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AN INTEGRATED APPROACH TO AMD MITIGATION THROUGH SULFIDE REMOVAL FROM TAILINGS

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Dissertation in fulfilment of MSc in Chemical Engineering
SYNOPSIS

The formation of acid mine drainage (AMD) from the microbial oxidation of sulfides in mineral waste deposits is one of the major challenges facing the mining industry worldwide. Growing environmental awareness and subsequent changes in legislation has focused research in addressing the prevention of pollution by AMD. Current waste management approaches focus on deposition techniques to control AMD formation and on remediation. However, these approaches do not remove the risk of AMD generation and are yet to be proven effective in mitigating long-term acid generating potential. In compliance with the principles of pollution prevention, addressing waste at its source, the aim of this work is to remove the risk of AMD generation by focusing on the removal of sulfides from potentially acid generating tailings prior to disposal. The objectives set out to address sulfide removal from tailings, through the use of flotation, to effectively reduce environmental burden and to assess the benefits of desulfurisation through the use of laboratory scale static and kinetic AMD prediction tests and resultant potential for metal deportment.

This was conducted through a case study to assess the tools and criteria required to aid in the development of effective waste management strategies for long-term AMD mitigation. The case study was carried out on a porphyry-type copper sulfide sample with typical tailings characteristics. It had a total sulfur content of 3.84%, the majority occurring as pyrite but it also contained chalcopyrite, with a copper content of 0.16%. The sample was found to be significantly acid generating in preliminary tests. Environmentally sensitive co-elements were identified with ICP-MS.

Desulfurisation was assessed in batch flotation tests using a dithiophosphate collector. Results showed that in a multi-stage flotation test it is possible to produce bulk sulfide-lean tailings with a total sulfur content of 0.21%, with the majority of sulfides concentrated in a low volume residue accounting for just 10% of the total mass processed. The experiments also highlighted the differential rates of flotation of chalcopyrite and pyrite, providing opportunity to recover values from the tailings.

Static AMD prediction tests, acid base accounting (ABA) and net acid generation (NAG), provided qualitative classification showing the sulfide-lean tailings to be non acid forming. However, the results carried high uncertainty and limited interpretation of the relative timescales of AMD generation processes. The development of a biokinetic test provided kinetic data relating the rates of acid generating and consuming reactions, in a microbial environment, and confirmed non acid forming status of the sulfide-lean tailings.

The kinetic tests also provided suitable leachate for the study of the environmental risk of metal mobility. Ranking elements with the use of a risk potential factor (RPF) highlighted that by removing sulfides, and thus removing the potential of acid
generation maintaining moderate pH, there is a general decrease in risk as mobility is reduced. However the results indicated that this is not necessarily the case for all elements, as shown for manganese.

The methods used in this project have outlined a generic assessment approach for desulphurisation following 4 steps: Tailings characterisation by mineral and elemental analysis, sulfide separation maximising value recovery and minimising environmental burden, AMD prediction and environmental risk assessment.

This work aids decision making in assessing waste management options for AMD mitigation through an integrated approach to design segregated, well characterised bulk tailings for disposal with minimal environmental burden, containing sulfides of significant AMD risk in a low volume stream which is more easily managed for AMD prevention. This provides scope on a case-by-case basis for value recovery as well as potential for waste recycling, reuse and by-products. The approach taken by this project is in line with the philosophies of the Minerals-to-Metals Research Initiative at the University of Cape Town as well as current research world-wide, and is significant in that it takes a new approach to conventional waste management, without presenting new technology.

Recommendations to continue this research include the refinement of the methods used, in particular the biokinetic test, and validation of the approach in a site specific case study. This will provide scope for the development of flowsheet options for sulfide separation, assessment of disposal options, as well as an economic feasibility study, comparing the cost of desulphurisation with conventional tailings management.
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GLOSSARY

List of abbreviations used in this work

ABA    Acid base accounting – static test method for determining AMD potential
AMD    Acid mine drainage, also known as acid rock drainage (ARD) or acidic metalliferrous drainage. These terms are generally used interchangeably; in this text AMD refers to contaminated acidic leachate from sulfide oxidation in mineral waste deposits.
ANC    Acid neutralising capacity
Fe(II) Ferrous iron – iron in 2\textsuperscript{nd} oxidation state
Fe(III) Ferric iron – iron in 3\textsuperscript{rd} oxidation state
Fe\textsuperscript{2+} Free ferrous ions in solution
Fe\textsuperscript{3+} Free ferric ions in solution
ICP-MS Inductively coupled plasma-mass spectrometry – Element analysis technique
K-NAG Kinetic net acid generation (see NAG)
MPA    Maximum potential acidity
NAF    Non acid forming
NAG    Net acid generation – a static test method for determining AMD potential
PAF    Potentially acid forming
ROM    Run-of-mine – high grade ore selected for beneficiation
RPF    Risk potential factor
S\textsubscript{T} Total sulfur
UC     Unclassified or uncertain
XRD    X-ray diffraction – Mineralogical analysis technique

Definitions of mineralogical terms

Chalcophilic Elements which form sulfide minerals
Lithophilic Elements which form oxide minerals, including silicates and carbonates
Porphyry Relatively low grade ore deposit with finely dispersed sulfide mineralisation
Chapter 1

INTRODUCTION

The mining industry produces large amounts of waste, typically accounting for 98% of total solids mined, some 52% of which is attributed to milled flotation tailings (Mitchell, 2000). Deposition of sulfidic mine waste frequently results in the generation of acid mine drainage (AMD). Increasing information on the impacts of AMD, increased water scarcity and public sensitivity to environmental issues surrounding mine wastes has resulted in tighter regulations on waste management and disposal. Hence, projects aimed at addressing AMD issues and challenges are increasingly important. Activities of organisations such as the International Council on Mining and Metals (www.icmm.com) and the International Network for Acid Prevention (www.inap.com.au), among others, are evidence of this.

This project focuses on the integrated management of sulfidic tailings, with a view to mitigating the associated AMD risks and liabilities effectively. Specifically, the focus is on removing of the risk of AMD formation from a tailings deposit, rather than simply managing the risk.

1.1. Background

The generation of AMD is caused by natural weathering of sulfide minerals liberated through mining operations. These minerals are commonly present as pyrite ($\text{FeS}_2$), pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), arsenopyrite ($\text{FeAsS}$) as well as other metal sulfides, in coal, base metal (most commonly Cu, Ni, Zn and Pb) and some gold deposits (Broadhurst et al., 2007). Figure 1 describes likely sources of AMD from gold and base metal sulfide ore beneficiation processes.

![Diagram of AMD generation](image)

Figure 1: Generic block flow diagram indicating sources of AMD from hard rock sulfide ore beneficiation (after Broadhurst, 2007)
Exposure of liberated sulfides in waste rock, tailings deposits and depleted leach heaps to moisture and atmospheric oxygen creates conditions supporting microbially catalysed oxidation, generating both ferric iron and acid as leaching agents. Acidification of the moist environment promotes further weathering and mobility of metal species previously locked within underground rock matrices.

Deportment of this acidic water by precipitation percolating through waste deposits can have negative impacts on surrounding environments with pollution plumes forming through contamination of groundwater and alluvial water systems. Acidic leachate also frequently contains elevated concentrations of toxic metal ions and soluble salts extending beyond the containment area (Broadhurst et al., 2007). An example of sulfate contamination from a tailings deposit is shown in Figure 2 (Duthie and Souster, 2008). This can affect agricultural land use in the surrounding area and impact drinking and sanitation water availability for surrounding communities, as well as causing ecotoxicological damage to local flora and fauna (Naiker et al., 2003).

The need to prevent contamination of natural resources, particularly water and soil, by AMD is now generally accepted. A number of techniques have been developed for and employed in the control of AMD over the past two to three decades (INAP, 2009; Blowes et al., 2005). Current commercial approaches focus mainly on deposition techniques for residues which increase chemical and physical stability to reduce AMD formation from the waste materials, or on treatment of AMD generated, or both. These approaches include subaqueous disposal, seals and covers, backfilling and active and passive remediation. The long-term impacts of current AMD management practices are not well understood and it is well recognised that the long term risk of AMD remains.
Remediation is a costly and difficult process requiring active management long after mine closure (Muguet et al., 2009; Potter et al., 2009; McCombe, 2009). Growing awareness of these shortcomings coupled with trends in modern industry towards sustainability has placed pressure on traditional mining practices to become proactive in complying with sustainable development and cleaner production principles (van Berkel, 2007). However, mines are still typically averse to process changes and new technologies. In particular, there is a need for new approaches in tailings management for the prevention of post-closure AMD impacts and risks in perpetuity, ideally through the removal of sulfides prior to disposal. This provides opportunities for integration of conventional unit operations and disposal methods simultaneously removing environmental risk and maximising resource recovery. Such an approach is consistent with the philosophy of the Minerals to Metals Research Initiative at the University of Cape Town, and is supported by recent research world-wide (Benzaazoua et al., 2008; Chan et al., 2008; McCallum and Bruckard, 2009).

1.2. Problem statement

Current practices in AMD mitigation from waste deposits, and in particular from flotation tailings, are of an “end-of-pipe” nature and are yet to be proven sufficient to prevent post-closure impacts and guarantee a walk-away status. Research is required to develop sulfide tailings management systems which remove the long-term risk of AMD generation such that the environmental burden is lifted.

1.3. Research objectives

The objective of this project is to explore the feasibility of an integrated approach for tailings management and AMD mitigation based on the removal of sulfide minerals prior to disposal. More specifically, this project aims to address the following research questions:

i. Is it possible to physically remove the sulfide components of tailings to ensure long-term AMD mitigation?

ii. Are current prediction techniques adequate in assessing the long-term AMD generating potential and subsequent environmental burden of desulfurised tailings?

iii. What information, procedures or tools are required in assessing and comparing alternative flowsheets for the integrated management of sulfide tailings to reduce the post-closure risks of AMD?

In answering these questions, this work aims to bring together understanding of concepts and knowledge in different areas of research relevant to the study of AMD mitigation, and in so-doing to assist the mining industry in their endeavours to more effectively manage large volume solid wastes.
1.4. Thesis structure

Chapter 1 introduces the project, gives background information in the development of the problem statement and project objectives and introduces the key research questions. Chapter 2 reviews relevant literature, based on the project background and research questions posed. Chapter 3 draws on the literature to develop the conceptual tailings management approach and research hypothesis and to direct the case study selection and scope. The empirical methodologies and results for the case study used to explore the research hypothesis are presented in Chapters 4 and 5 respectively. Finally, Chapter 6 concludes the study with a summary and discussion of key findings of the research. This chapter also highlights the significance and limitations of the project and makes recommendations for further work. This structure is outlined in Figure 3.

Figure 3: Schematic outline of the thesis structure
Chapter 2

LITERATURE REVIEW

In line with the key questions posed in Section 1.3, the literature review outlines the processes and factors contributing to AMD generation, environmental implications of AMD and preventative measures currently employed in industry. Techniques available for the prediction of AMD in assessment of environmental burden are also discussed.

2.1. AMD formation

2.1.1. AMD generation by sulfide oxidation

Acid mine drainage is caused by the microbially catalysed oxidation of sulfide minerals. Excavated sulfide material, typically pyrite (FeS$_2$), exposed to air and water is reactive with potential for generation of AMD. Two of the major residue sources of AMD are waste rock and tailings surface deposits from sulfide bearing ores mined either underground or in open pits. AMD generation from only these sources is discussed here, although the principles of generation apply to all sources of available sulfide.

The oxidation of metal sulfides, as illustrated for pyrite, follows the set of exothermic reactions outlined in Eq. 1 to 4 (Parker and Robertson, 1999; INAP, 2009). These reactions can occur either abiotically or biotically, however microbial activity mediates and greatly enhances the sulfide oxidation processes through the regeneration of aqueous ferric iron (Fe$^{3+}$) and acid as leach agents.

\[
\begin{align*}
\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \\
\text{FeS}_2 + 7\text{Fe}(\text{SO}_4)_3 + 8\text{H}_2\text{O} & \rightarrow 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \\
\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ 
\end{align*}
\]

Eq. 1

Eq. 2

Eq. 3

Eq. 4

Sulfide oxidation requires both water and oxygen (Eq. 1). Fe$^{3+}$ is well known to be a rapid oxidant or leach agent of sulfide minerals (INAP, 2009), as shown in Eq. 2. Ferric iron is generated by the oxidation of ferrous iron by Fe oxidising micro-organisms, requiring O$_2$ and CO$_2$. Sulfur oxidising micro-organisms are responsible for the generation of sulfate (SO$_4^{2-}$), also producing acid. Iron, which precipitates from the AMD solution as a ferric hydroxide giving the reddish rust colour associated with AMD, produces further acid as shown in Eq. 4. As the oxidation reactions are exothermic, through the life cycle of the deposit temperatures tend to rise and have been known to reach as high as 70°C in places (Lefebvre et al., 2001).
2.1.2. Factors influencing AMD formation

Factors which influence the kinetics of sulfide oxidation include microbial activity, temperature and pH, physical characteristics of the material and ferrous/ferric equilibrium. These are discussed extensively in literature (Johnston and Murray, 1997; Blowes et al., 2005; INAP, 2009) and are summarised below.

**Microbial activity**

At neutral to alkali pH pyrite oxidises chemically, but this reaction is slow. In the presence of acid, acidophilic micro-organisms mediate the oxidation of pyrite, oxidising Fe$^{2+}$ to Fe$^{3+}$, and oxidise intermediate sulfur compounds producing SO$_4^{2-}$, generating a highly acidic product. The roles of ferrous iron and sulfur oxidising micro-organisms are described in Figure 4.

![Figure 4: Schematic of pyrite oxidation by acidophilic bacteria; FOB: ferrous oxidising bacteria, SOB: sulfur oxidising bacteria (Bryan, 2006)](image)

Common ferrous iron-oxidising bacteria found in acid generating deposits include *Acidithiobacillus ferrooxidans*, *Leptospirillum ferriphilum* and *Leptospirillum ferrooxidans*. These live in similar habitats. *A. ferrooxidans* prefers slightly higher temperatures (optimum 35°C) and less extreme pH conditions, pH 1.0 to 3.5, with an optimum of 2 (Gould and Kapoor, 2003). *Acidithiobacillus thiooxidans* is the most common species responsible for the oxidation of S$^{2-}$ and S in the formation of H$_2$SO$_4$ (Parker and Robertson, 1999). It has similar optimal conditions to *A.* and *L. ferrooxidans*, at pH 0.5 to 4.0 and temperature range of 25 to 30°C (Gould and Kapoor, 2003). There are many other species present in typical mine residues. Details can be found in Gould and Kapoor (2003) and Bryan (2006).

One of the key factors in sustaining the oxidation of pyrite and other metal sulfides is the ferric to ferrous ion ratio. Ferric iron provides a catalyst for the oxidation reaction. Micro-organisms catalyse the conversion of ferrous to ferric iron and thus play an integral part in the process.
Climate and physical conditions
Climatic conditions, including temperature, rainfall and the nature of the surrounding area, have an important role in AMD formation. Figure 5 shows the movements of water through and around a residue deposit. The amounts of evaporation, run-off and water percolation are all affected by the climatic conditions in the area of the deposit.

![Figure 5: Hydrological flow through a mine residue deposit (Hansen, 2004)](image)

Hot, dry areas are noted for their high level of evaporation, affecting the saturation level within a deposit, especially in the upper reaches. Rainfall and further addition of slurries to the deposit reintroduces water, creating conditions for the generation of AMD. In areas of high rainfall, large quantities of water percolate through the deposits causing higher levels of leachate. The level of rainfall also affects the amount of run-off and erosion of deposits, affecting deposit covers. The characteristics of the surrounding area also play an important role. The soil or rock type on which a deposit is situated affects the rate of movement of leachate from the deposit to groundwater systems.

Air and water availability
As discussed above, water and O$_2$ are required for sulfide oxidation and O$_2$ and CO$_2$ are essential in sustaining microbial populations. Thus, air diffusion and water percolation within a deposit provide the conditions for acid generation. Lefebvre et al. (2001) conducted an extensive study on transport processes within waste rock deposits, highlighting the importance of gas diffusion and convection in sustaining AMD generating reactions. Garcia et al. (2005) confirmed through experimental work, the requirement for both air and water in the formation of acidic leachate from a pyrite-containing tailings dam.

Mineralogy and processing techniques
Both the mineralogy of the ore body and the processing techniques used in beneficiation influence the character of the waste deposit. Sulfide minerals present in a deposit, including pyrite (FeS$_2$), pyrrhotite (Fe$_{1-x}$S) and, to a lesser extent, trace
amounts of value-containing minerals, such as chalcopyrite (CuFeS$_2$) not recovered through concentration processes, are key minerals to which AMD is attributed (Broadhurst, 2007). Acid generation from sulfide oxidation can be counterbalanced by the presence of acid consuming gangue minerals within a deposit. These produce basic conditions in solution, thus acting as a buffer for acid produced through sulfide oxidation. Gangue minerals which are known to have neutralisation capacity include carbonates, aluminosilicates and oxyhydroxides (Blowes et al., 2003).

The nature and behaviour of the wastes is also influenced by the upstream processes of mineral beneficiation operations, including liberation (or comminution) and separation techniques. Apart from chemical composition, these processes dictate the particle size distribution and extent of liberation in waste deposits. In processes such as flotation, dependent on differences in hydrophobicity to separate minerals of value (Wills, 1997), particle sizes are required to be very small (generally below 150 µm) to increase value recovery. This liberates potentially acid generating minerals, increasing oxidation rates and thus the rate and extent of AMD generation. Reduced particle sizes also affect the multiphase flows within a deposit, reducing the permeability through a reduction of the void volume (Wu et al., 2007). Waste rock deposits with larger particles, although having a higher permeability, extend the time of potential risk through reduced liberation of sulfide minerals. An example of the effects of extent of liberation on contaminant deportment is shown in Figure 6 (Tran et al., 2003).

![Figure 6: Example of availability of cations for deportment from waste deposits based on particle size for tailings and waste rock (Tran et al., 2003)](image)

**Physical structure of tailings deposits**

The physical structure of tailings impoundments plays an important role in AMD as it can define the multiphase movements within a deposit, controlling the flow rates of air
and water. Clay or other impermeable layers within or under the deposit reduce leaching to ground water, whilst soil covers over the deposit prevent evaporation, air diffusion, or rainfall percolation. The way in which material is added to a deposit can also affect the potential for acid production, such as co-disposing waste rock and mill tailings to reduce permeability of air and water. These preventative measures are discussed further in Section 2.3.

Tailings dam failure can cause damage through mass movement of slurry as well as pollution through contamination of natural water systems. To prevent leaching through dam walls and provide security against dam failure, especially with the ever increasing size of tailings dams, adequate design and construction is required, taking into account factors such as hydrology, site location and construction materials. Operating procedures should focus on water management and adequate monitoring during the deposition of tailings aid in preventing failure (DME WA, 1999). The International Commission on Large Dams (ICOLD) now has a committee dealing with tailings dams and waste lagoons to provide a standard to which tailings impoundments should be constructed to ensure safety (Penman, 1999).

2.2. Environmental implications of AMD generation

Where acid is formed within waste deposits, it is transported by water flow through the deposit. This acidic leachate may be carried into surface and groundwater systems. The spread of leachate with groundwater movement in aquifers, or through soil systems, forms a pollution plume of acidic waters, containing high levels of sulfate and many other toxic products. This hydrodynamic movement and pollution plume generation is described simply in Figure 7, where contaminated leachate moves with natural water flows below the water table (see, for example, the sulfate contamination plume shown in Figure 2, Chapter 1).

![Figure 7: Movement of leachate and formation of pollution plume from a tailings deposit, after Broadhurst et al. (2007)](image)

The nature of groundwater movements can vary from site to site. In sites where groundwater velocities are low, a long lag time could exist between the onset of leachate and the first indications of contamination of groundwater. This slow
movement, coupled with relatively slow oxidation rates as discussed above, could also prolong the spread of acidic and contaminated water for hundreds of years after mine closure, making remediation complex (Broadhurst et al., 2007; Bryan, 2006; Blowes et al., 2005).

The acidic environment created by sulfide oxidation promotes the deportment of acid soluble and ion exchangeable metals from the stable, solid phase of minerals also liberated through the mining process. Table 1 gives some of the elements found within a complex porphyry-type ore which could pose an environmental threat. These are grouped based on their typical natural abundance.

