration rate were kept constant at 1200 rpm and 7 L/min respectively. A pulp density of approximately 7.5% was used.

6.3.2.1 Effect of frother dosage

The effect of frother dosage on mass and sulphur recovery was investigated using MIBC dosages of 0.06, 0.08 and 0.10 kg/ton. In Figure 49, sulphur recovery (sulphur mass in concentrate * 100 / sulphur mass in feed) over time is shown as a function of MIBC frother dosage with the PAX concentration kept constant at 1.8 kg/ton. The frother dosage had a significant effect with the sulphur recovery increasing from 50% to 70% with an increase in MIBC concentration from 0.06 to 0.08 kg/ton. Increasing the frother dosage to 0.01 kg/ton, however, had no significant effect on sulphur recovery.

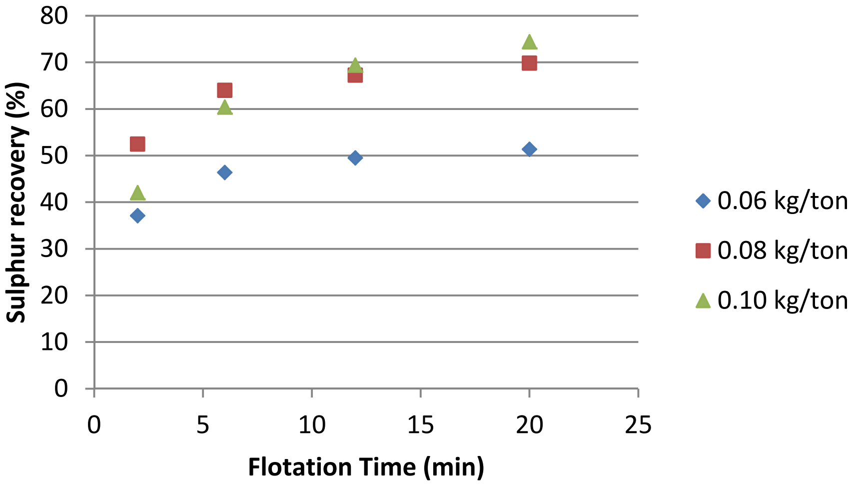


Figure 49: Sulphur recovery of CeBER leached, Fairview arsenopyrite concentrate samples at different MIBC frother concentrations, PAX dosage was kept constant at 1.80 kg/ton

While sulphur was recovered to the concentrate stream, the majority of the feed mass remained in the tails. Figure 50 details the total mass and sulphur recovery to the concentrate after flotation as a function of frother dosage with the PAX collector concentration kept constant at 1.8 kg/ton. While the sulphur recovery reaches 70% at an MIBC concentration of 0.08 kg/ton, the mass recovery increases from 18% at a concentration of 0.06 kg/ton to 33% with the similar increase. Similar to the sulphur recovery however, the mass recovery does not increase significantly at a frother dosage of 0.10 kg/ton. The difference in recoveries of the total mass and sulphur illustrates the effectiveness of froth flotation at these conditions in the physical separation of sulphide minerals to form a sulphur-rich concentrate while the majority of the mass remains in the sulphur-lean tails stream.

To investigate the associate effect of the sulphur removal on the ARD potential of the product streams, ABA and NAG ARD experiments were conducted on the feed, concentrate and tailings samples.

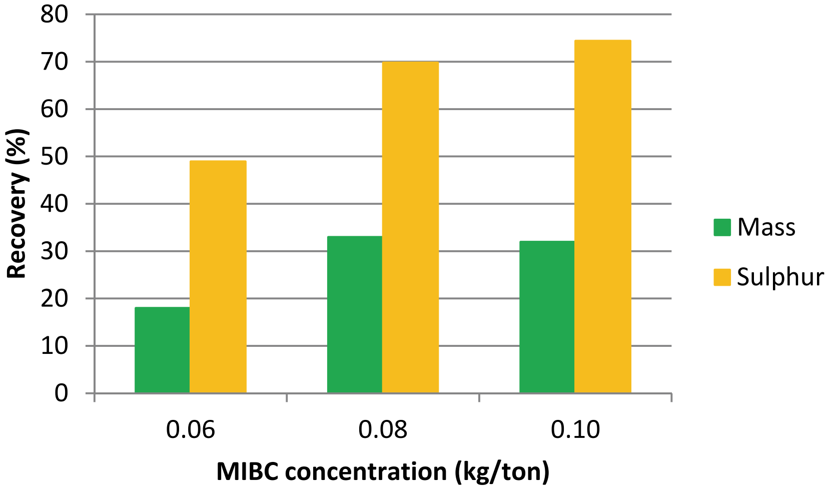


Figure 50: Mass and sulphur recovery from the CeBER-leached BIOX concentrate to the flotation concentrate at differing frother dosages with PAX concentration kept constant at 1.80 kg/ton

6.3.2.2 Acid Rock Drainage prediction results

Table 36 shows the results of the ABA experiments for the feed, concentrate and tailings stream as a function of frother concentration. The sulphur grade increased from 2.03 ± 0.13% in the feed to 4.72, 4.15 and 3.89% in the concentrate streams for MIBC dosages of 0.06, 0.08 and 0.10 kg/ton respectively. The decreasing sulphur grade is indicative of the increase in mass recovery associated with increasing frother concentration. In addition, although the sulphur grade is highest with an MIBC concentration of 0.06 kg/ton, the highest sulphur grade in the tails stream corresponds to the lowest associated sulphur recovery at this condition.

The ANC of the sample decreases with an increase in the sulphur grade, compounding the acid producing potential values of these streams. The production of a sulphur rich concentrate stream is associated with an increase in the NAPP of the stream from 67.5 kg H_2SO_4/ton in the feed to 140.1, 122.7 and 113.2 kg H_2SO_4/ton for the concentrates produced with MIBC concentrations of 0.06, 0.08 and 0.10 kg/ton respectively. All of these resulting concentrates are classified as acid forming (AF) by the ABA experiments.

The purpose of this separation is to achieve a bulk tailings fraction which is not acid generating. The sulphur grade of all the tailings streams was lower than their corresponding concentrates. For the tailings generated using flotation at 0.06 kg/ton MIBC, the low sulphur recovery to the concentrate resulted in an acid forming tailings stream. In contrast, the resulting tails from flotation using 0.08 and 0.10 kg/ton MIBC were classified as potentially acid forming (PAF). Further test work was therefore necessary to classify these samples more accurately.

Table 36: Acid-base accounting results for the preliminary experiments using CeBER-leached BIOX concentrate using different frother dosages.

Frother Dosage [kg/ton]	**Sample Origin**	**Sulphur Grade [%]**	**ANC** [kg H_2SO_4/ton]	**MPA** [kg H_2SO_4/ton]	**NAPP** [kg H_2SO_4/ton]	**ARD Classification**
N/A	Feed	2.03 ± 0.13	3.06 ± 0.3	70.5 ± 3.8	67.5	AF
0.06	Concentrate	4.72	4.40	144.5	140.1	AF
	Tails	1.10	4.86	33.	28.9	AF
0.08	Concentrate	4.15	4.48 ± 0.45	127.1	122.6	AF
	Tails	0.62	5.24 ± 0.22	19.0	13.7	PAF
0.10	Concentrate	3.89	5.84 ± 0.31	119.0	113.2	AF
	Tails	0.64	7.02 ± 0.28	18.4	11.3	PAF

*AF = Acid forming, PAF= Potentially acid forming

Further ARD classification was carried out by using a combination of the ABA and NAG pH, with the results shown graphically in a characterisation plot (Figure 51). The NAPP value on the x-axis was calculated from the ABA results while the NAG pH was measured after the complete reaction of the sample with a known quantity of 15% H_2O_2 solution.

Although the majority of the sulphur in the feed stream was recovered successfully to the concentrates at all three frother concentrations, the grade of the remaining tails resulted in all three samples were classified within the potentially acid forming region as indicated in Figure 51. The classification of the tailings as potentially acid forming suggested that an investigation into using a 2^{nd} flotation stage under optimal MIBC and PAX conditions is required, as a means of further decreasing the ARD potential. This investigation has yet to be completed

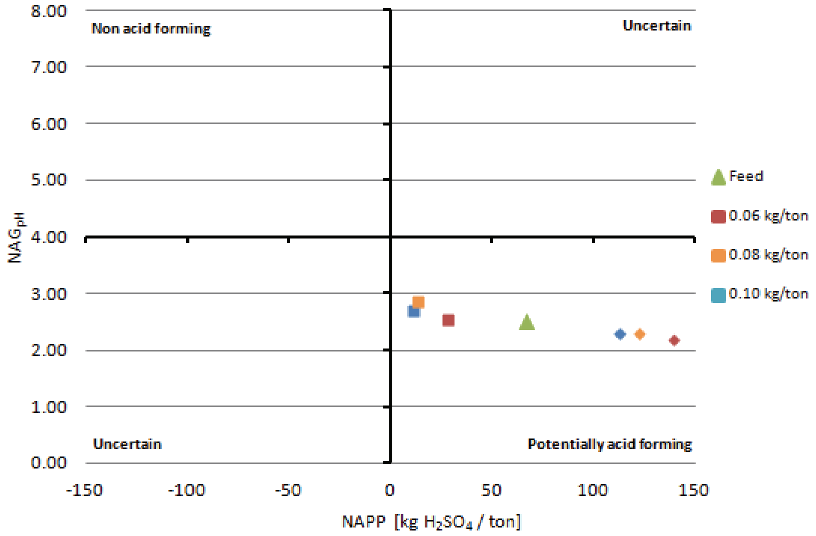


Figure 51: Characterization plot showing effectiveness of froth flotation on reduction of ARD potential of the CeBER-leached BIOX concentrate at differing frother dosages for the feed, concentrate (♦) and tails (■).

6.3.2.3 2nd Stage flotation of the CeBER leached, Fairview arsenopyrite concentrate

The two-stage flotation experiments were conducted in duplicate on two CeBER leached, arsenopyrite concentrate samples. The MIBC and PAX dosages for both flotation stages were kept constant at 0.08 and 1.8 kg/ton. The separation achieved in the mass and total sulphur of the feed sample is presented in Figure 52.

Approximately 47 and 91% of the mass and total sulphur of the feed sample was recovered during the two stage flotation process, with the first flotation stage accounting for 38 and 75% respectively. The remaining 53 and 9% from the feed formed the tails stream from the second flotation stage.

The ARD potentials of the concentrates and tails streams resulting from the two-stage froth flotation experiments are presented in Figure 53. Average values are presented with error bars indicating ARD static tests performed in triplicate. Although 91% of the total sulphur from the feed was recovered to concentrates 1 and 2, enough total sulphur remained in the tails 2 stream to classify the sample “marginally” potentially acid forming. This continued acid generating potential was due to the low relative ANC values as indicated earlier in Table 36.

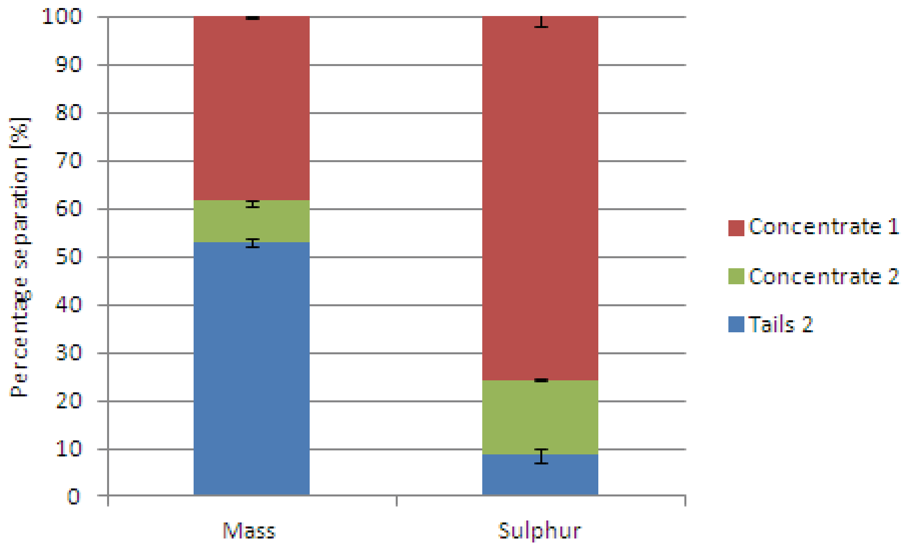


Figure 52: Separation achieved using a two-stage, froth flotation process on the CeBER leached, arsenopyrite concentrate. MIBC and PAX dosages were kept constant at 0.08 kg/ton and 1.8 kg/ton respectively.

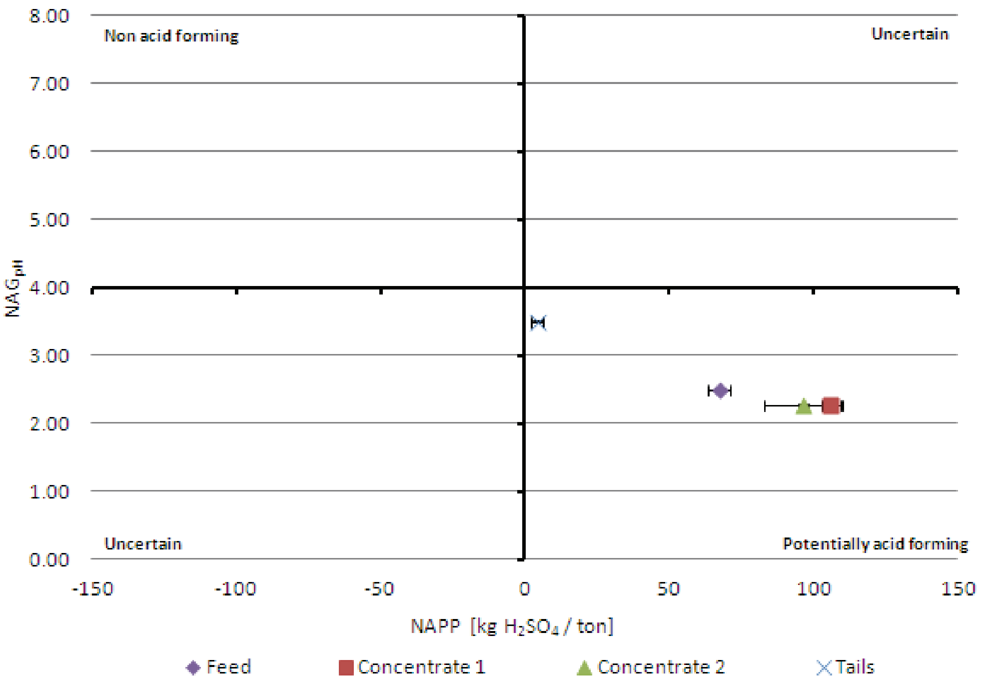


Figure 53: Characterization plot following two-stage froth flotation process on the ARD potential for two CeBER leached, arsenopyrite concentrate samples at an MIBC and PAX dosage of 0.08 and 1.8 kg/ton respectively.

6.3.3 Desulphurization of the Fairview tailings (from concentrator circuit)

Following the preliminary results which demonstrated the feasibility of froth flotation for the physical separation of sulphide minerals, the experimental test-work was extended to a Fairview tailings sample taken after the concentrator circuit on the Fairview Mine at Barberton. For this investigation, the collector concentration (PAX) was varied between 0.17 kg/ton and 2.33 kg/ton with an MIBC dosage of 0.08 kg/ton and 0.06 kg/ton used.

