



# **AN INVESTIGATION INTO ACCELERATED LEACHING FOR THE PURPOSE OF ARD MITIGATION**

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**Dissertation in partial fulfilment of MSc in Chemical  
Engineering**



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## Synopsis

World-wide, acid rock drainage (ARD) is one of the biggest environmental challenges facing environments with current or previously active mining activities. Formed from the exposure of sulphide mineral to both water and air, and catalyzed by naturally occurring iron- and sulphur-oxidizing micro-organisms, ARD pollution is predominantly associated with the mining of sulphidic ores and coal. Of particular concern are the large volumes of mining wastes from which the generation of ARD and the associated pollution effects often persist over tens to hundreds of years after mining operations have ceased. Current ARD management strategies focus on the prevention of ARD through mineral waste deposition or remediation options once ARD has formed. These strategies, however, do not remove the risk of ARD generation in the future.

The aim of this study was to investigate the removal of the potential for ARD generation from a low-grade copper waste rock through the accelerated removal of the sulphur components via reaction. The three waste rock samples used in this investigation had total sulphur grades of between 2.20 and 3.20 % with the majority of the sulphide present as pyrite, chalcopyrite and galena. Significant quantities of non-sulphide associated iron minerals, predominantly magnetite, were also present in the three samples. The waste rock samples were sourced from mining operations in Chile and South Africa and had a  $D_{80}$  of approximately 0.8 cm. All three waste rock samples were potentially ARD generating.

The study into desulphurization was conducted using laboratory scale bioleach column reactors with an investigation into the application of favourable growth and colonization conditions for iron- and sulphur-oxidizing micro-organisms. The first phase of experiments investigated the effects of feed solution acidity, aeration, increased temperature and the addition of an easily accessible microbial energy source in the form of pyrite concentrate on the rate of ARD generation. To assess the effect of these conditions on the rate of desulphurisation, an estimate of the expected time required for complete solubilisation of the sulphide fractions under the selected conditions was developed. This estimate, the Terminal Duration (TD), was determined from extrapolation of the steady leach rate of the copper, iron and sulphur. Characterization of the ARD potentials of the feed and solid residues was assessed by carrying out static ARD characterization tests, acid-base accounting tests and net acid generation tests. These tests allowed for the changes in ARD potentials of the solid phases to be investigated.

From the bioleach column experiments, the variable with the greatest effect on the rate of ARD generation was the acidity of the feed solution, resulting in an approximate 20-fold reduction in the time necessary for total sulphur removal as compared to a water feed. Aeration of the bioleach column and an increase in the system temperature also decreased the time necessary for complete removal of the ARD forming components. The addition of a 1% (w/w) pyrite concentrate (in the absence of the associated increase in operating temperature expected within a waste dump) had the opposite effect.

Results from the static ARD characterization tests confirmed the trend in the metal and sulphur removal observed from the bioleach column results. However the static characterization results carried high uncertainties which limited the interpretation and application in predicting the time necessary for complete ARD generation. Thus, the estimated time necessary for total ARD generation determined from the liquid phase leachate data from the bioleach columns and the ARD characterization test results differed. Also highlighted were the differences in rates and magnitudes of decrease of the acid neutralizing and producing components within the waste rock samples.

A second phase of experiments investigated the differences in sulphide leaching and the rate of removal of acid neutralizing capacity (ANC) observed during the first set of experiments. This investigation was performed on a second waste rock sample using five replicate bioleach column experiments. The progression of ANC and sulphur removal during bioleaching was investigated by sacrificing one column every 10 days and analysing the ARD potentials of the solid residues. Significant differences were observed in the relative rates of ANC and sulphur removal from the waste rock using bioleaching. An observed 73 % reduction in the ANC over the first ten days of bioleaching was in contrast to the negligible difference observed in the total sulphur content quantified using LECO analysis. The shorter time frames also allowed for the refinement of the technique used in the estimation of the time necessary for total ARD generation, the terminal duration. The rapid mineral extraction observed over the initial ten days was excluded from the calculations to predict the terminal duration for ARD generation. Nevertheless, the misalignment between the duration estimations from the bioleach leach data and the static ARD characterization results persisted. This misalignment was due to the acidic nature of the feed solution, which reacted with the acid neutralizing components and led to the removal of the ANC. The presence of “acid-insoluble” sulphide minerals, however, prevented the total solubilisation of the sulphides within the waste rock over the same time period.

A third experimental phase was conducted to quantify the reproducibility in the bioleach columns as a possible explanation for the differences observed in the five replicate bioleach experiments. As an attempt to improve the reproducibility of the bioleaching experiments, an investigation in the use of an in-bed sampling method was tested in place of a number of bioleach columns. These experiments were not inoculated with bioleaching micro-organisms, to prevent any differences in the communities reflecting in the leachate data from the column experiments. Experiments were conducted with a water and an acidic feed solution on the second waste rock sample. With the exception of problems experienced with iron solubility under water fed conditions, good agreement was observed in the leachate results under both the water and acidic feed conditions, indicating the suitability of the in-bed sampling technique for studies of the leachate solutions from the bioleach columns. However, comparison of the solids results, in particular the ANC values under the water fed conditions, highlighted the limitations of the in-bed sampling technique with regards to the representative sampling of the residues within the bioleach column reactors. Thus, it was concluded that the in-bed sampling technique cannot replace a bioleach column reactor system for investigations which require sampling of the solid phase.

To inform the limitations of the experimental approach, an investigation was conducted into the choice of ARD characterization tests and the sources of associated experimental error. This investigation was conducted by performing different static characterization tests on one waste rock

sample in addition to a literature survey. Significant sources of experimental error associated with the static ARD characterization tests included the preparation of the sample, the choice of ANC test and the choice of method used in the quantification of the total sulphur content. It was demonstrated that sample variation could be overcome by appropriate sample preparation. The incremental Skousen test was selected for determining ANC and LECO analysis for MPA determination, with associated coefficient of variance quantified. The results of the biokinetic ARD characterization tests supported the classification of the static characterization tests and also highlighted the role of the ANC of a waste rock sample in its subsequent ARD generation.

The effect of an addition of easily accessible iron and sulphur for bioleaching micro-organisms on the rate of ARD generation was investigated on a waste rock with a different mineralogy and sulphur grade to that previously used. In addition, the refinement of the method used to estimate time necessary for complete ARD generation and the conclusions from the investigation into the ARD characterization tests were incorporated into this investigation. No significant differences were observed between the leachate profiles of the pyrite-supplemented and non-supplemented bioleach column results, in the absence of the increase in temperature expected at large scale.

Overall, the study found that the single most significant effect on accelerating the rate of ARD generation was the level of acidity supplied to the waste rock samples. Aeration and a rise in temperature of the waste rock samples also positively affected the rate of ARD generation. The effects of these conditions on the ARD potential of the solid phases of the waste rock, however, were not observed due to the inherent uncertainty in the static characterization tests used in the classification of the ARD potentials. Use of the biokinetic ARD characterization test supported the findings of the static ARD characterization tests.

Recommendations for further investigations include the application of the experimental protocols selected in further laboratory studies of ARD removal, the applicability of the conditions identified (especially pyrite addition to mediate an increase in waste rock dump temperature) to larger scale waste rock dumps, further investigation into the relative rates of ANC and total sulphur removal and a further investigation into the refinement of the biokinetic test for use on waste rock samples. Such investigations will allow for further development of accelerated leaching as a method for ARD mitigation through sulphide removal. In addition, the study of the relative rates of ANC and sulphur removal could inform proposed ARD mitigation techniques which focus on the co-disposal of acid neutralizing and acid forming materials for the *in-situ* neutralization of ARD.

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## List of Abbreviations

AAS	Atomic adsorption spectrometry
ABA	Acid base accounting
ABS	Autotrophic basal salts
ALD	Anoxic limestone drain
ANC	Acid neutralising capacity
ARD	Acid rock drainage
ICP-MS	Inductively coupled plasma-mass spectrometry
MPA	Maximum potential acidity
NAF	Non acid forming
NAG	Net acid generation
NAG <sub>pH</sub>	The pH of the post-boil, NAG solution after filtering
NAPP	Net acid producing potential
OLD	Oxic limestone drain
PAF	Potentially acid forming
ROM	Run-of-mine
TD <sub>Average</sub>	Terminal duration estimated using the initial and final data points only
TD <sub>Cu</sub>	Terminal duration estimated from the copper extraction data
TD <sub>Fe</sub>	Terminal duration estimated from the iron extraction data
TD <sub>Solid</sub>	Terminal duration estimated from the static ARD characterization results performed on the solid phase
TD <sub>Sulphur</sub>	Terminal duration estimated from the sulphur extraction data
WRC	Water Research Commission of South Africa
XRD	X-ray diffraction
XRF	X-ray fluorescence

# 1. Introduction

## 1.1. Background

Acid rock drainage (ARD) is the one of the biggest environmental challenges currently associated with the mining of sulphidic ores and coal. This form of pollution occurs as a result of any activities which expose sulphide minerals to both water and air, allowing for sulphide oxidation. The rate of ARD formation may be accelerated in the presence of naturally-occurring, iron- and sulphur-oxidizing micro-organisms which catalyse the sulphide oxidation reactions

The large quantities of waste generated from mining activities, estimated to be as much as 98% of total mined material (Mitchell, 2000), compound the ARD problem. ARD is thus of particular concern to countries with large, well established mining industries, especially in the coal, gold and base metal industries where pyrite is present in the mineral ore but its complete extraction is not required for recovery of the metals of value (Environment Australia, 1997). For example, a 1994 survey of mines, mineral processing and industrial mineral tailings in Canada (MEND, 1995) showed that 28% and 13% of the 7 billion tons of tailings and 6 billion tons of waste rock respectively were potentially acid forming. In addition, IWRI (2002) estimated that over 40% of mine wastes sampled from over sixty coal, gold and base metal mines were potentially acid forming.

In South Africa, ARD pollution occurs from wastes associated with predominantly the gold (McCarthy, 2011) and coal mining industries (Pinetown *et al.*, 2004). Recent focus on ARD pollution in South Africa is as a result of the media attention given to the decanting of ARD into the Western Basin of the Witwatersrand in 2008 (IMC, 2010). In fact, until the completion of storage and pumping facilities in late 2008, the South African Department of Environment and Tourism estimated that 15 mega litres per day of ARD flowed into water ways towards the Cradle of Humankind World Heritage Site (Oelofse *et al.*, 2007).

The ARD problem is compounded by the time-scales associated with ARD generation are of particular importance. The generation and effects of ARD persist over tens to hundreds of years (Koehnken *et al.*, 2003; Nordstrom & Alpers, 1999). For example, ARD has been well documented in the Rio Tinto River system for the last 200 years (Leblanc *et al.*, 2000).

Although media coverage of the ARD problem, especially in South Africa, is recent, its importance has been recognised for a long time. There have been many government-funded research projects detailing pollution associated with mining activities in South Africa (31 reports since 1989, IMC, 2010). In addition, research, mainly funded through the Water Research Commission of South Africa (WRC), has focused on understanding ARD generation, possible ARD treatment technologies, disposal of associated ARD brines, quantification of the ARD problems in focused areas of the country and characterisation of the waste heaps and their ARD potentials (IMC, 2010).

With respect to prevention of ARD formation, handling of mine wastes is important. Current prevention techniques aim to prevent water, oxygen or both contacting with the sulphide mineral surface (Johnson & Hallberg, 2005). This is commonly achieved through covering of the waste

materials with layers impervious to either one or both of these reactants. Long-term prevention of ARD has been investigated through removal of the sulphide component from ARD forming wastes (Benzaazoua, 2000). Although physical removal of the sulphide fraction has been demonstrated successfully for tailings samples using froth flotation (Kazadi Mbamba et al, 2012, Hesketh *et al.*, 2009, Benzaazoua, 2000), the volumes and sizes of waste rock associated with mining activities would necessitate the added costs of crushing and milling before this method could be implemented (Mitchell, 2000). Overall, although currently implemented prevention techniques are successful in the short term, they fail to remove the potential for ARD generation in the future (Cilliers, 2006)

## **1.2. Approach to sulphide removal through accelerated oxidation**

### **1.2.1. Problem Statement**

The large volumes of sulphidic mine wastes generated pose a significant problem in the prevention of acid rock drainage. The longevity of ARD generation highlights the economic burden of prolonged ARD treatment schemes which, although successful in the short-term, fail to remove the risk of future ARD generation. Research concerning the removal sulphide minerals from waste rock is necessary therefore for the development of strategies to mitigate future ARD generation from these mining wastes.

### **1.2.2. Project Approach**

The objective of this project therefore was to investigate the designed acceleration of ARD generation from waste rock dumps and whether its generation, under controlled conditions, can be accelerated to occur by mine closure. This aim was accomplished in two main sections: through the addition of conditions favourable for microbial growth and colonization and, secondly, through an investigation into methods employed to assess and characterise the ARD potential of the waste rock subsequent to accelerated generation. Bioleach column reactors were used to study ARD generation under several conditions. The conditions investigated included:

- i. The replacement of a water feed solution with acidified feed.
- ii. Aeration of the bioleach column reactors with air.
- iii. An increase in reactor temperature.
- iv. An increase in the iron and sulphur lixiviate sources through the addition of 1% (w/w) pyrite concentrate

In order to assess the effect of the conditions on the rate of ARD generation and the remaining potential for ARD production, it was necessary to investigate methods of assessment and characterisation of the ARD potentials of the solid, waste rock samples. This was achieved through an investigation into the following methods for ARD characterization:

- i. The use of Terminal Durations (TDs) for the estimation of the time remaining for ARD generation from bioleach column leachate data.
- ii. An investigation into the use of traditional static ARD tests for characterization of waste rock samples.

- iii. Assessment of the ARD potentials of waste rock samples using the biokinetic ARD characterisation test described by Hesketh *et al.* (2010)

In addressing the above objectives, the study aims to highlight key interactions using a range of waste rock samples. However, neither the optimization of sulphide removal, nor ideal pyrite supplementation, is prioritized.

### **1.3. Thesis Structure**

The general background, problem statement and project scope presented in Chapter 1 is followed by a review of relevant literature concerning ARD formation, solid waste characterisation, the environmental effects of ARD and remediation and management strategies, in Chapter 2. A description of the waste rock samples, experimental equipment and the methodologies used in this study are presented in Chapter 3. The results of the initial experiments, aimed at gaining an understanding into the effect of typical conditions experienced in waste rock dumps on ARD generation, are presented in Chapter 4. Following the results and conclusions drawn from these experiments, Chapters 5, 6 and 7 each present the results and discussion of further investigation into points of interest raised from the Chapter 4. These chapters detail an investigation into the rates of ARD generation, an investigation into an *in-situ* sampling technique and an experimental review of ARD characterisation techniques, respectively. Following the conclusions drawn from Chapters 5 through 7, the investigation into the effect of pyrite supplementation to waste rock dumps is revisited in Chapter 8. Finally, Chapter 9 concludes this study with a summary of the findings and recommendations for further work. A schematic of the thesis structure, providing further detail of its structure, is presented in Figure 1-1.

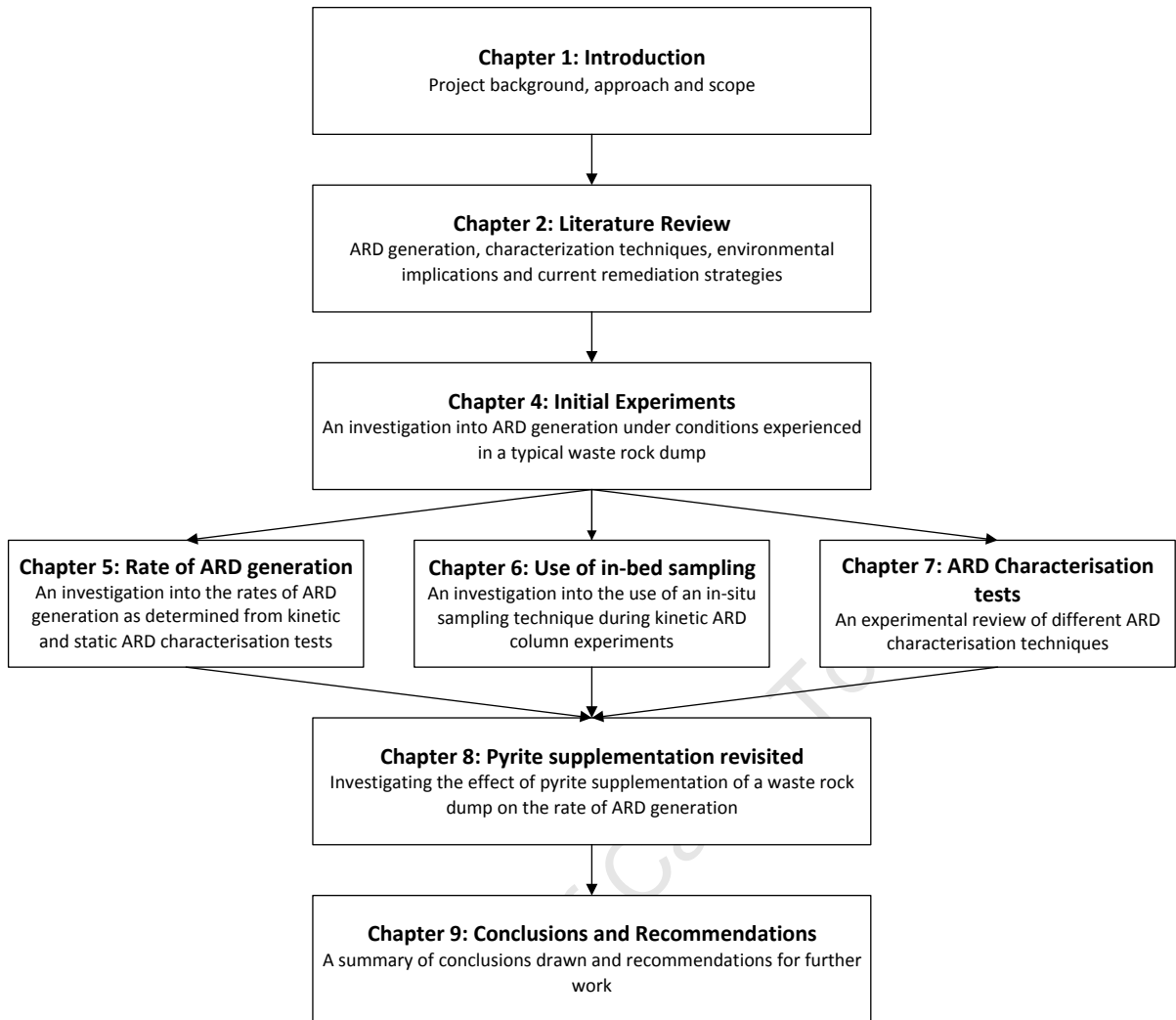


Figure 1-1: Schematic outline of the thesis structure.

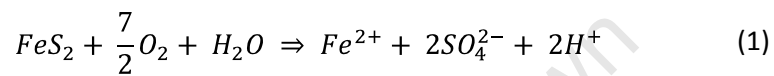
## 2. Literature Review

The literature review outlines the contributing factors to, and processes involved in, ARD generation, the current methods employed in the characterisation of the ARD potentials of solid wastes and the current and the environmental implications of acid rock drainage. Methods employed in the prevention and treatment of ARD are also discussed.

### 2.1. ARD Formation

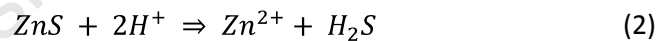
#### 2.1.1. ARD formation in an abiotic environment

When sulphide bearing minerals are exposed to both water and oxygen, there is a potential for the formation of ARD. Mineral oxidation occurs through reaction with oxygen with the aqueous system providing a reaction phase and subsequent transport of the soluble minerals and protons:

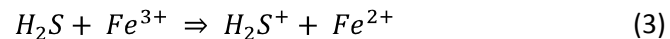


Although oxidation by oxygen is often the first step in ARD generation, it quickly becomes a secondary reactant in the presence of ferric iron, a stronger oxidizing agent. The mechanism for ARD generation depends largely on the acid solubility of the mineral. Schippers and Sand (1999) have proposed two different mechanisms for sulphide oxidation; namely, a polysulphide and thiosulphate mechanism for acid soluble and acid-insoluble minerals respectively.

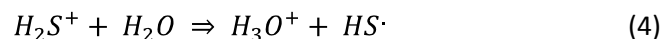
Acid soluble minerals undergo acid attack and are solubilized by  $H^+$  ions. This reaction pathway results in formation of hydrogen sulphide as a direct product from the mineral dissolution. Sphalerite is an example of an acid soluble mineral which undergoes dissolution as follows:



The sulphur species generated may undergo further oxidation to form polysulphides through reactions outlined by Schippers and Sand (1999). Firstly, hydrogen sulphide can be oxidized by ferric ions, forming a hydrogen sulphide radical.



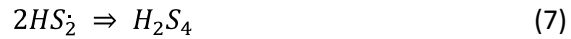
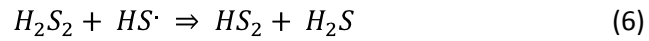
The hydrogen sulphide radical undergoes dissolution in an aqueous environment.



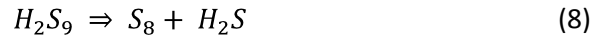
Two radicals may combine:



Reaction of the disulphide with another radical and subsequent dimerization enlarges the sulphide chain.

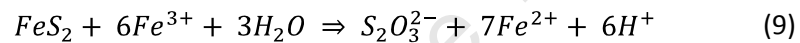


Further enlargement of the polysulphide chain occurs through similar reaction. In acidic solutions however, the polysulphides decompose to form elemental sulphur rings,  $S_8$ .

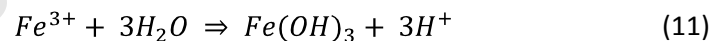


In an abiotic system, this elemental sulphur remains the most common sulphur product from dissolution of acid soluble minerals. Polysulphides can be oxidized either by oxygen or ferric iron to yield thiosulphates, however, formation of these is secondary (Steudel, 1996).

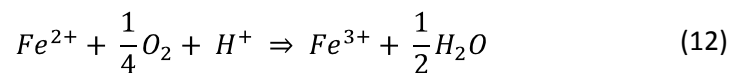
Minerals which do not undergo solubilisation via proton attack are termed "acid insoluble". Here, mineral solubilisation occurs through ferric iron attack with the sulphur component occurring as a direct thiosulphate product. This sulphur species then undergoes further oxidation leading to a final sulphate product.



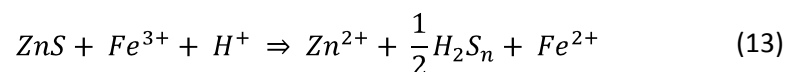
Thus, depending on the acid solubility of the minerals, the sulphur species within the abiotic acidic aqueous system include several different forms, the most common of which are elemental sulphur and sulphate. In addition to the acid solubility of the mineral, oxidation is also governed by the pH of the immediate environment. In systems above pH 3.5, the ferric ion precipitates via the following acid producing reaction:

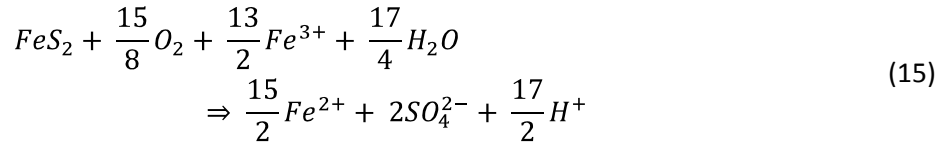
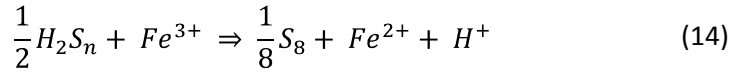


Although this reaction is acid forming, it also removes ferric ions from solution, potentially reducing the rate of ARD formation. At pH less than 3.5, ferric iron precipitation occurs to a lesser extent and ferric iron is regenerated naturally through the acid consuming oxidation of ferrous iron:



Although the ARD solution chemistry outlined above details both acid generating and consuming reactions, often depending on the pH of the solution, the overall mineral oxidation under acidic, abiotic conditions shows a net proton production, with Equations 13-14 and 15 for acid-soluble and acid-insoluble respectively.





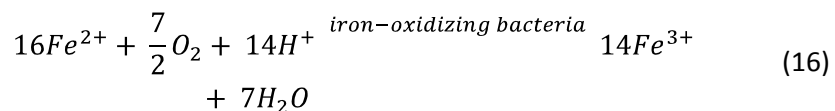
### 2.1.2. Factors governing ARD formation

The factors influencing the formation of ARD include the presence of micro-organisms, climate and the physical characteristics of the sulphide-bearing ore or waste material. These factors have been discussed extensively in literature (Blowes *et al.*, 2005; Johnston & Murray, 1997), and are discussed briefly.

#### The presence of micro-organisms

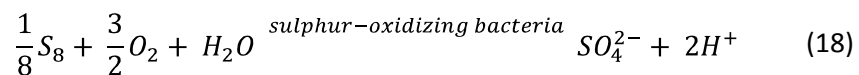
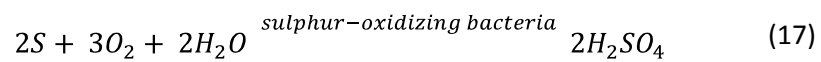
The role of microbial species on the formation of ARD is well recognised (Colmer *et al.*, 1950, as cited in Watling, 2006). Iron-oxidizing micro-organisms oxidize the ferrous iron dissolution product (Equation 1) to ferric iron (Equation 16). This species can further oxidize the mineral sulphide (Equation 9). Similarly, sulphur oxidizing micro-organisms are responsible for the oxidation of the sulphur species resulting from mineral dissolution (Equations 13-15), resulting in the production of protons and sulphate ions, two of the defining components of ARD (Johnson, 2003). Bioleaching micro-organisms therefore act as catalysts in the (re)generation of leaching agents (Equations 16-18), with the rate of leaching orders of magnitude greater in the presence of such micro-organisms (Nordstrom & Alpers, 1999).