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

<table>
<thead>
<tr>
<th>Mineral association</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major elements</td>
<td></td>
</tr>
<tr>
<td>Lithophilic*</td>
<td>Al, Mg, Ca, Na, K</td>
</tr>
<tr>
<td>Chalcophilic*</td>
<td>Cu, Fe, S</td>
</tr>
<tr>
<td>Minor elements</td>
<td></td>
</tr>
<tr>
<td>Lithophilic</td>
<td>Mn, Cr</td>
</tr>
<tr>
<td>Chalcophilic</td>
<td>Zn, Ni, Pb, Cd, Se</td>
</tr>
<tr>
<td>Trace elements</td>
<td></td>
</tr>
<tr>
<td>Chalcophilic</td>
<td>Co, As, Mo, Ag</td>
</tr>
</tbody>
</table>

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

Major lithophilic elements are commonly associated with silicate gangue minerals and are relatively abundant within the earth’s crust. They include the metals Mg, Ca, Na and K, which are salt forming in aqueous environments. Due to their relative abundance in the earth’s crust and presence in natural water bodies as necessary nutrients for flora and fauna, these are generally of lower risk. The minor elements listed make up both silicate and sulfide associated minerals, typically of lower natural abundance. However, in enriched ores these can be found in high concentrations and potentially pose environmental risk of contamination. Trace elements are generally associated with sulfide minerals. Although they are present in much smaller concentrations, the breakdown of sulfides in AMD generation can mobilise elements such as arsenic (As). Attenuation and solubilisation of As in acidic hydrodynamic flows can cause enrichment in mine water to toxic levels (Broadhurst, 2007).

Maluleke (2006) studied the reactivity of co-elements within a copper sulfide tailings under AMD conditions and showed that within weak acid systems significant amounts of major (Ca, Mn, Mg and Cu) and trace-minor metals (Cd, Co, Zn, Ni, Pb) may be mobilised and deported from a deposit. In stronger acidic environments there is the potential for further release, and thus bioavailability, of trace metals (As, Mo, Se) which would ordinarily be associated with secondary precipitates of oxidation products (Maluleke, 2006).
The release of these metals into natural water systems, lakes and rivers, can have detrimental effects on aquatic life through bioaccumulation of toxic metals to poisonous levels (Blowes et al., 2005). The concentrations of metals and sulfate, although aggravated by low pH conditions in mine water, are not necessarily limited to these conditions, as seen in the Ficklin plot in Figure 8 (INAP, 2009). This comprises global data across mine waters from all types of ore. In wetter areas, pollutant concentrations tend to be more diluted compared with drier climates, where reduced rainfall and evaporation can cause very acidic conditions with extremely high concentrations of metals and sulfate (Bryan et al., 2006). Some of the factors that govern the levels of contamination in leachate are shown on the plot.

Figure 8: Ficklin diagram showing sulfate concentrations in AMD environments (INAP, 2009)

The importance of the understanding and characterisation of trace metal contamination has been highlighted by a number of authors (Napier-Munn et al., 2008; Broadhurst, 2007; Warhurst and Noronha, 2000) and has been the focus of extensive research. Mineral waste deposits represent extremely complex systems of many elements. Some have severe environmental implications even at low concentrations and others place negligible burden even at relatively high concentrations. Adequate estimations of mobility and subsequent environmental risk are required so that focus can be placed on elements with greatest potential for environmental burden.

Broadhurst and Petrie (2010) describe a methodology for ranking elements identified to be deported through exposure to AMD conditions based on environmental significance. The use of a risk potential factor (RPF) allows comparison of the environmental risk posed by elements present in mine water by ranking them based on their natural abundance as well as their environmental threshold concentrations. Risk potential factors can aid in identifying the environmentally significant metals deporting from mineral waste deposits into the environment. This approach is used in this project and is described in Section 4.5.3.
2.3. AMD prevention

Poor understanding and management of mine waste deposits has led to widespread environmental degradation from acid mine drainage. The remediation of acidic and metal containing mine waters has become essential in areas which have had limited waste management and thus poor quality water, which in many cases, is evident in surrounding environments. Active treatment usually entails the collection and treatment of waters, neutralising pH and precipitating metals and salts. Although many improvements have been made in water treatment (Potter et al., 2009), it still lacks as a long-term solution, as mine wastes are known to produce acidic leachate long after mine closure (Bryan, 2006). Passive treatment is also used, including constructed wetlands for surface water treatment and permeable reactive barriers within aquifers for treatment of underground waterways. Although these biological systems can continue to operate successfully for years after mine closure, they require frequent monitoring and can fail under heavy contaminant loading or extreme pH levels (Blowes et al., 2005).

2.3.1. Conventional AMD prevention techniques

In order to avoid pollution from, and subsequent remediation of, AMD a number of preventative techniques have been developed which aim to manage AMD risk by controlling the conditions which lead to acid generation. Some of the conventionally used techniques are discussed here.

Seals and covers

Sealing layers under the site of a proposed dam can be laid below the deposit. Alternatively, a site can be chosen such that the underlying rock layers are of a non-permeable nature to prevent seepage to groundwater. Non-porous layers laid down can be clay-type soils, geopolymers or even plastic. The clay layers are more common owing to cost. Water which seeps from the tailings dam can thus be collected and treated. It is common to include a drainage layer for ease of water removal from the tailings (Martin et al., 2002).

Covers can also be laid over deposits, isolating potentially acid forming (PAF) material and reducing air and water flow. Several different top layers have been employed in the past. For example, sealing layers of impermeable clay soils are used to prevent infiltration of precipitation and surface water (Johnson and Hallberg, 2005) and saturated soil covers, comprising fine material with high water retention properties, are used to prevent air flux (Parent and Cabral, 2006). Erosion-preventing covers, comprising gravel-soil mixtures, are used to protect the contaminated tailings from future exposure. These barrier layers increase surface resistance and promote growth of vegetation to prevent erosion and percolation (Waugh et al., 1994). Covers with capillary barrier effect (CCBE) can also be employed. These are typically made up of multiple layers of clays, pebbles and sands, aimed at promoting surface water removal.
and vegetation growth whilst preventing air and water movements between sulfide waste material and the atmosphere (Gran et al., 2009; Johnston and Murray, 1997).

New approaches in order to improve cover efficiency and environmental performance are being investigated globally. Studies include work by Demers et al. (2008) who provide positive experimental results for the proposed use of sulfide-lean tailings as a protective physical barrier over potentially AMD generating tailings, integrating waste products as a cost effective waste management technique. Taylor et al. (2009) propose the use of alkali covers in order to passivate surface chemical oxidation within waste deposits. Although covers provide many advantages in preventing the physical and chemical processes which promote AMD formation and transport from deposits, the long-term effects are unknown and there is still potential for re-exposure through erosion in the future.

**Backfilling**

Backfilling provides an effective option for disposal, where tailings are disposed of in disused open-pit or underground workings, as an alternative to surface tailings impoundments. There are various types of backfill, including hydraulic, paste, rock and blended fill. These are described in more detail in literature (Engels & Dixon-Hardy, 2007; Dorricott and Grice, 2002). This review focuses on cemented paste backfilling (CPB) which has become a popular disposal method in recent years. In this process thickened tailings (typically 75-80 wt% solids) are mixed with a cementing binder before deposition in mine cavities, leaving a stable deposit of relatively high compressive strength.

CPB has several advantages as it removes the need for surface disposal as well as providing additional underground support in preventing subsidence and collapsing. It also provides opportunity for further value containing ore removal as the additional support from backfill removes the need for support columns. Most importantly, the potential for AMD production is greatly reduced as the binder acts to keep the saturation level of the deposit high, preventing oxidation of sulfide minerals (Dorricott and Grice, 2002).

There are disadvantages to backfilling, as the cementing does not allow further processing or reworking of the tailings without excavation or opportunities for remediation if AMD does occur. Short-term operating costs of backfilling are also higher than conventional surface disposal methods owing to binder costs and added transport of the material. Of particular concern with tailings of high sulfide content is the breakdown of backfill strength owing to the formation of expansive species, such as ettringite, through the reaction of sulfates with free calcium in the binder (Benzaazoua et al., 2004). Studies have been carried out testing the effects of high sulfide content on backfill strength (Fall and Benzaazoua, 2005). Positive results have been found in tailings of up to 12% sulfur, retaining unconfined compressive strength without sulfate
Another drawback is the economic and environmental cost of using cement products. Studies have shown that pulvurised fuel ash (PFA) exhibits pozzolanic properties when used in combination with CaOH binders, producing suitable fill material. This provides a suitable method of better environmental practice as well as reducing the waste generated from other industries (Chan et al., 2008).

The performance of backfilling is based on numerous factors, including particle size, mineralogy, tailings chemistry and pH, many of which are affected by the processing conditions, highlighting the need for integration between beneficiation and waste management in minerals processing (Dorricott and Grice, 2002; Benzaazoua et al., 2008; Chan et al., 2008).

**Blending and co-disposal**

Other techniques in tailings disposal include the use of blending or mixing of tailings and other waste products. One method of co-disposal is the mixing of fine tailings with coarser fractions. This has the advantage of reducing the permeability of the coarse waste rock, without the costs of additional treatment. The coarse fractions also provide physical stability to the fines deposits, reducing liabilities of dam failure caused by liquefaction in conventional tailings dams. Reduction in AMD potential is noted owing to the reduced air flow through co-disposed deposits, maintaining higher saturation levels and preventing oxidation. Benefits have been shown by various authors (Smith & Leduc, 2003; Wickland & Wilson, 2005; Wilson et al., 2009; Maddocks et al., 2009). Various methods for implementing co-disposal are available, including piping tailings into middle of waste rock dumps or layering waste rock and tailings.

The blending of acid consuming substances into potentially acid generating tailings aims to reduce the effects of sulfide oxidation (Johnson and Hallberg, 2004). These can include carbonate containing mine wastes, limestone and organic material which have high acid neutralising potential (Weber et al., 2004). Recent studies have shown that drawbacks of this method include ineffective neutralising due to channelling and the ultimate passivation of neutralisation potential. Researchers have offered alternative methods for in-situ neutralisation such as the use of alkali covers (Taylor et al., 2009).

Organic material can be used for the prevention and treatment of AMD. Blowes et al. (2003) propose mixing organic carbon into tailings deposits to create favourable conditions for the reduction of sulfide minerals in tailings, forming precipitates and thus reducing the generation of acid. Organic material can also be used in a barrier form to prevent migration of acid products out of dump sites. Challenges discussed include the method of inclusion of the organic material and its subsequent renewal as it must be placed below the phreatic surface in tailings to be productive.
2.3.2. Elimination of AMD potential by sulfide removal

The conventional methods for AMD prevention discussed above all deal with mitigation of AMD generation, without addressing the potential for AMD at its source (Mitchell, 2000). It has been identified by various authors (Cilliers, 2006; Napier-Munn et al., 2008) that in order to provide a long-term solution to AMD the potential for AMD generation must be addressed and eliminated. Research has shown that sulfide minerals in a waste deposit are responsible for the generation of AMD. Thus, the removal of sulfides removes the potential for AMD generation.

Selection of unit operations for sulfide removal

Sulfide removal can take place by reaction through (bio)leaching processes, producing liquid effluent streams which can be treated and managed in a reduced time-frame compared with those typical of AMD generation (Bryan, 2006), or by various physical separation processes, relying on differences in physical properties of species within a tailings stream (Wills, 1997). These can include gravity separation, magnetic separation, dense medium separation, screening, filtering and flotation, all common minerals processing techniques (Wills, 1997; McCallum and Bruckard, 2009). Flotation is a widely used process and is focus of this work. The importance of desulfurisation by flotation has been highlighted in studies by various authors over the last 15 years (Leppinen, 1997; Benzaazoua et al., 2008) with interest intensifying in recent years.

Conventional sulfide flotation

The process of flotation employs differences in physico-chemical mineral surface properties for the selective separation of specific minerals in a slurried ore, which is sparged with air to provide a gas-liquid interface. The use of organic chemicals, known as collectors, to enhance the hydrophobicity of mineral surfaces allows particles to attach to air bubbles within a flotation cell and be transported to the froth phase and thus concentrated, as explained in Figure 9.

![Figure 9: Schematic diagram describing flotation in a batch flotation cell](image-url)

Particles must be relatively small, for adhesive forces to carry a particle and frothers are used to give strength to air bubbles such that they can support mineral attachment in the froth (Wills, 1997). Various properties of the pulp, such as pH and redox potential, influence mineral surface properties and collector efficiency.
Chapter 2  

Flotation is commonly used for sulfide mineral separation and the recovery of pyrite is a well-known process. Collectors most commonly used for sulfide flotation are bivalent sulfur-based (sulphydryl) anionic chemicals, such as xanthates and dithiophosphates, which have good collection power and offer high selectivity towards sulfide minerals.

The slurry pH plays an important role in flotation as it affects the electrochemical properties of, and thus the collector adsorption onto, mineral surfaces (Laskowski, 2008; Wills, 1997). For specific collectors a critical pH exists which controls the collection of minerals. Critical pH characteristics are used to depress certain minerals for selectivity of a desired product, and can be used in flotation control. This is shown in Figure 10 for a dithiophosphate collector, which indicates that at higher pH values (pH > 9) chalcopyrite is floated selectively. However, a decrease in pH increases the floatability of other sulfide species, including pyrite.

![Figure 10: Example of pH effects on dithiophosphate collector concentration in flotation (Wills, 1997)](image)

Flotation has been used in the past to recover high purity pyrite successfully using standard copper flotation systems (US EPA, 1993; Broekman and Penman, 1991). These processes were designed for economic gain and only run when a market for pyrite existed. Although the environmental benefit was considered, this was not the primary focus. These processes do provide a precursor to flotation desulfurisation providing the technical feasibility of such a process without large capital investment.

The use of flotation for tailings desulfurisation

The extensive knowledge in industry of the processes of sulfide and, in particular, pyrite flotation can be used in implementing flotation as a technique for environmental desulfurisation. Various authors have studied the use of flotation for the desulfurisation of tailings, covering a wide range of different sulfide ores, including base metal porphyry, massive sulfide and gold and silver bearing sulfide ores. A summary of various desulfurisation tests is given in Table 2, showing the sulfur content and subsequent AMD potential, shown as net acid production potential (NAPP), recoveries achieved through experimentation and the type of collector used.
Table 2: Summary of literature results of desulphurisation by flotation

<table>
<thead>
<tr>
<th>Ore type by target values</th>
<th>Sr (wt%)</th>
<th>NAPP (kg H₂SO₄/ton)</th>
<th>Removal of S (%)</th>
<th>Collector type</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu, Au Ni, Au, Cu Ag, Zn, Pb</td>
<td>3.37</td>
<td>9.08</td>
<td>0.29</td>
<td>1.44</td>
<td>*n. a.</td>
<td>Xanthate</td>
</tr>
<tr>
<td>Au</td>
<td>2.3 - 3.7</td>
<td>51 - 98</td>
<td>89</td>
<td>*n. a.</td>
<td>Amine</td>
<td>Integrated waste management</td>
</tr>
<tr>
<td>Zn, Cu</td>
<td>5</td>
<td>9.38</td>
<td>146</td>
<td>280</td>
<td>90</td>
<td>91</td>
</tr>
<tr>
<td>Au, Cu</td>
<td>2.89</td>
<td>3.4</td>
<td>-43</td>
<td>77</td>
<td>90</td>
<td>Xanthate</td>
</tr>
<tr>
<td>Zn, Cu, Ag, Cu, Cu, Ag, Au</td>
<td>16.2</td>
<td>24.2</td>
<td>366</td>
<td>632</td>
<td>95</td>
<td>96</td>
</tr>
<tr>
<td>Cu, Zn</td>
<td>4 - 8</td>
<td>n. a.</td>
<td>n. a.</td>
<td>Xanthate</td>
<td>Reduced S. Value recovery of Cu, Zn, Ag and Au.</td>
<td>Leppinen et al. (1997)</td>
</tr>
</tbody>
</table>

*n. a. – results not available

Table 2 shows sulfur removal efficiency for a wide range of sulfide tailings with sulfur content as high as 24% in some cases. AMD potential varied from acid consuming (NAPP of -43 in kg H₂SO₄/ton) to highly acid forming (NAPP 588-632 kg H₂SO₄/ton). Sulfur removal ranged from 79% to 96% across literature sources and qualitative results indicated low residual sulfur in desulphurised tailings thus reducing AMD potential, shown by AMD prediction tests. These data give an indication of the applicability of flotation desulphurisation across ore types of vastly differing mineralogy and quality.

Site specific optimisation studies, such as the work by Benzaazoua and Kongolo (2003), which investigated operating conditions and reagent use for desulphurisation provide insight for processing ores of similar characteristics. In general, the use of sulfydryl collectors has been shown to be effective, in particular the use of xanthate collectors. They are also cost effective compared with other reagents (Benzaazoua and Kongolo, 2003). The use of amine collectors has been successful at pilot scale for gold bearing ores which are processed with cyanidation as cyanide is known to inhibit xanthate efficacy (Benzaazoua et al., 2008). Collectors are not necessarily the major expense in terms of reagents and assessment of a process should consider requirements of all reagents such as pH regulators and activators (Wills, 1997).

Leppinen et al. (1997) showed that desulphurisation, as well as producing tailings with negative NAPP values, provided opportunities for additional recovery of values of Cu and Zn, as well as minor Ag and Au, in their study. This has been reiterated in recent work by McCallum and Bruckard (2009) through the development of a methodology for assessing options for benign tailings production, the diagnostic separation of sulfide tailings (DSST). This work highlights opportunities for the production of benign tailings as well as by-products through various unit operations, including flotation.
Bois et al. (2004) conducted cost estimations for desulfurisation in a conceptual process. Their study used recently published data for a range of typical processing and disposal scenarios and compared the estimated costs of desulfurisation with conventional tailings management techniques. The results are shown in Figure 11. Considering that the use of covers (CCBE) does not remove potential long-term risk and underwater disposal displays poor water management especially in arid or semi-arid regions, as well as posing geotechnical risks, the authors have shown that desulfurisation provides a comparable alternative. Difficulties in assessing and evaluating novel strategies in waste management have been highlighted (Cilliers, 2006) owing to limitations and difficulties in the assessment of the actual cost of long-term tailings management across a broad spectrum of sites employing different techniques in waste management (Mitchell, 2000).

Figure 11: Comparison of cost estimations of desulfurisation compared with other AMD prevention methods (Bois et al., 2004)

Separated tailings fractions have provided researchers with opportunities to investigate disposal options. Integration of desulfurisation with paste backfill of high sulfide tailings has been researched for tailings from gold processing (Benzaazoua et al., 2008). This research found that a sulfide-rich tailings fraction can be successfully backfilled, with the sulfide content increasing backfill strength in some cases. A parallel study proposed the use of the sulfide lean fraction as a cover material for existing waste with AMD potential (Demers, 2008). These studies highlight the potential for desulfurisation as a feasible management alternative and the value of integration of waste management alternatives in AMD mitigation. The integration of mine closure planning through the life of the mine allows for the provision of the costs of closure whilst cash flows in the operation are high, rather than accepting the burden of post closure waste management costs after income from mining activities has ceased (Warhurst and Noronha, 2000).

The positive findings across a wide range of tailings characteristics highlight the efficacy of flotation as a feasible method of desulfurisation to provide benign tailings of low AMD risk. Flotation desulfurisation presents opportunities to increase value recovery as well as explore disposal options which minimise environmental burden.
2.4. Techniques for determining AMD generation potential

Prediction of the acid generating potential of a tailings or waste rock deposit is vital for the effective management or treatment of mine wastes. Within a deposit containing sulfide minerals which are potentially acid generating (PAG), there is also the possibility that minerals are present which consume acid generated. The dissolution of acid consuming minerals, such as carbonates, oxyhydroxides and alumino-silicates, present in the deposit can neutralise acidic conditions (Blowes et al., 2003). Understanding the mineralogy of sample and the interactions between the soluble phases is key in aiding prediction of the potential for AMD generation.

A selection of methods used to determine the potential for a deposit to produce or consume acid are reviewed below. These include the accelerated chemical tests, acid base accounting and net acid generation, as well as long-term kinetic tests, which take into account relative weathering rates. The use of medium-term microbial tests is also reviewed.

2.4.1. Acid base accounting

Acid base accounting (ABA) tests provide worst case scenario predictions for AMD generation as a balance between acid generation and acid neutralisation. The net amount of acid produced by a mine residue, or the net acid production potential (NAPP) can be calculated as the difference in the maximum potential acidity (MPA) and acid neutralisation capacity (ANC), measured as an equivalent kg of $\text{H}_2\text{SO}_4$ produced per ton, or kg $\text{CaCO}_3$ by some authors (Smart et al., 2002):

$$\text{NAPP} = \text{MPA} - \text{ANC} \quad \text{Eq. 5}$$

MPA is calculated based on the total sulfur assay. It is assumed that all the sulfur in the sample is in a form available for acid production, such as pyrite or pyrrhotite. This assumption can cause an over-estimation of NAPP without adequate sulfur speciation if sulfur is also present as sulfate, native sulfur, or lesser acid producing sulfides (such as galena).