6.3.3.1 *Effect of collector dosage*

The effect of PAX concentration was investigated using dosages ranging from 0.17 kg/ton to 2.33 kg/ton while the MIBC frother concentration was kept constant at 0.08 kg/ton. Figure 54 shows the sulphur recovery over time as a function of PAX concentration. The sulphur recovery increased with increasing collector concentration up to a dosage of 1.67 kg/ton. The experimental error between repeats, shown as error bars for the flotation experiments conducted at 1.00 kg/ton PAX, indicated a relative error of between 1 and 3% over the 20 minute flotation duration. A maximum sulphur recovery of 72% to the flotation concentrate was obtained at a PAX concentration of 1.67 kg/ton.

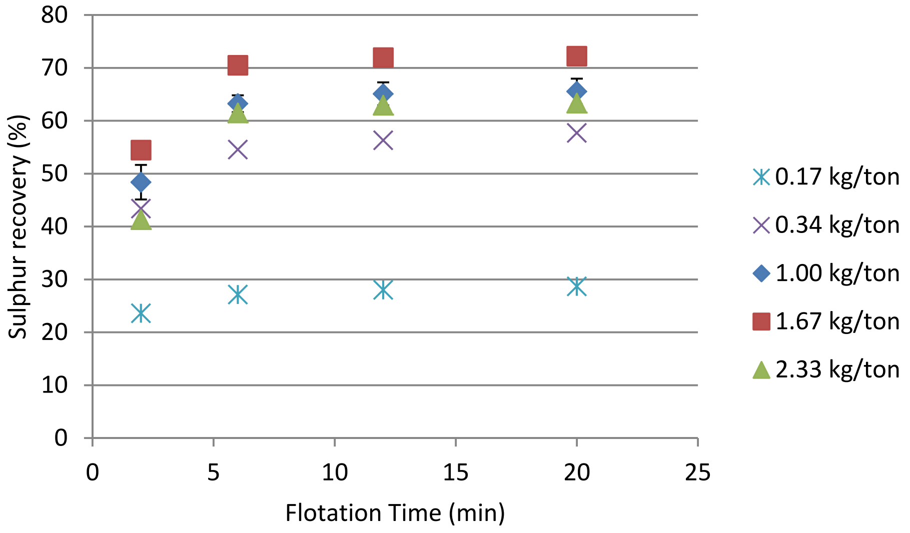


Figure 54: Sulphur recovery with time at differing PAX dosages with the MIBC concentration constant at 0.08 kg/ton

While sulphur recoveries above 70% were achieved, there was no selective accumulation of the sulphur in the concentrate stream. Figure 55 shows that while the sulphur recovery increased with increasing PAX concentration, the mass recovery increased at the same rate. The similar mass and sulphur recoveries at concentrations above 0.34 kg/ton, suggested no physical concentration of the sulphur into a specific fraction occurred.

However, at a PAX concentration of 0.17 kg/ton, sulphur analysis showed a sulphur recovery of 29% with an associated mass recovery of 46%. This indicated that, at this PAX concentration, sulphur was recovered to the tails rather than the concentrate.

As a result of the above findings, an investigation of a lower frother concentration for use in the flotation of this tailings sample was performed. An MIBC concentration of 0.06 kg.ton was used; the resultant sulphur recoveries are presented in Figure 56. At a PAX concentration of 0.34 kg/ton, decreasing the MIBC concentration decreased the sulphur recovery from 58% to 43%. The sulphur recoveries obtained for the other PAX concentrations remained unchanged; hence this result supported the findings of the preliminary study (Section 6.3.2).

Although the sulphur recovery decreased from 58% to 43% at a PAX concentration of 0.34 kg/ton, there was no change in the mass recovery (Figure 57). Therefore, similarly to the results for a PAX concentration of 0.17 kg/ton in Figure 55, the sulphur was effectively concentrated to the tails product stream. The relative mass and sulphur recoveries for the higher PAX concentrations, however, remained the same, showing no concentration effect.

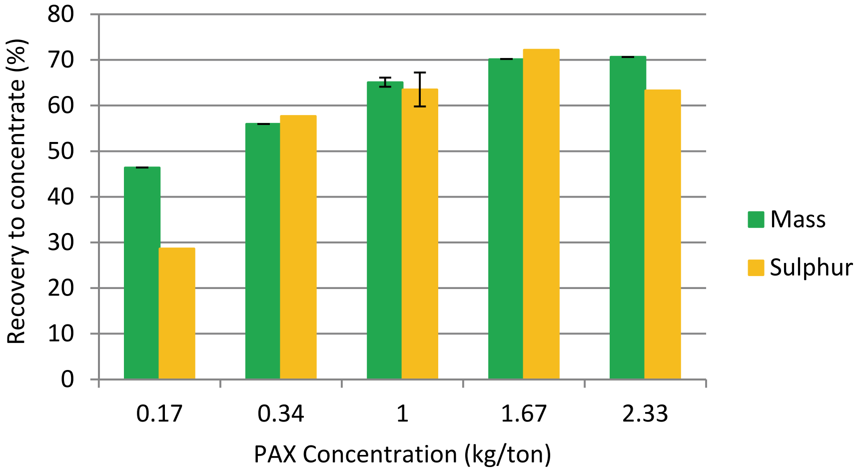


Figure 55: Mass and sulphur recoveries at different PAX dosages, MIBC constant at 0.08 kg/ton.
**Test carried out at 1.0 kg PAX per ton was done in duplicate.*

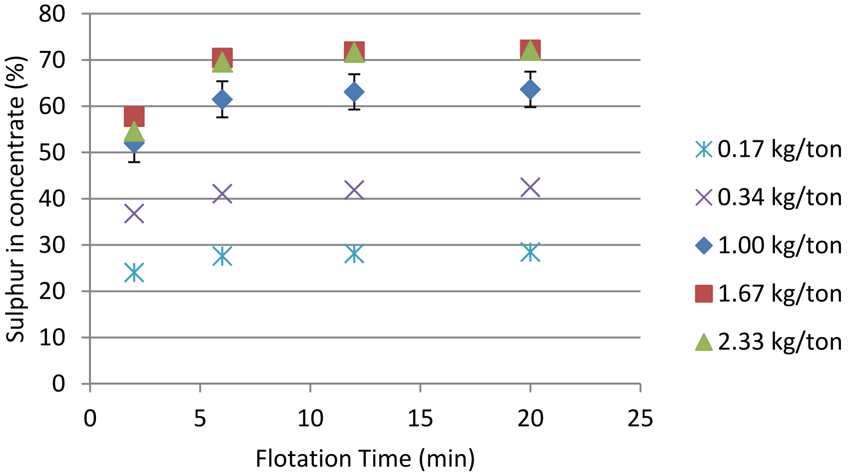


Figure 56: Sulphur recovery with time for different PAX concentrations with the MIBC dosage kept constant at 0.06 kg/ton

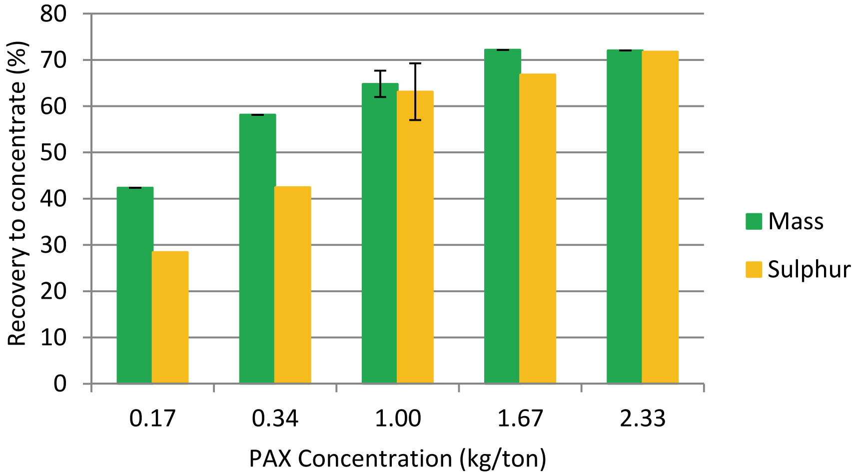


Figure 57: Mass and sulphur recovery as a function on PAX dosage, MIBC constant at 0.06 kg/ton.
** The test conducted at 1.0 kg/ton PAX was repeated in duplicate*

6.3.3.2 Acid Rock Drainage potentials

Although the sulphur recovery was above 50% for all flotation experiments using PAX collector concentrations of 0.34 kg/ton and above for processing of the tailings from the concentrator circuit, the sulphur grade in the concentrate streams decreased from 1.68 ± 0.11% in the feed to between 0.36 and 0.55% in the concentrate streams for all PAX concentrations. Similarly, the sulphur content of the tailings decreased. This decrease demonstrated a loss of sulphur from the solid material (Figure 55, Table 37). This finding was corroborated by the blue-green colour of the filtrate liquor, which suggested the presence of soluble copper metal species and associated counter-ions.

A sulphur imbalance was evident from the comparison of MPA values of the feed and the sum of those values pertaining to the corresponding concentrate and tailings streams. The decrease in sulphur grade in the absence of a corresponding decrease in ANC values, resulted in the low NAPP values presented. The majority of the concentrate and tailings streams were therefore classified as potentially non-acid forming (PAF), as shown in Figure 58 and Figure 59.

Table 37: Acid-base accounting results for the Fairview tailings subsequent to flotation of the tailings from the concentrator circuit with variable PAX collector concentrations using 0.08 kg/ton MIBC frother.

Collector Dosage [kg/ton]		**Sulphur Grade [%]**	**ANC** [kg H_2SO_4/ton]	**MPA** [kg H_2SO_4/ton]	**NAPP** [kg H_2SO_4/ton]	**ARD Classification**
N/A	Feed	1.68 ± 0.11	27.15 ± 0.36	51.36 ± 3.40	24.21	AF
0.17	Concentrate	0.36	28.55 ± 0.37	11.02	-17.53	PAF
	Tails	0.78	25.06 ± 0.36	23.75	-1.32	PAF
0.34	Concentrate	0.41	24.58	12.48	-12.10	PAF
	Tails	0.38	18.07	11.64	-16.44	PAF
1.00	Concentrate	0.55	30.06 ± 0.69	16.88	-13.18	PAF
	Tails	0.48	17.80 ± 1.25	14.69	-3.11	PAF
1.67	Concentrate	0.51	29.04	15.49	-13.54	PAF
	Tails	0.46	19.01	14.01	-5.00	PAF
2.33	Concentrate	0.52	28.83 ± 1.29	15.82	-13.01	PAF
	Tails	0.72	19.40 ± 1.20	22.09	2.7	AF

*AF = Acid forming, PAF= Potentially acid forming

As a result of the PAF classification from the ABA results, additional NAG experiments and a combined characterization plot were necessary to further characterise the ARD potentials (Figure 59). With the exception of the tails stream from the flotation performed at a PAX collector dosage of 2.33 kg/ton, the other concentrate and tailings streams were all classified as non-acid forming; in contrast with the feed which was classified within the “uncertain” region.

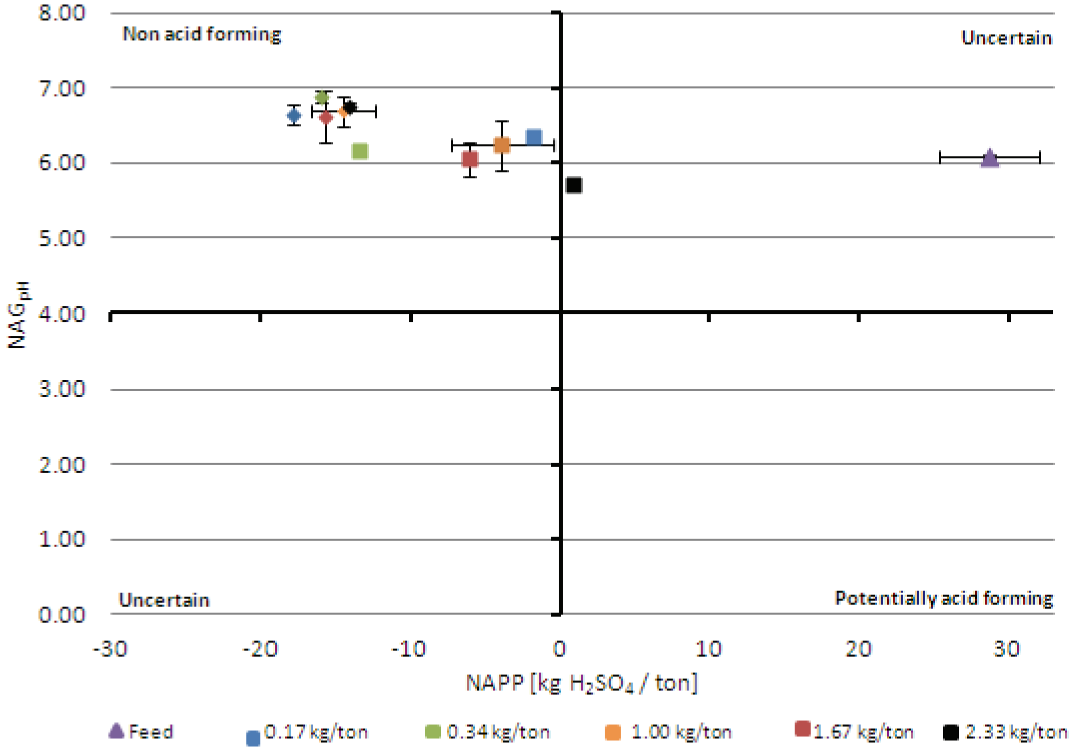


Figure 58: Characterization plot showing feed, concentrate (♦) and tailings (■) samples for different PAX collector concentrations at an MIBC dosage of 0.08 kg/ton

Acid Base Accounting (ABA) test results performed on samples from the flotation experiments at lower MIBC concentrations of 0.06 kg/ton are presented in Table 38. An accumulation of sulphur was observed in the tails stream for the flotation experiments performed at 0.17 and 0.34 kg/ton PAX. A loss of sulphur from the feed resulted in a decrease in the grade of both concentrate and tailings streams across collector concentration investigated.

Similarly to the results of the experiments conducted at an MIBC concentration of 0.08 kg/ton, the sulphur lost from the solid phases, together with the stable ANC values for the feed, concentrate and tailings streams, resulted in the low NAPP values and subsequently the ARD classification of potentially acid forming for all product streams across the collector dosages which were investigated.

Further classification of the concentrate and tailings streams from the flotation experiments conducted at a MIBC frother concentration of 0.06 kg/ton required the use of the NAG pH from the single-stage NAG experiment. The resulting characterization plot is presented in Figure 59.

With one exception, the flotation results at an MIBC concentration of 0.06 kg/ton were similar to those conducted at 0.08 kg/ton. The classification of the tails stream at a PAX concentration of 2.33 kg/ton shifted from “uncertain” to “non-acid forming.” This change in classification was due to an increase in the sulphur recovery at this PAX concentration. The concentrate and tailings streams at all PAX concentrations were classified as non-acid forming.

