A SYSTEMATIC APPROACH TO SULPHIDIC WASTE ROCK AND TAILINGS MANAGEMENT TO MINIMISE ACID ROCK DRAINAGE FORMATION

Report to the

WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

BACKGROUND AND RATIONALE

One of the major environmental issues in the mining industry is that of acid rock drainage (ARD), caused by the disposal of sulphide-bearing wastes. The legacy of the ongoing generation of ARD from the disposal of low grade dump rock, of tailings and from the mine site itself may continue for decades following active metal extraction. Acid rock drainage is recognised as a major challenge to South Africa owing to water scarcity, environmental impact of the polluted waters and the substantial cost of treatment. The latter is estimated to exceed R100 million per annum for one site only. Changes in legislation have put the burden of responsibility for perpetuity on mining companies. This, and understanding of the sheer magnitude of the problem, is driving a change in process thinking in order to reduce potentially harmful emissions from deposits and thus reduce long-term costs of tailings management and ARD remediation. Re-examination of the manner in which waste materials are disposed from the mineral processing and extraction stages of metal recovery is required to relieve the environmental burden created and reduce the time frame of risk. Particularly, the delay in the time of ARD formation is no longer acceptable and the need to remove the risk accepted.

In this study, the approaches to the removal of risk through removal of sulphur species were considered through both a paper-based review of key South African workings and a set of case studies addressing specific mineral wastes. Aspects of disposal of dump rock and tailings from mining operations processing mineral sulphides (especially pyrite) have been addressed, specifically with the focus of reducing capacity to form ARD 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) has been used to improve categorisation, separation and planned disposal of its components to mitigate ARD generation. While flotation and accelerated bioleaching have been used in the case studies to demonstrate sulphide removal by separation and reaction, a review of suitable unit operations is provided. Further, use of acid base accounting and net acid generation methods as static chemical methods for evaluating ARD potential was supported by the development of a biokinetic test for assessing ARD potential under an environment more cognisant with the ARD generating environment, as well as providing kinetic data over a shortened time frame to conventional kinetic tests. The biokinetic test also delivers solutions through which to analyse metal deportment through ARD.

OBJECTIVES AND AIMS

To meet the aims and objectives of the study, the following were addressed:

1. A framework for the discussion of the challenges of ARD in mineral processing.
2. A review of mineral resources and wastes in South Africa to highlight key contributors to ARD and to assess the potential of the material for sulphide removal through separation or accelerated oxidation.
3. A review of unit operations available for the removal of sulphidic materials through separation or accelerated oxidation.
4. Selection of appropriate tests for the quantification of ARD, and subsequent development of further tests, including biological tests and metal deportment.
5. A case study, centred on a specific mineral tailings, of the potential for ARD prevention through sulphide removal by flotation.
6. A case study of the potential for accelerated bioleaching for the removal of the sulphidic fraction from waste rock.

METHODOLOGY

Six components are included to meet the project aims and objectives: characterisation of the waste materials, review of appropriate unit operations, review of typical waste materials, study of removal of sulphide rich materials from tailings by physical separation (and its potential for recovery of values from the additional processing) through a case study, study of the removal of sulphide rich species from waste rock

through reaction using a case study. Both waste rock and finely divided tailings materials are considered with respect to their potential for ARD formation from waste material. Cross disciplinary expertise in mineral processing, bioprocessing and environmental engineering has been drawn into the study.

Specific emphasis has been placed on characterisation procedures of waste rock and tailings, through literature review on ARD formation as well as the in-house expertise. Through this characterisation, the sulphide-rich components requiring removal from the waste to prevent ARD formation are highlighted and the typical form and accessibility of these fractions considered to inform selection of appropriate unit operations. While some generic approach is useful, much value is lost by avoiding dealing with the complexity of specific ores in terms of their mineralogy, gangue materials, mineral dissemination, etc. Hence, the detailed characterisation has been undertaken through case studies using specific ore deposits. A case study was undertaken on base metal sulphide tailings in which physical separation of the sulphide species was mediated by flotation. A second case study on waste rock from a base metal sulphide deposit was treated to assess accelerated bioleaching as a means to remove the sulphidic fraction.

Success of these approaches was assessed through a combination of ARD potential tests, including acid base accounting (ABA) and net acid generation (NAG) tests as well as a biokinetic test developed through this project. Further to the impact of sulphide, the resultant metal deportment associated with ARD formation has been studied in these systems.

RESULTS AND DISCUSSION

The review of ARD-generating mineral wastes in South Africa has led to the highlighting of the following important sources of ARD: gold-bearing sulphidic ores, coal, PGM tailings (although low in sulphide, these are voluminous), base metal sulphide ores and antimony ores. The review of unit operations for sulphide removal has targeted specifically flotation, gravity concentrators and reaction through leaching as having potential for sulphide removal. Using these, a conceptual approach to the removal of sulphide has been prepared for the tailings mineral waste. This proposes the generation of an additional values stream (where appropriate), a sulphide rich tailings (of small volume) and a sulphide lean tailings accounting for the bulk of the tailings sample and benign with respect to ARD generation potential.

While a suite of chemical tests for ARD-generation potential have been selected for the study, their limitations are understood. These have been partly overcome by the development of a biokinetic test, providing relevant data more rapidly than the standard abiotic kinetic tests. Further refinement of this test to decouple the kinetics of acid neutralisation and acid generation is proposed.

A case study using flotation for the physical separation of sulphide from tailings allowed the demonstration of the concept of risk removal. Through this approach, a chalcopyrite rich values stream and two tailings streams were prepared. The small volume tailings stream, accounting for approximately 10% of the tailings, was characterised by an increased sulphide concentration of 3.9% while the bulk tailings stream (90% of the tailings by mass) contained 0.21% sulphide and was non-acid forming.

In the second case study using reaction to remove the sulphide fraction, the relative impacts of removal of acid neutralising and acid forming capacity were apparent, with the rate of the former exceeding that of the latter and being largely complete within 50 days. Further, the addition of a low amount of finely divided pyrite was demonstrated to augment biological sulphide oxidation and the concomitant sulphide removal.

While the preliminary case study on coal desulphurisation by flotation was unable to demonstrate significant separation of total sulphur from coal ultra-fines, both visual observation and net acid generation prediction tests demonstrated a significant separation of sulphidic sulphur, with the majority of the acid-generating sulphidic sulphur reporting to the concentrate fraction, resulting in an acid-forming concentrate while the residual tailings showed an increased NAG pH and reduced acid forming ability over the feed material.

CONCLUSIONS

In summary, the following project objectives have been met:

- Review, classification and characterisation of ARD generating mineral wastes in South Africa have been conducted, allowing identification of important materials for study.
- Unit operations available for sulphide removal have been reviewed.
- Characterisation methods to quantify ARD generation potential from waste rock have been reviewed and a sub-set selected for application. Further an additional biokinetic assay has been developed.
- Factors affecting the oxidation rate of metal sulphides have been reviewed. Further the potential for reduction of ARD generating capacity through accelerated bioleaching has been presented.
- Physical separation of sulphidic materials from tailings has been demonstrated to provide the major tailings fraction as non-acid forming while the reactive gangue may be contained in a small fraction of the tailings for additional recovery of values, utilisation of the sulphide or contained disposal.

RECOMMENDATIONS FOR FUTURE RESEARCH

Following the review of ARD-generating wastes in South Africa, it is recommended that the range of mineral wastes studied be expanded to include some of coal wastes, waste materials from gold-bearing ores and PGM ores while expanding work on base metal-bearing ores (nickel, copper and complex ores). In coal studies, it is recognised that sulphur is present in varied forms which need to be taken into account.

In the determination of ARD-generating potential, it is proposed that the biokinetic test be further refined to enable kinetic data to be collected in which acid neutralising capacity and acid generating capacity are decoupled and through which metal deportment can be studied.

The costing of the methods investigated for sulphide removal is required, both with respect to physical separation and reaction. Further, the extent of removal requires consideration. The processing of the waste removed, as a sulphide concentrate on physical separation or as a sulphate rich aqueous stream on reaction, requires further consideration in terms of the final fate of the sulphur species removed.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
ABA	Acid base accounting
ANC	Acid neutralising capacity
APP	Acid producing potential
ARD	Acid rock drainage
BSM	Basal salts medium
FOB	Iron oxidising prokaryotes
LCI	Life cycle inventory
MLA	Mineral liberation analysis
MPA	Maximum potential acidity
NAF	Non-acid forming
NAG	Net acid generation
NAG	Net acid generation
NAP	Net acid producing potential
NP	Neutralising potential
NPP	Net neutralising potential (NPP)
PAF	Potentially acid forming
PGM	Platinum group metal
PLS	Pregnant leach solution
QEM-Scan	Quantitative electron microscope scanning
ROM	Run off mine ores
SOB	Sulphur oxidising prokaryotes
TCLP	Toxicity characterisation leach protocol
TOC	Total organic acid
UC	Uncertain
XRD	X-ray diffraction
XRD	X-ray diffusion

1 INTRODUCTION

1.1 Background

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, of tailings and from the mine site itself is a global environmental issue for both closed and operational mines that may continue for decades, even centuries, following active metal extraction (Kalin et al., 2006). These tailings heaps typically contain significant amounts of finely ground sulphide minerals, often dominated by pyrite which is seldom targeted for economic value. Sulphide minerals are susceptible to oxidative dissolution wherever they are exposed to both air and moisture. Thus, in the oxic zone at the surface of waste heaps, sulphidic minerals are oxidised, contaminating water percolating through the heap. Depending on the nature and integrity of the surface bedrock underlying the heap, water draining these heaps may find its way into the wider environment as point or diffuse sources of pollution (Bryan, 2006). The dissolution of these sulphide minerals is in practice limited by the availability of the aqueous oxidant (Singer and Stumm, 1970; M^{c}Guire et al., 2001). In acidic environments, ferric iron is a more effective oxidant than oxygen and is the most important oxidant in the context of ARD genesis (McKibben and Barnes, 1986). A generalised equation for the oxidation of pyrite by ferric iron in the presence of water is given below.

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow 7Fe^{2+} + 6H^+ + S_2O_3^{2} \quad [1]$$

This results in the formation of ferrous iron (Fe^{2+}), proton acidity and thiosulphate. The activities of certain microorganisms dramatically increase the overall rate of mineral dissolution by as much as a million-fold (Singer and Stumm, 1970). This is the result of two critical microbial actions: (i) the oxidation of ferrous iron, and (ii) the oxidation of reduced inorganic sulphur compounds (RISCs), such as thiosulphate. A diagrammatical representation for the oxidative dissolution of pyrite by acidophilic prokaryotes is shown in Figure 1. In acidic environments (pH<3.5), ferrous iron is very stable and undergoes abiotic oxidation very slowly. Therefore, abiotic mineral dissolution occurs very slowly, due to the slow regeneration of ferric iron. However, under aerobic conditions some microorganisms oxidise ferrous iron rapidly:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad [2]$$

This provides a supply of ferric iron (Fe^{3+}) to the mineral oxidation pathways and prevents sulphide oxidation becoming limited by the concentration of available oxidant. Further, members of the microbial community oxidise reduced sulphur compounds such as polysulphides, elemental sulphur and polythionates, resulting in the production of sulphuric acid. This acidic pH decreases the precipitation of ferric iron, thereby maintaining its concentration in solution. Owing to the metabolic energy balance and aqueous chemistry, the greatest dissolution rates are observed when sulphur-oxidising microorganisms are present (M^{c}Guire et al., 2001). While iron is the most important metal in facilitating the process of sulphide mineral dissolution, any other metals within the mineral matrix are released at the same time. The general result of the reactions represented in Figure 1 is the formation of ARD, the often highly acidic, metal rich effluent draining both active and abandoned mine sites. It is a highly toxic and persistent legacy of sulphide mineral exploitation. The longevity of ARD genesis is one of the key aspects of the problem. Unlike other industries where cessation of operations will lead to a significant reduction in pollution, the reverse is often true for the mining industry. Uncontrolled oxidative dissolution of exposed sulphide minerals will lead to continuing pollution on a time scale often greater than the entire life of the mine.

Changes in legislation have put the burden of responsibility for perpetuity onto mining companies. This has led to a change in process thinking, in order to reduce potentially harmful emissions from deposits and thus reduce long-term costs of tailings management and ARD remediation, and to 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, the delay in the time of ARD formation is no longer acceptable and the need to remove the risk accepted. The mining industry is a major part of the industrial sector in South Africa and activities of this industry especially in the coal and gold sectors are accompanied by the generation of ARD. Its management thus

requires attention (Naicker et al., 2003). Some of the effects of ARD generation are highlighted in the following sections.

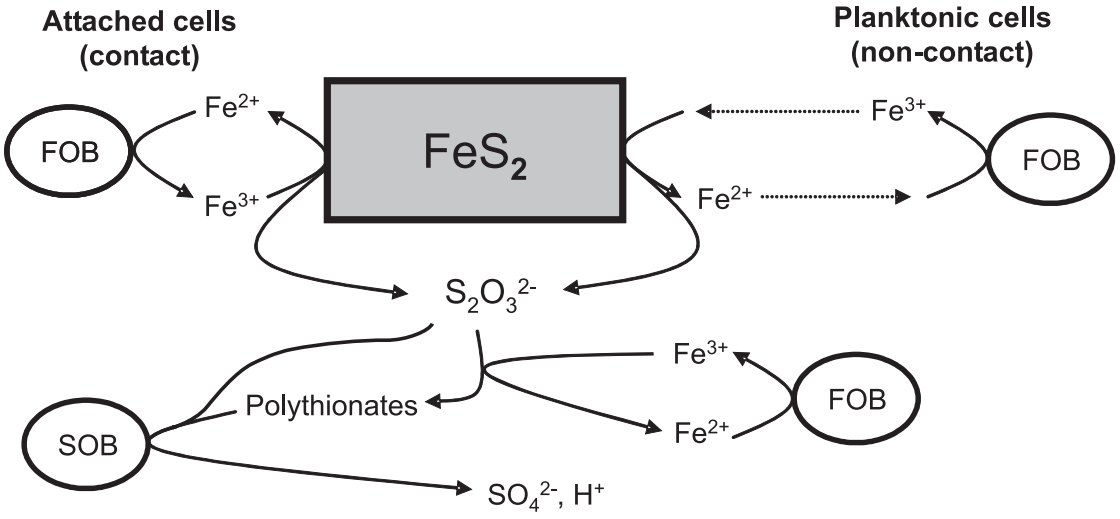


Figure 1: Hypothetical scheme for the oxidative dissolution of pyrite (FeS_2) by acidophilic bacteria, either by cells attached to the mineral surface or free-swimming (modified after Hallberg and Johnson, 2001). (FOB, iron-oxidising prokaryotes; SOB, sulphur-oxidising prokaryotes)

1.1.1. Environmental, Social and Economic Implications of ARD

Acid rock drainage causes remarkable environmental degradation. The main toxicants of ARD are sulphate, protons (acidity) and heavy-metals. Younger et al. (2002) identified six key areas, summarised in Table 1, in the generation of ARD that lead to environmental damage or pollution. These impacts result from different processes.

Table 1: Environmental effects of mining activity and ARD generation. Adapted from Younger et al. (2002)

Source	Effect
Excavation	Disruption of groundwater hydrology
Mineral processing e.g. bioleaching, milling and gold-mercury amalgamation	Polluted runoff
Dewatering *i.e.* draining water out of mining shafts	Water-table depression, reduction of groundwater resources, groundwater catchment modifications
Generation of ARD from pyrite	Discharge of contaminated leachate from mine tailings
Flooding of abandoned mine workings and water table rebound	Erosion, subsidence (sinkhole formation), accumulation of acid-generating salts
Discharge of untreated mine water after flooding	Contamination of surface water or overlying aquifers

It has been noted that the groundwater and soil in areas surrounding mining activities are often highly polluted with heavy metals and characterised by acidic pH, leading to the death of resident organisms, consequent reduction in biodiversity, reduction of water potability and availability for human use. An illustration of the extent of the ARD impact is given through the collection of statistics below. A comprehensive approximation of the worldwide pollution of water bodies by ARD in 1989 were approximately 19 300 km of streams and rivers, and 73 000 ha of lakes and reservoirs (Johnson, 2006). In the UK, 1000 km of rivers and waterways have been estimated to be impacted by ARD (Kroll et al., 2002). Further, Younger (2002) showed that over 5 000 km of waterways in Europe are probably polluted by ARD. The USEPA report (1997) indicated that coal mines in the Appalachian region of the North-eastern USA have degraded more than 12 000 km of streams. A countrywide estimation of ARD environmental pollution in USA was documented as follows: 7 000 km of streams and rivers, 23 000 ha of lakes and reservoirs (Kleinmann,

1989). In a report prepared by Rossman et al. (1997) for the Department of Environmental Protection, Pennsylvania, USA, it was stated that more than USD 5 billion was required for the rehabilitation of lands and streams polluted by ARD in Pennsylvania alone. Coal mining in the Witbank Coalfield of South Africa, has led to the extensive contamination of ground and surface water. Subsequently, this has resulted in the destruction of flora over an expanse of 3 ha where the seepage takes place (Bell et al., 2001). Termination of mining and dewatering activities is often associated with the restoration of the water table to its natural level, a phenomenon known as groundwater rebound. This may lead to uncontrolled ARD seepage into the surrounding areas that are topographically lower (Younger et al., 2002).

Schoeman and Steyn (2001) studied the process economics of the mine water (80 to 100 megalitre per day) treatment from the Grootvlei Proprietary, South Africa. They predicted the annual operating costs for reverse osmosis (RO), electrodialysis (EDR) and ion-exchange (GYP-CIX) treatment technologies to be 17.2, 6.7 and USD 8.6 million respectively. The presence of sulphate in potable water can cause a bitter and salty taste. The acceptable limit for taste is less than 250 mg/L (WHO, 2006). General water legislations allow for sulphate content of potable water in the range of 250 to 500 mg/L (WHO, 1996; USEPA, 1999). High sulphate concentration leads to increased water salinity. Ingestion of sulphate concentrations above 600 mg/L is known to cause disturbance in the human gastrointestinal tract. Sulphate content of ARD far exceeds this value. The toxic heavy metals dissolved by the ARD, including manganese, aluminium, iron, nickel, zinc, cobalt, copper, radium and uranium are all characterised by varying degrees of toxicity and radioactivity. Uranium and radium can cause cancer (Fernandes et al., 1995). Acid rock drainage pollution reduces farmland available for agricultural activities owing to salinity and acidity (Antunes et al., 2002) and causes deterioration of waterways leading to their reduced application for activities such as recreation and irrigation as well as destruction of vegetation (Lupankwa et al., 2006).

Sulphate build up in an aquatic environment may induce sulphide production, a compound that is lethal to several life forms. The malodorous characteristic of sulphide is also an environmental nuisance (Ghigliazza et al., 2000). Hence, sulphate removal in the treatment of ARD is imperative. Sediments of ARD-polluted water bodies are often covered with metal precipitates which hamper macroscopic life cycles and in turn impair the food chain resulting in the eventual loss of biodiversity (Ledin and Pedersen, 1996; Gray, 1997; Feng et al., 2000; Naicker et al., 2003).

1.1.2. Acid Rock Drainage Prevention

The impacts of ARD discussed above demonstrate the need to intensify research into its prevention. Preventative measures usually aim to prevent exposed sulphide minerals coming into contact with oxygen, moisture or both. Alternatively they inhibit the activity of mineral-oxidising microorganisms. Remedial methods aim to treat acidity and raise pH and remove metals by precipitation as hydroxides, carbonates or sulphides, or by adsorption. However, while various remediation schemes may be effective, they can be expensive, unpredictable and often simply transfer the problem from one place to another, leaving a toxic waste to be handled. Therefore, it is more pragmatic to handle the problem by removing or minimising the potential for mine wastes to generate ARD, where feasible. Prevention of ARD generation at the source has been considered to be a more cost-effective approach to managing it. Various methods for preventing ARD have been developed. To date, these have been aimed at limiting the exposure of the sulphidic phase to water and air or inhibiting the essential reactions of the generation process. In their review of ARD control options available, Johnson and Hallberg (2005) included the following: (i) sealing of abandoned underground mines thus preventing or diverting the movement of water and oxygen away from areas containing acid-producing rock; (ii) burying mine tailings under water, hence reducing the concentration of oxygen that comes into contact with the sulphidic phase; (iii) covering the dump with a sealing layer before underwater storage to augment the above approach; (iv) backfilling; (v) co-disposing waste tailings with alkaline materials (e.g. limestone, lime, cement kiln dust and fly ash) to neutralise the acid out-flow; (vi) preventing pyrite oxidation using phosphate salts to form a film on the sulphidic phase. Although these methods show that an understanding of the problem of ARD exists, they address the issue in an “end of pipe” approach and the long-term impacts are not well understood before implementation. A post-closure “walk-away” status is not guaranteed and remediation of ARD is a difficult and costly process.

The need arises for a more systemic or integrated approach to tailings management, the benefits of which have been emphasised in recent publications (Benzaazoua et al., 2008; Chan et al., 2008). This project seeks to expand approaches to ARD prevention through the removal of risk by the removal of the material implicated in ARD generation, rather than prevention of the reaction.

1.2 Problem Statement

In this project, we addressed aspects of disposal of dump rock and tailings from mining operations processing mineral sulphides (especially pyrite), specifically with the focus of reducing capacity to form ARD through removal of the sulphidic component of the waste. We sought to use the understanding of the factors governing ARD generation from dump rock and tailings (similar to those governing mineral bioleaching) with the view to the improved categorisation, separation and planned disposal of its components to mitigate ARD generation. This required identification of components responsible for ARD generation and characteristics of the waste for disposal to ensure minimisation and control of this generation. The project was scoped to address both tailings and dump rock.

Through the use of the 'sulphide-rich' and 'benign' gangue characterisation, we sought to propose improvements in waste disposal, largely through the removal of sulphides prior to disposal. This classification was developed based on an understanding of key features of the mineral ore governing ARD generation. The classification was used to propose appropriate removal of sulphide from the waste material using both separations and accelerated oxidation, allowing investigation of the ARD generation potential of 'benign' gangue alone compared with a combination of 'sulphide-rich' and 'benign' gangue. Further, the appropriate formats for disposal to minimise ARD formation was considered and the potential to derive value to offset processing costs were considered.

The overall objective, to be consistent with global sustainability and the systematic approach of the Minerals-to-Metals Research Initiative within the Department of Chemical Engineering at UCT, was to enhance the overall environmental performance of metal sulphide process operations, by both maximising economic and environmental efficiency and minimising environmental burden. In keeping with this approach, the project strives, in addition to its contribution to knowledge, to provide benefit to society through the essential role of water and necessity to maintain the quality of water bodies in mining areas, contribute to the economy through improved remediation approaches and protect to the environment through reduction in contamination of water resources, stable disposal of waste rock, and potential improved resource productivity.

1.3 Scope and Overview

The project centred on four major objectives:

- to characterise typical dump and tailings material in terms of 'sulphide-rich' components and 'benign' gangue material with respect particularly to ARD generation,
- to identify factors involved in controlling the oxidation of the metal sulphide material present in waste rock and tailings to ARD that can be manipulated to enable accelerated oxidation of the sulphide-rich material, particularly in terms of waste rock characteristics and also disposal conditions,
- to propose approaches to both the selection and separation of material for disposal, the removal (through reaction and separation) of active gangue implicated in ARD generation and the conditions of disposal to mitigate ARD generation and
- to propose approaches to the further processing of the 'sulphide-rich' fractions within the life of the mine, such as the accelerated bio-oxidation of the sulphide-rich material.

In conducting this project, the approach was divided into six components to meet the project aims and objectives. These included characterisation of the waste materials, review of appropriate unit operations for their processing, review of typical waste materials, study of removal of sulphide rich materials from tailings, study of the removal of sulphide rich species from both tailings and waste rock and their subsequent benign disposal, and recovery of values from the additional processing. Both waste rock in the form for dumping as well as finely divided tailings materials were considered in terms of potential for ARD formation. These two types of waste were handled through the case study focus of two postgraduate student projects, with one focussing only on tailings and their disposal and the second on both tailings and dump rock. The study has been augmented through the involvement of four Honours level students, allowing extension of the analysis

of methods for characterising ARD generation potential and preliminary studies on ARD from coal. The principal researchers provided cross disciplinary expertise in mineral processing, bioprocessing and environmental engineering. The project was scoped into nine deliverables over a two year period. These are provided in Table 2.

Table 2: Project deliverables and schedule

Deliverable number	Deliverable Description
1	Review of unit operations for sulphide removal
2	Review of mine wastes
3	Review of waste rock characterisation procedures
4	Feasibility study 1
5	Report on capacity development
6	Refinement and selection of waste rock characterisation
7	Feasibility study 2
8	Report on capacity development
9	Final report

2. OVERVIEW OF TYPICAL ARD GENERATING MINERAL WASTES IN SOUTH AFRICA

Acid rock drainage (ARD) is formed through the weathering of sulphide minerals in surface waste deposits and surface and subsurface voids (open pits and underground workings) as a consequence of the extraction and processing of hard-rock ore or coal. The focus here is on the characteristics, origins and sources of ARD-generating mineral wastes *i.e.* those wastes generated from mineral extraction and processing containing naturally-occurring sulphide minerals.

2.1. Classification of ARD-Generating Mine Wastes

The terms used to describe the various forms of waste and their definitions vary quite considerably in different parts of the world and are frequently associated with some controversy (Van Zyl et al., 2002). Furthermore differences in terminologies are used in the coal mining and hard-rock mining (*i.e.* extraction of metal-bearing minerals) and industrial mineral sectors. This sub-section is concerned with the terms used to describe various forms of sulphidic mineral waste and their definitions.

Solid and slurry wastes containing naturally-occurring sulphide minerals can be broadly defined as those arising from the mining, extraction and processing of sulphide-bearing mineral deposits, with a view to separating the targeted mineral(s) from the non-valuable component (gangue). Such wastes include waste rock and overburden from hard-rock and coal mining; tailings arising from the physical concentration and, in some cases leaching of hard-rock ores ahead of metal recovery; spent ore from the heap leaching of crushed run-of-mine ores (ROM); and discards and ultra-fine slurry from the screening and washing of ROM coal ores. Acid rock drainage may also be generated by stockpiles of low-grade sulphide ores. In reality the distinction between low-grade ore and waste rock or overburden is an economic one. Low-grade ores generally have a higher grade than waste rock and have the potential to be economic in the future but are considered sub-economical at the time of mining. In some cases these stockpiles are used for blending with higher grade ores or processed separately in heap leach operations, but in many cases may ultimately be left as waste and need to be rehabilitated as waste.

In Table 3, a consistent set of definitions of terminology to describe mine wastes associated with ARD generation is provided and set in context.

Table 3: Terminology for sulphidic mineral waste and ore stockpiles

Waste Terminology and Description		Other Terminologies	Associated Waste Deposit Terminology	Comments
Solid Waste	***Solid waste*** is the general term to describe the various solid and/or slurry materials remaining after removal of the targeted materials		Deposits, storage facilities, disposal facilities, piles, dumps	The European Economic Community (EEC) define waste as "any substance or object the holder discard, intends to discard or is required to discard" (European Waste Framework Directive 2006/12/EC, as amended by Directives 2006/12/EC and 2008/98/EC)
	Mineral waste is solid waste arising specifically from the extraction and primary beneficiation of naturally-occurring minerals	Mine residue(1)		(1) DWAF and DME in South Africa define mine residues as any debris, discard, tailings, slimes, screening, slurry, waste rock, foundry sand, beneficiation plant waste, ash and any other waste product derived from or incidental to the operation of a mine or activity, and which is stockpiled, stored or accumulated for potential re-use or recycling or which is disposed off.
	Sulphidic mineral waste is solid waste containing naturally-occurring / chemically sulphide minerals			Includes wastes from the extraction and processing (initial beneficiation) of sulphide-bearing ores, with a view to separating the targeted mineral(s) from the non-valuable (gangue) minerals.

Table 3 continued: Terminology for sulphidic mineral waste and ore stockpiles

Waste Terminology and Description	Other Terminologies	Associated Waste Deposit Terminology	Comments	Waste Terminology and Description
Mining Wastes	***Waste rock*** is the barren or uneconomic mineralized rock that has been mined, but is not of sufficient value to warrant treatment and is therefore removed ahead of processing	Mine rock	Dumps	The term "waste rock" is normally associated with hard rock mining – although overburden is sometimes used in the case of waste rock from open-pit mining
	Low-grade ore stockpiles usually consist of run-of-mine ore which has been mined and stockpiled with intention to process in the future, but is often left as 'waste'.		Stockpiles	The distinction between waste rock/overburden and low-grade ore is usually an economic one, and may vary from site-to- site and year-to-year.
	Overburden is the material (rock and soil) above the mineral resource that must be removed in order to mine the mineral resource	Spoil	Deposits, dumps	Normally used in reference to coal mining but also sometimes hard-rock mining (see above)
Ore processing wastes	***Spent ore*** is the rock remaining after recovery of metals and some soluble constituents through heap leaching and heap rinsing of ores		Facilities, piles	
Ore processing wastes	***Tailings*** are the solid product of ore treatment and concentration processes that are considered too low grade to be treated further. Tailings are the finely ground host rock materials which have been processed for the separation of desired mineral values	Slimes (1); Sands (2)	Impoundments; dumps and piles (sand); dams and ponds (slimes)	Normally used in reference to processing (initial beneficiation) of hard rock ores. (1) Slimes generally refers to finely divided tailings material (96% <0.427 mm) normally deposited as a slurry into a dam (2) Sands is used in reference to coarser, sand grain size tailings (typically 90% 2 mm)
	Coal discards are the solid wastes from coal cleaning of insufficient commercial value due to high ash content/low calorific value	Rejects	Dumps	
	Ultra-fine coal slurry contains coal which is too fine to be beneficiated effectively using conventional techniques.		Ponds	

2.2. Origins and Sources of ARD-Generating Mineral Wastes: A Generic Overview

As indicated in the previous section, sulphidic mineral wastes are generated from the initial beneficiation or processing of sulphidic ore bodies, and their ARD forming characteristics are thus dependent on:

(i) the characteristics of the ore (*i.e.* their origins);
(ii) the processes applied in their generation (*i.e.* their source); and
(iii) the design, maintenance and/or rehabilitation of the disposal facilities (*i.e.* their management).

Sulphidic wastes are generated during the extraction and processing of sedimentary coal and sulphidic metal-bearing ores.

2.2.1. Metal Bearing Sulphide Ores

In terms of ore characteristics, sulphide ores are generally considered to be metallic ores in which the valuable or targeted minerals are present as, or associated with, sulphides. In accordance with Broadhurst (2007), metals (including metalloids) forming minerals with sulphides and/or sulphide analogues (selenides, tellurides, arsenides and antimonides) include:

- Iron Fe: Occurs in abundance in nature in the form of both oxides and sulphides. Iron sulphides pyrrhotite, marcasite and, in particular, pyrite are the most commonly occurring sulphide minerals, and are largely considered to be sub-economic (*i.e.* as unwanted gangue)
- Base metals Cu, Ni, Co, Zn and Pb: Copper is the most noble of the base-metals and sometimes also occurs in the native state. These elements are often referred to as chalcophiles
- Semi-metals: As, Sb, Bi, Tl, In, Cd, Hg
- Semi-noble to noble metals Ag, Au, platinum group metals (PGMs): These metals often termed siderophiles, and frequently occur in their native state (*i.e.* as metals or metal alloys).

Although considerably enriched relative to their average crustal abundance, the minerals of the valuable and thereby targeted metals (base metals; (semi) noble metals; and certain semi-metals) are frequently only present as minor components. Sulphide ores are thus comprised mainly of deposits of “valueless” or sub-economic elements and their associated minerals, commonly termed gangue, hosted within barren or country rock. Gangue minerals can be in the form of non-valuable sulphides, particularly those of iron and arsenic (pyrite, pyrrhotite, arsenopyrite) or oxides (both simple and complex) commonly associated with sulphides. In accordance with the review conducted in a previous study by Broadhurst (2007), the latter include oxyanions (sulphates, borates, phosphates and, particularly, carbonates) of divalent metal cations (magnesium, barium and, particularly, calcium); the simple oxides of alkali metals and silica (e.g. quartz) and, to a lesser extent, halides. Further details pertaining to sulphide mineral and element associations in metal-bearing ores are detailed in Appendix I.

2.2.2. Extraction and Processing of Metal-Bearing Sulphide Ores

As a result of the relatively small quantities of targeted metals and their associated minerals in sulphide ores, the non-product (waste) outputs are generally voluminous, particularly those arising from the initial ore preparation and processing stages *i.e.* waste rock and tailings from mineral processing operations. Mining, or the process of raw ore extraction, forms the first processing stage in the commercial exploitation of all primary mineral resources, and can be defined as the act of separating the valuable mineral-bearing ore body from the host rock through physical extraction and crushing, as shown in Figure 2. In order to gain access to the ore, underground and, in particular, surface mining entails the removal of large quantities of material, commonly referred to as waste rock, mine waste or overburden. In reality the distinction between ore (commonly referred to as ROM ore) and waste rock or overburden is an economic one, with material containing less than the cut-off grades being considered as waste, and disposed of on a waste dump. According to Thornton (1983), and consistent with the figure quoted by Warhurst (2000), 1 ton of ROM ore corresponds on average to 1 ton of waste rock. This figure can, however, vary quite substantially, with open pit mining of low-grade ores (for example copper porphyry deposits) resulting in waste rock to ROM ore mass ratios of almost 2:1. Mining typically results in 90-95% recovery of the valuable or targeted element-bearing minerals, with waste rock consisting mainly of crushed host rock, as well as 5-10% of the valuable or targeted metal. In general waste rock and overburden facilities are constructed on natural terrain. Although it is now commonly recognised that such dumps may result in ARD if they contain sulphide minerals (*i.e.* are

derived from the mining of sulphide ore deposits), waste rock dumps generally remain poorly characterised and their potential for ARD generation largely unknown.