There are a number of accepted tests for ANC. The original ANC test was developed by Sobek et al. (1978). The acid neutralisation capacity is found by back titration after reacting the sample with HCl to dissolve available acid consuming minerals, such as carbonates. Different methods for conducting ANC tests, such as the Skousen siderite correction test (Stewart et al., 2006), have been developed to better represent the natural environment. The Skousen method includes the addition of hydrogen peroxide ($\text{H}_2\text{O}_2$) to oxidise aqueous $\text{Fe}^{2+}$, providing a more accurate measure of neutralisation capacity (Stewart et al., 2006; Maluleke, 2006). This is required since some carbonate minerals, although acid buffering when reacted, produce further acid on hydrolysis and precipitation of metal ions (Fe, Mn, Al) in an oxidising environment. The following reactions (Eq. 6-8) for siderite ($\text{FeCO}_3$) aid in explanation.
In standard Sobek ANC tests on a siderite containing sample, a dark green Fe$^{2+}$ precipitate forms, indicating the dissolution of the FeCO$_3$ mineral (Eq. 6) and thus buffering of acid. However, in natural AMD systems the oxidation of Fe(II) by microorganisms (Eq. 7) is inevitable and thus on precipitation of Fe(III), acid is re-released (Eq. 8), with no overall acid consumption. Thus in the siderite correction tests, oxidation of Fe$^{2+}$ by H$_2$O$_2$ better represents a natural system.

These tests are quick to carry out, inexpensive and provide a preliminary prediction for potential to generate acid. However, they do have limitations in prediction. The MPA does not account for sulfur speciation which could lead to an over-estimation of acid potential. The ANC does not take into account relative reactivity of acid consumption, nor provide comparison with kinetics or lags in acid generation. It is recommended that a combination of tests is used for better prediction (Smart et al., 2002; Stewart et al., 2006).

2.4.2. Net acid generation tests

Net acid generation (NAG) tests are designed to mimic natural chemical processes by accelerating the weathering of acid forming sulfide minerals and allowing the acid consuming and producing reactions to take place simultaneously. Acid is produced by oxidising available sulfur species with H$_2$O$_2$ following Eq. 9.

$$\text{FeS}_2 + \frac{15}{2}\text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ + 4\text{H}_2\text{O}$$  Eq. 9

Back titration of the liquor produced to pH 4.5 accounts for H$_2$SO$_4$ generated from sulfide oxidation. Acid buffering between pH 4.5 and 7 accounts for acidity from the hydrolysis and precipitation of divalent metal ions, such as Cu$^{2+}$ and Zn$^{2+}$, in accordance with Eq. 10.

$$\text{Me}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Me(OH)}_{2(s)}$$  Eq. 10

Results are shown in two ways: the final pH of the oxidised sample (NAG pH), giving an indication of the state of the final product; and as an equivalent mass of sulfuric acid produced per ton of ore (kg H$_2$SO$_4$/ton) at pH 4.5 and pH 7 (Maluleke, 2006; Stewart et al., 2006).

The kinetic net acid generation (KNAG) test, an extension of the static NAG test, aims to assess the kinetics of sulfide oxidation by continuous monitoring of temperature and pH, providing a profile of relative reactivity of the accelerated oxidation of the sample.
2.4.3. Interpretation of the static test results

Classification of samples based on the results of these tests is not necessarily an exact prediction. However, it does give guidelines for AMD generation and aids in sample comparison. Table 3 gives AMD classifications for the ABA and NAG tests. Combining results of the acid base account and net acid generation tests can provide a clearer picture of the AMD potential of a waste sample.

Table 3: Guidelines for classification in AMD tests (Broadhurst et al., 2007; Stewart et al., 2006)

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
<th>Units</th>
<th>Classification guideline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Base Account</td>
<td>NAPP &gt; 20</td>
<td>kg $\text{H}_2\text{SO}_4$/ton</td>
<td>Acid forming&lt;br&gt;Potentially acid forming (PAF)&lt;br&gt;Non acid forming (NAF)</td>
</tr>
<tr>
<td></td>
<td>-20 &lt; NAPP &lt; 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NAPP &lt; -20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Acid Generation</td>
<td>NAG pH &lt; 4.5 &amp; NAG$_{\text{pH}}&gt;10$</td>
<td>kg $\text{H}_2\text{SO}_4$/ton</td>
<td>Acid Forming&lt;br&gt;Potentially acid forming (PAF)&lt;br&gt;Non acid forming (NAF)</td>
</tr>
<tr>
<td></td>
<td>NAG pH &gt; 4.5 &amp; NAG$_{\text{pH}}$=5-10</td>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>Kinetic NAG</td>
<td>Temp peak lag &gt; 3hrs</td>
<td></td>
<td>PAF with slow reaction kinetics</td>
</tr>
<tr>
<td></td>
<td>Temp peak lag &lt; 15 min</td>
<td></td>
<td>PAF with fast reaction kinetics</td>
</tr>
<tr>
<td>Combined static tests</td>
<td>NAG pH &lt; 4.5 and NAPP &gt; 0</td>
<td></td>
<td>Potentially acid forming (PAF)&lt;br&gt;Non acid forming (NAF)</td>
</tr>
<tr>
<td>(Figure 12)</td>
<td>NAG pH &gt; 4.5 and NAPP &lt; 0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

Smart et al. (2002) propose the use of a geochemical classification plot combining the results of the ABA and NAG tests for AMD classification. An example is shown in Figure 12, displaying the regions of AMD classifications as outlined in Table 3 for combined tests. Liao et al. (2007) also propose a classification based on graphical display of NAG results, putting results into categories, based on their potential for AMD generation.

![Figure 12: Example of the AMD classification plot describing regions of classification (after Stewart et al., 2006)](image)

Other tests exist to enhance the predictability and interpretation such as the generation of acid buffering characteristic curves (ABCC), which are used to give an indication of reactivity and rates of dissolution of acid consuming species, enhancing ANC.
prediction (Stewart et al., 2006). Although these tests give in depth information relating to gangue geochemistry, they fail to relate rates of acid consumption with those of generation. These limitations of relative rate information, as well as not taking into account microbial interactions, put static chemical tests at a disadvantage.

2.4.4. Kinetic chemical tests

In order to enhance the findings of static prediction tests and address some of the shortcomings of these tests, various kinetic tests are available. These tests give the opportunity to study the various dynamic factors which influence AMD generation, including weathering cycles, dissolution lag times, microbial activity and the relative reactivity of minerals within a sample. They range from bench scale shake flask tests to large scale physical dumps (INAP, 2009; Blowes et al., 2005; Villeneuve et al., 2009; Hornberger and Brady, 1998).

The two most common laboratory tests are the humidity cell test and leach column test, both of which provide long-term dynamic weathering data. Humidity cell tests follow standard procedures (ASTM D5744-96) subjecting samples to wet and dry tests in aerated conditions (INAP, 2009). Leach column tests do not have standard procedures, but are typically carried out on a larger scale, designed to test a variety of factors in long-term AMD generation and contaminant mobility (INAP, 2009; Smart et al., 2002).

Although many long-term kinetic tests have been developed over the last 50 years (INAP, 2009), there are still varieties in apparatus used as well as a lack of standard test procedures. This makes the interpretation and meaningful comparison of results difficult between studies of differing ore bodies or waste samples (INAP, 2009; Villeneuve et al., 2009; Hornberger and Brady, 1998). Kinetic tests also typically take an extended time period of months to years to produce significant results, if at all (Brown et al., 2009; Villeneuve et al., 2009). They can thus be expensive compared with quick static tests and are known to be unreliable in quantitatively simulating actual AMD processes, owing, in part, to the physical constraints of testing equipment. It is thus advised in literature that tests are run in conjunction with static tests and designed with specific objectives in mind to produce significant results (Blowes et al., 2005; Hornberger and Brady, 1998).

2.4.5. Microbial prediction tests

Many of the problems highlighted in the use of current static and kinetic tests can potentially be addressed through the use of standardised biohydrometallurgical tests. Shake flask tests are commonly used in bioleaching studies to test microbial efficiency under sulfide oxidising conditions. They also provide opportunities to study trace-minor co-metal deportment under a leach environment (Bryan et al., 2006). The processes which govern the formation of AMD are the same as those which control the leaching of sulfide minerals for value recovery, as discussed in Section 2.1. Therefore, AMD can
be studied with methods similar to those which have shown success in microbial leaching lab experiments. Shake flask tests give insight into the efficiency of microbial colonies under controlled conditions, are able to give microbial oxidation and leaching rates as well as element dissolution and mobility rates. However, they are not commonly used in AMD prediction.

Microbial oxidation tests have been proposed previously for prediction of AMD generation potential. In the British Columbia Research Confirmation Test Acidithiobacillus ferrooxidans is added to an acid stabilised (pH 2.5) suspension of 15-30 g mineral sample of size 200 μm and incubated at 35°C. The pH is maintained below pH 2.8 for the first three days to allow for microbial adaptation whereafter additional sample of half the initial mass is added. The solution pH is tested regularly. If it increases 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 may be acid forming. Issues arising from literature have been highlighted, mainly around the acidification of samples to the ideal conditions for microbial activity as well as inconsistencies in microbiology. This tends to give an over-estimation of final acidity, and removes the opportunity to study initial AMD generation at natural pH ranges (Bruynesteyn and Hackl, 1984). Although these tests take into account the microbial influence of AMD, they fail to give significant insight into relative reaction rates and the results are viewed in a manner equivalent to static tests, not making use of kinetic data nor metal deportment, limiting the application of these tests in supporting the findings chemical tests in AMD prediction.

2.5. Summary of the literature review

This literature review has highlighted the scale of the problem of acid mine drainage from flotation tailings and the shortcomings associated with conventional tailings management approaches and techniques. The review has shown that options do exist for the integration of waste management through the use of desulfurisation which guarantees a walk-away status. The advantages of using flotation as a feasible method of desulfurisation of tailings have been highlighted, providing opportunities to effectively remove AMD potential from sulfide tailings. Although the use of desulfurisation enables waste management to move towards a sustainable approach to tailings with a long-term view, this does require careful planning and a good understanding of all aspects of a particular operation. AMD prediction is possible through the use of static laboratory test methods. However, the resultant data is limited to first order predictions, providing a need for improved kinetic tests for quantitative prediction. In order to gain an accurate picture of long-term AMD potential the use of a combined suite of tests is recommended and should draw on the wealth of knowledge generated through heap bioleaching research. The information gathered in this review has been used in developing a research hypothesis and approach, outlined in Chapter 3, in order to address the research objectives outlined in the introduction.
Chapter 3

DEVELOPING THE HYPOTHESIS AND SCOPE

3.1. A conceptual approach to integrated tailings management

Current methods for preventing AMD formation are effective in the short term, but they do not remove the potential for acid generation in perpetuity by the fact that the sulfide minerals responsible for AMD potential are still present in tailings deposits.

In order to adhere to the fundamental principles of pollution prevention, as outlined in literature (INAP, 2009), processes should be planned and designed systematically such that pollution is addressed at or as close as possible to its source within a process. Identifying the source of AMD generating components within a minerals beneficiation process can be aided through classification of individual minerals within a waste stream based on their role in AMD generation. Benign or “passive” minerals are those which may add to the overall volume of a tailings stream but do not require additional treatment in disposal in order to prevent environmental burden. “Active” components, on the other hand, do require additional processing or resources to prevent AMD generation, based on the proposed classification by Cilliers (2006).

The active components in the case of sulfide tailings are the sulfide minerals themselves. The two main sources of sulfide in tailings are non-valuable minerals, such as pyrite, and valuable sulfides which are not recovered in the beneficiation process (Napier-Munn et al., 2008). These sulfides typically make up a relatively small component of the total mass of tailings, but their inclusion means that large volumes of waste require attention to prevent the long-term potential for AMD generation. However, by removing these sulfide minerals from the tailings, they can be contained or treated separately in a smaller and thus more easily managed volume.

Cilliers (2006) proposes an additional desulfurisation step to the beneficiation chain which includes the conventional tailings stream in the process, viewing it as an intermediate product rather than a waste. As such it can be optimised to produce benign tailings, thus removing the long-term potential for AMD generation. This is shown in Figure 13.

![Figure 13: Proposal for separation of sulfides and benign tailings (after Cilliers, 2006)](image-url)
Literature has outlined various techniques for sulfide removal currently employed in industry, as discussed in Section 2.3.2, which can be used within an integrated strategy for AMD mitigation (Wills, 1997; McCallum and Bruckard, 2009). Froth flotation, in particular, has been highlighted as an effective separation method for the removal of potentially AMD generating sulfide minerals, producing sulfide-lean tailings. Flotation is particularly feasible in processes which already employ flotation for mineral beneficiation. This highlights the potential for operators in minerals processing to incorporate sustainable waste management strategies without relying on novel technologies.

The classification of tailings streams into sulfide-rich and sulfide-lean fractions provides opportunities to assess potential resources for reuse, by-products and alternatives for safe disposal, in keeping with the proposed principles for mineral waste management, where deposits are stable, inert and contained, providing environmental security in perpetuity (Franks et al., 2009). Various authors have discussed the importance of integrating waste management into beneficiation processes to reduce the long-term impacts of AMD through proper planning for mine closure (Dhar, 2000; Warhurst and Noronha, 2000; Bezuidenhout, 2007; Napier-Munn et al., 2008). Combining the concepts discussed above, a conceptual approach for the integration of flotation desulfurisation into a generic base metal beneficiation process has been developed and is described in Error! Reference source not found. (page 26). It outlines waste management options for reduced environmental risk, employing conventional methods for disposal discussed in the literature review (Section 2.3). This approach is summarised in Hesketh et al. (2010).

Downstream options for a sulfide enriched stream include potential uses in hydrometallurgy, through the production of sulfuric acid, or as a source of ferric iron to accelerate heap leaching operations or accelerated AMD control in waste rock. This is currently under investigation by a concurrent project at UCT (Harrison et al., 2010). This stream offers opportunities for increased value recovery through the concentration of trace components in this low volume stream as demonstrated by McCallum and Bruckard (2009). Studies have also shown the potential for backfilling high sulfide tailings, both increasing backfill strength and decreasing sulfide oxidation potential (Benzaazoua et al., 2008). Backfilling requires the production of paste, created by thickening tailings and thus encourages the recycling of process water. It also requires a binder for cementation which provides opportunities for integration of other industrial wastes, such as pulverised fuel ash (PFA) known for its cementing properties, as described by Chan et al. (2009).

The production of benign tailings, as well as producing waste with a greatly reduced potential for AMD generation, offers further opportunities, including the recovery of water through thickening. The co-disposal of benign tailings with waste rock as a cemented paste rock can aid in reducing the AMD potential by reducing permeation of
Figure 14: Conceptual flowsheet describing the integration of desulfurisation and disposal options into a generic base metal beneficiation process
water and air into waste deposits (Wickland and Wilson, 2005). It can also provide cover material used in prevention of AMD from existing tailings or waste rock deposits (Demers et al., 2008). In the absence of better alternatives, this waste can be disposed of in conventional tailings deposits without the threat of AMD generation. The success of downstream disposal methods is highly dependent on site and on process specific criteria. This highlights the need to integrate mineral processing operations and subsequent mineral waste disposal for maximum environmental benefit.

Although it is important to consider options for disposal or reuse of mineral wastes, the key driver for this project is the production of sulfide-lean tailings with negligible environmental burden, providing reduced capacity for AMD generation over the long-term. To achieve the aims of benign tailings, adequate assessment of environmental risk is required. Literature has outlined the importance of characterisation to quantify long-term environmental risk of mineral waste deposits, both through effective prediction of AMD generation potential (see discussions in Section 2.4) and the subsequent environmental burden of acidic and metal-contaminated leachate (Section 2.2). Limitations of current AMD prediction techniques motivate the need for kinetic tests to provide a reliable and realistic measure of long-term acid generating potential, to quantify the reduction in environmental risk of sulfide-lean tailings.

3.2. Statement of the hypotheses

In line with the proposed approach outlined in Section 3.1 above and the outcomes of the literature review in Chapter 2, the following hypotheses are put forward:

i. The long-term AMD risks associated with sulfide tailings can be effectively prevented by removing sulfides prior to disposal using flotation techniques.

ii. The combined application of both laboratory-scale static and biokinetic prediction methods is required to provide adequate assessment of the long-term benefits of flotation desulfurisation in mitigating AMD related environmental risk.

3.3. Research approach and scope

The approach taken by this project aims to fulfil the overlying objectives by providing experimental results to support the hypotheses outlined above. A case study on typical porphyry-type sulfide tailings from a major North American copper processing operation has been conducted. Porphyry deposits make up a large proportion of base metal sulfide ores world wide, accounting for ½ the world’s mine production and 93% of the US mined copper production (Broadhurst et al, 2007). Previous studies at the University of Cape Town (Broadhurst et al, 2007; Maluleke, 2006) have, furthermore, shown that flotation tailings from this particular operation are acid generating with high pyrite content (~7%).
The case study aimed to achieve three objectives:

i. To assess the technical feasibility of conventional flotation desulfurisation to effectively remove sulfide from porphyry copper sulfide tailings through laboratory experiments in flotation.

ii. To assess techniques for AMD prediction through comparison of standard static tests and the development of a microbial kinetic test to evaluate and compare the acid generating characteristics of the desulfurised tailings.

iii. To address the environmental implications of desulfurisation by focussing on both AMD generation potential and metal deportment in acidic leach conditions.

These objectives aim to fulfil the overarching objective of the project in assessing the tools and criteria required to effectively implement waste management for long-term AMD mitigation by sulfide removal. The site specific nature of mineral beneficiation operations requires that individual processes must be assessed independently. As this study is not linked to a particular operational site, it does not attempt to optimise the desulfurisation process, nor does it entail a detailed evaluation of options for the downstream management of the separated tailings fraction. Rather, the aim is to provide a proof of concept, in line with the approach outlined in Error! Reference source not found., as well as a set of generic tools and criteria that can be used in the evaluation of desulfurisation approaches for a variety of site-specific case studies. In addition it should be noted that without experimental optimisation or detailed process considerations, an economic assessment of the process would not be meaningful and thus is considered to be beyond the scope of the project.
Chapter 4

EXPERIMENTAL METHODS AND MATERIALS

The experimental work for this case study was divided into 4 main tasks, as described in Figure 15. Firstly, the sample was characterised, described and compared with typical tailings. Experiments in desulfurisation were conducted using bulk sulfide flotation and sequential flotation tests. AMD prediction methods were conducted by static and kinetic methods. Finally, the environmental risk of desulfurised tailings was assessed, through analysis of co-element deportment in flotation as well as element mobility in the kinetic leach tests.

![Figure 15: Schematic approach to experimental methodology](image)

This chapter describes the tailings sample selected for the case study and includes descriptions of experiments and procedures used in the completion of the case study. Details of all experimental methodologies can be found in the Appendices.

4.1. Tailings sample characterisation

4.1.1. Description of sample used in this study

The sample selected for this study, is a ROM ore sample, however it is of low grade and has chemical and mineralogical characteristics in line with the typical characteristics of porphyry tailings (Broadhurst, 2007). In this work it is described as conventional tailings and provides the feed material for flotation desulfurisation. The samples were collected from a porphyry copper sulfide ore deposit where flotation is used for mineral concentration. The samples have a total sulfur ($S_T$) content of
3.84 ±0.35% and Cu grade of 0.16 ±0.04% by mass. Semi-quantitative XRD (Appendix A 1.2) indicated pyrite (FeS$_2$) and chalcopyrite (CuFeS$_2$) as major sulfide minerals and calcite (CaCO$_3$) as the major carbonate. Siderite (FeCO$_3$) is typically associated with porphyry-type ores (Broadhurst et al., 2007) and was noted by the presence of readily soluble Fe$^{2+}$ in preliminary ANC tests. Silicate minerals make up the majority of the gangue, dominated by quartz (64%), and to a lesser extent, phyllosilicates such as biotite and chlorite (12%). Table 4 details the sulfide mineral analysis of the sample and compares it with typical ore characteristics from literature (Broadhurst, 2007). Mineral grades are calculated on the assumption that all copper and sulfur are present as sulfides, based on the XRD analysis (Appendix A 1.2). This sample has significant sulfide content, mostly occurring as pyrite. This sample also has a small component of value mineral (0.47% chalcopyrite).

Table 4: Sulfide mineral characteristics of porphyry-type copper ore

<table>
<thead>
<tr>
<th></th>
<th>Typical porphyry tailings analysis (%)</th>
<th>Analysis of samples used in this study (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (LECO)</td>
<td>2 – 11</td>
<td>3.84 ± 0.35</td>
</tr>
<tr>
<td>Cu (AAS)</td>
<td>0.08 – 0.15</td>
<td>0.16 ± 0.04</td>
</tr>
<tr>
<td>Fe (AAS)</td>
<td>1 – 10</td>
<td>8.07 ± 1.43</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.23 – 0.43</td>
<td>0.47 ± 0.12</td>
</tr>
<tr>
<td>Pyrite</td>
<td>2 – 18</td>
<td>7.03 ± 0.69</td>
</tr>
</tbody>
</table>

*(Broadhurst, 2007)*

Literature has highlighted the importance of characterisation of environmentally significant elements within tailings. Identification of a range of elements which could be of environmental burden was achieved through ICP-MS analysis on acid digested samples. The findings are shown in Table 5. Results were compared with predicted ranges for porphyry tailings (Broadhurst et al., 2007) and enrichment relative to the average crustal abundance was calculated based on data published by Broadhurst and Petrie (2010).