Table 38: Acid-base accounting results for flotation experiments performed on the Fairview tailings sample with varying PAX collector concentrations, using a constant MIBC frother concentration of 0.06 kg/ton

Collector Dosage [kg/ton]	**Sample Origin**	**Sulphur Grade [%]**	**ANC [kg H_2SO_4/ton]**	**MPA [kg H_2SO_4/ton]**	**NAPP [kg H_2SO_4/ton]**	**ARD Classification**
N/A	Feed	1.68 ± 0.11	27.15 ± 0.36	51.36 ± 3.40	24.21	AF
0.17	Concentrate	0.37	28.57 ± 0.46	11.47	-17.10	PAF
	Tails	0.69	21.25 ± 0.85	21.21	-0.04	PAF
0.34	Concentrate	0.40	25.68	12.31	-13.36	PAF
	Tails	0.76	23.25	23.19	-0.05	PAF
1.00	Concentrate	0.49	29.94 ± 0.85	15.13	-14.80	PAF
	Tails	0.44	21.92 ± 1.32	13.43	-8.49	PAF
1.67	Concentrate	0.46	26.89	14.11	-12.79	PAF
	Tails	0.59	19.89	18.18	-1.71	PAF
2.33	Concentrate	0.52	28.46	16.03	-12.42	PAF
	Tails	0.53	18.96 ± 0.61	16.25	-2.71	PAF

*AF = Acid forming, PAF= Potentially acid forming

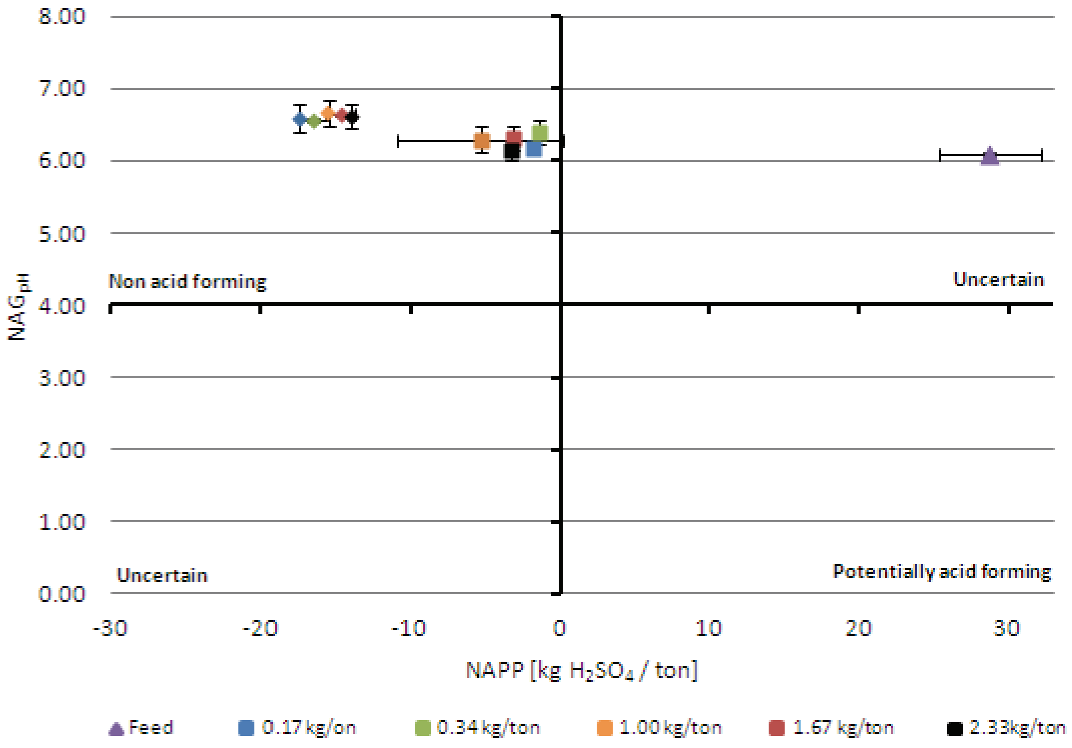


Figure 59: Characterization plot showing feed, concentrate (♦) and tailings (■) samples for different PAX collector concentrations at an MIBC dosage of 0.06 kg/ton

The discrepancy in sulphur grade between the feed, concentrate and tailings streams may have been as a result of the presence of soluble sulphur species within the feed samples. The observed colour of the flotation filtrate also supported the possibility of the presence of soluble metal species within the feed samples. Since no reaction of the sulphur species was expected as a result of flotation experiments, it was possible to combine the calculated sulphur masses from the concentrate and tailings streams to calculate the non-soluble sulphur grade of the feed sample.

The resulting sulphur grade back-calculated across all flotation experiments was estimated to be 0.52 ± 0.05%. The difference between this calculated value and the LECO counterpart was postulated to be due to the soluble sulphur species, at a grade of approximately 1.16 ± 0.23%.

Simple wash experiments were performed on four Concentration Circuit tailings samples to ascertain the amount of sulphur lost through washing. LECO analysis was performed on both the pre- and post-washed solid samples, with the wash water analysed for sulphate. A loss of 42 ± 11% of the total sulphur from the solid phase on washing, with an increase in SO_{42}- concentration in the liquid phase, confirmed the presence of a soluble, sulphate species.

6.4 CONCLUDING REMARKS

The use of froth flotation as a means of physical separation of sulphide minerals from gold-bearing ores was demonstrated successfully on the Fairview arsenopyrite concentrate sample leached in the CeBER laboratories. The effect of MIBC frother concentration on the mass and sulphur recoveries was investigated, with recovery increasing with an increase in frother dosage up to a concentration of 0.08 kg/ton.

Acid rock drainage (ARD) prediction tests on the resulting concentrate and tailings streams, however, revealed that the sulphur grade of the tailings was not reduced sufficiently, given the present ANC of the sample, to restrict the possible generation of ARD. Therefore, even though physical sulphide separation was achieved, a totally benign tailings stream was not achieved. The addition of a 2nd flotation experiment resulted in an average overall recovery of 47% and 91% of the available mass and total sulphur from the two feed samples respectively. This overall separation however did not allow for the complete removal of the ARD risk from the CeBER leached, Fairview arsenopyrite samples. To address the potential of achieving complete removal of ARD risk, further research should focus on optimization of the separation by flotation or other separation steps as well as considering the mineralogical arrangement of the residual sulphide, in terms of its occlusion or liberation, to determine the feasibility of such separation.

The investigation into the effect of varying the collector concentration on the sulphur recovery from a Fairview tailings (concentrator circuit) feed sample was conducted using the optimal frother dosage from the preliminary experiments. The PAX collector concentration had little effect on the sulphur recovery at dosages above 0.17 and 0.34 kg/ton, for the 0.08 and 0.06 kg/ton MIBC frother experiments respectively. In addition, little physical accumulation of sulphur was suggested by the observed mass and sulphur recoveries at these PAX collector concentrations. At dosages where a significant difference was observed between the mass and sulphur recoveries, the majority of the sulphur was reported in the tailings product streams. This was an unexpected finding and suggests that the choice of flotation chemicals requires review.

The ABA and NAG results for the flotation experiments conducted at both MIBC frother concentrations showed that although the feed samples were classified as acid forming and “uncertain” respectively, the concentrate and tailings streams, with one exception, were classified as non-acid forming. This discrepancy between feed and product streams was explained through back calculation of the feed sulphur grade using the mass of sulphur reporting to the concentrate and tailings streams. It was found that approximately 0.52 ± 0.05% of the reported 1.68 ± 0.11% sulphur remained within the solid phase after flotation, with the difference lost to the flotation liquor. Simple wash experiments were performed to verify the existence of the soluble sulphate species. LECO analysis of the solid phase both pre- and post-washing indicated the loss of 42 ± 11% of the total sulphur, with sulphate analysis of the post-wash liquor indicating the presence of SO_{42}-.

CHAPTER 7: REVIEW OF DISPOSAL STRATEGIES

7.1 FORMS OF WASTE FOR DISPOSAL

In the treatment options proposed to date for the prevention of ARD, two approaches have been taken. In the first, the sulphide fraction is removed from the tailings or ultrafine waste product, often with the associated improvement in value recovery. This leads to three output streams: the additional recovered product, the sulphide rich concentrate and the benign tailings. In the second approach, the lack of liberation of the sulphide prevents its physical separation; hence reaction is used, resulting in a sulphate rich waste stream and a sulphide lean waste rock in the best case.

Based on these treatment options, the following output streams require assessment in terms of their potential use for generation of new products in accordance with the principles of industrial ecology (in addition to the extended recovery of the main product):

- The sulphide concentrate (as a finely divided particulate material)
- The benign tailings
- The sulphate solution

7.1.1 The sulphide concentrate

It is desirable to concentrate the sulphide fraction into a stream representing the minimum mass recovery of the waste stream treated while maximising sulphur recovery. This is governed by the liberation of the sulphide and the selectivity of the separation process. In the separation processes demonstrated to date in this project, the sulphide content of the concentrate from the coal desulphurisation lay in the range 2.6 to 18.7% by mass (Kazadi Mbamba et al., 2012; Amaral Filho et al., 2012). In the desulphurisation of tailings from base metal recovery, investigated by Hesketh et al. (2010a), the sulphide concentrate contained up to 4% sulphur. All samples were acid forming and were amenable to bio-desulphurisation.

7.1.2 The non-sulphide tailings

The bulk mass recovery of each separation represented the non-sulphide tailings. This material typically had a sulphide content of less than 0.3% by mass and was demonstrated to be non-acid forming through each of the NAG, ABA and biokinetic tests. The properties of these benign tailings depend largely on the gangue mineralogy. In most cases studied, these were dominated by silicates and oxides and carried some acid neutralisation capacity.

7.1.3 The sulphate solution

Where the sulphide fraction was removed by reaction, a bio-generated leach environment was provided. Depending on the efficiency of the leach process, the sulphate concentration in solution can be expected to vary up to 80 g/l. The solutions are typically acidic (pH 1.0 to 2.3) with soluble iron present predominantly as ferric iron at a concentration of 0.1 to 5 g/l. The presence of additional metal ions in solution is a function of the gangue mineralogy.

7.2 MAGNITUDE OF WASTE STREAMS FOR DISPOSAL

The production of mineral wastes is significant. On average, 40 tons of solid waste are generated per capita per year, including several tonnes of slag, sludge, ash and contaminated soil, as well as 25 kg of white and brown goods (household appliances, electronics, etc.). The mineral wastes generated with respect to metal extracted vary with ore body and metal. An order of magnitude is derived by considering the global extraction of metals in 1988 and the associated ore mined, and waste generated, shown in Table 39A. To account for the growth in metal use with the emergence of developing nations in Asia, the metal extraction figures from 1988 can be compared with those of 2010 / 11, presented in Table 39B. Where these metals are associated with mineral sulphide ores, the waste materials have a potential for ARD generation. Further coal wastes also contribute to ARD.

Table 39 World production and use of key metals. A.) World extraction of metals in 1988: mined, extracted and waste generated (kMT). Sourced from Ayres and Ayres (1996); B.) Current (2010-2011) annual extraction of key metals globally (US Geological Survey 2012).

A	**Gross mass of ore (kMT)**	**Metal content (%)**	**Net mass of metal (kMT)**	**Mine and mill waste (kMT)**
Aluminium	97 660	37.3	36 400	61 220
Chromium	14 000	32.5	4 207	10 000
Copper	>1 750 000	0.5	8 450	>1 740 000
Gold (1979)	170 000	<0.001	1.19	170 000
Iron	953 000	59.0	564 400	390 000
Manganese	30 500	28.0	8 540	22 000
Nickel	80 000	1.0	835	79 000
Platinum group (1979)	30 000	<0.001	0.20	30 000
Zinc	220 000	3.22	7 115	213 000

B	**Global amount extracted (thousand metric tons metal)**		**Global amount extracted (thousand metric tons gross)**	
Metal	**2010**	**2011**	**2010**	**2011**
Aluminium	40 800	44 100		
Chromium			23 700	24 000
Copper	15 900	16 100		
Gold	2.56	2.70		
Iron	1030 000	1 100 000		
Manganese			13 900	14 000
Nickel	1 590	1 800		
Platinum group (Pt & Pd)	0.394	0.399		
Zinc	12 000	12 400		

The South African coal industry disposes of the major fraction of the 12 million tonnes of ultrafine coal waste generated annually. Even some twenty years ago, it was estimated that over 500 million tonnes of solid waste were generated by the mining industry in Canada each year (Hassani *et al*., 1994). India generates some 960 million tonnes of solid waste annually, as by-products of the industrial, mining, agricultural and municipal sectors. Of this, some 290 million tonnes are generated by the industrial and mining sectors, and 4.5 million tonnes are hazardous (Pappu et al., 2006).

As an example, the kyanite mine in Central Virginia, USA, produced 90 000 tons of the aluminosilicate mineral kyanite per year in 2003 and currently produces 150 000 tons per year. This mineral is used in brake shoes and pads, sanitary ware, floor and wall tiles, etc. Associated with this production are three waste streams: a silicate-rich stream containing quartz, muscovite and hematite; a magnetic stream containing magnetite, pyrrhotite and charcoal and a pyrite rich waste stream. Over the past 60 years, these have accumulated 27 million, 3.57 million and more than 380 000 tonnes of waste respectively (Schellenbach and Krekeler, 2011).

7.3 POTENTIAL USES OF THE PYRITE RICH FRACTION

7.3.1 Manufacture of H_2SO_4

Metal sulphides, typically pyrite, can be oxidised to metal oxide at high temperature through a roasting process. The gas SO_2 is formed in the roasting process, and can be converted to H_2SO_4. This is a well-established process, with improvements to the process patented as long ago as 1933 (Clark, 1933). Its economic feasibility varies with geographic location. By using O_2 in place of air for pyrite roasting, one can decrease the gas flow rate by nearly a third, thereby reducing roasting time and intensifying conversion. This allows reduced capital expenditure and a shortened payback period.

The oxidation reactions are highly exothermic, so heat recovery and integration should be included in this process. This energy integration is currently a focus in the large scale sulphuric acid manufacture through pyrite oxidation in China (400 000 t.p.a).

H_2SO_4 is required by a number of sectors, including the mining industry and fertiliser manufacture for the agricultural sector. It is currently a limiting commodity in South Africa, in short supply. Where used for fertiliser, it is particularly important that no toxic heavy metals such as mercury (Habashi, 1978) and arsenic

(Lindau, 1977) pollute the resulting acid. This can be achieved by introducing gas cleaning equipment at the SO_2 stage.

Additional value can be unlocked by using pyrite cinder resulting from the oxidation process to produce paint pigment. Pyrite cinder, the iron oxide (γ-Fe_2O_3 and Fe_3O_4) remaining in the reactor after the sulphur has been oxidised for H_2SO_4 production, can be roasted to produce hematite (α-Fe_2O_3) (Shoumkova, 2003). The hematite can then be used as a red pigment for cement and paint.

7.3.2 Pyrite and its role in compost manufacture or nutrient availability

The addition of pyrite in the production of wheat straw compost has been suggested to assist in retaining the ammonia in the compost and to make the phosphate component accessible. The latter is readily made bio-inaccessible through chelation and precipitation (Bangar *et al*., 1989). Obviously in such an application, it must be assured that the addition of pyrite and its subsequent acidification does not introduce the mobilisation of heavy metals, associated with either the pyrite or material to be composted.

7.3.3 Production of ferric sulphate and ferrous sulphate heptahydrate

Pyrite can be used to produce ferric sulphate coagulant and ferrous sulphate heptahydrate using a heap leaching setup (Colling et al., 2011; Vigânico et al., 2011). The acidic leachate leaving the heap leach is recirculated to the heap until the concentration of ferric ions reaches an acceptable level. In the case of ferric sulphate production, the leachate is then concentrated through evaporation and the resultant concentrated solution used as-is. For the production of ferrous sulphate heptahydrate, the ferric ions are reduced to ferrous ions by exposure to UV light, potentially the sun, and the ferrous sulphate crystallises. The ferrous sulphate may need to be washed and dried subsequent to crystallisation.

Both ferric sulphate and ferrous sulphate are used as coagulants in waste water treatment. Ferrous sulphate heptahydrate is also used to control anaemia in mammals and as a fertiliser.

7.3.4 Secondary lead refining

In the purification of hard lead for the production of battery grids, removal of copper and tin is important in order for the lead-antimony product to conform to Deutsches Institut für Normung (DIN) standards (Rabah et al., 1999). For the refining of hard lead, the alloy is melted, where after pyrite is added while stirring (Rabah et al., 1999). A layer of copper- and tin-rich slag forms on top of the lead and is separated from the lead. Addition of sodium hydroxide in the stirring phase was found to enhance copper removal efficiency (Rabah et al., 1999). This process naturally requires a pure pyrite stream, as introduction of impurities to the lead during the refining stage should be avoided.