The diversity of the microbial populations in the waste rock dump or tailings impoundment is governed by the temperature and pH of the environment as well as the concentrations of ferrous and ferric iron, sulphur species and oxygen in solution (Rohwerder *et al.*, 2003). Although significant temperature gradients may exist within active heap bioleaching systems due to the exothermic nature of the sulphide oxidation, average temperatures within waste rock dumps are usually within the mesophilic temperature range (Olsen *et al.*, 2003) owing to the lower availability of mineral sulphide and thereby heat of reaction generated. At these temperatures in acidic environments, the most important, and consequently most well studied, iron- and sulphur-oxidizing species which have a direct influence on the rates of ARD formation are *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans* and *Leptospirillum ferriphilum* (Plumb, 2008). Other micro-organisms reported include *Acidithiobacillus caldus*, *Sulfolobus metallicus* and *Metallosphaera* species (Watling, 2006; Hallberg & Johnson, 2001). The indirect role of iron-oxidizing micro-organisms on ARD generation through their oxidation of the ferrous to ferric iron has been outlined previously (Watling, 2006):



Microbial ferric regeneration has been reported as  $10^6$  times faster than chemical ferrous oxidation by oxygen at mesophilic temperatures (Watling, 2006), with the speed of regeneration playing an

important role in the rate of ARD generation through the maintenance of the desired ferrous / ferric ratio (Rohwerder et al, 2003). Although *Acidithiobacillus ferrooxidans* has the ability to oxidize both ferrous iron and sulphur species, sulphur-oxidizing bacteria are also commonly found in waste heaps and dumps. Such species include *Acidithiobacillus thiooxidans*, *Acidithiobacillus caldus* and *Sulfobaccillus sp* (Bryan, 2006; Watling, 2006). The presence of these sulphur oxidizing bacteria results in the oxidation of the thiosulphate, other sulphur intermediates, hydrogen sulphide & elemental sulphur to sulphate (Equations 17 & 18).



In well established ARD generating systems, the extent of this oxidation is such that the majority of the sulphur in the aqueous phase is present as sulphate (Johnson, 2003).

The rate of biotic ARD generation is governed by factors affecting the extent of microbial growth and colonization with waste heaps (Watling, 2006) and the activity of these microbial populations. These factors are discussed in detail elsewhere (Franzmann *et al.*, 2005; Rohwerder *et al.*, 2003; Boon & Heijnen, 1998). The main factors are briefly discussed below.

One of the main factors concerning the presence of micro-organisms in waste rock heaps is the necessity for the correct pH environment. The acidophilic microbial species generally only occur in environments below pH 3 (Watling, 2006). A limited number of species have been found at the mid-pH range and may be responsible for promoting oxidation and iron precipitation (Johnson & Hallberg, 2003). The temperatures experienced in waste rock heaps also influence the presence of bioleaching micro-organisms, with different species having optimal growth conditions at different temperatures (Rawlings *et al.*, 1999; Johnson & Hallberg, 2003). The availability of easily accessible iron and sulphur energy sources for micro-organisms and the presence of favourable attachment sites also contribute to the extent of microbial growth and colonisation within waste heaps (Schippers & Sand, 1999).

In addition, favourable conditions for micro-organisms may only develop over long periods of time (Bryan, 2006). This is especially true in waste heaps where limited processing of the waste ore has occurred (Price, 2003). This time period, and associated microbial presence, plays a large role in the possible extent of ARD formation and the time period over which this formation occurs (Environment Australia, 1997).

### **The role of climate and environment**

The conditions present in the natural environment surrounding waste deposits has a large effect on the formation of ARD. In particular, temperature, humidity and the ratio of precipitation to evapotranspiration are the three main aspects of climate which affect ARD formation (Plumlee, 1999). The oxidation of sulphide minerals may be enhanced in humid climates, due to the warm temperature and high humidity, with the high ambient temperatures increasing the rate of the

oxidation and providing more favourable conditions for leaching micro-organisms as compared to colder climates (Borek, 1994). An increased abundance of water in sulphide wastes in humid climates also promotes the formation of ARD through the supply of necessary water to the mineral surface. In contrast, ARD formation in arid and cold arctic conditions is hampered by the lack of sufficient water and low temperatures respectively (Plumlee, 1997).

The net flow of water within sulphide waste environments affects ARD composition. The ratio of precipitation to that of evaporation may not only change the rate of ARD formation but also the quality of the resulting pollution (MEND, 1994). In wet areas where precipitation dominates, larger volumes of ARD may be produced. The pollution, however, is often more dilute and of a higher pH than ARD formed from similar wastes in dry climates (Plumlee *et al.*, 1999).

### **Mineral composition and physical characteristics of mine wastes**

The response of mining wastes to conditions favourable for ARD formation is ultimately governed by the composition and physical characteristics of the wastes themselves. The composition affecting ARD formation includes the relative abundance of acid-generating and acid-neutralizing minerals, and the textures of the minerals present in the wastes (Plumlee, 1997). Physical characteristics of the mine wastes include the size of the waste particles and the permeability of mine wastes (Environment Australia, 1997).

The minerals present within a waste body influence the potential for, and rate of, ARD formation. Acid generated from a mine waste is dependent on the sulphide minerals present in the waste, their resistance to weathering and the products of the mineral oxidation (Plumlee, 1997). Whereas iron sulphide minerals generate acid upon oxidation with oxygen, other metal sulphides tend only to produce acid upon oxidation with ferric iron (Nordstrom & Alpers, 1999). Acid produced from sulphide oxidation may be partially neutralized by acid-consuming minerals, often in the form of carbonates, present in the mine waste (White *et al.*, 1999).

The rate at which different minerals weather or react with acid vary substantially between minerals and are a function of the grain size, texture and trace metal content (Plumlee, 1997). The increased surface area of finer grain particles as compared to larger grains often leads to an increased rate of oxidation (White & Jeffers, 1994). These authors also observed differences in oxidation rates between pyrite minerals with different textures, with framboidal pyrite weathering faster than euhedral pyrite under the same conditions. The presence of trace metals either within the crystal structure or as inclusions of other minerals, often increases mineral oxidation due to strains present in the crystal structure (Jambor, 1994).

The nature of the mining wastes is also influenced by the extraction and processing methods used in the mining operations. The largest effect is on the particle size and mineral liberation of the mine wastes (Plumlee, 1997). The size of the waste particles dramatically influences the rate of mineral oxidation, with an inverse relationship between size and oxidation rate most common (Wu *et al.*, 2007). Particle sizes also affect mineral liberation and permeability of mine wastes. A decrease in particle size is most often accompanied by an increase in mineral liberation, with the result an increase in the rate of mineral oxidation (Tran *et al.*, 2003).

## 2.2. ARD Characterization

Determination of the potential for ARD formation from waste rock is necessary for the adequate planning and commissioning of strategies to minimize the associated environmental impacts through appropriate disposal of mining wastes. Although several local environmental factors play a role in ARD formation, the primary potential is classified from characterisation of the waste ore. Broadly, this characterisation of ARD generation potential is achieved through the quantification of the acid-generating and acid-consuming components present within a sample. Balancing these components, and studying their interaction, relative weathering rates and environmental situation leads to the characterization of ARD generation potential. To enable prediction of ARD, these characterization results are combined with water transport and mineral contacting characteristics at the local geographic scale. Outlined below are several strategies for the characterisation of ARD generation potential from ore samples.

### 2.2.1. Static ARD Characterization

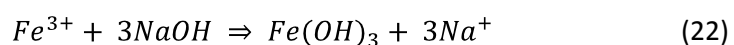
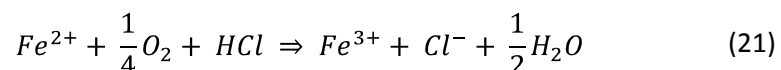
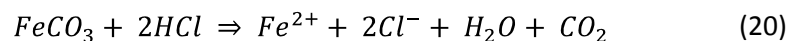
Static ARD tests are chemical tests designed to quantify the acid-neutralizing and acid-generating components present in an ore sample. These tests provide a relatively quick method for this determination and are often used as a screening tool for ore characterisation with the results dictating the necessity of further characterisation work (Lapakko, 2002).

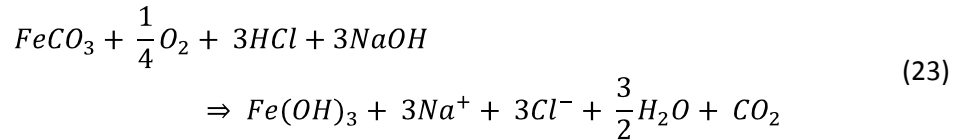
#### Acid Base Accounting

The most commonly used static test, known as Acid-Base Accounting (ABA, Fergusson & Erickson, 1988), balances the acid-generating and acid-consuming components within a sample to classify the sample as “acid-forming”, “non-acid forming” or “uncertain” (Stewart *et al.*, 2006). ABA tests are calculated from the difference between the acid neutralizing capacity (ANC) and the maximum potential acidity (MPA) of a sample with the resulting net acid producing potential (NAPP) having units of equivalent kilograms  $H_2SO_4$  per ton or kilograms  $CaCO_3$  per ton (Smart *et al.*, 2002; Miller & Jeffery, 1995):

$$NAPP = MPA - ANC \quad (19)$$

The ANC value of a sample is experimentally determined via back titration after acid addition. The standard ANC test was developed by Sobek *et al.* (1978) using HCl in the acid digestion, with the quantity and molarity based on a preliminary reactive carbonate test. Variations in ANC determination stem mainly from the presence of siderite in the ore sample (Jambor *et al.*, 2000).





The overall reaction of siderite with HCl (Equation 23) shows a consumption of equimolar amounts of acidity (HCl, Equations 20-21) and base (NaOH, Equation 22). During the Sobek ANC test however, complete oxidation of the Fe<sup>2+</sup> ions to Fe<sup>3+</sup> ions is not guaranteed. This leads to an overestimation of the ANC value (Skousen *et al.*, 1997).

The most commonly used method to account for the role of siderite is the Skousen Method (Skousen *et al.*, 1997) which involves the addition of H<sub>2</sub>O<sub>2</sub> in order to oxidize the ferrous iron to ferric iron before back titration. Variations in the method and amounts of H<sub>2</sub>O<sub>2</sub> added in the ANC test procedure are reported (Weber *et al.*, 2004a).

The maximum potential acidity of an ore sample is estimated from the total sulphur content. Once obtained, it is assumed that all the sulphur present is available for acid production and that this production follows the stoichiometry of pyrite oxidation. The assumption of complete oxidation allows for the easy calculation of the MPA value (Weber *et al.*, 2004a).

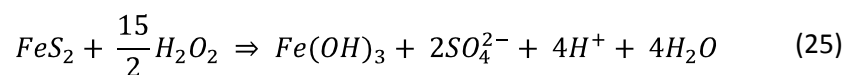
$$MPA = Total\ Sulphur\ \% * 30.6 \tag{24}$$

The assumptions that all sulphur is available for acid production and that this production follows pyrite stoichiometry may cause an overestimation of the NAPP value. This is especially true for samples where sulphur is present as sulphates or organic sulphur (Kania, 1998). This overestimation of the NAPP value led Lapakko (2002) to suggest that classification results using the ABA test represents a worst case scenario for ARD formation.

### Net Acid Generation

In conjunction with the ABA tests, net acid generation (NAG) experiments are used to classify the ARD forming potentials of ore samples. The use of both methods can highlight potential issues in the ANC and MPA estimations and reduces the likelihood of mis-classification of ore samples (Stewart *et al.*, 2006).

In NAG tests, the reaction of ore samples with a 30% H<sub>2</sub>O<sub>2</sub> solution allows for simultaneous acid-generation and acid-neutralization (Adam *et al.*, 1996). Acid-generation is facilitated through reaction of the sulphide species with the H<sub>2</sub>O<sub>2</sub>, with the level of neutralization dependent on the ore composition.



Following reaction, the measurement of the solution pH (NAG<sub>pH</sub>) and its subsequent back titration, firstly to a pH of 4.5 and secondly to pH 7.0, allows for quantification of the equivalent net acid production potential of a sample. Titration to pH 4.5 accounts for the acidity produced from sulphide oxidation while titration to pH 7.0 accounts for the acid generation from the hydrolysis and

precipitation of divalent metal ions (Stewart *et al.*, 2006). Results of NAG experiments are reported as either  $NAG_{pH}$  values, used in classification plots together with the NAPP values (Broadhurst *et al.*, 2007, Miller *et al.*, 1997) or as an equivalent mass of  $H_2SO_4$  produced per ton of ore (Stewart *et al.*, 2006).

### Representation of static test results

Results of static ARD tests are used to classify the acid-forming potential of ore samples. These potentials are presented using two different approaches. In tabular form (Table 1.1), potentials are classified according to a combination of the NAPP and  $NAG_{pH}$  values (Stewart *et al.*, 2006).

Table 2-1: Ore sample classification using NAPP and  $NAG_{pH}$  results (after Stewart *et al.* 2006).

NAPP Result [kg $H_2SO_4$ / ton]	$NAG_{pH}$ Results	Sample Classification
$NAPP \leq 0$	$NAG_{pH} \geq 4.5$	Non-acid forming
$NAPP \leq 0 \ \& \ NAG_{pH} \leq 4.5$ or $NAPP \geq 0 \ \& \ NAG_{pH} \geq 4.5$		Uncertain
$NAPP \geq 0$	$NAG_{pH} \leq 4.5$	Acid forming

These results can also be presented graphically using an ARD classification plot, shown in Figure 1.1 (Broadhurst *et al.*, 2007; Miller *et al.*, 1997).

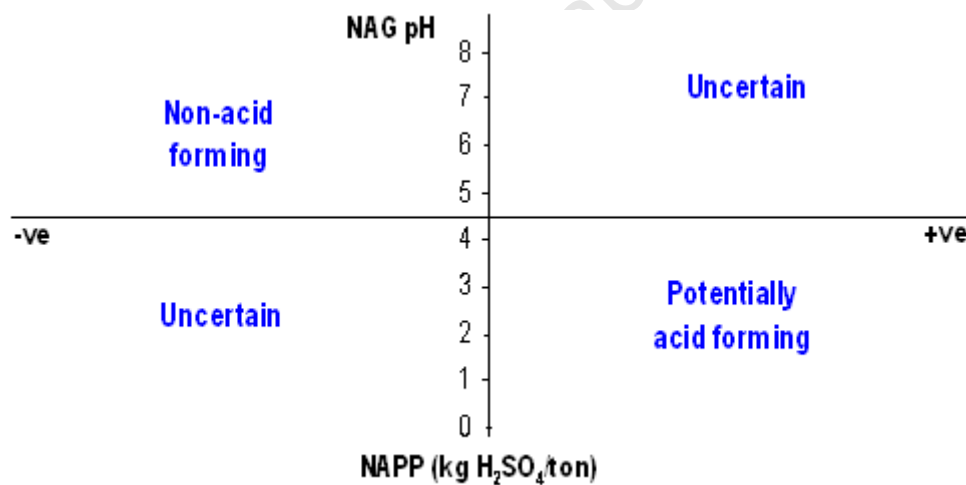


Figure 2-1: ARD classification plot from Hesketh (2010), after Miller *et al.*, 1997

Other ARD classification techniques have been proposed. For example, Stewart *et al.* (2006) proposed generating acid buffering characteristic curves which detail the relative reactivity and rates of the measured ANC. This technique necessitates the completion of additional static tests, thus increasing the time and complexity of the characterization methods. In addition, this technique fails to link the extent of acid consumption and acid generation (Hesketh, 2010). ARD characterization using mineralogical analyses of the samples has also been proposed. Characterisation of the mineralogy of waste rock samples has been recommended for use in conjunction with static ARD tests for ARD characterisation (Parbhakar-Fox *et al.*, 2011). The texture and composition of the mineral samples would be used to inform on the quantification of sulphide and acid neutralizing components, with consideration of the relative reactivities and available surface areas. The use of

mineral characterisation techniques however is limited (Parbhakar-Fox *et al.*, 2011), especially in the characterization of waste rock samples.

Overall, commonly used static tests provide a quick and easy screening tool for the characterisation of ARD potential of ore samples; with these two advantages of the well-established methods providing a barrier for others (Stewart *et al.*, 2006). Limitations of the static tests include the lack of information on the rate of ARD formation or neutralisation (Lapakko, 2002), and particularly their relative rates (Harrison *et al.*, 2010; Hesketh *et al.*, 2010), overestimations and inaccuracies due to the use of strong oxidants not found in waste heap environments (e.g. H<sub>2</sub>O<sub>2</sub>), not taking biological interactions into account, the use of finely ground samples and increased sulphide liberation for waste rock samples and difficulties experienced when comparing results from different techniques.. Certain laboratory techniques, especially in the determination of the percentage total sulphur, also contribute to limitations with respect to reproducibility and accuracy (Kania, 1998).

### 2.2.2. Kinetic tests for ARD Characterization

Kinetic tests for ARD characterization have potential to give distinct advantages over their static counterparts. In particular, the additional rate information informs the more realistic estimation of the potential lag periods before ARD formation, the duration of the potential ARD formation, the relative contributions of the acid forming and neutralizing components and the effectiveness of control measures used to limit sulphide oxidation (Lapakko, 2002). Kinetic ARD techniques range in size from laboratory scale tests to large scale physical dump sites (Blowes *et al.*, 2003).

As a direct extension of a static ARD test, kinetic NAG experiments involve the continuous measurements of the pH and temperature during reaction of the sample with H<sub>2</sub>O<sub>2</sub> (Lapakko, 2002). Although providing information concerning the rate of reaction of the sample with H<sub>2</sub>O<sub>2</sub>, data from these experiments may, at best, provide worst case scenario data. In addition, this test work is time consuming and contains all the limitations of static NAG experiments (Stewart *et al.*, 2006).

The most commonly used laboratory scale chemical tests to provide kinetic data on ARD generation include flask experiments, leach columns and humidity cell experiments (Environment Australia, 1997) which aim to simulate the mineral weathering and ARD formation under exposure to moisture and oxygen. Humidity cell experiments (Caruccio 1968, as cited in Lapakko, 2002) are used to assess relative ARD formation potential between ore samples (Mitchell, 2000) and determine rates of mineral dissolution under moist disposal conditions. The assumption that the waste rock is exposed to moist condition at all times provides a major source of error for this technique and may lead to an overestimation in the ARD potential and rate of formation (Lapakko, 2002).

Column leach experiments aim to simulate natural conditions for ARD generation. Kinetic leach column experiments have advantages in that several factors may be assessed independently (Mitchell, 2000) and that these experiments offer a relatively simple method for assessment of potential remediation options (Environment Australia, 1997). Major disadvantages in using column leach experiments are the time necessary to simulate ARD generation (Lapakko, 2002), especially in the later stages and with low sulphide waste ores, and the lack of standard operating procedures (Smart *et al.*, 2002).

Shake flask experiments are used as a rapid method for investigation of ARD formation (Lapakko, 2002). These often necessitate the milling of ore samples and thus do not represent field conditions accurately. The reduction in particle size also leads to an over-estimation of the rate of ARD formation (Mitchell, 2000) and potentially its extent. These rates can only be considered on a relative basis or to inform modelling for predicting ARD generation.

The main limitations in the use of kinetic experiments for the characterization of the ARD potentials lie in the time required for accurate assessment (Villeneuve *et al.*, 2009) often leading to added expense in comparison to static tests. Reduction in the experimental time precludes accurate representation of field conditions (Lapakko, 2002). The use of harsh chemicals, especially in static tests, also often leads to over-estimation of ARD formation, representing a worst case scenario.

### **2.2.3. Biological ARD characterization**

Chemical ARD characterization tests provide limited insight into the role of micro-organisms on the rate of ARD generation (Hesketh *et al.*, 2010). Inclusion of a microbial component in ARD characterization has been suggested previously, with the proposed experimental tests utilising shake flask experiments on finely ground samples inoculated with micro-organisms implicated in the bioleaching of mineral sulphides (Bruynesteyn & Hackl, 1984).

Limitations of such shake flask experiments, however, include the necessary acidification of the samples to ideal conditions for the microbial species used. This tends to overestimate the acidity and prevent the study of initial ARD generation within natural pH ranges (Hesketh *et al.*, 2010). The study of the interactions between the different microbial species found at ARD sites (Bryan *et al.*, 2006) may also be limited where a single microbial species is used. Hesketh *et al.* (2010) proposed the use of a refined biokinetic shake flask experiment using a mixed microbial culture for the characterisation of ARD from tailings samples. In addition, the authors found good comparison between the data obtained using static tests and biokinetic shake flask results. The use of shake flask experiments to characterise the potential for ARD generation from waste rock is, however, limited due to the necessary milling of the solids samples.

Although column leach experiments are often used for bioleaching studies, use of such experiments for ARD characterization is limited. This is mainly due to the extended durations necessary for experimentation especially where conditions are setup to mimic weathering rather than forced accelerated leaching conditions. In addition, inclusion of the microbial species into such experiments is seen to increase the necessary duration further (Hesketh *et al.*, 2010). Concerns surrounding the relevance of the laboratory microbial populations compared to those found in natural ARD environments also limit the use of microbial ARD characterization experiments (Mitchell, 2000).

## **2.3. Environmental effects of ARD**

Upon entering a local ground or surface water system, toxic mine drainage elements may be transported causing pollution far from the ore waste dump site. Although dilution, by a local water source, of slow-forming ARD may mitigate environmental damage in the immediate environment (Kleinmann, 1990), more often this transport increases the pollution range (Blowes *et al.*, 2003). Environmental effects from toxic mine drainage are dependent on the rate of ARD generation, its

concentration and the duration of formation. Often, a long time span occurs between the waste rock disposal and observable pollution (Price, 2003), the latter may persist for tens or hundreds of years. The potential pollution damage to both terrestrial and aquatic environments may occur as a direct result of the acidic pH of the waste drainage or due to the elevated concentrations of sulphate and dissolved metal ions.

ARD constituents and their concentrations are dependent on the mineralogy of the waste rock. In this way, the effect of ARD varies between geologies and locations. Often however, the metals released as a consequence of mineral-sulphide oxidation or subsequent acid leaching of associated minerals and gangue material represent the largest threat to both terrestrial and aquatic environments (MEND, 1997). Literature on the effects of ARD and its components on plants and animals is extensive (Duruibe *et al.*, 2007; Lennteck, 2004). It is not the aim of this study to present in depth analyses of these effects, however, some general commentary concerning heavy metal toxicity on plants and animals is discussed.

Many studies have focused on the effects of heavy metal accumulation on plants. The uptake of some metal species has been linked to a reduction in photosynthesis in some plant species (Rabe *et al.*, 1982), possibly due to the replacement of Mg within the chlorophyll molecule. Other consequences of metal pollution include a reduction in plant respiration (Singh & Yadava, 1986), the inhibition of nutrient uptake (Peterson & Healey, 1985) and a breakdown of plant membrane integrity (Singh & Yadava, 1986). Some plant species have shown the ability for induced metal toxicity resistance (Shehata & Whitton, 1982) which may have parallels for behaviour in natural environments (Kelly, 1999). Such tolerances may lead to accumulation of metal species without a direct pollution effect for the plant (Krieger *et al.*, 1999). This absorption and accumulation of metal species may also play an important role in the availability of these toxic elements for animal species.

The consensus amongst animal species is that metal toxicity most commonly manifests as hypoxia of body tissues (Burton *et al.*, 1972, as referenced in Kelly, 1999). Other effects of metals on animals include anemia (Tewari *et al.*, 1987) and increased heart rate (Hughes & Tort, 1985), possibly due to the interference of other metals with iron in the synthesis of haemoglobin (Jackim, 1973, as referenced in Kelly, 1999). Genetic mutations have also been observed in marine invertebrates (Gibbs *et al.*, 1987). Levels of exposure do not have to be at lethal dosages before the effects of metal pollution are observed in animals with metabolic costs being observed from exposure to low, non-lethal toxic metal levels (Collvin, 1985).

Metal toxicity is affected by certain factors in the polluted environments (Kelly, 1999). Campbell & Stokes (1985) observed the dependence of speciation of Al, Cu, Mn and Pb on solution pH with direct consequence in lower accumulation levels in animals (Harrison *et al.*, 1986). Studies have also shown a link between water hardness and metal toxicity with lower toxicity in hard water systems (Winner & Gauss, 1986; Mance, 1987). Other components present in polluted waters also affect the toxicity of the metals. The presence of natural chelating agents have been shown to increase lethal concentrations of metals in aqueous systems (Winner & Gauss, 1986) while the presence of phosphorous has shown mixed results in the effect it plays on metal uptake by organisms (Peterson & Healy, 1985; Shehata & Whitton, 1982). Overall however, metal pollution as a consequence of acid

mine drainage formation negatively impacts environments both in the immediate locality of the solid mine wastes but also in associated natural water systems, due to pollution mobility.

## **2.4. Remediation and Management**

Although characterisation of ARD generation potential informs prediction of ARD generation and enables management schemes to be designed and implemented, waste management at mine sites remains a complex issue. The difficulty lies in the large quantities of waste rock, process tailings and wastewaters generated from mining and mineral processing activities. Remediation and management systems for ARD producing mine wastes are often grouped into two main categories: prevention of ARD formation or the treatment of ARD. These categories are not mutually exclusive, with a combination of the two management systems used in some cases. Options for both ARD prevention and treatment are discussed in this section.

### **2.4.1. ARD Prevention Techniques**

Problems associated with ARD prevention include the volumes of waste rock generated by mining operations, the necessary continual disposal from operating mining operations and the necessary monitoring of the disposal sites for ARD formation. Disposal techniques aim to limit the access of oxygen or water, both necessary for ARD formation, to the sulphide mineral surface. This is commonly achieved through covering of the waste materials to prevent water and/or oxygen infiltration (Johnson & Hallberg, 2005). The long-term success however, is dependent on the integrity of the cover being maintained.

Removal of the sulphide component from ARD forming wastes is an attractive method for the prevention of ARD generation (Benzaazoua, 2000). Although physical removal of the sulphide fraction has been demonstrated successfully for tailings samples using froth flotation (Kazadi Mbamba et al, 2012, Hesketh *et al.*, 2009, Benzaazoua, 2000), the volumes and sizes of waste rock associated with mining activities would necessitate crushing and milling before this method could be implemented (Mitchell, 2000).

Engineered soil covers are used primarily for ARD prevention from waste rock dumps (Mitchell, 2000). These are often constructed using several different compacted layers of different particle sizes to minimize oxygen diffusion (EPA, 1995). Layers range from large sized gravel and or vegetation to prevent erosion, fine sand or silt layers to limit oxygen diffusion and impervious layers to prevent water infiltration (Ledin & Pederson, 1996). Impervious layers are often constructed of finely grained silt, impermeable clay or synthetic materials (Johnson & Hallberg, 2005; Kleinman, 1990 ; EPA, 1995). Vegetation often forms the outermost layer which, in addition to minimizing erosion, aids in stripping the oxygen from the soil layer and improves the aesthetics of the mine spoils (Kleinmann, 1990 ; Ledin & Pederson, 1996). An impermeable base is often included in waste rock dump design to prevent infiltration of any ARD formed into groundwater systems. This may be constructed using natural impermeable rock layers or wholly constructed of nonporous clay-based soils or plastic polymers (Kleinmann, 1990). Studies have also suggested the use of alkali covers which, in the event of water infiltration and subsequent dissolution, coat the sulphide minerals in an inert salt layer (Taylor *et al.*, 2009). The inclusion of fly ash and sewerage as cover additives to both

add an impermeable layer and promote the growth of vegetation has been suggested (Neuschütz *et al.*, 1999).