The major elements analysed were largely consistent with literature predictions. Ca showed no significant enrichment relative to crustal abundance. Al was found to be below the predicted range and, as with Mg, concentrations were lower than natural occurrence. Although Manganese (Mn) is typically presented as a minor to moderately abundant lithophiilic element, it exhibited significant enrichment (ratio of 2.2). It was thus grouped with the major metals. Minor metals Cr and Ni showed higher concentrations than predicted ranges, reflected in the enrichment ratios of 1.7 and 3.3 respectively. Apart from cobalt (Co) which had low relative abundance, metal analysis indicated significant enrichment (ratios of 4.6 to 38) of all the trace chalcophile elements analysed, including As, Mo and Cd, which are commonly associated with sulfide minerals. Trace elements were all within predicted ranges for porphyry tailings.
Table 5: Total metal analysis by ICP-MS of co-elements in the porphyry-type tailings sample

<table>
<thead>
<tr>
<th></th>
<th>Literature* (mg/kg)</th>
<th>Total metal concentration in sample (mg/kg)</th>
<th>Enrichment ratio#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;1000 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>4000 – 45000</td>
<td>38949 ±253</td>
<td>1.1</td>
</tr>
<tr>
<td>Al</td>
<td>40000 – 100000</td>
<td>8891 ±1233</td>
<td>0.1</td>
</tr>
<tr>
<td>Mg</td>
<td>2000 – 26000</td>
<td>7174 ±63.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Mn</td>
<td>100 – 2000</td>
<td>2213 ±6.66</td>
<td>2.2</td>
</tr>
<tr>
<td>Minor elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>10 – 200</td>
<td>326 ±1.40</td>
<td>3.3</td>
</tr>
<tr>
<td>Ni</td>
<td>1 – 50</td>
<td>178 ±3.03</td>
<td>2.4</td>
</tr>
<tr>
<td>Zn</td>
<td>15 – 500</td>
<td>135 ±3.99</td>
<td>1.7</td>
</tr>
<tr>
<td>Trace elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;100 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>5 – 100</td>
<td>72.9 ±1.18</td>
<td>4.6</td>
</tr>
<tr>
<td>Mo</td>
<td>1 – 500</td>
<td>28.6 ±0.72</td>
<td>19</td>
</tr>
<tr>
<td>As</td>
<td>2 – 550</td>
<td>15.6 ±2.76</td>
<td>8.7</td>
</tr>
<tr>
<td>Co</td>
<td>0.3 – 15</td>
<td>10.0 ±2.90</td>
<td>0.4</td>
</tr>
<tr>
<td>Ag</td>
<td>0.2 – 10</td>
<td>2.67 ±1.07</td>
<td>38</td>
</tr>
<tr>
<td>Cd</td>
<td>0.2 – 60</td>
<td>1.00 ±0.18</td>
<td>5.0</td>
</tr>
</tbody>
</table>

* Typical porphyry Cu tailings predictions (Broadhurst et al., 2007)
# Relative to crustal abundance (Broadhurst and Petrie, 2010)

In preparation of flotation experiments, samples were milled to 70% passing 150 µm with a steel rod mill. A milling curve was established for the ore to get a standard grind time, found to be 7 min 44 s. The milling curve can be found in Appendix A 2.1.

4.1.2. Chemical assay methods

Various methods for mineral and elemental analysis and characterisation were used throughout the experiments described in this chapter. These are presented here.

Total sulfur analysis

Total sulfur analysis was conducted using LECO S632 sulfur analysis equipment, which employs thermal decomposition combustion infrared spectrophotometry. Sulfur analysis was conducted by the analytical laboratory in the Department of Chemical Engineering.

Mineral Fe and Cu analysis in solid samples

The Fe and Cu content of tailings samples was measured by atomic absorption spectrometry (AAS), using Varian SpectrAA 30 equipment, on total acid digestion solutions of known sample mass. Total acid digestion was carried out using HF/HCl, HNO₃ and HClO₄. The detailed method can be found in Appendix A 1.1.
Trace-minor metal analysis

Trace-minor metal analyses were conducted using Inductive Coupled Plasma–Mass Spectrometry (ICP-MS) by the Department of Geology at UCT. Solid samples were prepared by the acid digestion method discussed above and dried down twice with HNO₃ to remove traces of HCl, as required for ICP-MS analysis.

Analysis of Fe in solution

Ferrous and total iron in solution was determined colorimetrically using the 1-10 phenanthroline method (Komadel and Stucki, 1988). Analysis was conducted on a Helios α UV-Vis spectrophotometer, at wavelength 510. Fe²⁺ concentration was calculated against a standard curve.

4.2. Flotation experiments

Batch flotation experiments were conducted in order to test the feasibility of using flotation for desulfurisation of sulfide tailings using standard batch flotation methods for copper sulfide concentration. Previously, similar flotation tests, as described by Reddick et al. (2009), focused on recovery of valuable sulfide minerals. Some modification was made to improve the bulk recovery of sulfides. However, optimisation of flotation was not complete as this was beyond the focus of the study. The flotation tests and methods are described here with additional experimental detail presented in Appendix A 2.

Experiments were conducted in a 3 litre modified Leeds batch flotation cell, using 1.13 kg milled sample. The cell was agitated at 1200 rpm and aerated at 5 l/min (Reddick et al., 2009). All experiments were conducted at ambient temperature, approximately 22°C. The collector used was a dithiophosphate collector, CYTEC S8985, which was used in previous flotation studies at UCT (Reddick et al., 2009; Maluleke, 2006) and by industry for chalcopyrite flotation in copper recovery circuits. This collector was designed for selectivity towards chalcopyrite. However, it also showed strong collecting properties with pyrite (Day, 2002). The frother used for the experiments was methyl isobutyl carbinol (MIBC). This was chosen based on its use in industry for this ore. MIBC is an inexpensive and readily available chemical by-product which produces a stable but brittle froth structure.

A typical copper sulfide ore would be floated at high pH to ensure copper selectivity (US EPA, 1993). The pH of the slurry is known to have an important influence on pyrite flotation. Good recoveries at the natural pH of the slurried ore (~pH 6) indicated that this is within the flotation window for pyrite for this particular collector, i.e. below the critical pH, above which pyrite would not be collected. Thus the flotation experiments were conducted without changes to the natural pH of the slurry.

The objective of these experiments was to achieve a target sulfide concentration in tailings such that acid generation did not result to show a proof of concept. As such, the
operating parameters of the flotation cell such as air flow rate, froth depth and stirrer speed were not investigated. All tests were carried out using 30 g/ton of frother.

Single stage experiments were conducted to find operating conditions which favoured bulk floatability of sulfide minerals. The effect of collector concentration was tested with 4 tests of increasing dosage at 12, 15, 27 and 36 g/ton. Tests studied the effects of residence time on sulfide removal over a flotation time of 15 min.

Once the responses of the flotation system were better understood, a final set of focused multi-stage experiments were conducted. The multiple stage float was carried out with 4 sequential collector additions of 9 g/ton each. Flotation times were 8 min for the first stage and 5 min for the subsequent stages. All concentrates and tailings collected were dried, weighed and representatively sampled for analysis.

The initial target for desulfurisation was based on previous research in AMD prediction on flotation tailings from this ore (Maluleke, 2006), where the neutralising capacity tests on samples indicated ANC values in the range of 26 to 28 kg H$_2$SO$_4$/ton. In acid base accounting, a sample is deemed non acid forming at a NAPP of -20 kg H$_2$SO$_4$/ton. Thus, to achieve non acid forming tailings, a preliminary target for sulfur content of the final tailings was calculated from the maximum potential acidity using Eq. 5 (Section 2.4.1) and Eq. 11 (Section 4.3.1). The theoretical target total sulfur content for non-acid forming tailings was approximately 0.25% S$_T$ in the final tailings.

4.3. AMD prediction by chemical tests

Preliminary chemical AMD prediction was conducted by acid base accounting and net acid generation methods described in Section 2.4. These methods are outlined here.

4.3.1. Acid base accounting (ABA)

Maximum potential acidity (MPA)

The MPA was calculated stoichiometrically from the total sulfur (S$_T$) content, as found through LECO tests, in units of kg H$_2$SO$_4$/ton of ore (Eq. 11), based on the assumption that all sulfur in the sample forms H$_2$SO$_4$.

$$MPA = 30.6 \times (S_T)$$  \hspace{1cm} Eq. 11

Mineralogy by XRD indicated sulfides as the only sulfur-containing minerals within the sample. It was thus accepted that the S$_T$ content was available for acid production.

H$_2$O$_2$ siderite correction ANC test

Owing to the presence of siderite in the sample identified in mineralogy studies, the H$_2$O$_2$ siderite correction ANC test, as developed by Skousen et al. (1997), was used for determination of the ANC in order to avoid over-estimations of the neutralisation capacity, as found by Maluleke (2006).
The fizz rating and back titration experiments for the determination of the acid neutralisation capacity were carried out as outlined in the methods described in Appendix A 3.1.

The ANC was calculated from the experimental findings of the $\text{H}_2\text{O}_2$ siderite correction test using Eq. 12. Results were reported as an equivalent mass of acid consumed, in kg of $\text{H}_2\text{SO}_4$, per ton of sample (kg $\text{H}_2\text{SO}_4$/ton).

$$\text{ANC} = \left[\frac{\text{Vol}_{\text{HCl}} - \text{Vol}_{\text{NaOH}} \times C}{W}\right] M_a \times 49$$  \hspace{1cm} \text{Eq. 12}

where $M_a$ is the molarity of HCl (M), $W$ is weight of sample (g) and $C = (\text{Vol}_{\text{HCl}} \text{ in blank})/(\text{Vol}_{\text{NaOH} \text{ titrated in blank}})$ to take into account the differences in molarity between the acid and base solutions. A stoichiometric conversion factor of 49 gives results in kg $\text{H}_2\text{SO}_4$/ton.

### 4.3.2. Net acid generation (NAG) tests

**Single addition NAG test**

Net acid generation experiments were conducted following the methods outlined in Appendix A 3.2. The filtered residues were analysed for total sulfur with LECO to assess the extent of sulfide oxidation. Results noted were pre-boil and after-boil pH, $\text{NAG}_{\text{pH 4.5}}$ and $\text{NAG}_{\text{pH 7}}$, calculated from back titration volumes by Eq. 13 in units of kg $\text{H}_2\text{SO}_4$/ton of ore.

$$\text{NAG} = \frac{49 \times V \times M}{W}$$  \hspace{1cm} \text{Eq. 13}

where $V$ is the volume of NaOH (ml); $M$ is the molarity of NaOH and $W$ is the weight of sample (g).

**Sequential NAG test**

The sequential NAG test is carried out following the same procedure as the single addition NAG test; however, after filtering, the residues were retained and the procedure repeated until no further reaction with $\text{H}_2\text{O}_2$ was noted and the after-boil pH was above pH 4.5. The sequential NAG was calculated with Eq. 13, using the cumulative volume of sequential additions of NaOH.

**Kinetic NAG test**

The kinetic NAG test provides an assessment of the relative reactivity of a sample. The procedure for the single addition NAG test was followed whilst continuously monitoring and recording the temperature and pH of the solutions after the addition of $\text{H}_2\text{O}_2$. The profiles of the temperature and pH changes were plotted against time to assess the
reactivity of samples. The lag time was recorded as the time taken for the temperature to reach a maximum after the catalytic decomposition of the H$_2$O$_2$.

4.4. Biokinetic tests for AMD prediction

Microbial activity is recognised to contribute towards the generation of AMD-forming conditions. In order to assess generation of acid and metal dissolution under microbial leach conditions, leach tests were conducted on 7.5 g samples of flotation feed, high sulfide and low sulfide tailings. Samples were added to 150 ml autotrophic basal salts medium at pH 2 (Bryan et al., 2006). Both abiotic tests and inoculated tests were conducted in triplicate. The latter were inoculated with Acidithiobacillus ferrooxidans, Leptospirillum ferrophilum, Sulfo bacteri um benefaciens and Acidithiobacillus caldus. These were maintained at 37°C on an orbital shaking bench at 150 rpm for 90 days. Redox potential (measured using a Crison ELP 21 Eh meter against a silver/silver chloride reference electrode (+199 mV vs. SHE)), pH, ferrous and total iron in solution were measured at regular intervals. Microbial population sizes were estimated by viable population plate counts using the method described by Miles and Misra (1938) on suitable gelled media (Johnson and McGuiness, 1991) and modified further by Bryan et al. (2006). Counting of colonies was conducted under a microscope. After completion of the tests, leach liquors were retained for elemental analysis by ICP-MS.

4.5. Co-element deportment and environmental risk

4.5.1. Total metal deportment in the desulfurisation process

To test the effects of flotation desulfurisation on the co-element deportment to tailings, ICP-MS analyses were conducted to find total major, minor and trace metal compositions within the feed and desulfurised tailings fractions. Total acid digestion methods were used, as described for AAS analysis; however, these included a double dry down step with HNO$_3$ to ensure all HCl was removed before ICP-MS analysis.

4.5.2. Leachability of co-metals under biokinetic test conditions

Leachate samples collected from the biokinetic tests were filtered and made up to standard volumes. Analysis was conducted by ICP-MS and results compared with total metal analysis of the feed and desulfurised tailings samples.

4.5.3. Environmental risk assessment

Ranking of environmental significance of co-elements was conducted using risk potential factors (RPF), calculated by Eq. 14 (Broadurst and Petrie, 2010):

$$\text{RPF}_i = \frac{C_i^2}{ARC_i \times BC_i}$$  

Eq. 14
where $AC_i$ is the available concentration (ppm), in this case leachate concentrations from biokinetic shake flasks; $ARC_i$ is the environmentally accepted concentration (ppm), with water quality standards for drinking water used as a proxy measure; $BC_i$ is the natural background concentration (ppm), using the average crustal abundance for individual elements as a proxy measure.
Chapter 5

RESULTS AND DISCUSSION

This chapter covers the results of the experimental case study. The feasibility of flotation to achieve tailings desulfurisation using standard copper flotation techniques is presented. The results of the chemical AMD prediction tests carried out on the feed sample and desulfurised tailings are then discussed. Further, the development of a biokinetic AMD prediction test is described and its results compared with the chemical tests typically used. Finally, metal deportment predictions are presented.

5.1. Flotation for tailings desulfurisation

Although not typically practiced, the feasibility of using flotation desulfurisation for the removal of pyrite from tailings has been demonstrated previously (Bois et al., 2004; Benzaazoua et al., 2008). Experiments on the sample described in Chapter 4 were conducted to determine favourable conditions for desulfurisation and show the feasibility of using flotation as an effective means of desulfurisation.

5.1.1. Single stage flotation experiments

To test conditions for effective desulfurisation, bulk sulfide flotation tests were conducted at the natural pH of the slurry, assessing the effects of increased collector concentration and residence time. Detailed results of these experiments are outlined in Appendix A 4.1.

The results of increasing collector additions for 15 min flotation tests are summarised in Table 6. A final S_T content of the bulk tailings of 0.66 ±0.03 wt% was achieved with 36 g/ton collector addition, removing 84% of pyrite from the bulk tailings to leave a sulfide-lean tailings counting for over 90% of the total mass of the feed tailings.

Table 6: Effect of collector on sulfide removal in single stage flotation tests, floated for 15 min at pH ~6

<table>
<thead>
<tr>
<th>Collector addition (g/ton)</th>
<th>Feed tailings S_T content (wt%)</th>
<th>Final tailings S_T content (wt%)</th>
<th>Mass deportment to tailings (%)</th>
<th>Extent of S_T removal from feed (%)</th>
<th>Extent of Cu removal from feed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>4.16</td>
<td>3.58</td>
<td>97.6</td>
<td>14</td>
<td>70</td>
</tr>
<tr>
<td>15</td>
<td>4.28</td>
<td>2.2</td>
<td>95.0</td>
<td>46</td>
<td>86</td>
</tr>
<tr>
<td>27</td>
<td>3.73</td>
<td>1.1</td>
<td>91.0</td>
<td>75</td>
<td>96</td>
</tr>
<tr>
<td>36</td>
<td>3.64</td>
<td>0.66</td>
<td>91.9</td>
<td>84</td>
<td>100</td>
</tr>
</tbody>
</table>

Increases in collector addition from 27 to 36 g/ton improved the S_T removal but did not significantly influence the mass % reporting to the tailings, indicating better bulk sulfide...
separation efficiency at higher collector concentrations. The final $S_T$ content is, however, still above the target value of 0.25% $S_T$. Although poor $S_T$ recovery was seen at low collector additions, significant copper was removed at 12 g/ton collector. Some 70% of copper was removed, compared with only 14% total sulfur removal. A comparison of the effect of collector concentration on the relative removal of copper and sulfur (Figure 16) highlights the selectivity of the dithiophosphate collector to chalcopyrite at the natural pH of the slurry. The preferential separation of chalcopyrite is most noted at low collector addition (12 to 15 g/ton).

![Graph showing effect of collector addition on total sulfur and copper removal](image1.png)

*Figure 16: Effect of collector addition on total sulfur and copper removal in single stage flotation tests (error bars denote variance in mass balance calculations)*

The effect of flotation time on the relative removal of chalcopyrite and pyrite with 36 g/ton of collector is illustrated in Figure 17.

![Graph showing pyrite and chalcopyrite removal over time](image2.png)

*Figure 17: Pyrite and chalcopyrite removal as a function of flotation time for single stage tests at 36 g/ton collector, error bars denote standard deviation for $n=2$*
At 36 g/ton collector addition, the rate of flotation of both chalcopyrite and pyrite minerals decreased significantly after the first 6 minutes of flotation, with the majority of bulk sulfide removal occurring within a period of 10 minutes. After this, the rate of flotation was seen to plateau, resulting in 84% $S_T$ removal after a total flotation period of 15 minutes (see Table 6). The flotation of chalcopyrite is, furthermore, seen to be more rapid than that of pyrite, reaching 80% removal from tailings after just 3 min float time compared with less than 50% removal of pyrite.

5.1.2. Multi-stage flotation desulfurisation tests

The results presented in Section 5.1.1 demonstrate that sulfide recovery responded well to increases in the concentration of collector at the natural pH of the slurry. To improve overall sulfide recovery and thereby achieve a final tailings product with less than the targeted 0.25% $S_T$, sequential flotation experiments were conducted. These tests also provided an opportunity to explore the possibility of selective flotation for value recovery by manipulating the differential effects of time and collector addition on the relative extents of removal of chalcopyrite and pyrite seen in the single stage tests. On the basis of the results of the single stage tests, collector additions of 9 g/ton were added over 4 stages to a total of 36 g/ton. A conditioning step was included between each stage.

Results of the multi-stage experiments are summarised in Table 7.

*Errors denote standard deviation, n=3

With a total collector addition of 36 g/ton over four stages, the residual sulfur in the tailings was reduced to 0.21 ±0.01%, implying a removal of sulfur from the tailings of 95.1%. The desulphurised tailings contained 89.7% of the feed tailings, comparable with the total mass deportment to tails of 91.9% for only 84% $S_T$ removal under single stage flotation conditions. The greatest sulfide removal was noted in stages 2 and 3, accounting for some 76% of overall sulfur removal. The residual sulfur content in the tailings after each stage is displayed in Figure 18.
Figure 18: Residual $S_T$ (wt %) in tailings after each stage of collector addition, standard deviations for n=3

Figure 19 compares the cumulative removal of pyrite and chalcopyrite per stage addition of collector. Consistent with the results of the single stage tests, the extent of removal of chalcopyrite relative to pyrite was greatest in the 1st stage of flotation. At 9 g/ton collector addition approximately 60% of chalcopyrite was removed in 8 min, compared with less than 10% pyrite removal; however, the actual mass of copper recovered was in the same order of magnitude as that of pyrite. This confirmed the selectivity of the chosen flotation reagents to chalcopyrite, which required shorter residence times and lower collector concentrations than pyrite for effective removal. The subsequent stages showed significant increases in bulk sulfide removal compared with the single stage tests at 36 g/ton collector addition. This provides opportunity for selective removal of valuable copper-bearing sulfides from the bulk sulfides of little value but significant AMD potential (in this case, pyrite).

On this basis it is proposed that tailings desulphurisation be conducted in two steps: a value recovery step (Stage 1) and a bulk sulfide removal step (the cumulative sulfide removal over Stages 2 to 4). This approach, presented schematically in Figure 20, results in three product streams: a value product which could be recycled to the conventional flotation circuit, a sulfide-rich tailings stream of low volume, and a sulfide-lean tailings fraction.
Chapter 5

Results and discussion

Figure 20: Two step approach to desulfurisation incorporating value recovery and bulk sulfide removal

Mass flows and stream compositions across the multi-stage batch flotation experiments are detailed in Table 8. From a conventional tailings feed with low value but significant acid generating sulfide content, a value concentrate containing 5.67 wt% copper was produced with 9 g/ton collector in Stage 1. Stages 2 to 4 cumulatively produced a sulfide-rich tailings stream of less than 9% of the total mass, containing 81% of the sulfur in the feed. The remaining sulfide-lean tailings comprised nearly 90% of the feed with greatly reduced sulfur content ($S_T$ 0.21%).