Addition of pyrite has also been successfully used to extract copper and other base metals from copper refining slag (Arslan et al., 2002; Tümen et al., 1990) through roasting and leaching.

7.3.5 Copper smelting

Pyrite can be added as auto-thermal feed for copper smelters, thereby reducing the electricity demand of the smelter by releasing the heat of oxidation (Crump, 1925). The high heat of oxidation of the pyrite almost exclusively heats the smelter contents to a point where the matte and slag forms separate from each other (Peters, 1907).

This technique is well known and is currently in use at Zambian copper smelters. The pyrite that is added is purified by flotation; however it needs to be of a high quality to avoid introducing impurities to the copper product. This method of copper smelting is especially useful in an environment where other fuel, in either the form of coke or electricity, is expensive or difficult to obtain as well as where pyrite is relatively abundant. Disposal of emissions must obviously be addressed.

The process allows for the production of sulphuric acid, which can be used in the other processes related to the companies' activities.

7.3.6 Chrome (VI) reduction

The chrome (VI) ion is a by-product of chromite refining, pulp and pigment production, and stainless steel production, amongst others (Kim et al., 2002). It is problematic due to its high mobility and toxicity, in addition to being a class A human carcinogen (Kim et al., 2002). Treatment processes for water or other materials contaminated with chrome (VI) normally include the reduction of chrome (VI) to chrome (III) and the subsequent precipitation of the insoluble chrome (III). Lin and Huang (2008) have shown that pyrite can be used in chrome reduction. This process may be a cost-effective way to treat chrome (VI) laden effluent from industries in Mpumalanga.

7.3.7 Cemented paste backfill

This option has been suggested to be especially relevant to underground mines that use waste backfill to aid the stabilising of mine roofs. The cemented paste provides structural support for the mine while mining activities take place (Benzaazoua et al., 2008). Cement and blast furnace slag can neutralise acid produced by the sulphide-rich tailings. The extent to which the cement and slag neutralise the acid produced by the oxidation of sulphides has not been quantified; this means that rigorous research is still needed before its recommendation and potential implementation, particularly to address whether this presents a long term solution. Research on physical strength and long-term stability is needed to enhance the long term strength since preliminary tests have shown the cemented paste's strength to deteriorate with time (Benzaazoua et al., 2008).

7.3.8 Pyrite in solar panels

Pyrite is one of 23 semiconductor materials for photovoltaic applications that have been identified with potential to lower their cost substantially relative to silicon. It is the most abundant of these and is non-toxic. Pyrite has a very high absorptive coefficient ($\sim 5 \times 10^5$ cm^{-1}) and a suitable energy band gap (e.g. ~ 0.95 eV) for photovoltaic energy conversion (Bi et al., 2011, Wadia et al., 2009, Schellenbach and Krekelar, 2011). Hence it could become a really important PV material in thin film PV units such as solar panels. It is well recognised that the elements which are most exploited currently, will be constrained by availability in the large scale application of PV systems. Wadia et al. (2009) suggest that pyrite could be responsible for electricity generation some 2 to 3 orders of magnitude greater than silicon. Studies are underway currently to provide a rigorous understanding of the photovoltaic properties of pyrite, on which to base decisions on its potential (Bi et al., 2011; Hu et al., 2012).

Pyrite applications have not yet been demonstrated sufficiently, with the best efficiency reported at 2.8%, where a minimum of 4% is required to compete. This is attributed to phase impurities and thermodynamic instability. Various approaches to overcome these limitations, including the generation of nano crystal films (Bi et al., 2011), are under consideration. As yet, questions as to whether thin film technology is required or alternative non-conventional approaches may prove successful remain unanswered (Wadia et al., 2009). For the application of mineral wastes, purity is likely to be a constraining issue.

7.3.9 Pyrite in micro and nano linear actuators

The application of pyrite in nano and micro linear actuators is dependent on the weakly magnetic properties of pyrite and its response in the presence of a strong electric field (Cazacu et al., 2010). For this application pyrite is incorporated into a heat-cured silicone rubber film, less than a millimetre thick. Ground reduced pyrite was found to be better suited to the application than unprocessed pyrite. The processing is likely to be complex and may require high purity pyrite. This application will still require some research.

7.3.10 Magnetic susceptibility following dielectric heating

By selective dielectric heating of pyrite in coal, its separation can be improved by increasing its magnetic susceptibility in proportion to the time and power of the treatment (Bluhm et al., 1986). Pyrite and ash are predicted to heat 1.3 to 3.3 times faster than clean coal and have been shown experimentally to heat 1.9 to 2.6 fold faster when heated by dielectric heating at 2.45 GHz. This difference in heating rates may assist in the liberation of the sulphide from the coal.

7.3.11 Heat generation in the bioleaching process

It is well recognised that the ferric leaching of chalcopyrite for extraction of copper proceeds efficiently at temperatures of 60 to 100°C while being too slow under ambient conditions for commercial exploitation. In the minerals bioleaching process for recovery of copper from low grade chalcopyrite ores, thermophilic conditions must be established. Owing to the exothermic nature of pyritic oxidation, it is proposed that this may be achieved by the inclusion of sufficient finely divided and well liberated pyrite to drive the temperature of the ore bed up. This could be provided by the pyrite concentrates separated from sulphidic tailings. The solubilisation of the pyrite in the bioleach environment would also increase the availability and inventory of the acid and ferric iron leach agents, provided that a favourable pH environment is maintained to minimise jarosite formation.

7.3.12 Other applications

The presence of mineral sulphides in coal acts as a heat sink such that the heat release rate does not follow expected Arrhenius kinetics. Further this effect is pronounced beyond that predicted from the heat sink argument, indicating physicochemical effects of disseminated mineral (Beamish and Aristoy, 2008). This impacts heat recovery from coal, and also highlights the heat capacity of pyrite of 517 J/kg/°C.

Pyrite can be used in glass pigment applications, such as the manufacture of brown bottles. Pyrite absorbs ultraviolet light, reducing deterioration of light sensitive compounds when stored in these bottles.

Pyrite can also be used to prepare sulphite cellulose (Lindau, 1977).

7.4 REVIEW OF POTENTIAL PRODUCTS FROM THE SOLUBLE SULPHATE STREAM

Where waters which are high in sulphate and iron are allowed to evaporate from evaporation ponds, secondary minerals may form; e.g. melanterite and hexahydrite were identified at the Iron Duke pyrite mine in Mazowe Valley, Zimbabwe. These minerals are acid generating, hence de-commissioning and rehabilitation measures are required to precede mine closure (Ravengai et al., 2004). Hence, it is desirable to remediate the sulphate containing streams which have been generated. In the context of de-sulphurising waste rock through accelerated reaction, it is favourable in the first instance to derive useful product from the liberated sulphate, considered below. In the absence of this, remediation of the acidic sulphate stream is required.

7.4.1 Formation and use of gypsum

Gypsum or calcium sulphate dehydrate is formed when sulphuric acid reacts with calcium carbonate to form an insoluble precipitate and is a common approach to the removal of sulphate from acidic waste waters. This synthetic gypsum can be used interchangeably with mined gypsum, allowing conservation of natural reserves while using waste resources. There are a wide range of uses for gypsum in the building industry, including the finishes of walls and ceilings as dry wall or plasterboard, a plaster ingredient, a component of Portland cement in sandlime bricks and fibrous gypsum boards. Plaster developed from waste gypsum has shown improved engineering properties (Pappu et al., 2007).

In addition, gypsum is used as a fertiliser and soil conditioner, as a coagulant, in healthcare products, in plaster of Paris, etc. Phosphogypsum has been proposed as a soil conditioner for calcium and sulphur deficient soils (Pappu et al., 2007), where the absence of heavy metals can be ensured. Its use as a soil conditioner is recent (Agrawal et al., 2004). Where ammonium sulphate is present in the gypsum, it has fertilizer value (Pappu et al., 2007). In India, some 6 million tons of waste gypsum are generated annually (Pappu et al., 2007).

7.4.2 Sulphate reduction to elemental sulphur or to sulphide for metal precipitation

It is well recognised from the copious literature on the biological treatment of acid rock drainage that the sulphate in solution may be biologically reduced to sulphur or sulphide. Most typically, this process cannot be controlled to stop at the sulphur intermediate. Rather, the resultant H_2S may be used for the selective precipitation of metals which are present as metal sulphides, and their subsequent recovery. Alternatively, it may be partially oxidised, through the control of the oxygen environment, to yield elemental sulphur. South Africa remains a net importer of elemental sulphur, despite its extensive sulphate pollution problem. Currently studies are underway to control the oxidation to yield sulphur directly through the use of floating sulphur biofilms (van Hille, 2012).

While these processes are theoretically attainable and have been demonstrated at a pilot scale, their commercial exploitation is not yet cost-effectively demonstrated. Further optimisation, and an accurate estimation of the environmental cost, is required.

7.4.3 Provision of acidity in mineral processing

Acidity is a key requirement for the leaching of base metals from oxide ores and some sulphide ores. This provides a potential source of acidity where the processes are in geographic proximity.

7.4.4 Production of coagulants

The coagulant poly-alumino-sulphate compares well to standard coagulants used to remove colour and dissolved organic matter. Poly-alumino-sulphate can be produced from iron-containing acidic sulphate solutions such as formed through the bioleaching of pyrite (Menezes et al., 2010). In the first stage, the solution is aerated at pH 2.5 to 3.0 to convert all ferrous iron present to ferric iron. The pH is increased to pH 5.0 by addition of NaOH, enabling the selective precipitation of iron and aluminium as hydroxides while preventing precipitation of manganese and zinc. The precipitate is washed and dissolved in sulphuric acid to form the coagulant solution (8.7% Fe, 3.3% Al). On use at a concentration of 0.4 mM, a daily flow-rate of 1200 m^3 of the acidic sulphate solution will enable formation of 45 m^3 of the coagulant. This is sufficient to treat water for 740 000 people (Menezes et al., 2010).

Ferric sulphate can also be recovered from the reaction solution from the bioleaching of pyrite and used as a coagulant (Menezes et al., 2010).

7.4.5 Ferric oxide nanoparticles

Ferric oxide (Fe_3O_4) nanoparticles can be prepared from the acidic sulphate solutions generated on the bioleaching of pyrite (Menezes et al., 2010). These require appropriate surface chemistry to suit application. Potential applications include use in immunoassays, in enhancement of the contrast in magnetic resonance imaging, for detoxification of biological fluids, drug delivery and cell separation (Gupta and Gupta, 2005). Lee et al. (2007) report the use of coated ferric oxide nanoparticles in *in vivo* cancer imaging, allowing use of magnetic resonance imaging concomitantly with optical fluorescence imaging. Applications such as these will require preparation of high purity solutions from which to generate the nanoparticles.

7.4.6 Inorganic pigments

Following formation of the acidic sulphate solution containing iron and metals mobilized from the waste ore, a sludge may be produced on treatment with limestone, lime, soda ash, caustic soda, ammonia, kiln dust or fly ash. Where the iron concentration is high, this may be aerated to achieve ferric hydroxide as a major product. Owing to the inorganic heavy metal content of the resultant sludge, this has potential for use in inorganic pigments (Marcello et al., 2008). Obviously the pigment properties will depend on the gangue mineralogy and cannot be generalized. These can be used in paint, resin, polymer and ceramics.

7.5 USES AND DISPOSAL OF BENIGN TAILINGS

7.5.1 Benign tailings and tailings dams or impoundments

Most mining tailings generated in South Africa are disposed of in tailings dams or impoundments. This holds for many mining countries, except those constrained by land availability. Canada reports a big push towards underground disposal of mining wastes. Desulphurisation of tailings to achieve a bulk benign, unreactive tailings, particularly with respect to ARD generation, and a small volume of reactive tailings follows the premise of “Design for closure”. The cost of rehabilitation of non-acid generating tailings dams has been estimated at ten-fold less than that of acid-generating sites, e.g. 10 000 CAD$/hectare for benign tailings dams relative to 100 000 CAD$/hectare for acid-generating sites (Aubertin et al., 2002, cited by Benzaazoua et al., 2007).

Desulphurised tailings which are shown as non-acid forming can be used as cover material for tailings impoundments to replace water as a covering for the exclusion of oxygen. This is important for the closure phase. It has been demonstrated at Doyon mine, Quebec, Canada (Benzaazoua et al., 2007) and provides a valuable use for the desulphurised tailings generated through the separation methods described above.

Agrawal et al. (2004) prepared a comprehensive article on opportunities for utilisation of mining wastes to enhance resource productivity. They indicate that the tailings from the HZL zinc plant in Chanderia, India are disposed to tailings dams or backfill, or used in constructing embankments, mine roads, playgrounds, or as land fill. It is interesting that, in this review, Agrawal et al. (2004) do not discuss disposal or re-use of these wastes. This is indicative of the unmet potential of these waste streams.

7.5.2 Tailings Disposal and Backfill

Tailings disposal requires potential to concentrate the tailings slurry to ensure that on settling, the water fraction can be suitably reduced. This is important, both for disposal to traditional tailings ponds (although not always achieved) and for backfill. This requires a good understanding of the dewatering of these tailings slurries, as well as their rheology as a function of solids content. The latter informs their pump-ability and ability to deliver to desired disposal locations. As an example, Nguyen and Boger (1998) studied the rheology of clay-based coal tailings. Here, it is demonstrated that by increasing the slurry concentration from the typical 17 wt% to between 40 and 50 wt%, the pumping energy was decreased, mechanical wear reduced owing to reduced velocities and the disposal volumes greatly decreased. These findings strongly motivate improved attention to disposal of concentrated tailings slurries in the future.

Increasingly, tailings are disposed of as paste backfill, which consists primarily of mineral ore tailings and small amounts of cement, mixed to provide a flow-able, and pump-able suspension that can be transported over fairly long distances horizontally but which has a structural strength following curing at its final destination. Increasing backfill also flows by gravity down the mineshaft and into the voids of the exploited mine. To achieve this, the flow-ability of the non-Newtonian fluid is important. The paste is prepared from dewatered tailings, cement (3-5%) and water to achieve a consistency of slump concrete and a solids concentration of 70 to 85% (Brackebusch, 1995; Fall et al., 2005). The advantages of paste backfill include reduced mine dewatering and increased stability. The approach can be used for both underground and “on surface” disposal.

Underground disposal of tailings is increasingly considered from the environmental impact perspective, both as a disposal site for tailings (reducing the requirement for surface tailing impoundments) and owing to the potential to reduce the reactivity of the tailings (owing to reduced access to oxygen and water). Further, by creating cemented tailings backfill, the stability of the exploited underground workings can be improved by providing ground support for the mine structures and preventing or minimizing subsidence occurring on the surface (Kesimani et al., 2005; Fall et al., 2008). These improve the safe working environment. The role of tailings in backfill for stabilising the underground workings has long been recognised. In 1992, Cooke et al. acknowledged the positive role of silicate backfill in stope support applications, owing to its early fill strength, reduced run-off of water and solids and associated reduction in shrinkage. To achieve the support and stability, the microstructure of the hardened backfill is important in determining the mechanical strength and durability (1.5 to 3.5 MPa). To date, the cost of surface disposal in tailings dams remains less than that of backfill (Hassani et al., 1994); however, the cited advantages of backfill as well as the increasing legislative and social requirement to minimise negative environmental impact implies that this approach requires rigorous assessment.

The key factors to consider in cemented tailings backfill include providing the required compression strength, a consistency that will meet the slump requirements and a high solids concentration (70-85%) while minimising cost. The largest contributor to cost is the binder, contributing up to 75% of the cost. Variables identified in the study of Fall et al. (2008) to affect the performance properties include the particle size of the tailings, tailings’ density, cement content and the water to cement ratio. Particularly the fraction of tailings passing 20 µm affects the resultant porosity, water retention and strength (Fall et al., 2005). While increasing the binder added increases strength, it also increases cost substantially (Fall et al., 2005), requiring a compromise to be reached. Further, increasing binder concentrations are required with increasing tailings density, correlating to increased sulphur content, to achieve the required strength. The effect of the mineralogy and petrography of the tailings material on the performance of the cemented paste backfill (CPB) has not yet been rigorously considered, and is expected to be an important variable.