In some cases the ROM ore is suitable for direct marketing or for economic extraction of the valuable constituents by means of relatively inexpensive heap leach techniques. In the majority of cases, however, the ROM ore needs to be separated further from the gangue in order to produce a product suitable for sale (in the case of industrial, non-metallic minerals) or further metallurgical processing (in the case of most metal-bearing minerals), as illustrated in the middle block of Figure 2. Concentration, which is also referred to as mineral processing or initial beneficiation, can be defined as the separation of mineral phases by physical means (*i.e.* through the use of processes that do not result in chemical changes to the mineral component of the ore). The primary objective of concentration processes is to separate the valuable commodity-bearing minerals from the non-valuable minerals, thereby producing a concentrate, which has a smaller volume but higher-grade than the ROM ore, and a large volume discard tailings stream containing the majority of the gangue (non-valuable) minerals. In the case of complex ores, physical processing techniques are frequently also used to separate valuable minerals from each other. Mineral processing or concentration systems typically consist of three unit operations, *viz*. milling; followed by physical solid-solid separation of the liberated minerals; and finally dewatering for the recovery of water from both the concentrate and tailings outputs.

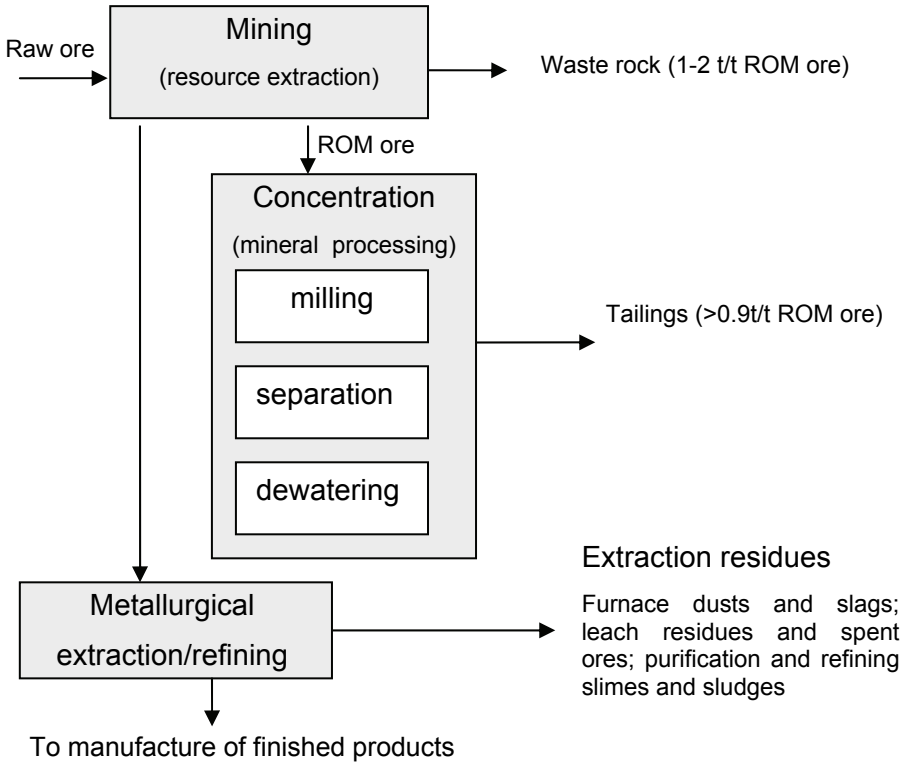


Figure 2: Typical mining and beneficiation flow sheet for the primary metal resource industry (Broadhurst, 2007)

The primary objective of milling (or comminution) is to reduce the size of the mineral particles to physically liberate the minerals from each other, prior to separation. The size at which adequate liberation is achieved is dependent on the characteristics of the ore, and to a lesser extent on the physical separation processes. In the case of metallic mineral resources, particularly low-grade non-ferrous metal deposits, it is normally necessary to grind the ore relatively finely (<<1 mm) in order to achieve acceptable recovery and concentration of the valuable constituents. Milling is generally followed by physical solid-solid separation of the liberated particles. A number of physical mineral processing or concentration methodologies and associated reactor technologies exist, the selection of which is mainly dependent on the physical and chemical differences between the minerals requiring separation *viz*. classification (grain size); gravity separation (density and size); heavy medium separation (density); magnetic separation (magnetic

susceptibility); electrostatic separation (electric conductivity); and froth flotation (surface chemistry). These technologies and their dependency on particle size are detailed further in Appendix I.

Because of the complexities of the ore mineralogy, no mineral separation process is fully effective in separating all feed particles into the desired products, even if they have been fully liberated by comminution ahead of separation. Whilst the efficiencies (in terms of recovery of the targeted commodity) of the mineral processing operations are typically between 90 and 95%, Hayes (1985) reports that between 20 and 30% of the contained value may be lost during mineral separation in the case of complex polymetallic sulphide ores. As in the case of mining, the mass flows during concentration are largely dependent on the grade of the ROM ore. In the case of low-grade metallic ores, particularly non-ferrous ores, tailings typically account for 90% of the ROM ore.

2.2.3. Coal Ores and Processing

Coal is formed over millions of years from compacted plant material. The major elements present in coal are thus essentially those present in plants, such as carbon, hydrogen, nitrogen and sulphur. Inorganic material, such as clay and rock, is also present in coal, with smaller amounts of sulphides, carbonates and silica. The latter forms the ash produced from coal combustion. Many of the elements of environmental concern present in coal are mainly associated with sulphide minerals in the ash and include As, Cd, Cu and Se. As in the case of metal-bearing sulphide ores, coal is prepared for down-stream processing (power-generation, metallurgical applications, etc.) to produce a waste stream (discard) containing the majority of the ash-forming minerals, and a “clean” coal product with a higher calorific value. The ratio of discard to ROM coal is, however, considerably lower than the ratio of tailings to metal-based ROM ore, with discards amounting to approximately 22% of the ROM coal (DME, 2001). The steps in the coal preparation process include screening and washing, as shown in Figure 3.

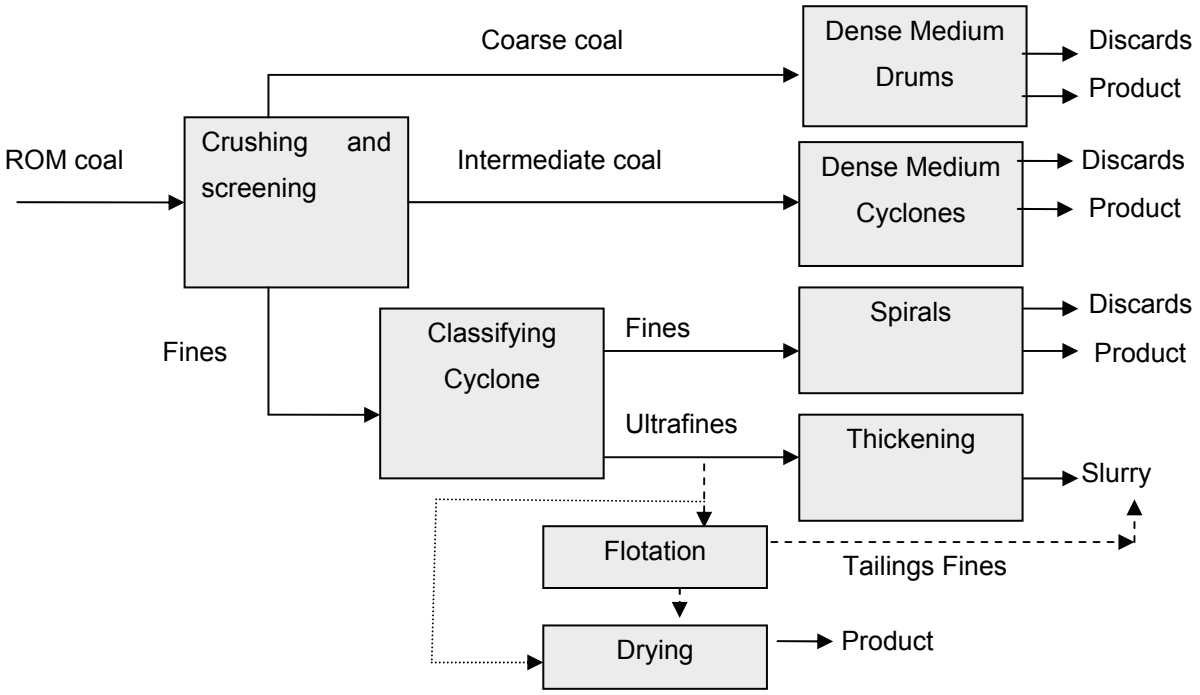


Figure 3: Block flow diagram of the coal washing process (Adapted from Reddick, 2006)

Washing is a water-based process with the techniques varying in accordance with the particle sizes of the screened coal fractions. Although the ARD generating properties of coal wastes, particularly discards, is known to be linked to the sulphur content, sulphur speciation in coal deposits and processing streams remain uncertain.

2.3. The Deportment of Sulphur during Extraction of Sulphidic Metal-Bearing Ores and Coals

Of key concern in terms of ARD formation and impacts is the concentration and speciation of sulphide minerals in the ore body, and their subsequent deportment to the waste outputs during ore extraction and processing. It should, however, be noted that a higher concentration of gangue (*i.e.* non-valuable or sub-economic) sulphide minerals such as pyrite, pyrrhotite and arsenopyrite, in ore deposits does not necessarily translate to higher sulphide content in waste outputs from mineral processing operations. The extent to which the sulphide in the ore deports to the tailings also depends on the association of the gangue sulphide with the targeted valuable minerals.

- Gangue sulphide minerals which are chemically bonded to or encapsulate the targeted minerals are recovered in the product stream (concentrate) during mineral processing. In such cases the sulphide mineral impacts the further processing of the values.The tailings generated during processing of such ores have lower gangue sulphide concentrations than the ROM ore, although sulphide separation is never 100% complete.
- Gangue sulphide minerals which are not bound to the targeted minerals are largely removed to tailing or discard wastes during processing. These sulphide minerals do not impact the further processing for value recovery. In such cases the sulphide concentrations in the tailings or discard wastes are higher than in the ROM ores.

The ARD generating potential of waste deposits from the extraction and processing of sulphide ores is, furthermore, dependent on the size or volumes of wastes. Large volumes of tailings containing relatively low levels of sulphide can result in an equally large (or larger) ARD pollution plume than smaller volumes of tailings with higher levels of sulphide.

2.4. Origins, Sources and ARD-Generating Characteristics of Sulphidic Wastes in South Africa

A summary of the key characteristics of sulphidic ores and associated wastes in South Africa is provided in Table 4. More detailed information is provided in Appendix 2. Commodities recovered from sulphide-bearing ores in South Africa include coal, gold, PGMs base metals (copper, nickel, lead and zinc) and antimony. Local ores in which the gangue sulphide minerals are present largely associated with the value components include the PGM ore bodies and the refractory gold ores in the Barberton Greenstone Belt in Mpumalanga. Passive sulphide gangue minerals are typically associated with Witwatersrand gold ores, massive base-metal sulphide ores, and coal deposits. Selected results from a previous life cycle inventory (LCI) analysis of the local industry, presented in Figure 4 (Stewart, 1999, summarised by Stewart and Petrie, 2006), shows the generation of large quantities of wastes by the gold, PGM and coal industry sectors, most of which occur in the form of sulphide-bearing waste rock and tailings. Whilst the gold and coal sub-sectors are commonly associated with ARD pollution of water resources, tailings from the PGM sector - although generated in high volumes - have low sulphide content, and are not generally considered to be acid generating. The LCI data in Figure 4 also indicates that the primary processing of base metal sulphide ores in South Africa generates relatively small volumes of solid waste, in comparison to other local mineral industry sub-sectors. Nevertheless these wastes often contain high concentrations of sulphide minerals (up to 30%), and thus have the potential for significant contamination of local water sources and soils (see discussion in Table 4).

A detailed assessment of the ARD generating potential of sulphidic wastes in South Africa is, however, limited by the lack of (readily) available data and information. For the most part sulphide wastes, particularly waste rocks and tailings which have not (yet) given rise to serious ARD pollution problems, appear to remain poorly characterised, and their long-term ARD risks largely unknown.

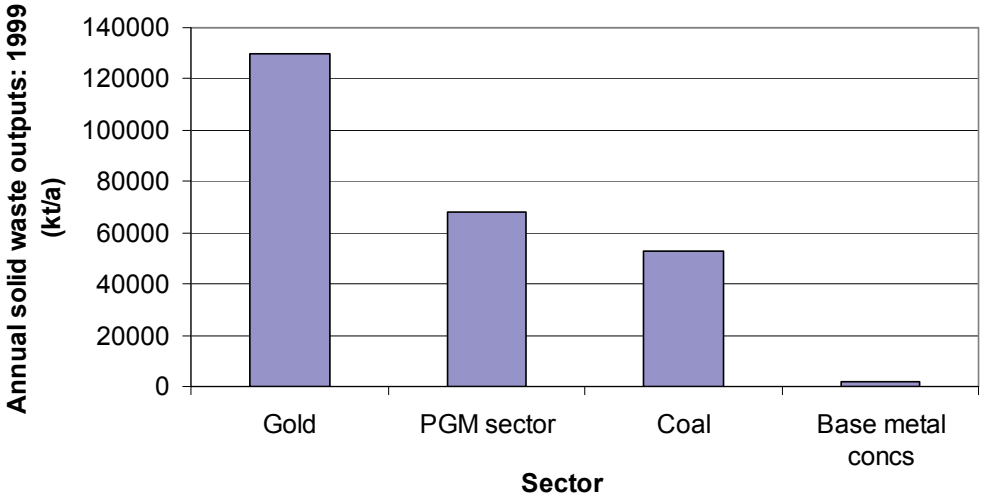


Figure 4: Total solid waste outputs for selected local minerals industry sectors (Stewart, 1999)

Table 4: Key characteristics of sulphidic ores and associated wastes in South Africa

Associated Commodity	Deposit Location	Ore Description	Sulphidic Wastes and Associated ARD Risks
Gold	Witwatersrand Basin: The East Rand Goldfield; the Central Rand Goldfield, the West Rand Goldfield; the Klerksdorp (Kosh) Goldfield ; and the Free State Gold field	Placer gold deposits. Gold generally occurs in a native form often associated with pyrite, carbon and uranium, with quartz being the main gangue material. Sulphide mineral content varies between 2.6-11% (Marsden and House, 2006)	• ***Concentration tailings****:* Historical deposits of sands and slimes (approximately 240 covering an area of 400 km^2) have resulted in extensive generation of ARD, with elevated concentrations of heavy metals such as Co, Ni and Zn and (in some cases) uranium (Coetzee, 2004; Mphephu et al., 2004a and 2004b; Oelofse et al., 2007, Smith, 2005) • ***Waste rock****:* Sulphide content and ARD generating potential of waste rock currently unknown. • ***Cyanidation leach tailings****:* Residues from the cyanide leaching of Witwatersrand gold ores have been found to contain significant quantities (0.5-0.7%) of unreacted sulphide sulphur (Genmin, 1991).
	Barberton Greenstone Belt in Mpumalanga	Gold occurs as free gold and associated with sulphide minerals, pyrite and arsenopyrite, and to a lesser extent pyrrhotite (1.3-4% sulphur)	• ***Concentration tailings*** containing residual sulphide such as arsenopyrite, pyrrhotite and pyrite (Swash, 1988). Potential for ARD generation unknown. • *Waste rock:* Extensive ARD generation due to weathering of sulphide minerals in waste rock dumps at Bien Venue reported (Bullock et al, 2004)
Coal	Numerous coalfields mainly in Mpumalanga, but also Limpopo, Gauteng, Free State and Kwazulu-Natal	Coal with inorganic material (ash) such as clay and rock, and smaller amounts of sulphides (typically in the range 1-3% S; mainly as pyrite), carbonates and silica.	• ***Overburden:*** sulphide content and ARD generating potential of overburden material is unknown. • ***Discards:*** Relatively high ash and sulphur content (typically 1-5%, but can be as high as 13%), mainly in the form of pyrite in ash. Considered to pose a considerable pollution threat as a result of ARD generation as well as spontaneous combustion (DME, 2001; Hansen, 2004; Pinetown et al., 2007; Reddick, 2006) • ***Ultrafine slurry***: Higher calorific value and lower sulphur content (typically <3%) than discards. Also considered to pose a high ARD risk (DME, 2001; Reddick 2007). • ***Coal stockpiles***: Coal in SA is largely net acid generating, and stockpiles can release ARD (Hodgson, 1998).

Associated Commodity	Deposit Location	Ore Description	Sulphidic Wastes and Associated ARD Risks
Base metal sulphides- Active operations	Aggeneys copper-lead-zinc-silver deposits in the Northern Cape- Gamsberg, Black Mountain and Broken Hill mines	Exhalative complex sulphide ore bodies, containing galena, sphalerite and chalcopyrite which together with pyrite and pyrrhotite achieve massive sulphide proportions (up to 50%)	• ***Waste rock****:* Characteristics unknown, may vary from mine-to-mine • ***Concentration tailings****:* High pyrite content (30%). Although acid generating, environmental risk is considered low due to location and associated poor water quality (Duthie and Souster, 2007)
Base metal sulphides- Active operations	Copper: carbonatite igneous complex at Palabora	Copper sulphides in banded carbonatite, with magnetite, apatite and silicates; and trace amounts of other sulphides	***Waste rock and concentration tailings****:* Sulphide content and ARD potential unknown, but sulphides are expected to be low and wastes unlikely to be acid generating (high neutralising capacity)
	Nkomati nickel deposit in Mpumalanga	Two zones exist (i) a massive sulphide zone containing pentlandite with pyrite and pyrrhotite; and (ii) a mineralized zone containing low sulphides	***Waste rock and concentration tailings****:* Sulphide content and ARD generating potential unknown-potentially significant for wastes generated from the massive sulphide zone.
Base metal sulphides: Defunct operations	Prieska copper-zinc sulphide deposits and O 'Kiep copper sulphide deposits in the Northern Cape (Beale, 1985; Van Niekerk and Begley, 1991)	Both massive sulphide deposits with pyrite and possibly pyrrhotite as gangue sulphide minerals	***Defunct waste rock and concentration tailings deposits****:* Sulphide content and ARD generating potential unknown; expected to be significant but risks may be considered low due to location.
	Zn-Pb Pering deposit (Van Niekerk and Begley, 1991)	Disseminated deposit with minor quantities of gangue sulphides hosted in dolomite (Coetzee, 1976; Van Niekerk and Begley, 1991)	***Defunct waste rock and concentration tailings deposits****:* Sulphide content and ARD generating potential unknown, although sulphides may be present in relatively low concentrations, ARD neutralising capacity may be significant, due to carbonaceous nature of host rock.
PGMs	The Western, Eastern and Northern limbs of the Bushveld Igneous complex (Becker et al., 2008; Conradie, 2006; Schouwstra and Kinloch, 2000)	Merensky and Platreefs: PGE and PGM associated with nickel (pentlandite), copper (chalcopyrite) and iron (pyrrhotite and pyrite) sulphides UG2 reef: lower sulphide mineral content with higher iron oxides and chromite.	***Waste rock and concentration tailings****:* Sulphide content and ARD generating potential unknown, but generally considered negligible. Nevertheless residual sulphides can be expected to be present in wastes, albeit at low levels, due to incomplete recoveries during flotation.
Antimony	The Murchison Greenstone belt in the Northern Province	Stibnite veins and disseminations in host quartz-carbonate rocks, with accessory sulphides arsenopyrite and pyrite	***Waste rock and concentration tailings****:* Sulphide content and ARD generating potential unknown. Although residual sulphides may occur at relatively low concentration levels, ARD neutralising capacity may be significant due to carbonaceous nature of host rock.

3. UNIT OPERATIONS FOR SULPHIDE REMOVAL THROUGH SEPARATION OR REACTION

3.1. Introduction

In this project, the potential for prevention of ARD formation was investigated through the removal of sulphur-containing compounds from the mineral ore waste materials in order to create a small volume reactive or active waste product and a large volume waste product which is largely benign (Cilliers, 2006; McCallum and Bruckard, 2009) and can be used for its structural properties. Ideally the sulphide removal results not only in minimizing the reactive waste with ARD producing capacity, but also allows the identification of potential value for components of the resultant streams. Two major approaches were used in this study: removal through physical separation and removal through reaction. In order to assess potential approaches to each of these, a review of unit operations within the minerals processing industry was required both in terms of physical separations and in terms of reaction processes.

3.2. Review of Unit Operations for Physical Separation of Sulphide Containing Materials

Physical separations are based on the following properties: particle density, particle size, particle magnetism, surface properties including hydrophobicity and charge. These allow separation based on the associated driving forces; namely, gravity, centrifugal force, magnetic field, buoyancy and electrical field. Those unit operations typically used in the minerals industry include screening, gravity concentration, cyclones, dense medium separation, froth flotation, magnetic and electrical separation, sedimentation and filtration (Wills and Napier-Munn, 2006). The application of such physical separation in the prevention of ARD is driven by the tendency of sulphide minerals to be concentrated in the finer fractions relative to silicates and aluminosilicates, the characteristic higher density of sulphide minerals over alumino-silicate materials, and the ability to modify surface properties of sulphide minerals separately from silicates and aluminosilicates (McCallum and Bruckard, 2009). For example, McCallum and Bruckard (2009) demonstrated that with sample copper and nickel tailings, some 40 to 75% of the total sulphur present occurred in the fraction of fines passing 38 μm.

Gravity concentrators separate particles as a function of their relative specific gravity and typically their motion through a fluid. They have been applied across a specific gravity range of 1.3 (coal) to 7.5 (galena) (Wills and Napier-Munn, 2006). Efficiency of separation is affected by particle size distribution, with the presence of very fine particles causing an increase in suspension viscosity, hindering efficiency of separation. As a result the feed to gravity concentrators is usually pre-treated to remove oversize particles by screening and fines by de-sliming. Typical unit operations used to effect gravity concentration include jigs, spirals, shaking tables, pneumatic tables and centrifugal concentrators (Wills and Napier-Munn, 2006). While cyclones achieve separations based on settling velocity, governed by particle size and density, dense medium separation can offer an advantage over these by enabling efficient separations at the required density with close control of the density selected for separation being attainable (Wills and Napier-Munn, 2006). Such separations have been used commonly in the pre-concentration of minerals and in the preparation of clean coal from high ash coal. These separations may be achieved in a range of flow-through configurations including drums and cones or in centrifugal devices such as cyclones or whirlpools.

Froth flotation represents the central unit operation in separations for mineral processing. The principle of separation centres on differences in surface properties between the mineral and gangue phases present. Further, these properties can be controlled by the addition of frothers to alter surface properties at the gas-liquid interface and collectors to alter surface properties at the solid liquid interface. Flotation is a complex process influenced by contacting regime, bubble properties, pH, particulate characteristics and chemical additives, amongst others, and has been comprehensively reviewed (Harris 1982; Harris et al., 2002). Magnetic separations exploit the differing magnetic properties across minerals and gangue materials, resulting in focused applications. Diamagnetics are repelled towards the minimum magnetic field intensity, while paramagnetics move toward the greatest intensity. Examples of minerals separated through magnetic separations include hematite (Fe_2O_3), magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), pyrrhotite (FeS), chromite ($FeCr_2O_4$) and wolframite ($(FeMn)WO_4$). Mostly the magnetic properties are attributed to iron in the ferromagnetic form (Wills and Napier-Munn, 2006). Electrical separations exploit differences in electrical conductivity across minerals and gangue. Application is limited to dry sands and is restricted by particle size and the ideal flow of particles in a single layer (Wills and Napier-Munn, 2006).

Typically selective sulphide separations have been used to optimise value recovery only; however, it is known that these separations provide a technically feasible option for removal of sulphide not associated with the value from its tailings. Most commonly, pyrite (FeS_2) falls within this category. This has potential to introduce a level of primary integration of ARD prevention into the upstream mineral processing flow sheet. To date, the use of such separation has been driven by economic incentives rather than environmental concern (USEPA 1993; Broekman and Penman, 1991). Combining improved understanding of waste characterisation based on process conditions and characteristics of ores (Broadhurst, 2007), an opportunity exists for ARD prevention to be integrated into mineral processing employing physical separation, thereby addressing the costs of the ongoing legacy of ARD by removing its risk of formation from treated tailings. McCallum and Bruckard (2009) investigated different separations approaches across four tailings samples with the same aim as this study, the minimisation of sulphide content and thereby ARD generation potential. The tailings samples studied may be characterised as follows: magnetite rich sulphide tailings from a sulphide copper deposit; pyrite and pyrrhotite rich tailings from a nickel deposit containing disseminated and massive sulphides; monzonite porphyry silicate/ aluminosilicate rich tailings from a massive low grade gold-copper sulphide deposit; lead-zinc concentrator taiings from a silver-lead-zinc deposit. McCallum and Bruckard demonstrated appropriate separations of sulphur-containing fractions following gravity concentration using two heavy liquids of specific gravities of 2.85 and 3.75. Following treatment of four different tailing samples, separate product streams were achieved of which one was high in silicate sand (45-91%) while low in sulphur (0.8-0.4%) across four cases while the other was a crude iron sulphide heavy fraction in three cases. Using magnetic separation by a Readings dry magnetic separator, a high grade iron magnetic fraction containing 43 to 60% Fe while low in sulphur at some 0.3 to 0.5% was achieved with the first two tailings samples. In all four cases, flotation using a PAX collector resulted in the formation of a low volume stream containing the bulk sulphide product at S concentrations of 28%, 25%, 6.6% and 6.12% across the four samples, representing up to 79% recovery of the sulphide. The high volume stream was expected to represent a benign flotation tailing; however ARD generation potential was not assessed quantitatively.

Flotation was selected as the unit operation to explore the technical feasibility of separating the sulphide rich fraction of flotation tailings from the benign fraction and assess the environmental risk of such separation products in terms of ARD potential. Specifically, the concept, as outlined in Figure 5, centres on the concentration of the reactive sulphide-containing material into a small volume stream (sulphide rich tailings), while rendering the major portion of the tailings sample benign (sulphide lean tailings). The latter may be disposed by conventional methods with little or no risk of ARD formation. The case study is presented in Chapter 5.

Selection of flotation is based on selectivity and controllability of the separation as well as the common implementation of flotation processes in mineral processing; thereby allowing both ease in further processing of the waste tailings as well as retrofitting of the process to separate sulphide containing material as an integral part of the concentration regime. The removal of sulphur components from tailings developed through the concentration of base metals, especially copper, by physical separation was studied. The work of McCallum and Bruckard (2009), reported during the lifetime of this WRC project, supports this selection of flotation. Benzoaazoua et al. (2008) have shown that non-selective flotation is a feasible and cost effective option for separating sulphides from tailings. This produces two tailings waste fractions, a benign tailings stream with greatly decreased acid generation potential and a sulphide rich tailings stream. Various methods have been explored for disposal of the separated tailings. It has been proposed that the benign fraction can be used in co-disposal techniques with waste rock, decreasing its capability to generate acid, through reduced permeation of O_2 and water, or used as cover on existing tailings dumps. It has also been proposed that the sulphide rich fraction can be used in backfilling operations with good strength properties or, based on knowledge of mineral sulphide bioleaching, subjected to accelerated oxidation for generation of heat and acid required in mineral beneficiation operations.

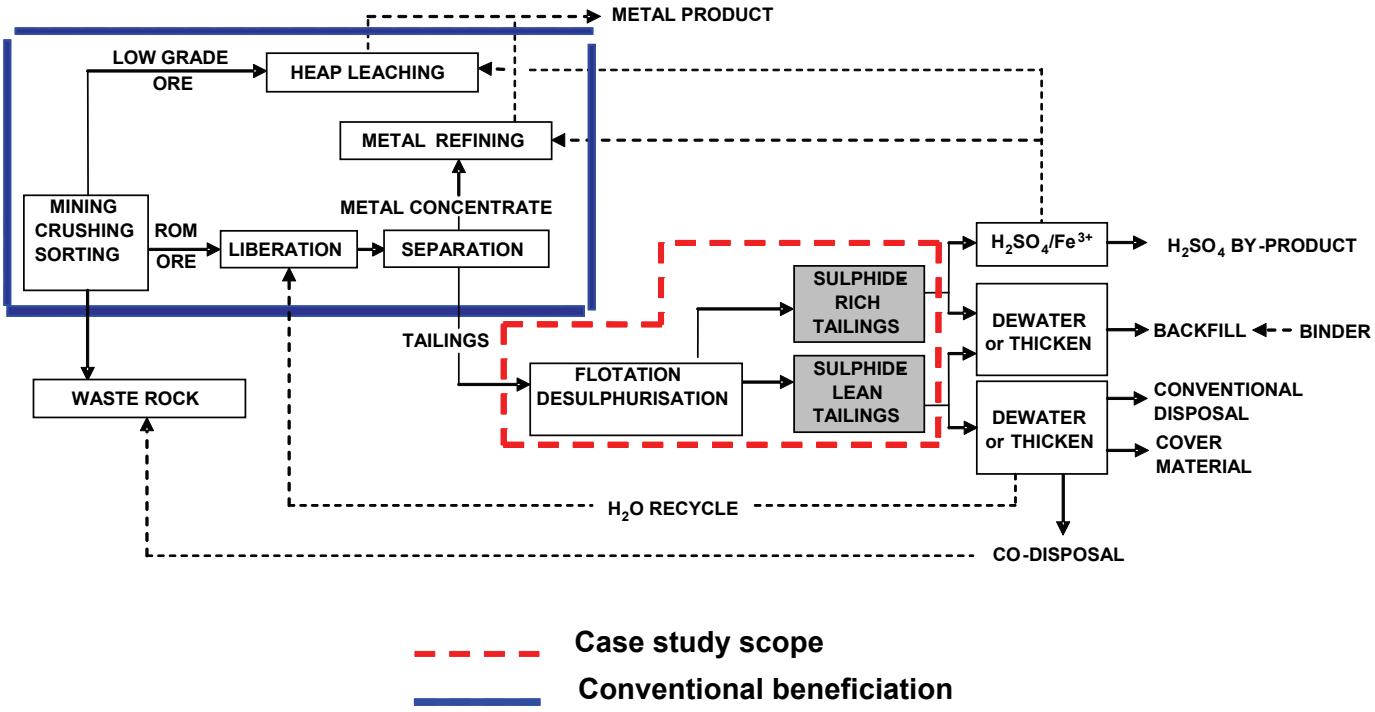


Figure 5: Conceptual flowsheet describing the integration of desulphurisation and disposal options into a generic base metal beneficiation process

3.3. Review of Unit Operations for Removal of Sulphide Containing Materials by Reaction

Mine and mineral processing sites give rise to huge amounts of waste materials. Excavated material that has a metal content that is too low to be processed economically is dumped in spoil heaps, along with mine overburden. Additionally, ores are often processed to concentrate desired metal sulphides prior to smelting. Concentration procedures, such as flotation, involve grinding the ore and treating it to make the target mineral fraction float; hence are not applicable to the treatment of dump and waste ores of low mineral content.

Acid rock drainage arises from oxidation following the exposure of sulphide minerals such as pyrite, contained in waste rock, closed mining sites and coal tailings, to atmospheric oxygen and moisture, representing a reaction approach. By accelerating the microbial decomposition of sulphidic mineral wastes, drainage can be intercepted as a contained pregnant leach solution (PLS) rather than released as environmentally damaging ARD (Bryan, 2006). In the reaction approach, research in mineral bioleaching has demonstrated the solubilisation of base metal sulphides through ferric and acid leach agents, with their subsequent regeneration through the microbial oxidation of the resultant ferrous iron and reduced sulphur species. Similarly abiotic leaching may result under acid and ferric rich conditions, where oxidation is driven by elevated temperature and elevated partial pressure of oxygen. This approach does not require the same degree of sulphidic mineral liberation as the physical separation above, hence it forms a potential approach for the risk reduction through decreasing potential for ARD generation from waste or dump rock. Further, re-processing of polluting waste heaps and tailings deposits, using refined modern methods to exploit more marginal materials, could lessen their environmental impact with immediate effect as well as remove the risk of delayed environmental impacts in future years, decades or centuries whilst providing an additional source of metals that would otherwise be lost. In this WRC project, mineral bioleaching under acidophilic microbial conditions was selected to investigate potential for the removal of sulphur compounds through solubilisation by reaction.

4. WASTE ROCK CHARACTERISATION IN TERMS OF ARD POTENTIAL

4.1. Introduction

The ability to predict the acid generating potential of a particular ore body or mineral type would assist greatly in the design phase of new operations and the management of waste and tails in existing operations and legacy sites. The two primary goals of predictive testing are the characterisation of a discrete volume of material in terms of acid generating potential and the prediction of drainage quality based on the rate of acid generation. The quality of the predictive information may be affected profoundly by the sampling protocol and the choice of predictive tests.

Tests are classified as either static or kinetic and the choice of which tests to use is typically affected by understanding of the geology, cost and time available. This section provides an overview of the most widely employed test protocols and highlights the advantages and limitations of these. Similar information is available in the Global Acid Rock Drainage (GARD) guide (INAP, 2009), prepared by the International Network for Acid Prevention (INAP).

Ideally, characterisation of the material should be performed during the exploratory phase of a new operation, where information may be obtained from outcrop exposures, exploration drill samples, geological sections and core assays. The sampling techniques employed to evaluate material in terms of recoverable resources are similar to those used in predictive testing for acid generation which facilitates this process. However, in most cases testing will be confined to waste rock dumps and tailings impoundments at operational or legacy sites.

4.2. Sampling

The purpose of predictive testing is to allow for classification and planning of waste disposal or management, based on the predictive quality of drainage from that material. The samples must be selected in order to account for both the type and volume of material and also for variability of materials that will be exposed with time. For these reasons the selection of samples has important implications for subsequent testing.

There are several opinions concerning the number of samples required during a fixed-frequency sampling regime. These range from a minimum of one to as many as 50 samples per million tons of significant rock type. A significant rock type is one which represents more than 1-2% of the total rock volume. The prescription of a fixed number of samples has been criticised, particularly with respect to waste rock dumps where the method of construction, typically end dumping from trucks, results in heterogeneous deposits. Tailings dumps are more uniform and consequently easier to characterise, although samples should be taken from various depths to determine if oxidation is occurring. It is important to ensure that the collected samples provide the best representation of the sampled body as individual sample data are normally composited to provide an overall picture of a waste pile or tailings impoundment.

Handling, storage and period between sampling and analysis are important factors as each of these may influence the physical and chemical characteristics of the sample. In particular, issues such as contamination of drill core samples by drilling lubricant and the addition of material during milling need to be considered.