Although common, the use of covers rarely prevents ARD formation completely but rather reduces the volumes of ARD produced (Kleinmann, 1990). Most importantly, covers do not remove the risk of future ARD generation, but rather delay it as long as the cover integrity is maintained. In addition, some disadvantages to the use of covers for waste rock include: the large volumes of waste rock produced from mining activities resulting in a shortage of cover material; the cost of effective cover design and maintenance, especially valid in the use of synthetic covers; and the lack of knowledge around the long-term performance of covers in the prevention of ARD formation (Johnson & Hallberg, 2005). The greatest advantage to engineered soil covers, however, is the low level of maintenance required (MEND, 1994).

A cover of water may also be used to limit the oxygen availability at the mineral surface (Plumlee & Logsdon, 1998). Abandoned mine shafts may be flooded and sealed to prevent oxygen ingress. Sealing of the shafts may be accomplished using the waste rock or tailings from the mining operations. After the consumption of the oxygen in the water cover, typically 7 -10 mg/L at temperatures between 15 – 25 °C and 1 atm pressure (Sandler, 1998), ARD formation is minimized by the slow rate of oxygen transfer and the complete sealing of the mine shafts (Johnson & Hallberg, 2005). Water covers are often used to minimize ARD formation from processing tailings (MEND, 1996). Here however, the effectiveness of the covers is reliant on the complete and constant covering of the material by water. The use of water covers is limited by availability of water resources and the adequate ability to prevent the inflow of oxygen-containing waters (Johnson & Hallberg, 2005).

Combined reduction of the access of water and oxygen to the reactive sulphide minerals, and possible maintenance of a neutral pH despite sulphide oxidation can be achieved through the co-disposal of reactive sulphide tailings with inert or neutralizing components (Mehling *et al.*, 1997). Compacted waste rock, co-disposed with an inert material could limit water infiltration and thus ARD formation (Kleinmann, 1990). The theory behind co-disposal with a neutralizing agent is the *in-situ* neutralization of ARD formed (Maddocks *et al.*, 2009). Neutralizing components used can include carbonate minerals or organic material (Weber *et al.*, 2004a). Co-disposal components may also be chosen to encourage the passivation of the sulphide minerals (Evangelou, 1998). Limitations of co-disposal include the passivation or depletion of the neutralizing components and the ineffective ARD neutralization due to channelling (Plumlee & Logsdon, 1998).

To further limit the rate of ARD formation and aid in its prevention, the use of bactericides as additives to waste rock dumps has been investigated (Johnson and Hallberg, 2005; Ledin & Pederson, 1996; Erickson & Kleinmann, 1985; Schippers *et al.*, 2000). Here, the aim is to prevent the oxidation of the iron- and sulphur-containing minerals by micro-organisms by limiting their growth or colonisation of the mineral surface and thus limit the subsequent ARD formation. Limitations of bactericides, especially in the absence of covers, are the necessity for repeat application (Plumlee & Logsdon, 1998) and their variable effectiveness in the short and long term (Shippers *et al.*, 2000; Sand *et al.*, 2006; Johnson & Hallberg, 2005).

Although prevention techniques are often successful in reducing the volumes of ARD formed or delaying its onset, to date, they seldom prevent ARD formation completely. The ever present potential of the waste rock for ARD formation, lack of knowledge regarding the long-term performance of the techniques utilized, and the necessity for maintenance and monitoring suggests that current prevention techniques are not the optimum long term solution to ARD prevention.

#### 2.4.2. Treatment of Acid Mine Drainage

Treatment management schemes are employed after liquid drainage has been produced, either where generation prevention techniques have not been used or have failed. Treatment of mine drainage focuses on the removal of the toxic elements to country-dependent environmental levels, subsequent to discharge into the surrounding environment. Treatment schemes fall into two main categories, depending on the energy inputs into the systems used: either active or passive treatment systems.

Younger *et al.* (2002) defined treatment of ARD as active when it was achieved by methods requiring ongoing inputs of energy from non-renewable resources. Treatments could also necessitate the use of chemical or biochemical reagents. Treatment plants, situated on or close to the mine site, typically include multiple unit operations and require the ongoing manning by operators. Advantages of utilizing active treatment plants include the use of well understood technologies, designs that are easily adaptable to differing ARD compositions, a smaller footprint, and treatments that allow for the efficient conversion and precise control of effluent quality. The capital and ongoing operating and maintenance costs however constitute the main disadvantage in the use of active treatment plants (Younger *et al.*, 2002).

Passive treatment is defined as: *"The deliberate improvement of water quality using only naturally available energy source, in systems which require only infrequent maintenance in order to operate effectively over the entire system design life"* (Younger *et al.*, 2002). The development of passive treatment systems stemmed from observations of water quality exiting natural wetlands (Walton-Day, 1999), with initial applications limited to waste waters from coal operations (Younger, 2000). Today, passive treatment schemes are utilized for drainage with many different compositions including base metals (Wildeman & Updegraff, 1998; Eger *et al.*, 2000; O'Sullivan *et al.*, 2001; Gusek & Wildeman, 2002) and uranium mining operations (Noller *et al.*, 1994). Although early passive treatment systems resembled wetlands in construction and appearance, more modern systems consist of a number of stages, each stage utilized to treat different aspects of the mine drainage, operating in series or parallel, or a combination (Johnson & Hallberg, 2005). Advantages of passive systems over the active equivalent include the low operating and maintenance costs and typical use of non-hazardous reagents. The major disadvantages in the use of passive treatment schemes include the large land requirements, large capital costs required for construction, difficulties in achieving and maintaining adequate exit water qualities and the limits on effluent flow rates and volumes (Younger *et al.*, 2002).

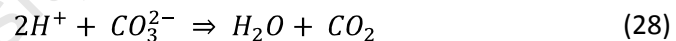
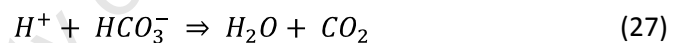
The major problems with ARD treatment include the use of hazardous chemicals, problems experienced in achieving and maintaining water quality when dealing with multi-metal ARD waste and the problems of dewatering and handling of the, often toxic, multi-metal sludge generated as a

by-product of the treatment processes (Karthikeyan *et al.*, 1995; Fan & Anderson, 1995; Younger *et al.*, 2002). Whether through active or passive means however, the main foci of the treatment of mine drainage are correction of the pH and reduction of the metal and dissolved salt concentrations (Akcil & Koldas, 2006). Each of these is discussed further with specific references to the methods and reagents most commonly employed in both the active and passive treatment of mine drainage.

### Neutralisation of ARD

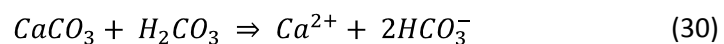
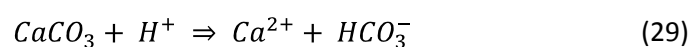
The pH of the ARD controls the metal solubility and thus their mobility. Many metals, for example Cu, Fe, Zn and Cd, are soluble at both high and low pHs but form insoluble hydroxyl compounds in the neutral pH region (Nordstrom & Alpers, 1999). This property remains the focal point for metal removal from ARD. The differences in solubility of metal hydroxides or metal sulphides at different pHs also allows for the possible recovery of metals from waste streams for subsequent commercial use. While this remains an expensive option requiring staged neutralizing and separation processes, it is becoming increasingly favourable due to the potential value of the recoverable metal salts.

Correction of pH to values within the neutral range is accomplished through the addition of neutralizing compounds to the ARD. In the case of ARD, the amounts of neutralization must be sufficient to neutralize the acidity of the drainage, counter protons formed from metal hydrolysis and to cause the precipitation of metal species. Neutralization of acidic drainage is most commonly performed through the reaction of protons with hydroxyl ions (Equation 26) or dissolved carbonate species (Equation 27).

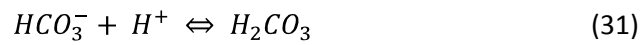


In active treatment processes, commonly used neutralizing compounds include  $Ca(OH)_2$ ,  $CaO$  and  $NaOH$  (Younger *et al.*, 2002; Skousen, 2002). The choice of reagent is governed by the necessary level of pH increase, the cost of the reagent, its ease of handling and reactivity (Younger *et al.*, 2002). The required pH level is governed by metal solubility and thus the metal content of the mine drainage. The cost of reagent is often linked to the volumes and acidity of waste water. Phipps *et al.* (1991), showed the cost effectiveness of  $NaOH$  and  $Ca(OH)_2$  at low acidity, low throughput and high acidity, high throughputs respectively over a five year period.

Carbon dioxide concentrations play a large role in the neutralization of acidity, in that, release of  $CO_2$  drives Equations 27-28 to the right. Calcite, commonly used in the treatment of ARD, is directly proton consuming and results in the release of bicarbonate ions (Equation 29).



Further, the presence of the bicarbonate ions also buffers the resultant treated solution with its ability to either consume or produce protons in the equilibriums reached between the carbonate - bicarbonate and bi-carbonate - carbonic acid



These reactions highlight the importance of the behaviour of CO<sub>2</sub> in ARD treatment systems, with the amount of CO<sub>2</sub> and the composition of the mine drainage important when determining the amounts of carbonate neutralizing reactant necessary (Hedin *et al.*, 1994b; Rose & Cravotta, 1998; Rose, 1999). The solubility and rate of mass transfer of CO<sub>2</sub> to the liquid phase also determine the kinetics of neutralization (Cravotta & Watzlaf, 2002).

Alkalinity addition in passive systems is constrained by the focus on naturally-available energy sources (eg: flow via gravity) and the need for only infrequent system maintenance. Additions of alkalinity in passive systems therefore are often infrequent. Some passive systems use anoxic limestone drain (ALD) channels, trenches filled with crushed limestone, to add alkalinity (Brodie *et al.*, 1993). Research into the uses and limitations of such systems has focused on the chemistry of the limestone dissolution, the reaction rates obtainable with differing ARD compositions and the kinetics of calcite dissolution (Rose, 1999). ALDs also exhibit problems with effluents with elevated oxygen, iron and aluminium concentrations owing to precipitation of the metal hydroxides onto the crushed limestone (Hedin *et al.*, 1994b). To counter this, oxic limestone drains (OLD), which limit the oxygen availability to the reaction surface, are also used. (Skousen *et al.*, 1998). The use of such systems has shown limited effects of iron precipitation on the limestone dissolution and subsequent neutralizing ability (Skousen *et al.*, 1998; Gusek & Wildeman, 2002). The majority of passive treatment systems employ both ALDs and OLDs to add alkalinity to ARD (Brodie *et al.*, 1993).

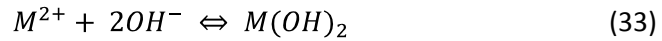
### **Removal of metals in ARD treatment**

The role of metals in the toxicity of ARD has been discussed previously. The removal of these components forms an important part in the treatment of mine drainage. As previously mentioned, metal solubility is linked closely to the drainage pH; with this property often forming the basis for metal removal. However, pH correction alone however is often not enough to remove metal species to potable water quality standards. Table 2-2 presents the limits of metal concentrations in drinking water.

Many studies have investigated the removal of metals from effluent streams (Kurniawan *et al.*, 2006), with the technologies including chemical- and bio-precipitation, ion exchange, adsorption, physical filtration and solvent extraction (Blais *et al.*, 2008). The most commonly used method of metal removal from effluent streams in active treatment processes is precipitation (Levasseur *et al.*, 2005).

Metals are most commonly removed through the precipitation of hydroxide and sulphide metals salts (Blais *et al.*, 1999), with metal hydroxide precipitation widely used in industry (Lewis, 2010). Metal hydroxides are formed through the addition of Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, NaOH or NH<sub>4</sub>OH, and

formed according to Equation 33. The acidic nature of ARD however often precludes the use  $\text{Ca(OH)}_2$  due to the formation of secondary precipitates, most notably gypsum, which, in processes not designed for gypsum production, leads to excess necessary reagent and leads to an increase in sludge disposal costs (Blais *et al.*, 2008).



The majority of metal hydroxides precipitate at pHs above 5 (Lewis, 2010; Blais *et al.*, 2008). Figure 2-2 shows metal hydroxide solubility as a function of pH of many metals.

**Table 2-2: Maximum metal concentrations of drinking water standards (From Blais *et al.*, 2008)**

Metals	Maximum concentration limits [mg/L]	Source
Antimony	0.006	U.S. National primary drinking standards - 1994
Arsenic	0.05	U.S. National primary drinking standards - 1994
Beryllium	0.004	U.S. National primary drinking standards - 1994
Cadmium	0.005	European economic community water standards - 1980
Chromium	0.05	European economic community water standards - 1980
Copper	1.0	U.S. National primary drinking standards - 1994
Mercury	0.001	European economic community water standards - 1980
Lead	0.05	European economic community water standards - 1980
Nickel	0.05	European economic community water standards - 1980
Selenium	0.01	European economic community water standards - 1980
Silver	0.01	European economic community water standards - 1980
Thallium	0.0005	U.S. National primary drinking standards - 1994
Zinc	5.0	U.S. National primary drinking standards - 1994

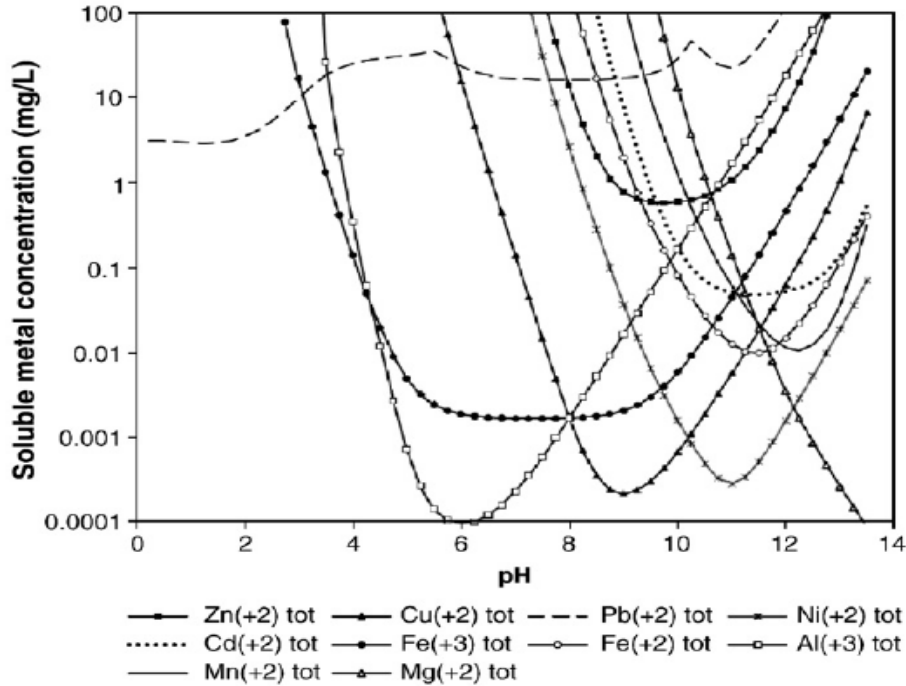


Figure 2-2: Calculated metal hydroxide solubilities as a function of pH (From Lewis, 2010)

Although not as widely used, sulphide precipitation offers some advantages of the use of hydroxide precipitation. Sulphide precipitates have a lower solubility (Figure 2-3), faster reaction rates, better selectivity and the potential for metal sulphide recovery (Lewis, 2010; Blaise *et al.*, 2008). However, sulphide precipitation is often more difficult to control, more costly, and more hazardous due to the potential formation of  $H_2S$  in acidic conditions (Veeken & Rulken, 2003). Under these conditions, it is often necessary to initially neutralize with NaOH before the addition of the sulphide chemical (Charerntanyarak, 1999). Metal sulphide precipitation occurs via Equation 34, with  $Na_2S$ , NaHS and  $H_2S$  the most commonly used sources of sulphide (Blaise *et al.*, 2008).



Many precipitation processes often include the use of coagulating agents such as aluminium and iron salts to aid precipitate separation (Duan & Gregory, 2003). In addition, flocculation chemicals are often added to increase the size of the precipitates and aid in sludge dewatering (Viadero *et al.*, 2006). Organic polymers, made of modified polyacrylamide (Viadero *et al.*, 2006), iron/cationic and aluminium/ cationic polymer blends are also used (Tandrus, 2000).

The separation of metal precipitates is usually performed using settling tanks, followed by active sludge dewatering via filtration (Blaise *et al.*, 2008), with the composition and physical characteristics of the precipitation sludge affects its handling and disposal. The long term environmental stability of these sludges has been the focus of many studies (Kalin *et al.*, 2006; Zinck, 2004; Fiset *et al.*, 2003, Zinck, 1997). Zinck *et al.* (1996) estimated that 6.7 million tons of sludge from ARD treatment plants was produced per year. Ledin & Pederson (1996) concluded that although treatment of ARD is technically feasible, the generation of unstable secondary wastes is a potential environmental concern for the future (Kalin *et al.*, 2006).

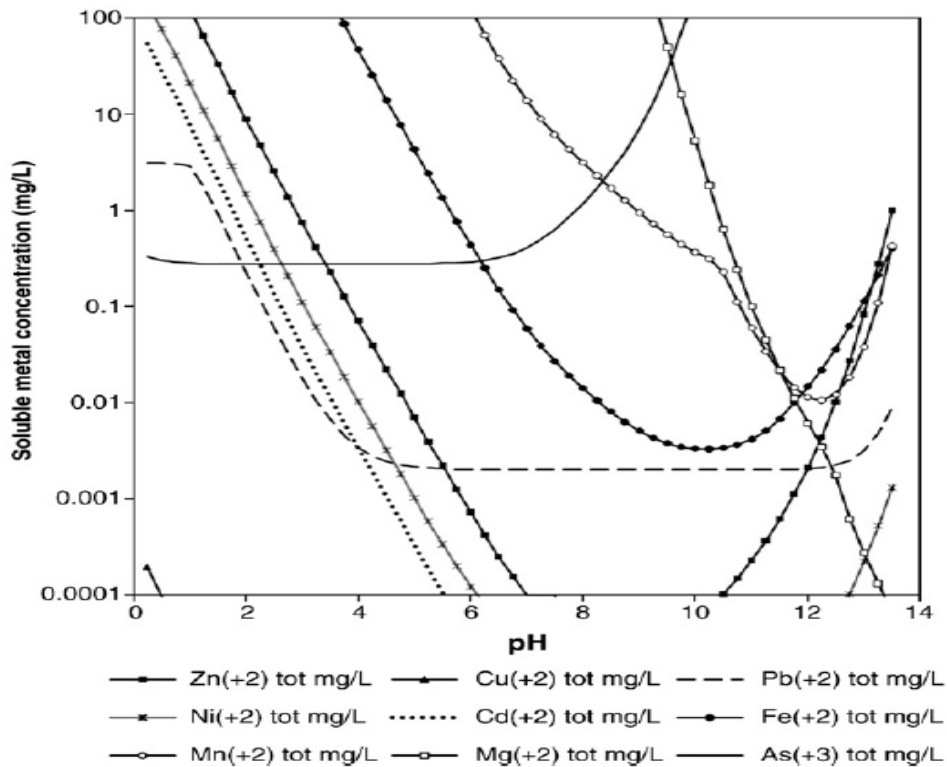


Figure 2-3: Calculated metal sulphide solubilities as a function of pH (From Lewis, 2010)

In passive treatment systems, where the process control is minimal, metal removal often occurs in conjunction with the pH correction. This often leads to metal precipitation within anoxic limestone drain systems but is less of a problem when utilizing oxic limestone drains. This problem is overcome in SAPS systems through stripping of the oxygen from the drainage prior to reaction with the alkalinity-adding reagent.

The use of ion-exchange and adsorption processes in the passive treatment of ARD is well documented (Karathanasis & Thompson, 1991; Machemer & Wildeman, 1992). Ion exchange however, although perhaps the dominant removal process for some metals, is not a reliable, long-term treatment process; with the possible release of metals in the advent of a pH shock to the system (Karathanasis & Thompson, 1991). In addition, although both ion-exchange and adsorption may have the potential to contribute to metal removal initially in constructed wetland systems (Machemer & Wildeman, 1992), the size of passive treatment systems, as compared to drainage volumes necessitating treatment, often limits the long term ability for metal removal (Walton-Day, 1999).

### The removal of sulphur in ARD treatment

The presence and role of sulphur and sulphur-containing compounds, both in reduced and oxidized forms, in ARD is discussed in Section 1.2. Due to the presence of sulphur-oxidizing bacteria within ARD systems, sulphate is usually the dominant sulphur form found in ARD waters; with its removal often necessary to meet environment discharge regulations. Table 2-3 details the permissible sulphate concentrations in drinking waters from around the world.

**Table 2-3: Sulphate concentration guidelines in drinking water for several countries**

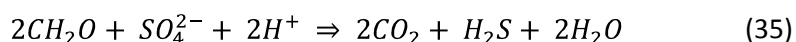
Country	Max permissible SO <sub>4</sub> <sup>2-</sup> [mg/L]	Source
N/A	500	WHO, 2004
USA	250	USEPA, 1995
Canada	500	Health Canada, 2012
Australia	250	NHMRC, 2011
South Africa	200	DWAF, 1996

The removal of sulphate during pH correction and metal precipitation often fails to reduce sulphate concentrations to these permissible levels. Neutralized ARD typically contains sulphate concentrations between 1000 – 2000 mg/L (Kempton *et al.*, 2003). These authors have also modelled the effectiveness of sulphate removal through lime addition. This is limited by the solubility of the gypsum product, with the theoretical minimum sulphate concentration remaining in waste waters above pH 8.0 of 650 mg/L (Kempton *et al.*, 2003).

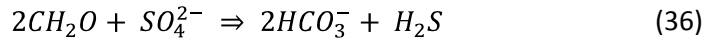
Methods for the removal of sulphates from waste waters include the addition of concentration processes, most notably membrane separation technologies (Kempton *et al.*, 2003), to existing neutralization processes or the reduction, either chemically or biologically, and subsequent precipitation of metal sulphides from solution (Benner *et al.*, 1999). Biological treatment technologies usually exhibit cost benefits (van Hille *et al.*, 2012, Kempton *et al.*, 2003) and, due to its natural occurrence by sulphur reducing bacteria in wetlands (Benner *et al.*, 1999), are often viewed as more environmentally friendly (Wieder & Lang, 1992).

Biological, sulphate reduction can be achieved using sulphur-reducing bacteria, the use of which also necessitates the presence of both a carbon source and electron donor. The selection of an electron donor and carbon source for active biological reduction processes is dependent on the treatment efficiency and the cost of the substrate (van Houten *et al.*, 1994). Electron and carbon sources include: sewerage sludge, animal manure, agricultural wastes, lactate, pyruvate and ethanol (Liamleam & Annachatre, 2007).

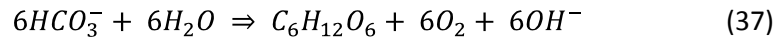
In addition to sulphate reduction, biological reduction may increase the alkalinity of the ARD, promoting the precipitation of metal –sulphide complexes and allowing for the incorporation of the reduced sulphur species into the organic sulphur compounds. The generation of alkalinity from sulphate reduction is dependent on the pH of the waste waters. At pH below 4.5, microbially mediated sulphate reduction consumes protons with CO<sub>2</sub> as a by-product through the following reaction (Kalin *et al.*, 2006).



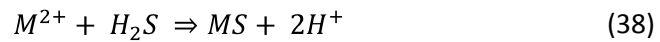
Here, the CH<sub>2</sub>O represents a simple organic source for the micro-organisms. The CO<sub>2</sub> produced, once the solubility limit has been reached, may escape the system in gaseous form and thus not contribute to the pH of the system. At pHs greater than 4.5, bicarbonate ions are produced rather than gaseous CO<sub>2</sub>. The presence of the bicarbonate ions also buffers the solution, with the potential to further consume or produce protons (Equations 36-38) depending on the equilibria formed.



Further alkalinity may be produced by the presence of photosynthetic micro-organisms within the reduction environment. Here, the micro-organisms consume the bi-carbonate ions, producing a strong basic product (Johnson & Hallberg, 2005).



The possibility of alkalinity generation is also affected by the presence of metals as free cations within the waste drainage, and their possible reaction with the H<sub>2</sub>S product formed from the sulphur reduction.



Sulphate reduction often occurs in conjunction with metal reduction; predominantly with the reduction of ferric to ferrous iron (Sheoran *et al.*, 2010). Reactions occurring here often potentially result in a net consumption of protons and neutralization (Schindler *et al.*, 1986). As a consequence, metal removal is also achieved through sulphur reduction with up to 95% removal of Fe, Zn, Mn, Ni and Cd being reported in pilot scale bioreactors (Dvorak *et al.*, 1992).

Off-line sulfidogenic bioreactor systems represent active sulphate reduction processes which operate with separate hydrogen sulphide production and metal precipitation circuits (Johnson & Hallberg, 2005). The Thiopaq system uses two distinct micro-organism populations to form hydrogen sulphide and precipitate metals and, with the use of sulphide oxidizing micro-organisms, to convert any excess hydrogen sulphide to elemental sulphur (Boonstra *et al.*, 1999). The Biosulfide System (Rowley *et al.*, 1997) uses two independent biological and chemical processes to form hydrogen sulphide and treat ARD. Sulphur reducing bacteria are used to produce hydrogen sulphide, which is then used to precipitate metal species from the ARD.

Improvement of water quality by natural wetlands (Wieder & Lang, 1992) led to the research into and construction of artificial wetland systems for the treatment of ARD, with the sulphate reduction and metal precipitation are performed by naturally occurring micro-organisms. The presence of plants in such constructed systems is generally not necessary for ARD treatment (White *et al.*, 2011, Johnson & Hallberg, 2005) and variants of constructed systems which do not support plant growth are utilized (Johnson & Hallberg, 2005). A variant of the constructed wetland, permeable reactive barriers allow for the *in-situ* treatment of ARD and can be installed directly into polluted aquifers (Benner *et al.*, 1997). Water leaving the aquifer flows directly through this barrier, which is constructed to promote the growth of sulphate reducing bacteria (Benner *et al.*, 1999).