Limited papers in peer reviewed journals are available on the potential for acidification of sulphur compounds present in backfill (Benzaazoua et al., 2004, Thomson et al.,1986, Benzaazoua et al., 2007). It is expected that, owing to the reduced porosity and permeability of these tailing deposits as well as the lack of oxygen availability underground, acidification is reduced significantly. Benzaazoua et al. (2004) demonstrated that the sulphide content of the tailings which are added in the cemented paste backfill influenced the strength of the CPB, with this being a function of the binder type. The mechanical properties improved with increasing sulphide, especially above 12% sulphur. This was attributed to either the increasing volume fraction of binder (owing to its addition on a mass basis) or the precipitation of sulphate-based secondary minerals, enhancing cohesion, as a function of increasing sulphate availability. It was noted that extensive precipitation of sulphate hydrates resulted in sulphate attack, decreasing structural strength.

Further, while oxidation rates of sulphide minerals are decreased by the exclusion of water and air, these can still oxidise in the cemented paste backfill, leading to acid generation. The reduced internal pH in the CPB destabilises the cement hydrates and can reduce durability (Benzaazoua et al., 2004b). The combination of the binder, tailings and mixing water characteristics and ensuing likelihood of acidification influence the strength and subsequent deterioration of the CPB.

Benzaazoua et al. (2007) carried out a pilot scale relating to this by desulphurisation of the tailings from the Doyon gold mine operation in Abitibi, Quebec, Canada. These acid-generating tailings generated at the Doyon mine were 3 wt% sulphur (mainly as pyrite), in the presence of silicates (quartz, muscovite and chlorite) with a specific gravity of 2.83. Their particle size was characterised by a D_{10} of 4 µm, a D_{50} of 22 µm and a D_{90} of 100 µm. This was desulphurised by flotation to produce a low sulphide tailings that were non-acid generating and a reactive tailings from the sulphide concentrate of the separation process, the latter containing 12% sulphide. This acid forming sulphide-rich tailings was used to prepare cemented paste backfill with the addition of 5% by mass binder of Portland cement (30%) and blast furnace slag (70%). Following curing, it was demonstrated that the CPB demonstrated adequate strength as well as improved environmental behaviour compared with no treatment.

Kesimal et al. (2005) presented a study on the disposal of tailings from a massive sulphide mineral ore processing plant for the recovery of copper and zinc from an underground mine in Turkey. Two tailings were studied, both high in sulphides (mainly as pyrite) in the presence of Fe_2O_3 as major component (50 to 60%) with a specific gravity of 4.40 and 4.67 respectively. Their particle size was characterised by a D_{10} of 3.5 and 3.0 µm, a D_{50} of 12 and 9 µm and a D_{90} of 50 and 32 µm. These were formed into CPB using pozzolanic materials such as fly ash, silica fume and blast furnace slag with Portland cement. The study highlights the significant impact of tailings properties on the mechanical strength of the CPB achieved and also suggests that the long term deterioration seen in the mechanical strength of the CPB may result from the oxidation of the sulphide fraction, particularly pyrite, and subsequent acidification with breakdown of the cementious components.

7.5.3 Use of benign tailings in the co-disposal of waste rock to reduce acidification

As discussed in Section 3.1, the acidification of waste rock with the subsequent formation of ARD requires the presence of a microbial community, water and oxygen. Through the co-disposal of non-acid forming tailings (preferably with acid neutralising capacity) and waste rock, it is anticipated that the permeability of the deposit can be minimised to prevent acid forming conditions. Some aspects of this have been investigated previously. For example, Doye and Duchesne (2005) consider co-disposal with alkaline materials to resist formation of acidic conditions. Misra et al. (1996) demonstrated the improved cementation and stabilisation of tailings in the presence of fly ash. The formation of cemented layers within the deposit was shown to reduce the porosity with potential to impact ARD generation (Blowes et al., 1991; McGregor and Blowes, 2002) while cementation in general stabilised the mine tailings (Misra et al., 1996; Choi et al., 2008) This concept is under study (Section 3) and forms a potential sink for benign, non-acid forming tailings.

7.5.4 Use of benign tailings in the construction of wetlands

Constructed wetlands are finding increasing application for the passive treatment of waste streams, through mimicking naturally occurring ecosystems. Silicate rich waste streams have been proposed as suitable constructed wetland media for remediation processes (Schellenbach and Krekeler, 2011). Criteria to be met for this use include appropriate grain size (D_{10} of 0.3 to 2.0 mm, D_{60} of 0.5 to 8.0 mm) and a low Cu content. Further, no mineral deportment should occur and sulphide minerals, likely to cause acidification should be absent (Giese et al., 2011). For a depth of constructed wetland of 1.5 m, a waste stream of average specific gravity of 2.2 will require 33 000 tons per 1 ha of wetland. This bulk usage is appropriate for the use of large volume mining wastes.

It must be noted that mine wastes with toxic heavy metal content should not be mixed with, or allowed to contaminate, soils that will support the growth of plants for animal or human consumption. Cobb et al. (2000) demonstrated that the presence of lead, cadmium, arsenic and zinc in mine waste and in waste-amended soils used for cultivation of vegetables both stunted the growth of the plants (lettuce, radishes, beans and tomatoes) and were accumulated in either the leaves (lettuce and radishes), roots (lettuce, beans, tomatoes, less in radishes) or fruits of the plant, leading to their accumulation in the bodies of animals or humans which are feeding on these plants.

7.5.5 Road construction

The use of silicate-based benign tailings is fairly widely reported for road construction, both of mine roads and of standard paved roads (Agrawal et al., 2004; Pappu et al., 2007). The hard-packing typical of these tailings provides a very durable road surface, even in the absence of pavement. It has been noted that care is required to ensure that metal deportment from such structures to surrounding agricultural land does not occur, supporting the use of benign, non-acid forming tails that do not contain mobilisable heavy metals.

7.5.6 Mine tailings as a cement additive

Against the backdrop of some 300 million tonnes of industrial and mining wastes generated per year in India, building materials are increasing steeply in cost. Examples include the increase in cement from INR (Indian rupee) 1 .25 /kg (US$ 23 per ton) in 1995 to INR 3,75 / kg (US$ 69 per ton) in 2005 to INR 5.4/kg (US$ 100 per ton) in 2013, sand has increased fourfold over the period 1995 to 2005 while bricks increased from INR (Indian rupee) 0.66 /kg (US$ 12 per ton) to INR 1.90 /kg (US$ 35 per ton) over the same 10 year period. Further, the demand for these compounds has increased steeply. The demand for concrete has increased by 50% over the 10 year period. To meet these demands and mitigate the steep cost increase, it is desirable to use the inorganic waste as building material components; however the heterogeneity of these wastes poses a challenge. Uses are sought in cement, bricks, blocks, tiles, paint aggregate, concrete, ceramic products and fuel. Most of the discard from coal waste is used as filler in road embankments. Residues leaving the coal combustion stage (CCRs) may be used in cement, concrete, bricks, backfill, road construction, adhesives, wall board, etc. (Pappu et al., 2007).

The use of mining waste products in the making of cementious products was included in the 1988 patent of Philip et al. from the O'Kiep Copper Company. The patent refers to Portland cement and suggests that these additives are of particular interest where prepared for ballast, rather than structural strength.

Celik et al. (2006) investigated the use of tailings from the extraction of gold from ore as an additive for Portland cement. Prior to use, these tailings from the plant in Bergama, Turkey (94.5% SiO_2 with 1-2% each of Al_2O_3, Fe_2O_3, K_2O; D_{10} = 2.80 µm, D_{50} = 28.8 µm, D_{90} = 75.1 µm) were treated to remove free cyanide and to stabilise the heavy metals present. Dried tailings were added to the cement clinkers across a concentration range of 5 to 25%. The addition of fly ash and silica fume in combination was also considered. The compressive strength properties of the resultant Portland cement were compared with the properties of cement with conventional additives. Up to 25% gold tailings in the cement clinker produced cement of appropriate standard. Blending with silica fume and fly ash increased the compressive strength values. It must be noted that this varies with source of fly ash.

Sobolev and Arikan (2002) report on High Volume Mineral Additive (HVMA) cement comprised of Portland cement, cement clinker, gypsum, mineral additive and an admixture Supersilica (a reactive silica based complex admixture). These are ground together in the ball mill to allow the production of a wide range of concrete products, including high-performance concrete with good compressive strength (140 MPa) while using a substantial fraction of inexpensive and readily available mineral wastes. While their testwork focuses on sand, blast furnace slag and fly ash, they recognise the role of mineral tailings. These are governed by defined standards, including the need to demonstrate binding or pozzolanic properties that provide a synergistic effect and compatibility with Portland cement. Further, the fraction of inexpensive mineral additives can be altered from a low level in high strength cement to up to 70% in low cost cements. The environmental benefits include the use of mining wastes, the conservation of energy and resources, and the reduction of emissions.

7.5.7 Glass or rock wool and glass ceramics from silicate tailings

Rock-wool is produced industrially and used for acoustic and thermal insulation, withstanding temperatures to 1300°C. It is currently made from naturally occurring basalt sands through a process of melting and recrystallization (Marabini et al., 1998). Similarly, glass ceramics are made by melting or sintering balsalt sands and sea sands. Basalt sand contains approximately 50% SiO_2 as the main ingredient, with CaO, Fe_2O_3, MgO and Al_2O_3 being the remaining key components. For rock wool, a characteristic basicity index of unity is required where this can be estimated as:

$$\frac{(SiO_2 + Al_2O_3)}{[CaO + MgO + Fe(tot)]} \approx 1 \qquad [7.1]$$

This can be manipulated by the ratio of oxides present, either through adding basalt or basic quarry waste. Marabini et al. (1998) suggest that silicate tailings can be converted to glass ceramics by starting with a finely divided material with a basicity index of 1, melting this at 1000 to 1600°C to form a bubble free melt. The material is then poured onto a steel plate at 600°C. For the rock wool, the melt is spun (Marabini et al., 1998). The required properties of these products were obtained on manufacture from silicate tailings.

7.5.8 Recovery of other metals

Depending on the gangue mineralogy of the benign tailings fraction, it may be appropriate to recover other metal components from this fraction prior to its disposal. A number of rare metals are associated, for example, with the ash phase of coal. A number of these are of importance in the electronics industry, hence new sources are required.

7.6 DISPOSAL OF SULPHIDE FRACTIONS AND SLUDGES FROM SULPHATE TREATMENT

Where no use is available for the sulphide fraction, this will require disposal with containment to minimise the presence of oxygen, water and micro-organisms to prevent ARD, as is required for all acid-forming tailings. The advantage of the pre-treatment is that the mass of tailings requiring contained disposal is greatly reduced. Alternatively, the sulphide rich fraction can undergo bio-desulphurisation should the use for the soluble sulphate be preferred.

7.7 CONCLUSION

Following the generation of both desired and waste streams in the prevention of ARD, it is important that each of these finds an appropriate use or disposal route. The review undertaken has illustrated that a broad spectrum of approaches are possible. While some of these are only relevant to small volumes of the effluent streams, they may have the potential to generate a product of value to contribute to the costs of ARD prevention, e.g. rock wool. Further, these routes may conserve other resources. In addition to these, applications processing large volumes of materials are required to meet the flows within these systems.

A matching of the potential stream sizes which are generated with the demand for suggested products will be useful to determine the fraction of materials to be considered for disposal. This has the potential to maximise resource productivity and allow an industrial ecology approach to be implemented. However, the analysis is required on a regional basis and will vary from region to region.

CHAPTER 8: FLOTATION DESULPHURISATION PLANT DESIGN FOR COSTING SULPHIDE REMOVAL

8.1 INTRODUCTION

Acidic drainage as a result of mining and mineral processing activities is a reality in South Africa. ARD remediation measures in-place are variable, not only in South Africa but worldwide. Desulphurisation of coal fines by flotation is a potential method to control acidic drainage. A two stage flotation process is proposed, as described in Chapter 5. This yields a saleable mineral product, a low volume sulphide rich fraction and a benign tailings fraction. The three products of this flotation process all have revenue generating potential subject to further investigation, as discussed in Chapter 7. This may make this process economically feasible and is important in cases of abandoned mines where capital to finance remediation is not easily accessible.

The aim of this chapter is to develop the framework for providing an order-of-magnitude cost estimate for a conceptual two-stage coal flotation desulphurisation plant with a capacity of 100 t/h. This model is based on the specific project assumptions and is therefore indicative only. It is expected to be subject to change as assumptions are improved. The accuracy of the order-of-magnitude estimate is within ± 30% to ± 50%; the assumptions that have been made follow the guidelines for making such estimates.

The plant has been designed to treat nominal coal fines from a dump of an abandoned mine in the Witbank/Middleburg coal field. It was the practice for some coal mines without fines beneficiation plants to dump the untreated material. Although termed “fines”, these dumps frequently contained significant quantities of +850 µm material.

8.2 PROJECT SCOPE

The scope of the project is an ultrafine coal flotation plant with a milling circuit, two stages of flotation and a dewatering circuit. The basis of the proposed flowsheet follows the process shown in Figure 61. Milling is included to allow the coal to be floated at -150 µm. The plant products include a clean coal concentrate, a sulphide-rich concentrate and a sulphide-lean flotation tailings (benign).

The plant capacity is in the order of 720,000 tonnes per annum. Yearly production includes:

- 576,000 tonnes of clean coal,
- 57,600 tonnes of sulphide-rich concentrate and
- 86,400 tonnes of benign tailings.

There is a domestic market for a fine coal product with a calorific value in the order of 23 MJ/kg. Export markets, such as India, also exist subject to product quality requirements. The project life is set at 15 years and plant availability at 82%. The chosen plant location is Middleburg, a coal mining area in South Africa. Due to the already existing mining activities in Middleburg, it is assumed that transport networks, water supply and labour are readily available. The climate consists of wet summers and dry winters. The summer season is from October to February and temperatures average 26°C. The winter season is from April to August and temperatures average 8°C.

8.3 PROCESS DESCRIPTION

The plant throughput is 100 t/h and the feed consists of coal fines. The process flow includes milling, flotation and dewatering as shown in Figure 61.

8.3.1 Milling Circuit

A front end loader tips the feed into the receiving bin, from which it is conveyed to the mill by means of a plate feeder. Water is added to form a slurry. The mill reduces the particle size to 80% passing 150 micron. Process water is added to the mill product sump to obtain the required feed density to the hydrocyclones. The hydrocyclone classifies the particles through the action of centrifugal forces. The mill is in closed circuit with the hydrocyclones: the cyclone underflow is returned to the mill while the overflow proceeds to the flotation circuit.

8.3.2 Flotation Circuit

The two stage flotation circuit consists of coal and sulphide flotation. The cyclone overflow (P_{80}: -150 µm) is conditioned in a tank to which flotation reagents are added. Oleic acid acts as a collector for the oxidised coal and MIBC promotes froth formation. The slurry enters the first stage flotation bank where clean coal is floated and recovered as concentrate. The first stage tailings flow to the second stage conditioning tank where the sulphide flotation reagents are added. PAX acts a sulphide collector, MIBC promotes froth formation and dextrin acts as a coal depressant. The slurry then flows into the second stage flotation bank, where sulphide is floated and recovered as concentrate, and a sulphide-lean stream is recovered as tailings. The three products from the flotation circuit flow to the dewatering circuit.

8.3.3 Dewatering circuit

Clean coal concentrate, sulphide-rich concentrate and sulphide-lean tailings have high moisture content and these are pumped to the plate and frame filter presses and thickener. Filter presses are used to recover water from the coal and sulphide concentrates. The tailings are thickened and filter presses are used to recover water. The recovered water is pumped and re-used as process water. The dewatered products are conveyed to stockpiles.