4.3. Physical and Mineralogical Information

Important information on the material of interest can be gathered prior to testing by characterising its physical and mineralogical properties. Particle size is the most relevant physical property as it relates to the reactive surface area, which influences reaction rates and duration as well as the porosity and permeability of the solids. In addition, the presence of alteration layers (oxidation products or precipitates) on the surface can affect the results of subsequent leach tests. A number of mineralogical techniques are available, which provide information on the specific composition of the material and distribution of the various mineral phases. These techniques range from relatively simple and inexpensive, such as optical microscopy, through electron microscopy, X-ray diffraction (XRD) and diffusion (XRF) to advanced analyses requiring complex and expensive equipment, such as mineral liberation analysis (MLA) and quantitative electron microscope scanning (QEM-Scan). They provide information on the composition of the sample and provide details on

the crystal habit and distribution of the component minerals. This information can be used to identify sulphide minerals that release limited or no acidity upon oxidation, to identify fine grained or framboidal sulphides which would enhance their rate of oxidation and identify passivation of sulphide grains, which would reduce oxidation rate.

4.4. Static Tests

Static tests can be considered as initial screening tests. The most widely used static assessment methods are the acid-base accounting (ABA) and net acid generation (NAG) tests. The static tests provide information on the absolute potential of the material to generate ARD and do not take into account reaction kinetics. For the static tests a representative subsample from the bulk should be split and pulverised. The recommended particle size for static tests varies from -23 µm to -240 µm, depending on the source of the method. Pulverising enhances sample homogeneity and increases the reactive surface area. Based on the practical difficulty associated with generating sufficient sample material of -23 µm and mineral liberation issues at the upper end of the scale, -75 µm (-200 mesh) is often used. Pulverising the sample increases the reactive surface area which may liberate material which is unlikely to be exposed in the field. As such, static tests often represent a worst case scenario.

4.4.1. $pH_{1:2}$ and $EC_{1:2}$ Tests

These tests provide a measure of the inherent acidity or alkalinity of the material and also its potential to release salinity elements upon exposure to water. The procedure involves preparing a slurry at a solid to liquid ratio of 1:2 (w/w) using deionised water. The slurry is stirred briefly and allowed to stand for 24 hours prior to measurement. This test also provides useful information if the sample has been partially oxidised under humid, but non-saturated conditions. This can lead to the formation of acid generating salts, such as ferrous-ferric hydroxysulphates and jarosites, on the mineral surface. The salts may be readily soluble, rapidly releasing oxidisable and hydrolysable ions into solution.

4.4.2. Acid-Base Accounting (ABA)

The acid-base accounting test was originally developed in 1974 to evaluate coal mine waste and was modified in 1978 by Sobek and associates. Acid-base accounting (ABA) involves a series of static tests that evaluate the balance between acid generating and acid consuming reactions. The acid generating reactions are primarily the oxidation of sulphide minerals, while acid consuming reactions include the dissolution of carbonates, the weathering of silicates and the displacement of exchangeable bases.

These tests have been described by a number of agencies and environmental consulting companies and the terminology and way of expressing the results may change, the underlying principle remains the same. The maximum potential acidity (MPA, also referred to as acid producing potential (APP)) is derived by from an analysis of the total sulphur content of the material. This value is multiplied by a factor of 30.6 to represent the MPA as kg H_2SO_4 per ton of material. It is based on the reaction of pyrite under oxidising conditions:

$$FeS_2 + {}^{15}/_4O_2 + {}^{7}/_2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad [3]$$

The method is conservative as it assumes all S exists as pyrite, while in reality sulphate and native sulphur are non-acid forming, while a number of mineral sulphides (covellite, chalcocite, sphalerite, galena) release less or no acidity upon oxidation (Smart et al., 2002). If the mineralogy of the sample is known, the MPA value can be adjusted to account for non-acid generating sulphides. North American test protocols represent the final value in terms of kg $CaCO_3$ per ton, in which case a factor of 31.25 is used to multiply the S value (Stewart et al., 2006).

The acid neutralising capacity (ANC, also referred to as neutralising potential (NP)) is determined by reacting the sample with a standardised acid solution and then back-titrating to determine how much acid has been consumed by reacting with the sample. An initial “fizz test” is performed by adding a few drops of 8% HCl to the sample and gauging the extent of reaction. Based on the strength of reaction the volume and concentration of acid to be used in the test is selected. The standard test requires the heating of the sample-acid mixture to 80-90°C to accelerate the reaction. Following cooling, deionised water is added to make up a

standard volume (125 mL) and the sample is back-titrated to pH 7.0. A few drops of 15% H_2O_2 are added as the pH approaches pH 5.0 to promote ferrous iron oxidation. ANC is calculated using the formula below:

$$ANC = [Y \times M_{HCl} / wt] \times C \quad [4]$$

where : Y= (vol of HCl added) – (vol of NaOH titrated×B)
B= (vol of HCl in blank) / (vol of NaOH titrated in blank)
M_{HCl}= molarity of HCl
wt= sample weight (g)
C= conversion factor (49.0 to express results as kg H_2SO_4/t)

As with the MPA value, results from this test can be expressed in terms of kg $CaCO_3$/t.

The ANC test has been criticised for its tendency to overestimate the neutralising capacity as a result of the use of strong acid and the heating of the sample, both of which may lead to the reaction of minerals such as iron and manganese carbonates which would not normally react under environmental conditions. In certain situations the ANC may be underestimated as a result of metal hydroxide precipitation during the back-titration (Stewart et al., 2006).

If the sample contains significant amounts of siderite ($FeCO_3$) the ANC may be overestimated using the standard protocol as the neutralising effect of the carbonate is accounted for, but the acid generating effect of ferrous oxidation, hydrolysis and precipitation is not adequately accounted for. An alternative method, involving the addition of extra H_2O_2 and an extended reaction time, has been proposed to account for siderite in the sample (Skousen et al., 1997; Stewart et al., 2006).

The values for acid producing and neutralising potential are combined to determine the net acid producing potential (NAPP) or net neutralising potential (NPP), if $CaCO_3$ is used as the basis. Alternatively an ANC/MPA ratio is used to indicate a relative margin of safety within a material. “Safe” values in literature range from one to three, but it is generally accepted that a value over two signifies that there is a high probability the material will remain neutral.

4.4.3. Modified Acid-Base Accounting

This method is based on the same principles as the standard ABA, but has been modified to address some shortcomings. The MPA is calculated using sulphide sulphur rather than the total sulphur value. The ANC is determined over a longer period of time (24 hours), but does not involve heating the sample so less reactive carbonates should remain stable (USEPA, 1994). A number of other variations exist, such as the British Columbia Research Initial Test (BC) and the alkaline production potential:sulphur ratio (APP:S), but all are based on the same principle. Variations include changes in the particle size and final expression of the data. These alternative methods have the same inherent shortcomings as the standard ABA (USEPA, 1994).

4.4.4. Net Acid Generation (NAG) Test

The NAG test involves the addition of hydrogen peroxide to the test material to accelerate the oxidation of reduced sulphur species (Stewart et al., 2003a). Acid produced during the oxidation reaction may be neutralised simultaneously by alkaline material in the sample, resulting in a direct measurement of the net amount of acid generated by oxidising the sample. This is quantified by back-titrating and the final value is again expressed in terms of kg H_2SO_4/t. The back-titration is performed to two endpoints, with the titration value at pH 4.5 giving a measure of proton acidity as well as acidity from soluble iron and aluminium hydrolysis and precipitation. The titration value at pH 7.0 further includes metal ions which precipitate as hydroxides between pH 4.5 and pH 7.0.

A number of variations of the NAG test exist, with the three most common being the single addition NAG, the sequential NAG and the kinetic NAG. The single addition NAG involves a single addition of 250 mL 15% hydrogen peroxide (H_2O_2) to 2.5 g of pulverised (-75 µm) sample. The sample reacts for 12 hours after which it is heated to decompose unreacted peroxide. The NAG pH is recorded, the sample filtered and the filtrate back-titrated. The NAG value is determined using the equation below:

$$NAG\ (kg\ H_2SO_4/t) = (49 \times V \times M) / W \quad [5]$$

where: V= volume of NaOH used in titration (mL)
M= concentration of NaOH used in titration (moles/l)
W= mass of sample (g)

If the NAG pH≥4.5 the material may be classified as non-acid forming. For samples where the NAG pH<4.5 the sample may be classified as potentially acid forming with a secondary classification based on the calculated NAG value. A calculated NAG below 5 kg H_2SO_4/t places the material in the lower capacity group while a value above 5 indicates a higher potential acid forming capacity.

The single addition NAG has been shown to underestimate acid generating potential when the pyritic sulphur content of the material exceeds 1%. Hydrogen peroxide undergoes catalytic degradation when exposed to sulphide mineral surfaces or oxidation products. Where pyritic sulphur content exceeds 1% the potential exists for the peroxide to degrade prior to complete oxidation of the minerals. In this situation the sequential NAG test is preferable. The sequential NAG test follows a similar protocol except that when the sample is filtered at the end of the first test the solids are not discarded, but are retained to be used as the starting material for the second NAG test. This process is repeated until the NAG pH≥4.5 or the calculated NAG value becomes insignificant. As an example, laboratory test work (data not published) on a waste rock sample with a sulphur content of 3.16% required five NAG tests before no further acidity was generated. A single addition NAG test resulted in a 40% underestimation of the acid generating potential.

A third variation on the NAG test is the kinetic NAG. In this case the pH, temperature and conductivity are continuously measured for the duration of the oxidation phase. This provides an indication of the rate of mineral oxidation and also the relative rate of acid generation and consumption. Data generated using the same material described in the previous paragraph showed an initial increase in the NAG pH to pH 5.0 and the pH only dropped below pH 4.5 after 60 minutes. This indicates that the kinetics of carbonate dissolution is faster than sulphide oxidation, even under accelerated oxidation conditions. This type of information is important in assessing how the material will behave when exposed to the environment.

Analysis of the NAG test liquor prior to titration to determine cation and anion concentrations can provide valuable information on the liberation of heavy metals and other environmentally detrimental components which may exist as sulphides or acid labile minerals. In many cases this information would be more relevant than a TCLP or acid rain leach test.

Samples which contain significant amounts of organic material can affect the accuracy of the NAG test due to oxidation of the organic material by the peroxide, potentially resulting in underestimation of the acid generating capacity (Stewart et al., 2003b). It is therefore important that static tests are not performed or considered in isolation and that data from the different types of static tests are used to reach a conclusion on the material being tested. Figure 6 shows an example of a geochemical classification plot which utilises NAG pH and NAPP data to classify material as non-acid forming (NAF), potentially acid forming (PAF) or uncertain (UC). A generalised flowchart describing the process of evaluating samples by static tests is presented in Figure 6 (Smart et al., 2002).

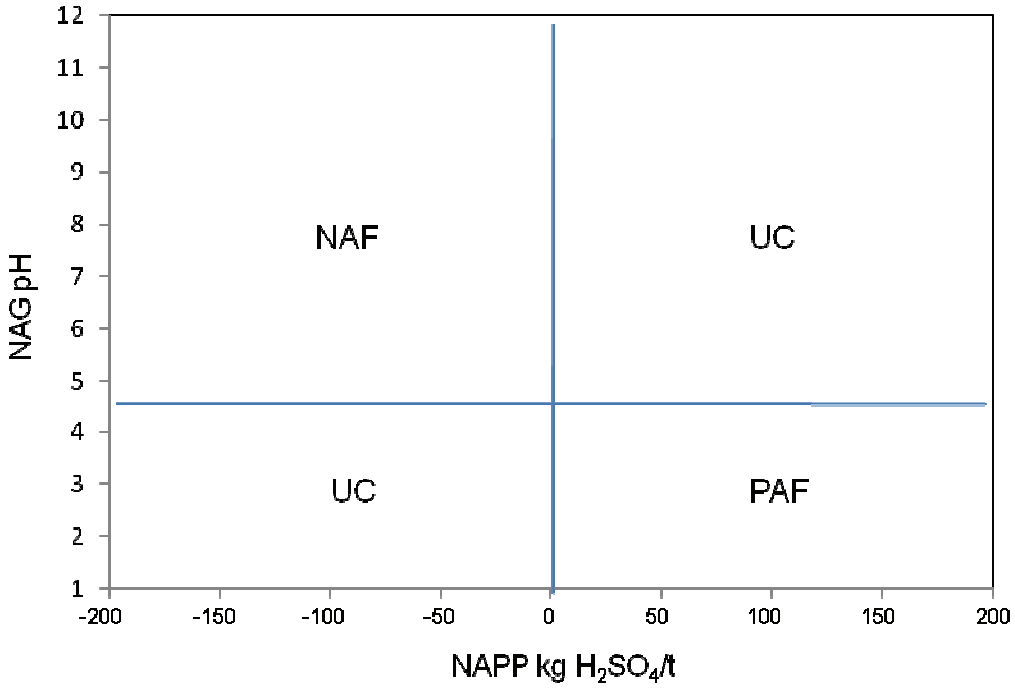
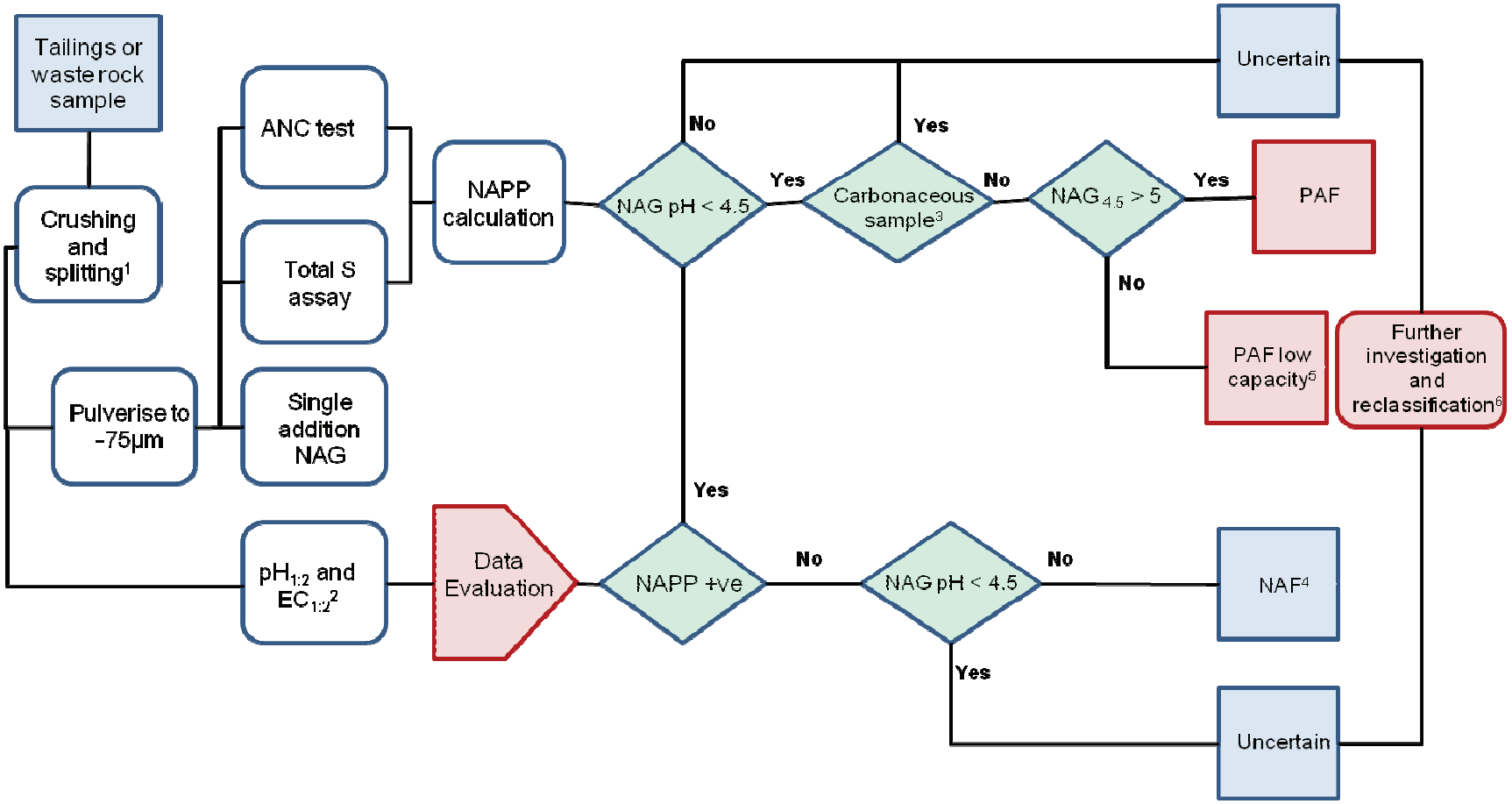


Figure 6: Example of a geochemical classification plot (Smart et al., 2002). Zones in the plot refer to non-acid forming (NAF), potentially acid forming (PAF) or uncertain (UC)

4.5. Kinetic tests

Kinetic tests attempt to mimic natural oxidation and weathering reactions in the field. They typically involve a larger volume of sample and tend not to require fine particle sizes. Kinetic tests provide information on the rate of sulphide mineral oxidation and give an indication of likely drainage quality. However, unlike static tests which provide information in a short period of time, the majority of kinetic tests reported to date require operation for months or even years to provide meaningful information and as a result are significantly more expensive. Kinetic tests can vary in terms of scale from shake flasks to field scale test dumps (Smart et al., 2002). An additional advantage over static tests is that variables which could influence the rate and extent of acid generation in the field can be tested under relatively controlled conditions. These variables include temperature, irrigation rate and the presence of iron and sulphur oxidising microorganisms. A number of popular kinetic tests are summarised in Sections 4.5.1 to 4.5.5. Further, the development of a biological kinetic test is presented in Section 4.5.5.2 with potential to provide good insight into ARD generation potential, including kinetic data.



[1]Sample preparation may include crushing to nominal-4 mm and splitting of a representative sample from the bulk. Core and rock samples require crushing before splitting. Drill chips and tailings do not normally require crushing.
[2]pH and EC measurements provide information on readily available acidity and salinity. Measurements best carried out on crushed rather than pulverised sample.
[3]Organics may interfere with NAG tests, particularly in coal samples with >5% TOC
[4]Further evaluation recommended for samples with high S (> 2%) and high ANC (ANC/MPA <1.5)
[5]Further investigation recommended to determine acid forming capacity when S > 1% and NAG/NAPP ratio < 0.5
[6]Further investigation required to classify samples with conflicting NAG and NAPP results, samples with high TOC

Figure 7: Flow chart showing ARD screening tests, decision nodes and ARD rock categories (Adapted from Smart et al., 2002)

4.5.1. Shake Flask Tests

Kinetic tests conducted in shake flasks typically utilise the smallest sample volume of all kinetic tests. The material is normally crushed to -75 µm (200 mesh) or smaller which increases surface area and leads to an increased oxidation rate. The material is typically suspended in distilled water, although nutrients may be added, and shaken for the duration of the test. Samples are periodically removed and analysed for pH, sulphate and dissolved metals. Where tests need to be run for extended periods additional water needs to be added to maintain liquid volume, but this can complicate data interpretation. Due to the small scale and relatively simple operation large numbers of replicates are possible, allowing a number of variables to be tested simultaneously.

4.5.2. Humidity Cell Tests

Humidity cells are among the most popular kinetic test. While there is no uniform design or methodology for operating humidity cells, the underlying principle is consistent. The material is packed into a reactor (column or box) with air inlet and outlet ports. The cell is typically operated for a minimum of 10 weeks, during which a cycle of aeration with dry air, moist air and flushing with a predetermined volume of distilled water is repeated. This is intended to mimic changes in atmospheric conditions with periodic rainfall events and should be adjusted to mimic local climatic conditions. Following the flushing events the leachate is collected and analysed for pH, acidity, alkalinity, redox potential and cation and anion concentrations. Humidity cells may be inoculated with iron and sulphur oxidising microorganisms.

4.5.3. Leach Column Tests

Leach columns are an extension of the humidity cell concept and are typically packed with 2-5 kg of crushed material or tails, which is a greater mass than a typical humidity cell. Water is periodically flushed through the column to create a wet-dry cycle which simulates oxidation and flushing events. The columns are operated under the assumption that oxygen is not limiting and aeration may be required where for larger columns. Leach columns are typically operated using a weekly wet-dry cycle, where water is added at a rate of 100 mL/kg and a monthly flushing cycle where water addition during one week of the month is increased 4-5 fold. The analyses performed on the leachate are similar to those used in humidity cell tests.

The major drawback of humidity cell and kinetic column tests is the time required to generate meaningful data, which may often run into years. This time period can be reduced by operating the columns in a similar fashion to bioleach columns, where rapid oxidation of the mineral for recovery of valuable metals is desired. In this case irrigation is continuous and the feed solution may be acidified or supplemented with iron and nutrients. The rationale behind the accelerated leach tests is that microbial colonisation of waste rock or tailings with a significant sulphide mineral content is inevitable, given their ubiquitous association with this type of material and the rate of acid generation and metal liberation from colonised material is of particular interest as this represents the most aggressive phase. Column temperature may also be controlled, depending on the sulphide mineral content of the material, to mimic heating of the material due to mineral oxidation.

4.5.4. Field Tests

Field scale testing involves the construction of test piles of waste rock on a lined bed to prevent seepage of the leachate. The size may vary from 800 to over 2 000 tons, depending on land availability and the particle size is generally not reduced, as is the case in other kinetic tests. In most cases active irrigation is not used (USEPA, 1994).

4.5.5. Biological Shake Flask Tests

A significant shortcoming of the standard kinetic tests is the tendency to ignore the influence of microbial activity. While humidity cells or leach columns may become colonised by microbes associated with the material, this does not occur in a controlled or reproducible manner. There is currently no widely accepted standard protocol which accounts for microbial activity. The GARD guide (INAP, 2009), which “is intended as a state-of-the-art summary of best practices and technology” does not consider the catalytic effect of iron and sulphur-oxidising microbes in any of the predictive tests. The following section reviews previous attempts to incorporate microbial activity and presents a refinement of the technique, with sample data, developed during this project.

4.5.5.1. Review of previous use of biological shake flask tests

Attempts have been made to develop kinetic tests which account for microbial activity, although they have not been widely accepted. An example of such a test is the British Columbia Research Confirmation Test developed by Duncan and Bruynesteyn (1979). *Acidithiobacillus ferrooxidans*, an iron oxidising bacterium, is added to an acid stabilised (pH 2.5) mineral suspension and incubated at 35°C. The pH is maintained at below pH 2.8 for the first three days to allow for microbial adaptation after which additional sample material is added. The solution pH is tested regularly and if it increases to above pH 3.5 the test is terminated and the sample can be classified as most likely non-acid forming. A decrease in solution pH indicates microbial activity and provides a strong indication that the sample will be acid forming.

4.5.5.2. Further development of the biological shake flask test

In this study, we have initiated further refinement of the biokinetic shake flask test, owing to its great potential to show tendency for ARD formation through microbial colonisation. Further to this the test demonstrates the combined impact of biologically leachable material with the inhibiting or neutralising environments or both. Legislation has placed the burden of responsibility of waste dumping for perpetuity onto mining companies, thereby changing process thinking in order to enable these risks to be monitored carefully over the long term time period to calculate the overall risk. Through the use of finely milled whole ore or tailings, the potential for microbially-mediated ARD formation is characterised, while minimising the time of assay required. The environments used both mimicked the biologically active environment that may develop with time as well as investigating the potential to generate such an environment. The methodology developed to date is presented, whereafter a preliminary data set comparing a subset of results is presented.

Methodology of biokinetic shake flask tests

In order to assess generation of acid, sulphate and metal dissolution under leach conditions, finely milled samples in the size range 37-75 μm were leached in shake flask tests. An ore loading of 7.5 g was added to 150 mL basal salts medium (BSM) in the presence of 0.5 g/L total iron (65% as Fe^{2+}, 35% as Fe^{3+}) at pH 2. Both abiotic tests and inoculated tests were conducted. The latter were inoculated with *Acidithiobacillus ferrooxidans, Leptospirillum ferriphilum* and *Acidithiobacillus caldus* at 10^6 cell/mL each. These were incubated at constant mesophilic temperature with agitation for 90 days. Redox, pH, ferrous iron, total iron in solution and sulphate in solution were monitored. Further, the leaching of abiotic controls, biotic flasks without pH control and biotic flasks with pH control were compared.

The samples presented in this study were drawn from the case study using sulphide separation by flotation to minimise the ARD generation potential of tailings sources from Kennecott as presented in Sections 5.2 and 5.3.

Sample results of biokinetic shake flask test

The pH, ferric iron and redox potential profiles obtained with time of incubation of the shake flasks are presented in Figures 8, 9 and Figure 10. On bioleaching of all the feed and tail materials, an initial increase in pH resulted from the acid leaching of gangue material (the gangue material of these Kennecott ores are well recognised to be acid consuming). While the initial rate of increase was the same in all cases, this deviated at approximately seven days of leaching with the rate of increase maintained only in the low S tails. The rate of increase decreased with increasing S availability. In both the feed and high S tails, the maximum pH (pH 2.8 and 3.4 respectively) was attained at day 18 whereafter a decreasing pH was observed until this stabilised in the range pH 2.2-2.3. This phase of decreasing pH corresponded to an increase in ferric iron concentration and redox potential, indicating the presence of biological activity driving ferrous iron oxidation. Although not monitored, the simultaneous oxidation of S compounds was expected. These oxidation reactions resulted in the concomitant generation of Fe^{3+} and H^+ leach agents and the ongoing release of acid, sulphate and metal ions into solution in the form of ARD. Rigorous analysis of the relative changes in pH, ferric iron generation across the time frame provides information on the competition between neutralisation and acidification of the gangue and sulphide phases, thereby informing the picture of ARD potential.

Of particular interest was the comparison of the bioleach profiles of the low S tails conducted with and without pH control. In the absence of pH control, the pH of the bioleach of the low S tail sample continued to

increase with time, unlike the high S (>2% S) samples. A maximum pH between 4.80 and 5.10 was reached and maintained between day 45 and the end of the leach. Under these conditions of increasing pH, regeneration of ferric iron through biological iron oxidation catalysed by *Acidithiobacillus* and *Leptospirillum* species did not occur, hence a decrease in both Fe^{3+} concentrations was observed from day 4 such that ARD generation did not occur. This was accompanied by a decrease in redox potential. Where the pH of the bioleach was maintained at conditions optimal to the *Acidithiobacillus* and *Leptospirillum* species inoculated, generation of ferric iron, accompanied by increasing redox potential was observed from day 4 to day 18, with the Fe^{3+} concentration increasing to approximately 550 mg/L. This Fe^{3+} concentration was maintained from day 18 to day 31 whereafter a gradual decrease was observed. Under all conditions, the ferrous iron concentration remained below 40 mg/L, indicating that the rate of bacterial oxidation was not rate limiting. From Figure 8, it can be seen that the acid consuming reactions were complete or balanced by the acid-generating bioleaching from day 18. This is consistent with the pH maxima observed on leaching of materials with a higher S content and is a characteristic dominated by the gangue composition. On comparison of the bioleach assays with and without pH control, it was seen that while the low S material can support a small amount of leaching and thereby ARD generation under acidic conditions, the gangue composition prevents these conditions being established in the absence of external acid addition. This was due to conditions unfavourable to the microbial system being established before sufficient leaching occured. This illustrated the interaction between biological acid generation and abiotic acid consumption. Further, the biological tests provide a measure of the potential for conditions favourable to bioleaching to be established, whereas the static chemical tests assume that this leaching would occur in all cases.

Finally, it is recognised that while a material may contain a mineral-gangue combination such as in the low S tails above, where active bioleach conditions were not naturally established, the disposal of such material in the presence of an acid generating material would result in the liberation of the sulphide fractions of both, aggravating ARD generation.

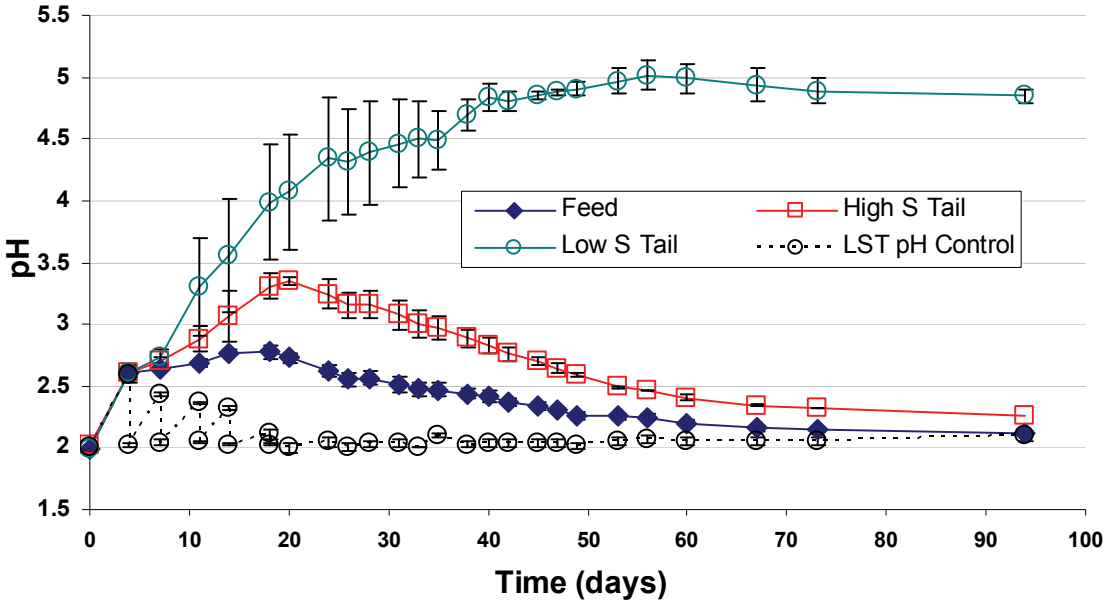


Figure 8: The pH profile obtained on bioleaching of finally milled tailings samples of varying S concentration following inoculation with a mixed mesophilic culture. Error bars denote standard deviation (n = 3).

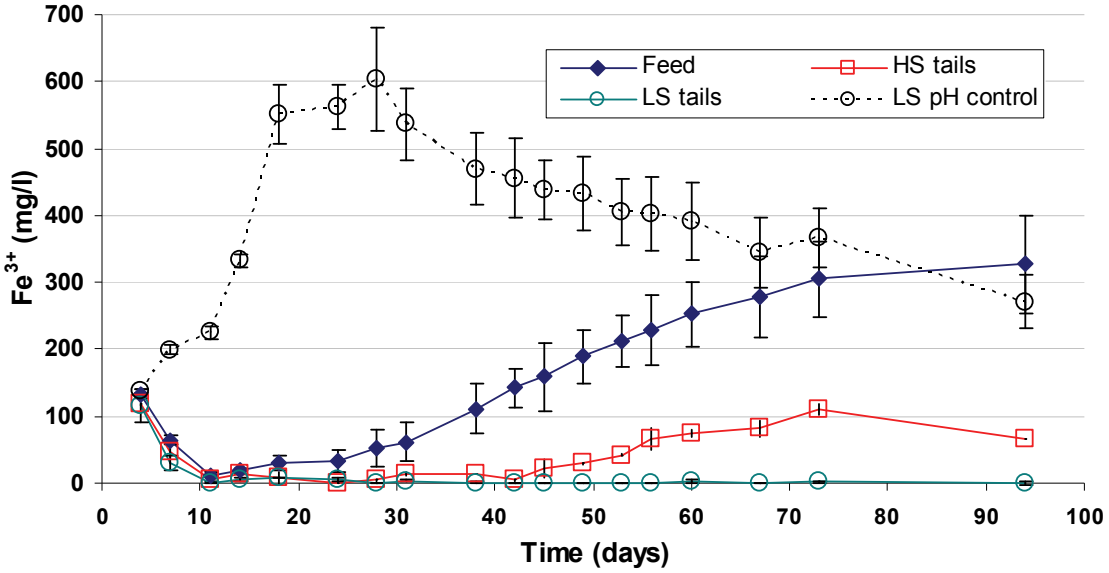


Figure 9: The profile of ferric iron concentration obtained on bioleaching of finally milled tailings samples of varying S concentration following inoculation with a mixed mesophilic culture at a starting concentration of 0.5 g/L soluble iron. Error bars denote standard deviation (n = 3).

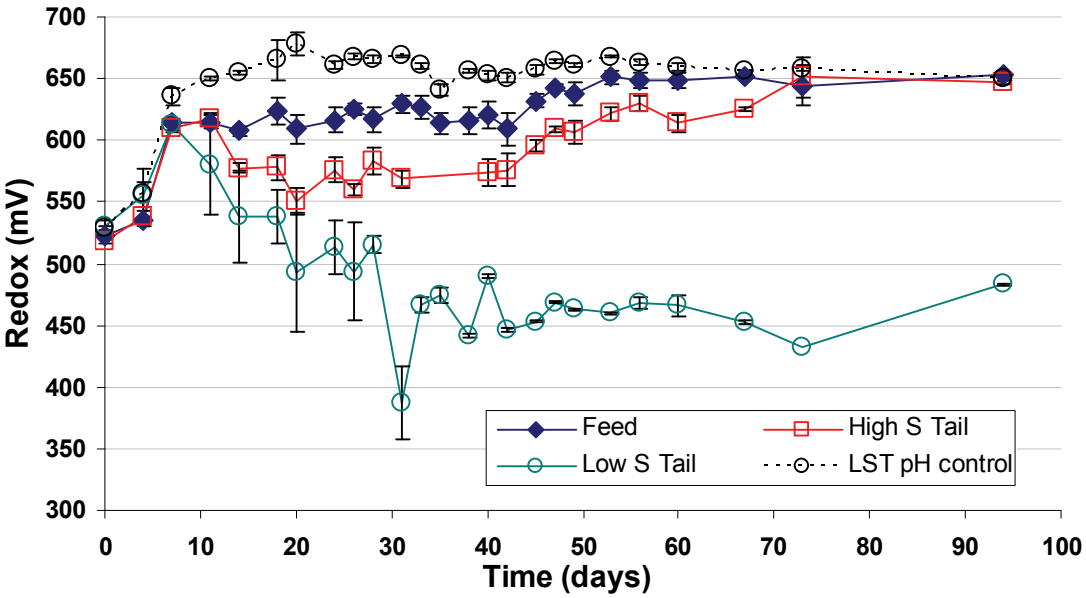


Figure 10: The redox potential profile obtained on bioleaching of finally milled tailings samples of varying S concentration following inoculation with a mixed mesophilic culture. Error bars denote standard deviation (n = 3).