Table 8: Summary of mass balance results for step-wise flotation experiments

<table>
<thead>
<tr>
<th>Stream</th>
<th>Mass fraction (%)</th>
<th>$S_T$ content (wt %)</th>
<th>Copper content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Tailings</td>
<td>100</td>
<td>3.8</td>
<td>0.16</td>
</tr>
<tr>
<td>Value product (Stage 1)</td>
<td>1.5</td>
<td>21.0</td>
<td>5.7</td>
</tr>
<tr>
<td>Sulfide-rich tailings (Stages 2-4)</td>
<td>8.7</td>
<td>33.7</td>
<td>0.39</td>
</tr>
<tr>
<td>Sulfide-lean tailings (Stages 2-4)</td>
<td>89.7</td>
<td>0.21</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The results are displayed schematically in Figure 21 which includes standard deviations across the triplicate tests.

Figure 21: Schematic of relative mass flows for pyrite, chalcopyrite and gangue in the multi-stage tests
5.2. Prediction of AMD potential of desulfurised tailings

Verification is required to show that AMD generation potential has indeed been mitigated on achieving sulfide-lean tailings of 0.21% $S_T$ such that they can be deposited without environmental risk. Static and kinetic tests are typically used to build an informative picture of AMD potential from tailings, as discussed in Section 2.4. Tests selected for this study included acid base accounting, net acid generation and biokinetic prediction tests which were developed from shake flask bioleaching methods. This section discusses the use of these tests in assessing the tailings produced by desulfurisation.

5.2.1. Static AMD prediction test results

Acid base accounting (ABA)

ABA tests were conducted across full range of tailings produced through flotation in order to find the range of $S_T$ content for which successful desulfurisation was achieved. Selected results of the tests, showing samples in each AMD class, are detailed in Table 9. The removal of sulfur from tailings has a marked effect on AMD potential through a reduction in maximum potential acidity (MPA) from 118 to just 6.42 kg $H_2SO_4$/ton, whilst the acid neutralising capacity (ANC) remained unaffected.

Table 9: Selected results of acid base accounting tests

<table>
<thead>
<tr>
<th>$S_T$ %</th>
<th>MPA</th>
<th>ANC</th>
<th>NAPP</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.84 ± 0.3</td>
<td>118 ± 10.6</td>
<td>23.2 ± 5.52</td>
<td>94.8 ± 15.8</td>
<td>Acid forming</td>
</tr>
<tr>
<td>0.67 ± 0.03</td>
<td>20.4 ± 0.779</td>
<td>23.1 ± 4.27</td>
<td>-2.64 ± 5.05</td>
<td>Potentially acid forming</td>
</tr>
<tr>
<td>0.21 ± 0.01</td>
<td>6.42 ± 0.002</td>
<td>28.7 ± 3.57</td>
<td>-22.3 ± 3.57</td>
<td>Non-acid forming</td>
</tr>
</tbody>
</table>

*Errors denote standard deviations across repeat experiments

Figure 22 shows results of the ANC tests as a function of sulfide concentration as well as the average across all samples (24.9 ±3.79 kg $H_2SO_4$/ton). The ANC was independent of sulfide content, indicating that desulfurisation of the feed tailings did not inhibit the ability of gangue minerals to act as a buffer for AMD generation. Also indicated on Figure 22 are the boundaries of classification for acid base accounting (NAPP = -20 kg $H_2SO_4$/ton and 20 kg $H_2SO_4$/ton). For these particular tailings, the desulfurised samples below $S_T$ of 0.25% are classified non-acid forming (NAF) and samples of greater than 1.5% $S_T$ considered acid forming.

The poor reproducibility associated with the ANC values can be attributed to heterogeneity of samples as well as error in measurement and its subsequent propagation. Across the 11 samples displayed, the ANC ranged from 18.9 to 31.8 kg $H_2SO_4$/ton, giving a relative standard deviation of 14.3%. Variance in sulfide content was 9.0%, based on feed sample heterogeneity.
Apart from poor reproducibility, the acid base accounting methods also have limitations through possible over-estimations of both the MPA and the ANC. The MPA is based on a total sulfur assay, assuming that all sulfur exists as sulfide and will produce acid. It does not take into account sulfates or other forms of sulfur. Nor does it account for trace sulfide minerals such as galena (PbS) which may exist below the detection limit of XRD and, although adding to total sulfur content, may not contribute to acidity in sulfide weathering (Smart et al., 2002; da Silva, 2004). The ANC of a sample may also be over-estimated owing to the low pH levels at which the tests are conducted. It is plausible that not all acid consuming species are available for neutralisation. These limitations, coupled with poor reproducibility, give high uncertainty in the results. Hence, classification of samples by acid base accounting only provides a preliminary assessment of AMD potential.

**Net acid generation (NAG) tests**

Net acid generation tests were conducted to enhance the prediction of AMD by studying the accelerated chemical oxidation of sulfide minerals. Single addition, sequential and kinetic test results are discussed below.

**Single addition net acid generation tests**

The results of the single addition NAG tests are displayed in Table 10, giving preliminary AMD classification based on Table 3, Section 2.4.3. In accordance with the single stage NAG tests, tailings with a $S_T$ content of greater than 1% have NAG pH values of less than pH 4.5 and are thus classified as acid forming. The sulfide lean tailings fraction (0.21% $S_T$) exhibited a NAG pH of greater than 4.5 and NAG$_{pH7}$ of less than 1 kg H$_2$SO$_4$/ton and was thus classified non acid forming (NAF).

A comparison of NAG$_{pH7}$ and NAG$_{pH4.5}$ results indicates that the majority (60-70%) of acid generated by the tailings with $S_T$ values of greater than 1% can be attributed to
oxidative dissolution of sulfides and iron precipitation (See Eq. 9 in Section 2.4.2). Nevertheless secondary precipitation of divalent metal ions, in accordance with Eq. 10 in Section 2.4.2, also results in significant acid generation for these samples, indicative of oxidation of base metal sulfides, such as chalcopyrite, and possibly also metal occlusions in pyrite.

Table 10: Selected single addition NAG results

<table>
<thead>
<tr>
<th>S %</th>
<th>After-boil NAG pH</th>
<th>NAG(_{pH4.5}) (kg H(_2)SO(_4)/ton)</th>
<th>NAG(_{pH7}) (kg H(_2)SO(_4)/ton)</th>
<th>S(_T) oxidised (%)</th>
<th>AMD classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.84</td>
<td>2.57</td>
<td>16.5</td>
<td>26.8</td>
<td>37</td>
<td>Acid forming</td>
</tr>
<tr>
<td>0.97</td>
<td>2.84</td>
<td>8.47</td>
<td>12.2</td>
<td>81</td>
<td>Acid forming</td>
</tr>
<tr>
<td>0.21</td>
<td>5.71</td>
<td>n/a</td>
<td>0.81</td>
<td>87</td>
<td>NAF</td>
</tr>
</tbody>
</table>

The results of % S\(_T\) oxidised in Table 10, also show that a single addition test does not account for the full potential of acid generation by pyrite, particularly in samples with higher sulfur content. At a S\(_T\) grade of 3.84%, the addition of peroxide only oxidised 37% total sulfur (as measured by LECO), compared with 87% sulfide oxidation of the desulfurised tailings. The under-estimation of net acid generation in the single addition NAG tests owing to incomplete oxidation is reported in literature (Stewart et al., 2006). The exothermic temperature increase caused by pyrite oxidation decomposes peroxide, thus limiting sulfide oxidation (Sapsford et al., 2008).

Sequential net acid generation tests

Sequential NAG tests were conducted to ensure that all sulfide minerals were oxidised in order to get a more accurate estimate of quantitative net acid generating potential. The experimental steps of the single addition NAG test were repeated until no further reaction was noted, indicating complete oxidation of sulfides. Table 11 indicates the results of the 5 stage sequential experiments conducted on the high sulfide tailings (3.84% S\(_T\)). The cumulative acid generation shows the majority of sulfide oxidation, both as a result of sulfide oxidation (accounting for 67% of total acid) and precipitation of divalent ions, takes place in the early stages (1-3) where the NAG pH was below pH 3. Negligible oxidation occurred after the 4\(^{th}\) stage (NAG pH 4.56 ±0.99).

Table 11: Sequential NAG results for sample of sulfur content of 3.84%

<table>
<thead>
<tr>
<th>Stage</th>
<th>NAG pH(^*)</th>
<th>Cum. NAG(_{pH4.5}) (kg H(_2)SO(_4)/ton)(^*)</th>
<th>Cum. NAG(_{pH7}) (kg H(_2)SO(_4)/ton)(^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.77 ± 0.22</td>
<td>17.3 ± 11.8</td>
<td>28.0 ± 6.30</td>
</tr>
<tr>
<td>2</td>
<td>2.31 ± 0.15</td>
<td>54.9 ± 3.44</td>
<td>70.1 ± 1.46</td>
</tr>
<tr>
<td>3</td>
<td>2.89 ± 0.94</td>
<td>66.9 ± 7.36</td>
<td>84.2 ± 11.8</td>
</tr>
<tr>
<td>4</td>
<td>4.56 ± 0.99</td>
<td>67.1 ± 7.56</td>
<td>86.0 ± 11.3</td>
</tr>
<tr>
<td>5</td>
<td>5.32 ± 0.57</td>
<td>67.1 ± 7.56</td>
<td>88.0 ± 11.2</td>
</tr>
</tbody>
</table>

\(^*\)Errors calculated as standard deviation for n=3
Figure 23 displays the sequential NAG pH values comparing sample results of varying ST content. As shown, the number of stages required to reach complete oxidation (where final pH of the solution is above pH 4.5) decreased with the ST content in the tailings. For the sample of 0.21% ST only a single stage was required, compared with the sample of 0.65% which required 3 stages to ensure complete oxidation. Where experiments were run in triplicate, error bars of standard deviation are shown. This highlights the poor reproducibility in the tests which could lead to uncertainty in assessing samples based solely on their NAG pH.

Figure 23: After boil NAG pH for tailings samples of varying sulfur content

Figure 24 displays a plot of the single addition NAG pH against the cumulative NAGpH7 (kg H2SO4/ton) as a function of ST. This provides graphical classification for the samples based on their AMD potential (Hansen, 2004; Liao, 2007).

Figure 24: Net acid generation test results of samples of varying ST content indicating acid generation potential classifications
Samples with NAG pH below pH 4.5 and NAG\sub{pH7} over 50 kg H\textsubscript{2}SO\textsubscript{4}/ton are considered highly acid forming. Tailings samples containing more than 1% S\textsubscript{T} fell in this category. Samples containing between approximately 0.3% and 1% S\textsubscript{T} were found to be moderately acid forming with NAG\sub{pH7} between 5 and 50 kg H\textsubscript{2}SO\textsubscript{4}/ton and NAG pH below pH 4.5. Samples, such as 0.3% S\textsubscript{T} with low NAG\sub{pH7} (below 5 kg H\textsubscript{2}SO\textsubscript{4}/ton) but NAG with pH below pH 4.5 are unclassified and require further testing to confirm AMD potential. A tailings sample with NAG pH greater than 4.5 and NAG\sub{pH7} below 5 kg H\textsubscript{2}SO\textsubscript{4}/ton are considered non acid forming (NAF). This was seen for the sulfide-lean tailings samples of 0.21% S\textsubscript{T}.

**Kinetic net acid generation (K-NAG) tests**

The kinetic NAG test was carried out on both high sulfide (3.84% S\textsubscript{T}) and desulfurised samples (0.21% S\textsubscript{T}). The kinetic tests give an indication of pyrite availability and insight into relative reaction kinetics for pyrite oxidation. Figure 25 compares desulfurised tailings with untreated tailings over 3.5 hours of reaction with H\textsubscript{2}O\textsubscript{2}.

![Figure 25: Kinetic NAG temperature profile](image)

The temperature profiles for the sulfide containing samples (3.84% S\textsubscript{T}) display a peak in temperature at around 3 hours of reaction time. This indicates the presence of a significant amount of pyrite available for oxidation and thus AMD potential, as the temperature peak is caused by catalytic decomposition of the H\textsubscript{2}O\textsubscript{2} owing to the exothermic reaction of pyrite oxidation. The lag time from the start of the test to the peak in temperature is an indication of sulfide reactivity. The high sulfide samples tested here, although significantly acid generating, exhibit slow reaction kinetics under NAG test conditions. It has been proposed that a relationship exists between the lag time in a K-NAG test and the lag time for acid generation in column leaching experiments (Stewart et al., 2006), although Sapsford et al. (2008) have claimed that this trend is sample specific. There was no rise in temperature in the sulfide-lean tailings sample (0.21% S\textsubscript{T}) indicating that there was no significant amount of pyrite available for oxidation. Sapsford et al. (2008) confirm that samples with low sulfide
content will not exhibit an exothermic spike as little or no oxidation by H\textsubscript{2}O\textsubscript{2} takes place. The increase in temperature caused the decomposition of H\textsubscript{2}O\textsubscript{2} at which point oxidation reactions ceased. This caused incomplete oxidation of the sulfides, as discussed for the single addition NAG tests.

**Combined classification of static predictions**

Direct quantitative comparison of ABA and NAG tests results is not meaningful owing to the differences in test conditions and assumptions made in the test methods. In NAG tests the neutralising capacity for a low acid generating sample may not be fully realised. However, ABA assumes that the ANC is constant for a given gangue mineralogy, thus over-estimating neutralisation potential.

Owing to the uncertainty highlighted in both the NAG and ABA test results, Smart *et al.* (2002) proposed the use of a geochemical classification plot, which combines the NAG pH with the NAPP results to give a more informed picture of AMD potential. The classification plot (Figure 26) provides an opportunity to compare and validate the static test results. The findings are qualitative, and still show a degree of uncertainty, especially for samples of lower S\textsubscript{T} content.

![Figure 26: AMD classification plot comparing acid base accounting results with the NAG pH](image)

Table 12 outlines classifications of the ABA and NAG tests for the range of samples displayed in Figure 26, indicating the combined classification as introduced in Table 3, Section 2.4.3. For samples of higher S\textsubscript{T} content (2.9 to 3.84%) and the desulfurised sample at 0.21% S\textsubscript{T} there was agreement in classification. However, for the samples of S\textsubscript{T} content between 0.3 and 1% there were discrepancies or uncertainty in classification.
Table 12: Comparison of static AMD test classifications

<table>
<thead>
<tr>
<th>$S_T$ (%)</th>
<th>ABA</th>
<th>NAG</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.84</td>
<td>Acid forming (AF)</td>
<td>Highly AF</td>
<td>PAF</td>
</tr>
<tr>
<td>2.80</td>
<td>AF</td>
<td>Highly AF</td>
<td>PAF</td>
</tr>
<tr>
<td>0.97</td>
<td>Potentially AF (PAF)</td>
<td>Moderately AF</td>
<td>PAF</td>
</tr>
<tr>
<td>0.67</td>
<td>PAF</td>
<td>Moderately AF</td>
<td>UC</td>
</tr>
<tr>
<td>0.30</td>
<td>PAF</td>
<td>Uncertain (UC)</td>
<td>UC</td>
</tr>
<tr>
<td>0.21</td>
<td>Non acid forming (NAF)</td>
<td>NAF</td>
<td>NAF</td>
</tr>
</tbody>
</table>

Although the static tests have provided detailed predictions for AMD potential, the poor reproducibility, coupled with low accuracy, gives high uncertainty in the quantitative results. The static tests thus provide a useful preliminary classification method, but lack the capability to produce accurate quantitative results. The static tests also failed to predict the relative rates of acid production and neutralisation. Oxidation of pyrite is slow, predicted to take hundreds of years in a tailings deposit (Hansen, 2004) whereas the dissolution of carbonate minerals is known to be rapid, even in neutral conditions. The static tests did provide qualitative information on pyrite oxidation as shown in the K-NAG results, but did not give an indication of the interaction between generating and neutralising processes, an important factor to consider in an open flow-through system typically found in mineral waste deposits. The static chemical tests also do not provide any information regarding the microbial oxidation processes which govern AMD generation as explained in Section 2.4.3, and cannot be ignored if a realistic assessment of AMD generation is required.

5.2.2. Biokinetic AMD prediction test results

The pH trends in literature generally show that there is a very different rate in dissolution of acid consuming minerals to that of the acid forming oxidation of sulfides. Research has also shown that sterile systems, without microbial activity, rarely exist (Bryan, 2006). This highlights the importance of studying the kinetics of the subprocesses and understanding the system in terms of both geochemistry and microbiology. The former can, in theory, be addressed in standard kinetic tests such as column and humidity cell tests; however, these can take up to a year to produce significant results and are thus often impractical to use (INAP, 2009).

In order to address the shortcomings of the results of the suite of static AMD prediction tests discussed in Section 5.2.1 and the limitations of current kinetic test methods, the biokinetic shake flask test was developed following shake flask test methodology commonly used to examine microbial efficiency in bioleaching, which follows the same mechanisms as AMD generation. Tests were carried out on the flotation feed, ($S_T$ 3.84%) a high sulfide tailings ($S_T$ 3.40%) and a desulfurised tailings ($S_T$ 0.21%), as outlined in Figure 21. In all cases, the initial pH in the test was pH 2.0 and this was allowed to vary as a function of the reactions occurring. In addition, the desulfurised
sample was leached under pH controlled conditions at pH 2.0 to assess the reactivity of the sulfide-lean tailings fraction exposed to an acid environment.

**Time course results of the biokinetic tests**

Results are shown for variation in pH (Figure 27), ferric concentration (Figure 28) and redox potential (Figure 29) over the time course of 94 days. For ease of description of the results, the figures have been divided into regions I to IV, based on the general trends in pH.

*Figure 27: pH as a function time for biokinetic tests, error bars denote standard deviation, n=3*

*Figure 28: Ferric iron concentration in solution as a function of time in biokinetic tests, n=3*
Initially, an increase in pH across all tests, including an un-inoculated abiotic test, was seen owing to leaching of rapidly soluble acid consuming minerals under the acidic conditions at the start of the tests. This is consistent with the static acid neutralisation capacity findings. After 5 days of leaching, an increase in redox potential (to above 600 mV) and ferric iron concentration was seen in the inoculated tests, indicating the onset of microbial activity, oxidising the ferrous iron available from the dissolution of siderite ($\text{FeCO}_3$). Conversely, no increase in redox potential was observed in the abiotic test which remained below the initial value of approximately 460 mV over 20 days. The ferrous iron concentration in solution was also measured, however results are not shown as the concentration remained low (below 40 mg/l) throughout the inoculated tests, owing to the presence of iron oxidising micro organisms.

Under all conditions associated with a pH increase exceeding pH 2.6 from 5 to 18 days (region II), precipitation of ferric iron from solution was observed. This is shown in Figure 28. The pH trends diverged during this period as the rate acid generating reactions surpassed those of acid consumption. The rate of increase in pH declined with increasing sulfide content. The feed and high sulfide tailings reached their maximum pH values (pH 2.8 and 3.4 respectively) at around 18 days. In comparison, the pH of the desulphurised sample ($S_T 0.21\%$) continued to increase at a constant rate to above pH 4 after 18 days, and showed a concomitant decrease in redox potential owing to the precipitation of $\text{Fe}^{3+}$ from solution at higher pH levels.

From day 18 (region III), acid generating reactions dominated in the samples containing 3.40% and 3.84% sulfur, indicating a depletion of available acid neutralising minerals. This is shown by a decrease in the pH of the solutions and the regeneration of $\text{Fe}^{3+}$ in solution. In the presence of the microbial culture, the oxidation of pyrite...
brought Fe$^{3+}$ and H$^+$ ions into solution, which promoted further leaching of sulfides, as described in Figure 4, Section 2.1.2. The pH stabilised at around pH 2.2 after day 70, indicating significant acid generation potential from these samples. The sulfide-lean tailings sample (0.21% S$_T$) stabilised at around pH 4.9 after 50 days (region IV), and showed no further Fe$^{3+}$ regeneration through to the end of test. The redox potential remained below 500 mV, indicating the inhibition of microbial activity, and thus no further AMD generation.

The desulphurised sample was also subjected to reaction under pH control by adding H$_2$SO$_4$ after sampling every 2 to 3 days to maintain a solution pH of 2.0. This was only required up until day 18 (regions I and II on Figure 27), whereafter available acid consuming minerals had been depleted and no further pH adjustment was made. During this period the gangue minerals in the tailings consumed an equivalent of 24.5 ±3.7 kg H$_2$SO$_4$/ton. The redox potential remained high (above 650 mV) and the soluble ferric iron concentration increased to 550 mg/l in 18 days, providing evidence of microbial activity under these pH conditions, which are optimal for Acidithiobacillus and Leptospirillum species. The high Fe$^{3+}$ concentration was maintained until day 31, whereafter a gradual decrease was observed, most likely owing to the precipitation of jarosite (KFe$_3$(OH)$_6$(SO$_4$)$_2$), indicated by the yellow colour of the precipitate.

The controlled pH test investigated the reactivity of sulfide-lean tailings at low pH as well as the potential to maintain acid generating conditions in the event of the material being exposed to microorganisms in an acidic environment. This scenario may arise in cases where the tailings are co-disposed with acid generating material or acidic waters or where weathering continues following the depletion and removal of acid neutralising capacity in a flow through system.