Advantages of active processes include the predictability of process performance, selective metal precipitation and recovery, and lower residual sulphate concentrations as compared to passive systems (Johnson & Hallberg, 2005). The capital and operational costs associated with active processes however remain their largest disadvantage. In passive systems, the necessary land surface area often prohibits the implementation of such systems. The long-term replenishment of organic

feed sources within these systems is also an area of concern (Dollhopf *et al.*, 1988) and may lead to increased operational costs in passive systems.

Overall, treatment of mine drainage remains complex due to the often competing reactions involved in the pH correction, reduction in ionic strength and the removal of the toxic elements from the waste waters. In addition, economic factors compete with the selection of the optimum treatment option (Plumlee & Logsdon, 1998). This is especially true for waste rock systems, where the low mineral grades and large volumes highlight the longevity of ARD formation (Walton-Day, 1999). ARD generation in such systems remains problematic with the current options limited to ARD containment and treatment (Plumlee & Logsdon, 1998). This, coupled together with the lack of long-term prevention mechanisms, may necessitate the indefinite treatment of ARD, during the life-time of the mining operations, but, more importantly, long after the termination of any mining activity in the area.

## 2.5. Project Motivation

The large sulphide-containing, waste rock volumes and the longevity of the ARD generation form two of the main problems associated with ARD from waste rock. In addition, current ARD prevention techniques, although successful in the short-term, fail to remove the potential for its generation in the future (Cilliers, 2006). Controlled removal of the active components, the sulphide-bearing minerals, presents the most effective prevention treatment for ARD.

Physical separation of the sulphide components from waste rock is not feasible owing to limited sulphide mineral liberation; hence its removal by reaction only can be considered. In particular, the use of biohydrometallurgical processes, designed for the large solid phase volumes associated with waste rock, offer potential for the removal of sulphide components through oxidation. This allows for the potential metal concentration from the low-grade wastes into small-volume liquid streams (Bruckard & McCallum, 2009). The production of a liquid effluent stream also allows for easier treatment schemes, while the augmenting of oxidation conditions allow reaction over reduced time frames as compared to typical ARD generation (Bryan *et al.*, 2006).

The role and favourable conditions for growth and colonisation of bioleaching micro-organisms is well documented (Watling, 2006), with studies linking microbial activity to the rate of ARD generation (Smart *et al.*, 2002). Since favourable conditions for bioleaching micro-organisms within waste rock dumps typically only develop after an extended lag period (Hesketh *et al.*, 2010), promotion of favourable bioleaching conditions may lead to a decrease in this lag time period and an overall increase in the rate of ARD generation.

The aim of this project therefore was to investigate the designed acceleration of ARD generation from waste rock dumps and whether its generation, under controlled conditions, can be accelerated to occur by mine closure. This aim was accomplished in two main sections: through the addition of conditions favourable for microbial growth and colonization and, secondly, through an investigation into methods employed to assess and characterise the ARD potential of the waste rock subsequent to accelerated generation.

In the completion of this project, it is acknowledged that limitations exist in the use of laboratory-scale column experiments to simulate ARD generation from commercial-scale waste rocks dumps. The applicability of laboratory-scale experiments may explain the some of the discrepancies reported between laboratory results and field test-work (Crock *et al.*, 1999), hence laboratory results must be interpreted appropriately. In particular, the reduction in particle size often leads to increased reaction rates as compared to field studies (Jennings *et al.*, 2008). Comparative studies have shown large differences when comparing the weathering rates between laboratory-scale column experiments and kinetic field columns containing 1.6 tons of waste rock, with the observed differences due to differences in particle size (Stromberg & Banwart, 1999). Although direct comparison of weathering rates is often not possible, changes in leachate quality in laboratory column tests does often follow the general trend of complementary field studies (Smith *et al.*, 2013). In particular, through linking these tests through appropriate modelling approaches, improved value of the laboratory data is achieved (Simunika *et al.*, 2013).

University of Cape Town

### 3. Material and Methods

The experimental work conducted in this case study was divided into two main categories. Constructed waste rock samples firstly underwent bioleaching in laboratory bioleach columns. Secondly, acid mine drainage testing was conducted on the resultant solid phase. Both of these experimental categories required ore preparation. This, along with the experimental apparatus, procedures and analysis protocols used in the study are described.

#### 3.1. Materials

##### 3.1.1. Waste Rock Samples

Three copper-bearing waste rock samples were used in this study. Samples A & B, described in Appendix 11.1, were sourced from a commercial bioleaching operation in Chile, South America. Waste rock sample C was a mix of two bioleaching ore samples from Chile, South America, a zinc-bearing waste rock and a zinc concentrate from South Africa.

XRD analysis, provided by the ore suppliers and confirmed by analysis performed at the University of Cape Town, indicated that pyrite (2.6 %, 0.8 %), chalcopyrite (1.3 %, 1.8 %) and galena (1.7 %, 2.4 %) were the main sulphidic components in waste rock A and C respectively. Copper was the majority metal in the ores and, in addition to the chalcopyrite, was present in trace amounts (< 0.2 weight %) as chalcocite, covellite, bornite and enargite. Gangue components were dominated by quartz (40 %, 39 %), mica (21 %, 5.5 %) & magnetite (16 %, 17 %) for waste rock A and B respectively. Ore mineralogies and grades for waste rock samples A, B and C are presented in Appendix 11.1.

Where pyrite was added to leaching experiments, an 86% (XRF analysis) pure concentrate was utilized.

##### 3.1.2. Bioleaching Micro-organisms

The specific species used were obtained from the German culture collection DSMZ: *Acidithiobacillus* (*At.*) *ferrooxidans* DSM 584, *At. caldus* DSM 8584 and *Leptospirillum* (*L.*) *ferriphilum* ATCC 49881. Unless otherwise stated, all stock cultures were maintained in 1 L shake flasks with a 700 mL working volume, agitated at 120 rpm on an orbital shaker. *At. ferrooxidans* was grown at pH 1.6 in modified 9K medium, consisting of the following (g/L):  $(\text{NH}_4)_2\text{SO}_4$  (2.0),  $\text{K}_2\text{HPO}_4$  (0.5),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (0.5), KCl (0.1),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (20.0). *At. caldus* was grown in similar media excluding  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and with an additional 1 g/L of  $(\text{NH}_4)_2\text{SO}_4$  and 5 g/L elemental sulphur. *Leptospirillum ferriphilum*, agitated at a rate of 400 rpm, was grown in a 1 L continuous stirred tank reactor (CSTR) at a dilution rate of 0.021 /h and pH 1.30. The reactor feed contained the following components (g/L):  $(\text{NH}_4)_2\text{HPO}_4$  (0.53),  $(\text{NH}_4)_2\text{SO}_4$  (1.83),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (5.0),  $\text{K}_2\text{SO}_4$  (1.11) as well as 10 mL/L Vishniac solution containing:  $\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$  (1.0),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (1.0),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (1.0),  $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$  (0.5),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (5.0),  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.5),  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (0.5), added to 15 g/L EDTA dissolved in 6% KOH. The *Leptospirillum ferriphilum* strain was originally obtained from a continuous tank bioleaching mini-plant, treating a pyrite concentrate from Gamsberg, South Africa, and was maintained at a residence time of 72 h.

### 3.1.3. Experimental Equipment

#### Bioleach column experiments

A system of polyvinyl chloride (PVC) laboratory scale column reactors (Figure 3-1) were used in the bioleaching of the constructed waste rock samples. The reactors were 1.1 m in height and had an internal diameter of 0.1 m. Each column held approximately four kilograms of ore, with a void volume of approximately 40%. The temperature of the bioleach was controlled via an external heating coil; with temperature sensors located on the external surface of the columns and internally within the ore bed. The columns were insulated to promote heat retention.

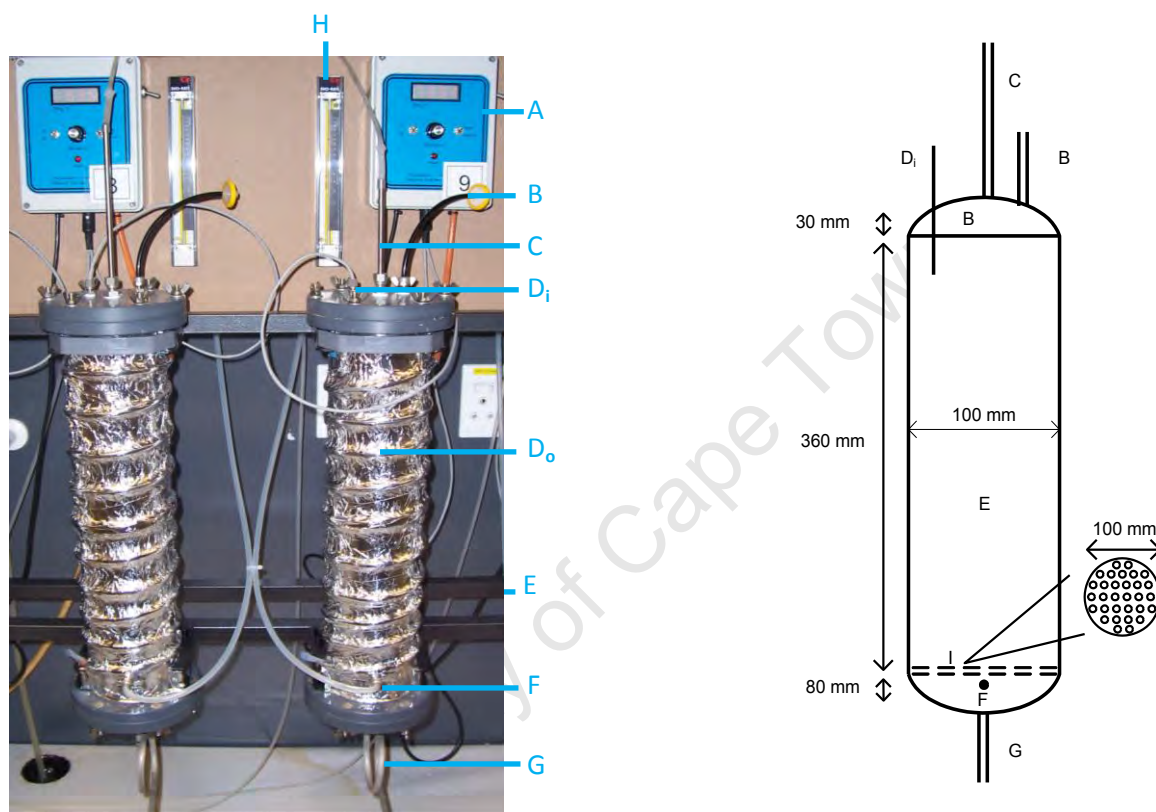


Figure 3-1: Bioleach column reactor system after Harrison *et al.* (2010)

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

## 3.2. Experimental Procedures

### 3.2.1. Preparation of solid samples

#### Preparation of waste rock samples for column experiments

##### Representative Sampling

To ensure uniformity across the column experiments, waste rock samples were split into representative samples using an ore riffler in the Centre for Mineral Research Laboratories at the

University of Cape Town. Separation was conducted using the entire ore sample and ending with the necessary number of 4 kg ore samples.

#### **Preparation of waste rock for ARD analysis**

After bioleaching experiments, leached waste rock samples were removed from the column, washed with distilled water and dried before undergoing further mineral processing in preparation for ARD test work.

#### Milling

The entire leached waste rock sample was milled for 15 minutes using a rod mill with a working volume of approximately 30 L. Ten, 1.2 kilogram, 290 mm × 25 mm stainless steel rods were used in the milling process. After milling, the ground material was passed through a 200 µm sieve.

#### Representative Sampling

In order to ensure representative samples were used in the ARD tests, the finely milled ore was split using a Dickie & Stockler, 10-pot rotary riffler. The resulting two hundred gram sample was split further using an 8-way Fritsch rotary sample divider. From this, between 7-10 grams were obtained.

#### **Preparation of waste rock for XRD analysis**

In preparation for X-ray diffraction analysis, milled ore samples were micronized using a McCrone Micronizer. Approximately 30 mL of a 30% acetone-water mixture was added to the micronizing chamber containing approximately 2 g of milled ore sample. Each sample was micronized for 15 minutes, with the resultant slurry collected in a 150 mL Erlenmeyer beaker. This was filtered and allowed to dry overnight at room temperature.

### **3.2.2. Bioleach column experiments**

Column experiments were conducted on waste rock under differing conditions to investigate the rate of generation and composition of the resulting ARD.

#### **Column loading**

The waste rock sample, prepared by representative sampling, was agglomerated prior to being loaded in the bioleach column reactors. A liquid mixture containing 4.7 mL, 96-98% H<sub>2</sub>SO<sub>4</sub> and 50 mL H<sub>2</sub>O was added to approximately 4 kg of dry constructed, waste rock. Where applicable, the pyrite concentrate was mixed with the waste rock at this stage. After mixing, approximately 10 mL, containing 10<sup>9</sup> cells of each microbial species used, was added to the agglomerated waste rock. The samples were mixed before being loaded into the reactors to achieve a final moisture content of approximately 5.5%.

#### **Column Operating Procedure**

Unless otherwise stated, bioleach columns were fed continuously from the top via Masterflex pumps at a rate of approximately 40 mL per hour. Where aerated, compressed air flowed into the column from below through an air distributor at a rate of 12 L/min. Leachate solution was collected on a continuous basis from the bottom of the columns using 5L sample containers.

### **Column sampling procedures**

The leachate deriving from the column experiments was sampled on a daily basis. Of the approximate 940 mL of liquid collected over the 24 hour period, a 25 mL sample was sent for copper analysis. A further 25 mL sample from the bulk volume was used for the pH, redox potential and iron analyses.

### **End of experiment procedures**

Once the bioleaching experiment phase had been completed, the bioleaching columns were stopped and left overnight to allow any remaining leachate solution to drain from the column reactors. This solution was analysed as above.

The solid phase was removed from the columns and washed before milling. The pH of the wash solution was determined by the pH of the experimental feed. Where a bioleach column had an acidic feed, the pH of the wash solution was between pH 1.2 and pH 1.5. In the case of a water-fed column experiments, distilled water was used to wash the ore. Two litres of washing solution was added to the ore solids in a bucket, mixed by hand, and allowed to settle before the solution was drained through a 150  $\mu\text{m}$  sieve. The liquid phase was discarded and the solids were allowed to dry for 7 days at 32 °C before being packaged and weighed.

### **In-Bed Sampling Technique**

In-bed sampling was conducted following the procedure developed by Chiume *et al.* (2012), using the experimental conditions as outlined above. Approximately 300 grams of solid (wet mass) was removed from the lower portion of the in-bed sampled column on a weekly basis for use in ARD characterisation tests. The use of in-bed sampling was limited to one set of column experiments.

### **Column Reproducibility Tests**

Unless otherwise stated, reproducibility tests were performed using the column operating procedures as outlined above. For column experiments performed over varying durations, the sampling and end of experiment procedures remained the same as those stated above.

## **3.3. Analytical Methods**

### **3.3.1. Solution analysis**

Analyses of the leachate solution resulting from the bioleach column and the liquid phase in the flask experiments are described.

#### **pH and redox potential measurements**

The pH of the leachate solutions resulting from the bioleaching and flask experiments was measured with use of a Metrohm 713 pH meter. Redox potential measurements were made using a Metrohm 704 Eh meter against a silver/ silver chloride reference electrode.

#### **Copper concentration**

The copper content of the leachate solution was quantified by atomic absorption spectrometry (AAS) using a Varian SpectrAA 30 spectrometer incorporating Spectra AA 100/200 version 1.1 software by the analytical laboratory in the Department of Chemical Engineering at the University of Cape Town.

### **Ferrous and total iron concentrations**

Ferrous iron concentrations were determined colourimetrically using the 1-10 phenanthroline method using a Helios  $\alpha$  UV-Vis spectrophotometer at 510nm (APHA, 1998). Total iron was measured using the same method by adding excess hydroxylamine to the sample, promoting the reduction of any  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  (APHA, 1998). Concentrations were quantified against a standard curve.

### **Sulphate concentration**

The sulphate concentration in the leachate was measured turbidimetrically using the method outlined by the American Public Health Association (APHA, 1995). Measurements were conducted using a Helios  $\alpha$  UV-Vis spectrophotometer at 420 nm. Concentrations were quantified against a constructed standard curve.

### **3.3.2. Analysis of solid samples**

Total sulphur quantification from solids samples were conducted using LECO analysis, combined digestion and ICP analysis and x-ray diffraction. Three methods were employed to facilitate comparison of the values obtained from each method.

#### **LECO Analysis**

LECO analysis quantified the percentage total sulphur in a sample using thermal decomposition combustion infrared spectrophotometry by way of the LECO S632 sulphur analyser. The analysis was done by the Analytical Laboratory staff in the Department of Chemical Engineering at the University of Cape Town.

#### **Digestion & ICP Analysis**

Quantification via digestion and ICP was performed by the staff of the analytical laboratory in the Department of Chemical Engineering at the University of Cape Town. The methods employed were developed in house, with samples sequentially digested using concentrated solutions of hydrochloric, hydrofluoric and nitric acids.

#### **X-ray Diffraction Analysis**

X-ray diffraction was conducted using and performed by the Analytical Laboratory in the Department of Chemical Engineering at the University of Cape Town.

#### **Quantification of copper and iron**

Quantification of the copper and iron content of the waste rock was performed through a combination of acid digestion and atomic absorption spectrometry. Sample digestion was performed sequentially using concentrated hydrochloric, hydrofluoric and nitric acids. AAS analysis was performed using a Varian SpectrAA 30 spectrometer incorporating Spectra AA 100/200 version 1.1 software by the analytical laboratory in the Department of Chemical Engineering at the University of Cape Town.

### 3.4. Acid Rock Drainage Tests

#### 3.4.1. Static Tests

Acid base accounting (ABA) and net acid generation experiments were conducted to quantify the ARD potential of the ore samples. All test work was conducted in triplicate and averages reported.

#### Acid base Accounting (ABA)

Quantification of the net acid generation via acid base accounting uses the difference between the maximum potential acidity (MPA) and the acid neutralizing capacity (ANC) of the ore samples.

$$NAPP = MPA - ANC$$

This difference is reported as a net acid producing potential value (NAPP) with units of kg H<sub>2</sub>SO<sub>4</sub> / ton of ore.

#### Maximum potential acidity (MPA)

The maximum potential acidity of the samples was calculated using the sulphur content determined via LECO analysis (Section 2.6.2) and the assumption that all the sulphur present undergoes complete oxidized to form sulphuric acid.

$$MPA = 30.6 * S_{Total}$$

The total sulphur is in the form of a percentage value; giving the MPA value units of kg H<sub>2</sub>SO<sub>4</sub> / ton of ore.

#### Acid neutralizing capacity (ANC)

Acid neutralization capacity was determined experimentally using the method outlined by Skousen *et al.* (1997) as one of the ore constituents was thought to have a siderite component. For comparison, the Sobek (Sobek, 1978) and Standard Skousen (Skousen *et al.*, 1997) methods were performed on selected samples.

The volume and molarity of the HCl solution to be used in the ANC experiments was determined through a Fizz rating test (Sobek, 1978), performed by adding 1-2 drops of concentrated acid to 0.5 g of solid sample. The reaction was classed according to the intensity of the visible and audible fizz.

For the Skousen methodologies (Skousen *et al.*, 1997), a 2 g milled ore sample was measured into a 250 mL Erlenmeyer flask. An appropriate quantity of HCl solution at the appropriate concentration was added as per the fizz rating. De-ionized water was used to make up the total volume to 100 mL. The flask was then covered and allowed to stand overnight. The solution was boiled gently for five minutes and filtered through 500 µm filter paper to recover the filtrate.

The Incremental Skousen method was performed as outlined by Lawrence and Wang (1997). Ten drops of a 30 % H<sub>2</sub>O<sub>2</sub> solution were added to the collected filtrate. This was allowed to stand for 15 minutes before titration using diluted NaOH (concentration determined by fizz rating) to a pH of 4.5. These steps were repeated until a steady pH value of 4.5 was obtained. After being allowed to stand overnight, the pH was corrected pH 7.0. Again, ten drops of a 30 % H<sub>2</sub>O<sub>2</sub> solution were added to the filtrate, the flasks left for 15 minutes, and the pH corrected pH 7.0; repeated until a stable pH was reached. The process of a 24 hour wait, addition of ten drops of 30% H<sub>2</sub>O<sub>2</sub>, 15 minute wait, and

titration to a stable pH value of 7.0 was repeated over a 72 hour period, with the total volumes of dilute NaOH used over the 4 day period recorded.

The Skousen (Skousen et al., 1978) method differs from the Incremental method in the addition of the H<sub>2</sub>O<sub>2</sub>. Here, the addition of the ten drops, 30 % H<sub>2</sub>O<sub>2</sub> was replaced with the addition of a 5 mL aliquot of 30 % H<sub>2</sub>O<sub>2</sub>, and 15 minutes waiting period, with 5 minute boiling step.

The Sobek ANC method was followed as per Sobek et al. (1978). After addition of the HCl volume and 20 mL distilled water to a 2 g ore sample, the solution was heated for two hours at a temperature of 80 – 90 °C. The solution was made up to the 120 mL before being titrated with a dilute NaOH solution to a pH of 7.0. This titration was repeated over 72 hours.

To calculate the ANC value, the exact mass of the ore sample, the molarity of the NaOH sample and the volume of NaOH were compared to those obtained when using a blank sample.

$$ANC = \frac{Volume_{HCl} - Volume_{NaOH} * C * M_{acid} * 49}{W_{sample}}$$

Where M<sub>acid</sub> is the molarity of the acid (M), W<sub>sample</sub> the mass of the sample (g) and “C” takes into account the differing molarities of the NaOH and HCl solutions.

$$C = \frac{Volume_{HCl \text{ in Blank}}}{Volume_{NaOH \text{ titrated in Blank}}}$$

A conversion factor of 49 results in the ANC units of kg H<sub>2</sub>SO<sub>4</sub> / ton.

### Net acid generation (NAG)

Net acid generation experimental work was carried out using hydrogen peroxide to oxidize all acid generating components of the ore sample actively. Test work was conducted following the method outlined by Miller et al. (1997).

Approximately 2.5 g of milled sample was measured into a 500 mL Erlenmeyer flask. To this was added 250 mL of 15% H<sub>2</sub>O<sub>2</sub> solution, corrected to a pH of between 4.5 and 5.5 using a 5 M NaOH solution. The mass of the flask was recorded and was allowed to stand overnight.

After 24 hours, the flask was boiled for a minimum of two hours or until no more effervescence was observed. Once all the H<sub>2</sub>O<sub>2</sub> had been removed, distilled water was used to correct the mass and the pH was measured and recorded. The sample was cooled and allowed to settle. Prior to filtering, the mass of the filter paper was recorded. Both the filtrate and the filter cake were recovered from the filtering process. The filtrate was titrated against a 0.1 M NaOH solution to a pH of, firstly, 4.5 and, secondly, 7.0, with the volumes of NaOH recorded for both pH values. The filter cake was recovered and once again reacted with a 15% H<sub>2</sub>O<sub>2</sub> solution, with the mass of sample lost, as unrecoverable from the filter paper, recorded. This was repeated until the pH of the filtrate had a value of 4.5 or greater. The NAG values for each titration were calculated using the following equation:

$$NAG = \frac{49 * V * M}{W}$$

where V is the total volume of NaOH used in each titration step (mL), M is the molarity of the NaOH solution used and W is the mass (g) of ore sample used in each reaction step. The inclusion of the constant, 49, in the equation allows for units of NAG of kg H<sub>2</sub>SO<sub>4</sub> / ton ore.

### 3.4.2. Biokinetic, accelerated weathering test

The acid production potential of the sample under microbial oxidation conditions and over time was investigated through biokinetic flask tests to characterise accelerated weathering leading to ARD. The method used by Hesketh *et al.* (2010) was followed.

Autotrophic basal salt (ABS) medium (150 mL) at a pH of 2.0, was added to 7.5 g milled ore samples in 250 mL Erlenmeyer flasks. Flasks were inoculated with a mixed consortium of *Acidithiobacillus ferrooxidans*, *Leptospirillum ferriphilum*, *Sulfobacillus benefaciens* and *Acidithiobacillus caldus* and were maintained at 37°C on an orbital shaker at 150 rpm. Two different sets of experiments were conducted. In the first set, the pH was corrected to pH 2 by adding concentrated H<sub>2</sub>SO<sub>4</sub> on every sample day. This was continued until the pH fell below 2.0. The amount of concentrated H<sub>2</sub>SO<sub>4</sub> was recorded in each instance. In the second set of flasks, the pH was not controlled but was allowed to vary according to the acid producing and neutralizing ore components. Biokinetic flask experiments were run over a 75 day period.

Flasks were sampled every alternate day according to the following procedure. Once the flasks had been removed from the orbital shaker, distilled water was used to correct for volume lost due to evaporation. Flasks were allowed to settle before the pH was recorded and H<sub>2</sub>SO<sub>4</sub> added if applicable. The redox potential and a 100 µL sample was taken for iron analysis before the flasks were returned to the orbital shaker.

### 3.4.3. Terminal duration estimations

A simple method was developed in this study for the estimation of the time necessary for complete solubilisation of the mineral sulphide, equating to complete ARD generation, was developed using a linear extrapolation of the copper, iron and sulphur extraction curves. Similarly, a linear extrapolation of the NAPP and NAG results was used for terminal duration estimations for the static ARD test results. Detailed calculations for these methods is presented in Appendix 11.4

## 3.5. Experimental Approach

Accelerated leaching under different conditions was studied using laboratory scale, bioleach column reactors. Experiments were conducted under varying conditions to assess the effect of operating conditions on the rate and composition of ARD generated from the waste rock samples. Following bioleaching, static ARD characterization tests were conducted on the solids material to investigate the change in the ARD potentials of the solid phase.

Further column experiments were conducted to investigate the variability in the leaching data as a result of the inherent experimental errors associated with laboratory scale bioleach column reactor

experiments. In addition, the use of an in-bed sampling technique performed on one reactor was investigated as a replacement for five individual bioleach columns.

An investigation into the use of difference static characterization tests on one waste rock sample was performed to highlight the applicability of the different methods for use on waste rock samples. Biokinetic ARD characterization tests were also performed in order to assess the applicability of this test on waste rock samples and to highlight the advantages of this characterization tests over the static methods.

Lastly, the effect of an addition of an easily accessible iron and sulphur lixiviate source of the rate of ARD generation was investigated on a waste rock sample with differing composition as to that investigated earlier. The findings of previous chapters were integrated into this investigation.