Fresh water is collected in a tank and is pumped to the process plant. The recovered water from the flotation products is pumped and used as process water. Spillages in the plant are recovered by sump pumps and fed to the process.

8.4 PROCESS DESIGN

In order to come up with the cost estimates, the feed throughput, separation efficiency and plant capacity were estimated as reported in Table 40.

Table 40: Design assumptions

Parameter	Value
Feed throughput	100 t/h
Coal yield	80 t/h
Sulphide fraction concentrate	8 t/h
Benign tailings	12 t/h
Operating hours	8400
Plant availability	82%
Plant capacity	720000 t/annum

The design criteria are summarised in Tables 41 to 45. These are based on the following estimates or assumptions:

A: Assumed based on project information
B: Determined from calculation/models
C: Estimate – rule of thumb

The feed particle size distribution is given in Figure 60. The process flowsheet is shown in Figure 61 and the material balance is shown in Figure 62.

Table 41: Feed characteristics

Parameter	Units	Value	Source
Feed size	µm	+850	A
Moisture content	% w/w	8	C
Ore Bond work index	kWh/t	13	C
Coal yield	%	80	A
Sulphide recovery	%	8	A
Design bulk density	ton/m^3	0.8	C
Ore density	ton/m^3	1.4	C
Net acid generation	kg H_2SO_4/ton	NAG pH < 4.5 $NAG_{pH7} > 10$	A
Net acid production potential	kg H_2SO_4/ton	> 20	A

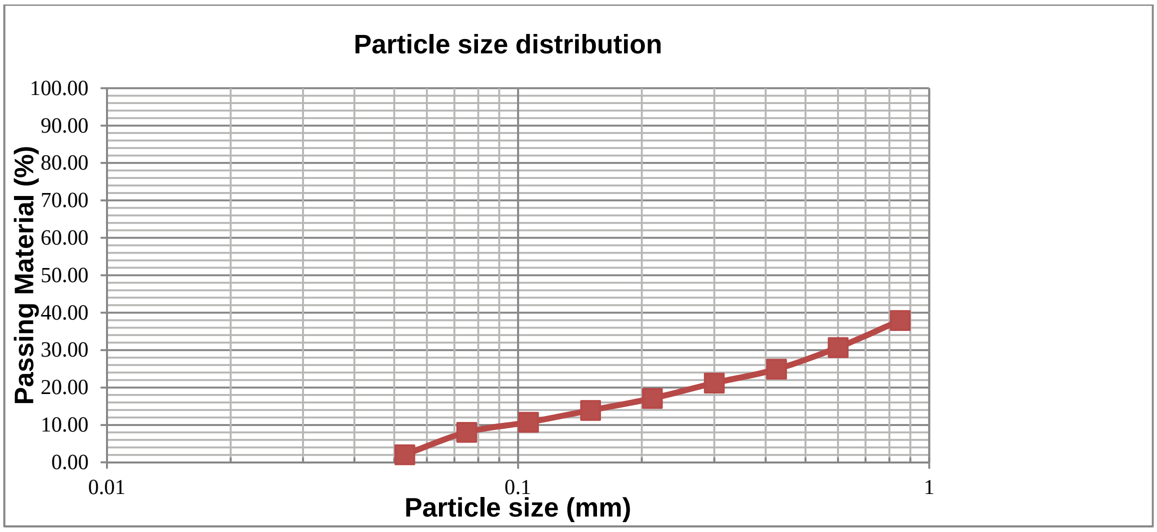


Figure 60: Particle size distribution

Table 42: Milling circuit

Parameter	**Units**	**Value**	**Source**
Plant throughput	t/h	100	A
Ore envelope	µm	+850	A
Mill throughput	t/h	350	B
Fresh feed	t/h	100	A
Ball mill circulating load	%	250	C
Product size: P_{80}	µm	150	C
Hydrocyclone feed density	% v/v	14	C

Table 43: Flotation circuit

Parameter	**Units**	**Value**	**Source**
First stage flotation			
Conditioning time	min	5	A
Coal flotation cells	-	7	B
Retention time	min	5	B
Feed solids	% w/w	10	C
Yield	%	80	A
Concentrate: net acid generation	kg H_2SO_4/ton	NAG pH < 4.5 $NAG_{pH7} > 10$	A
Concentrate: net acid production potential	kg H_2SO_4/ton	> 20	A
Second stage flotation			
First stage tailings: second stage feed	t/h	20	B
Conditioning time	min	5	A
Sulphide flotation cells	-	11	B
Retention time	min	20	B
Feed solids	% w/w	3	B
Yield	%	40	A
Sulphide concentrate	t/h	8	B
Sulphide concentrate: net acid generation	kg H_2SO_4/ton	NAG pH < 4.5 $NAG_{pH7} > 10$	A
Sulphide concentrate: net acid production potential	kg H_2SO_4/ton	> 20	A
Benign tailings	t/h	12	B
Benign tailings: net acid generation	kg H_2SO_4/ton	NAG pH > 4.5	A
Benign tailings: net acid production potential	kg H_2SO_4/ton	< -20	A

Table 44: Dewatering circuit

Parameter	**Units**	**Value**	**Source**
Coal concentrate plate and frame filter press			
Ore envelope: F_{80}	µm	150	A
Feed solids	% w/w	20	C
Filter cake solid	t/h	80	B
Filter cake moisture	% v/v	20	C
Sulphide concentrate plate and frame filter press			
Ore envelope: F_{80}	µm	150	A
Feed solids	% w/w	20	C
Filter cake solid	t/h	8	B
Filter cake moisture	% v/v	20	C
Tailings thickener			
Ore envelopes: F_{80}	µm	150	A
Feed solids	% w/w	2	B
Underflow	m^3/h	27	B
Overflow	m^3/h	637	B
Solids moisture	% w/w	60	C
Tailings plate and frame filter press			
Feed solids	% w/w	40	C
Filter cake moisture	% v/v	20	C

Table 45: Reagents

Parameter	**Units**	**Value**	**Source**
First stage flotation			
Collector: Oleic acid	kg/tonne	2.79	A
Frother: Methyl isobutyl carbinol (MIBC)	kg/tonne	0.28	A
Second stage flotation			
Collector: Potassium amyl xanthate (PAX)	kg/tonne	2.33	A
Frother: MIBC	kg/tonne	0.11	A
Depressant: Dextrin	kg/tonne	0.93	A
Flocculant			
Polymer	kg/tonne	0.07	C

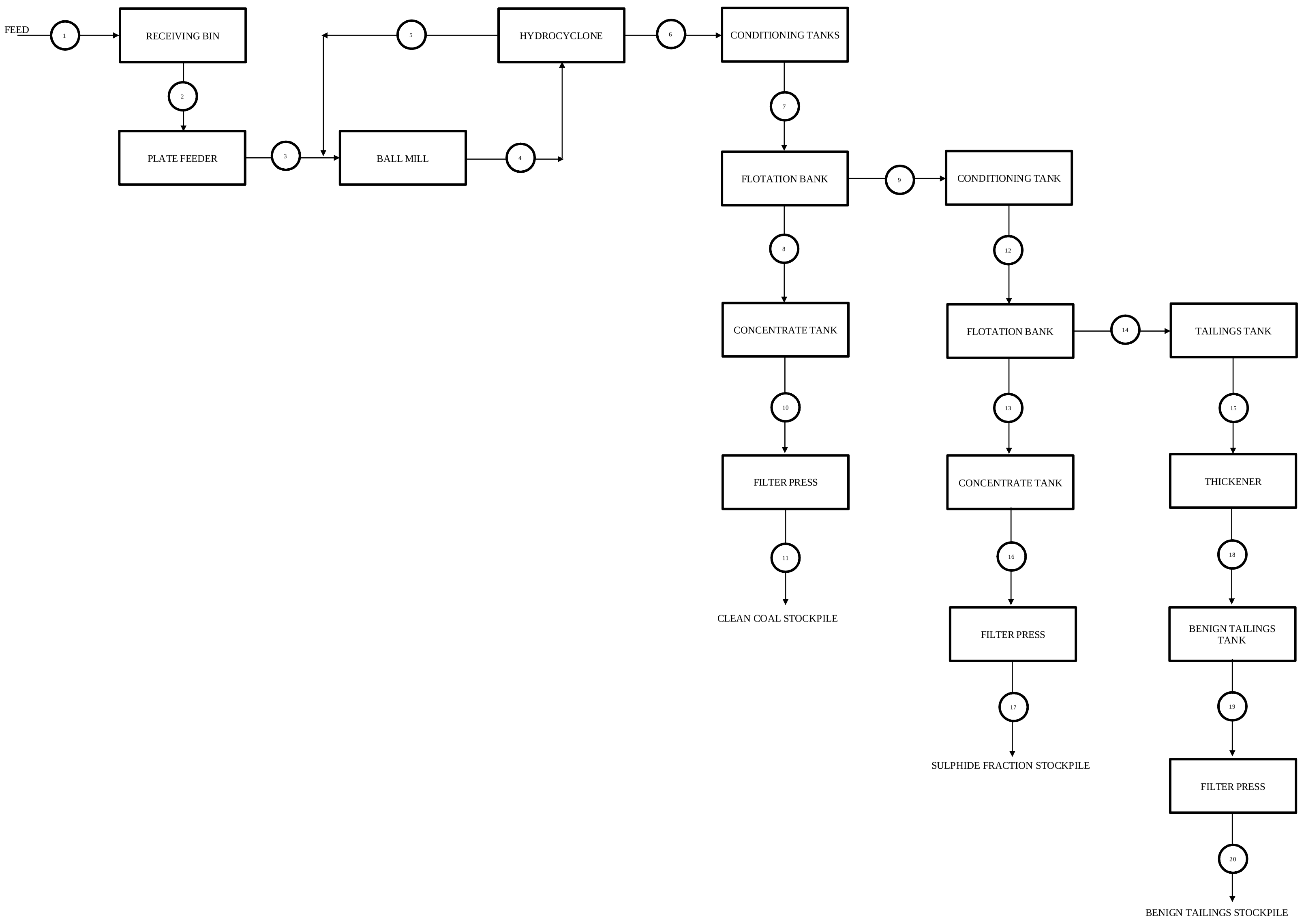
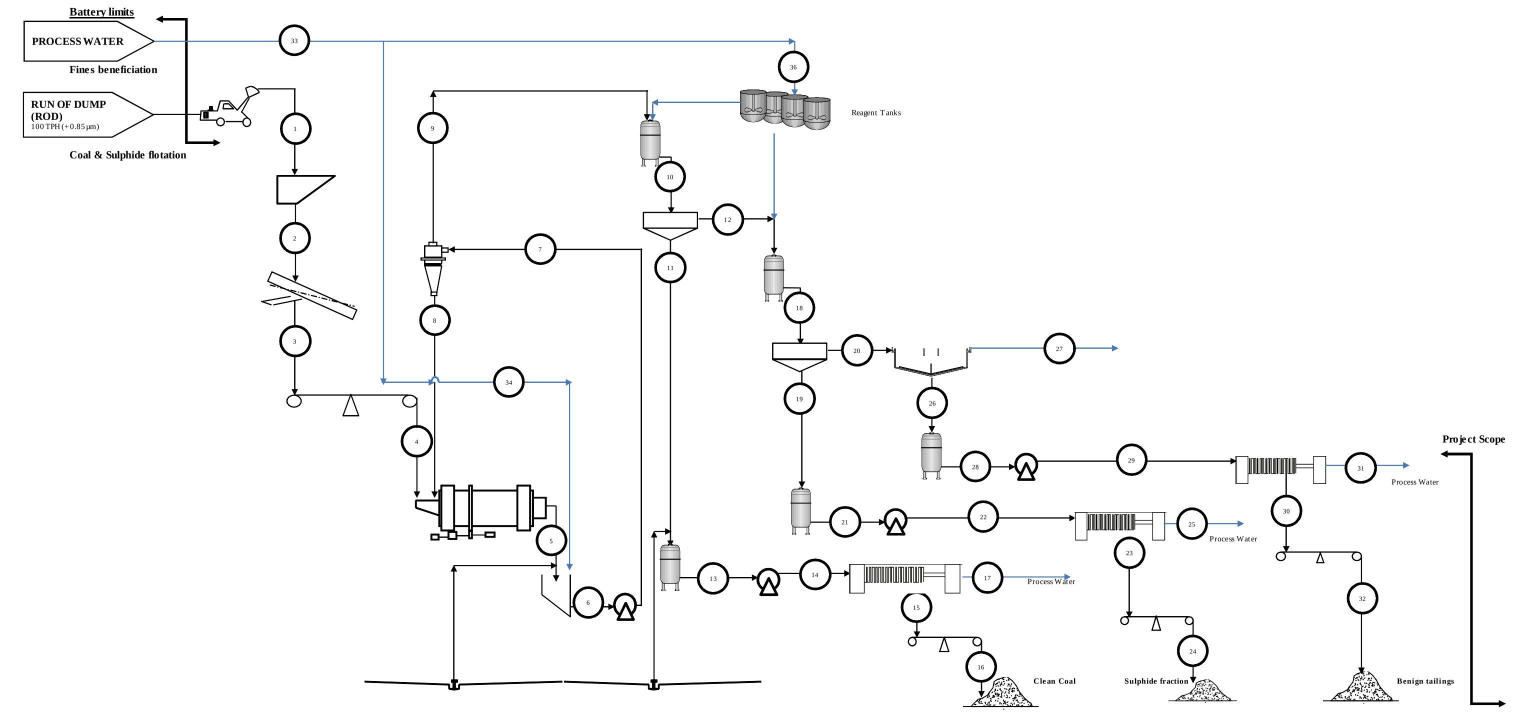


Figure 61: Process flowsheet for desulphurisation of fine coal



Process Stream	ROD	Bin	Plate Feeder	Conveyor Belt	Ball Mill Discharge	Surge Tank Discharge	Classification Cyclone Feed	Cyclone Underflow	Cyclone Overflow	Conditioning Tank Discharge	1st stage Flotation Concentrate	1st stage tailings	Clean Coal Slurry	Filter Feed	Clean Coal	Clean Coal	Filtered Water	2nd Stage Flotation Feed
Stream No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
Solid feedrate [t/h]	100.0	100.0	100.0	100.0	350.0	350.0	350.0	250.0	100.0	100.0	80.0	20.0	80.0	80.0	80.0	80.0	0.0	20.0
Water feedrate [m^3/h]	8.0	8.0	8.0	8.0	467.7	1416.7	1416.7	467.7	949.0	949.0	320.0	629.0	320.0	320.0	14.3	14.3	305.7	629.0
Slurry feedrate [m^3/h]	79.4	79.4	79.4	79.4	717.7	1666.7	1666.7	646.3	1020.4	1020.4	377.1	643.3	377.1	377.1	71.4	71.4	305.7	643.3
Slurry feedrate [t/h]	108.0	108.0	108.0	108.0	817.7	1766.7	1766.7	717.7	1049.0	1049.3	400.0	649.0	400.0	400.0	94.3	94.3	305.7	649.0
Slurry density [t/m^3]	1.36	1.36	1.36	1.36	1.14	1.06	1.06	1.11	1.03	1.03	1.06	1.01	1.06	1.06	1.32	1.32	1.00	1.01
Solids volume fraction	100%	100%	100%	100%	35%	14%	14%	25%	7%	7%	15%	2%	15%	15%	80%	80%	0%	2%
Solids mass fraction	100%	100%	100%	100%	43%	20%	20%	35%	10%	10%	20%	3%	20%	20%	85%	85%	0%	3%
Ore S.G. [t/m^3]	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40

Process Stream	2nd Stage Concentrate	2nd Stage Tailings	Sulphide Concentrate	Filter Press Feed	Sulphide Fraction	Sulphide Fraction	Filter Press Recovered Water	Thickener Underflow	Thickener Overflow	Benign Tailings Slurry	Benign Tailings Slurry	Benign Tailings	Filter Press Recovered Water	Benign Tailings	Process Water Feed	Reagent Make-up Water	Cyclone Feed Water
Stream No.	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**
Solid feedrate [t/h]	8.0	12.0	8.0	8.0	8.0	8.0	0.0	12.0	0.0	12.0	12.0	12.0	0.0	12.0	0.0	0.0	0.0
Water feedrate [m^3/h]	32.0	597.0	32.0	32.0	1.4	1.4	30.6	17.9	579.1	17.9	17.9	2.1	15.8	2.1	49.8	0.4	949.0
Slurry feedrate [m^3/h]	37.7	605.6	37.7	37.7	7.1	7.1	30.6	26.5	579.1	26.5	26.5	10.7	15.8	10.7	49.8	0.4	949.0
Slurry feedrate [t/h]	40.0	609.0	40.0	40.0	9.4	9.4	30.6	29.9	579.1	29.9	29.9	14.1	15.8	14.1	49.8	0.4	949.0
Slurry density [t/m^3]	1.06	1.01	1.06	1.06	1.32	1.32	1.00	1.13	1.00	1.13	1.13	1.32	1.00	1.32	1.00	1.00	1.00
Solids volume fraction	15%	1%	15%	15%	80%	80%	0%	32%	0%	32%	32%	80%	0%	80%	0%	0%	0%
Solids mass fraction	20%	2%	20%	20%	85%	85%	0%	40%	0%	40%	40%	85%	0%	85%	0%	0%	0%
Ore S.G. [t/m^3]	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40

Figure 62: Process flow diagram for desulphurisation of fine coal using two-stage flotation

8.5 SITE REQUIREMENTS

8.5.1 Power supply

Electrical power is needed to run the flotation plant. Process plant power consumption in the order of 2 MW is estimated and electrical grid connections are assumed to be available. Provision is made for a generator in case of power cuts or power interruptions for essential equipment. Fire extinguishers and carbon dioxide protection for electrical substations are to be in place.