**Microbial population activity**

The effects of microbial activity were shown in results of redox potential and ferric concentration. In order to confirm the microbial population density sustained in each of the experiments, viable population counts were carried out with serial dilutions. Results after 48 days of the experiment are shown in Figure 30.

![Figure 30: Viable population count after 48 days, showing population density for each test](image-url)
Healthy populations were supported by the conditions found in both experiments with higher sulfide content. Of interest is the population difference between the two tests of sulfide-lean tailings (0.21% Sₜ). The sample which was not pH controlled revealed microbial populations two orders of magnitude lower than that of the sulfide containing samples; however, the same ore sample under low pH conditions maintained a higher population density until day 48 of the experiment, despite limited availability of sulfide mineral and ferrous iron. The presence of both iron oxidising and sulfur oxidising species was seen, identified visually through the shape and colour of individual colonies under the microscope.

### 5.2.3. Comparison of test results of biokinetic with static tests

In order to validate the findings of the biokinetic tests, a comparison of the test results with the findings of the static tests was conducted, looking at the neutralising potential as well as the pH conditions created by sulfide oxidation. The test results are compared in Table 13. The acid consumption of the pH controlled low desulfurised tailings was calculated by converting pH into concentration of H⁺ ions. The acid addition, and thus consumption was equivalent to 24.5 ±3.7 kg H₂SO₄/ton of sample, which equates to the predictions of the ANC static test (24.9 ±3.8 kg H₂SO₄/ton). The classifications of AMD potential in the tests are also in agreement, indicating that the desulfurised tailings are non-acid forming.

**Table 13: Comparison of biokinetic and static AMD test results**

| Sample      | Sₜ (%) | Static tests | Biokinetic test | pH day 73
|-------------|--------|--------------|-----------------|----------
|             |        | NAG pH | *ANC (kg H₂SO₄/ton) | Classification | Eq. NP (kg H₂SO₄/ton) | Classification |
| Feed        | 3.84   | 2.36   | 24.9 ±3.8 | Acid forming | 2.15 | # n. c. | Acid forming |
| High S Tails| 3.40   | 2.61   | 24.9 ±3.8 | Acid forming | 2.32 | n. c. | Acid forming |
| Low S Tails | 0.21   | 5.71   | 24.9 ±3.8 | Non-acid forming | 4.89 | 24.5 ±3.7 | Non-acid forming |

*average for all tests

The pH data at day 73 of the biokinetic test is plotted against the single addition NAG pH as a parity chart in Figure 31. Although some variation in pH values was found there exists a relationship between the values at different levels of sulfide content. An R² value of 0.9968 was found for a straight line fitted to the data. Discrepancies (as indicated by the slope of 0.84) can be accounted for by incomplete oxidation in NAG tests and acid added for basal salts pH regulation in the biokinetic tests. The pH comparison is thus qualitative, but the close relationship between the static and biokinetic pH test results highlights the efficacy of the results and validates the findings.
Chapter 5   Results and discussion

Comparison of the tests in terms of time or rate based results highlights the limitations of the static tests, as seen in the interpretation of the pH trends, which give meaningful insight into the interactions of the acid consuming and acid generating reactions. Although the material had a significant ANC (~25 kg H$_2$SO$_4$/ton), this was mainly owing to rapid consumption of carbonate-type minerals, which were consumed in the early stages of the experiment (less than 20 days). In an open system typical of a mineral waste deposit, this would mean that the majority of acid consuming capacity would most likely be lost in the early stages of the life of the deposit, compared with the relatively long time scales seen in sulfide oxidation, with slower kinetics as found in the kinetic NAG tests. The delayed onset of acid generation is demonstrated by significant pH decrease in the biokinetic tests only after day 20, continuing until day 70. Although neutralisation potential exists as found by the static ANC tests, the biokinetic tests show that this is not necessarily available for acid consumption across the time frame for AMD generation, and thus in a typical AMD scenario the acid potential will be greater than that assessed by static testing alone.

The batch biokinetic tests have clearly demonstrated their potential to provide improved understanding of AMD potential over static tests within a practical time frame. Furthermore, these biokinetic tests provide appropriate leachates for the study of metal deportment, as is discussed in Section 5.3.

5.3. Metal deportment in desulfurised tailings

As outlined in the literature (Section 2.2), one of the major environmental issues associated with the generation of AMD is the mobilisation and subsequent deportment of major, minor and trace metals by the acidic environment caused by sulfide oxidation. An analysis of metal deportment and mobility was conducted by ICP-MS, in order to assess the impacts that desulfurisation has on these potentially harmful metals.
5.3.1. Deportment of metals to desulfurised tailings

Total metal analyses were conducted on the desulfurised tailings and the results compared with the co-element analysis of the feed tailings material (Table 5, page 31), to evaluate deportment of environmentally significant metals to the sulfide-lean tailings fraction. Results of ICP-MS analysis on total digested desulfurisation feed and tailings samples are shown in Table 14 and Figure 32 (a, b and c). Experimental errors shown in the results are as provided by ICP-MS analysis.

Table 14: Total metal analysis of desulfurisation feed and sulfide-lean tailings indicating the mass balanced % metal in feed reporting to tailings

<table>
<thead>
<tr>
<th>Element</th>
<th>Metal concentration of feed sample (mg/kg)</th>
<th>Metal concentration of sulfide-lean tailings (mg/kg)</th>
<th>Fraction reporting to tailings (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>38949 ±253</td>
<td>42213 ±52.9</td>
<td>97.2</td>
</tr>
<tr>
<td>Al</td>
<td>8891 ±1233</td>
<td>9845 ±309</td>
<td>99.3</td>
</tr>
<tr>
<td>Mg</td>
<td>7174 ±63.0</td>
<td>7022 ±32.5</td>
<td>87.8</td>
</tr>
<tr>
<td>Mn</td>
<td>2213 ±6.66</td>
<td>2301 ±44.8</td>
<td>93.3</td>
</tr>
<tr>
<td>Minor elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>326 ±1.40</td>
<td>288 ±0.09</td>
<td>79.4</td>
</tr>
<tr>
<td>Ni</td>
<td>178 ±3.03</td>
<td>160 ±0.08</td>
<td>80.7</td>
</tr>
<tr>
<td>Zn</td>
<td>135 ±3.99</td>
<td>99.7 ±0.08</td>
<td>66.3</td>
</tr>
<tr>
<td>Trace elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>72.9 ±1.18</td>
<td>37.3 ±0.23</td>
<td>45.9</td>
</tr>
<tr>
<td>Mo</td>
<td>28.6 ±0.72</td>
<td>13.3 ±0.01</td>
<td>41.9</td>
</tr>
<tr>
<td>As</td>
<td>15.6 ±2.76</td>
<td>1.89 ±1.20</td>
<td>10.8</td>
</tr>
<tr>
<td>Co</td>
<td>10.0 ±2.90</td>
<td>3.55 ±0.03</td>
<td>31.8</td>
</tr>
<tr>
<td>Ag</td>
<td>2.67 ±1.07</td>
<td>1.02 ±3.17</td>
<td>34.2</td>
</tr>
<tr>
<td>Cd</td>
<td>1.00 ±0.18</td>
<td>0.35 ±1.52</td>
<td>31.5</td>
</tr>
</tbody>
</table>

As expected from literature (Broadhurst, 2007), the major lithophilic metals (Ca, Mg, Al and Mn), all of which are associated typically with silicate and carbonate minerals, reported almost entirely (88 to 99%) to the sulfide-lean tailings fraction. Significant deportment (66 to 81%) to this tailings fraction also occurred in the case of the minor elements (Cr, Zn and Ni) which indicated that these minerals were also predominantly present as, or associated with, lithophilic minerals, such as oxides and silicates. As a result of these, and total mass, deportment trends, no significant decrease in the concentration of these lithophilic elements after tailings desulfurisation by flotation was observed. This is shown in Figure 32 a and b.

In contrast, there was partial deportment to both the sulfide-rich and sulfide-lean tailings fractions of the trace chalcophilic elements, including lead (Pb), molybdenum (Mo), cobalt (Co), silver (Ag), cadmium (Cd) and, in particular arsenic (As) of which only 11% reported to the desulfurised tailings. As a result of this partial deportment, the
concentrations of these elements in the desulfurised tailings was significantly lower than in the feed tailings, as shown in Figure 32 c. This could have significant implications in terms of environmental impact, as many of these trace elements are acutely to highly toxic, and pose a considerable risk to natural and human environments even at relatively low concentration levels (Broadhurst, 2007).

![Figure 32 a, b and c: Total metal concentrations of feed and desulfurised tailings by ICP-MS analysis](image)

### 5.3.2. Mobility of metals in biokinetic leach tests

Although it has been shown that desulfurisation removes some environmentally significant elements, there is still potential for contamination of leachate by elements present in the tailings. In order to test whether these elements mobilise under leach conditions, ICP-MS analysis was conducted on the leachate generated over the 94 days of the biokinetic tests, discussed in Section 5.2.2. Table 15 gives the concentrations of the elements leached in the biokinetic tests from the feed tailings ($S_T$ 3.84%) and sulfide-lean tailings ($S_T$ 0.21%) conducted with and without pH control. The extent of mobilisation of the total element concentrations of the feed and desulfurised tailings during biokinetic leaching, showing leached metal as a % of total metal in the solid fraction, is presented in Figure 33.

The extent of mobility of the majority of elements in the bioleaching tests of both the feed and tailings samples with no pH control exhibited low (10-20%) to negligible (less than 10%) mobilisation. Exceptions to this included manganese (62-77%), zinc (46-100%) and cobalt (95-100%). The extent of mobilisation is governed by primary mineral dissolution as well as secondary attenuation reactions, including precipitation, entrainment and adsorption (Broadhurst, 2007). Although a detailed study of the reaction mechanisms governing element dissolution behaviour is beyond the scope of this project, the trends seen in the results in Table 15 and highlighted in Figure 33 are consistent with predictions in literature (Broadhurst, 2007). Mn, Zn and Co are all known to exhibit low attenuation potential, whereas trace chalcophilic elements
generally exhibit low availability due to precipitation and adsorption reactions.

Table 15: Results of element mobility in biokinetic leach test conditions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Leachable concentration (mg/kg)</th>
<th>Extent of mobilisation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>*Feed tailings</td>
<td>Desulfurised tailings</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*no pH control</td>
</tr>
<tr>
<td>Ca</td>
<td>2806</td>
<td>1786</td>
</tr>
<tr>
<td>Al</td>
<td>283</td>
<td>3.2</td>
</tr>
<tr>
<td>Mg</td>
<td>1352</td>
<td>753</td>
</tr>
<tr>
<td>Mn</td>
<td>1696</td>
<td>1423</td>
</tr>
<tr>
<td>Cr</td>
<td>5.9</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>17.8</td>
<td>9.9</td>
</tr>
<tr>
<td>Zn</td>
<td>257</td>
<td>46.2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>Mo</td>
<td>0.04</td>
<td>0.008</td>
</tr>
<tr>
<td>Co</td>
<td>9.5</td>
<td>5.4</td>
</tr>
<tr>
<td>As</td>
<td>0.48</td>
<td>0.08</td>
</tr>
<tr>
<td>Ag</td>
<td>0.02</td>
<td>0.002</td>
</tr>
<tr>
<td>Cd</td>
<td>0.16</td>
<td>0.06</td>
</tr>
</tbody>
</table>

* final pH of 2.1
$ final pH of 4.9
$ pH controlled at pH 2.0

Figure 33: Extent of element mobility in biokinetic shake flask tests

A comparison of the results of the sulfide-lean tailings for the uncontrolled test (with a final pH of 4.9) and the test controlled at pH 2.0 shows the effect of pH on element mobilisation. The role of pH in controlling element mobility is discussed in literature (Broadhurst, 2007) and is known to enhance primary dissolution as well as control
element attenuation through precipitation and adsorption reactions. The low pH conditions increased mobilisation of all elements to some extent, with greatest increases noted for Al, Zn and As. In particular, at pH 2.0 leachable arsenic was increased to concentrations greater than that of the feed material, despite only 11% As deportment to tailings, as seen in the results in Section 5.3.1.

5.3.3. Effect of desulphurisation on environmental significance

The results in Table 15 describe metal availability under the biokinetic leach conditions, but the data does not provide an indication of the level of threat or toxicity that a mineral waste deposit may have on the environment. The use of an environmental indicator, such as a risk potential factor (RPF) described by Broadhurst and Petrie (2010), provides an opportunity to rank elements based on the environmental significance of their deportment potential. In the absence of site-specific data, the RPF (Eq. 14 in Section 4.5.3) compares available metal concentrations in a sample to naturally acceptable levels, in this case, the average crustal abundance as a proxy measure for background concentration levels and drinking water standards as a proxy measure for water quality standards (Broadhurst and Petrie, 2010). Table 16 classifies the elements mobilised in the biokinetic tests based on their RPF values calculated from the leachable concentrations discussed in Section 5.3.2. Detailed results of RPF calculations are displayed in Appendix A 4.4.

Table 16: Ranking of metal mobility on environmental significance for selected co-elements

<table>
<thead>
<tr>
<th>Environmental Significance</th>
<th>RPF/1000</th>
<th>Feed tailings (S$_T$ 3.84%) final pH 2.1</th>
<th>Sulfide-lean tailings (S$_T$ 0.21%) final pH 4.9</th>
<th>Sulfide-lean tailings Controlled pH 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>High A</td>
<td>1000-10000</td>
<td>Mn</td>
<td>Mn</td>
<td>Mn</td>
</tr>
<tr>
<td>B</td>
<td>100-1000</td>
<td>Ni, Zn</td>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>C</td>
<td>10-10</td>
<td>As, Mo, Cd, Al, Ca, Mg, Cr, Mo, Ag, Pb</td>
<td>As, Mo, Cd, Ni, Zn, Al, Ca, Mg, Cr, Mo, Ag, Pb</td>
<td></td>
</tr>
<tr>
<td>Moderate</td>
<td>0.1-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Negligible</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Following methodology described by Broadhurst and Petrie (2010), in both the feed and desulphurised tailings leachates the only element which posed significant environmental risk was Mn. This is attributed to its high level of mobility at all pH levels tested (pH 2.0 to 4.9), as discussed in Section 5.3.2, coupled with strict requirements for drinking water. As shown in Table 16, all other elements displayed low to negligible environmental risk under the conditions of the three biokinetic tests, indicating that the desulphurisation process did not have an effect on the classification of environmental risk for this particular study.

The calculated RPF values are shown graphically in Figure 34, also indicating the zones of classification. Although there was no change in the RPF classification of
elements during desulfurisation, when comparing the absolute values for the feed and desulfurised tailings a decrease in RPF was seen after desulfurisation. This is particularly notable in chalcophilic metals, such as As, Ag and Cd. The decrease in RPF is affected by deportment behaviour in the flotation process, which showed significant removal of chalcophiles, and by pH, influencing attenuation reactions. Oxidation of sulfides in the feed sample reduced the leachate pH, subsequently mobilising a greater concentration of metals. The effects of pH are particularly noted in the pH controlled sulfide-lean sample, in which the RPF values were significantly increased from the leachate sample at pH 4.9, in some cases to values higher than that of the acid generating feed tailings. This is highlighted for elements such as Al and As, both of which have low attenuation potential but at low pH levels their environmental risk increased two orders of magnitude, as measured by the RPF methodology.

![Figure 34: Trace element risk potential factor (RPF/1000) showing classification](image)

Although this method of ranking elements provides an indication of which elements have the highest risk, the classification is qualitative and the actual environmental threat may be enhanced or reduced based on many factors, mostly around the physical environment, as discussed in Section 2.2. Waste deposits in high rainfall areas has greater permeation and thus greater leaching rates than drier areas, but the increased flows also have a diluting effect on metal concentrations, masking the level of contamination. However, the RPF values have provided an opportunity to compare risk across pH changes, and have highlighted the implications that acidic conditions have on metal mobility and subsequent environmental risk. This becomes an important consideration in tailings disposal management as although the desulfurised tailings are not acid forming, they could still present significant environmental risk if exposed to acidic conditions, negating the positive attributes of AMD mitigation through sulfide removal.
Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

Current methods in AMD prevention typically focus on controlling the processes, or the subsequent remediation, of AMD generation, but are yet to be proved sufficient in preventing long-term environmental burden. Consistent with the principles of pollution prevention (INAP, 2009) and emerging legislative trends, there is a need for new approaches in AMD mitigation to reduce the long-term risk of AMD generation. However, the development of new approaches in waste management to reduce environmental impact is currently limited by a lack of quantitative research in this area (Mitchell, 2000; McCallum and Bruckard, 2009). This is aggravated by the fact that industry has previously relied on historical precedents rather than scientific research in the development of waste management techniques and typically operates with the sole aim of maximising economic value.

In this project, options for developing a conceptual integrated approach to AMD mitigation, through sulfide removal from flotation tailings, have been explored in a laboratory based case study. This study, conducted on a porphyry-type copper sulfide tailings set out to achieve three main objectives in addressing the problem of long-term AMD generation potential in tailings deposits. Firstly, the study explored the feasibility of removing the AMD risks through the physical separation of acid generating sulfides from tailings. Secondly, the study assessed the use of both static and kinetic methods to predict and quantify the benefits of flotation desulfurisation in effectively mitigating AMD generation potential. Lastly, the study aimed to show the environmental significance of desulfurisation by focusing on the deportment of potentially harmful co-elements in a leaching environment.

The key findings of the case study, in light of the objectives mentioned above, are summarised and the methodology used is discussed, as a framework for desulfurisation assessment, in Section 6.1. In Section 6.2 the research hypotheses are interrogated and the significance of this study highlighted and, finally, recommendations for further work are outlined in Section 6.3.

6.1. Outcomes of the case study

The experiments in the case study were carried out on a porphyry-type copper sulfide sample with characteristics typical of conventional tailings. It had a total sulfur content of 3.84%, mostly occurring as pyrite, and was classified as acid forming in preliminary AMD prediction tests. A minor copper content of 0.16% Cu was also identified. The key findings of the experimental case study are discussed below.
6.1.1. Summary of the results of the case study

**Flotation desulfurisation**

Based on findings in literature (Section 2.3.2), flotation was selected for the physical removal of sulfides from the tailings sample described above. Step-wise batch flotation tests with a dithiophosphate collector showed that in 4 stages, the addition of a total of 36 g/ton of collector enabled the removal of over 95% of total sulfur ($S_T$), leaving the bulk (90% of total mass) of the tailings with a $S_T$ content of just 0.21%. The case study conducted here also highlighted opportunities to recover minor valuable minerals by making use of the difference in flotation rates between pyrite and chalcopyrite. On this basis, a value rich product with a copper content of 6% and a sulfide content of 21% was generated in an initial flotation stage, prior to the separation of tailings into sulfide-rich and sulfide-lean fractions. Thus, opportunities are created to develop tailings desulfurisation processes which minimise environmental burden whilst maximising economic return on investment.

**AMD prediction**

Prediction of the AMD potential of the sulfide lean tailings, as a method of quantifying the benefit of the desulphurisation process, was carried out with both static and biokinetic tests. Static testing methods included acid base accounting (ABA) and net acid generation (NAG) tests. ABA showed that desulphurised tailings containing 0.21% $S_T$ were non acid forming, with a NAPP of -22.3 kg $H_2SO_4$/ton, compared with feed tailings NAPP of 94.8 kg $H_2SO_4$/ton. The samples had an average acid neutralisation capacity (ANC) across the feed and desulphurised tailings of 24.9 ±3.57 kg $H_2SO_4$/ton, which remained unaffected by the flotation process. The results of the net acid generation tests provided validation of the classification of tailings samples. However, the two static tests were carried out on a different basis and thus the NAG did not add to the quantitative assessment of AMD potential. Kinetic NAG tests provided qualitative insight into the potential kinetics of sulfide oxidation, but they were limited in their ability to predict relative rate information between acid consuming and acid generating processes. They also did not consider the microbial influence on AMD generation.

The development of a biokinetic test based on standard shake flask tests used in bioleaching studies both validated and complemented the static chemical tests, by providing further insight into the relative rates of acid generating and acid consuming reactions in a microbially oxidising environment. Although the biokinetic test results confirmed that the desulphurised tailings were non acid forming, they also showed that the extent to which the sample is considered acid neutralising, as determined by the static AMD prediction tests, may be misleading, as readily soluble acid consuming minerals could be leached and transported from a deposit before the onset of sulfide oxidation. The use of a pH controlled biokinetic test also provided insight into the enhanced reactivity of desulphurised tailings in acidic conditions, particularly in terms of increased metal mobility, as discussed in the following section.
Co-element deportment and environmental risk

The use of biokinetic tests provided suitable leachate for the study of mobility and environmental risk of co-existent elements, which frequently occur in acidic leachate from tailings deposits at elevated and potentially harmful concentration levels. The deportment and associated environmental risk of selected elements was evaluated through chemical analyses of the solid tailings and biokinetic leach liquors, and subsequent ranking and scoring of relative environmental risk, under the biokinetic leach conditions, using risk potential factors (RPF). Co-element RPF was calculated on the basis of leachable concentrations, drinking water standards (as a proxy measure of environmentally acceptable concentration levels) and average crustal abundance (as a proxy measure of background concentration levels), in accordance with the method developed by Broadhurst and Petrie (2010).