**Table 3-1: Summary of experiments performed detailing the aim of each experiment, the experimental system used, the waste rock sample, the experimental conditions and the chapter wherein the results are presented.**

<b>Aim of Experiment</b>	<b>Experimental system</b>	<b>Waste rock sample</b>	<b>Experimental Conditions</b>	<b>Thesis Chapter</b>
Investigating the effect of leaching conditions on the rate of ARD formation	Bioleach column reactors	Sample A	Standard conditions with varying temperature, aeration and feed composition	Chapter 4
Investigating the differences in rates of decrease of ANC & MPA	Bioleach column reactors	Sample B	Standard conditions at 32 °C	Chapter 5
Investigating the use of in-bed sampling for the <i>in situ</i> sampling of bioleach column reactors	Bioleach column reactors	Sample B	Standard conditions at 32 °C	Chapter 6
An experimental review of ARD characterization methods	Flask experiments	Sample A & B	Various conditions as outlined by each characterization methods	Chapter 7
Investigation into the addition of a pyrite concentrate for enhanced ARD generation	Bioleach column reactors	Sample C	Standard conditions with varying feed composition	Chapter 8

## **4. Investigation into ARD Generation from Waste Rock**

### **4.1. Introduction**

To date, studies have focused on the potential for ARD to form from waste rock, with little attention on the effect of operating conditions on ARD generation. The initial experimental work presented here aimed to gain an understanding into ARD generation from waste rock and the effects of regulatory factors typically found in waste dumps or used to mitigate ARD generation. The effects of acidity, temperature, aeration and a pyrite addition were investigated.

Laboratory scale, bioleach column reactors were used to simulate conditions in the waste rock dump. The preparation of the waste rock followed a typical heap bioleaching agglomeration protocol to stimulate microbial colonization and reduce the experimental duration. While this is not fully representative of dump conditions, it allowed the ARD formation to be aggravated, thereby allowing experiments to be conducted in a feasible timeframe. The leachate solution was sampled with measurements of the pH, redox potential, ferrous and total iron concentrations performed. The redox potential, a measure of the ferric to ferrous ratio, was used as a indication of the microbial activity within the bioleach system owing to the catalytic acceleration of ferrous iron oxidation. A major limitation in using the redox potential, however, is that it gives no indication of the activity of pure sulphur-oxidizing microbial species. In addition, although all column experiments were inoculated with identical cultures, any subsequent changes in microbial population were not investigated.

Two extreme scenarios were investigated using typical dump conditions and typical heap bioleaching operating conditions, the former representing slow ARD generation and the latter accelerated. Furthermore, the typical heap bioleaching experiment was used as a control for investigations into the effects of temperature, aeration and pyrite addition.

### **4.2. Leachate profiles under typical conditions in the waste rock dump**

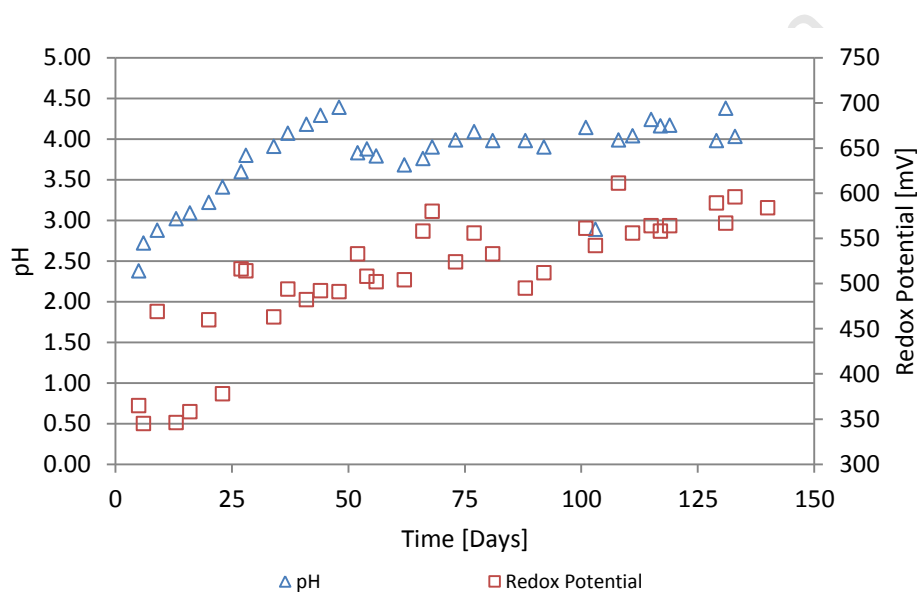
Untreated waste rock dumps are exposed to weather elements, the most important being rainfall, temperature and airflow. Following ARD generation, rainfall run off may carry toxic elements into the local water systems. To simulate ARD generation under these conditions, inoculated bioleach columns were irrigated continuously for 24 hours, twice weekly with water. The use of inoculum was chosen to accelerate the generation of the conditions typical in the dump over time.

A solution flow rate of 40 mL/h, corresponding to 36 mm per day of rainfall, was chosen. While this was chosen to enable comparison with heap leach data, this amount of rainfall is not uncommon in some of South Africa's mining areas ([www.saexplorer.co.za](http://www.saexplorer.co.za)). In addition, a high irrigation rate was utilized to minimize the duration of the experiments. Leachate samples were collected and analysed for pH, redox potential and the concentrations of ferrous iron, total iron and copper.

The pH of the leachate solution (Figure 4-1) rose over the first 35 days from an initial approximate value of pH 2.0, to approximately pH 4.0 which was maintained for the remaining duration of the experiment. The low initial value was a direct result of the acid agglomeration process, with pH conditions suitable for bioleaching micro-organisms. The increase in pH can be attributed to the acid

neutralization capacity of the waste rock. Although the final pH lies outside the optimum for bioleaching micro-organisms (Watling, 2006), the stable pH below that of the feed suggests some microbial activity after the 35 day period.

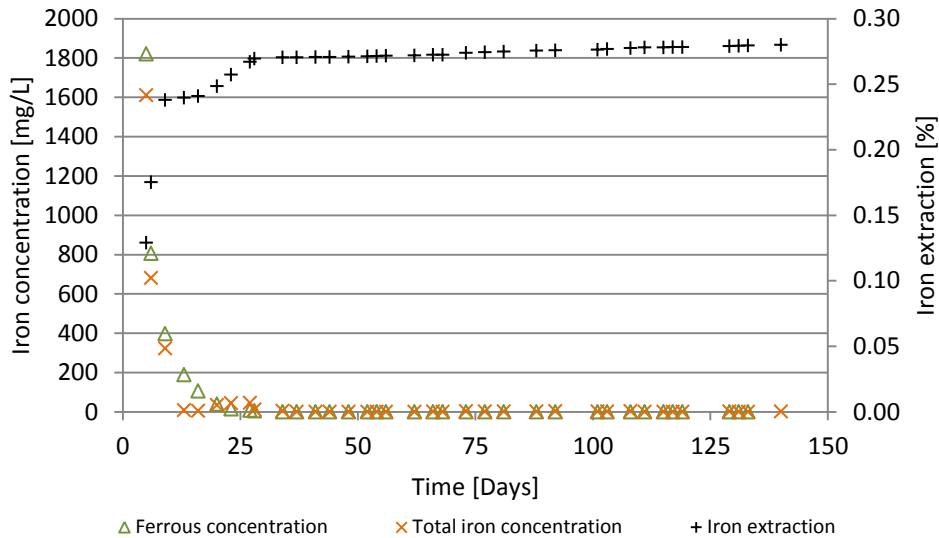
The redox potential profile is also presented in Figure 4-1. During the initial acid mineral leaching following agglomeration, iron was released as ferrous iron. Since, the ferrous iron concentration in the leachate was higher than the ferric concentration, the redox potential was low. The rise in redox potential over the course of the experiment was consistent with oxidation of the ferrous iron to the ferric form. The large changes experienced at day 9 (470 mV) and day 20 (460 mV) were due to the intermittent feeding of the bioleach columns. A potential of 550 mV indicating an oxidizing environment present in the column, was reached after 75 days and suggests microbial regeneration of ferric iron at a faster rate than the mineral leaching under these conditions (Breed & Hansford, 1999).



**Figure 4-1: pH and redox potential profiles for intermittent irrigation of agglomerated and inoculated waste rock with water.**

The initial high iron concentrations of approximately 1800 mg/L shown in Figure 4-2, were due to leaching of acid soluble minerals by the  $H_2SO_4$  added during agglomeration. Subsequently, the soluble iron concentrations decreased to below 100 mg/L for the duration of the experiment. Ferrous iron was the dominant species until day 60. Thereafter, ferric iron outweighed ferrous iron concentrations in the column system. This is in agreement with the redox potential data, with the low relative ferrous abundance in the leachate suggesting microbial activity.

Iron concentrations removed from the waste rock remained low for the duration of the experiment. Iron extraction increased to 0.29% over 144 days, corresponding to a removal of 1.3 g of iron from the 4 kg column containing a total of 474 g of iron. The low observed total iron concentrations observed in the leachate solution were as a result of iron precipitation due to the pH conditions within the bioleach column.



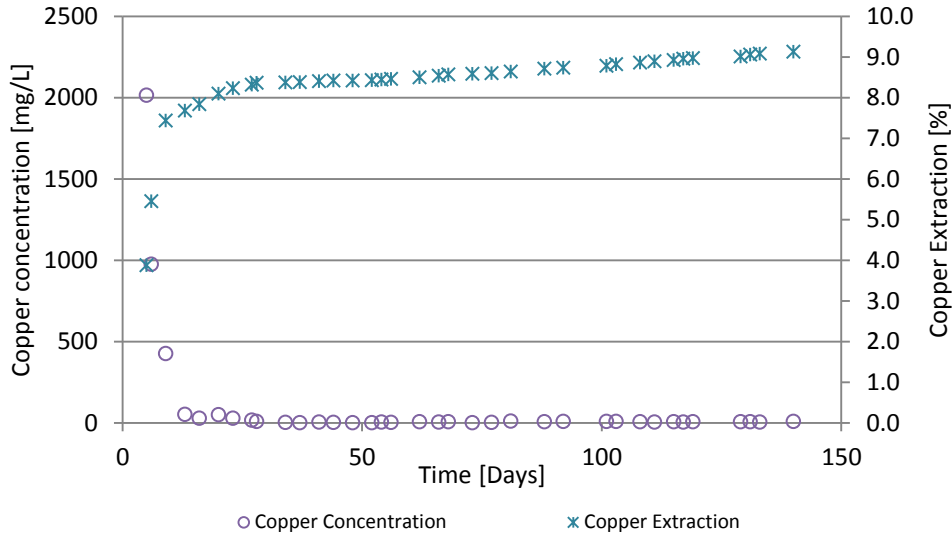
**Figure 4-2: Ferrous, total iron concentrations in leachate and iron extraction profiles for intermittent irrigation of agglomerated and inoculated waste rock with water.**

Copper concentrations in the leachate solution were measured due to the dominance of this metal in the waste rock sample. The waste rock sample contained 7 % (w/w) sulphide minerals, of which, 61 % were copper sulphides. Thus, copper extraction was used as a proxy for the oxidation of sulphide minerals and associated ARD generation, owing to less interference by precipitation as compared to iron.

The initial high concentrations of copper were due to the acid leaching of acid soluble metal sulphides during agglomeration (Figure 4-3). The sharp decrease in concentration was due to washout of solubilised copper on initiation of irrigation. The subsequent low copper concentrations suggested continued, slow sulphide mineral leaching over the duration of the experiment.

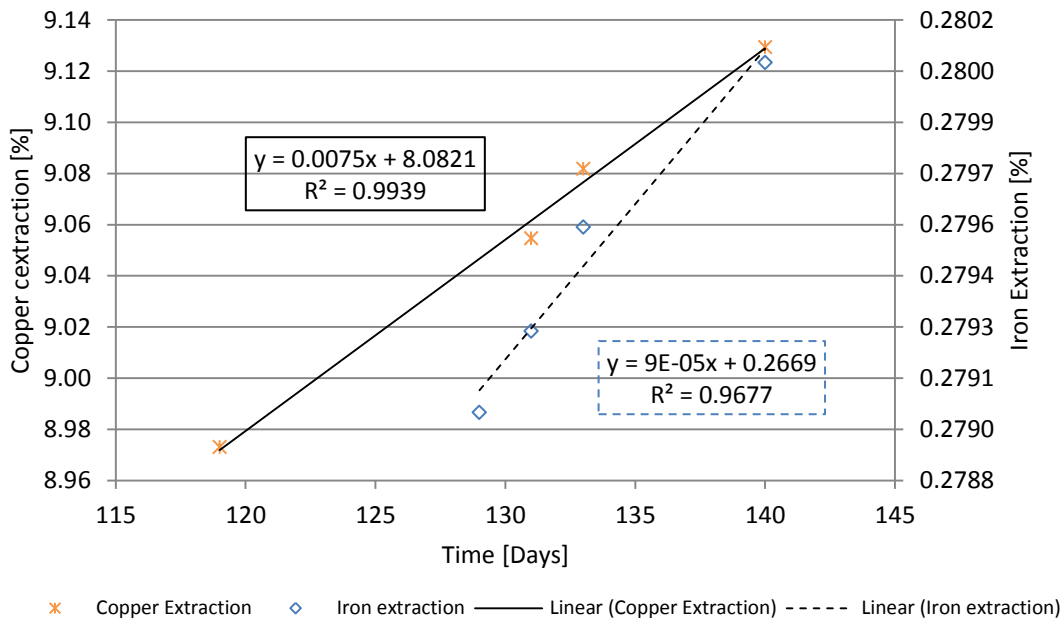
The rapid, initial acid leaching during agglomeration is observed over the first 10 days in Figure 3.3. This early phase accounted for 7.7% of the total copper available and 89% of the total copper extracted over the 144 days of the experiment. Leaching thereafter was dominated by slower, continued oxidation of the residual sulphide minerals which was responsible for the remaining 11% of copper extracted. Over the period 27 to 144 days, the rate of copper extraction remained unchanged indicating that on-going copper leaching may be expected over an extended time frame. This continuous metal extraction is also indicative of the longevity of the ARD associated with sulphide-bearing waste rock.

The difference in extraction of the iron and copper suggested low chalcopyrite leaching throughout the experiment. In addition, precipitation of iron within the leach column was expected given the pH of the leachate solution. On termination of the experiment and removal of the solid phase, a yellow-orange precipitate was observed, lending credence to the iron precipitation occurring within the bioleach column.



**Figure 4-3: Copper concentration and extraction profiles for intermittent irrigation of agglomerated and inoculated waste rock with water.**

By using the mineral extraction data as a proxy for sulphide mineral oxidation, a basic estimation for the duration of ARD formation, the “Terminal Duration” (TD), was estimated through linear extrapolation (Figure 4-4) of the terminal data points. To determine the amount of time necessary for a representative estimation of the necessary duration required for total copper ( $TD_{Cu}$ ) and iron ( $TD_{Fe}$ ) removal, several values were estimated using a varying number of terminal data points corresponding to the number of days leaching continued before termination of the experiment. These are presented in Table 4-1.



**Figure 4-4: Linear extrapolation of the final four data points for copper and iron extraction resulting in an estimation of the Terminal Durations for ARD formation under intermittent irrigation with water.**

The TD values estimated from differing numbers of terminal data points varied for both the TD<sub>Cu</sub> and the TD<sub>Fe</sub>. The TD<sub>Cu</sub> values showed good agreement for all except the estimate using the 10 days. This observation is due to a slight increase in the rate of leaching over this final period. For the TD<sub>Fe</sub> therefore, it was necessary to include a large set of terminal data points to obtain a more accurate estimate. The TD<sub>Cu</sub> was under the intermittent water fed condition was estimated using an average of the last three values in Table 4-1 as 30 ± 1 years.

The TD<sub>Fe</sub> estimates showed some inconsistencies between the estimates using different numbers leaching durations. Here however the TD<sub>Fe</sub> estimated from the final 10 days matched that using the final 40, 50 and 60 days. Due to the pH condition at which this experiment was conducted however, especially given the iron solubility at pH values above pH 3.5, this similarity could not necessarily be extended to other experimental conditions. The TD<sub>Fe</sub> was therefore estimated using the last three values in Table 4-1 to be 3034 years.

**Table 4-1: TR<sub>Cu</sub> and TR<sub>Fe</sub> estimations using variable terminal data points for the intermittent irrigation of agglomerated waste rock with water**

<b>Terminal</b> leaching duration corresponding to number of data points used [days]	TD <sub>Cu</sub> [years]	TD <sub>Fe</sub> [years]
10	25	3034
20	33	3413
30	32	3901
40	30	3034
50	31	3034
60	31	3034

These basic estimations are most likely an under-estimation of the true time periods necessary for total ARD generation due to the assumption of constant extraction rate used. Further, acidified agglomeration of the waste rock at the start of the experiment is expected to have accelerated leaching. In reality, the rate of extraction will most likely decrease with copper- and iron-sulphide removal, thus extending the total ARD generation time.

In addition, copper sulphides only accounted for 61% of the total sulphide content of the waste rock, with the difference being made up by galena (PbS, 24 %) and sphalerite (ZnS, 15 %). The use of copper extraction as a proxy for the ARD formation time period is valid however due to the acid soluble nature of the galena and sphalerite; resulting in quicker leaching times for these minerals as compared to, for instance, chalcopyrite; the predominant copper-sulphide present in the waste ore selected. In addition, given that iron precipitation was expected and observed at the pH levels of the leachate solution, the use of copper extraction as a proxy for the duration of ARD formation was more appropriate than iron extraction.

### **4.3. Leachate profiles under typical heap bioleaching conditions (bioleach control experiments)**

The extent of ARD generation is recognized to be dependent on the irrigation rate (in Section 3.2, 36 mm per day) and the degree of acidification. Typical waste heap acidification usually occurs over a long time period and is most often due to the action of bioleaching micro-organisms (Harris &

Ritchie, 1983; Morin *et al.*, 1994). To simulate an extreme case scenario for the rate of ARD formation following the onset of acidification once a microbial population is established, typical heap bioleaching conditions were used. These conditions actively encourage mineral sulphide oxidation. The conditions were chosen to minimize the experimental time period necessary. In this extreme case, the acidification of the feed solution to pH 1.15 and the addition of nutrients, as described in Section 2.4, were included. In addition, the column experiments were feed continuously rather than intermittently as before. All other operating variables were maintained the same as the intermittent-water experiment (Section 3.2).

The pH of the leachate rose initially from that of the feed, pH 1.15, to pH 1.4 over the first two days of experimentation (Figure 4-5). Thereafter it declined gradually to a value approximately matching that of the feed. The initial rise in pH was due to the reaction of the acid added with the acid neutralizing components within the waste sample.

The redox potential remained steady at approximately 400 mV over the initial 20 days before a rapid increase to 550 mV over a 4 day period. A constant, gradual increase thereafter resulted in a value of approximately 670 mV by the completion of the experiment. The low redox potential over the first 20 days indicated the dominance of ferrous over ferric iron and suggested an absence or low level of a microbially-mediated oxidative environment. In the presence of sulphidic minerals, a redox potential exceeding 550 mV (Breed & Hansford, 1999) is generally attributed to result from an active culture of ferrous iron oxidizing micro-organisms.

In comparison with the profiles observed under water-fed conditions, the acidic feed conditions provided a more favourable environment for the acidophilic micro-organisms. This translated an active microbial population being established more rapidly, as suggested by the redox potential. The higher final potential attained suggested increased microbial activity as compared to the water-fed experiment.

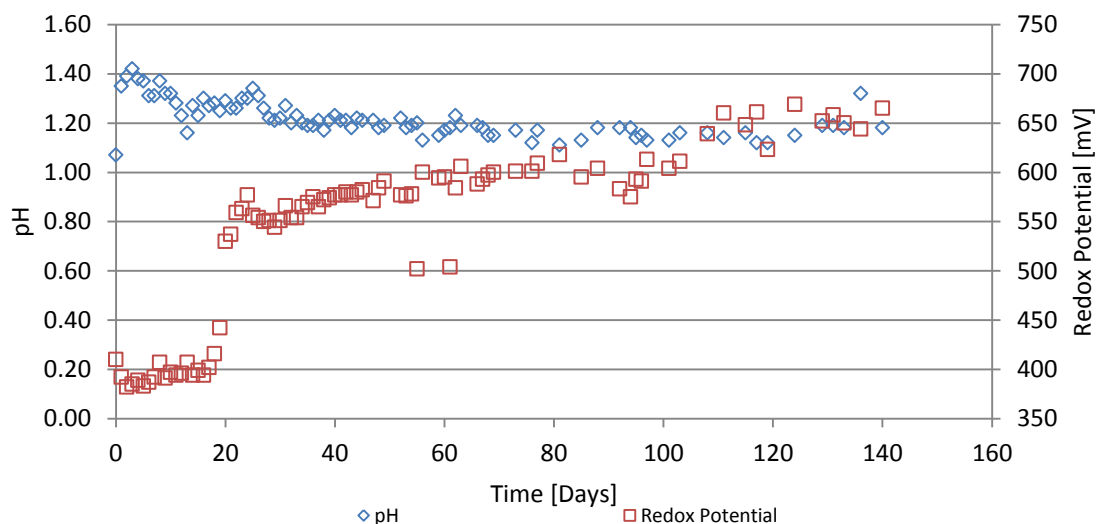
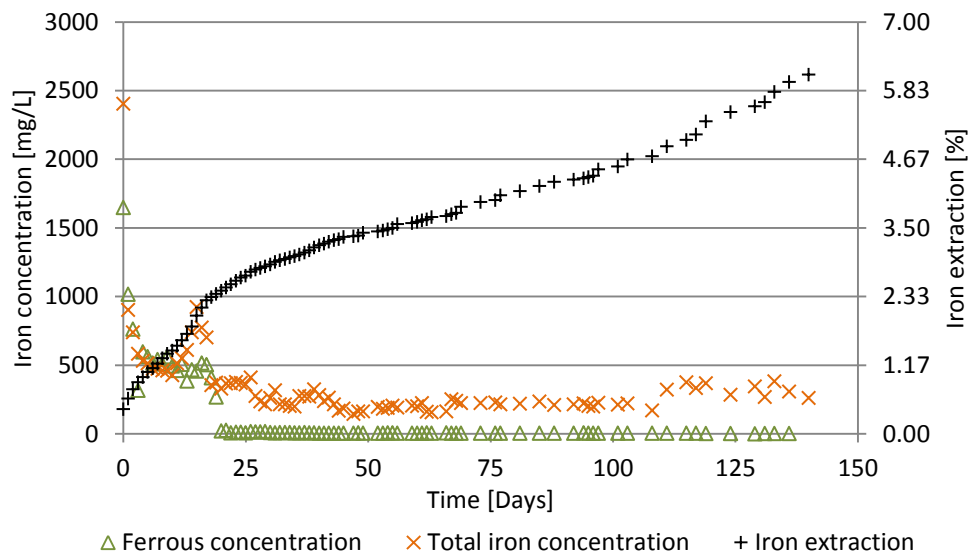


Figure 4-5: The pH and redox potential profiles following continuous irrigation of agglomerated and inoculated waste rock with acidified media (typical of bioleach conditions).

The increases in redox potential were mirrored by the relative dominance of the ferric over the ferrous iron concentrations (Figure 4-6). The ferrous concentration decreased rapidly from approximately 1700 mg/L at the start of the experiment to 500 mg/L over the initial 4 days of leaching. The ferrous concentration decreased further through 279 mg/L to below 50 mg/L between 20 and 22 days. In contrast, the total iron concentration remained above 150 mg/L for the duration of the experiment, with an average concentration of 235 mg/L after day 30. This ferric dominance corresponds to the high Eh period and is proposed to correspond to the onset of microbial activity. Comparison with the feed concentration of approximately 200 mg/L shows the slow, continuous leaching of iron from the waste rock.

Over the initial 15 days, the high iron concentrations were due to the acid leaching during agglomeration. This phase corresponds to the period of low redox potentials (400 mV) and displayed the most rapid rate of iron extraction due to washout of the iron solubilised in the ferrous form during the agglomeration process. Corresponding to an increase in redox potential due to ferrous-oxidizing microbial activity, extraction between days 15 and 100, represented the change from acid leaching to ferric iron dominant leaching. Although precipitation may have occurred within the leach column and thus the exiting iron concentrations may not have been a true reflection of the total amount of solubilised iron, the stable iron concentration profiles observed during this period suggested a stable rate of iron extraction. The increase in the total iron concentrations in the leachate and thus the rate of iron extraction over the final 40 days coincided with an increase in the redox potential from 600 mV to approximately 640 mV. As the ferrous concentration remained low, the increased amounts of soluble iron were predominately in the ferric form. The 6 % iron extraction achieved after 144 days under typical heap bioleach conditions can be compared with the 0.28 % observed with an intermittent water feed solution.



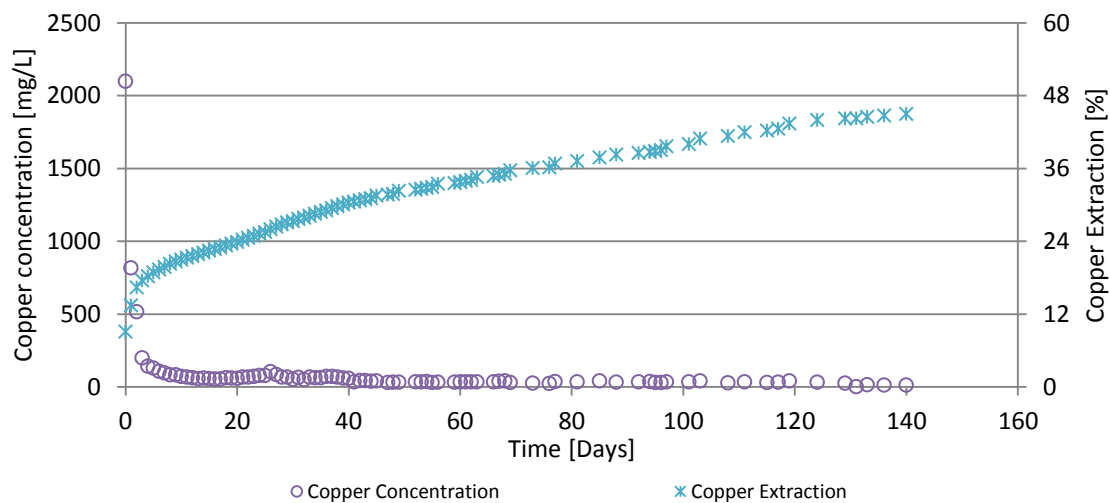
**Figure 4-6: The iron concentration and extraction profiles following continuous irrigation of agglomerated and inoculated waste rock with acidified media (typical of bioleach conditions).**

The copper concentration and extraction profiles are presented in Figure 4-7. The copper concentration decreased rapidly from 2100 mg/L to approximately 200 mg/L over the initial 3 days. This rapid phase of leaching was due to copper extraction from acid leaching during the

agglomeration process. Extraction from day 3 to 20, detailed the transition from acid leaching to copper extraction via ferric oxidation of the mineral sulphides. This transition was substantiated by the rise in redox potential from 400 mV to 600 mV over the duration of this period. The slower rate of ferric oxidation as compared to acid leaching was highlighted by the changes in copper concentration. Metal concentration decreased steadily from those initially experienced to value below 50 ppm after 40 days of leaching. These continuous, low copper concentrations once again imply the long-term nature of ARD formation from waste rock.