4.5.5.3. Conclusion

The biokinetic shake flask test described above provides information on the relative kinetics of acid-consuming and acid-generating reactions that cannot be obtained from typical static tests. Inoculation of the flasks with iron and sulphur oxidising bacteria facilitated the catalysis of the mineral oxidation reactions, as would occur in the field, providing relevant data more rapidly than standard abiotic kinetic tests. One limitation of the assay is that it is a batch reaction. In the case of the material tested alkalinity was liberated from the gangue which, in the case of the LST sample, increased the pH to the point where microbial activity was inhibited. In reality the liberated alkalinity would be flushed out, increasing the potential for subsequent microbial activity and oxidation of the sulphides. The assay is currently being refined to include periodic replacement of the liquid fraction with fresh media, in an attempt to better represent reality.

5. CASE STUDY 1: REMOVAL OF SULPHIDE FROM TAILINGS BY FLOTATION AND ITS SUBSEQUENT IMPACT ON ARD POTENTIAL

5.1. Introduction

This experimental case study formed part of the development of an integrated approach to tailings management aimed at addressing the shortcomings of current methods of tailings disposal (see discussions in Chapter 3). The focus of this case study was on the use of froth flotation for the removal of sulphides from tailings generated through minerals processing. These tailings are one of the major sources of ARD, typically comprising 30% to 50% of total mineral waste in hard-rock mining (see Figure 2, Chapter 2).

The study here aimed to demonstrate the technical feasibility of flotation desulphurisation, at laboratory scale, and the subsequent environmental benefit of producing benign tailings. The latter was assessed with the combined use of static chemical and biokinetic ARD prediction tests. The experiments were conducted on a copper sulphide ore of typical porphyry characteristics, previously well characterised in research at UCT (Maluleke, 2006, Broadhurst et al., 2007) and known to be acid generating.

5.2. Experimental Test Work

In order to test the feasibility of the conceptual approach presented in Chapter 3, flotation tests were carried out on a typical copper sulphide ore. Static chemical and biokinetic shake flask ARD prediction tests were conducted on products to assess the performance of these tests in terms of ARD mitigation.

5.2.1. Ore Description

An oxidised low grade porphyry copper ore with a sulphur grade of 3.84 ±0.35% (determined using a LECO S632 sulphur analyser) was used as an example of sulphidic ore. The copper grade was measured as 0.16±0.04% by atomic absorption spectrometry (AAS). Qualitative XRD indicated pyrite and chalcopyrite as major sulphide minerals. Carbonates present included calcite and siderite which are typically associated with porphyry type ores (Broadhurst et al., 2007). Silicate minerals made up the majority of gangue, dominated by quartz (64%).

Table 5 gives details of the sulphide mineral analysis of the ore and a comparison of typical ore characteristics from literature (Broadhurst, 2007). Mineral grades were calculated assuming all copper and sulphur are present as sulphide based on the qualitative XRD data. Crushed ore samples of 1.13 kg were milled to 70% passing 150 µm with a steel rod mill before flotation.

Table 5: Sulphide mineral characteristics of porphyry ore

	Typical porphyry analysis (%) (Broadhurst, 2007)	**Analysis of samples used in this study (%)**
S (LECO)	2 – 11	3.84 ± 0.35
Cu (AAS)	0.5 – 1	0.164 ± 0.04
Fe (AAS)	1 – 10	8.07 ± 1.43
Chalcopyrite	1.5 – 2	0.47 ± 0.12
Pyrite	2.5 – 18	7.03 ± 0.69

5.2.2. Flotation Tests

Flotation experiments were carried out on milled ore slurry in a 3 litre modified Leeds batch flotation cell at 30 wt% solids. The reagents used were a dithiophosphate based promoter, from CYTEC Mining Chemicals (Day, 2002) which is used onsite for copper flotation, and methyl isobutyl carbinol (MIBC) frother. All experiments were conducted at the natural pH of the slurry in tap water (± pH 6). The air flow rate and impeller speed were kept constant at 5 L/min and 1200 rpm. Collector concentration was varied to manipulate pyrite recovery. Samples collected were analysed for iron, copper (AAS) and sulphur (LECO). The desulphurised tailings were split into representative samples for use in ARD prediction tests.

5.2.3. ARD Prediction Tests

The following static and kinetic tests were used for prediction of ARD generation potential:

(i) Acid base accounting (ABA)

- maximum potential acidity (MPA) calculated based on the LECO sulphur grade of the sample.
- acid neutralisation capacity (ANC) is calculated by reacting the sample with HCl to dissolve available acid consuming minerals such as carbonates. Due to the presence of siderite in the gangue material the Skousen method of ABA was used (Maluleke, 2006). Back titration with NaOH gives an equivalent acid consumption, expressed as kg H_2SO_4/ton of tailings.
- net acid production potential (NAPP) where NAPP= MPA – ANC (Stewart et al., 2006).

(ii) Net acid generation (NAG)

with results shown in two ways: as NAG pH *i.e.* the final pH of the oxidised sample, giving an indication of the state of the final product; and as an equivalent mass of sulphuric acid (kg H_2SO_4) produced per ton of ore (Stewart et al., 2006).

(iii) Biokinetic shake flask tests, (as discussed in Chapter 4).

Table 6 gives guidelines for classification of samples based on the results obtained through the ABA and NAG tests as well as combined results for use in ARD classification plots where discrepancies in the results occur. These classifications are used to characterise the tailings produced through flotation experiments in order to assess the environmental performance of the desulphurisation experiments.

Table 6: Guidelines for classification of ARD prediction test results (Hansen, 2004; Stewart et al., 2006)

	Result	Units	Classification guideline
Acid base account	NAPP>20	kg H_2SO_4/ton	Acid forming
	-20<NAPP<20	kg H_2SO_4/ton	Potentially acid forming
	NAPP<-20	kg H_2SO_4/ton	Non acid forming
Net acid generation	NAG pH<4.4	pH	Potentially acid forming
	NAG pH>4.4	pH	Non acid forming
	$NAG_{pH4.5}$ > 0	kg H_2SO_4/ton	Acid forming due to free acid
	NAG_{pH7} > 0	kg H_2SO_4/ton	Acid from metal ions in solution
Combined static tests	NAG pH<4.5 and NAPP>0		Potentially acid forming
	NAG pH>4.5 and NAPP<0		Non acid forming
	If either of these criteria fail, the results are considered uncertain and further testing is required for classification		

5.3. Results and Discussion

5.3.1. Separation of Residual Sulphides by Flotation

The extent of pyrite recovery, and hence of the effectiveness of desulphurisation, was determined as a function of collector dosage in batch floats. Table 7 gives the results of preliminary tests in terms of the sulphur content of the samples before (feed) and after (tailings) desulphurisation. These results show that the removal of pyrite from the tailings was dependent on the collector dose, with high recoveries being achieved at collector dosages exceeding 27 g/ton.

Table 7: Results of changes in S% in tailings with collector dosage

Collector addition (g/ton)	Pre-desulphurisation S (%)	Post-desulphurisation S (%)
12	4.16	4.06
15	4.28	2.20
27	3.73	1.10
36	3.64	0.66

Note: All tests conducted at natural pulp pH (~pH 6), and a 15 min float period.

In order to test the option of running two flotation stages in series, a float was run using step-wise increases in collector dosage from 9 g/ton to 36 g/ton. As illustrated in Figure 11, collector dosage was found to have a far greater effect on pyrite recovery than on chalcopyrite recovery. Hence, whilst a low collector dose (9 g/ton) resulted in low pyrite recoveries (<6%), a recovery as high as 95% was achieved at a collector dosage of 36 g/ton. On the other hand, the majority of the chalcopyrite recoveries occurred at relatively low collector dosages (9-18 g/ton).

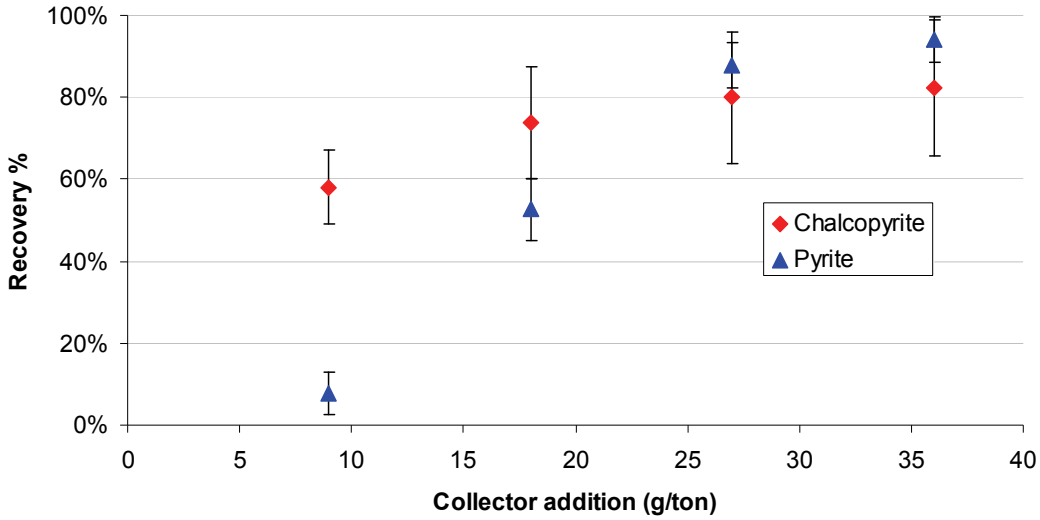


Figure 11: Change in mineral recovery with collector addition on batch flotation of porphyry ore. Error bars denote standard deviation (n = 3).

This differential effect of collector dosage creates the opportunity for value recovery from tailings by using low initial collector dosages to remove small quantities of easily floatable value mineral (chalcopyrite), and subsequently increasing collector dosage to remove pyrite, leaving a predominantly sulphide free tailings. This concept is presented schematically in Figure 12, which shows the calculated proportional mass flows for chalcopyrite, pyrite and gangue in a two-stage flotation process.

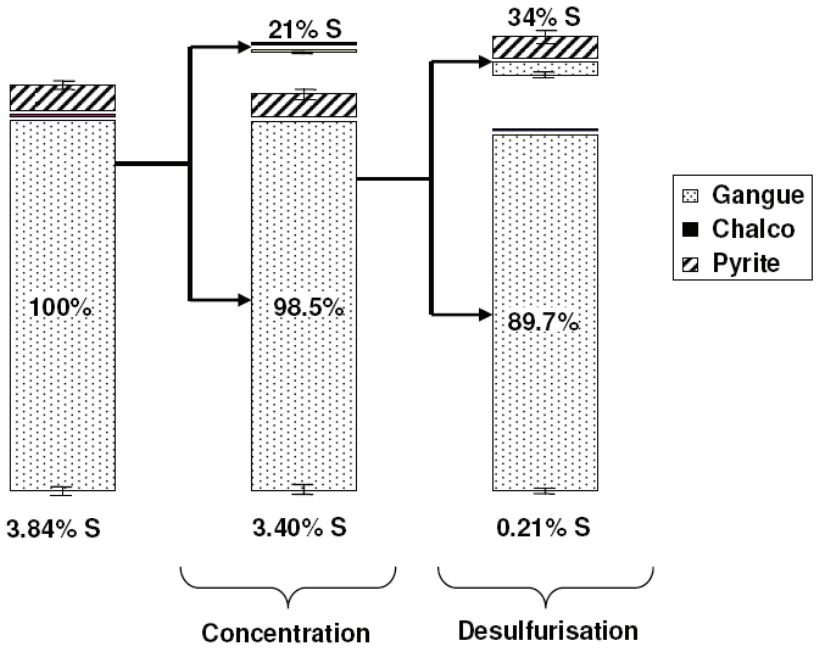


Figure 12: Schematic of mass flows in two-stage flotation for separation of active components from gangue indicating relative mass flow and sulphur grade of each stream

The first flotation stage, termed the concentration phase, produced a concentrate constituting only a small portion (1.54%) of the total feed by mass, but containing 58% of the chalcopyrite. The first-stage tailings constituted the vast majority of the feed material, and had a sulphur content of 3.4%, occurring predominantly as pyrite. The second flotation stage, termed the desulphurisation stage, produced a sulphide-rich phase (34% sulphide) of relatively small volume (8.7% of the total feed by mass), termed the sulphide-rich tailings fraction. The remaining benign tailings (the sulphide-lean tailings fraction) accounted for 89.7% of feed by mass, with a greatly reduced sulphur grade (0.21% S).

5.3.2. Acid Rock Drainage Risk Assessment of the Tailing Fractions by Static Testing

The ARD potential of the various tailings produced through flotation was assessed using acid base accounting (ABA) and net acid generation (NAG) static tests. The results of the ABA tests are summarised in Table 8.

Table 8: ABA results for tailings samples of varied sulphur grade

Sample	S Grade	MPA	ANC	NAPP	Classification
	%	[kg H_2SO_4/ton]			
1	3.8%	115.0	27.5	87.7	Acid forming
2	2.2%	67.3	25.0	42.3	Acid forming
3	1.0%	31.7	26.3	5.37	PAF
4	0.21%	6.6	28.7	-22.1	NAF

As the samples were from the same ore body, the acid consuming gangue minerals present were similar. Hence ANC values did not vary greatly for the different tailings samples and can be considered as largely independent of the desulphurisation process. However, a decrease in the sulphur content of the sample greatly reduced the maximum potential acidity (MPA), and thus the net acid producing potential (NAPP). Based on the ABA classification criteria presented in Table 6, samples 1 and 2 with higher sulphur grades (3.8% and 2.2% respectively) were both acid forming. At a sulphur grade of 1.0%, the sample became potentially acid forming (PAF), with a sulphur grade of 0.21% resulting in a non-acid forming (NAF) classification. The classification of the tailings samples as a function of ANC and sulphur grade is depicted graphically in Figure 13.

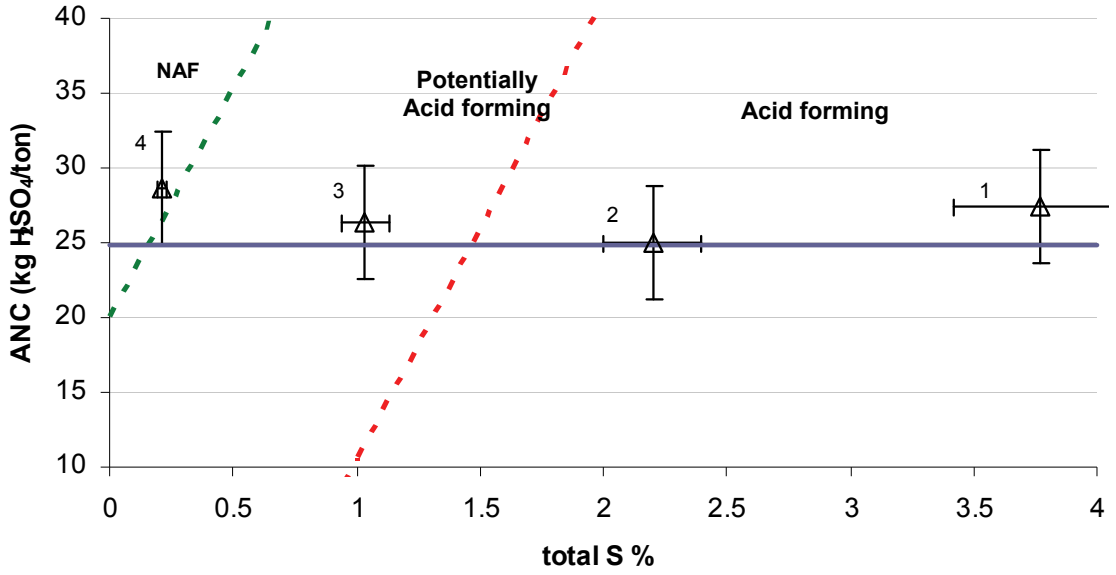


Figure 13: Acid Base Accounting results: ANC vs. S grade (%) for selected tailings samples. Error bars denote experimental variance across all samples testes.

The results of the single addition net acid generation (NAG) tests are summarised in Table 9. As in the case of the ABA test results, only the low sulphur tailings (sample 4 with 0.21% S) are classified as non-acid forming.

Table 9: Single addition NAG results for samples of decreasing residual sulphur content

Sample	S_T (mass %)	After boil NAG $_{pH}$	$NAG_{pH4.5}$	NAG_{pH7}	Sulphur Oxidation (%)	ARD classification
			(kg H_2SO_4/ton)			
1	3.84	2.57	16.5	26.8	37%	Acid forming
3	1.04	2.84	8.47	12.2	81%	Acid forming
4	0.21	5.71	0	0.81	87%	Non acid forming

The NAG pH is plotted as a function of the NAPP results, derived from the ABA tests, in Figure 14. In accordance with the combined classification criteria outlined in Table 6, flotation tailings with sulphur grades of >0.7% lie in the lower right-hand quadrant and are potentially acid forming. As the sulphur grade decreased, the points shifted towards the non-acid forming region, becoming non-acid forming at grades of 0.21%. Flotation tailings with intermediate sulphur grades (0.3% and 0.67% S) lie in the bottom left-hand "uncertain" region of Figure 13, and hence remain unclassified.

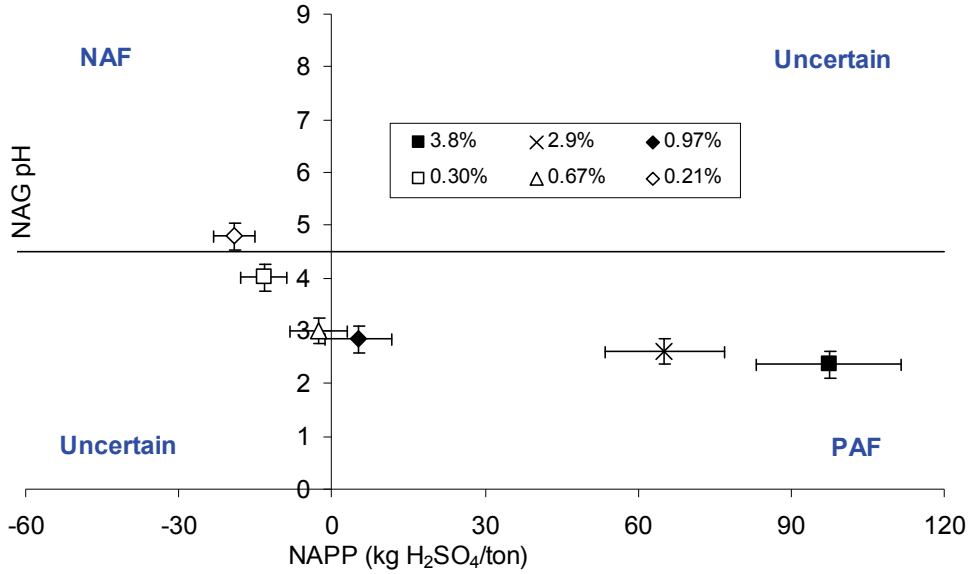


Figure 14: Acid rock drainage classification plot for tailings samples of different sulphur content

5.3.3. Acid Rock Drainage Risk Assessment of the Tailing Fractions: Biokinetic Shake Flask Tests

Biokinetic ARD prediction tests were conducted in order to cover the shortcomings of the static tests, including the lack of indication of acid and base interactions, and their relative timescales, and the availability and suitability of the sulphide mineral for bio-oxidation in a leach environment. Detailed results for the biokinetic shake flask tests conducted on low sulphide tailings (LST containing 0.21% S), high sulphide tailings (HST containing 3.40% S) and feed tailings (3.84% S) have been presented and discussed in Chapter 4. These results confirmed the low ARD potential of the low sulphide (0.21% S) tailings fraction under non-acidic conditions, as derived from the two-stage desulphurisation flotation process presented in Figure 12. The biokinetic tests further showed that the acid neutralising capacity of the acid consuming reactions was short-lived for tailings that have not been desulphurised (HST and feed samples), and that if disposed of these tailings will definitely generate acid over the long-term.

A comparison of the results of the static chemical and the biokinetic tests (Table 10) indicated that the NAG pH values generated during the NAG tests were similar to the final pH values obtained for the biokinetic shake flask tests (leach period of 73 days). The acid neutralising capacity (ANC) values for all samples, derived from the static acid base accounting (ABA) prediction test, furthermore corresponded to the amount of acid consumed during the pH-controlled biokinetic test *i.e.* 25 kg H_2SO_4/ton. The good correlation of results indicates that the static tests provide a relatively accurate measure of the long-term acid generating potential in the case of this material.

Table 10: Comparison of static and biokinetic test data

Sample	S%	Static tests[1]		Biokinetic test	
		NAG pH	ANC (kg H_2SO_4/ton)	pH Day 73	Classification
Feed	3.84%	2.36	24.9 ± 3.79	2.15	Acid forming
High S Tails	3.40%	2.61		2.32	Acid forming
Low S Tails	0.21%	4.79		4.89	Non-acid forming[2]

(1) Detailed results provided in Hesketh et al., 2010a
(2) Under conditions with no external acid addition

5.4. Conclusion

The results of this case study demonstrate that the long-term ARD risks associated with base metal sulphide tailings can be mitigated by means of desulphurisation using standard flotation techniques. The results of this research project also illustrate that the conceptual approach outlined in Chapter 3 provides opportunity for the simultaneous recovery of metal values from the conventional tailings waste stream. On the basis of the flotation test results, a two-stage desulphurisation process has been proposed for the desulphurisation of typical porphyry-type copper sulphide tailings. This process gives rise to a chalcopyrite-rich concentrate and two tailings fractions, *viz* a small volume, sulphide-rich fraction containing the majority of the acid-forming pyrite, and a large volume, sulphide-lean fraction with sulphur grades as low as 0.21% S. The benefits of the two-stage desulphurisation process have been confirmed through ARD prediction techniques, which have shown the sulphide-lean tailings fraction to be non-acid forming. The application of biokinetic shake flask tests served to both complement and enhance the results of the static chemical (ABA and NAG) ARD prediction tests, providing valuable informative data on microbial activity and its role in the kinetics and mechanisms of ARD generation.

6. CASE STUDY 2: REMOVAL OF SULPHIDE FROM WASTE ROCK AND TAILINGS BY ACCELERATED OXIDATION AND ITS SUBSEQUENT IMPACT ON ARD POTENTIAL

6.1. Project Approach

To accomplish the acceleration of the microbial leaching of sulphide mineral wastes, either as the first step for re-processing mineral scarce waste heaps or to reduce the future polluting capabilities of the waste, it is necessary to understand which factors are affecting microbial activity, and manipulate them so as to optimise mineral oxidation. Two key aspects which can affect the microbial population of a heap are pH and aridity (Bryan *et al*., 2006). While the most extreme conditions may cause indigenous microbial communities to be restricted in composition, these populations may still be capable of extensive mineral oxidation. Rather, the availability of inorganic nutrients, energy source, oxygen and the sulphide mineral substrate are the most pertinent consideration in terms of nurturing microbial colonisation and activity to ensure the rapid leaching of the available sulphide fraction before final disposal.

The efficient translocation of liquid through the heap must also be considered. This relates to two aspects: the transfer of nutrients and oxygen to the microorganisms, and the removal of oxidation products. As mineral oxidation progresses, the precipitation of metals such as iron in the form of jarosites within the heap will occur. If there is insufficient liquid movement, the formation of hardpans due to this precipitation may form a natural barrier to oxygen and moisture, reducing the immediate output of polluted effluents (Schippers *et al*., 2001), and allowing these to remain within the heap or dump as a environmental risk. Therefore, the construction and packing of the heap must be carefully controlled.

The effluent from an efficiently irrigated dump operation can then be collected and recovered in much the same way as for a conventional heap leaching operation. The advantage of such bioaugmentation where metal recovery is not targeted is that the otherwise protracted release of ARD could be condensed to a confined time horizon with collection and remediation of leachate, e.g. by active treatment with lime. The implementation of processes such as these could improve mineral resource productivity and protect its equally valuable natural environment to improve public perception of the industry and environmental stewardship. Most importantly, the approach may provide a route to limit the long-time liabilities of the mining site.

6.2. Experimental Materials and Methods

6.2.1. Column Reactors

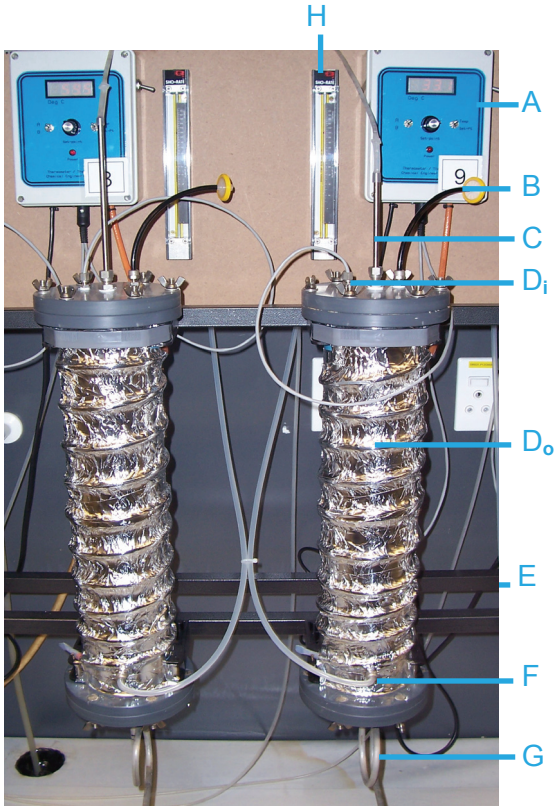
A column reactor system was used to simulate the heap or dump bioleach system. Polyvinyl chloride (PVC) columns were used as seen in Figure 15. The columns were insulated and temperature controlled by a heating coil positioned on the external surface. A temperature controller unit was employed with temperature sensors positioned on the external column surface (inside the insulating layer) and inside the packed ore bed. Where aeration was specified, compressed air flowed into the column from the bottom through an air distributor. The effluent pipe was coiled in design to minimise air loss by short-circuiting. The column reactors had a working volume of approximately 3140 cm^3 with a 40% void volume.

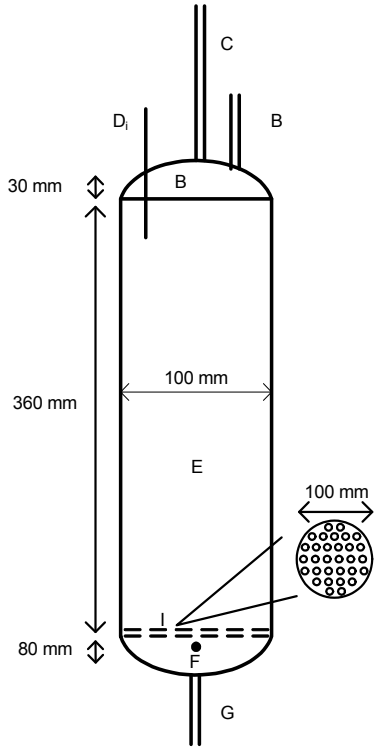
6.2.2. Bacterial cultures

Mesophilic bacterial cultures were employed to facilitate the leaching process. The specific species used were obtained from the German culture collection DSM: *Acidithiobacillus ferrooxidans* DSM 584, *Acidithiobacillus caldus* DSM 8584 and *Leptospirillum ferriphilum* ATCC 49881.Unless otherwise stated, all stock cultures were maintained in 1 L shake flasks with a 700 mL working volume, agitated at 120 rpm on an orbital shaker. *Acidithiobacillus ferrooxidans* was grown at pH 1.6 in modified 9K media, consisting of the following components (g/L): $(NH_4)_2SO_4$ (2.0), K_2HPO_4 (0.5), $MgSO_4.7H_2O$ (0.5), KCl (0.1), $FeSO_4.7H_2O$ (20.0). *Acidithiobacillus caldus* was grown in similar media excluding $FeSO_4.7H_2O$ and with an additional 1 g/L of $(NH_4)_2SO_4$ and 5 g/L elemental sulphur.

Leptospirillum ferriphilum, agitated at a rate of 400 rpm, was grown in a 1 L CSTR at a dilution rate of 0.021 /h and pH 1.30. The reactor feed contained the following components (g/L): $(NH_4)_2HPO_4$ (0.53), $(NH_4)_2SO_4$ (1.83), $FeSO_4.7H_2O$ (5.0), K_2SO_4 (1.11) as well as 10 mL/L Vishniac solution containing: $ZnSO_4.2H_2O$ (1.0),

$CoCl_2.6H_2O$ (1.0), $MnCl_2.4H_2O$ (1.0), $CuSO_4.2H_2O$ (0.5), $FeSO_4.7H_2O$ (5.0), $Na_2MoO_4.2H_2O$ (0.5), $CaCl_2.2H_2O$ (0.5), added to 15 g/L EDTA dissolved in 6% KOH. The *Leptospirillum ferriphilum* strain was originally obtained from a continuous tank bioleaching mini-plant, treating a pyrite concentrate from Gamsberg, South Africa, and was maintained at a residence time of 72 hours.





A-Temperature control unit
B-Air outlet
C-Feed inlet
Di-Inside temperature sensor
Do-outside temperature sensor
E-packed bed
F-air inlet
G-leachate outlet
H-rotameter
I-perforated metal disc

Figure 15: Bioleach column reactor system

6.2.3. Ore Mineralogy

The experiments were conducted using the ore of the mineralogy detailed in Table 11.

6.2.4. Analytical Procedures

The bioleaching performance and potential for ARD formation was determined by investigation of pH, redox potential and iron liberation and speciation. The ARD potential was determined using ABA methods.

Sample pH measurements were taken using a Metrohm 704 pH meter and probe. Redox potential measurements were taken using a Metrohm 704 pH meter equipped with a combined Pt.Ag/AgCl electrode. The redox electrodes were tested on a daily basis by measuring a Crison standard redox solution of 468 mV at 25°C.

Atomic absorption spectroscopy (AAS) was used to determine Fe^T (total iron) concentration in the leachate. A Varian Spectra AA-200 Atomic absorption spectrophotometer incorporating Spectra AA 100/200 version 1.1 software was utilised. The Fe^{2+} concentration was measured colorometrically using the 1-10 phenanthroline method (Eaton *et al*., 1998). The 1-10 phenanthroline complexed with Fe^{2+} to form an orange/red compound which was quantified by measuring absorbance at 510 nm. The Fe^{3+} concentration was calculated by subtracting the Fe^{2+} concentration obtained either from the 1-10 phenanthroline assay or from the redox potential by calculation using the Nernst equation, from the total iron concentration obtained by AAS.

Acid base accounting was used in the calculation of net acid producing potential (NAPP), calculated as the difference between the theoretical maximum potential acidity (MPA) based on S content and the experimentally determined acid neutralising capacity (ANC) values of the sample. For comparison, the net acid generation (NAG) value for each experiment was also determined experimentally. These tests are reviewed in Section 4.4 while the experimental protocols used are presented in Section 5.2.3.

Table 11: Ore mineralogy used in bioleach column experiments

Mineral	Chemical Formula	Weight percent [%]
Chalcopyrite	$CuFeS_2$	1.28
Pyrrhotite 3T	Pyrrhotite	0.45
Sphalerite	ZnS	0.45
Pyrite	FeS_2	2.64
Chalcocite	Cu_2S	0.13
Covellite	CuS	0.20
Bornite	Cu_5FeS_4	0.07
Enargite	Cu_3AsS_4	0.07
Galena	PbS	1.71
Rutile	TiO_2	0.13
Goethite	FeO(OH)	0.07
Hematite	Fe_2O_3	0.13
Alunite	$KAl_3(SO_4)_2(OH)_6$	0.33
Svanbergite	$SrAl_3(PO_4)(SO_4)(OH)_6$	0.40
Apatite	$Ca_5(PO_4)_3(OH, F, Cl)$	0.00
Hornblende	$Ca_2(Mg, Fe, Al)_5 (Al, Si)_8O_{22}(OH)_2$	1.32
Magnetite	Fe_3O_4	16.59
Quartz	SiO_2	40.14
Mica		21.70
Amphibole	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$	0.59
Kaolinite	$Al_2Si_2O_5(OH)_4$	4.88
Albite	$NaAlSi_3O_8$	3.76
Na orthoclase		1.91
Plagioclase	$(Na, Ca)AlSi_3O_8$	1.12
Biotite	$K(Mg, Fe)_3AlSi_3O_{10}(F, OH)_2$	0.33

6.3. Experimental Approach 1: Factors Influencing Leach Rate

6.3.1. Introduction

In the first phase of experimental work, column leach experiments at the 4 kg scale under a range of conditions both simulating the waste rock dump and conditions for enhancement of sulphide mobilisation were carried out to ascertain key factors influencing microbial leach rates. The experimental setup is shown in Figure 15. The following factors were studied with respect to the rate of sulphide mobilisation from a waste or low grade ore containing some 2% S as pyrite and chalcopyrite:

- Acidity of irrigation stream
- Iron content of irrigation stream
- Presence of pyrite
- Operating temperature
- Availability of oxygen
- Irrigation rate

6.3.2. Operating conditions

The first experiment (Experimental set 1) sought to compare the rate of establishment of a leaching environment under intermittent irrigation with water (simulating rain) with those typically used in intentional bioleaching environments (acidic water in the presence of dissolved iron with an adequate supply of oxygen). Further comparisons investigated the temperature of the operation and the availability of oxygen and of

sulphide mineral in the form of pyrite, the latter influencing iron availability, acid generation and heat generation. Operating conditions are given in Table 12. Each column was charged with 4 kg agglomerated ore at the beginning of the run. Agglomeration was conducted using an acid water solution consisting of 50 mL H_2O / kg ore and 3.7 mL H_2SO_4/kg ore.