The results highlighted that the desulfurisation process had little effect on the concentrations of major and minor lithophilic (silicate and oxide forming) elements, many of which determine the acid neutralising capacity (ANC) of sulfide tailings. This is consistent with the findings of the ABA prediction tests, which showed that the ANC of the various porphyry-copper tailings samples remained constant, regardless of the extent of desulfurisation. In contrast, trace chalcophilic (sulfide forming) elements showed partial deportment to both tailings fractions, thus significantly reducing the concentration of these elements, which include many of the environmentally significant elements, such as Pb, Mo, Cd, Ag and As, in the desulfurised tailings. Also, the higher pH values in the leach solutions generated during the biokinetic leaching of desulfurised tailings (final pH of 4.9 relative to the feed tailings of final pH 2.1) reduced the mobility of the majority of elements.

The use of risk potential factors (RPF) showed that the combined effects of partial deportment and reduced leachability resulted in a general decrease in the environmental risks associated with co-elements for the desulfurised tailings, particularly in the case of Al, Zn and, to a greater extent, As. A notable exception was manganese. Consistent with previous findings (Broadhurst et al 2007), manganese was found to be highly leachable under all pH conditions, and posed a significant risk to the environmental in both the feed and desulfurised tailings. The results also highlighted the extent to which the leachability and thus the environmental risk of co-elements is enhanced with exposure to acidic conditions, even after desulfurisation.

6.1.2. A generalised framework for the assessment of tailings desulfurisation for AMD mitigation

The methods used in this case study have produced well characterised tailings, which are segregated and classified into bulk tailings with no AMD generation potential and a low volume residue requiring containment or treatment. These methods can be further developed into a generic approach for the systematic assessment of the viability of
options for mitigating AMD potential from sulfide tailings on a case-by-case basis. The proposed approach outlined in Figure 35, consists of four main areas, namely, tailings characterisation, evaluation of suitable sulfide separation techniques, laboratory scale AMD prediction and environmental risk assessment.

Each area of assessment applies scientific techniques or tools, typical examples of which are outlined in Figure 35. These are discussed in further detail below.

**Tailings characterisation**

Conventionally, tailings characterisation has been based only on requirements for compliance (McCallum and Bruckard, 2009). Research by Broadhurst (2007) and Maluleke (2006) looked at sulfide content, taking into account AMD potential and economic value, as well as mineralogy and metal distribution for porphyry-type tailings and has shown that thorough characterisation is required to predict environmental performance. In this case study, mineralogy by XRD provided semi-quantitative identification of sulfide minerals of value and acid generating potential, as well as gangue minerals with neutralisation potential. XRD lacks sensitivity for low concentrations (less than 2-3%), and thus is only considered acceptable for primary assessment. However, in conjunction with techniques such as atomic absorption spectrometry (AAS), LECO sulfur analysis and inductively coupled plasma-mass spectrometry (ICP-MS), which provide detailed elemental analysis, further characterisation is possible. Sample characterisation could be enhanced through mineral speciation across size distributions, sequential chemical extraction (SCE) to study mineral behaviour (Maluleke, 2006), sulfur speciation for ore bodies in which sulfur exists in different forms, as well as detailed mineralogical tools, such as scanning electron microscopy (SEM). These enhanced tests were not conducted in this study as
the tailings samples had been previously well characterised, but they should be considered for a poorly characterised sample.

**Sulfide separation**

The case study has shown that the separation of sulfides to produce bulk tailings of low sulfide content has direct positive effects in mitigating long-term AMD potential, as well as improving trace value recovery. Although this work focused on the use of flotation for desulfurisation, there are a number of other physical methods, including size, gravity and magnetic separations, which can be used to target specific minerals, either of value or environmental significance, enabling the design of tailings for long-term surety. Methods should be assessed in each site specific case, as they could show varying potential for different ore types. Sulfide separation techniques to produce bulk sulfide-lean tailings, removing the majority of sulfides to a concentrated stream, have been the subject of world-wide research (Benzaazoua et al., 2008; Napier-Munn et al., 2008; McCallum and Bruckard, 2009), including the development of a systematic methodology for the assessment and beneficiation of tailings, namely the diagnostic separation of sulfide tailings (DSST), as described by McCallum and Bruckard (2009).

**Acid mine drainage prediction**

AMD prediction tests carried out in the case study have shown that static tests can adequately classify a sample, but have a large associated region of uncertainty. Further, to get an in-depth understanding of the long-term behaviour of tailings, kinetic testing is required. The biokinetic shake flask test developed offers a viable alternative to standard kinetic tests, such as humidity cell and leach column tests, providing confirmatory AMD classification as well as useful information on the relative rates of acid generating and consuming reactions under microbial oxidation conditions in comparatively short experimental time frames of 2 to 3 months.

**Environmental risk assessment**

Further assessment is required in order to assess the potential environmental risk associated with AMD generation, as discussed in Section 2.2, typically caused by acidic conditions and high concentrations of metals and sulfate salts in solution. In this case study, elemental analysis by ICP-MS was used to evaluate co-element deportment during flotation desulfurisation, as well as leachability under biokinetic test conditions. A screening assessment of relative environmental risk was subsequently conducted through the application of risk potential factors (RPF), in accordance with the methodology described by Broadhurst and Petrie (2010). Although it was beyond the scope of this case study, it is recognised that a comprehensive environmental risk assessment requires quantitative prediction of the time-related generation and dispersion of contaminants. This entails site-specific predictive modelling supported by detailed empirical data and information, as discussed by Hansen et al. (2008).
6.2. Concluding remarks

The overall objective of this thesis was to explore the feasibility of an integrated approach for tailings management through the mitigation of the long-term environmental risk of AMD by sulfide removal from tailings. The approach taken in this thesis addressed the overall objective with a case study, which has outlined a systematic approach and the tools needed to assess options for effective desulfurisation to aid in the development of an integrated cleaner production solution to the long-term mitigation of AMD.

6.2.1. Validation of the hypotheses

This thesis aimed to explore two main hypotheses in meeting the overall objective, as described in Chapter 3. The hypotheses are reiterated and discussed here.

The long-term AMD risks associated with sulfide tailings can be effectively prevented by removing sulfides prior to disposal using flotation techniques.

The study has shown that flotation provided an effective method for sulfide removal and produced desulfurised tailings containing just 0.21% $S_T$, with the majority of sulfides concentrated in a low volume stream of 10% of the total mass processed. The removal of sulfides from the tailings significantly reduced the maximum potential acidity by sulfide oxidation from 118 to 6.4 kg $H_2SO_4/ton$. The flotation results also showed that opportunities to recover further value from tailings are potentially feasible with flotation optimisation in a two step process.

The combined application of both laboratory-scale static and biokinetic prediction methods is required to provide adequate assessment of the long-term benefits of flotation desulfurisation in mitigating AMD related environmental risk.

The development of a biokinetic AMD prediction test has enabled a detailed assessment of the relative kinetics of acid generating and consuming reactions under microbial leach conditions. The classification of AMD potential was consistent with the findings of standard chemical static prediction tests. The combination of kinetic and static prediction test results effectively described AMD potential, and highlighted the non acid forming potential of desulfurised tailings produced through flotation. The kinetic tests have further shown the importance of understanding the relative time scales of acid generation and consumption within long-term AMD formation. The kinetic tests also allowed investigation co-element mobility under a range of pH conditions, assessing the potential for environmental risk. Although there was reduced risk for the majority of elements, owing to moderate pH levels from a reduction in acid generation, not all risk was removed, in this case manganese. This highlighted the importance of thorough characterisation in assessing, and thus mitigating, environmental risk.
6.2.2. Significance of this study

The holistic approach taken in this case study of desulfurisation, whereby waste is treated within the process system boundaries, has provided a set of tools which can be generically applied for the assessment of site specific scenarios for the prevention of long-term AMD generation, thereby removing environmental risk rather than managing it. The design of well characterised, segregated tailings enables more informed decision making in the development of new waste management strategies for long-term AMD mitigation, to maximise resource use and value recovery, whilst minimising environmental burden.

This research is consistent with the latest trends in world wide research to improve the sustainable approach to minerals processing where there is a need for broader thinking. It is in line with the philosophies of the Minerals-to-Metals Research Initiative at the University of Cape Town, under which this project has been conducted. Research focuses on the importance of planning for closure, and supports the need for integration of waste management to ensure environmental security and reduce legislation enforced remediation or post closure mitigation costs (Warhurst and Noronha, 2000).

6.3. Recommendations for further work

As discussed in Chapter 3, the scope of this project focused on a proof-of-concept for the application of flotation in the effective desulfurisation of tailings and mitigation of the associated environmental risks of AMD. As such, the methods used in the case study did not attempt to optimise the desulfurisation process nor provide detailed evaluation of the implementation of desulfurisation in a waste management strategy. However, the findings and methodologies of the study provide motivation and guidance for further developmental and optimisation work, covering both site specific application of the approach, as well as fundamental research and development.

Recommendations for site specific studies

The unique characteristics of ores and related beneficiation processes in the mining industry require consideration of site specific factors to validate the commercial application of the approach and methodologies presented in this work. Site specific studies will provide scope for the development of flowsheet options for the integration of sulfide removal from tailings into the beneficiation process, thus optimising conventional processing techniques for maximum economic benefit, whilst minimising environmental burden. A site specific study will also provide opportunity for the downstream management of separated tailings fractions. This will include consideration of responsible disposal methods, such as backfilling or co-disposal techniques discussed in Section 2.3.1, as well as potential for resource recovery, process recycling and by-products in an integrated waste management scheme, such as that proposed by Chan et al. (2008). Flowsheet development should include an economic analysis to
provide motivation for the selection of a proposed approach to waste management. An economic assessment of desulfurisation feasibility should compare the costs of desulfurisation with conventional disposal options and AMD remediation, as well as assessing possible revenue through by-products. The benefits of industrial collaboration for the development of integrated waste management techniques has been highlighted, by example, in work by Benzaazoua et al. (2008) and Demers et al. (2008).

**Fundamental research and development**

Recommendations for fundamental research include the further development and refinement of some of the tools and techniques which support the protocol for the assessment of desulfurisation opportunities (shown in Figure 35, Section 6.1.2).

Further development of alternative physical separation techniques for sulfide removal from tailings is recommended, such as screening or classification based on size class. Application of such techniques, either as an alternative or in combination with flotation may reduce reagent and other operating costs associated with flotation desulfurisation.

The biokinetic tests developed in this study also require further research and development. Whilst they provide valuable data on the relative kinetics, the low initial pH used to enhance microbial activity, and thereby reduce the time scales of the tests, affects the ability to interpret kinetic data. The batch tests also do not represent an open flow-through system, as found in mineral waste deposits, adequately. Refinement of these tests across a range of samples and through the introduction of semi-batch or continuous tests will focus interpretations of the results and assist in developing a test which can be used with confidence for kinetic AMD prediction. A study of the relationships between the biokinetic tests and chemical AMD prediction tests, such as the kinetic NAG test and the acid buffering characteristic curve (ABCC), is also recommended.
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A 1 CHEMICAL CHARACTERISATION

A 1.1. Analysis methods

A 1.1.1. Total acid digestion for AAS and ICP-MS

i. Weigh approx. 0.1g sample into 250ml Erlenmeyer flask

ii. Add 10ml HCl/Hf mixture in ratio 4:1 to flask and heat to boiling

iii. Add 10ml HNO₃ to flask and boil until vol. approx. 2ml

iv. Add 5ml HClO₄ and boil until vol. approx. 2ml.

v. For ICP-MS, step iv. is repeated twice with HNO₃ to remove trace Cl.

vi. Make up volume to 100ml, filter with Whatman no. 1 filter paper.

Analysis by AAS: %Me = R (ppm) / [100 * mass sample (g)]

A 1.1.2. Mineralogical characterisation by X-ray diffraction (XRD)

The mineralogical composition of samples was analysed by the Department of Geology at the University of Pretoria using X-ray diffraction (XRD). The samples were prepared for XRD analysis using a back loading preparation method and were analysed with a PANalytical X’Pert Pro powder diffractometer with X’Celerator detector. The phases were identified using X’Pert Highscore Plus software.

A 1.2. Tailings sample characterisation results

Table A1: XRD data of ore sample (Dept. of Geology, University of Pretoria)

<table>
<thead>
<tr>
<th></th>
<th>wt%</th>
<th>(3sigma)</th>
<th>Description</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almandine</td>
<td>2.82</td>
<td>0.69</td>
<td>Garnet</td>
<td>Fe₃Al₂(SiO₄)₃</td>
</tr>
<tr>
<td>Biotite</td>
<td>8.51</td>
<td>2.7</td>
<td>phyllosilicate</td>
<td>K(Mg, Fe)₂AlSi₃O₁₀(F, OH)₂</td>
</tr>
<tr>
<td>Calcite</td>
<td>2.95</td>
<td>1.02</td>
<td>carbonate</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>1.95</td>
<td>0.42</td>
<td>sulfide</td>
<td>CuFeS₂</td>
</tr>
<tr>
<td>Chlorite</td>
<td>3.48</td>
<td>1.86</td>
<td>phyllosilicate</td>
<td>(Mg,Fe,Ni,Mn,Al)Al₂Si₅O₁₀(OH)₈</td>
</tr>
<tr>
<td>Diopside</td>
<td>1.47</td>
<td>0.9</td>
<td>pyroxene</td>
<td>MgCaSi₂O₆</td>
</tr>
<tr>
<td>Microcline</td>
<td>3.08</td>
<td>0.81</td>
<td>Feldspar</td>
<td>KAlSi₅O₈</td>
</tr>
<tr>
<td>Pyrite</td>
<td>11.45</td>
<td>0.72</td>
<td>sulfide</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Quartz</td>
<td>64.29</td>
<td>2.82</td>
<td>silicate</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>
Table A2: Feed sample variance in $S_T$, Fe and Cu analysis.

<table>
<thead>
<tr>
<th>Sample no</th>
<th>$S_T$ % (LECO)</th>
<th>Fe % (AAS)</th>
<th>Cu % (AAS)</th>
<th>Chalco % (calc)</th>
<th>Pyrite % (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.60</td>
<td>9.11</td>
<td>0.149</td>
<td>0.432</td>
<td>6.60</td>
</tr>
<tr>
<td>2</td>
<td>4.28</td>
<td>8.80</td>
<td>0.130</td>
<td>0.374</td>
<td>7.89</td>
</tr>
<tr>
<td>3</td>
<td>4.06</td>
<td>8.69</td>
<td>0.111</td>
<td>0.320</td>
<td>7.50</td>
</tr>
<tr>
<td>4</td>
<td>4.26</td>
<td>8.95</td>
<td>0.144</td>
<td>0.415</td>
<td>7.84</td>
</tr>
<tr>
<td>5</td>
<td>3.87</td>
<td>11.0</td>
<td>0.159</td>
<td>0.459</td>
<td>7.09</td>
</tr>
<tr>
<td>6</td>
<td>3.77</td>
<td>8.66</td>
<td>0.184</td>
<td>0.531</td>
<td>6.88</td>
</tr>
<tr>
<td>7</td>
<td>3.83</td>
<td>8.61</td>
<td>0.186</td>
<td>0.537</td>
<td>6.99</td>
</tr>
<tr>
<td>8</td>
<td>3.73</td>
<td>8.65</td>
<td>0.193</td>
<td>0.557</td>
<td>6.80</td>
</tr>
<tr>
<td>9</td>
<td>4.76</td>
<td>8.71</td>
<td>0.169</td>
<td>0.489</td>
<td>8.75</td>
</tr>
<tr>
<td>10</td>
<td>3.55</td>
<td>7.36</td>
<td>0.176</td>
<td>0.508</td>
<td>6.48</td>
</tr>
<tr>
<td>11</td>
<td>3.85</td>
<td>7.43</td>
<td>0.183</td>
<td>0.527</td>
<td>7.03</td>
</tr>
<tr>
<td>12</td>
<td>3.37</td>
<td>7.15</td>
<td>0.256</td>
<td>0.738</td>
<td>6.07</td>
</tr>
<tr>
<td>13</td>
<td>3.67</td>
<td>8.97</td>
<td>0.206</td>
<td>0.594</td>
<td>6.68</td>
</tr>
<tr>
<td>14</td>
<td>3.56</td>
<td>5.40</td>
<td>0.140</td>
<td>0.404</td>
<td>6.53</td>
</tr>
<tr>
<td>15</td>
<td>3.28</td>
<td>5.20</td>
<td>0.150</td>
<td>0.433</td>
<td>6.00</td>
</tr>
<tr>
<td>16</td>
<td>3.80</td>
<td>6.70</td>
<td>0.168</td>
<td>0.486</td>
<td>6.95</td>
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<tr>
<td>17</td>
<td>4.00</td>
<td>7.74</td>
<td>0.078</td>
<td>0.226</td>
<td>7.41</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>3.84</strong></td>
<td><strong>8.07</strong></td>
<td><strong>0.164</strong></td>
<td><strong>0.472</strong></td>
<td><strong>7.03</strong></td>
</tr>
</tbody>
</table>

*Standard deviation

Please see Appendix A 3.4 for ICP-MS elemental analysis of co-metals in sample.
A 2  FL OTATION EX PERIMENTS

A 2.1.  Milling curve
Milling curve as established to find time for approximately 70% passing 150 µm, as specified by Reddick et al. (2009).

![Milling curve graph]

Figure A1: Milling curve developed to find grind time for 70% passing 150 µm

A 2.2.  Single stage flotation experimental details

Table A3: Single stage flotation conditions

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Porphyry Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of ore</td>
<td>1.13 kg</td>
</tr>
<tr>
<td>Milling: Time</td>
<td>7 min 44 s</td>
</tr>
<tr>
<td>Water addition</td>
<td>600 ml</td>
</tr>
<tr>
<td>Impeller speed</td>
<td>1200 rpm</td>
</tr>
<tr>
<td>Collector:</td>
<td>Cytec S-8985</td>
</tr>
<tr>
<td>Concentration (g/ton)</td>
<td>12, 15, 27, 36</td>
</tr>
<tr>
<td>Conditioning time</td>
<td>2 min</td>
</tr>
<tr>
<td>Frother: (stage 1)</td>
<td>MIBC</td>
</tr>
<tr>
<td>Concentration</td>
<td>30 g/ton</td>
</tr>
<tr>
<td>Conditioning time</td>
<td>1 min</td>
</tr>
<tr>
<td>Aeration rate</td>
<td>5 l/min</td>
</tr>
<tr>
<td>pH of Feed</td>
<td>not adjusted (~6)</td>
</tr>
<tr>
<td>Total Float time (min)</td>
<td>15 min</td>
</tr>
</tbody>
</table>
Table A4: Experimental procedure for a bulk sulfide float

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Feed sample and pH</td>
</tr>
<tr>
<td>2</td>
<td>S-8985 Addition</td>
</tr>
<tr>
<td>3</td>
<td>MIBC Addition</td>
</tr>
<tr>
<td>4</td>
<td>Air on</td>
</tr>
<tr>
<td>6</td>
<td>Concentrate(C)1 collection</td>
</tr>
<tr>
<td>9</td>
<td>C2 collection</td>
</tr>
<tr>
<td>13</td>
<td>C3 collection</td>
</tr>
<tr>
<td>18</td>
<td>C4 collection, air off</td>
</tr>
<tr>
<td>18</td>
<td>T1 and 2 sample</td>
</tr>
</tbody>
</table>

All samples were oven dried at 70°C and representatively sampled for analysis.