Thereafter, copper extraction was governed by mineral leaching through ferric attack. Although the redox potential increase from 600mV to 660mV was suggested as the reason for the increase in the rate of iron extraction, a similar increase in extraction rate is not observed in the copper extraction curve. This is due to chalcopyrite being the predominant copper sulphide within this waste rock. The refractory nature of the chalcopyrite prevented total dissolution prior this stage. The increase in redox potential therefore had minimal impact on the rate of copper leaching as chalcopyrite dissolution favours lower potentials (Third *et al.*, 2002).

In comparison with the 9% copper extracted under intermittent, water fed conditions, approximately 45% of the copper within the ore body had been removed. Of particular importance was the extent to which the acidic environment accelerated the copper leaching. This is highlighted by the 17% copper extraction observed after 5 days of leaching with an acidic feed solution as compared to the 9% after 140 days under intermittent water irrigation.



**Figure 4-7: Copper concentration and extraction profiles following continuous irrigation of agglomerated and inoculated waste rock with acidified media (typical of bioleach conditions).**

The  $TD_{Cu}$  and  $TD_{Fe}$  were estimated using differing numbers of terminal leaching data points (Table 4-2). Favourable microbial conditions, established the use of typical heap bioleaching conditions, resulted in an average 16 and 512 fold decrease in the  $TD_{Cu}$  and  $TD_{Fe}$  respectively as compared to those estimated from the intermittent, water-fed experiment. The  $TD_{Cu}$  and  $TD_{Fe}$  were estimated using an average of the last three values in Table 4-2 (data from 40-60 days of leaching) as  $1.6 \pm 0.1$  and  $7.4 \pm 0.6$  years respectively.

**Table 4-2: Estimated total extraction durations from TDCu and TDFe following continuous irrigation of agglomerated and inoculated waste rock with acidified media (typical bioleach conditions)**

<b>Terminal</b> leaching duration [days]	TD <sub>Cu</sub> [years]	TD <sub>Fe</sub> [years]
10	2.8	6.5
20	2.4	2.8
30	1.8	6.5
40	1.6	6.8
50	1.5	7.5
60	1.5	7.9

Comparison of the leachate profiles and estimated rates of ARD formation under intermittent water-fed conditions and those present under continuous irrigation of acidified water supplied with key nutrients, typical of heap bioleaching systems, has shown that providing favourable conditions for the growth and colonization of bioleaching micro-organisms within the waste heap can increase the estimated rate of ARD formation. In particular, the effect of an acidic medium over a near-neutral water feed was apparent. The acidic environment within the heap, in addition to the leaching of acid-soluble minerals, stimulated microbial growth and colonization, with direct consequence of further, microbially mediated sulphide oxidation. These two experiment systems therefore provide extreme scenarios for the rate and duration of ARD generation and the subsequent leachate profiles.

#### **4.4. The effect of aeration on ARD rate of formation and leachate quality**

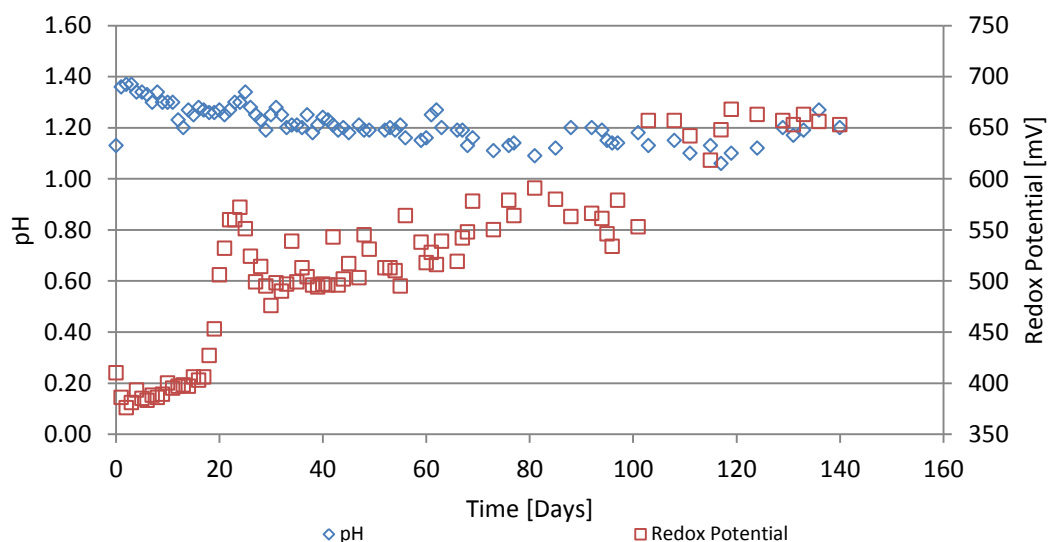
To establish the increased leaching efficiency associated with purpose-designed heap bioleaching operations is costly, due to capital and operating costs involved with feed irrigation and aeration of the heaps. Hence, use of these operating conditions for the acceleration of ARD from waste rock dumps may be both technically and economically unfeasible. Since natural irrigation is often available to waste rock dumps, an investigation into the role of aeration within the waste rock dumps is useful to provide a further understanding of its on the bioleaching system.

The presence of air is key component in ARD formation. As such, limiting air availability within a waste rock system is a method employed in ARD prevention techniques. Constructed covers however often fail to prevent the formation of ARD entirely but rather work on reducing the volumes of ARD generated (Kleinmann, 1990). Further, the long term integrity of the covers cannot be guaranteed without maintenance (Johnson & Hallberg, 2005). Hence, future ARD generation cannot be completely discounted.

To simulate an oxygen and carbon dioxide scarce environment within a waste rock dump, no air was fed to the experimental column. In addition, nitrogen gas was purged through the column after loading, with subsequent sealing of the gas inlets and outlets. The column however was not hermetically sealed, as this would not represent typical waste rock dump conditions accurately. The column was fed with an acidic feed solution as in Section 3.3.

The initial increase in leachate pH to 1.4 and subsequent steady decrease to a value corresponding to that of the feed (Figure 3-8) is similar to the pH profile experienced under typical bioleaching conditions in which the superficial gas velocity on aeration was 12 L/min (Figure 3-5). The initial increase in pH was due to the acid neutralisation reactions taking place on agglomeration of the waste rock, with the subsequent gradual decrease due to net result of further neutralization and the washout of the neutralised leachate.

The low redox potential values over the first 20 days mirrored the profile observed under typical heap bioleaching conditions. Although a similar rapid rise in potential was observed from 403 mV at day 16 to 560 mV at day 22, indicating the onset of bioleaching, this increase was not sustained in the manner observed in the typical bioleach condition experiment and decreased to 500 mV at day 27. The gradual increase in potential from 500 mV to 580 mV between days 27 and 80 was in direct contrast to the rapid increase to this same level over a 10 day period as shown in Figure 4-5. This suggests that the absence of aeration of the system has a negative effect on the microbial activity within the bioleach column, explained by the chemoautotrophic nature of the bioleaching microorganisms. The redox potential attained by the end of the experiment was similar to that observed under typical heap bioleaching conditions.

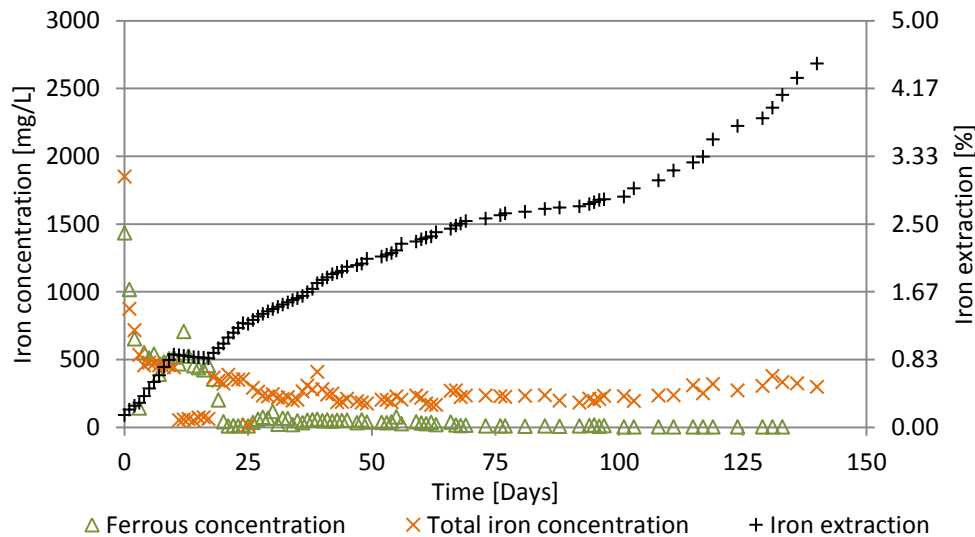


**Figure 4-8: pH and redox potential profiles on continuous irrigation of agglomerated and inoculated waste rock with acidified media under oxygen limitation**

The initial decreasing trend observed in the iron concentration under limited aeration (Figure 3-9) was similar to that experienced under typical heap bioleaching conditions (Figure 3-6). This initial iron in the leachate was due to the acid mineral leaching during agglomeration, eluted by the feed solution. As compared to the profiles observed under typical heap bioleaching conditions, lower total iron concentrations were experienced throughout the experiment. By the end of the experiment, 4.5 % of the iron in the waste rock had been removed as compared to 6.1 % under typical heap bioleaching conditions.

Lower comparable iron recovery was experienced under acid leaching (the initial 15 days), acid and ferric leaching (days 15 to 100), and under ferric-dominated leaching (the final 40 days ). Under

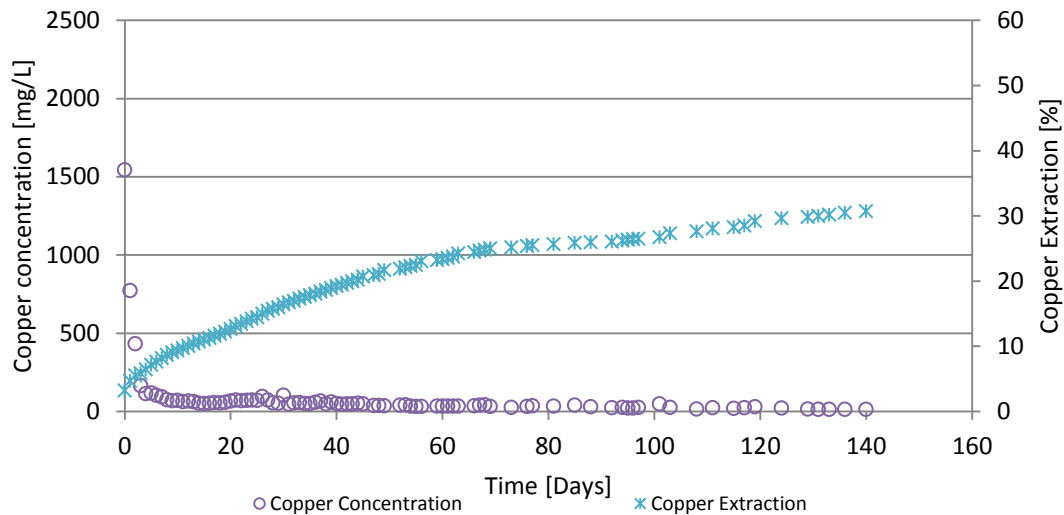
limited aeration, the rate of iron recovery was also lower in each of these phases as compared to the bioleach control experiment with the exception of the final 40 days which showed good comparison with those rates achieved under typical aerated heap bioleaching conditions. This suggests that although initially hindered by limited aeration, the microbial population was significant enough by the end of the experiment to ensure similar rates of iron dissolution between the two experimental conditions.



**Figure 4-9: Iron leachate profiles on continuous irrigation of agglomerated and inoculated waste rock with acidified media under oxygen limitation.**

The initial copper concentrations observed over the initial 3 days were due to the elution of copper leaching during acid agglomeration (Figure 4-10). Acid leaching was also responsible for the copper extracted up until day 10, as the redox potential remained at approximately 400 mV. The change in the rate of copper extraction after approximately 10 days occurred without a significant change in the redox potential. This suggests that this rate change was due to changes in the solid phase, either mineralogical or due to particle sizes, rather than a change in the oxidative environment within the bioleach column. The change in the rate of metal extraction at approximately day 70 occurred simultaneously with a change in the redox potential to values greater than 550 mV.

Although the copper concentration and extraction profiles are similar in trend to the profiles experienced under typical heap bioleaching conditions (Figure 3-7), less copper metal was extracted. Comparison of the copper extraction highlighted the role of aeration in ARD formation when, initially, and in the absence of an active microbial population, only half the copper was extracted as compared to the same time period under typical heap bioleaching condition. Overall by the completion of the experiment, 4.5 % copper was leached under conditions with no aeration as compared to the 6.1 % under typical bioleach conditions.



**Figure 4-10: Copper concentration and extraction profiles on continuous irrigation of agglomerated and inoculated waste rock with acidified media under oxygen limitation**

The averages of the  $TD_{Cu}$  and  $TD_{Fe}$  values estimated using 40 to 60 days of data (Table 4-3) led to an estimation of  $2.3 \pm 0.1$  and  $7.8 \pm 1.0$  years for complete copper and iron extraction respectively. Comparison of the time for complete extraction of copper under typical bioleach conditions, a value of  $1.6 \pm 0.1$  years, confirmed the negative effect of limited air availability on the rate of sulphide mineral oxidation.

Larger inconsistencies were observed between the  $TD_{Fe}$  values as compared to the  $TD_{Cu}$  estimates. The  $TD_{Fe}$  under non-aerated and the bioleach control conditions were similar at  $7.8 \pm 1.0$  and  $7.4 \pm 0.6$  years respectively. This similarity was in contrast with the lower total iron extraction experienced under oxygen limitation conditions. This suggested that aeration did not significantly affect the rate of leaching of iron-containing minerals within the waste rock sample. The discrepancies between the  $TD_{Fe}$  values and the relative iron extractions highlight a possible limitation with the method used for the terminal duration estimation.

**Table 4-3:  $TD_{Cu}$  and  $TD_{Fe}$  estimates on continuous irrigation of agglomerated and inoculated waste rock with acidified media under oxygen limitation**

<b>Terminal</b> leaching duration [days]	$TD_{Cu}$ [years]	$TD_{Fe}$ [years]
10	3.2	5.4
20	2.9	5.8
30	2.4	6.2
40	2.3	6.8
50	2.3	8.1
60	2.4	8.6

Non-aeration of the simulated waste rock dump resulted in a decreased extraction of copper and iron over the 144 day period. The higher estimated  $TD_{Cu}$  indicated the effect of prolonging ARD generation as compared to a typical bioleach condition. The extent of mineral leaching however suggested that although no mechanical aeration occurred, air infiltration into the bioleach system

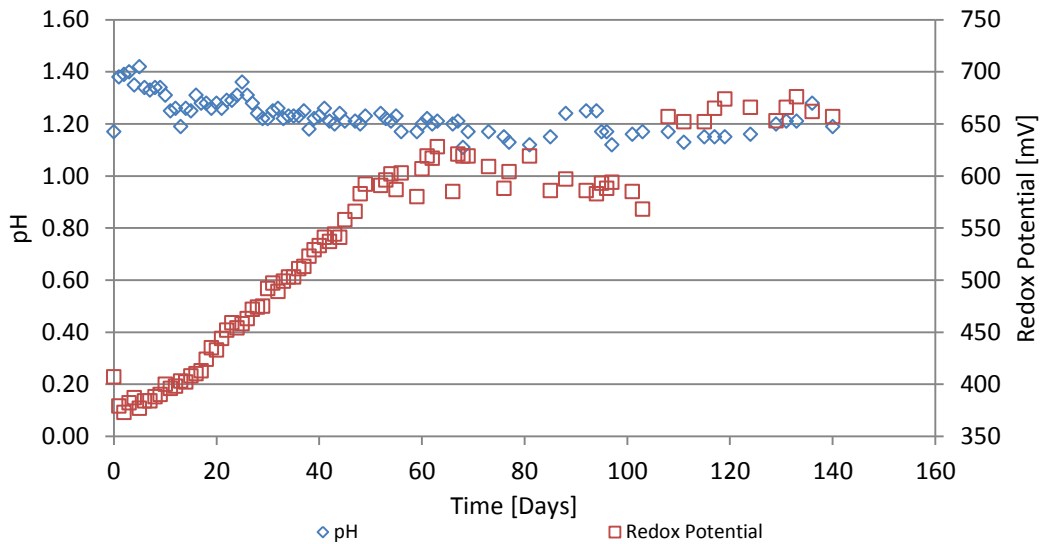
was sufficient to stimulate microbial activity and promote both abiotic and microbially-mediated sulphide oxidation. The similar infiltration of air into typical waste rock dumps results in the gradual growth and colonization of bioleaching micro-organisms and ultimately the formation of ARD.

#### **4.5. Effect of temperature increase on the rate of ARD formation and leachate quality**

In the presence of microbial activity and exothermic mineral leaching reactions, the temperature within the rock heap or dump operations often varies from ambient at the outer edge, based on the balance between heat generation and heat loss to the environment, to those temperatures suitable for moderate and thermophilic bioleaching micro-organisms near the centre of the heaps or waste dumps where heat loss to the surroundings is limited (Rawlings *et al.*, 2003). The increases in temperature experienced within waste dumps are a direct result of the exothermic nature of the mineral leaching and ferrous oxidation reactions and is dependent on the sulphide grade of the ore.

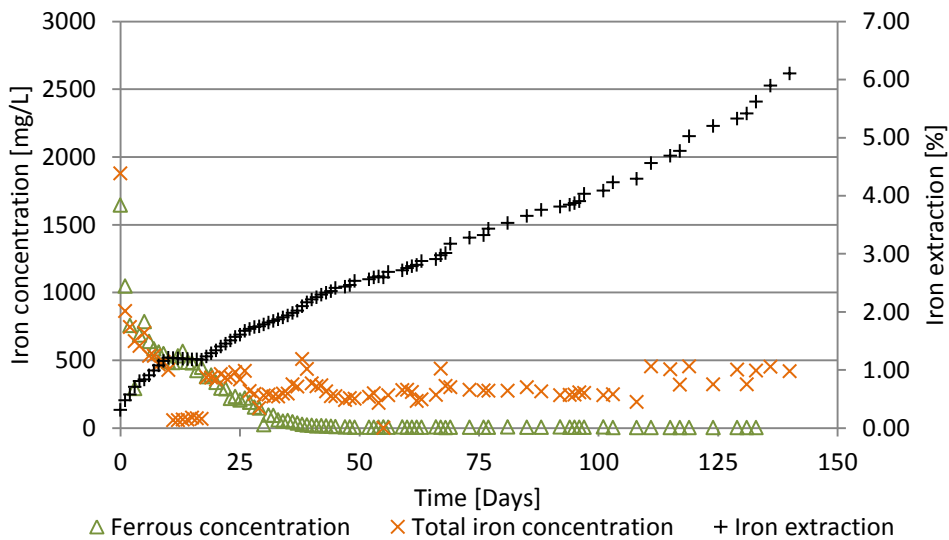
Thermodynamic theory dictates that the chemical rate of ARD production should increase with an increase in temperature. However, bioleaching micro-organisms are active in defined temperature ranges (Fransmann *et al.*, 2005). The overall effect of an increase in temperature is therefore dependent on the microbial species present. For this particular investigation, a mixed mesophilic culture was utilized and the temperature of the leach column maintained at 42°C, compared with 32°C in the remaining experiments. Fransmann *et al.* (2005) studied the effect of temperature on the rates of iron and sulphur oxidation for a range of bioleaching micro-organisms. For the purpose of the mixed microbial population used in this study, 42 °C formed the upper bound of the operating temperature range.

The pH profile (Figure 3-11) of the leachate generated at 42 °C was similar to that under the typical heap bioleach conditions and in a non-aerated environment at 32 °C. The redox potential profile (Figure 3-11) showed a gradual increase to a value of 600 mV over a period of 60 days, stabilization at this value for approximately 40 days and finally a jump to a potential of 660mV after 100 days of experimentation. This is in contrast to the typical bioleach conditions where a sudden increase in potential to 550 mV was observed at 20 days.



**Figure 4-11: pH and redox potential profiles on continuous irrigation of agglomerated and inoculated waste rock at 42°C with acidified media**

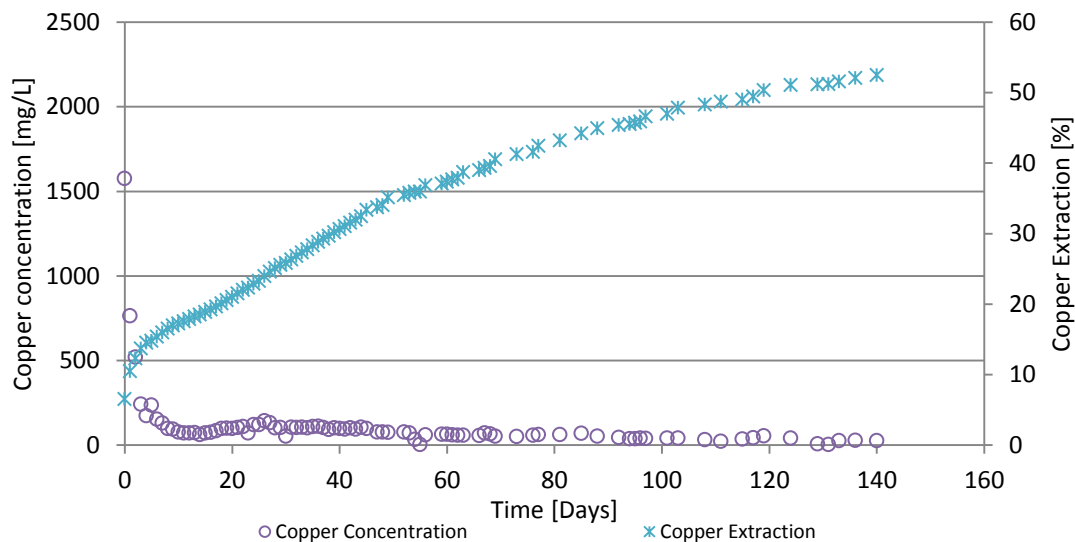
The rate of iron extraction was divided into two phases (Figure 4-12). Acid leaching of the waste rock sample occurred over the initial 12 day period. The rate of leaching under elevated temperatures was higher than the corresponding phase under typical bioleach conditions. The short time period however resulted in less iron being extracted at the elevated temperature. The constant rate experienced over the remainder of the experiment, regardless of the potential of the leachate solution, suggested that iron extraction was governed by the operating temperature of 42°C rather than availability of ferric iron or any changes in the mineralogy of the waste rock sample. Overall, a similar amount of iron was extracted as compared to typical bioleach conditions at 32°C.



**Figure 4-12: Leachate iron concentration and extraction profiles on continuous irrigation of agglomerated and inoculated waste rock at 42°C with acidified media**

Figure 4-13 details the copper concentration and extraction curves with three distinct phases of copper extraction observed. The rapid initial copper extraction over the first three days due to acid-leaching of copper-containing minerals during the agglomeration process. Acid leaching was the

dominant mechanism for copper and iron liberation up until approximately day 40, where the redox potential reached 550 mV. Thereafter, the increasing potential values suggested microbially-dominated, ferric leaching was dominant. The slower rate of copper extraction over the final 90 days of the experiment, together with the abundance of chalcopyrite with the waste rock sample, suggested the dominance of chalcopyrite leaching during this phase. By the end of the experiment, 53 % of the copper was extracted at an operating temperature of 42 °C as compared to 45% under typical bioleaching conditions at 32 °C.



**Figure 4-13: Copper concentration and extraction profiles on continuous irrigation of agglomerated and inoculated waste rock at 42°C with acidified media**

The dominance of chalcopyrite leaching at the later stages of the experiment was suggested for all leaching conditions investigated. In conjunction with thermodynamic theory therefore, it was expected that less time would be required for the complete removal of the sulphide components at elevated temperatures as compared to those experienced at 32 °C. In addition, it is known that chalcopyrite leaching is favoured at elevated temperatures (Rawlings *et al.*, 2003). This was indeed the case, with estimate for  $TD_{Cu}$  of  $1.3 \pm 0.1$  years (Table 4-4) as compared to the estimate of  $1.6 \pm 0.1$  years for the  $TD_{Cu}$  for the 32 °C experiment. A 10 °C rise in temperature of the experimental bioleach column therefore resulted in an approximate 19 % decrease in the estimated time necessary for complete ARD generation. The  $TD_{Fe}$  was estimated at  $6.0 \pm 0.5$  years (Table 4-4), once again a 19% difference from the estimate at 32 °C of  $7.4 \pm 0.6$  years.

**Table 4-4:  $TD_{Cu}$  and  $TD_{Fe}$  estimates for continuous irrigation of agglomerated and inoculated waste rock at 42 °C with acidified media**

<b>Terminal</b> leaching duration [days]	$TD_{Cu}$ [years]	$TD_{Fe}$ [years]
10	1.5	4.2
20	1.7	4.8
30	1.4	5.2
40	1.4	5.4
50	1.3	6.1
60	1.2	6.4

An increase in the temperature of the simulated waste heap increased the copper extraction but with a negligible effect on percentage iron extraction as compared to extraction at 32 °C. The same however was not observed in the Terminal Duration estimations, which showed a 20% decrease in the necessary time for total ARD generation from both copper and iron extraction data. The exothermic nature of sulphide oxidation is expected to provide enough heat to raise the temperatures of such waste dumps (Rawlings *et al.*, 2003; Franzmann *et al.*, 2005) Thus, the temperatures within waste rock dumps have been observed to increase far above ambient with an increase in the release of ARD a result (Schippers *et al.*, 1995).