Table 12: Experimental conditions under which Experimental Set 1 of leach columns was operated to simulate sulphide removal from waste rock through bioleaching

Column No	Temperature [°C]	Aeration Rate	Feed		Pyrite Content	Microbial Content (per species)
			Rate	Composition		**$1*10^{12}$**
1	32	12 L/hr	Intermittent *	Water	-	$1*10^{12}$
2	32	12 L/h	40 mL /hr	0.2 g/L Total Fe#	-	$1*10^{12}$
3	32	12 L/h	40 mL /hr	0.2 g/L Total Fe#	1%	$1*10^{12}$
4	42	12 L/h	40 mL /hr	0.2 g/L Total Fe#	-	$1*10^{12}$
5	32	Flush with N_2 at start	40 mL /hr	0.2 g/L Total Fe#	-	$1*10^{12}$
6	32	12 L/h	Intermittent **	Water	-	$1*10^{12}$

* irrigated for two 24 hour periods per week
** irrigated for one 24 hour period per week
# supplied in the ratio Fe^{2+}: Fe^{3+} of 0.7:1.3
shaded areas represent deviation of column conditions from the standard operating conditions.

6.3.3. Results

On comparing the establishment of bioleaching following intermittent irrigation with water or operation under typical bioleaching conditions of acidified water containing dissolved iron, oxygen and CO_2, it was clearly seen that acidification of this waste ore / tailings body was not achieved on irrigation with water over a 140 day period. Effluent pH in the range pH 3.0 to 4.5 resulted (Figure 16). This illustrates the long term nature of ARD generation and thereby long term liabilities. Further, owing to the dependence of iron precipitation on pH as well as the absence of dissolved iron in the feed stream, the residual soluble iron concentration remained extremely low (<10 mg/L) as shown in Figure 17, thereby restricting the process of the establishment of biological leaching conditions and a realistic assessment of ARD potential over the extended duration of the experiment. This is supported by the low level of copper liberation from these tailings under irrigation with water (Figure 19). However, the potential for ARD generation remains over the extended time frame. On operating these column experiments with an acidic, iron-bearing feed, typical of heap and dump bioleaching (columns 2 to 5), the pH of the effluent was maintained below pH 1.5 in all cases (data not shown), resulting in a dissolved iron concentration in the range 170 to 450 mg/L (Figure 18), demonstrating a release of iron from the ore. Column 2 provided the control experiment, with conditions most closely representing bioheap leach environment. Analysis of the redox potential profile (Figure 17), the iron in solution (Figure 18) and the copper extraction (Figure 19) demonstrated that, in the absence of sufficient provision of oxygen through aeration, the rate of sulphide mineral oxidation was reduced. While the provision of pyrite facilitated the more rapid establishment of a high redox potential (650 mV), no improvement in the leaching of the sulphide minerals within the tailings sample could be detected using copper extraction presented in Figure 19 as the marker. However, owing to the column dimensions, the anticipated increase in operating temperature was not achieved. Increase in operating temperature to 42°C through heating was shown to impact on the leaching of sulphide minerals (Figure 19), resulting in extraction of 35% of copper in >140 days compared with 28 to 30% at 32°C.

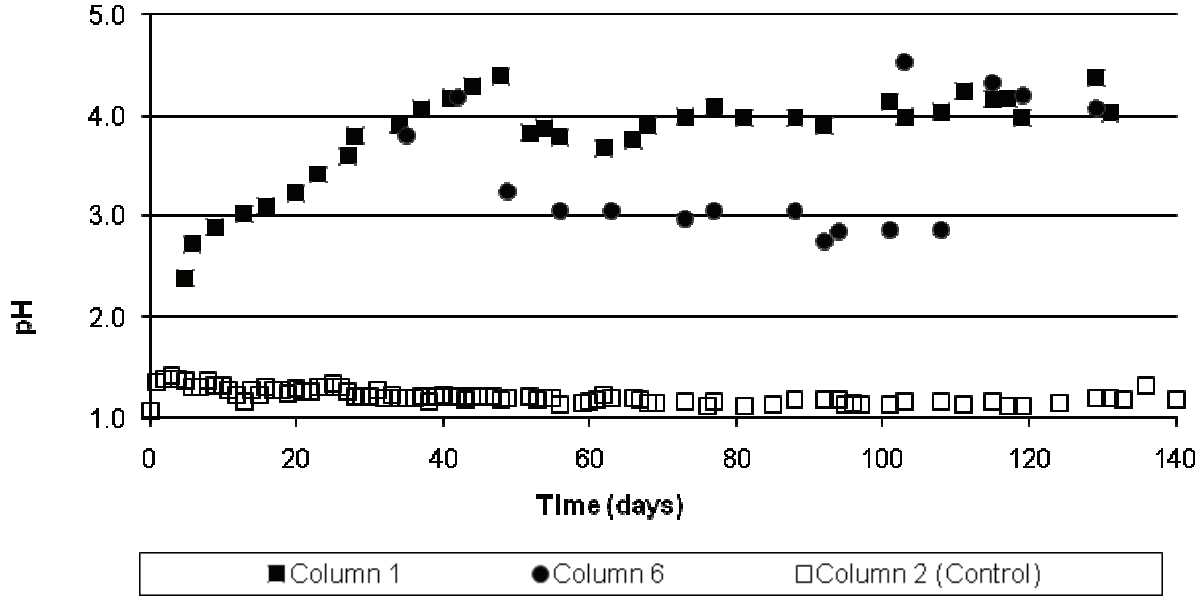


Figure 16: pH profile following irrigation of waste rock with water or acidified irrigant carrying dissolved iron. Column 1 was irrigated for two 24 hour periods per week while column 6 was irrigated for one 24 hour period per week typical of humidity cell operation. Column 2 was irrigated continuously with acidified water containing 0.2 g/L Fe.

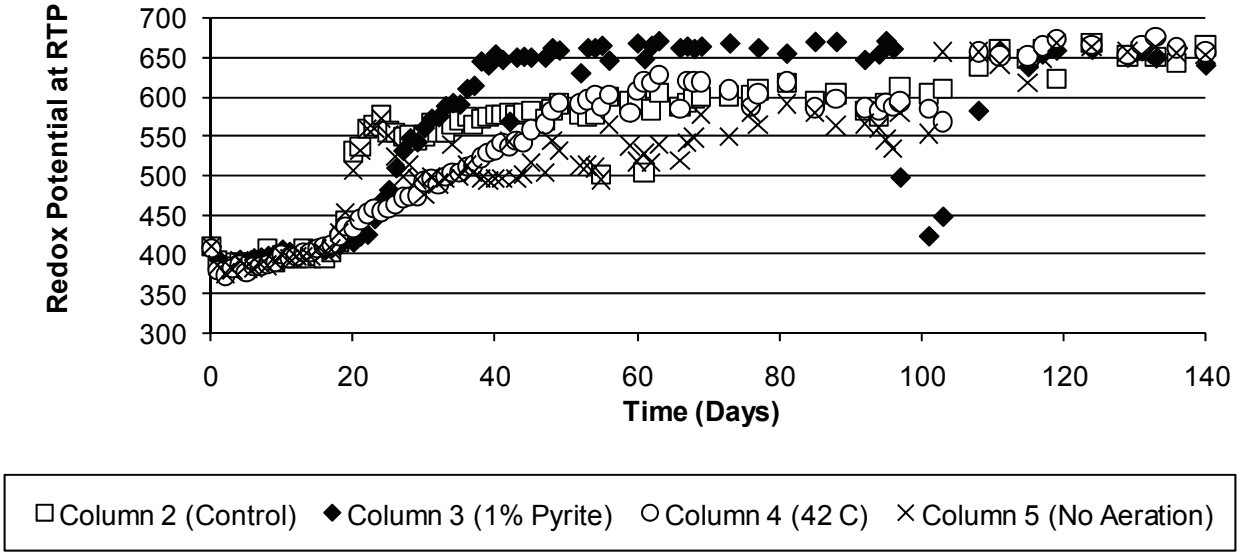


Figure 17: Redox potential of PLS from waste rock in column bioleach reactors operated under conditions defined in Table 12

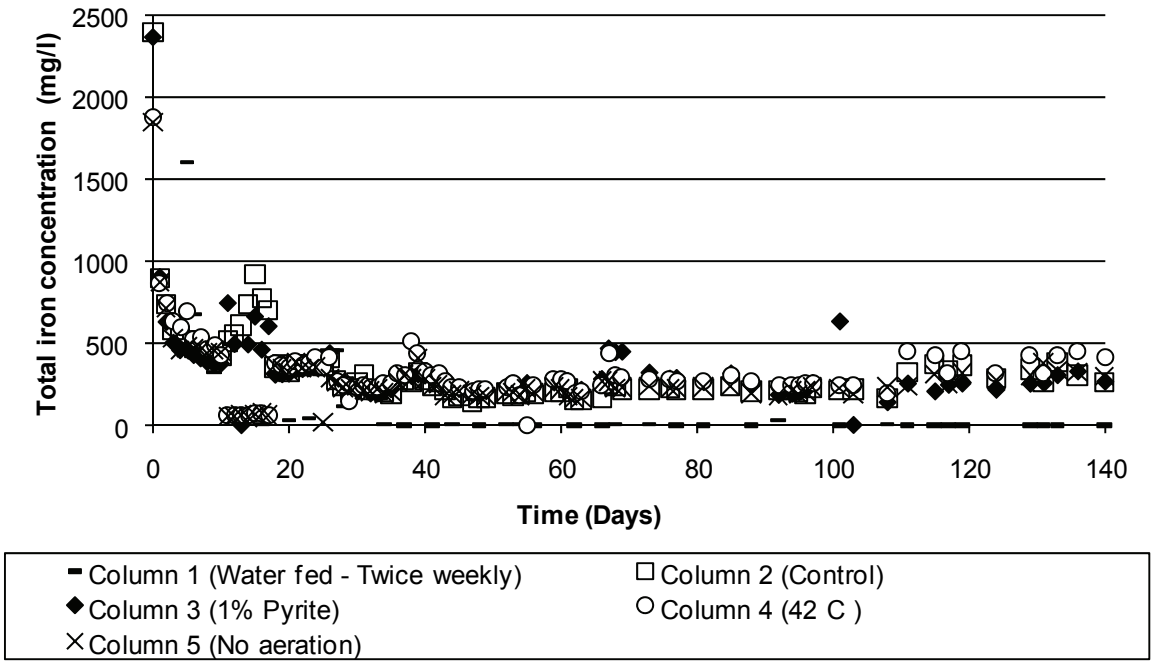


Figure 18: Total dissolved iron concentration in PLS from waste rock in column reactors operated under conditions defined in Table 12

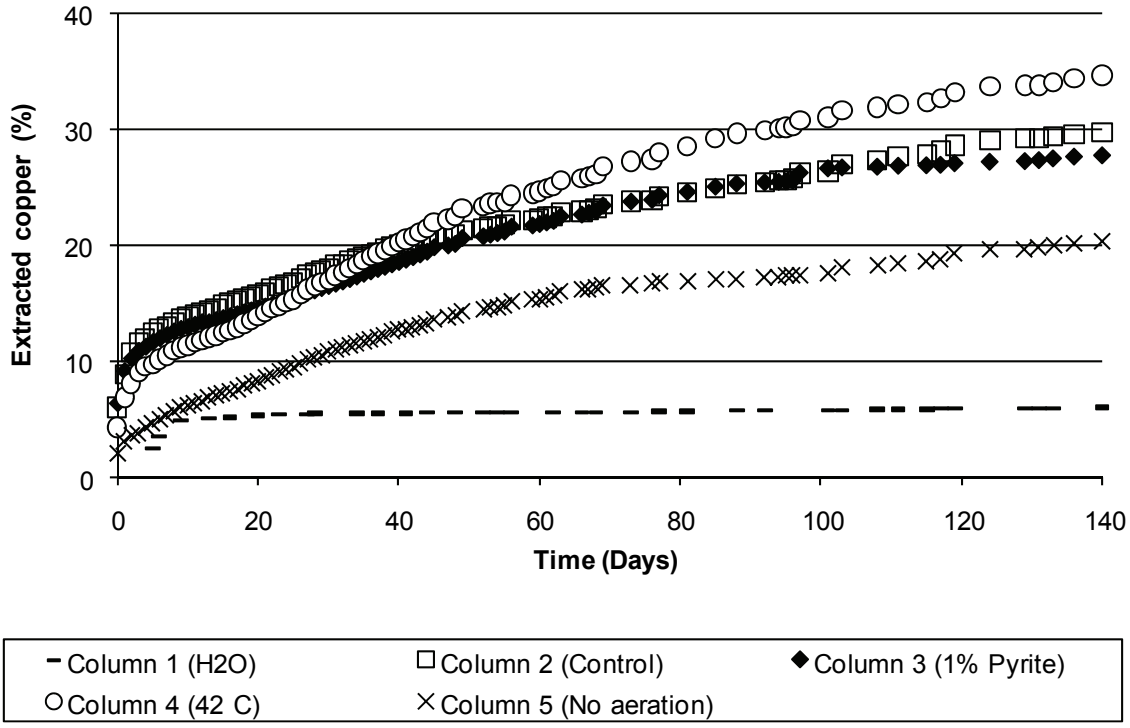


Figure 19: Extraction of copper from waste rock in column bioleach reactors operated under conditions defined in Table 12

The differences between the water-irrigated and acid-fed columns observed from the pH, dissolved iron and mineral extraction were not observed in the ARD generation data. Table 13 shows the potential of the ore sample to generate acid as well as the neutralising capacity of the samples both before and after the 140 day period.

The net acid producing potential (NAPP) values, a combination of the maximum acidity potential (MPA) and the acid neutralising capacity (ANC) of the sample, show that only the addition of pyrite had a positive effect in decreasing the ARD generation potential when compared with the starting material. Further, these results suggest that running bio-leach columns at all other conditions actually increases the potential for acid production. Considering the acid production potential and the neutralising capacity of the sample separately provides added clarity. The MPA uses the sulphur content of the sample and assumes total oxidation thereof to calculate the maximum amount of acidity which can be generated. Comparing these values, shown in Figure 20, the experiment with added pyrite showed the largest decrease in MPA of 25%, despite the addition of sulphur associated with the 1% pyrite addition.

Table 13: Acid base accounting results from experimental approach 1 (defined in Table 12)

Column	Difference	NAPP	MPA	ANC	NAG
		kg H_2SO_4/ton	kg H_2SO_4/ton	kg H_2SO_4/ton	kg H_2SO_4/ton
1	H_2O Fed	46	45	-1	50
2	Control	45	46	2	51
3	1% Pyrite	38	35	-2	44
4	42 °C	45	47	2	43
5	N_2 Flush	49	50	1	54
Feed Ore	-	40	47	7	56

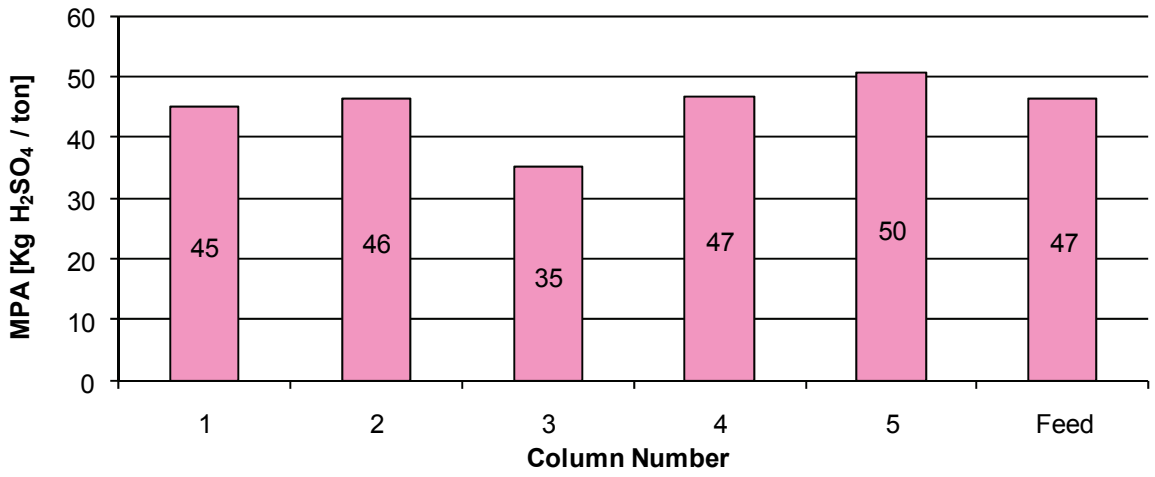


Figure 20: Maximum potential acidity (MPA) results for leach columns operated under conditions defined in Table 12

The second contributor to the NAPP is the acid neutralising capacity (ANC) of the samples. Figure 21 shows this value for columns 1-5 as well as the feed material. In all cases, the inherent neutralising capacity of the ore after 140 days leaching has decreased by at least 70%. The negative values, as shown in Figure 21, are values obtained experimentally. In reality, a negative neutralising capacity should be read as a "zero" neutralising capacity rather than an 'acid generating capacity'.

Even in the water-irrigated experiment (column 1), the neutralising capacity of the ore is diminished completely, illustrating aqueous dissolution under neutral conditions. This fact compounds the ARD formation potential as the neutralising capacity of the waste rock is removed on irrigation prior to ARD formation, negating potential for *in-situ* acid neutralisation.

Since the NAPP value is a combination of the MPA and ANC values, the observed increase in the potential of the samples to produce acid after the experiment is not an increase in its acid-forming material, but is a decrease in its inherent acid neutralisation capacity compared to the feed material.

In the absence of an oxygen provision (column 5), a substantial microbial population could not be established. This led to the longer time period necessary to achieve the same redox potential level as those attained under conditions resembling heap bioleaching (Figure 17). It also resulted in the slower mineral

dissolution rate shown in Figure 19. The lack of a microbial leaching environment resulted in a decrease in the neutralising capacity of the waste ore but not in the ARD formation potential. Subsequently, similar to the water-fed system, the potential for the formation of ARD over the 140 days increased due to the decrease in the intrinsic neutralising potential of the ore.

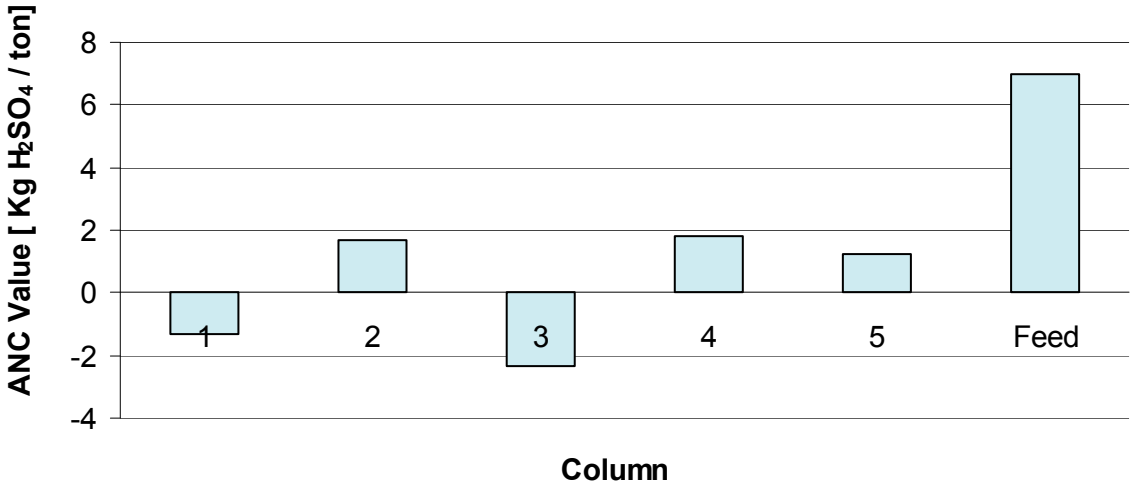


Figure 21: Acid neutralising capacity (ANC) results for experimental leach columns set 1

There is also a discrepancy between the mineral dissolution and the decrease in acid producing potential. Although increased operating temperature showed an increase in the rate of mineral dissolution, this did not correspond to a decrease in MPA. These discrepancies indicate that a reduction in mineral sulphide content does not necessarily correlate directly with a reduction in ARD formation potential; a result also indicated when one considers the net acid generation (NAG) presented in Table 13. The experimentally determined NAG values are comparable with the theoretical MPA values and the resultant NAPP, shown in Figrue 22.

The two acidity measurements of the waste sample, the MPA and the NAG, are determined differently. The MPA value is a theoretical calculation using only the sulphur content of the ore. The NAPP represents the difference between this and the acid neutralising potential (ANC), whereas the NAG is an experimentally determined value which takes into account the sulphide content, the non-sulphide acid generating content and the inherent neutralising capacity of the sample. The difference between these values is a compound measure of the non-sulphide acid generating capacity and the total inherent neutralising capacity of the sample.

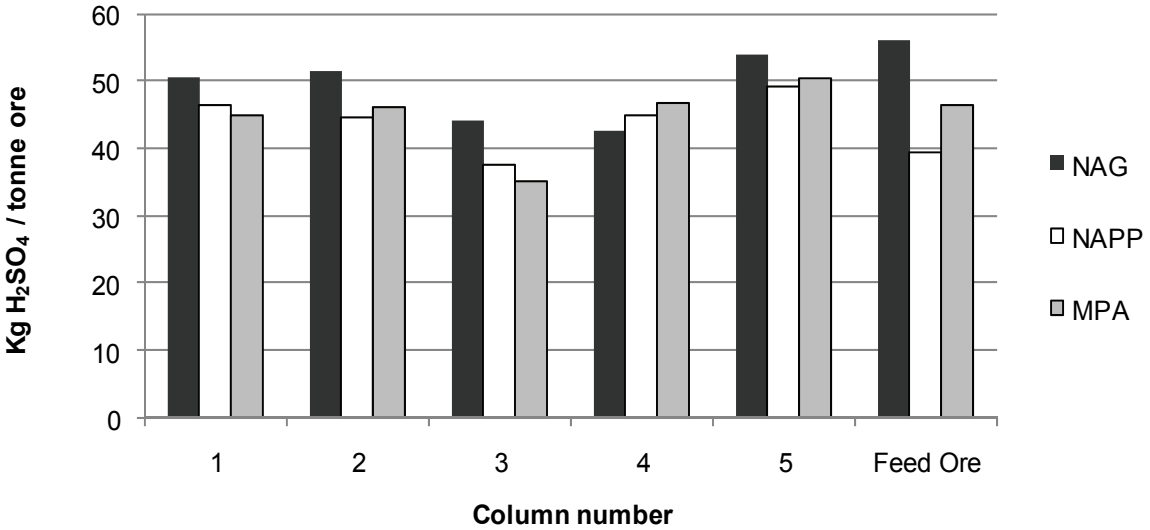


Figure 22: Comparison between theoretical maximum potential acidity (MPA) and experimental net acid generation (NAG) values for experimental leach columns set 1

In contrast with the net acid producing potential results, the increased operating temperature (column 4) reduced the experimentally determined acid generating capacity to the same level as that obtained through the addition of pyrite concentrate (column 3) after 140 days. These results suggest that the addition of pyrite was more successful in reducing the sulphide content of the waste ore while the increase in temperature had more of an effect on the other acid producing components. The addition of pyrite reduced the sulphide content from 47 to 35 effective kg H_2SO_4 producing potential per ton. This condition provided the lowest MPA, NAPP and NAG results and was selected for further study.

6.4. Experimental Approach 2: Loss of ARD generation potential with leach time

6.4.1. Introduction

The second phase of the experimental work focused on the reduction of the ARD potential after the initial 50 days following the agglomeration, active inoculation and pyrite addition. During experimental approach 1, a 50 day leaching period was required for the establishment of a stable microbial environment observed from the sustained increase in redox potential, corresponding to active ferrous iron oxidation and plentiful ferric leaching reagent (Figure 17). The pyrite addition experiment performed during the first phase was repeated with five replicate columns. One column was sacrificed every ten days to provide ore for ARD prediction tests. In this way, information was obtained about the changes in ARD potential before the establishment of a stable microbial population. The column leach equipment, shown in Figure 15, was used.

6.4.2. Operating conditions

The second experiment was conducted to replicate and expand the data obtained from the pyrite addition experiment (column 3) of experimental phase 1. The release of sulphur-containing compounds and associated metal mobilization in the system was studied through the period prior of microbial colonisation. Each column was charged with 4 kg agglomerated ore. Agglomeration was conducted using an acid water solution consisting of 50mL H_2O / kg ore and 3.7 mL H_2SO_4/kg ore. Five bioleach column reactors were operated under the same conditions as column 3, described in Table 12 (1% pyrite added, inoculation at 10^{12} cells of each species per ton ore, 32°C, aeration rate of 12 L/h and feed irrigation rate of 0.040 L/ h containing 0.2 g Fe^{2+} per litre). These columns were operated for 10, 20, 30, 40 and 50 days thereafter they were sacrificed for ARD analysis of the solid phase.

6.4.3. Results

The five columns showed good reproducibility with the trends of mineral dissolution, sulphate release and microbial population establishment following one another, and column 3 of the first experimental phase, closely. Figure 23 indicates the microbial colonisation of the column reactors resulting in establishment of a ferric environment and high redox potential in less than 30 days of the 50 day period. Data collected from the experiment run under typical bio-leaching conditions (column 2 of experiment 1, no added pyrite) is super-imposed. The increased redox potential in the presence of pyrite was due to the increased soluble iron released through the oxidation of the added pyrite.

Similarly, on comparison of the copper dissolution in Figure 24, the dissolution rate is similar for all the columns. The control column from experimental approach 1 showed a faster acid leach rate initially over the first 5 days compared to the columns with added pyrite, followed by a slightly decreased bioleach rate between days 10 and 50. This is also observed in Figure 19 over the same time period.

On comparison of the sulphate concentrations exiting the bioleach column reactors (Figure 25:), it is clear that the rate of sulphur released from all the columns is similar across the pyrite-containing column reactors. The concentration of sulphate in the PLS stream decreased rapidly over the first five days, representing the wash through of acid soluble material, before stabilising at a concentration of some 2 g/L above that of the entering acid feed (Figure 25:).

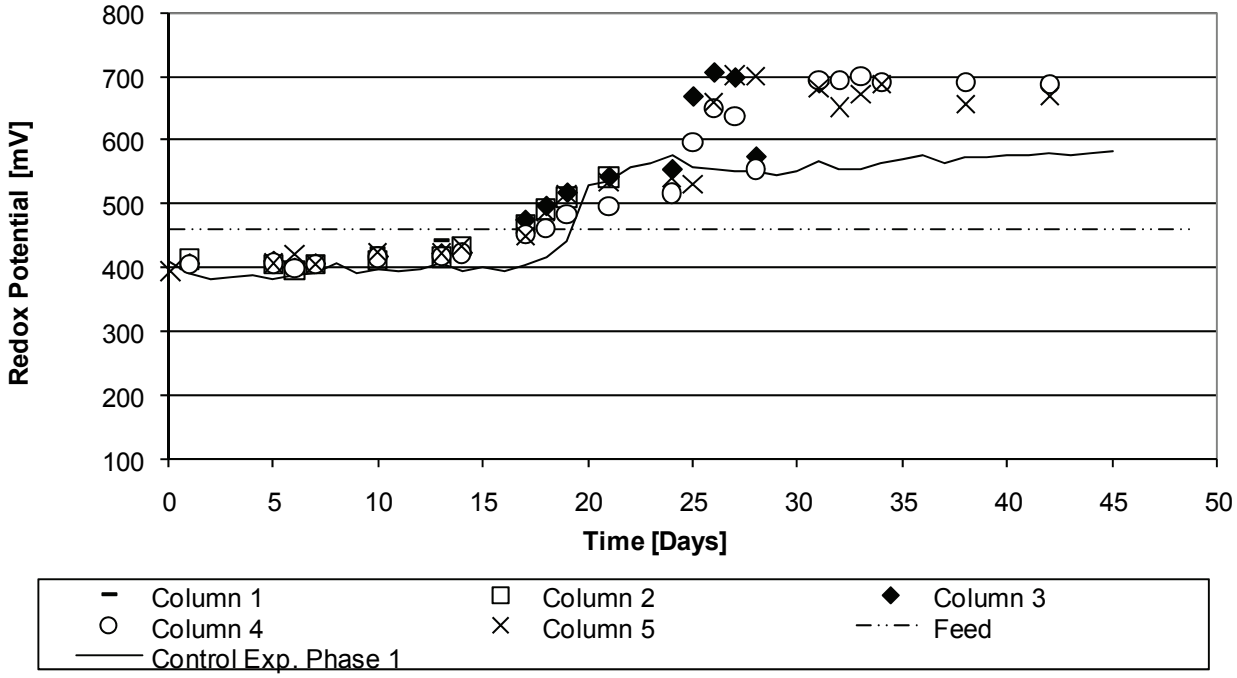


Figure 23: Redox potential in pregnant leach solution for bio-leach columns during approach 2

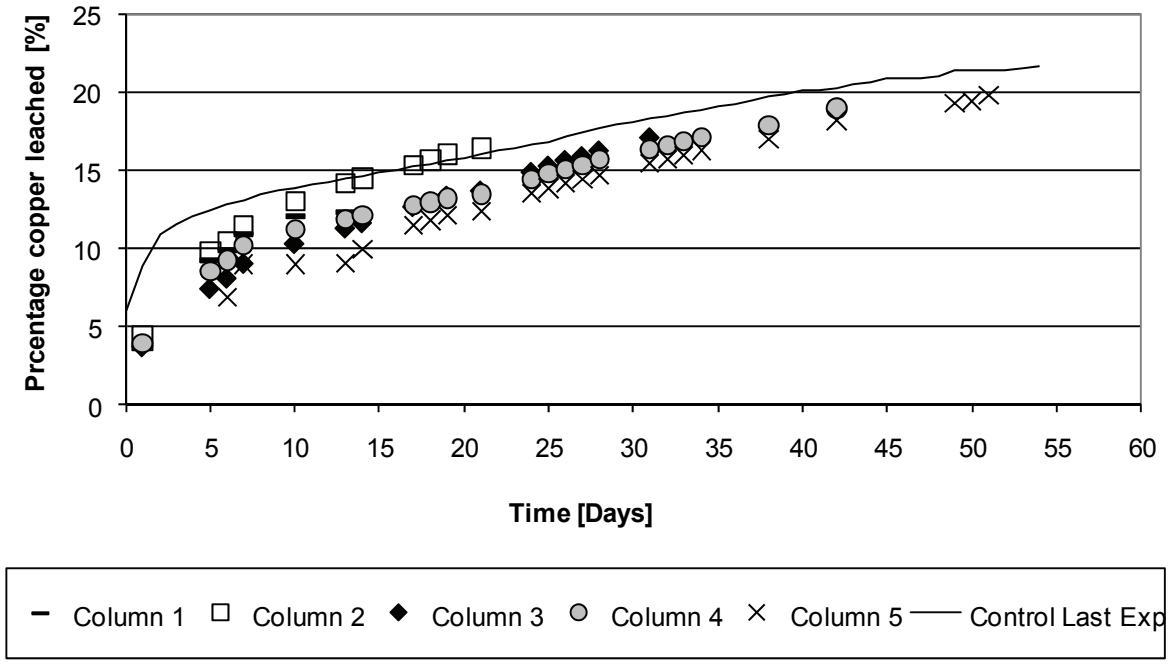


Figure 24: Copper dissolution for bio-leach columns during approach 2 showing the control column from experimental approach 1

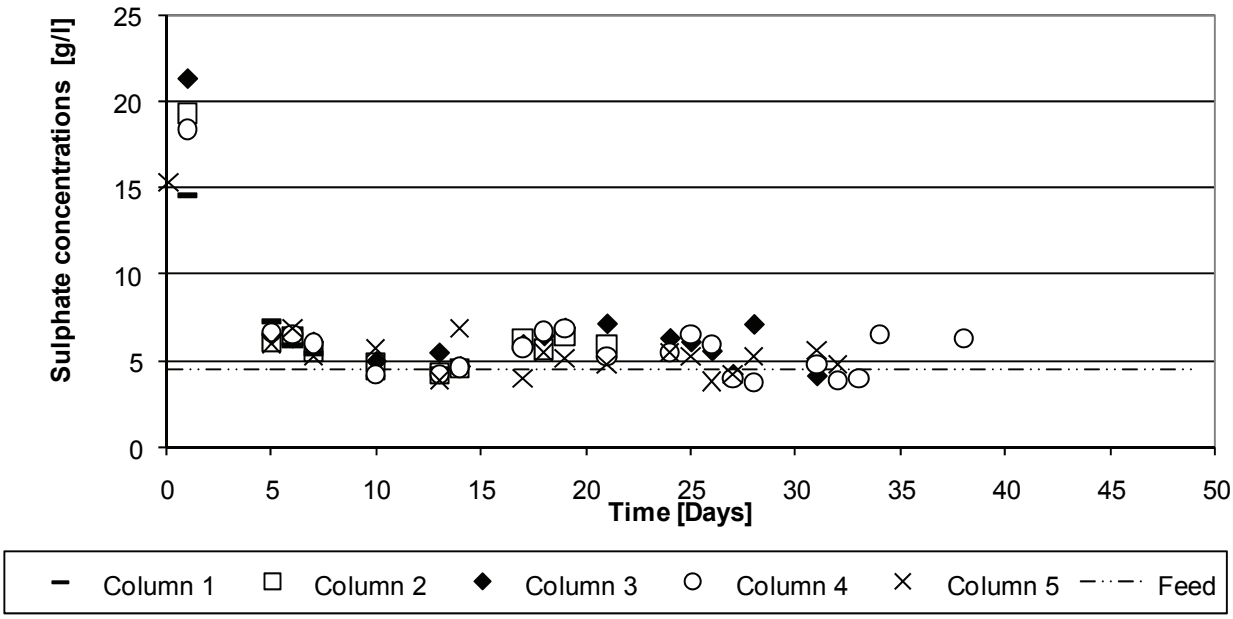


Figure 25: Sulphate concentrations in the PLS for the second experimental approach

The reproducibility of the rate of mineral dissolution, of sulphate liberation and the microbial population establishment, supported the assumption that the changes in ARD potential across the columns represented the changes that would occur in one experiment over the same period.

Table 14: Acid base accounting results from experimental approach 2

Leach time (days) [Column]	NAPP kg H_2SO_4/ton	MPA kg H_2SO_4/ton	ANC kg H_2SO_4/ton	NAG kg H_2SO_4/ton
[Feed]	40	47	7	56
10 [1]	39	44	5	54
20 [2]	38	43	5	80
30 [3]	35	37	2	67
40 [4]	44	43	0	47
50 [5]	36	37	1	55
144 [3 ex expt 1]	38	35	-2	44

Since mineral dissolution increases over time, and all the copper bearing minerals are in sulphide complexes, it was expected that the sulphur content, and thus the maximum potential acidity (MPA) would decrease over time. Similarly, as shown in experimental approach 1, the acid neutralising capacity (ANC) of the waste ore was expected to decrease across the experiment. The ABA, as well as the experimentally determined net acid generation (NAG), values are shown in Table 14. The trend in ANC and MPA values decreased with time. In addition, there was a slight decrease in the net acid producing potential (NAPP) over the experimental period. Figure 26 shows the decrease in the MPA and ANC, including values obtained from the first experimental approach at 144 days.