8.5.2 Water supply

Water is used in the process plant, supporting facilities and human consumption. The dewatering circuit is designed to recover water from the products which is recycled for use in the plant, while plant spillages are pumped back into the process. A water circuit for fighting potential fire in all areas is required. Fresh water supply is assumed to be available from the local municipality and allowance has been made for the installation of water infrastructure.

8.5.3 Transport

Road and rail networks will provide access to the plant. Chemical reagents and other raw materials will be supplied by vendor vehicles to the plant. Plant personnel will travel by road. Clean coal product will be transported on rail wagons. Allowance has been made for transport networks to meet operational plant traffic.

8.5.4 Site structures

Process plant structures, workshop, laboratory, offices and stores are expected to be fit for intended purpose.

8.5.5 Labour

Labour required for construction purposes will be available in surrounding areas. It is assumed that local labour supply is available to meet operational plant requirements and can be easily trained.

8.5.6 Environmental impact and effluent disposal

The aim of flotation desulphurisation is to prevent formation of acidic water. Benign tailings formed as a result of flotation have the potential to be used as capping cover material, subject to further investigation. The sulphide product will be contained and handled in an environmentally acceptable manner. Allowance has been made for disposal costs. Potential for use as a product has not been included in this study.

8.6 EQUIPMENT LIST

A list of the major equipment including plate work considered for this estimate is included in the following Table 46. Equipment was designed with an average live capacity of 100 t/h.

Table 46: Major equipment list

Equipment	**Quantity**	**Capacity (Q)**
Milling section		
Feed bin	1	Q = 100 t/h Volume = 125 m^3
Plate feeder	1	Q = 100 t/h
Feed conveyor	1	Q = 100 t/h L= 30 m W = 600 mm
Mill sump tank	1	Q = 2500 t/h = 2600 m^3/h Volume = 20 m^3
Mill slurry pump	1	Q = 2500 t/h = 2600 m^3/h Diameter = 775 mm
Ball mill	1	Q = 718 t/h = 818 m^3/h Dia = 3.5 m EGL = 5.2 m
Hydrocyclone	2	Q = 2500 t/h = 2600 m^3/h Diameter = 800 mm
Flotation circuit		
Reagent tanks	5	Volume = 0.1 m^3
Conditioning tank	1	Q = 1020 t/h = 1049 m^3/h Volume = 90 m^3
Conditioning tank	1	Q = 643 t/h = 649 m^3/h Volume = 55 m^3
Flotation cells	7	Q = 1020 t/h = 1049 m^3/h H = 4 m Dia = 4.8 m Total volume = 165 m^3
Flotation cells	11	Q = 643 t/h = 649 m^3/h H = 2.4 m W = 4.2 m Total volume = 407 m^3
Flotation pump	1	Q = 643 t/h = 649 m^3/h Diameter = 530 mm
Dewatering circuit		
Tailings filter press	1	Q = 30 t/h = 27 m^3/h
Coal conveyor	1	Q = 80 t/h L = 30 m W = 600 mm
Sulphides conveyor	1	Q = 8 t/h L = 30 m W = 600 mm
Benign tailings conveyor	1	Q = 12 t/h L = 30 m W = 600 mm
Process water tank	1	Q = 950 t/h = 950 m^3/h Volume = 200 m^3
Sump pump	2	Diameter = 290 mm
Process water pump	1	Q = 950 t/h = 950 m^3/h Diameter = 775 mm
Fresh water pump	1	Q = 18 t/h = 18 m^3/h Diameter = 221 mm
Process water tank	1	Q = 950 t/h = 950 m^3/h Volume = 200 m^3

8.7 CAPITAL COSTS

Table 47 lists capital expenses for setting up a two stage flotation plant. Major equipment prices were obtained from vendors and rough cost estimations were made. The total capital expenditure is estimated at ZAR 198 million, based on the assumptions made. A contingency of 20% was assumed.

Table 47: Capital costs

Parameter	Estimation	ZAR (*1000)
Equipment	35%	53,000
Equipment delivery	7%	10,600
Equipment installation	10%	15,142
Instrumentation and controls	3%	4,542
Piping	7%	10,600
Electrical	8%	12,114
Buildings -structural steel	17%	25,742
Civil and earthworks	9%	13,628
Yard improvements	1%	1,514
Service facilities	3%	4,542
Sub-total (A)	100%	151,428
Engineering and supervision*	5%	7,571
Construction*	5%	7,571
Start-up costs*	1%	1,514
Contingency*	20%	30,285
Total cost	131%	198,371

*** these are based on the direct equipment cost (A)**

8.8 OPERATING COSTS

The factors contributing to the operating costs for the flotation plant are listed in Table 48. The total operating costs amount to ZAR 161 million per annum with a 20% contingency. The flotation reagent costs are particularly high and are summarised in the Table 49. Flotation reagents are highlighted as an area for further study for this application.

Table 48: Operating costs

Operating costs	
Parameter	**ZAR (*1000)**
Water	1,050
Electricity	21,000
Labour	16,800
Maintenance	2,650
Overhead	3,600
Laboratory	1,440
Reagents	70,738
Transport	14,400
Disposal cost	2,633
Contingency	26,969
Total cost	160,647

Table 49: Reagent costs

Reagent	Flow rate (t/h)	Flow rate (tonnes/year)	ZAR/year (*1000)
Collector: Oleic acid	0.279	2,099	57,852
Frother: MIBC	0.028	202	3,830
Collector: PAX	0.047	336	7,817
Depressant: Dextrin	0.019	134	1,238
Polymer	0.0008	7	272

8.9 CASH FLOW ANALYSIS

Based on the estimates of capital and operating expenditure, a net present value (NPV) of ZAR 50 million and internal rate of return (IRR) of 19% was calculated. Table 50 provides a summary of the cash flow analysis. Closure costs and taxes have been excluded in this estimation. The order of magnitude estimate is based on earnings before interest, taxes, depreciation and amortisation. Clean coal sales revenue generated based on the assumptions made is shown in Table 51.

Table 50: Project cash flow analysis

Valuation and assumptions		
	Value	**Unit**
Project NPV	50 million	ZAR
Discount rate	14	%
Internal rate of return	19	%
Assumptions		
Coal Price	349	ZAR/t

Table 51: Product Price Estimate

Product	Flow rate (t/year)	Unit Price (ZAR/t)	Revenue (ZAR/year)
Coal concentrate	576,000	349	201 million

As stated in Section 8.1, this model is not conclusive but rather a framework that will allow different process assumptions to be made, and different options to be evaluated, subject to the results of further test work.

8.10 SENSITIVITY ANALYSIS

Sensitivity analysis shows how positive and negative changes in the input variables may affect the project NPV. In Figure 63 to 68, the effect on NPV of specific project assumptions made such as coal price, yield, utilisation, reagent costs, capital and operating estimates are shown.

The base price for coal used is ZAR 349 per tonne. The effect on the project NPV of an increase in base price of up to 60% (ZAR 558 per tonne) and a decrease of up to 60% (ZAR 140 per tonne) is shown in Figure 63. The project NPV is sensitive to coal prices; a decrease in the market value of coal from the base will make the project unprofitable. There are potential uses for the sulphide concentrate and benign flotation tailings products subject to further investigation, with the result that additional revenue may be generated.

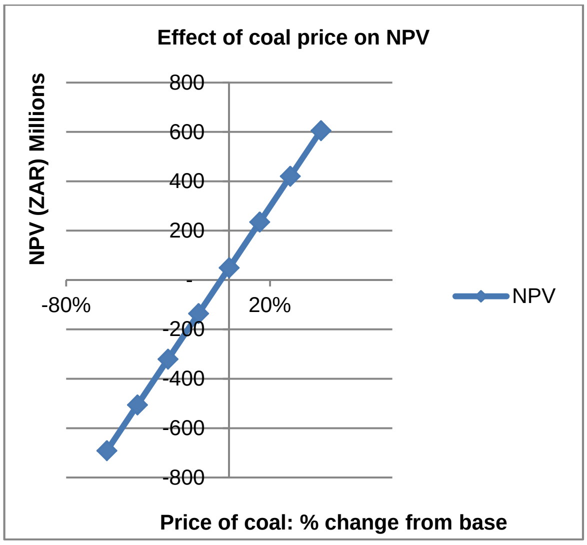


Figure 63: Sensitivity of NPV to coal price

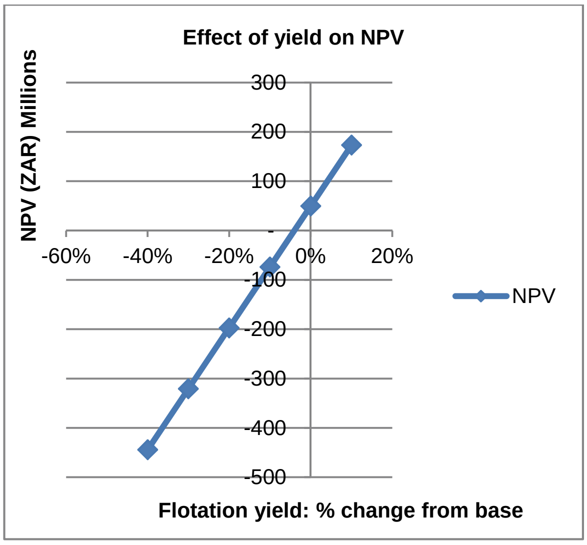


Figure 64: Sensitivity of NPV to flotation yield

Low yields of coal flotation result in low revenue and negative NPV values as shown in Figure 64. The base for coal yield is 80%, input variables are altered in the range +10% to -40%.

Capital costs have a minor impact on the project NPV. At above 20% change to the base value of ZAR 198 million, the project becomes less viable. The project is sensitive to operating costs, an increase to the base value of ZAR 161 million reduces project feasibility.

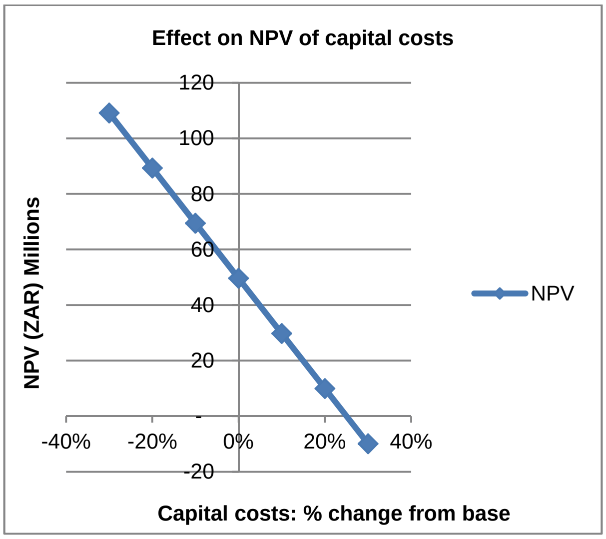


Figure 65: Sensitivity of NPV to capital costs

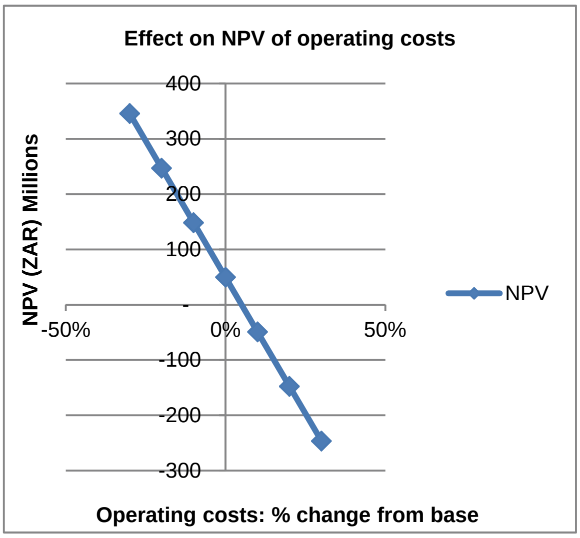
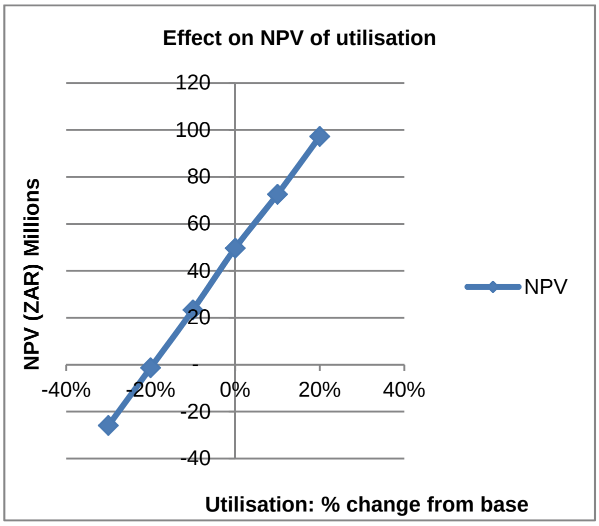


Figure 66: Sensitivity of NPV to operating costs

The base value for utilisation is 82%, at -20% change to the base the project NPV is negative. The base value for reagent costs is ZAR 71 million, at 5% change to the base value the NPV is zero. Subsequent research has shown that flotation reagent dosage can be reduced significantly up to a factor of 10%. This will have a positive impact on the project economics as reagent costs have the highest contribution to operating expenditure.

The project input variables: coal price, reagent costs, operating costs and coal yield have a significant impact on NPV.