#### **4.6. The addition of pyrite concentrate as a lixiviate source**

An easily accessible microbial energy source was added to increase the availability of iron and sulphur species in the simulated waste rock bed, with the added benefit of providing an additional acid source for the acid-leaching of waste rock components. Pyrite was chosen as the mineral additive due to its abundance and the fact that it provides energy for both iron- and sulphur-oxidizing microbial species. In the waste dump environment, oxidation of the added pyrite concentrate would also result in an increase in the temperature of the waste dump. Owing to the large surface area to volume ratio of the laboratory scale column reactors, however, this temperature increase is not observed in small scale laboratory columns. In addition, owing to the low pH of the feed solution, a discernible increase in acidity as a direct result of the pyrite addition was not expected.

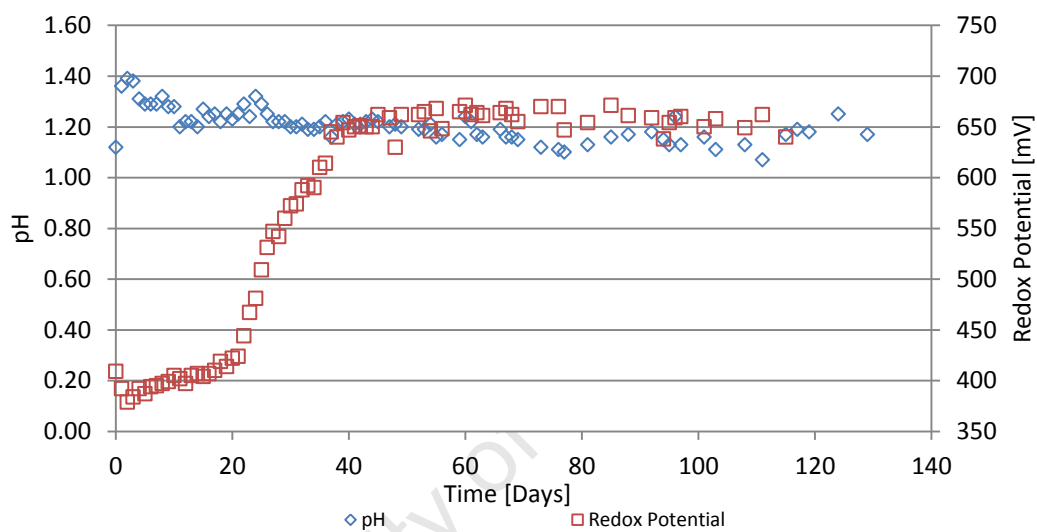
Chemical engineering theory, however, was used to quantify the expected temperature increase associated with the pyrite addition. Thermodynamic theory dictates that approximately 13 kJ of energy should be released per gram pyrite through the oxidation of pyrite mineral although microbial oxidation of pyrite has been shown to release between 9 kJ/g and 14 kJ/g depending on the microbial species (Rohwerder *et al.*, 1998). This energy will be partially converted to heat, resulting in heating of the mineral, water and air phases. Rigorous modelling is required to estimate effectively the temperature increase in the bed; however typical increases in a pyrite-rich heap leach environment have resulted in temperature of 40 to 70°C being reported (Rawlings, 1999).

The multifaceted effects of a pyrite addition therefore were studied separately. While the effect of an increase in acidity and temperature have been discussed previously in Section 4.3 and 4.5 respectively, the aim of the pyrite addition was to investigate the effect of an increase in the ferrous iron and sulphur species in the absence of the increases in acidity and temperature associated with pyrite oxidation.

It was expected that the increases in ferrous iron and sulphur species would serve as an easily accessible energy source for the bioleaching micro-organisms, thus encouraging their growth and colonisation. In addition, the increased iron in the system, once oxidized, would increase the supply of ferric iron under the acidic bioleach conditions. In this experiment, 1% (w/w) pyrite concentrate was added during the agglomeration process with all other operating conditions identical to the experiment under typical bioleaching conditions at 32°C.

The pH profile, shown in Figure 4-14, shows a similar trend to the other experiments under acidic feed conditions. The initial rise was due to reaction with acid-consuming components within the waste rock, with the subsequent gradual decrease a result of the pH of the feed and elution of the acid neutralising capacity.

The redox potential profile (Figure 3-14) showed a gradual increase to 420 mV over the first 20 days, then increases more rapidly to 650 mV by day 40. The redox potential, however, reached 650 mV more rapidly for this experiment than under typical bioleach conditions and elevated temperatures, where 650 mV was only reached after approximately 108 days. This suggested that a more active microbial population was established over a shorter time period, with the higher potential attained indicating an increased overall activity through the higher relative ratios of ferric to ferrous iron.

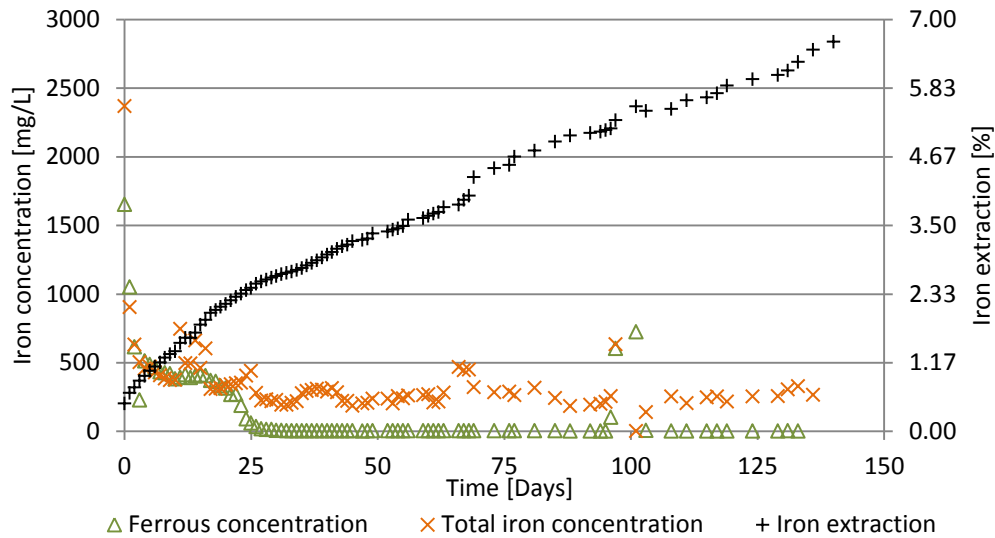


**Figure 4-14: pH and redox potential profiles of agglomerated and inoculated waste rock with 1% additional pyrite concentrate under continuous irrigation with acidified media.**

The ferrous iron concentration (Figure 4-15) decreased from an initial value of approximately 2400 mg/L to 450 mg/L over the first 15 days. Subsequently, the ferrous concentration decreased to 50 mg/L by day 25 and remained below 20 mg/L for the duration of the experiment. The total iron concentration followed a similar profile to that experienced in the bioleaching control. Once a stable oxidative environment was reached however, the average total iron concentration under pyrite-assisted leaching conditions exceeded that observed in the bioleaching control by an average of 30 mg/L. This suggested that more iron was extracted with the addition of 1% pyrite concentrate. This result was substantiated by the iron extraction profile, with extraction calculated as the iron removed as a percentage of the sum of the iron content of the waste rock and the amount of iron added in the pyrite content. The increased soluble iron was predominantly in the form of ferric iron.

The initial 25 days was dominated by acid leaching with iron extraction occurring before substantial microbial activity enabled a high ferric iron concentration to be maintained. Over this period, the iron extraction values were slightly lower than that experienced under typical heap bioleaching conditions. Extraction over the remainder of the experiment suggested steady, microbially-mediated, mineral sulphide oxidation. The sustained, faster rate of iron extraction experienced corresponded

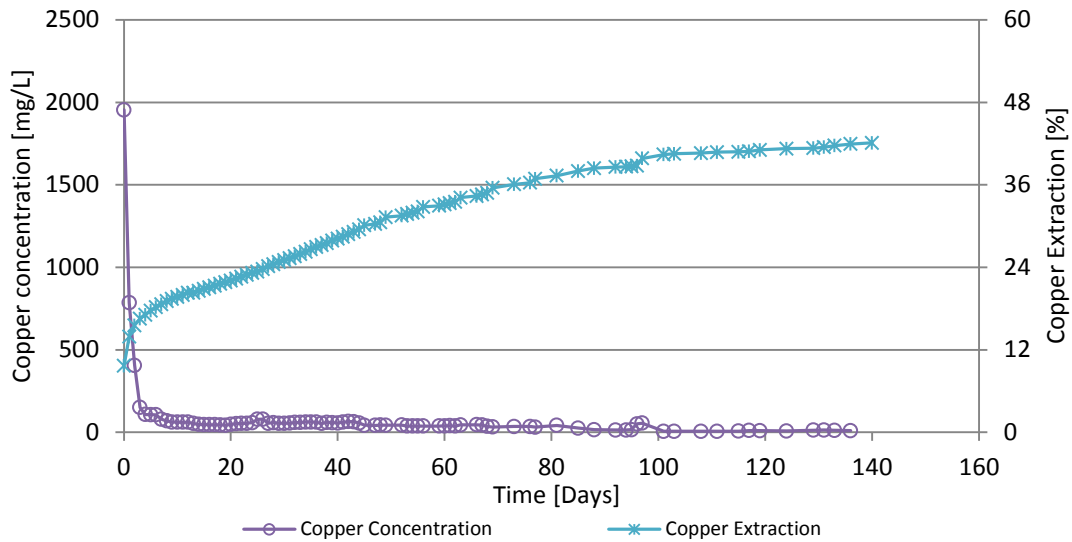
to the higher redox potential values attained. The rate of iron extraction was comparable with that experienced during the final phase of extraction in the bioleaching control. Overall, 6.6 % of the iron was removed from the waste rock under these conditions as compared to the 6.1 % under leaching at 42 °C or in the bioleaching control experiment.



**Figure 4-15: Iron leachate profiles of agglomerated and inoculated waste rock with 1% additional pyrite concentrate under continuous irrigation with acidified media.**

The copper concentration profile, presented in Figure 4-16, showed a similar trend to that observed in the bioleaching control. The rate of extraction was slightly lower over the first 80 days as compared to that observed for the control experiment. Although the extraction rate over the final 60 days is comparable, the overall extraction after the addition of pyrite concentrate was 42 %, as compared to the 45 % achieved in the bioleaching control. This difference however may be due to inherent differences between the waste rock samples as compared to the effect of a 1% addition of pyrite concentrate.

Although the addition of the pyrite concentrate did result in an increase in the ferric iron concentrations in the leachate solution, these increases did not result in a noticeable augmentation of the rate of copper leaching under these conditions. This is in agreement with van Hille *et al.* (2010) who showed a disconnect between ferric concentrations in the leach solution and the associated copper liberation for a low grade, chalcopyrite-dominated sulphide ore at similar conditions.



**Figure 4-16: Copper concentration and extraction profiles of agglomerated and inoculated waste rock with 1% additional pyrite concentrate under continuous irrigation with acidified media.**

The  $TD_{Cu}$  and  $TD_{Fe}$  estimates are presented in Table 4-5 as a function of terminal leaching duration. The average  $TD_{Cu}$  and  $TD_{Fe}$  for the pyrite column are  $2.8 \pm 0.3$  and  $9.3 \pm 0.1$  years respectively, calculated using data across the last 40 to 60 days. When compared to the bioleach control values of  $1.6 \pm 0.1$  and  $7.4 \pm 0.6$  respectively, these suggest a retardation in the rate of mineral extraction with the addition of 1% pyrite concentrate.

**Table 4-5:  $TD_{Cu}$  and  $TD_{Fe}$  estimations for continuous irrigation with acidified media of agglomerated and inoculated waste rock with a 1% pyrite concentrate addition**

<b>Terminal</b> leaching duration [days]	$TD_{Cu}$ [years]	$TD_{Fe}$ [years]
10	3.2	6.1
20	3.3	6.9
30	3.3	8.0
40	3.2	9.2
50	2.8	9.3
60	2.5	9.3

The addition of the 1% (wt) pyrite concentrate was intended as an easily accessible iron and sulphur source for the bioleaching micro-organisms, with the additional associated increases in temperature, acidity of the leachate solution and ferric iron concentration. These were intended to increase the rate of sulphide oxidation, either microbially or chemically, with the result a decrease in the necessary time for complete sulphide removal. Although the redox potential profile of the leachate solution indicated an increased relative ferric concentration as compared to that observed in the bioleach control experiment, this increase did not result in an increase in the rate of mineral sulphide oxidation, suggesting that mineral availability may have been the limiting factor.

Overall, the  $TD_{Cu}$  and  $TD_{Fe}$  estimates suggested that the addition of a 1% pyrite concentrate resulted in an increase in the time necessary for complete sulphide removal. This suggests that the increase in microbial activity and associated relative ferric concentration towards the end of the experiment

had negatively affected the rate of copper sulphide leaching which is in agreement with previous studies on low grade chalcopyrite ores at similar conditions. The observed 3% difference in copper extraction may be due to inherent differences between the waste rocks samples.

No noticeable increase in the temperature as a result of the pyrite oxidation of the experimental column was observed. This however was not unexpected due mainly to the dimensions of the laboratory columns and lack of insulation, thereby providing a relatively large surface area for heat loss. As a result, the chemical and temperature effects of a pyrite addition have been separated.

#### **4.7. Assessing ARD potential using ARD characterization tests**

Although information concerning the leachate quality and rate of ARD generation may be gained from the comparison of experimental bioleach columns at the different conditions, little information concerning the pre- and post-leaching potential for ARD generation is obtained from such experiments. For this, standard ARD characterization tests were performed on the solid phases from each leaching experiment to gain an understanding of the effect of leaching on reducing the subsequent ARD generating potential.

The common, static ARD characterization methods were used to quantify the inherent acid neutralizing and acid generating potentials of the waste rock samples. The neutralizing capacity was determined through an acid digestion and back titration with sodium hydroxide, with the maximum acid generating potential determined from the total sulphur grade. A balance of these gave an overall estimation of the net acid producing potential of the waste rock samples. In addition, experiments were performed using a hydrogen peroxide solution to oxidize the sulphide content of the samples fully and, using a sodium hydroxide titration, experimentally quantify the net acid generating potential. These characterization methods are outlined in Section 2.6.1. The ARD potential of a pre-leach feed sample was used as a comparison to investigate the changes in ARD potential as a result of the leaching experiments. Detailed calculations for the characterization tests are presented in Appendix 11.2.

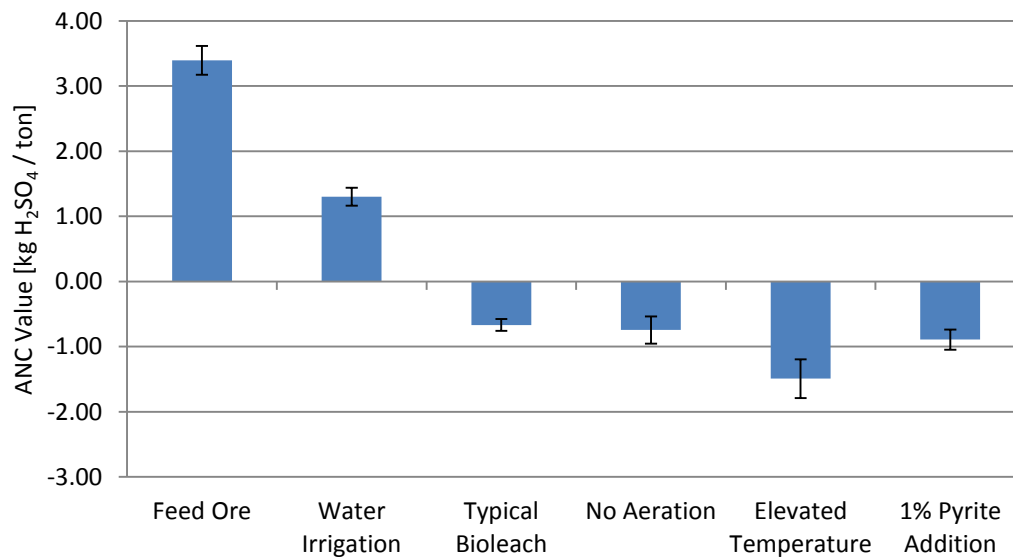
##### **4.7.1. Static ARD prediction experiments**

The results of the ANC static experiments are presented in Figure 4-17. Initially, the waste rock sample contained enough acid consuming material in one tonne to neutralize 3.4 kg H<sub>2</sub>SO<sub>4</sub>. The post leaching results indicate that after 144 days of column leaching, the ANC value decreased under all conditions.

The residual ANC following intermittent irrigation with water remained positive after the experiment, indicating the limited removal of the neutralizing components of the waste rock. The loss of ANC due to the acid added during agglomeration accounted for approximately 1.7 kg H<sub>2</sub>SO<sub>4</sub> / ton waste rock. Thus, the ANC value for the water-fed experiments indicated that in addition to the ANC removed during agglomeration, the equivalent of 0.4 ± 0.14 kg H<sub>2</sub>SO<sub>4</sub> / ton was removed from the waste rock at these conditions.

Under acidic feed conditions, the ANC of the waste rock was totally depleted under all operating conditions. The negative ANC values indicated the presence of acid-soluble, acid forming minerals or

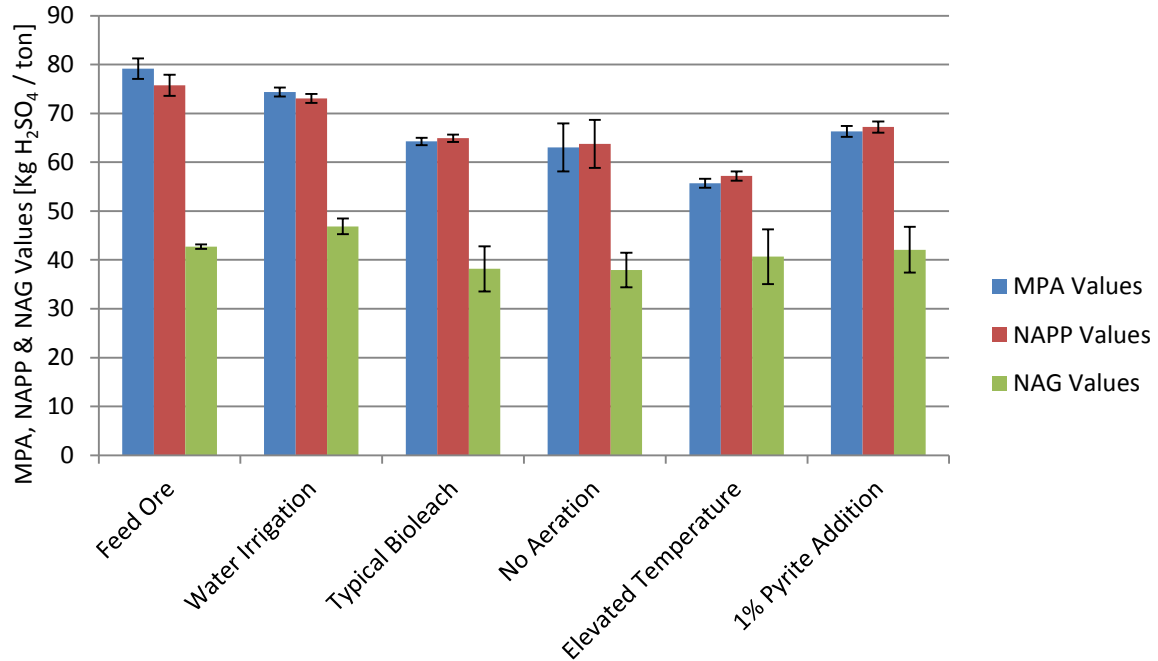
sets of acid forming reactions which occurred during the acid digestion of the sample. Larger negative values suggested the increased abundance of these minerals or reactions.



**Figure 4-17: Acid neutralizing capacity of agglomerated and inoculated waste rock samples after bioleaching for 144 days under different conditions**

The trends observed in the MPA and NAPP results (Figure 4-18) corresponded inversely with the copper extraction data where the largest removal of copper occurred at elevated temperatures and the smallest under water fed conditions. Of particular notice are the differences in the rates of decrease of MPA and ANC values. Over the course of the experiment, the ANC values decreased by 100% for all acid fed experiments. In comparison, the largest decrease in MPA value was 30 % at an elevated temperature over the same time period.

With the exception of the water fed column experiment, there was no statistical difference in the NAG values between the feed and the post-leach samples. The experimentally determined NAG values were also contrary to the theoretical NAPP values, with NAGs predicting approximately half the amount of acid generation with respect to the NAPPs. The experimental results for the water fed column indicated that the ARD potential of the waste rock increased after the leaching experiment was performed. This suggested that the removal of ANC during leaching was greater than the removal of the acid forming components under this condition.



**Figure 4-18: MPA, NAPP and NAG values for agglomerated and inoculated waste rock samples after bioleaching for 144 days under different conditions**

The static ARD characterization tests quantified the overall change in the pre- and post-leached ARD potentials. However, no information on the potential rate of ARD generation was obtained. The terminal durations were estimated from the static ARD test results using the changes in the ARD potentials between the feed and leached samples. This allowed for comparison with the terminal durations, with the aim of resolving the two data sets.

#### 4.7.2. Calculation and comparison of ARD generation rates

The concept of “terminal duration” was developed in this study to provide a measure of the rate of ARD generation and the longevity of the leaching problem. The detailed calculations developed for terminal duration are outlined in Appendix 11.4. The terminal durations estimated from the iron and copper extraction profiles for each of the leaching conditions investigated are presented in Table 4-6. With the exception of the water-irrigated experiment, the  $TD_{Cu}$  and  $TD_{Fe}$  estimates were all within the same order of magnitude. Leaching of the waste rock at the elevated temperature of 42 °C resulted in the lowest time estimated for complete ARD generation.

The terminal duration estimated for the water irrigated experiment differed by a factor of 10 and 210 in the copper and iron durations respectively. Under these conditions, the method of linear extrapolation of the extraction data did not take into account any precipitation, especially iron, which may have occurred within the bioleach column. This is particularly relevant in the water irrigated experiment where the pH of the leachate stabilized at approximately pH 4.0. Iron precipitation above pH 3.5 have been reported due to the low iron solubilities (Deveci *et al.*, 2004). In this case, any iron precipitate remaining in the bioleach column may re-solubilise if acidic conditions were introduced. Thus the potential for metal pollution from such a system remains.

**Table 4-6: Terminal duration estimations from the copper and iron extraction profiles for agglomerated and inoculated waste rock samples leached for 144 days under different conditions**

Leaching Condition	Terminal Duration [years]	
	TD <sub>Cu</sub>	TD <sub>Fe</sub>
Water irrigation	30 ± 1.0	3034 ± 0
Bioleach control	1.6 ± 0.1	7.4 ± 0.6
No aeration	2.3 ± 0.1	7.8 ± 1.0
Elevated temperature	1.3 ± 0.1	6.0 ± 0.5
1 % pyrite addition	2.8 ± 0.3	9.3 ± 0.1

Determination of the acid producing potentials of the solid samples allowed for a quantification of the change in ARD potential with time. From these data, it was possible to obtain estimations of the total necessary time for complete sulphide removal. The terminal duration from the solids (TD<sub>solid</sub>) were estimated using both the NAG and NAPP values and are presented in Table 4-7.

Direct comparison of the TD<sub>Cu</sub> and TD<sub>Fe</sub> estimates with those of the TD<sub>solid</sub> estimates for each column experiment was not possible due to the different methods used in each estimation. The TD<sub>Cu</sub> and TD<sub>Fe</sub> values were estimated using linear extrapolations of the copper and iron extraction curves while the TD<sub>solid</sub> values were estimated using the average rate of change of acid producing potentials of the solid samples. For the purpose of comparison with the TD<sub>solid</sub> estimates, terminal durations using linear extrapolation of the average rate of change of copper extraction over the 144 leaching period were calculated (TD<sub>average</sub>). The estimates however do not take into account the logarithmic nature of the copper extraction profile. These are presented in Table 4-7, with detailed calculations provided in Appendix 11.4.

Although the trend in the Average Rates as calculated from the leachate and NAPP values were similar, the ratio between these values varies from 0.3 to 1.5. There was also little agreement between the NAPP and NAG values. In particular, the NAG results showed no statistical difference between the feed and post-leached samples. In addition, there was a positive change in NAG value for the experiment under water irrigation, leading to an increase in the ARD potential over time.

**Table 4-7: Terminal duration estimations from the averages of the copper extraction profiles and the NAPP and NAG solids results for agglomerated and inoculated waste rock samples leached for 144 days under different conditions**

Operating Condition	TD <sub>average</sub> [years]	TD <sub>solid</sub> [years]	
		NAPPs	NAGs
Water Irrigation	16	10.7	N/A
Typical Bioleach	1.0	2.4	3.3
No Aeration	1.4	2.1	3.1
Elevated Temperature	0.8	1.2	8.0
1% Pyrite Addition	1.0	3.0	6.0

ARD characterization tests were conducted on the solid samples to gain an understanding on the effects of the leachate on the remaining potentials of the solid phase. The inherent neutralizing

capacity and the acid producing potential of the solids were quantified using common, static ARD characterization methods. While the ANC of the samples showed a total decrease for all experiments conducted using acidified media, a similar decrease in the acid producing potentials of the solids samples was not observed. Although the ANC for the water irrigated experiment decreased by over 50 %, the decrease in associated NAPP lay within experimental error of that of the feed sample. In addition, the NAG value for this experiment indicated an increase in net acid generation after bioleaching with a water feed solution.

Bioleaching at an elevated temperature of 42 °C resulted in the lowest time necessary for complete mineral sulphide removal. In comparison, the lack of aeration and addition of 1% pyrite concentrate by mass resulted in an increase in the terminal duration as compared to the bioleaching control experiment. Under water irrigation conditions, the solubility of iron species at the elevated pHs and probable iron precipitation resulted in a  $TD_{Fe}$  of 3034 years. In addition, the potential for re-solubilisation of the iron precipitate under acidic feed conditions indicated the lack of removal of the potential for ARD pollution in the future under these conditions.

Comparison of the terminal durations estimated from the leachate and solids data was achieved using linear extrapolation of the averages between initial and final copper extraction values. Although the trends between the  $TD_{solid}$  estimates from the NAPP values and the  $TD_{average}$  values were similar, the magnitudes of these values differed. In addition, there was little correlation between the  $TD_{solid}$  estimates from the NAPP and NAG data. The use of the  $TD_{average}$  for this purpose did not take into account the logarithmic nature of the copper extraction profile and thereby can only be considered as a relative indicator.