Of particular interest from the MPA data is the comparison of the final MPA values, and subsequent percentage total sulphur, obtained between the first and second experimental approaches. The majority of the sulphur species leached within 144 days was leached during the first 50 day period. The difference between an MPA value of 37, obtained after 50 days, and that of 35, obtained after 144 days, is the equivalent of 0.06% total sulphur. In this experimental setup, with a mass of approximately four kilograms, this is the equivalent to 2.6 grams of sulphur; equivalent to four percent of the starting total sulphur content of the waste ore sample used in the experiment. This is compared to the leaching of 20% of the total sulphur content over the first 50 days. The same decreasing trend is seen in the change in acid neutralising capacity (ANC), shown in Figure 26.

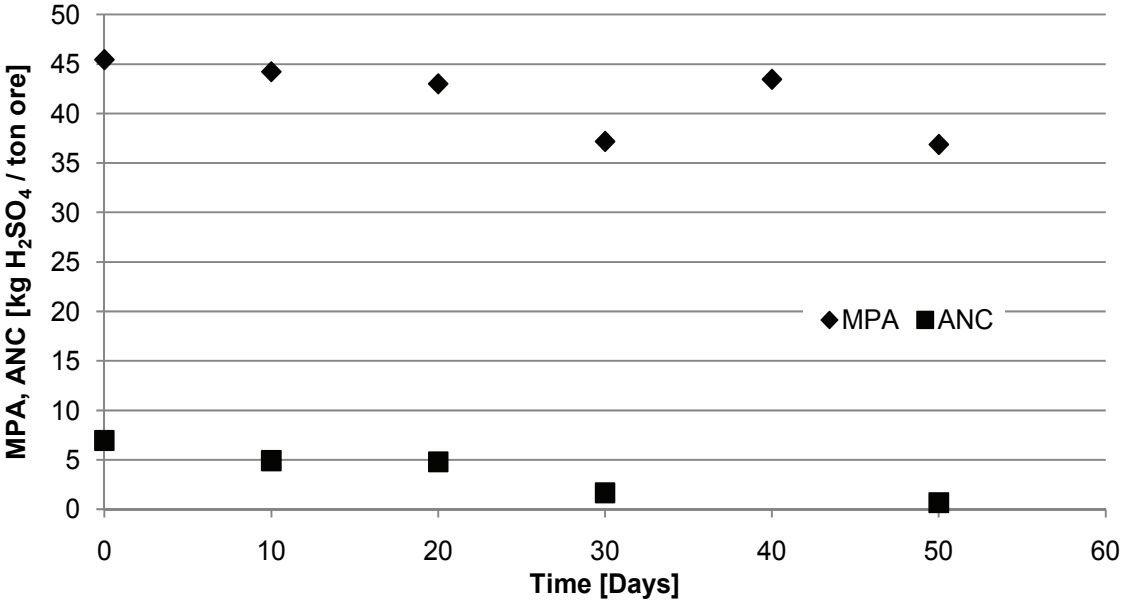


Figure 26: Theoretical maximum potential acidity values for the pyrite containing columns of experimental approaches 1 and 2

6.5. Experimental Approach 3

To shed light on the period required for leaching of sulphides from the low grade or waste ore, it is interesting to analyse sets of column data collected under heap leach conditions in related studies, particularly through looking at the compromised delivery of air, inoculum and irrigant. This is done through the analysis of data sets generated in the 4 kg leach columns described above where: 1. varying levels of inoculum were supplied, 2. the supply of Fe was compromised, and 3. nitrogen supplementation was used to nurture rapid colonisation of the ore bed. In future results, the effect of the rate of irrigation will be included.

Column experiments initiated with differing inoculation concentrations across the range 10^8 to 10^{12} cells per ton were shown to require differing time periods to achieve optimal leaching conditions (data not shown). Further, it has been shown that where the indigenous population is nurtured, bioleaching conditions are achieved; however a delay in the onset of leaching relative to the inoculated tests resulted in general. These data do show dependence on the ore mineralogy and ore bed conditions. Van Hille et al. (2010) studied the effect of availability of soluble iron, as well as the time period required for the onset of leaching, on the leach rate in column reactors using a low grade copper ore. While the initial rate of leaching increased with increasing iron concentration across the range 0.2 to 5 g/L, this increase was not proportional. Further, once the easily leached sulphide minerals had undergone dissolution, no further benefit of the high end of this iron concentration range was evident. Hence, sufficient available soluble iron is preferred to establish leaching conditions but not necessary above 0.5 g/L to sustain it.

Further, Van Hille et al. (2010) demonstrated that the extended lag period typical of the establishment of the colonised ore bed required for effective bioleaching can be reduced by the supply of a nitrogen source, preferably as an organic nitrogen source. On supply of yeast extract as soluble nutrient in the irrigation liquor at a concentration of 0.5 to 1.0 g/L, a more rapid onset of leaching and increased biological phase was observed. This resulted in an increase in the bioleaching of copper from the low grade ore of some 50 to 100% over the 60 day period investigated. The result is attributed to the high energy expenditure required to fix nitrogen by those microorganisms able to carry out these reactions. By provision of the combined nitrogen source, preferably in organic form, the energy saved can be directed into cell growth, thereby improving the biomass available to catalyse the provision of leaching agents. These related studies highlight the importance of availability of soluble iron, nitrogen as nutrient and a metabolically active inoculum in the acceleration of mineral bioleaching. Further analyses of these, and related operating parameters presented above, are required while using representative waste rock samples.

6.6. Conclusions

These studies have demonstrated the potential to manipulate the ARD generating potential in waste rock. Particularly, it has been shown that the acid neutralising capacity is altered rapidly (over 20 to 50 days) under irrigation in both acidic and neutral conditions. Reduction in sulphur content and metal mobilisation only occur under acidic conditions that support the development of microbial populations to re-generate the leach agents. The addition of pyrite, to supply sufficient iron in solution and heating through metabolic energy generation, was shown to augment the final reduction in sulphur content of the ore as well as reduce the ARD generating potential in terms of both NAG and NAPP. It is recognised that the accelerated leaching approach results in the generation of a sulphate and metal-rich water stream from which these compounds will require recovery to allow re-circulation of the water within the process. This shall be addressed in a follow on project (WRC project no. K5/2015). While production of gypsum for which a substantial market exists is considered to handle this sulphate rich stream, it is noted that polishing of the final water stream, or its use in a closed recycle would be necessary under this scenario owing to the residual sulphate concentration of some 1500 mg/L following gypsum precipitation.

7. CASE STUDY 3: PRELIMINARY STUDY OF THE REMOVAL OF SULPHIDE FROM COAL FINES AND TAILINGS BY FLOTATION TO MINIMISE SUBSEQUENT ARD IMPACT POTENTIAL

7.1. Introduction

7.1.1. Background and Motivation

As discussed in Chapter 2, conventional coal beneficiation (upgrading) at South African collieries produces large quantities of wastes in the form of discards and ultra-fine slurries. These wastes contain significant quantities of residual (and potentially saleable) coal as well as pyrite, and are a major source of ARD pollution in certain regions of South Africa (DME, 2001). South African coal mining and processing operations still emphasise an end-of-pipe approach in their management of ARD, with the focus being on chemical or biological treatment techniques, or both.

Previous studies have demonstrated the techno-economic viability of converting coal ultra-fines from local coal processing operations into a useful product through the application of coal flotation and dewatering techniques (Fickling, 1985; Harris et al., 1994). These techniques are now being applied in the beneficiation of ultra-fine coal slurries and historical slimes dam deposits at a number of local collieries. Although largely limited largely to laboratory-scale studies on American coal samples, reports in the literature also demonstrate the feasibility of using froth flotation techniques for the selective removal of pyrite from finely divided coal (Bethell and Luttrell, 2004; Liu and Somasundaran, 1994).

Consistent with literature reports and the proposed conceptual approach, previously outlined and demonstrated in Chapters 3 and 5 of this report respectively, two potential process options for both the selective removal of sulphide sulphur and recovery of coal from ultra-fines by means of flotation techniques were investigated (Figure 27). In process option 1, selective sulphide flotation was carried out initially to separate sulphide minerals (pyrite) from coal and other non-sulphide (ash-forming) minerals. This was followed by selective flotation and recovery of coal in the form of a saleable product. In the second option, coal was selectively recovered prior to the application of desulphurisation flotation to separate the acid generating sulphide from the non-acid forming gangue minerals.

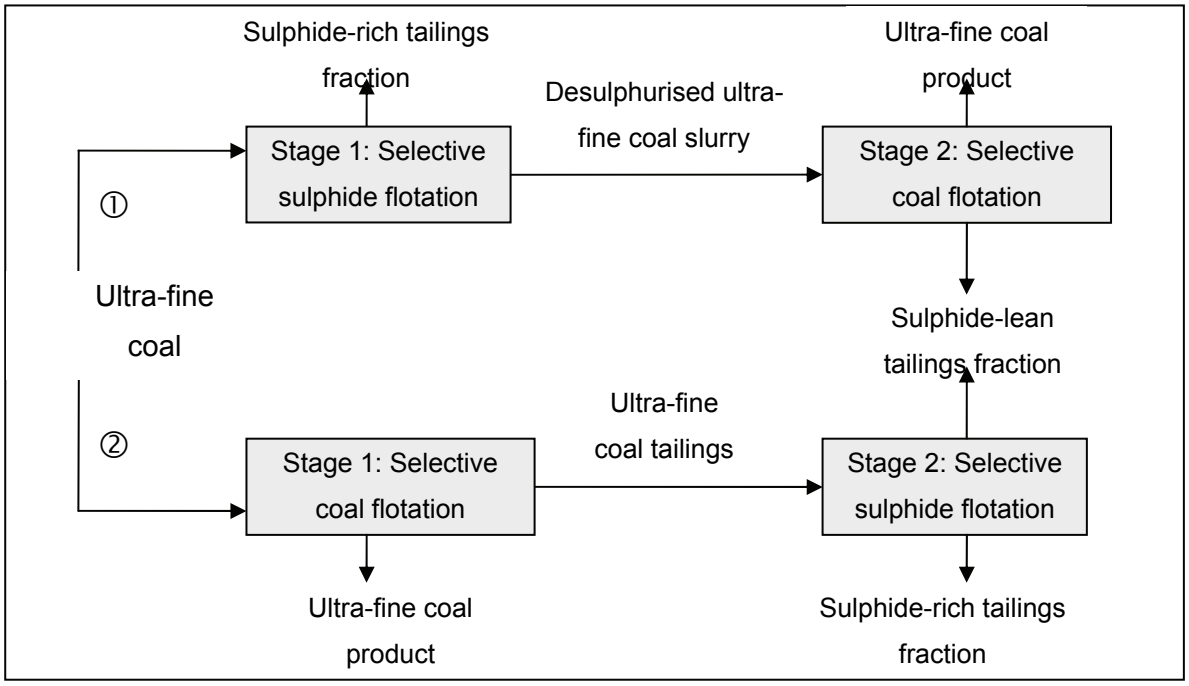


Figure 27: Process options for the mitigation of acid rock drainage (ARD) and recovery of coal from ultra-fines

7.1.2. Study Scope

The mini-case study conducted here formed part of an honours-level project, and entailed preliminary flotation and ARD characterisation test work with a view to establishing:

(i) the feasibility and/or challenges of selectively removing sulphide from a South African ultra-fine coal sample (*i.e.* stage 1, option 1 in Figure 27 above).
(ii) the effect of flotation desulphurisation on ARD generating potential.
(iii) knowledge gaps and requirements/opportunities for further research and development in this area.

7.2. Experimental

7.2.1. Sample Description

A sample of coal ultra-fines (particle size less than 120 µm) was procured from a local coal processing plant. Chemical analysis (see Section 7.2.3) indicated a total sulphur (S_T) content of 1.05% and an ash content of 23%. Liberated particle grains were clearly visible under a microscopic.

7.2.2. Flotation Test Work

Laboratory-scale flotation tests were conducted in a 3 litre modified Leeds batch flotation cell, to investigate the effects of frother addition and collection period on froth stability and sulphur recoveries. Experimental conditions are summarised in Table 15.

Table 15: Experimental conditions for the desulphurisation flotation test work

Coal depressant	Dextrose (2 g/kg sample)
Sulphide collector	Xanthate, SIBX (1g/kg sample)
Frother	Methyl isobutyl carbinol, MIBC (75-150 µL/kg sample)
Air flow rate	5 L/min
Impeller speed	1500 rpm
Collection period	10-30 minutes
pH	Natural (7.4-7.5)

7.2.3. Sample Characterisation

The ultra-fine coal feed sample, as well as selected flotation concentrate and tailings samples, were analysed for total sulphur (S_T) content, by means of LECO combustion analysis, and ash content, in accordance with South African National Standards (SANS) method 131:1997. The acid generating potential of these samples was assessed using the single stage net acid generation (NAG) empirical test method as described in Chapter 5[1]. Samples were classified according to the criteria outlined in Table 16.

7.3. Results and Discussion

7.3.1. Flotation Test Work

Scouting tests at an MIBC frother dosage of 75 µL/kg ultra-fine coal resulted in an extremely unstable froth. Froth stability improved significantly on doubling the frother dosage (to 150 µL/kg ultra-fine coal). Under these conditions separated pyrite particles were clearly observed on both the sides and bottom surface of the concentrate collector tray. The quantitative results for the duplicate test runs at a frother dosage of 150 µl/kg feed sample are summarised in Table 17 and Figure 28.

The results in Table 17 indicate that approximately half the feed sample (± 100g) reported to the flotation concentrate after a 30 minute collection period, along with approximately 54% of the sulphur (±1.3 g S_T) and 47% of the coal (± 76 g). Figure 28 shows that deportment of S_T to the concentrate was still occurring at a measurable rate after 30 minutes. The majority (approximately 80%) of the total S_T recovery, however, occurred within the first 20 minutes of collection. Calculation of the S_T: coal recovery ratios (Table 17), indicates negligible separation of total sulphur and coal under the selected test conditions.

[1] As no sulphur speciation analysis was conducted in these samples, the Acid Base Accounting method was not applied in the assessment of ARD potential (see Footnote 2 in Section 7.4)

Table 16: Criteria for the classification of ARD on the basis of NAG prediction tests

Classification	Parameters
Acid neutralising	NAG= 0 kg/t H_2SO_4; and NAG_{pH}>7.5
Non-acid generating	NAG= 0 kg/t H_2SO_4; and 4.5≤NAG_{pH} < 7.5
Low to moderately acid generating	NAG at pH 4.5 < 5 kg/t H_2SO_4 ; and NAG at pH 7.0 = 2-10 kg/t H_2SO_4 ; and NAG_{pH} < 4.5
Highly acid generating,	NAG>20 kg/t H_2SO_4; and NAG_{pH}<4.5

Table 17: Preliminary desulphurisation flotation test work results

	Extent of recovery (mass %)			Mass recovery ratios (sulphur:coal)
	Total mass	Total sulphur	Coal	
Run 1	54.4	52.2	49.4	1.04
Run 2	55.3	56.5	44.9	1.14
Mean	54.9	54.4	47.2	1.09

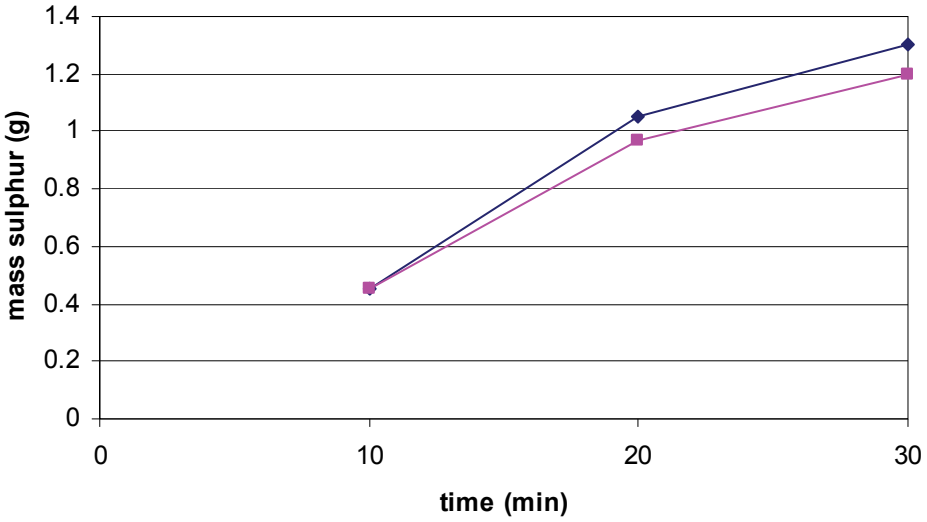


Figure 28: Mass recovery of total sulphur (S_T) as a function of concentrate collection period

7.3.2. Acid Rock Drainage Risk Potential Assessment

Table 18 summarises the results of the NAG tests carried out on the ultra-fine coal feed and output samples derived from flotation test run 1 (see Table 17 above). In accordance with the NAG test results, the ultra-fine coal feed and the flotation tailings were both potentially non-acid generating, whilst the flotation concentrate had a high acid generating potential. These results indicate that the flotation concentrate has a higher content of sulphide sulphur minerals and/or lower content of acid consuming minerals, despite only slight differences in the S_T contents. This is consistent with the visual observations which indicated selective deportment of pyrite to the flotation concentrate (see discussions in Section 7.3.1 above).

Table 18: Results of the NAG test work for ARD prediction

Sample	Total S (%)	NAG_{pH}	NAG (kg H_2SO_4/t)		Classification
			pH 4.5	pH 7	
Ultra-fine coal feed	1.11	5.2	0	3.3	Non-acid generating
Flotation tailings	1.15	6.5	0	0.4	Non-acid generating
Flotation concentrate	1.38	2.7	55.7	55.3	Highly acid generating

The results in Table 18 also indicate that the flotation tailings fraction has a slightly lower acid generating potential than the ultra-fine feed, indicative of a depleted sulphide sulphur (pyrite) content and/or higher content of acid consuming minerals in this fraction.

7.4. Conclusions and Recommendations

Preliminary desulphurisation flotation test work on coal ultra-fines failed to result in any significant separation of total sulphur (S_T) from coal. Nevertheless both the visual observations and net acid generation (NAG) prediction test results indicated appreciable separation of sulphide sulphur (pyrite) from other (organic) sulphur forms, with the majority of the acid-forming pyrite deporting to the concentrate fraction during flotation. Poor S_T:coal separation ratios thus appear to be largely due to inadequate depression of coal during desulphurisation flotation, with significant quantities of S_T occurring as non-acid forming organic sulphur, closely bound to or within the coal macromolecules.

On the basis of these results, the following recommendations are made:

- Flotation test work
  Preliminary test work results have indicated that the deportment of coal to the concentrate needs to be reduced significantly, in order for the process route entailing preferential desulphurisation flotation (*i.e.* process option 1 in Figure 27) to be viable. In this regard, further test work to investigate the effects of increasing dosages of dextrose depressant or the use of alternative types of depressants, or both, is recommended.

  Given the current problems with coal depression, it is also recommended that further test work be conducted on the alternative process route *i.e.* that entailing selective recovery of coal prior to desulphurisation flotation (process option 2 in Figure 27).

- Sulphide speciation and ARD characterisation
  The results of this preliminary study have also highlighted the need for a more quantitative understanding of sulphur speciation and deportment during flotation of coal ultra-fines. This understanding is required for the meaningful application and interpretation of both the flotation and ARD prediction tests[2]. It is thus recommended that techniques and protocols for the quantitative speciation of sulphur in coal and prediction of associated ARD, such as those developed by Miller (2008) and Stewart et al. (2009), be investigated and established prior to further flotation test work.

- Sample procurement
  Finally it should be noted that preliminary ARD prediction tests, reported in Table 18, indicated that the ultra-fine coal sample used in this study does not exhibit acid generating properties[3]. In order to provide sufficient justification for development of the ARD mitigation approach proposed here, it is further recommended that an ultra-fine coal sample with proven acid generating characteristics be identified, and procured for further test work in this area.

[2] The LECO combustion analysis method applied in this preliminary test work programme provides a measure of total sulphur only, resulting in an overestimation of the ARD generating potential when using conventional acid base accounting (ABA) methods.

[3] Visual observations indicate that this is possibly due to the high acid neutralising capacity of the ultra-fine coal sample, as opposed to a low pyrite content.

8. CONCLUSIONS

Acid rock drainage (ARD) is well recognised as a major threat in South Africa, resulting in the increasing acidity and salts loading of water bodies and leachates, particularly through the presence of sulphates and metals in solution. Such ARD streams are generated over extended time frames exceeding a hundred years in areas of South Africa with active mining and minerals processing of sulphide-containing ores. Hence the ARD problem is widespread and one extending into perpetuity. To handle this problem, both with respect to securing adequate quality water and in terms of the liabilities of those exploiting the mineral resources, it is necessary to both remediate contaminated areas and to stem the further production of ARD. This requires a rigorous knowledge base on ARD generation in its own right. Currently both the lack of technical prowess in this field and the lack of data on ARD-generating materials has resulted in limited prediction ability and thereby a limited ability to handle ARD prevention, in the long term, prior to costly remediation. This situation is aggravated by the waste nature of the resource responsible for ARD generation (tailings, waste rock, disused mine workings), resulting in little importance having been placed on characterising these materials.

Through review of waste rock in South Africa, its characterisation, potential for ARD generation and metal deportment, the importance of this study is realised. Specifically the following areas are highlighted as important from the perspective of ARD generation potential in South Africa: the coal industry owing to the presence of pyritic sulphur in coal, the gold industry owing to recovery from sulphidic ores in which the entire sulphide-containing fraction represents waste material, the PGM industry where, despite the low sulphur content of tailings and waste rock, the large volumes to be processed suggest the potential for significant ARD generation potential, the base metal industry in which lower volumes of waste rock of a higher sulphide content are processed, and the mineral sands industry. The case studies presented in this study have focussed primarily on sulphidic base metal containing ores, with preliminary work presented on coal. The scope of materials considered will be expanded in follow-on project, WRC K5/2015.

In this study, we present a new conceptual approach to the prevention of ARD formation, driven through a desire to remove the risk of ARD generation to the extent possible, rather than delaying its onset into perpetuity. The removal of the sulphur containing components is investigated through the application of traditional technologies. While the review of technologies available suggests a range of alternative approaches in solid-solid separations (Chapter 3), in this case froth flotation has been selected to demonstrate the potential to separate tailings into a major fraction that is benign with respect to ARD generation and a minor fraction of high sulphide content with associated potential for enhanced metal recovery. Secondly, bioleaching (exploiting the naturally occurring reaction set responsible for the generation of ARD) has been used to investigate the removal of the sulphide material from non-liberated waste rock through reaction, presenting a different approach. This allows the new approach to be built on the strength of a sound technology base in South Africa.

In conducting this study, the importance of good data is essential to ensure its value. Particularly the need to analyse the heterogeneous solids phase appropriately is essential. Review of the well accepted analytical tools for quantifying the ARD potential in Chapter 4 illustrated the limitations of current analyses for ARD prediction. Particularly the need to develop methodology around the characterisation of coal was highlighted and will be included in WRC project K5/2015. Further the limitations in the data available from static tests were recognised. For new insight into the ARD problem, it is necessary to understand the relative kinetics of ARD generation potential and ARD neutralisation potential. Static tests cannot provide this data while the well accepted humidity cell tests are too slow and labour intensive (running over more than 6 mo) as well as only being applicable to waste rock and not finely divided tailings material. To meet this need, the establishment of a new biokinetic assay is presented (Hesketh et al. 2010b), drawing on our knowledge base in mineral bioleaching to underpin its development. Through this test, a more realistic, but worst case scenario is built. The results from the biokinetic assay complement and validate those derived from traditional static tests. These are particularly important where static tests give ambiguous data. Further, the biokinetic test illustrates the need to account for sulphur removal and loss of acid neutralising capacity separately, owing to the differing time scales of these reactions.

The case study, presented using flotation to separate the tailings material from a base sulphide mineral deposit into a dominant fraction of benign material, clearly demonstrated the concept of mass reduction of

active or reactive tailings with potential for ARD generation. In this study, 85% of the tailings material was separated into a stream containing 0.2% S. This material was classified as non-acid forming, and hence benign with respect to acid generation. Further, recovery of 50% of the residual copper was achieved into a fraction of 4% of the tailings and the remaining S was concentrated into 11% of the original mass of the tailings at a high S concentration of 34%. This latter material may be suitable as a S-rich product or will require careful disposal of this much reduced volume. The case study also suggests the potential for the selection of separation steps based on the integrated optimisation of recovery of values and of generation of benign tailings as the major fraction for disposal. This approach facilitates the treatment cost of the waste processing being largely constrained within the active lifetime of the mine. The use of or disposal of the small volume, high S stream, typically high in pyrite content, requires consideration. It is anticipated that this material may have a role in the generation of acid or ferric iron as leach agents, the generation of sulphuric acid, or in stabilising of backfills.

In the case study of treatment of waste rock to reduce its sulphur content through bioleaching, a variety of conditions were investigated including the inoculation of ore, supply of O_2 and CO_2, supply of dissolved iron, temperature and enhancement of iron concentration and metabolic energy through pyrite addition. These studies demonstrated the gradual reduction in S within the ore body on bioleaching. The S reduction was accompanied by a decrease in MPA and NAG. However, the reduction in acid neutralising capacity accompanied leaching under all conditions investigated, including irrigation with neutral water. The rapid removal of acid neutralising capacity resulted in a maximum point in acid generation capacity, measured as NAPP, in some situations, particularly where S removal was limited. This highlights the importance of understanding the relative kinetics of removal of sulphur compounds and of acid neutralising capacity. It also highlights the limitations of the static tests for ARD potential measurement in which these components are not de-coupled on a kinetic basis. The treatment of ARD generating materials through bioleaching has been illustrated to reduce the ARD generating potential within the life of mine, through a novel approach. Analysis of the economic feasibility remains to be finalised; furthermore, the practicality of this approach requires analysis. Particularly, scenarios for the handling of the large volume sulphate rich effluent stream generated through this approach are required.

The preliminary case study on coal illustrated the difficulty in achieving separations of total sulphur (S_T) from coal for the particular coal sample used. This is postulated to arise from the nature of association of the organic S fraction with the coal matrix as well as inadequate depression of the coal during flotation. However, separation of the pyritic sulphur towards the small volume flotation concentrate resulted in the increasing acid forming nature of this fraction, classified as highly acid generating with a NAG_{pH} of 2.7. In turn, a slight increase in the NAG_{pH} of the flotation tailings relative to the feed was observed (6.5 and 5.2 respectively), corresponding to a slightly lower acid generation potential in the tailings. This is consistent with the reduction of pyritic sulphide in the tailings. These preliminary studies illustrate the potential for selective separation to provide tailings of low acid generating potential. However, further studies are required to provide a rigorous dataset and understanding of the potential.

In summary, the following project objectives have been met:

- A review, classification and characterisation of ARD generating mineral wastes in South Africa has been conducted, allowing identification of important materials for study.
- Unit operations available for sulphide removal have been reviewed.
- Characterisation methods to quantify ARD generation potential from waste rock have been reviewed and a sub-set selected for application. Further an additional biokinetic assay has been developed.
- Factors affecting the oxidation rate of metal sulphides have been reviewed. Further the potential for reduction of ARD generating capacity through accelerated bioleaching has been presented.
- Physical separation of sulphidic materials from tailings has been demonstrated to provide the major tailings fraction as non-acid forming while the reactive gangue may be contained in a small fraction of the tailings for additional recovery of values, utilisation of the sulphide or contained disposal.

9. RECOMMENDATIONS

Several recommendations are drawn from this study for further consideration. This study has focussed on base metal ore bodies with preliminary work conducted on coal. Following the review of ARD generation potential in South Africa, it is recommended that the following resources are included in future investigations: coal, gold-bearing ores in which pyrite represents a waste material, PGM ores which while low in sulphide are voluminous, base metal-bearing ores, and mineral sands.

While the biokinetic test presented provides improved data on ARD generating potential, it is recommended that this test be refined to enable kinetic studies in which the removal of acid neutralising capacity and of acid generating capacity are de-coupled. Further, refined quantitative analytical approaches are required to discern sulphur speciation in coal and its deportment through the separation to facilitate interpretation of results.

While the concept of sulphur removal from tailings through physical separation has been demonstrated to provide the major fraction of the tailings as a benign, non-acid forming material, it is recommended that this approach be validated across a range of tailing deposits or mineral processing streams. Further, additional studies to address uses or disposal routes for the reduced volume of material with a high pyrite concentration are required. It is recommended that a costing be conducted on this separation approach and that the integration of the separations to facilitate production of benign tailings and to recover maximum values be considered.

The bioleaching of waste rock has been shown to reduce ARD generating potential under conditions where an effective bioleach environment is established. However, the feasibility of the accelerated ARD route requires confirmation from a practical perspective. Particularly, the handling of the dissolved sulphate species and the recovery of the sulphate in a usable form such as gypsum requires investigation. Further, the potential for a closed water re-circulation loop should be considered.

In the coal studies, it is necessary to investigate a range of coal samples in which the sulphur presents in different ratios and associations with the coal. Furthermore, it is recommended that the deportment of coal to the concentrate requires reduction to enable the concentration of sulphide sulphur in a small volume fraction of the tailings. Alternative separation operations may also provide value in the desulphurisation of coal.