A 2.3. Multi stage flotation experimental details

Table A5: Multi-stage flotation experimental conditions

<table>
<thead>
<tr>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore: Porphyry Cu</td>
</tr>
<tr>
<td>Mass of ore 1.13 kg</td>
</tr>
<tr>
<td>Milling: Time 7 min 44 s</td>
</tr>
<tr>
<td>Water addition 600 ml</td>
</tr>
<tr>
<td>Impeller speed 1200 rpm</td>
</tr>
<tr>
<td>Collector: Cytec S-8985</td>
</tr>
<tr>
<td>Concentration 9 g/ton</td>
</tr>
<tr>
<td>Conditioning time 2 min</td>
</tr>
<tr>
<td>Frother: MIBC</td>
</tr>
<tr>
<td>Concentration 30 g/ton</td>
</tr>
<tr>
<td>Conditioning time 1 min</td>
</tr>
<tr>
<td>Aeration rate 5 l/min</td>
</tr>
<tr>
<td>pH of Feed not adjusted (~6)</td>
</tr>
<tr>
<td>Total Float time (min) 8 + 5 + 5 + 5</td>
</tr>
</tbody>
</table>
Table A6: Multi stage flotation experimental procedure

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Feed sample, pH</td>
</tr>
<tr>
<td></td>
<td>Collector addition 1</td>
</tr>
<tr>
<td>2</td>
<td>Frother addition</td>
</tr>
<tr>
<td>3</td>
<td>Air on</td>
</tr>
<tr>
<td>4</td>
<td>C1</td>
</tr>
<tr>
<td>5</td>
<td>C2</td>
</tr>
<tr>
<td>8</td>
<td>C3</td>
</tr>
<tr>
<td>11</td>
<td>C4, Air off, TAILINGS SAMPLE 1</td>
</tr>
<tr>
<td>0</td>
<td>Collector addition 2</td>
</tr>
<tr>
<td>2</td>
<td>Air on</td>
</tr>
<tr>
<td>7</td>
<td>C5, Air off, TAILINGS SAMPLE 2</td>
</tr>
<tr>
<td>0</td>
<td>Collector addition 3</td>
</tr>
<tr>
<td>2</td>
<td>Air on</td>
</tr>
<tr>
<td>7</td>
<td>C6, Air off, TAILINGS SAMPLE 3</td>
</tr>
<tr>
<td>0</td>
<td>Collector addition 4</td>
</tr>
<tr>
<td>2</td>
<td>Air on</td>
</tr>
<tr>
<td>7</td>
<td>C7, Air off, TAILINGS SAMPLE 4</td>
</tr>
</tbody>
</table>
A 3 AMD PREDICTION METHODS

A 3.1. Acid neutralising capacity (ANC) methods

A 3.1.1. Fizz rating

Approximately 0.5 g sample is reacted with 1-2 drops of 25% HCl. The reaction of carbonates within the sample is noted by an audible/visible fizz. The intensity of the fizzing is rated based on Table A7 for selection of HCl concentration and volume and NaOH concentration for use in ANC tests. If initial pH after acid digestion is outside of range pH 0.8-1.5, fizz rating must be adjusted accordingly.

Table A7: Fizz rating for acid and base requirements for ANC tests

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fizz Rating</th>
<th>HCl molarity (M)</th>
<th>HCl volume (ml)</th>
<th>NaOH molarity (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>0.5</td>
<td>4</td>
<td>0.1</td>
</tr>
<tr>
<td>Slight</td>
<td>1</td>
<td>0.5</td>
<td>8</td>
<td>0.1</td>
</tr>
<tr>
<td>Moderate</td>
<td>2</td>
<td>0.5</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>Strong</td>
<td>3</td>
<td>0.5</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>Very strong</td>
<td>4</td>
<td>1.0</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbonate</td>
<td>5</td>
<td>1.0</td>
<td>60</td>
<td>0.5</td>
</tr>
</tbody>
</table>

A 3.1.2. $\text{H}_2\text{O}_2$ siderite correction ANC test

Acid Digestion

i. Weigh duplicate samples of 2 g into 250 ml Erlenmeyer flasks.

ii. Add HCl according to fizz rating and make up to 100 ml with de-ionised water.

iii. Boil for 5 min

Back titration

i. Allow to cool and filter solution.

ii. Confirm liquor pH is between 0.8 and 1.5, according to fizz rating

iii. Using a burette, back titrate liquor to pH 4.5, recording NaOH addition.

iv. Add 5 ml 30% $\text{H}_2\text{O}_2$ and boil for another 5min

v. Back titrate to pH 7

vi. Leave solution for 24 hours

vii. Check pH and back titrate to pH 7.

viii. Add a further 5 ml $\text{H}_2\text{O}_2$, boil for 5 min.
ix. Repeat steps v. to viii. over 72 hours.

ANC is calculated by:

$$\text{ANC} = \frac{\text{Vol}_{\text{HCl}} \times M_a - \text{Vol}_{\text{NaOH}} \times C \times 49}{W}$$

Where $M_a$ is the molarity of HCl (M), $M_b$ is the molarity of NaOH (M), W is weight of sample (g) and $C = (M_a \times \text{Vol}_{\text{HCl}} \text{ in blank})/(\text{Vol}_{\text{NaOH}} \text{ titrated in blank})$ to take into account the differences in stoichiometry in the acid and base solutions.

**A 3.2. Net acid generation (NAG) test methods**

*Note: H$_2$O$_2$ must be at room temperature. Ensure that pH of H$_2$O$_2$ is > pH 4.5. Adjust with NaOH if necessary. Pyrite oxidation is an exothermic reaction, and solutions can "boil over". Caution must be taken.*

**A 3.2.1. Single addition NAG test**

i. Weigh 1.25 g sample into 250ml Erlenmeyer flask.

ii. Add 125ml 15% H$_2$O$_2$, cover, and allow to react for 24h in a fume hood.

iii. Measure pre-boil pH.

iv. Heat solution until effervescence stops or for a minimum of 2 hours.

v. Allow to cool, make up volume to 125ml with de-ionised water.

vi. Record after-boil pH.

vii. Filter, retaining solids residue and liquor.

viii. Back titrate with NaOH recording volume added at pH 4.5 and pH 7.

NAG is calculated by:

$$\text{NAG} = \frac{49 \times V \times M}{W}$$

Where $V = \text{vol. NaOH (ml)}$; $M = \text{molarity of NaOH}$ and $W = \text{weight of sample (g)}$.

**A 3.2.2. Sequential NAG test**

i. Carry out single addition NAG test as stage 1 of sequential NAG

ii. Repeat steps ii. to viii. on solid residue.

iii. Repeat until no effervescent reaction is seen and after-boil NAG pH is > pH 4.5.
A 3.3.  Biokinetic test methods

A 3.3.1.  Shake flask tests

All shake flask tests were conducted in triplicate.

i. Add 150ml autotrophic basal salts (ABS) solution to 250 ml Erlenmeyer flask.
ii. Fit a cotton wool bung, cover with foil and autoclave to sterilise ABS solution.
iii. After cooling, weigh in 7.5 g tailings sample to each flask.
iv. Inoculate with 0.75 ml mixed culture of iron and sulfur oxidising microorganisms.
v. Measure Redox potential and ensure pH is at 2.0, adjusting with H₂SO₄ if necessary.
vi. Weigh each flask and place in shaking incubator at 150 rpm at 37°C.
vii. Before sampling, weigh flask. Top up with de-ionised water to account for water loss by evaporation.
viii. Record pH, redox, ferrous and total iron concentrations every 2-4 days.

For the controlled pH test, at each pH measurement, if the pH has increased titrate with H₂SO₄ back to pH 2, recording the volume and molarity of acid added.

Ferrous assay is conducted following the 1-10 phenanthroline method (Komadel and Stucki 1988).

A 3.3.2.  Population density by viable plate counts

Viable plate counts using serial dilutions (Miles and Misra, 1938) were conducted on each sample after 6 weeks of testing.

i. Pipette 0.1 ml of leach solution into 0.9 ml ABS in a reaction tube and mix.
ii. Pipette 0.1 ml of the diluted solution from step i. into 0.9 ml ABS in a 2nd tube.
iii. Repeat for 6 dilutions.
iv. Spot 10 µm of each dilution onto gelled media (Johnson and McGuiness, 1991).
v. Place in incubator at 37°C until growth is noted.
vi. Using a microscope, count individual colonies in each spot.

Assuming each individual colony is grown from a single microbe, population density can be calculated, and verified, for each dilution.
A 4 EXPERIMENTAL RESULTS

A 4.1. Flotation results

A 4.1.1. Single stage flotation results

Table A8: Single stage flotation mass balance results at varying collector addition

<table>
<thead>
<tr>
<th></th>
<th>12g/ton</th>
<th>Total Mass (g)</th>
<th>S %</th>
<th>Fe %</th>
<th>Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>1091.5</td>
<td>4.16</td>
<td>8.95</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Concentrate</td>
<td>26.85</td>
<td>26</td>
<td>22</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Tailings</td>
<td>1064.7</td>
<td>3.58</td>
<td>8.63</td>
<td>0.078</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>15g/ton</th>
<th>Total Mass (g)</th>
<th>S %</th>
<th>Fe %</th>
<th>Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>1105.5</td>
<td>4.28</td>
<td>8.8</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Concentrate</td>
<td>54.98</td>
<td>35</td>
<td>32</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Tailings</td>
<td>1037.1</td>
<td>2.2</td>
<td>7.86</td>
<td>0.029</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>27g/ton</th>
<th>Total Mass (g)</th>
<th>S %</th>
<th>Fe %</th>
<th>Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>1128.1</td>
<td>3.73</td>
<td>8.65</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Concentrate</td>
<td>99.36</td>
<td>35</td>
<td>27</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Tailings</td>
<td>1019.4</td>
<td>1.1</td>
<td>7.17</td>
<td>0.074</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>36g/ton*</th>
<th>Total Mass (g)</th>
<th>S %</th>
<th>Fe %</th>
<th>Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>1094 ±15.6</td>
<td>3.64 ±0.51</td>
<td>6.51 ±1.7</td>
<td>0.11 ±0.05</td>
<td></td>
</tr>
<tr>
<td>Concentrate</td>
<td>89.61 ±3.73</td>
<td>40 ±1.2</td>
<td>27 ±2.1</td>
<td>1.5 ±0.09</td>
<td></td>
</tr>
<tr>
<td>Tailings</td>
<td>1004.6 ±11.8</td>
<td>0.66 ±0.03</td>
<td>5.72 ±0.96</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

*Standard deviation, n=2

A 4.1.2. Multi-stage flotation mass balance results

<table>
<thead>
<tr>
<th></th>
<th>Pyrite (g)</th>
<th>Chalcopyrite (g)</th>
<th>Total mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeat</td>
<td>1 2 3</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>Feed</td>
<td>75.0 51.9 77.7</td>
<td>4.9 3.52 4.11</td>
<td>1098 1076 1081</td>
</tr>
<tr>
<td>1</td>
<td>4.03 7.48 3.11</td>
<td>3.51 1.93 2.82</td>
<td>17.44 17.74 15.31</td>
</tr>
<tr>
<td>2</td>
<td>41.6 30.7 34.9</td>
<td>4.03 2.65 3.62</td>
<td>62.64 71.41 53.22</td>
</tr>
<tr>
<td>3</td>
<td>68.1 45.8 67.6</td>
<td>4.30 2.85 3.99</td>
<td>103.0 93.84 95.96</td>
</tr>
<tr>
<td>4</td>
<td>47.9 48.5 74.0</td>
<td>4.40 2.93 4.11</td>
<td>116.1 101.2 113.8</td>
</tr>
<tr>
<td>Tail</td>
<td>3.12 3.37 3.71</td>
<td>0.507 0.59 0</td>
<td>982.2 974.5 967.1</td>
</tr>
</tbody>
</table>
A 4.2. Acid base accounting (ABA) results

Table A9: ABA results

<table>
<thead>
<tr>
<th>S %</th>
<th>MPA (kg H₂SO₄/ton)</th>
<th>NaOH addition (ml)</th>
<th>ANC (kg H₂SO₄/ton)</th>
<th>NAPP (kg H₂SO₄/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.84 ± 0.34</td>
<td>118 ± 10.5</td>
<td>17.5</td>
<td>18.9</td>
<td>97.4 ± 14.3</td>
</tr>
<tr>
<td>3.73 ± 0.34</td>
<td>114 ± 10.3</td>
<td>17.9</td>
<td>27.5</td>
<td>86.7 ± 14.1</td>
</tr>
<tr>
<td>2.9 ± 0.26</td>
<td>88.7 ± 8.0</td>
<td>16.7</td>
<td>23.5</td>
<td>65.2 ± 11.8</td>
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<tr>
<td>2.2 ± 0.20</td>
<td>67.3 ± 6.1</td>
<td>18.1</td>
<td>25.0</td>
<td>42.3 ± 9.8</td>
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<tr>
<td>1.1 ± 0.10</td>
<td>33.7 ± 3.0</td>
<td>17.7</td>
<td>28.2</td>
<td>5.49 ± 6.8</td>
</tr>
<tr>
<td>0.97 ± 0.09</td>
<td>29.7 ± 2.7</td>
<td>16.65</td>
<td>24.4</td>
<td>5.25 ± 6.5</td>
</tr>
<tr>
<td>0.69 ± 0.03</td>
<td>21.0 ± 1.0</td>
<td>17.4</td>
<td>20.7</td>
<td>0.32 ± 4.8</td>
</tr>
<tr>
<td>0.65 ± 0.06</td>
<td>19.9 ± 1.8</td>
<td>18.15</td>
<td>25.5</td>
<td>-5.60 ± 5.6</td>
</tr>
<tr>
<td>0.3 ± 0.03</td>
<td>9.18 ± 0.8</td>
<td>16.75</td>
<td>22.5</td>
<td>-13.3 ± 4.6</td>
</tr>
<tr>
<td>0.22 ± 0.02</td>
<td>6.73 ± 0.6</td>
<td>17.4</td>
<td>31.8</td>
<td>-25.0 ± 4.4</td>
</tr>
<tr>
<td>0.21 ± 0.02</td>
<td>6.43 ± 0.6</td>
<td>16.55</td>
<td>25.6</td>
<td>-19.2 ± 4.1</td>
</tr>
</tbody>
</table>

Average ANC = 24.9 ± 3.57 kg H₂SO₄/ton.

A 4.3. Net acid generation (NAG) results

Table A10: Sequential NAG results

<table>
<thead>
<tr>
<th>S %</th>
<th>3.84%</th>
<th>2.9%</th>
<th>0.97%</th>
<th>0.65%</th>
<th>0.3%</th>
<th>0.21%</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAG pH</td>
<td>2.77 ± 0.22</td>
<td>2.61</td>
<td>2.84</td>
<td>3.00</td>
<td>4.01</td>
<td>5.71 ± 0.52</td>
</tr>
<tr>
<td>NAGₚH₄.₅</td>
<td>17.35 ± 11.8</td>
<td>19.69</td>
<td>8.47</td>
<td>4.65</td>
<td>0</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>NAGₚH₇</td>
<td>27.95 ± 6.30</td>
<td>27.89</td>
<td>12.18</td>
<td>7.24</td>
<td>1.54</td>
<td>1.00 ± 0.02</td>
</tr>
<tr>
<td>NAG pH</td>
<td>2.31 ± 0.15</td>
<td>2.56</td>
<td>3.15</td>
<td>3.11</td>
<td>4.60</td>
<td></td>
</tr>
<tr>
<td>NAGₚH₄.₅</td>
<td>54.92 ± 3.44</td>
<td>35.54</td>
<td>12.18</td>
<td>11.38</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>NAGₚH₇</td>
<td>70.15 ± 1.46</td>
<td>49.76</td>
<td>17.47</td>
<td>18.62</td>
<td>3.08</td>
<td></td>
</tr>
<tr>
<td>NAG pH</td>
<td>2.89 ± 0.94</td>
<td>2.53</td>
<td>3.09</td>
<td>5.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAGₚH₄.₅</td>
<td>66.92 ± 7.36</td>
<td>66.17</td>
<td>19.59</td>
<td>11.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAGₚH₇</td>
<td>84.16 ± 11.8</td>
<td>85.31</td>
<td>32.30</td>
<td>21.72</td>
<td></td>
<td></td>
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<tr>
<td>NAG pH</td>
<td>4.56 ± 0.99</td>
<td>3.64</td>
<td>4.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAGₚH₄.₅</td>
<td>67.13 ± 7.56</td>
<td>69.45</td>
<td>21.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAGₚH₇</td>
<td>86.03 ± 11.3</td>
<td>96.24</td>
<td>46.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAG pH</td>
<td>5.32 ± 0.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NAGₚH₄.₅</td>
<td>67.13 ± 7.56</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAGₚH₇</td>
<td>88.03 ± 11.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ NAGₚH₄.₅ and NAGₚH₇ units in kg H₂SO₄/ton
² Standard deviation, n=3
³ Standard deviation, n=2
### A 4.4. Results of co-element deportment and mobility by ICP-MS

**Table A11: Results of co-element characterisation and deportment in flotation desulfurisation**

<table>
<thead>
<tr>
<th></th>
<th>Crustal abundance (ppm)</th>
<th>Drinking water std (ppm)</th>
<th>Typical Porphry Tailings (mg/kg)</th>
<th>Total metal concentrations (mg/kg)</th>
<th>Feed enrichment ratio</th>
<th>Deportment to tailings (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>36300</td>
<td>100</td>
<td>9099</td>
<td>38949 ± 253</td>
<td>42213 ± 178</td>
<td>1.1</td>
</tr>
<tr>
<td>Al</td>
<td>81300</td>
<td>0.2</td>
<td>4986</td>
<td>8891 ± 1233</td>
<td>9845 ± 1386</td>
<td>0.1</td>
</tr>
<tr>
<td>Mg</td>
<td>20900</td>
<td>100</td>
<td>3202</td>
<td>7174 ± 63</td>
<td>7022 ± 40</td>
<td>0.3</td>
</tr>
<tr>
<td>Mn</td>
<td>1000</td>
<td>0.05</td>
<td>1244</td>
<td>2213 ± 6.7</td>
<td>2301 ± 3.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Minor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>100</td>
<td>0.5</td>
<td>270</td>
<td>326 ± 1.4</td>
<td>288 ± 1.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Ni</td>
<td>75</td>
<td>0.02</td>
<td>109</td>
<td>178 ± 3.0</td>
<td>160 ± 3.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Zn</td>
<td>80</td>
<td>3</td>
<td>118</td>
<td>135 ± 4.0</td>
<td>99.7 ± 3.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Trace</td>
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<tr>
<td>Pb</td>
<td>16</td>
<td>0.01</td>
<td>36.0</td>
<td>72.9 ± 1.2</td>
<td>37.3 ± 0.69</td>
<td>4.6</td>
</tr>
<tr>
<td>Mo</td>
<td>1.5</td>
<td>0.05</td>
<td>25.5</td>
<td>28.6 ± 0.72</td>
<td>13.3 ± 0.54</td>
<td>19</td>
</tr>
<tr>
<td>As</td>
<td>1.8</td>
<td>0.01</td>
<td>27.9</td>
<td>15.6 ± 2.8</td>
<td>1.89 ± 0.056</td>
<td>8.7</td>
</tr>
<tr>
<td>Co</td>
<td>25</td>
<td>1</td>
<td>18.5</td>
<td>10.0 ± 2.9</td>
<td>3.55 ± 2.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Ag</td>
<td>0.07</td>
<td>0.01</td>
<td>1.47</td>
<td>2.67 ± 1.1</td>
<td>1.02 ± 1.1</td>
<td>38</td>
</tr>
<tr>
<td>Cd</td>
<td>0.2</td>
<td>0.005</td>
<td>1.35</td>
<td>1.00 ± 0.18</td>
<td>0.350 ± 0.25</td>
<td>5.0</td>
</tr>
</tbody>
</table>

1 Broadhurst and Petrie (2010)
2 Maluleke (2006)
3 Standard deviation, as supplied by ICP-MS analysis
4 Ratio of feed total concentration to crustal abundance (BC)
5 Mass balanced % of feed reporting to tailings
### Table A12: Leachate element mobility results

<table>
<thead>
<tr>
<th></th>
<th>Leachate concentration (mg/kg)</th>
<th>Mobility: % of feed leached</th>
<th>RPF/1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>¹Tailings</td>
<td>²Tailings (pH 2)</td>
</tr>
<tr>
<td>Ca</td>
<td>2806 ± 30</td>
<td>1786 ± 0</td>
<td>3553 ± 5.8</td>
</tr>
<tr>
<td>Major</td>
<td>Al 283 ± 4.0</td>
<td>3.2 ± 2.0</td>
<td>397 ± 0.75</td>
</tr>
<tr>
<td></td>
<td>Mg 1352 ± 4.0</td>
<td>753 ± 8.9</td>
<td>1675 ± 15</td>
</tr>
<tr>
<td>Mn</td>
<td>1696 ± 2.2</td>
<td>1423 ± 9.0</td>
<td>1781 ± 51</td>
</tr>
<tr>
<td>Minor</td>
<td>Ni 17.8 ± 0.077</td>
<td>9.90 ± 0.02</td>
<td>16.6 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>Zn 257 ± 0</td>
<td>46.2 ± 0.07</td>
<td>107 ± 0.10</td>
</tr>
<tr>
<td>Trace</td>
<td>Pb 0.142 ± 0.0076</td>
<td>0.040 ± 0.005</td>
<td>0.048 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>Mo 0.035 ± 0.0045</td>
<td>0.008 ± 0.0001</td>
<td>0.125 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>As 0.477 ± 0.075</td>
<td>0.082 ± 0.005</td>
<td>0.709 ± 0.007</td>
</tr>
<tr>
<td></td>
<td>Co 9.52 ± 0.034</td>
<td>5.37 ± 0.02</td>
<td>7.81 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Ag 0.023 ± 0.015</td>
<td>0.002 ± 0.009</td>
<td>0.012 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>Cd 0.165 ± 0.0037</td>
<td>0.056 ± 0.0005</td>
<td>0.099 ± 0.006</td>
</tr>
</tbody>
</table>

¹Desulphurised tailings of 0.21% S, leached without pH adjustment
²Desulphurised tailings leached at controlled pH 2
³Standard deviation, as supplied by ICP-MS analysis