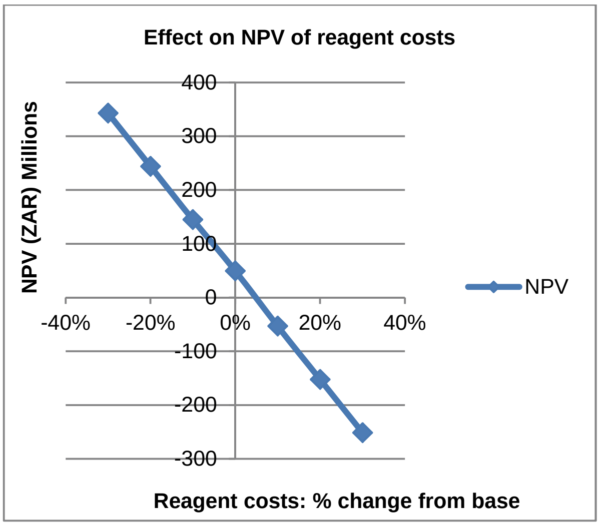


Figure 67: Sensitivity of NPV to utilisation

Figure 68: Sensitivity of NPV to reagent costs

8.11 CONCLUSION

The flotation desulphurisation flowsheet proposed follows a traditional coal flotation process flowsheet with an additional stage for sulphide flotation added. An order-of-magnitude estimate model is proposed for a new coal flotation desulphurisation plant. The preliminary financials based on specific project assumptions reflect possible viability. Further testwork and different process models will provide more information on economic viability of this approach. The process flowsheet is amenable to optimisation, subject to further investigations.

Sensitivity analysis shows the impact of the project assumptions made such as coal price, flotation yield, reagent costs, utilisation, operating and capital costs on project NPV. Further investigation into potential uses of the sulphide fraction and tailings fraction and the markets for these possible products may provide additional revenue sources to the project. It is important to consider that the waste stream from the coal plant is significantly reduced and can be contained, reducing waste handling costs not yet accounted for here. Coal remains an important commodity and source of energy for domestic and industrial consumers. In addition to the reduction of ARD generation potential, improved resource productivity is obtained for the coal mined.

This plant design has been based on treating coal fines from historical (dumped) tailings. Application of flotation desulphurisation to an operational mine may see some of the projected costs absorbed in the mine running costs and a reduction of waste streams. Specifically potential may exist to achieve these goals partly by including multi-decision making criteria into the selection of coal handling regimes.

CHAPTER 9: CONCLUSIONS & RECOMMENDATIONS

9.1 THE RESEARCH FOCUS

The ideal approach to handling of sulphidic waste rock is to prevent the potential for generation of ARD through the removal of the sulphide phase before its disposal, thus avoiding the need for long-term mitigation strategies. In the best case, this processing of waste rock prior to disposal should result in an increase in the recovery of values from the starting material and the re-allocation of waste materials as feedstocks for other uses. In this study, research has explored the potential to achieve the scenario just described through extension of the preliminary study on the prevention of ARD, initiated in WRC 1831/1/11.

Particularly, this project has aimed to establish the feasibility of the approaches proposed in the previous report and extend these. While the potential for the removal of sulphide from tailings was demonstrated in WRC 1831/1/11, in WRC K5-2015 its general application across tailings from various sources, the cost implications and disposal routes for the sulphide fraction removed have been investigated. With respect to removal by reaction, accelerated bioleaching has, to date, shown limited value. Potential exists to seek improvements and alternative reaction approaches have been proposed. For implementation of these, a good knowledge on the opposite approach of restricting waste rock dump permeability is essential and has been addressed.

The report on this study is structured to consider the following:

1. Review of current rock drainage prevention strategies
2. Review of ore bed permeability and its impact on ARD generation reactions
3. Experimental studies with respect to the effect of packing on bed permeability and leaching
4. Experimental studies on the effect of irrigation on colonization, moisture content and stagnant zones
5. Approaches to modelling and / or predicting bulk fluid flow in the rock bed
6. Further considerations of sulphide removal by reaction
7. Sulphide removal from tailings by separation across a variety of tailings materials, including a base mineral tailings (WRC 1831/1/11), coal fines and gold tailings, to establish the generic value of the approach
8. Potential uses for the streams generated by sulphide separation
9. Provision of a framework for costing of the sulphide separation, with preliminary insights.

9.2 PERMEABILITY, FLUID FLOW, MASS TRANSFER AND COLONISATION

It is well recognised that hydrology and mass transfer are factors in efficient bioleaching, hence these impact ARD formation. By restricting the ingress of water and oxygen, bioleaching reactions can be slowed and, with this, the generation of ARD. Current rock drainage prevention strategies focus on this limitation of provision of reactants through the use of covers and coatings. While these have been shown to be effective, the life span of their effectiveness remains in question, motivating the topic of this project in which, ideally, the risk of ARD formation is eliminated through the removal of the sulphide fraction. Where this is not possible due to limited liberation, prevention of the reaction is sought. In this report, the former is considered for tailings and finely divided waste rocks, and the latter for larger, unliberated waste rock.

Strategies to limit the permeability of waste rock dumps to restrict access of reactants were reviewed. Two predominant approaches were found: provision of borders or covers, and reduction of bed permeability through the co-mingling of waste rock with fine material. Discussion of the latter in the literature is limited.

Waste rock dumps are characterized by non-homogeneous flow and channelling. The impact of particle size distribution and irrigation rate on preferential flow patterns through well characterised materials under saturated conditions has been described; however this is poorly characterised in inhomogeneous ore beds characteristic of waste rock dumps. Further the influence of these on gas and heat transport further impacts ARD formation. Very few rigorous hydrology studies are reported and those that do exist relate to the smaller particle size distributions of soils, rather than waste rock dumps. These studies do provide useful insight of the interactions between flow patterns, microbial colonisation and clogging, be it with heterotrophic microbial populations in soils or precipitates in waste rock dumps. To date, most discussion of hydrology of waste rock dumps and low grade mineral heaps for extraction has been based on modelling studies. From the studies reported, the distribution of the heap between flowing liquid, stagnant liquid, particles and the gas phase is key. Recently, new approaches to the study of flow through partially saturated inhomogeneous rock beds using novel tomographic approaches have highlighted the poor understanding of this aspect and, consequently the limited value of current models, highlighting the critical need for fundamental developments in this area to allow for appropriate prediction and modelling.

In the light of the limitations of predictive studies, a series of experimental studies were undertaken. The limitations of these small scale studies is well established, hence these studies were used to establish trends, rather than specific flows. To inform the experimental study, preliminary work was conducted to establish methodology and provide proof of concept using a model solid system of glass beads and sand in 4 kg columns of 10 cm diameter. The model study has demonstrated that by including a fraction of fine particles with the waste ore in the dump, the permeability of this bed can be manipulated to reduce fluid flow, thus decreasing the supply of reactants to the reactive sulphide mineral sites. While a substantial reduction in permeability was achieved with a uniformly mixed system (co-mingling), the greatest impact was found on using layers of fine particles to reduce bed permeability. Permeability decreased, residence time increased and degree of saturation increased with decreasing particle size for uniformed sized particles. Most importantly, the model solid system supported the concept that by including a fraction of fine particles with the waste rock material in the dump, permeability can be manipulated and flow restricted, restricting access of reactants to the reactive sulphide minerals present.

Forced bioleaching studies were conducted with a low grade ore to compare leach rates of agglomerated and layered ore in the 4 kg columns of 10 cm diameter. It is evident from the study of packing configurations that the agglomeration of fine material onto coarse particles provides both enhanced permeability of the ore bed as well as providing a niche environment for microbial colonisation (Govender et al. in press). The absence of the agglomerated fine material reduced the residence time in the ore bed and slowed the leach rate and thereby ARD generation rate. In addition the introduction of layers of fine material further slowed the leach rate through decreased permeability. Importantly, colonisation of the waste rock dumps by iron-oxidising micro-organisms lead to the ongoing regeneration of leach agents, thereby de-coupling ARD generation from the flow of liquid and allowing continual generation across time. It is essential to provide tools by which to estimate the time scales for the onset of ARD formation under these differing packing and operational regimes. This is recommended as a key focus area for ongoing research.

The impact of flow rate on colonization and leaching was also studied experimentally. Here it was shown that the rapid irrigation rates result in a greater flow of micro-organisms through the bed while reduced irrigation rates encourage microbial colonisation of the waste rock bed. Preliminary data on associated leach rates of low grade ore as a function of irrigation rate are available. These data are important to predicting the colonisation of waste rock dumps where precipitation results in temporal regions of high and low flow.

Irrigation of the waste rock bed from a single point demonstrated that regions of differing moisture content develop. Where ‘drier’ regions with moisture content was around 7%, colonisation was not detected with methods used (<103 cells per kg), whereas in higher moisture zones around 10%, colonisation was significant (109-1011 cells per kg).

9.3 SULPHIDE REMOVAL

Previous studies on the removal of sulphide from tailings by separation were reviewed. This demonstrated that significant strides forward have not been reported in the open literature since WRC 1831/1/11. This highlighted the importance of conducting studies to validate the applicability to other tailings streams, as well as to characterise the nature of the resultant streams exiting the separation such that routes for their use or disposal can be considered.

Previous studies on the removal of sulphide by reaction were reviewed. Here limited work on accelerated bioleaching was reviewed. Most notably the use of potassium ferrate as an oxidizing agent and use of the Fenton reaction provide interesting approaches. The recent report on the Fenton reaction is confirmatory of recent work conducted in the CeBER laboratories at UCT with respect to bioleaching and opens a new and interesting avenue for consideration, which is recommended.

The studies on the removal of the sulphide fraction from tailings or finely divided waste material by flotation in order to remove the risk of ARD formation, initially reported in WRC 1831/1/11 for base metal tailings, have been extended considering also refractory gold ore tailings and fine coal. In all cases (8 sample materials), except one, flotation successfully removed the majority of the sulphide material into a concentrate stream, leaving the bulk of the tailings with very low residual sulphide. Using both static tests (acid-base accounting and net acid generation) and the newly developed biokinetic test, these bulk tailings were largely demonstrated to be non-acid forming and thereby benign. Further, in several cases, a further recovery of the "values" was also obtained. All streams have been characterised in terms of values, sulphide, ANC and ARD generating potential, providing a framework against which to access further use or disposal.

It is noted that the characterisation provided by static tests is limited. While the biokinetic test previously developed does provide extended information, its refinement to enhance the information provided is recommended. Further the use of mineralogy in assessing ARD generation potential is proposed.

9.4 POTENTIAL USES OF THE SULPHIDE AND BENIGN TAILINGS STREAMS

The potential uses of both the sulphide rich fraction and the sulphide lean tailings have been reviewed. The further use of the sulphide rich fraction has potential to avoid the need for its disposal with containment and, thereby, waste containment costs, while enhancing resource productivity. The further use of benign, sulphide lean tailings has potential to supply materials currently quarried, while reducing the tailings impoundments required and their associated economic and environmental costs. The review undertaken has illustrated that a broad spectrum of approaches are possible. While some of these are only relevant to small volumes of the effluent streams, they may have the potential to generate a product of value to contribute to the costs of ARD prevention. Further, these routes may conserve other resources. In addition to these, applications processing large volumes of materials are required to meet the flows within these systems. A matching of the potential stream sizes generated with the demand for products is recommended as this will be useful to determine the fraction of materials to be considered for disposal. This aspect is currently under consideration as the first stage of the follow-on study. This approach has the potential to maximise resource productivity and allow an industrial ecology approach to be implemented. However, the analysis is required on a regional basis and will vary from region to region.

9.5 ECONOMIC AND ENVIRONMENTAL EVALUATION

In order to establish a framework for the economic costing of the sulphide removal from tailings and fine waste materials, a flotation desulphurisation flowsheet has been proposed to follow the traditional coal processing flowsheet. This has been used as the basis for an order of magnitude estimate of a new fine coal desulphurisation plant using flotation and the performance estimated in Section 5. Based on assumptions specified, this preliminary costing has suggested potential for economic viability. A sensitivity analysis has been presented which targets, among others, value of the resource recovered, yield and reagent costs as key considerations for optimisation of the approach.

Further optimisation and modification of the flotation desulphurisation flowsheet is recommended in later studies to shed further light, beyond the sensitivity analyses presented. It is also recommended that the potential for implementing the potential uses of the resultant streams be considered in economic terms. Further environmental assessment, both with and without the utilisation of the resultant streams, is recommended.

9.6 SUMMARY OF KEY INSIGHTS

In summary, the following insights have been gained through this study:

1. In the absence of removal of the sulphide from waste rock and tailings, it is unlikely that ARD generation can be avoided in perpetuity.
2. The introduction of fines through co-mingling or establishment of layers within or on top of the waste rock dump reduces the permeability through the dump, but does not restrict leaching completely once microbial colonisation has been established. The rate of this leaching is affected by the ore packing.
3. The poor understanding of the fluid path through a heterogeneous bed under unsaturated conditions compromises the modelling approach on which most prediction of ARD formation from heaps has been based.
4. Where microbial colonisation of the waste rock dump occurs, the formation of ARD is continuous in time, de-coupled from the supply of irrigant. In this case, the irrigant serves to flush out the already formed ARD from the rock dump. The rate of flow of this irrigant (through dry and wet periods) influences both the flushing of ARD achieved and the colonisation of the rock surface.

5. With tailings or fine waste rock / coal, proof of concept has been shown across a variety of feed materials that removal of sulphide through separation using, for example, flotation may result in a bulk tailings sample which is benign with respect to ARD generation. The minority stream is enriched with the sulphide material and requires contained disposal or use.
6. A wide range of potential uses exist for both the sulphide rich stream and the sulphide lean stream resulting from the flotation separation. These include the generation of products such as sulphuric acid and cover materials for which there is significant demand in South Africa, amongst others.
7. A framework has been established for the costing of the separation approach. Preliminary analysis under specified conditions suggests potential for viability. Further sensitivity analyses highlight the cost of resource recovered, yield and reagent costs as key variables to be studied further.
8. The limitation of the suite of characterisation methods for ARD is noted. Static tests lack a kinetic framework. Biokinetic tests require refinement to consider the flow through environment and reduction in labour intensity. Humidity cell tests are too time consuming, requiring data collection for over a year.

9.7 RECOMMENDATIONS FOR FURTHER INVESTIGATION

Key recommendations for further work include the following:

1. Refinement of the tests available for the characterisation ARD potential are required. It is proposed that refinement of the biokinetic test be undertaken in terms of data analysis, kinetic information attainable and the potential of a flow through system. Further, characterisation based on mineralogy should be considered.
2. Improved understanding of fluid flow and fluid exchange within the unsaturated heterogeneous heap is required to inform the meaningful implementation of modelling approaches.
3. Further testwork on co-mingling and layering of fines in the reduction of ARD generation from waste rock dumps is required. Specifically this testwork should consider the use of the fine benign fraction from the separation process. Further the work should be conducted both on the 4 kg lab-scale as well as at the pilot scale on site. The latter will enable constraints to experimental interpretation to be removed.
4. Investigation of the use of chemical oxidants for the removal of sulphide in waste rock by reaction should be considered. Of specific interest here is the implementation of Fenton chemistry.
5. With respect to the sulphide separation from fine waste materials such as tailings and coal fines, the economic analysis needs to be rolled out to other systems to evaluate generic value. Further, environmental assessment is critical. Further experimental work is required to investigate the key parameters highlighted by these studies, e.g. reagent costs and the potential environment footprint associated with reagents. The potential for use of bio-flotation agents that can be generated on site and have a low environmental footprint should be investigated. Further to this, a proof of concept study is required at a larger scale, on site.
6. Expanded analysis of the potential use of streams generated through the separation is required. Particularly, the match between material availability and potential product demand is required, as is perceived value, technology availability, etc.
7. The current study has been restricted by access to representative samples of the waste rock, tailings samples and fine coal samples of interest. Assistance in securing appropriate and representative samples is a key requirement of further studies and it is recommended that these are secured with the help of industrial representatives. In addition, field sites should be sought for both the investigation of the use of fines in slowing ARD formation in waste rock dumps and for the demonstration scale proof of concept of the sulphide separation.

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