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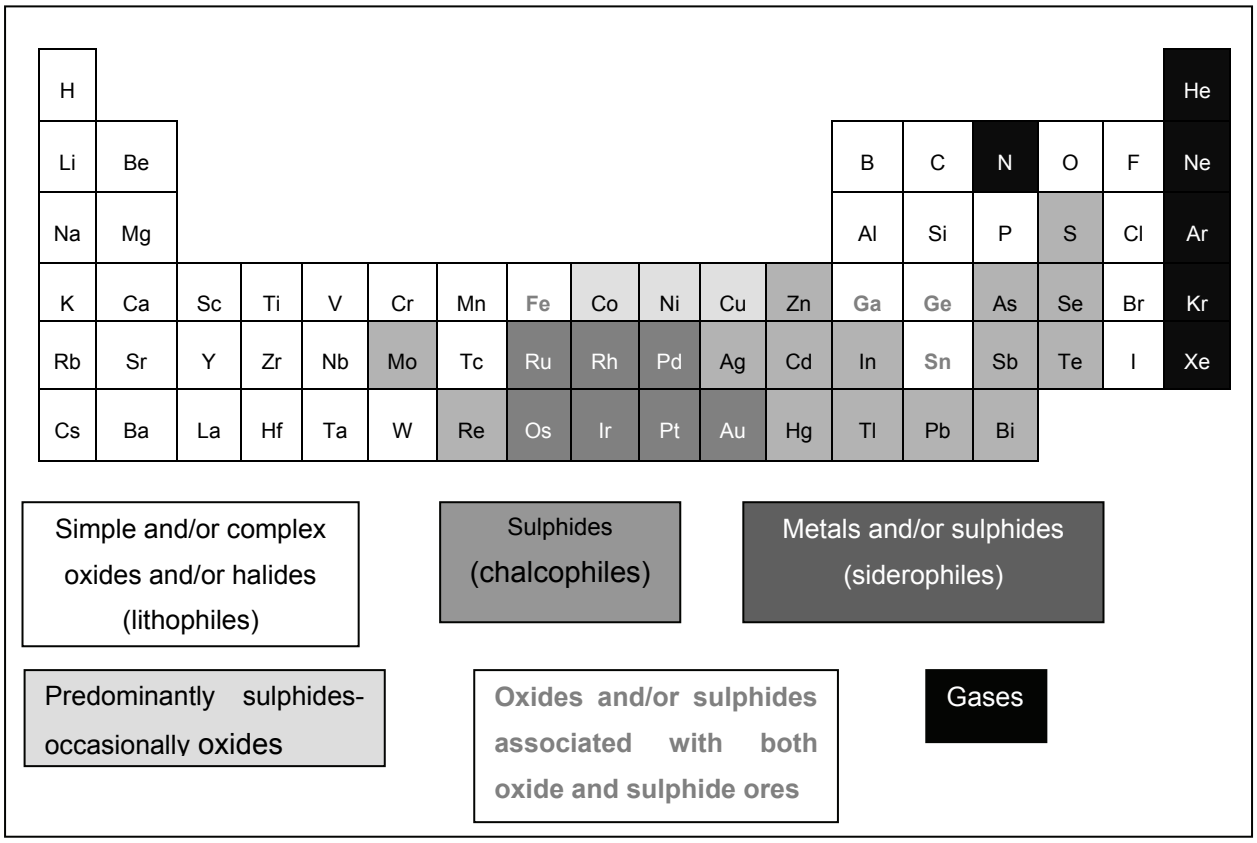
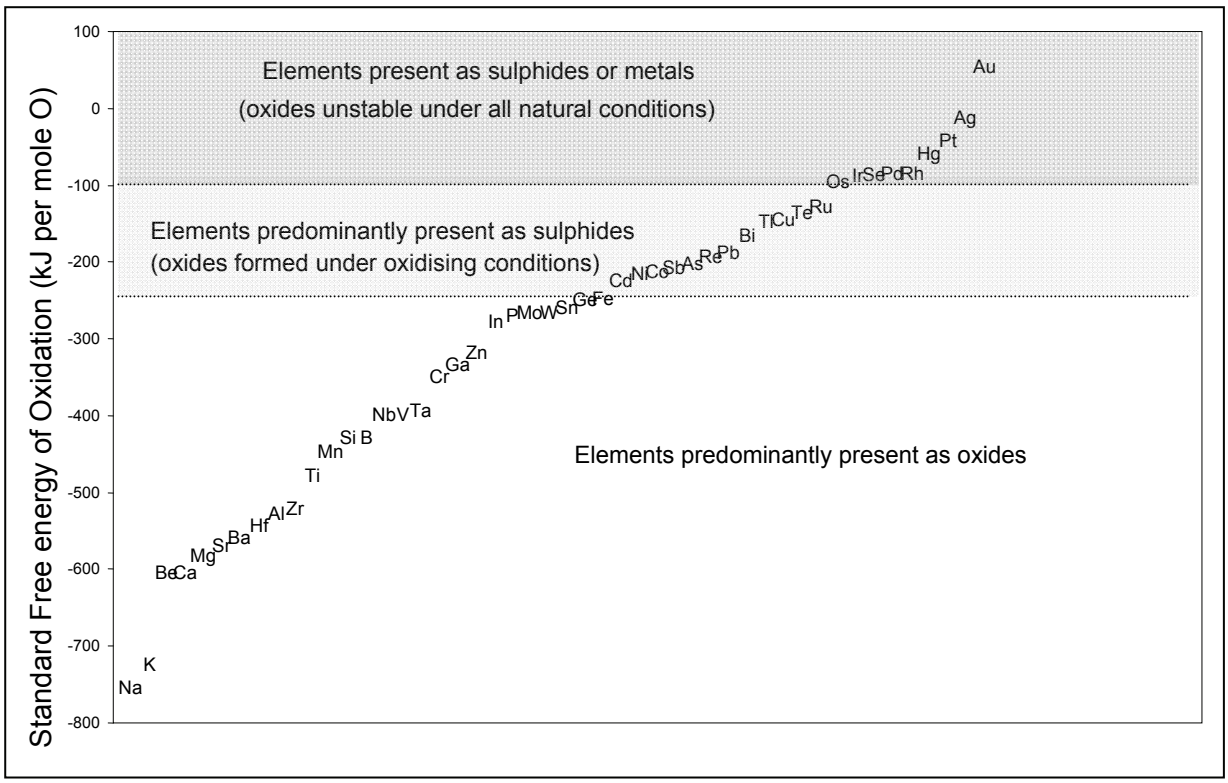
APPENDICES

APPENDIX 1: GENERIC ORIGINS AND SOURCES OF SULPHIDIC MINERAL WASTES (BROADHURST, 2007)

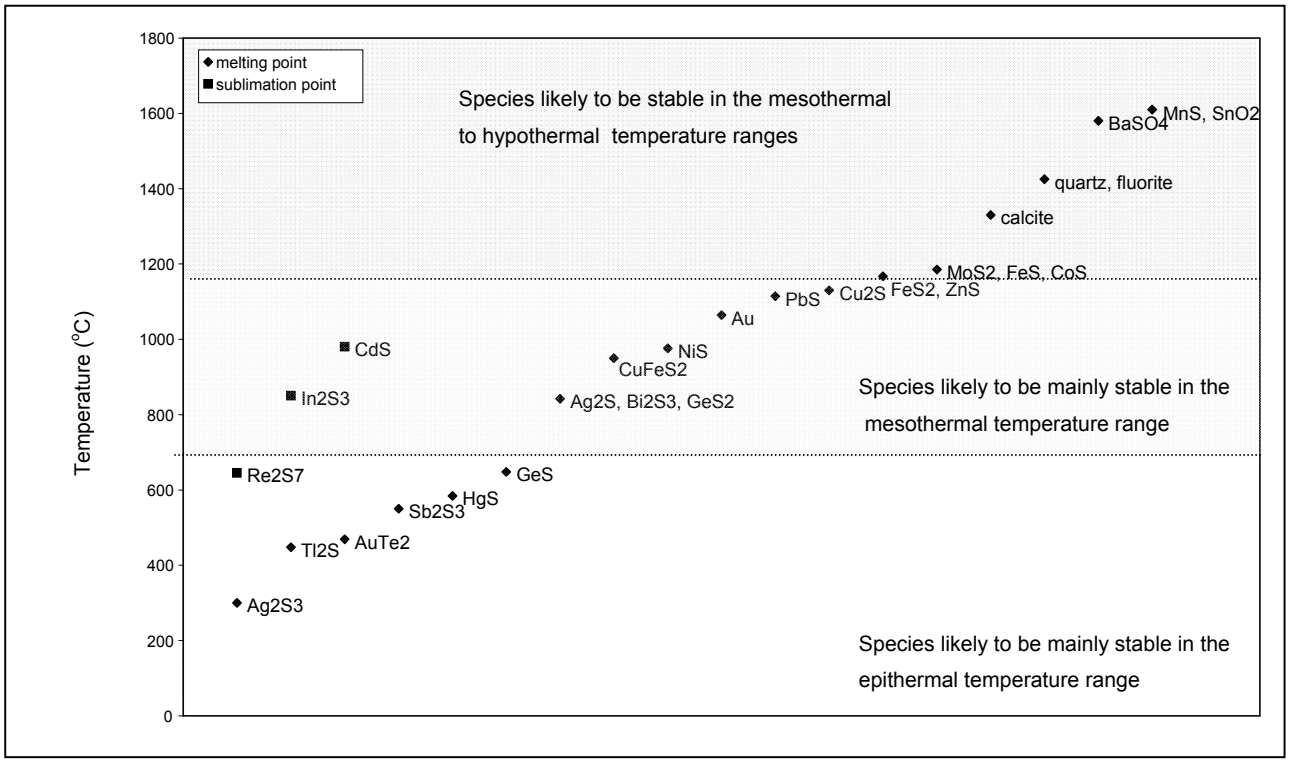
A1.1. Modes of occurrence of elements within the earth's crust



A1.2. The affinity of elements for oxygen



A1.3. Stable temperature ranges of hydrothermal minerals as a function of melting and sublimation points



A1.4. Mineral associations of hydrothermal deposits

Element	Mineral	Hydrothermal deposit class		
		Hypothermal	Mesothermal	Epithermal
Mo	Molybdenite (MoS_2)			
Sn	Cassiterite (SnO_2)			
As	Arsenopyrite (FeAsS) Orpiment/Realgar (As_2S_3)			
Fe	Pyrite (FeS_2) Marcasite (FeS_2) Pyrrhotite (FeS)			
Au	Native/ tellurides			
Zn	Sphalerite (ZnS)			
Pb	Galena (PbS)			
Cu	Chalcopyrite ($CuFeS_2$), tetrahedrite ($(CuFe)_{12}Sb_4S_{13}$); bornite (Cu_5FeS_4), covellite (CuS)			
Ag	Argentite (Ag_2S)			
Sb	Stibnite (Sb_2S_3)			
Hg	Cinnabar (HgS)			
Bi	Native bismuth Bismutite (Bi_2S_3)			
Co Ni	Cobaltite (CoAsS) Niccolite (NiAs)			
Si	Quartz (SiO_2) Adularia ($KAlSiO_3$) Topaz ($Al_2SiO_4(F, OH)_2$			
F	Fluorite (CaF_2) (Topaz, apatite)			
W	Wolframite ($(Fe, Mn)WO_4$) Scheelite ($CaWO_4$)			
Ca (Mg)	Ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) Calcite ($CaCO_3$) Dolomite ($CaMg(CO_3)_2$) (scheelite, fluorite)			
Mn	Rhodocrosite ($MnCO_3$) (ankerite, wolframite)			

Element	Mineral	Hydrothermal deposit class		
		Hypothermal	Mesothermal	Epithermal
Ba	Barite ($BaSO_4$)		═══	═══
P	Apatite ($Ca_5(PO_4)_3(F, Cl. OH)$)	═══		
B	Tourmaline ($NaFe_3Al_6(BO_3)Si_6O_{18}(OH)_4$	═══		
U	Uraninite (UO_2)		═══	

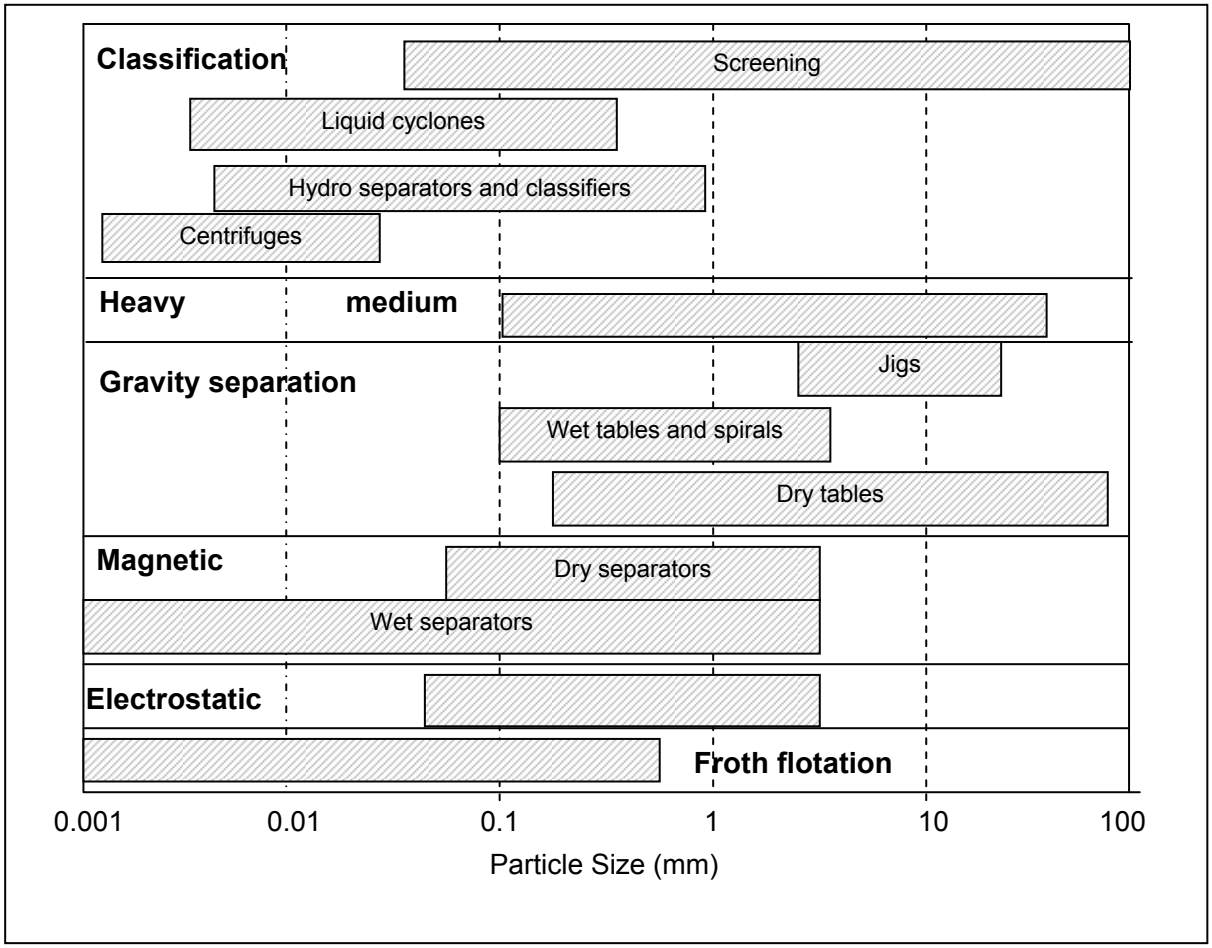
═══ Major association

═══ Minor association

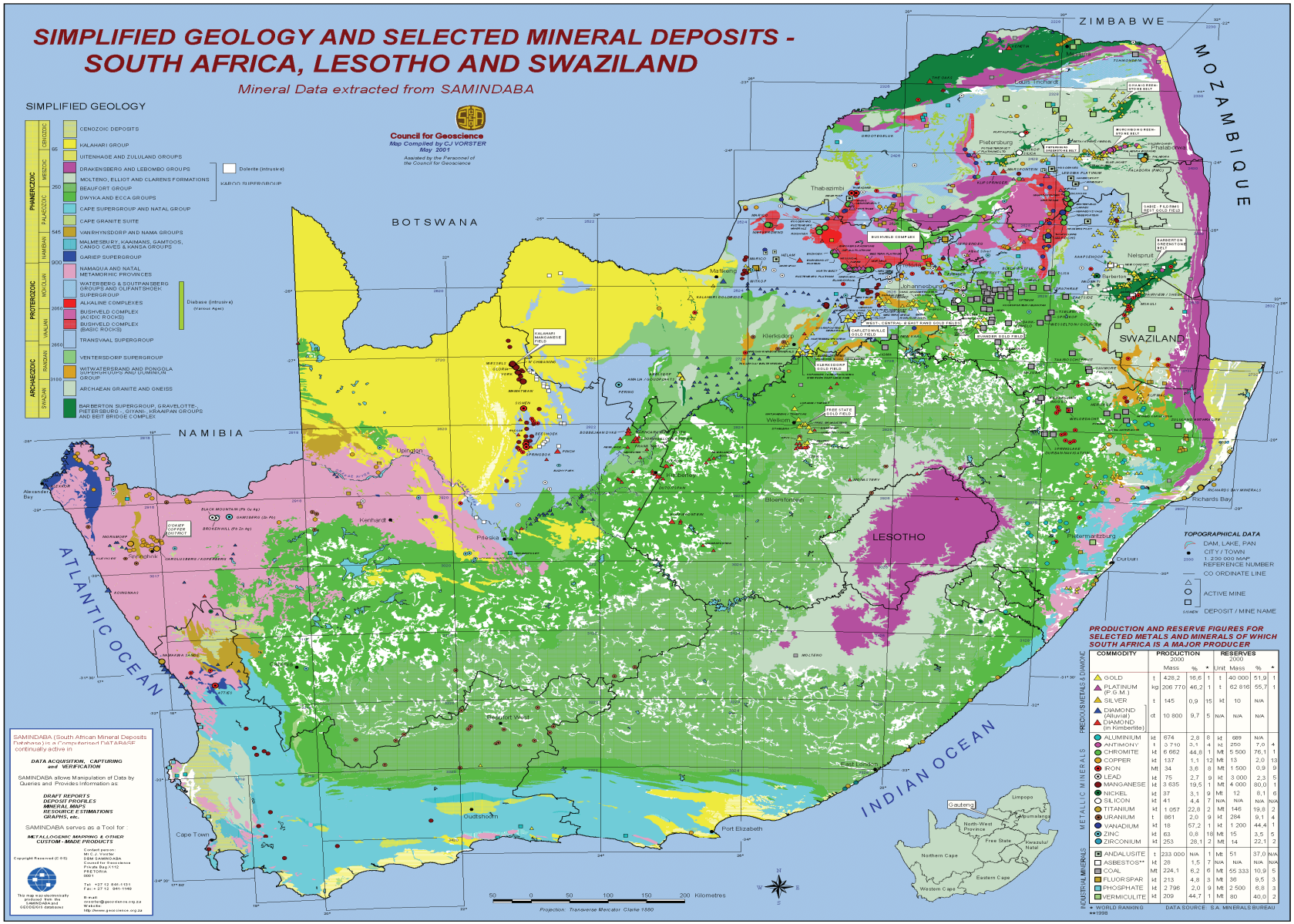
A1.5. Concentration methodologies and technologies as a function of solid-solid separation criteria

Separation criteria	Method type	Common separator technologies
Size only	Classification	Screens; liquid cyclones; hydroclassifers; centrifuges
Density only	Heavy medium separation	
Size and density	Gravity separation	Jigs; shaking tables; spirals
Magnetic susceptibility	Magnetic separation	Dry separators; wet separators
Electric conductivity	Electrostatic separation	
Surface chemistry	Flotation	Froth flotation

A1.6. Particle size range for various concentration methodologies and technologies



APPENDIX 2: ORIGINS AND SOURCES OF SULPHIDIC MINERAL WASTES

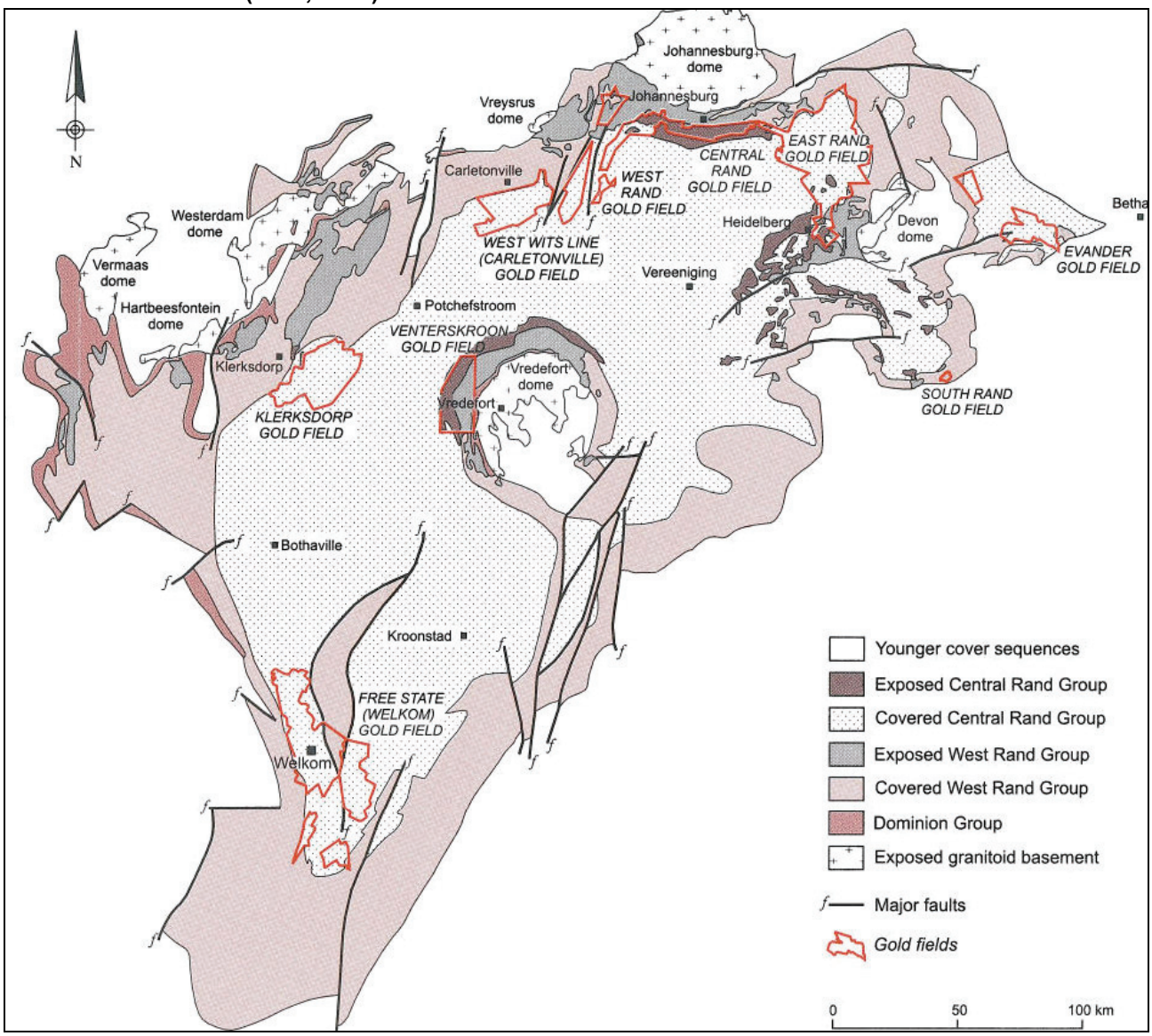


A2.1. Overview of South African Mineral Deposits (South African Council for Geoscience)

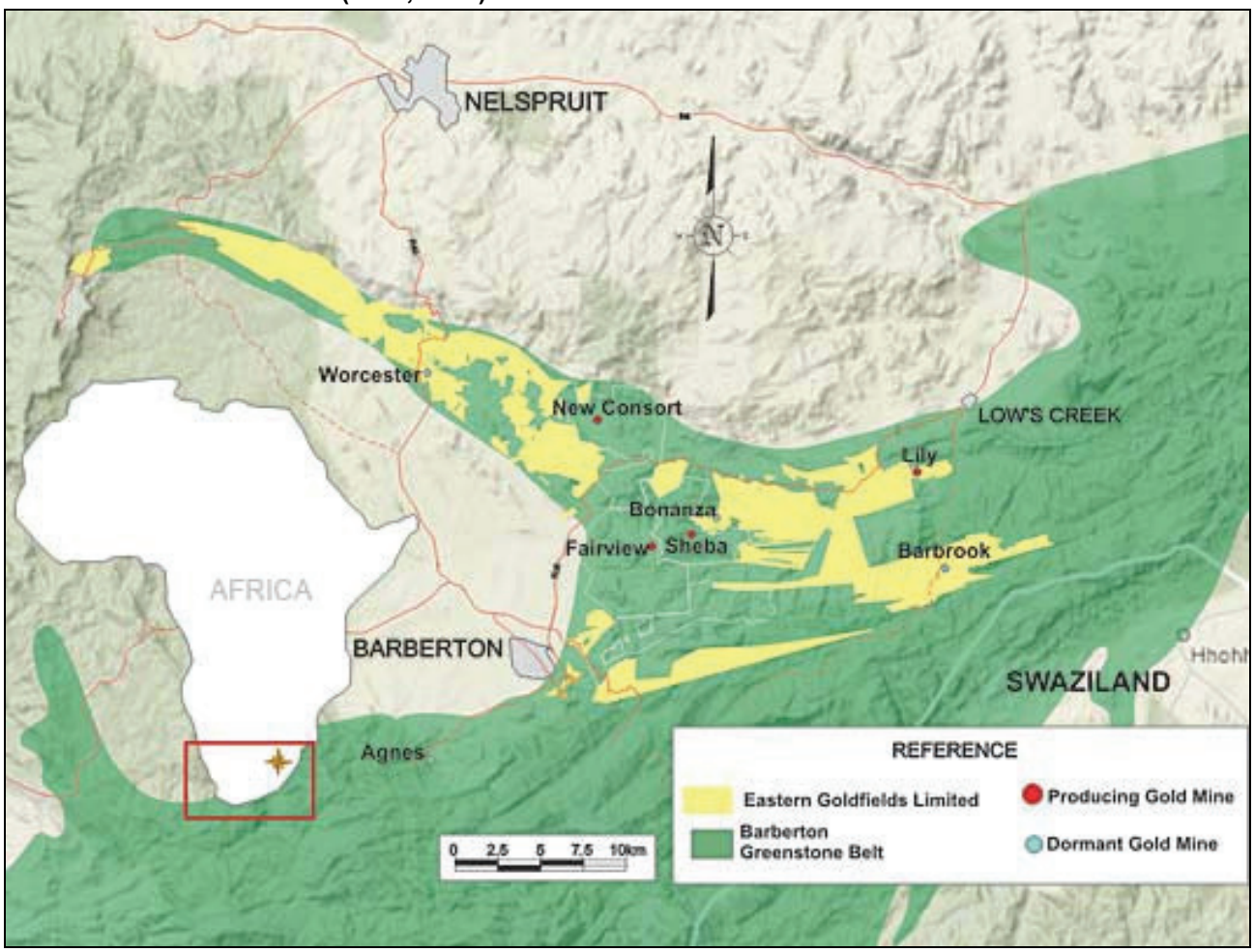
A2.2. Gold sub-sector

By far the most important occurrences of gold in South Africa are found within conglomerates of the Witwatersrand Basin, which contains seven exploited goldfields. South Africa does have other smaller gold producers outside of the Witwatersrand, in the form of Archaean greenstone belts. The main gold producing greenstone belts are the Barberton and the Kraaipan greenstone belts. The Barberton greenstone belt is situated in the Mpumalanga province, just north of Swaziland. The Kraaipan belt is located west of Johannesburg, near Kuruman. Other smaller belts exist in the Northern Province, but have been worked sporadically. Goldfields production outside of the Witwatersrand accounted for only 4% of the countries total gold production in 2006.

Witwatersrand Basin (DME, 2008)



Greenstone Barberton Belt (DME, 2008)



A2.2.1. Ore Processing and Waste Generation

Gold is produced in South Africa using three different process routes, as shown in the flowsheet (p. 99) below (Broadhurst et al., 2007). Gravity concentration followed by mercury amalgamation is the oldest technology and yields the lowest gold recoveries, and resulted in the recovery of relatively coarse gold only. This technology has been largely superseded by technologies based on cyanide dissolution. Within the cyanide dissolution based processes, older processes follow dissolution with filtration and subsequent cementation of gold from solution. More recently, semi-batch carbon-in-pulp or CIP adsorption has replaced clarification and cementation processes. Some plants may employ gravity concentration after comminution.

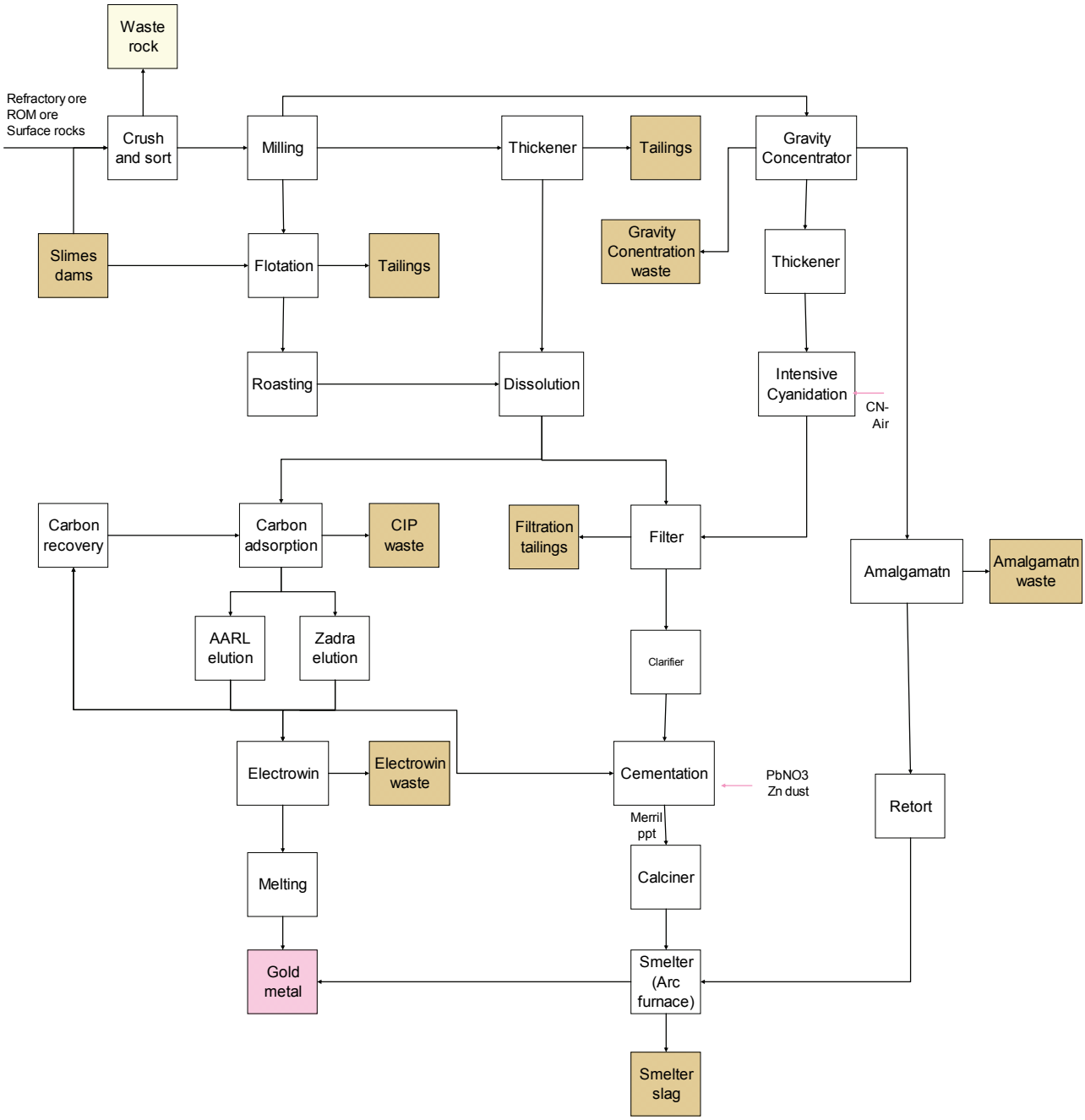
Extensive gold mining activities within the Witwatersrand Basin, has resulted in an estimated more than 270 tailings impoundments in this region, covering approximately 400 km^2 in surface area. Mine tailings are differentiated into two categories based on their material characteristics. These are slimes dams and sand dumps. Sand dumps have been generated during earlier periods, when ore crushing, e.g. by stamp batteries, produced a fairly coarse material. Slimes dams have been generated from 1940's with the introduction of cyanidation process, which requires the ore to be milled to a finer state. This has made sand dumps to be coarse (approximately 200 microns diameter) while slimes dams consists of fine materials (Mpephu et al., 2004a and 2004b).

Important in contributing towards gold production in the country today is the reworking and extraction of economic minerals from these slimes dams and mine sand dumps (e.g. the extraction of low concentrations of gold, silver, uranium oxide and pyrite (for sulphur) from slimes dams and mine dumps on the East Rand Goldfield by the East Rand Gold and Uranium Company Limited (ERGO)). In accordance with the Council for Geosciences, the chance of finding any more major gold deposits in Gauteng, in particular, is rather slim and future contributions are most likely to come from:

1. the reworking of existing slimes dams and mine dumps occurring all over the Witwatersrand;

2. the re-engineering and re-structuring of large, marginal mines into smaller, much leaner operations;
3. the scavenging of abandoned stopes where the pillar structures are mined, the stopes sweeped and vacuum cleaned and even the wood structures recovered from the stopes are burned and any gold trapped in it recovered; and
4. as in the case of the proposed Argonaut project, to extend workings further down dip.

The remaining active gold fields, such as the Greenstone Barberton goldfields in Mpumalanga, make a relatively small contribution to the production of gold in South Africa (approximately 4% of national production in 2006 (DME, 2008)).

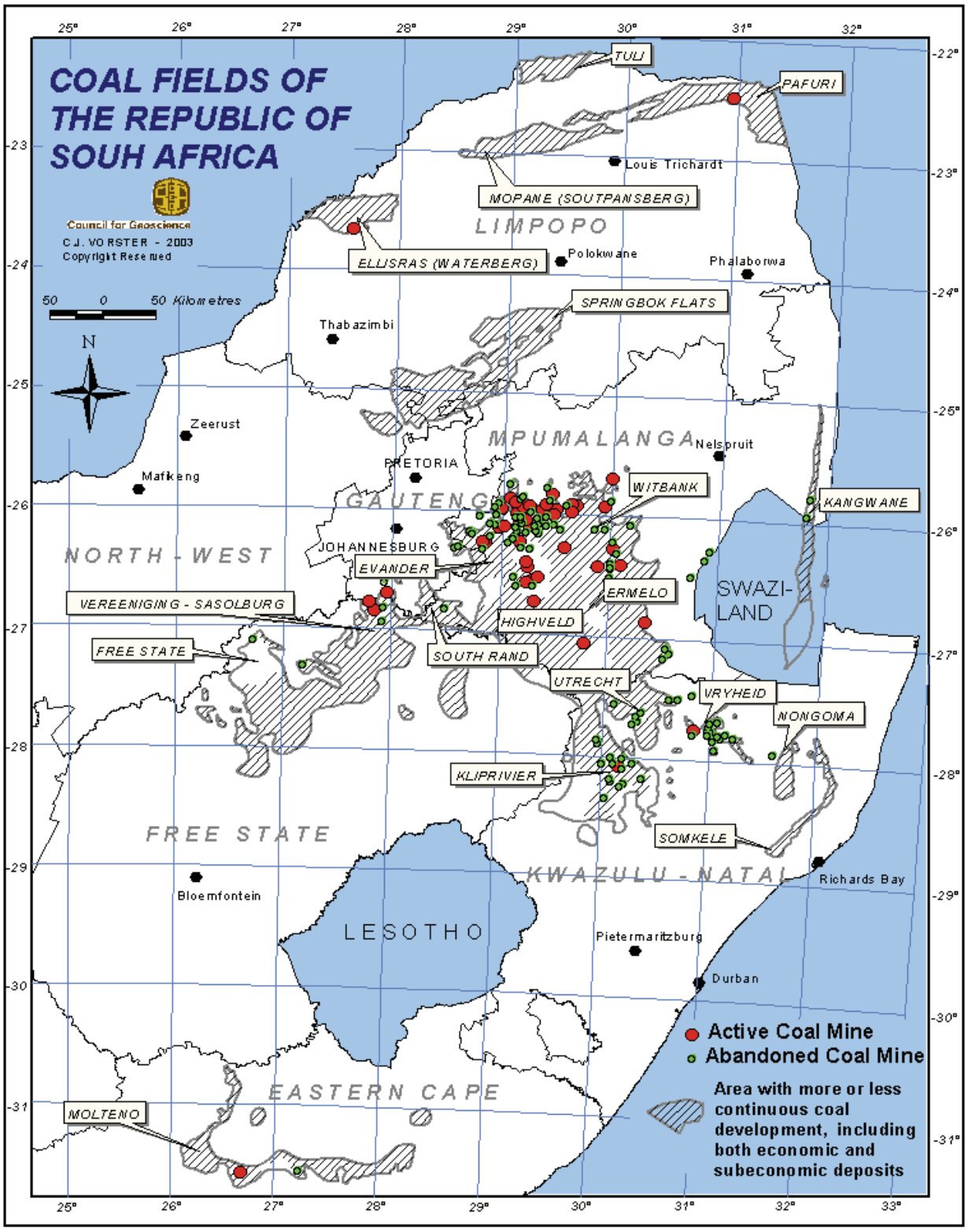


Gold processing flowsheet: South Africa (Broadhurst et al., 2007)

A2.3. Coal Sub-sector

South Africa produces nearly 250 Mt of saleable coal a year producing approximately 90% of South Africa's electricity. The so-called Witbank coalfields (Witbank-Middelburg, Ermelo and Stanferton-Secunda areas) in Mpumalanga, contains extensive coal reserves and is the country's most productive coalfield. Other coal

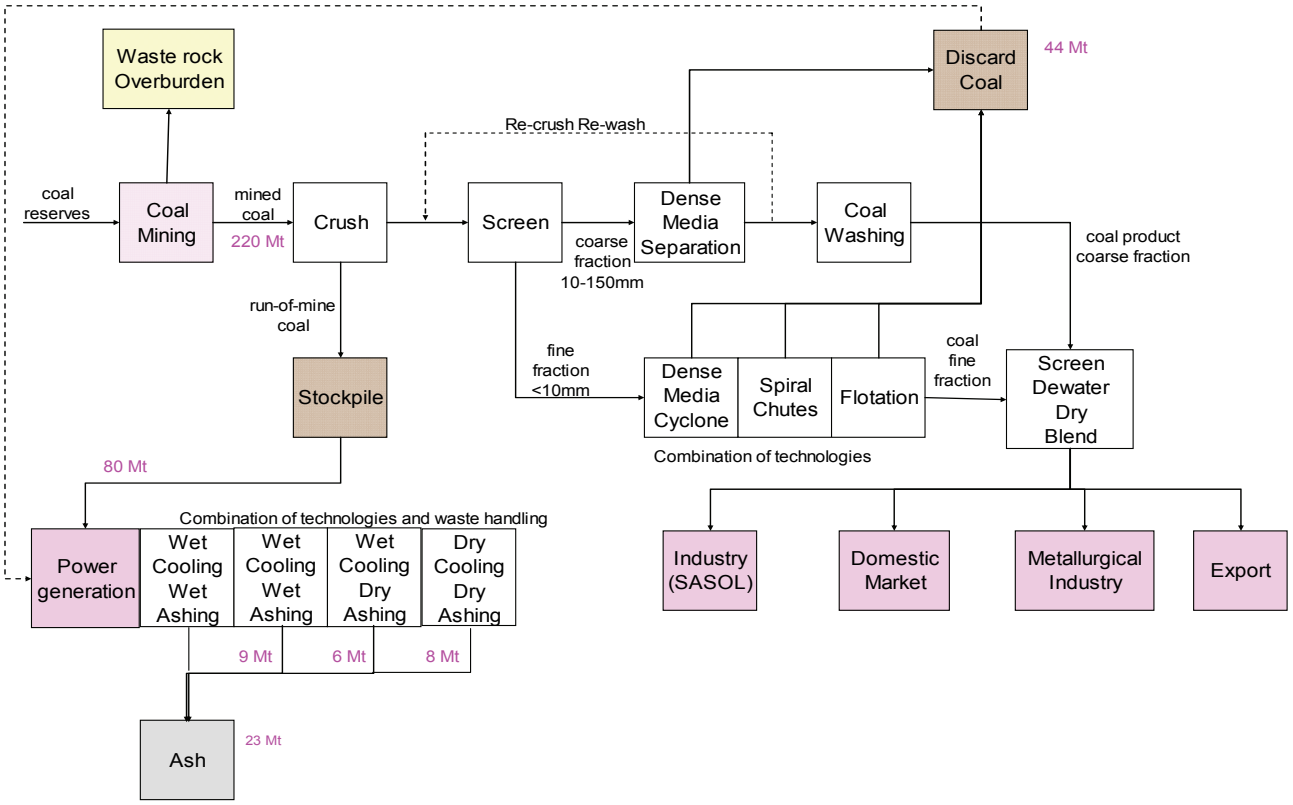
fields occur in the Free State; Vereeneging-Sasolburg; KwaZulu-Natal (small operations), with single large collieries near Ellisras (Waterburg coalfields) and Tshipise (Soutpansberg coal fields) (Jeffrey, 2005).



A2.3.1. Coal Processing

The quality of the coal found in South Africa is generally low, with a low heat value and high ash content- typically 20-30% (ESKOM, 2007) The sulphur content is relatively low (Mostly <2%) and is largely present inorganically in pyrite, which is present in the ash. In some cases ROM coal is sent directly to power generation, but for the most part it is processed to increase its calorific value. Firstly all material that has a low calorific value, such as stones, rocks, wood, etc. needs to be removed. This is achieved by crushing the ROM coal and then separating unwanted material physically. The coal is then screened to separate different

size fractions. The second process after crushing and screening is beneficiation. Coal is washed to reduce the ash content. Ash is removed since it is incombustible and reduces the total calorific value of the coal. The washing process typically involves a density-based separation of valuable coal from low-grade coal, with high ash content. Buyers usually specify the ash and sulphur content of the coal. The degree of coal washing is thus determined by these specifications, with more than 80% of South African coal is washed (DME, 2001, cited Reddick, 2006).



Coal sub sector process flowsheet (Broadhurst et al., 2007)

A2.3.2. Coal wastes

The sulphidic mineral waste streams from coal mining and processing include waste rock or coarse overburden from mining and discard coal and ultrafines from coal beneficiation processes. The process flowsheet also identifies coal stockpiles, on both the mine site and the power generation site, as a solid waste. This is because these temporary stockpiles give rise to impacts similar to those typically associated with solid wastes (Hansen, 2004; Notten 2001). Discards pose a particular threat to the surrounding environment through both ARD generation and spontaneous combustion, as a result of their relatively high sulphur and moisture content. Old (defunct) discard dumps in particular are considered to be one of the greatest polluters of the environment in certain regions of South Africa, particularly the Witbank region, polluting the atmosphere, rivers, ground water and the esthetics of the countryside (DME, 2001). Statistics revealed approximately 40 defunct discard dumps, most of which are smaller than 5 million tons. As the average life of the active discard dumps, smaller than five million tonne is 11 years, it is expected that these dumps will grow considerably (DME, 2001).

In a 2001 survey report, the South African Department of Minerals and Energy state:

Discard coal and slurry are currently being produced at annual rates in excess of 42 million and 11 million tonnes respectively. Utilisation of both discard coal and slurry is being practiced on some mines. Discard coal is being re-washed for power station feed, while slurry ponds are being re-treated by froth flotation, producing a saleable product, which is blended with coarser coal fractions and sold as export steam coal or power station feed. Treatment of slurry and the reclamation of slurry ponds for beneficiation by froth- flotation are being carried out by a number of mines. Beneficiation is carried out in either column flotation cells or in conventional tank type flotation cells. Product quality and recovery is normally good due to the better quality of the slurry when compared to the discard coal. With environmental laws becoming stricter, mines are paying greater attention to the methods of discard and slurry disposal.

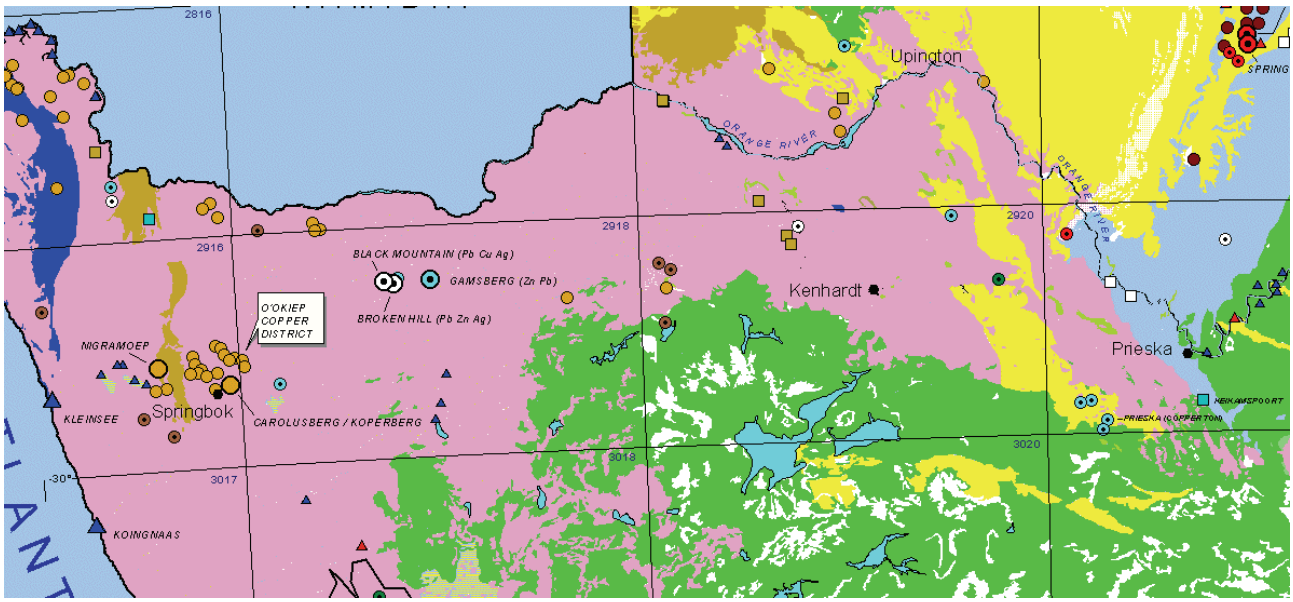
Discard coal is now being compacted and the discard dump clad with soil and vegetated. These rehabilitated dumps are potentially reclaimable, the discard being kept under non-oxidising conditions. A substantial amount of discard has either been tipped into opencast voids or mixed with opencast overburden material to fill voids left by the mining operation. This discard is considered un-reclaimable. Methods of slurry disposal have also changed considerably. Slurry is now pumped into the centre of the dump, the compacted discard forming a wall around the central slurry impoundment. This form of co-disposal will have a marked affect on the discard reclamation. Slurry is sometimes pumped onto the un-compacted discard coal resulting in a matrix, which does not require intensive compacting, to form a non-oxidising condition within the dump. This method of slurry disposal is known as integrated discard disposal and will also affect discard reclamation. Treatment of slurry and the reclamation of slurry ponds for beneficiation by froth- flotation are being carried out by a number of mines. Beneficiation is carried out in either column flotation cells or in conventional tank type flotation cells. Product quality and recovery is normally good due to the better quality of the slurry when compared to the discard coal.

A2.4. Base Metals Sub-sector

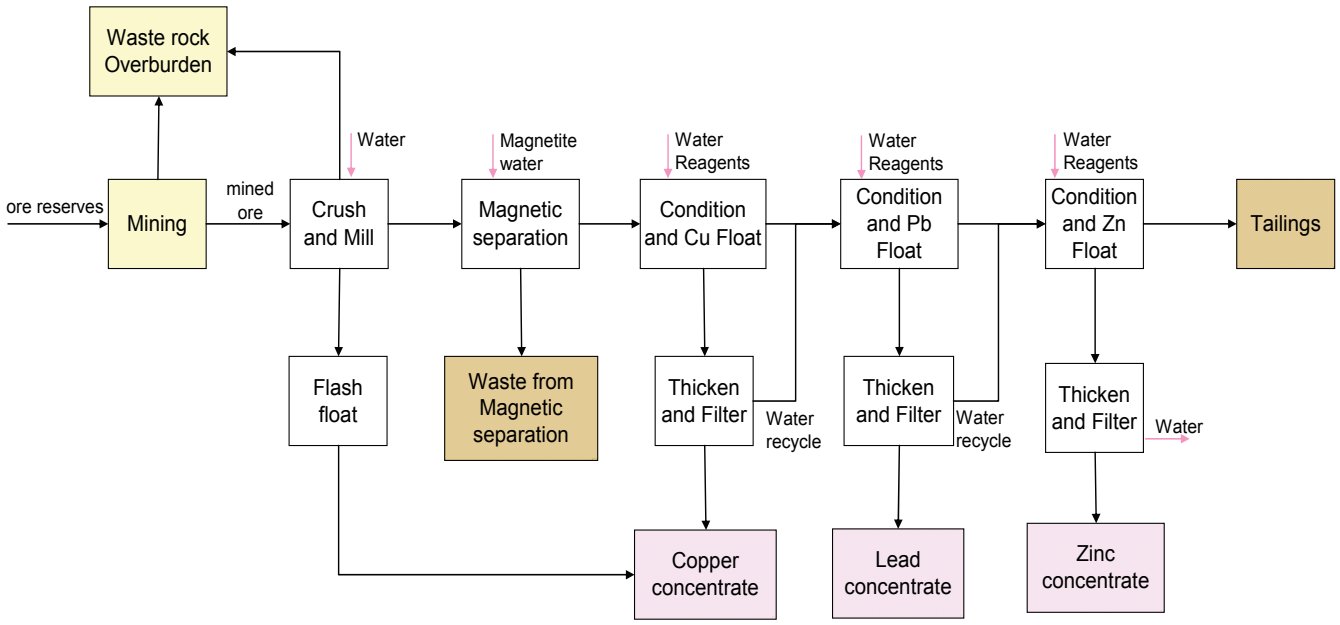
The majority of South Africa's copper and, particularly nickel, production is associated with the beneficiation of PGMs (see later discussion).South Africa's only primary nickel mine is the Nkomati mine situated in Mpumalanga. The so-called "Bon Accord" nickel sulphide deposit is unique and has two zones: A massive sulphide zone, containing pyrite, pentlandite and pyrrhotite, and a mineralised zone, with low sulphides. The only primary copper metal production in South Africa occurs at the Palabora Copper Mine. The Palabora igneous complex is unique in that the copper sulphides occur in veins of carbonatite, and is thus not a sulphide ore in the conventional sense. Copper, zinc and lead concentrates are also produced at the Black Mountain mineral processing plant from ore mined at the Broken hill, Swartberg (Black Mountain) and Gamsberg mines in the Aggeneys in the Northern Cape Province (see detailed discussion below).

A number of other base metal sulphide deposits have been mined and processed in the past, but operations have since shut-down:

- The zinc-copper ore body at Copperton in the vicinity of Prieska in the Northern Cape Province- a massive sulphide deposit with 30% pyrite, 1.74% copper and 3.9% Zn.
- The O'Kiep massive sulphide copper deposits near the town of Springbok in the north-west corner of the Northern Cape Province produced blister copper.
- The Pering zinc-lead deposit in the northern part of the Northern Cape Province- a disseminated galena and sphalerite deposit hosted in dolomite, with minor quantities of pyrite, chalcopyrite and carbonaceous shale.



Northern Cape Province base-metal deposits (From South African Council for Geoscience. See mineral deposit map in A2.1 for key to symbols)



Generalised flowsheet for the initial concentration of base metal sulphide deposits (Broadhurst et al., 2007)

Survey of the base metal sulphide ore deposits and beneficiation processes in the Aggeneys district (Hesketh, 2008)

Black Mountain minerals processing plant is owned and operated by Anglo Base Metals, producing lead, zinc, copper and silver from three mine sites, Broken Hill, Swartberg (Black Mountain) and Gamsberg. The plant is situated near the town of Aggeneys in the Northern Cape Province in South Africa.

The Aggeneys region, in which the Black Mountain plant is situated, forms part of the Bushmanland Group of the Namaqualand igneous complex, formed in the Proterozoic era. The ore bodies a sedimentary exhalative (SEDEX) deposit with high metal sulphide inclusions, in some cases containing up to 50% sulphides. The area comprises four major ore bodies, two of which, Black Mountain and Broken Hill, are presently being mined extensively, a third, Gamsberg, on a small scale to satisfy government legislation, and a fourth, Big Syncline, which, due to hardness of the surrounding rock, has not yet been mined (Gama Paulo, 2001). Studies have shown that the mineralogy of the three mines, shown on the map detail above, are very similar as they were formed from the same mineralizing fluid (Reid et al*, 1992). The ores from the three mines behave in similar ways and are thus processed through the same plant, although the primary minerals in each case differ, as shown in the table below.*

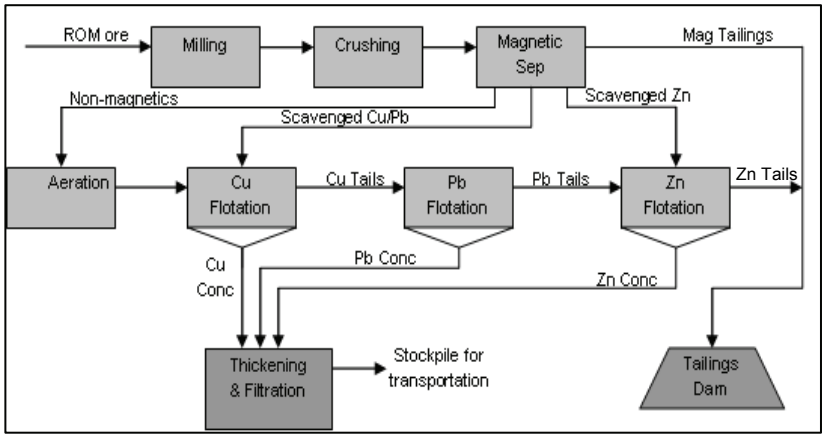
Ore grades of Aggeneys region

	Reserves (Mt)	*Pb %*	*Zn %*	*Cu %*	*Ag (g/ton)*	*Fe %*
Broken Hill	*0.41*	*3.57*	*1.77*	*0.34*	*48*	*~35*
Black Mountain	*1.47*	*2.67*	*0.59*	*0.75*	*30*	*~30*
Gamsberg	*142*	*0.55*	*7.1*	*0.02*	*6*	*~30*

The sulphide minerals of importance in this study are found in the following order of abundance: pyrrhotite, galena, sphalerite, chalcopyrite and pyrite (Frimmel et al.*, 1995). The major gangue minerals found with this ore body are magnetite (Fe_3O_4), quartz and micas. The sulphide minerals exist as massive, disseminated and layered forms within the ore bodies. Run-of-mine (ROM) ore from the mine sites, is crushed and milled to for feed for magnetic separation. The magnetic separation step removes magnetite, Fe_3O_2, and monoclinic pyrrhotite, FeS, reducing overall volume of material sent to the flotation circuit and thus improving residence times. Non-magnetic material is then fed to flotation, made up of three circuits. Firstly, copper is removed, then lead, and finally zinc. The zinc flotation tailings are then combined with tailings from the magnetic separation on the tailings dam.*

At the Black Mountain Mine site there are two waste rock dumps, one at Swartberg and the other at Broken Hill. These deposits take rock removed from the mines, which is deemed to be of little economic value, but requires removal for access to further mineral deposits within the mine. Currently, these rock dumps are not known to be acid generating due to the low sulphide value of the rock lining the ore deposits, but this needs to be verified.

Flowsheet of the Black Mountain operation



One Tailings dam exists receiving magnetic separation tailings, containing magnetite and monoclinic pyrrhotite, and 70% of flotation tailings from the zinc flotation circuit. The other 30% of the tailings is backfilled in disused mine workings. This tailings dam has a capacity of 25 MT covering 65ha. Currently, the dam stands at 35 m, with a maximum allowable height of 50 m. The composition of the tailings dam is given below (Duthie and Souster, 2007):

Copper 0.03%
Lead 0.50%
Zinc 0.30%
Pyrite 30 to 40%

There are plans to extend the tailings dam, to accept tailings until the estimated closure of the mine in 2013. Currently an EIA is being conducted by Oryx Environmental, with the proposed work to be carried out by Golder Associates. A pilot study is presently being conducted by Anglo Base Metals, to extent the backfilling operation from 30% to 70%. Should this study fail, the proposed extension to the tailings dam will include 100% of the tailings from the processing plant.

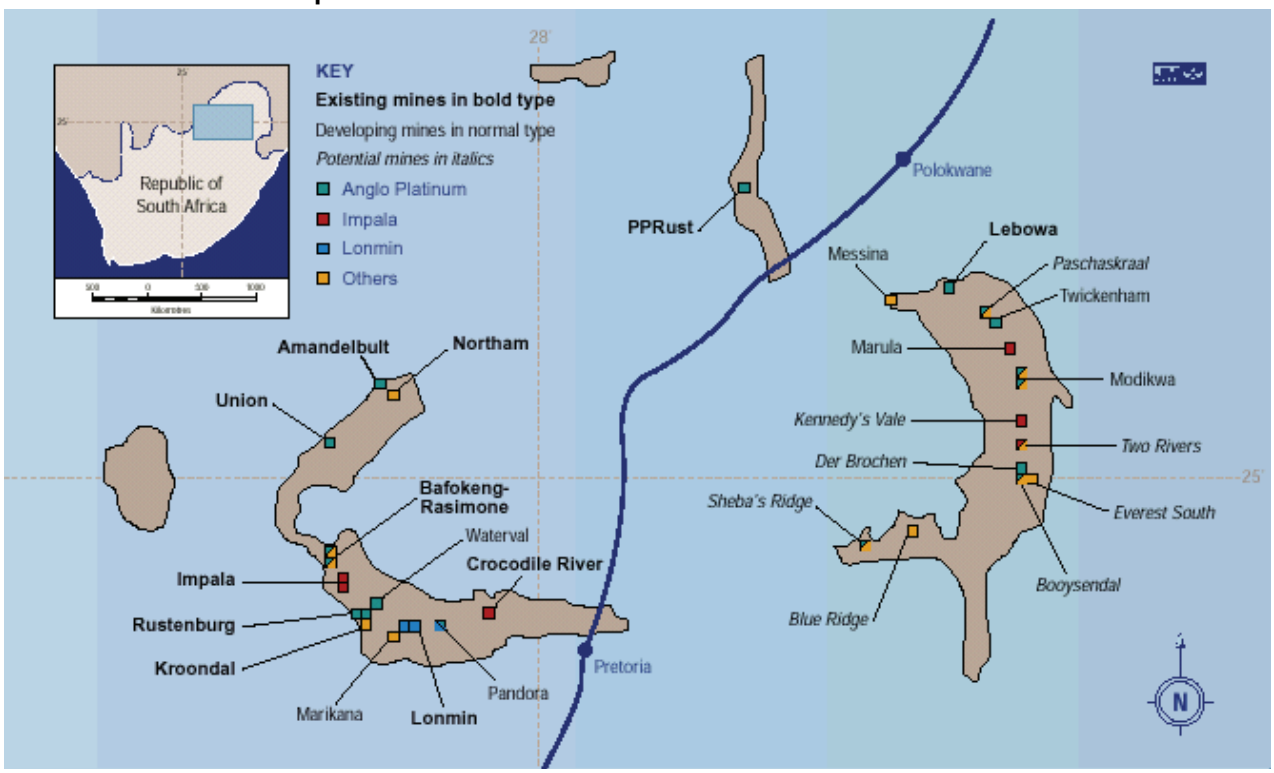
A2.5. Platinum Group Metals Sub-sector

The Bushveld Igneous Complex in South Africa boasts one of the world's foremost deposits of PGMs as well as economically recoverable amounts of copper, nickel, chromium and vanadium. There are three different reef types which are exploited by platinum mining companies; Merensky Reef, UG2 Reef and Platreef (Becker et al., 2008). The principal PGM-bearing horizons are the Merensky Reef and the Upper Group 2 (UG2) Reef, which occur around the Eastern and Western Limbs of the complex, while a third PGM-rich layer, the Platreef, is found only on the Northern Limb at the north-eastern edge. Although there are other deposits similar to Platreef in some respects, such as Sheba's Ridge, these have yet to be mined.

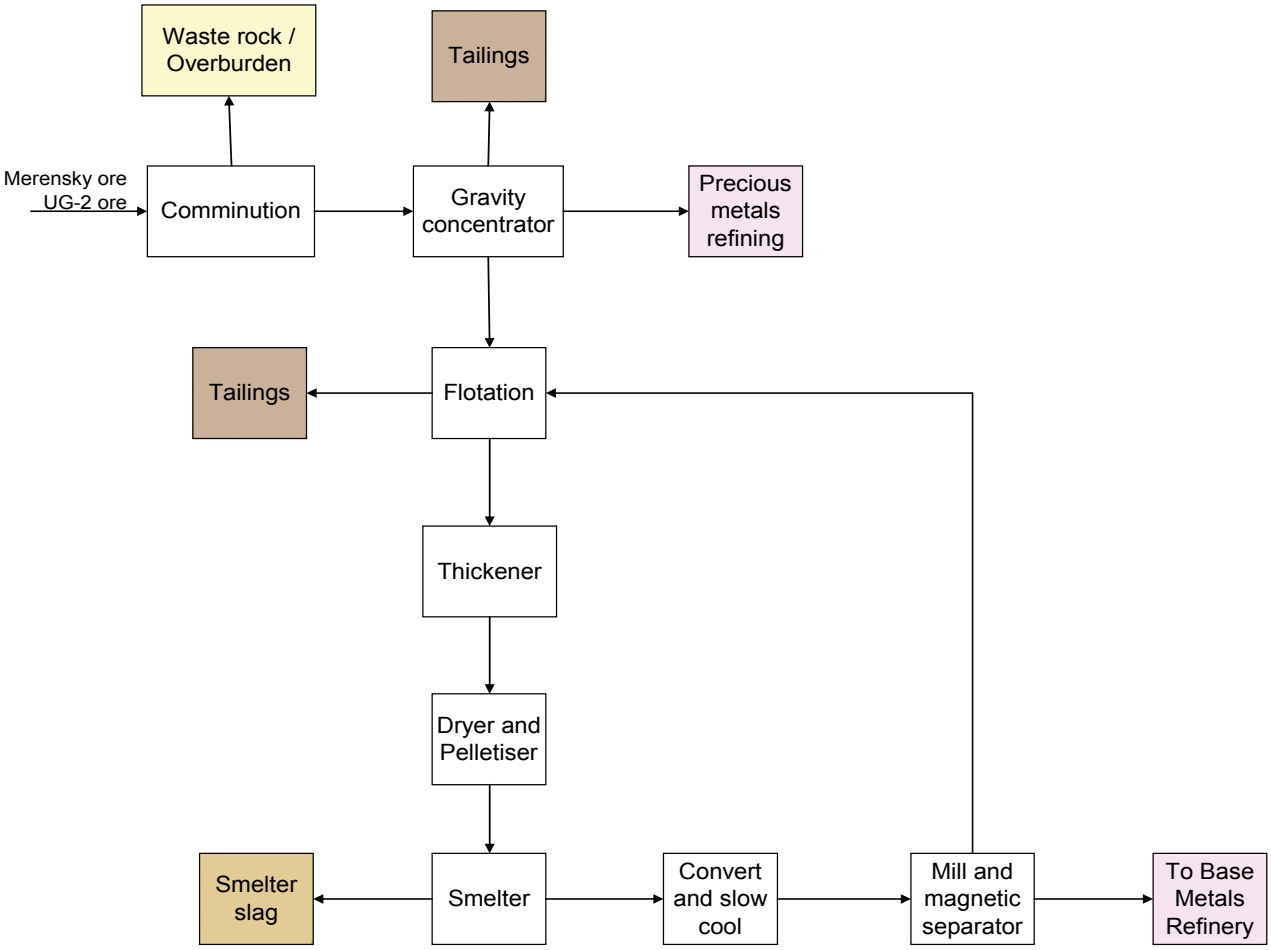
The Merensky Reef has been the principal source of PGMs since it was first worked in 1925. However, the other reefs have grown in importance, so that by 1999 the Merensky Reef accounted for just over 50% of all platinum-bearing ore processed in South Africa. Exploitation of the UG2 began in the 1970s and has steadily increased; in 1999, it was the source of 42% of ore processed and is now thought to exceed 50% across the complex. The UG2 is found at a vertical distance of between 16 and 400 metres below the Merensky Reef, depending on location. The Platreef, briefly mined in the 1920s, was first exploited on a large scale in 1993 and is gradually becoming a significant contributor of PGMs for Anglo Platinum. Angloplats Western Limb Tailings Retreatment (WLTR) plant, situated near the Brakspruit Shaft in Rustenburg, is also retreating old tailings from a number of dams in the Klipfontein and Waterval areas. The plant was commissioned at the beginning of 2004.

The Merensky and Platreef have a higher sulphide content- with which is the PGE and PGM are closely associated- and yield meaningful quantities of nickel and copper as by-products of PGMs. UG2 differs from Merensky in that it contains significantly more chromite and lacks the base metal sulphides and gold found in the Merensky ore, reducing the value of the ore, although it does contain a higher fraction of PGMs.

Southern Africa PGM Deposits



The solid wastes arising from the initial beneficiation of PGM ores include waste rock and overburden from mining and tailings from gravity concentration and flotation, and smelter slag.

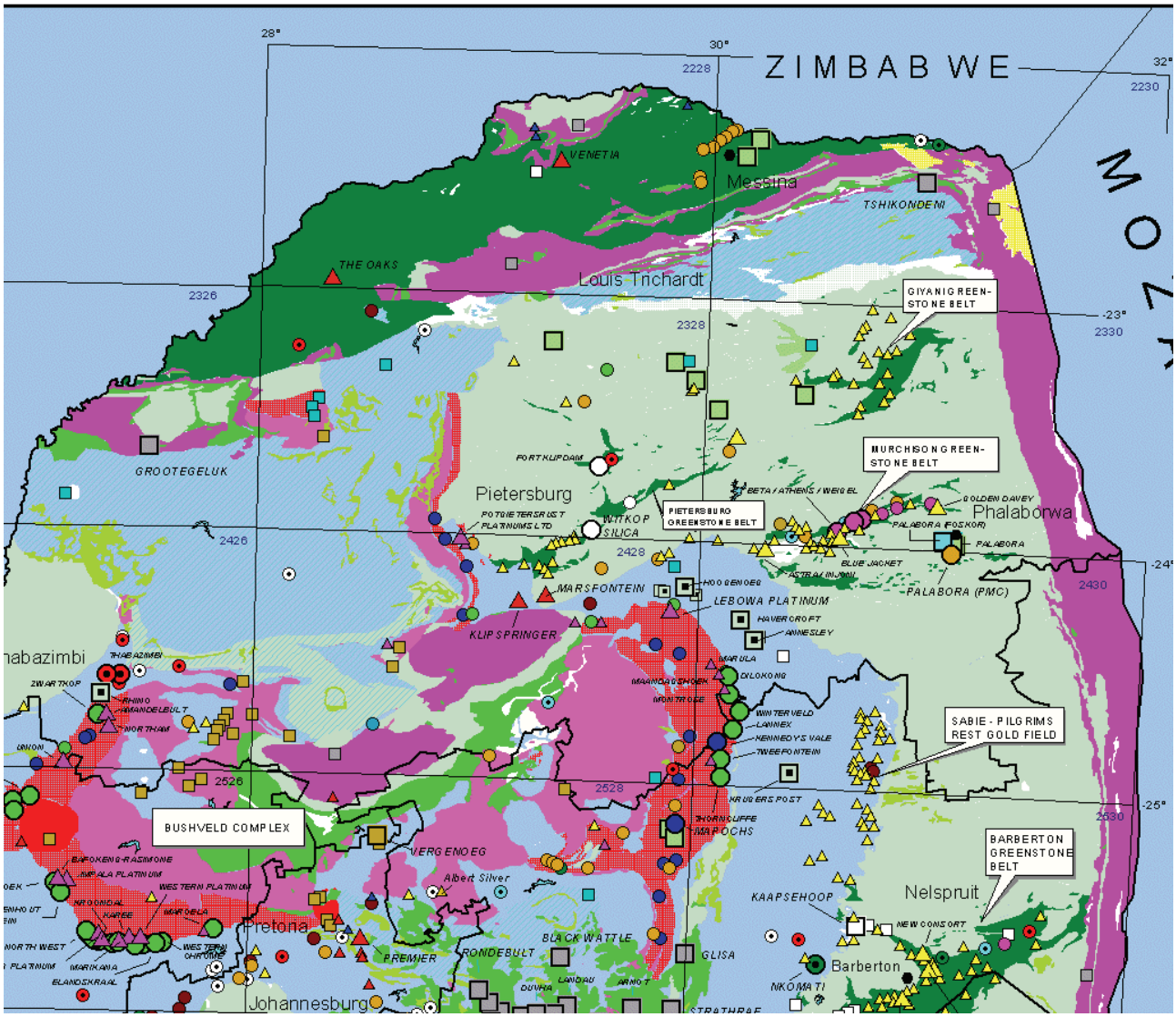


Initial beneficiation of PGM ores flowsheet (Broadhurst et al., 2007)

A2.6. Antimony Sub-sector

Stibnite (Sb_2S_3) ore on the local "Antimony Line" in the Murchison Greenstone Belt in the Northern Province is confined to a 10-25-m zone of massive quartz-carbonate rock in an envelope of schistose chloritic quartz-carbonate rock and talc-carbonate schist. Accessory sulphides include pyrite and, in particular arsenopyrite. Minor gold is present n all the main sulphide phases. This ore body feeds the only primary antimony mine in South Africa, Consolidated Murchison, which is the world's single largest producer of high grade antimony, and also the world's oldest known antimony deposit. The Metorex Group owns and operates Consolidated Murchison, which produces both antimony and gold by sublevel open stoping (Schwartz-Schampera and Herzig, 2001).

Limpopo Province antimony deposits (From South African Council of Geoscience. See mineral deposit map in A2.1 for key to symbols)



APPENDIX 3: DISSEMINATION OF RESEARCH TO DATE

	Authors	Title	Journal / conference
1	Hesketh AH, Broadhurst JL and Harrison STL (2008).	An integrated approach to mineral sulphide tailings management and ARD mitigation.	Mineral Processing 2008, August 2008, Cape Town.
2	Cilliers JJ and Harrison STL (2008).	Sustainability and the mineral engineering curriculum.	*IMPC Workshop on Education*, Beijing, China, Sept 2008.
3	Hesketh AH, Broadhurst JL and Harrison STL (2009).	An Integrated Approach to the Management of Sulphide Tailings and Mitigation of Acid rock drainage	ICARD, 22-25 June 2009, Sweden
4	Robert P van Hille, Andries W van Zyl, Nicholas R L Spurr and Susan T L Harrison	Investigating heap bioleaching: Effect of feed iron concentration on bioleaching performance	Bio- and Hydrometallurgy '09, April 6-7, 2009, Cape Town, South Africa
5	AH Hesketh, JL Broadhurst and STL Harrison	Mitigating the generation of acid rock drainage from copper sulphide tailings impoundments in perpetuity: An integrated management strategy	SRCR '09, 4-5 April 2009, Cape Town, South Africa
6	Johannes J Cilliers and Susan TL Harrison	Sustainability and the Mineral Engineering Curriculum	SRCR '09, 4-5 April 2009, Cape Town, South Africa
7	Susan T L Harrison, Alexander H Hesketh, Robert P van Hille and Jennifer L Broadhurst	Process decisions focused on the prevention of ARD formation on beneficiating sulphide minerals	17th Interational Biohydrometallurgy Symposium, 13-17 Sept 2009, Argentina
8	AH Hesketh, JL Broadhurst and STL Harrison	Mitigating the generation of acid rock drainage from copper sulphide tailings impoundments in perpetuity: An integrated management strategy	*Minerals Engineering* (2010) **23**, 225-229
9	S T L Harrison, A H Hesketh, R P van Hille and J L Broadhurst	Biokinetic test for the characterisation of ARD formation potential of sulphide mineral wastes	*Hydrometallurgy*, invited submission, in press