#### **4.8. Chapter Summary**

To gain an understanding of ARD generation from a copper-sulphide waste rock, laboratory scale bioleach column experiments were performed. Experiments were performed to simulate two extreme scenarios, that of slow ARD generation under intermittent water irrigation, and that of an accelerated scenario in which bioleaching micro-organisms colonise the waste rock under acidic feed conditions. The effect of a temperature increase, lack of suitable aeration and a 1% pyrite concentrate addition were investigated to gain an understanding of their effect on the rate of ARD generation and leachate quality.

Valuable information regarding the comparison of ARD generation under the different conditions was acquired. The largest effect on the rate of ARD generation was the establishment of acidity in the dump environment, most rapidly simulated by use of the acidic feed solution. Under irrigation with water in which a leachate pH of approximately 4.0 resulted, the rate of ARD generation was significantly lower than that experienced with an acidic feed, with the pH of the resulting leachate in the range 1.1 to 1.4. The acidic nature of the feed allowed for the extraction of the acid soluble minerals and provided favourable conditions for the growth and colonization of bioleaching micro-organisms.

The effects of limited aeration and temperature on the rate of ARD formation were in good agreement with the ARD theory as outlined in Section 1.2. An environment with limited aeration

showed a decrease in the rate of ARD formation due to the twofold effect of this limitation. Firstly, oxygen is used as an electron donor in sulphide oxidation, with the lack of this within the waste dump expected to result in a decrease in the rate of ARD generation. Secondly, the bioleaching micro-organisms used in this investigation used CO<sub>2</sub> to fix carbon for metabolic use, with a lack thereof resulting in the negative effect on microbial activity as indicated from measurements of the redox potential. Both cause a slower rate of sulphide oxidation and thus ARD generation. Following thermodynamic theory, the rate of ARD generation increased with an increase in the operating temperature of the bioleach column from 32 °C to 42 °C. This condition provided the highest overall copper extraction, with similar levels of iron extraction as the bioleach control experiment.

With the addition of an easily accessible nutrient source, the suggested activity of the micro-organisms increased over a shorter time period as compared to the other conditions investigated. A direct link between this increased activity and an increase in the rate of ARD generation however was not observed. Although the addition of a 1% pyrite concentrate by mass led to an increase in the percentage iron extraction from the waste rock, no such increase was observed in the extraction of copper metal. The additional potential benefits of the pyrite oxidation, namely the increased temperature and resulting increased soluble ferric concentration were not observed, owing to the experimental configuration.

Linear extrapolation of the copper and iron extraction curves was developed as a comparative indicator of the effect of leaching on the rate of ARD generation. Both the copper and iron extraction profiles were used in this estimation. Complications with iron solubility, especially within the pH range of the water irrigated experiment, resulted in extreme discrepancy between the water and acid irrigated experiments. Overall, leaching of the waste rock at an elevated temperature resulted in the lowest time estimated for complete sulphide removal.

Static ARD characterization tests were performed on the solid material after bioleaching. These experiments included the separate quantification of the inherent neutralizing ability and the acid producing potential of the waste rock. These were compared to that of the feed material to quantify the reduction in ARD potential through leaching. The ANC results demonstrated that regardless of feed acidity, inherent neutralizing capacity of the waste rock was lost. In the case of the water irrigated experiment, there was little associated reduction in the acid generating potential of the sample. Thus, under this condition, the inherent neutralizing capacity cannot be counted on to neutralize any future ARD generation. For the experiments performed with an acidic feed media, total removal of the ANC was observed. A smaller decrease in the percentage total sulphur indicated that the potential for ARD generation was much less affected by the leaching process under all conditions over the 144 day period. Sulphide removal was highest at the elevated temperature of 42 °C, with a 30% decrease in the theoretical ARD generation potential observed.

Conflicting results were obtained from experimental determination of the ARD potentials. NAG results showed no statistical difference between the pre- and post-leaching waste rock samples. The exception to this was the experiment performed with a water feed solution, which showed an increase in the ARD generation potential, consistent with the reduction in ANC observed for this sample.

In order to provide a comparison of the rate of decrease in ARD potential from the leachate and solids analysis, it was necessary to determine the terminal duration using the initial and final copper extraction percentages. Comparison of these values with those obtained from the NAPP and NAG experiments indicated that, although the values were similar in magnitude, a direct match was not achieved. The trend of the values between the leachate and NAPP results was consistent.

Although laboratory scale bioleach column reactors do not simulate waste rock dumps closely, useful information was obtained on a comparative basis on the effects of the conditions studied on the rate of ARD generation. Of particular interest was the differences observed in the rates of decrease of the neutralizing capacity and the acid generating potential of the waste rock samples. This difference could potentially, as observed in the water irrigated experiment, lead to an increase in the ARD generating potential of a waste heap with time.

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## 5. Rate of ARD generation from leachate and static test work

The differences observed in the rates of decrease of the neutralizing capacity and the acid producing potential during bioleaching has the potential for an increase in the overall ARD potential of a waste rock sample with time. To investigate the differences in the rates of decrease of the ANC and MPA bioleach column experiments were conducted over a shortened time frame, with solid sampling occurring at 10 day intervals.

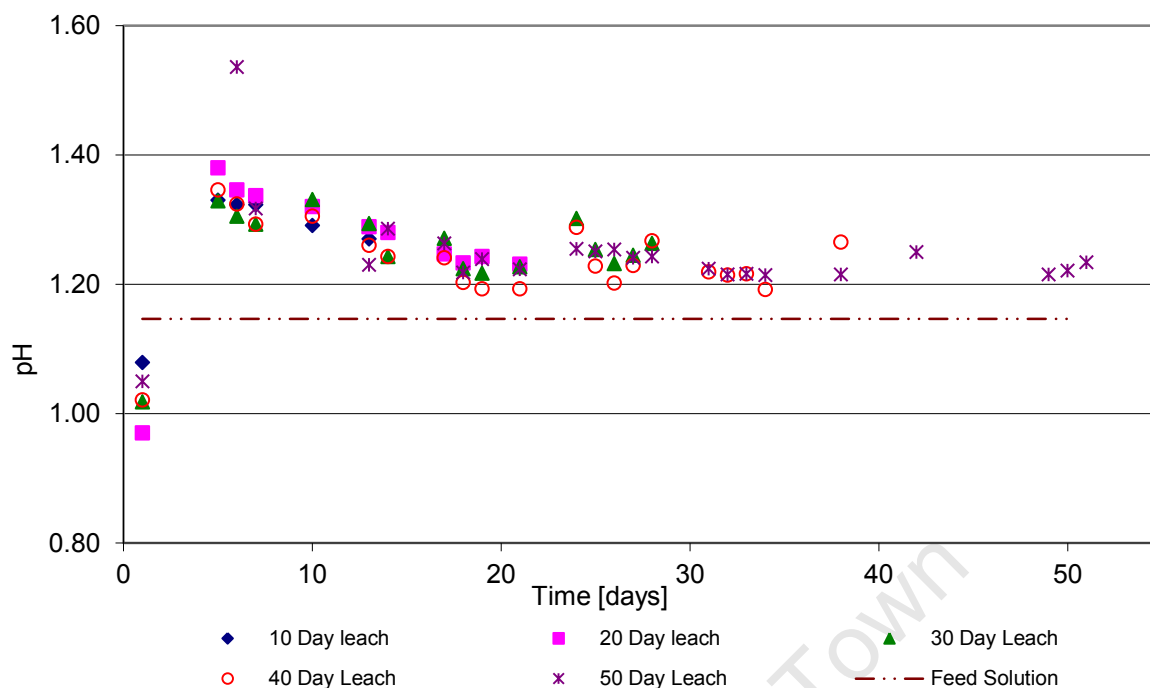
In addition, comparison of the  $TD_{Cu}$  and the  $TD_{average}$  from the ARD leachate solution indicated significant differences between the two estimated values due to the fitting of linear extrapolated data to the averages of the logarithmic extraction curves which was required due to the duration of the experiments. Similarly, estimates of the terminal durations from the leachate and solid ARD prediction experiments did not correspond. Over the shortened experimental durations therefore, a closer fit between the values estimated from the linear extrapolations and average-value extrapolations, and those obtained from the solids ARD prediction experiments was expected.

The bioleach column experiments were performed with the addition of 1% pyrite concentrate by mass. To gain an understanding of the changes in ARD generation with time, five, inoculated column experiments were run under identical conditions (32°C, aeration at 7 L / min., continuous irrigation with an acidified solution containing 0.5 g/L  $Fe^{2+}$ ). One column was sacrificed every ten days. Solid analysis was conducted on each of the column experiments, with the view to building a successive picture in the changes in the ARD potential with time.

As a consequence of the large variations observed in the rates calculated from the iron extraction profiles and the iron precipitation within the bioleach column, copper extraction alone was used as a proxy for ARD formation.

### 5.1. ARD leachate quality and generation rate

The importance of the acidic environment on the activity of bioleaching microbial species was discussed in Section 3.3. The pH profiles of the experiments followed a similar trend (Figure 4-1). Initially, the pH increased to pH 1.34 – 1.38, with exception of the 50-day column leach experiment which increased to pH 1.54, due to reaction of the acid with acid-neutralizing components within the waste rock sample. This was followed by a steady decrease, with the pH of all columns stabilizing at an approximate value of pH 1.2. The deviation in pH in the 50-day column may be as a result of slightly more acid consuming minerals present in this particular sample. While representative sampling procedures were used in the packing of these columns, it is well recognised that a degree of heterogeneity may be experienced where small scale experiments are conducted such that exact identical mineralogy and particle sizes between the columns is difficult to attain.



**Figure 5-1: pH profiles of five column experiments of agglomerated and inoculated waste rock with 1% additional pyrite concentrate following continuous irrigation with acidified media at 32 °C**

The similarity in the redox potential profiles, shown in Figure 4-2, indicated similar oxidative environments in each column. This suggested that microbial activity in each experiment was comparable, leading credence to the assumption of similar leaching in all columns. The redox potential of the pyrite-addition experiment operated under the same conditions over 144 days and presented in Section 3.6 is included in the comparison.

The redox potential profiles are approximately constant at 390 – 400 mV over the first 12 days, followed by a gradual increase up to a potential of approximately 520 mV by day 25, followed by a rapid increase to a potential of approximately 700 mV over a three day period. These were supported by iron measurements (data not shown).

In comparison with the profile observed previously (Figure 3-17), there is a strong correlation for the initial 25 days, with a potential of 550 mV attained by day 25. Thereafter, the potential increased steadily to a value of 650 mV by day 33. This difference may be due to differences in the microbial population or mineralogy. Although both samples were sourced from the same bulk, and thus the same bulk mineralogy, samples for the two different experiments were from different statistical splits. Similarly, although the microbial species were sourced from the same stock culture, these cultures were not static in the intermittent time period between the experiments.

With the exception of the 20-day leach experiment, the copper extraction profiles for the columns show similar values over the 50 day time period investigated (Figure 5-3). The similar trends in this copper extraction data supported the reproducibility of the bioleach column experiments. Although detailed comparison between the 144-day leach and the other durations is not relevant due to the differences in mineralogy, a similar copper extraction trend is observed. The enhanced copper

extraction in the 20-day column experiment may be as a result of mineralogical differences between waste rock samples.

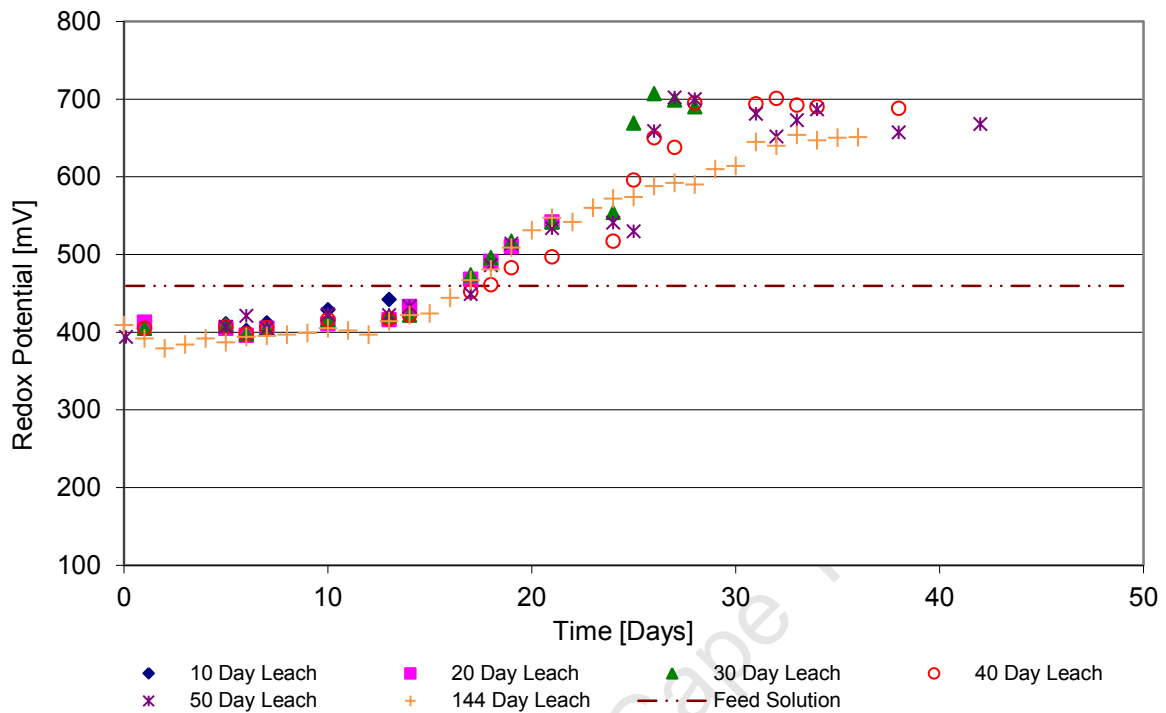


Figure 5-2: Redox potential profiles of five column experiments of agglomerated and inoculated waste rock with 1% additional pyrite concentrate following continuous irrigation with acidified media at 32 °C

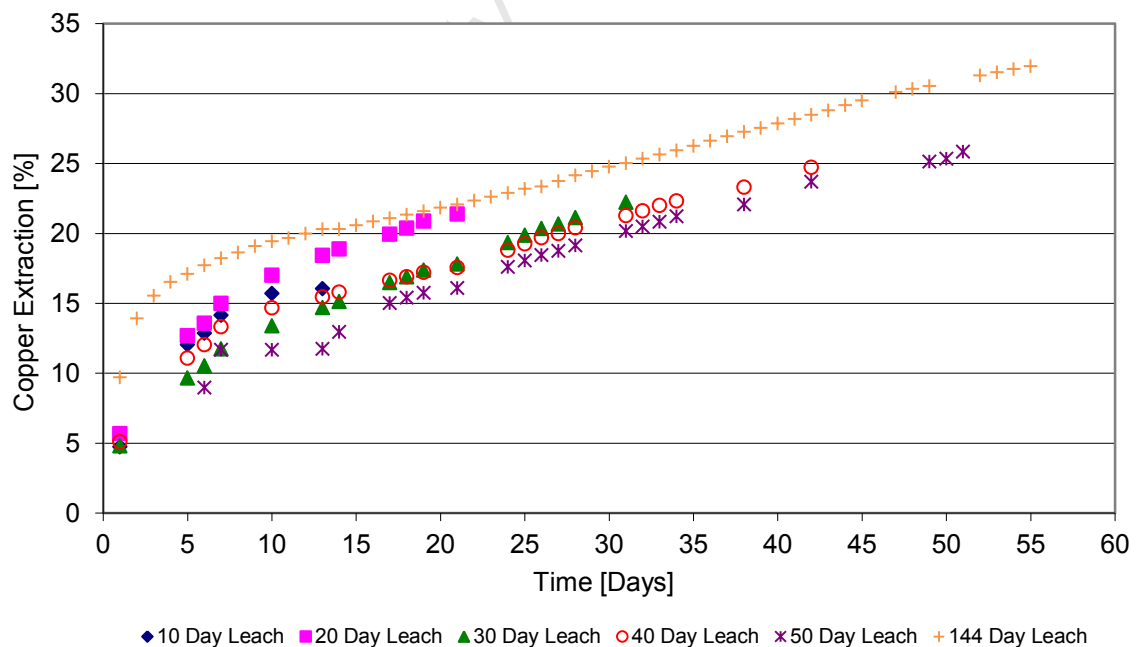
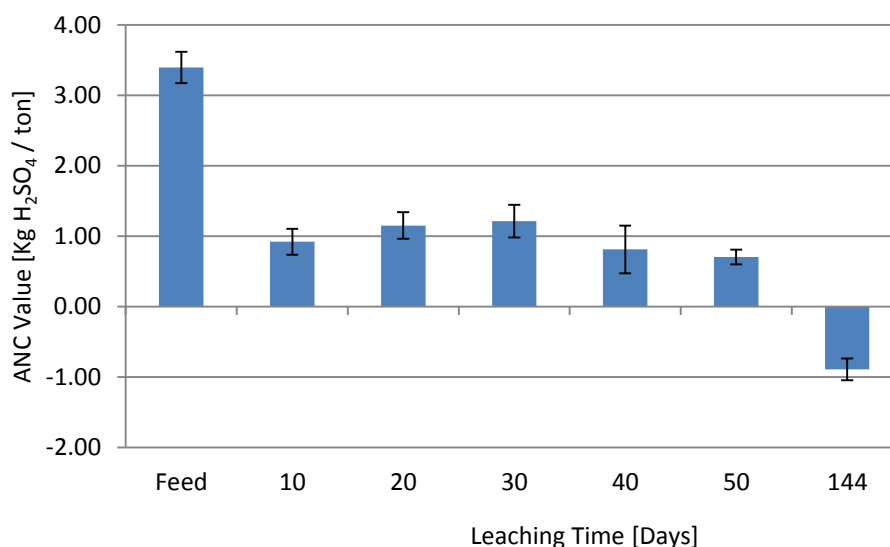


Figure 5-3: Copper extraction profiles of five column experiments of agglomerated and inoculated waste rock with 1% additional pyrite concentrate following continuous irrigation with acidified media at 32 °C

## 5.2. ARD static prediction experiments

At ten day intervals, a column experiment was sacrificed for solids analysis with static ARD prediction experiments conducted to determine the remaining ARD potential in the waste rock samples. The successive sacrificing of the 5 column experiments allowed investigation into the change in ARD potential with time. In addition, terminal durations were estimated from the leachate copper extraction profiles and from the results of the solid ARD prediction experiments.

The rapid decrease in the ANC observed in Figure 4-4 was due to reaction of the acid consuming components within the waste rock with the acid added during the experiment and the flow of feed solution through the column. During agglomeration, 1.7 kg H<sub>2</sub>SO<sub>4</sub> / ton of ore was added, accounting for an approximate 50% decrease in the ANC value. Further ANC was removed by the flow of solution through the column (regardless of pH, Section 3.2) and the generation of ARD from sulphide oxidation. That neutralizing capacity was present after the addition of approximately 1000 L (10 days of leaching at 40 mL / hr), suggested not all the ANC was in contact with the flowing solution. The rapid removal of the ANC suggested that microbially-mediated acid generation was not responsible for a significant decrease in the ANC value over the duration of the experiment. Although the 144-day ANC value pertains to a slightly different ore sample, the continuing trend in the decrease in ANC would be expected to be similar from this waste rock sample.



**Figure 5-4: ANC results from solids samples from five column experiments of agglomerated and inoculated waste rock with 1% additional pyrite concentrate following continuous irrigation with acidified media at 32 °C**

In contrast to the rapid ANC decrease, the decrease in MPA and NAPP was steady over the first 20 days (Figure 4-5), with an approximate 18% decrease over this period. No statistical difference in the MPA and NAPP values was demonstrated in the leached waste rock samples. The difference in the rates of decrease of the ANC and MPA suggested the quicker removal (as a percentage) of the acid consuming components, as compared to the acid generating components. This suggested the possibility for an overall increase in the ARD potential of a waste rock dump with time, until such time as significant acidification may potentially arise due to colonisation and decrepitation of rock exposing new mineral surfaces. The 144-day result suggested an overall statistical decrease in the percentage sulphur over an extended experimental duration.

Although the NAG values decreased with an increase in the leaching duration as expected, the error associated with this particular static test did not allow statistical significance for the apparent decrease to be demonstrated. These values therefore indicated no reduction in the experimentally determined, acid generating potential of the leached waste rock samples. As observed in Section 3.7.1, the NAPP and NAG experiments displayed conflicting results.

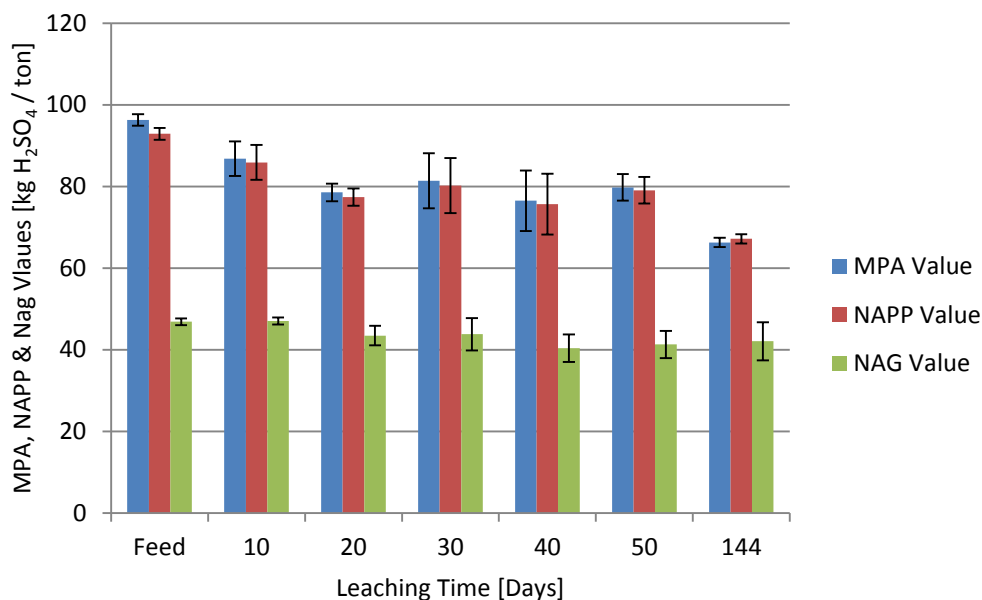


Figure 5-5: MPA, NAPP and NAG from solids samples from five column experiments of agglomerated and inoculated waste rock with 1% additional pyrite concentrate following bioleaching

### 5.3. Comparison of the rate of ARD formation as calculated from liquid and solid phases

The  $TD_{Cu}$  and  $TD_{average}$  were calculated from the leachate data using the copper extraction profiles, and compared. In addition, each of these was compared to equivalently estimated rates from the NAPP and NAG static test results, using linear extrapolation to estimate the time necessary for complete removal of the ARD potential.

#### 5.3.1. Comparison of the Terminal and Average Rates as calculated from the leachate

The  $TD_{Cu}$  values (Table 4-1) were estimated using the final phase, after 10 days of leaching, of the copper extraction profiles so as to exclude the extraction from the rapidly leached acid-soluble minerals which do not play a significant role in long-term ARD generation. This was substantiated by the redox potential which remained at approximately 400 mV for the first 10 days of leaching, indicate the dominance of acid leaching over this period. Significant extraction from non-acid soluble sulphide minerals was therefore not expected during this leaching stage. Thus, the  $TD_{Cu}$  value for the 10 day leach experiments was excluded.

The  $TD_{Cu}$  values were similar across the 50 day leaching experiments and were identical to the corresponding average values. This was expected due to the linear nature of the extraction profiles.

The average values for the  $TD_{Cu}$  and  $TD_{average}$  are  $0.7 \pm 0.1$  years. For comparison, the  $TD_{Cu}$  estimated between 10 and 50 days for the extraction data from the 144-day column experiment was 0.78 years.

The difference between the estimated  $TD_{Cu}$  over the 50-day experiment and that estimated from the pyrite supplemented column over 144 days (Section 3.6) indicated the decrease in leaching rate with an increase in experimental duration. With an approximate three-fold increase in experimental duration to 144 days, the terminal duration increased by a factor of four to  $2.8 \pm 0.3$ . The difference in values indicates the limitation of extrapolation of the extraction profiles over the shortened experimental duration and its significance in ultimate ARD generation rates.

**Table 5-1: Terminal duration estimations from copper extraction profiles for bioleach experiments on agglomerated and inoculated waste rock with 1% additional pyrite concentrate leached for different durations**

Leaching Duration	$TD_{Cu}$ [years]	$TD_{average}$ [years]
10 Days	N/A	N/A
20 Days	0.6	0.6
30 Days	0.6	0.6
40 Days	0.8	0.8
50 Days	0.7	0.7
144 Days	$2.8 \pm 0.3$	N/A

### 5.3.2. Comparison of the Average Rates from leachate and solids data

Similar to the estimations for the  $TD_{Cu}$  and  $TD_{average}$ , it was possible to estimate the terminal durations from the solid ARD characterization results using the 10-day leached sample as the “initial” point (data not shown). Although the observed trend in the  $TD_{NAPP}$  and  $TD_{NAG}$  values were similar, the validity of using the NAPP and NAG results for terminal duration estimations was questionable given the error associated with these static tests. Further therefore, no comparison between the rates from the leachate and solids data was possible.

## 5.4. Chapter Summary

The leachate profiles obtained from the five column experiments, conducted over 50 days, showed good agreement, indicating the suitability of using the liquid phase data to estimate progression of ARD generation. The large differences between the copper extractions experienced over the course of the initial 20 days of leaching, however, illustrated the variation typical in column leach tests. This difference may result from inherent mineralogical differences between the four kilogram samples, differences in packing and inherent experimental error in the laboratory scale bioleach column reactors.

ARD characterization data from the solid phases indicated the rapid removal of the ANC over the first 10 days of leaching, with no significant decrease in the ANC value observed over a 40 day period thereafter. A significant difference was observed between the magnitude of the reduction between the MPA and NAPP, and the ANC values. The errors associated with the static ARD experiments however prevented any significant difference in the NAPP and NAGs from being observed.

The terminal durations for ARD generation were estimated by excluding extraction which occurred during the predominantly acid-leaching, initial 10 days. The linear profile of the extraction curve subsequent to this period resulted in identical  $TD_{Cu}$  and  $TD_{average}$  estimates. In addition, the  $TD_{Cu}$

estimate for the 144-day column experiment was identical for the 50 day estimate. There was, however, no comparison between the terminal durations estimated from the copper extraction and the solids samples due to the errors in the static ARD characterization tests, which indicated no significant difference between MPA and NAPP values of the leached solid samples.

In addition to the large errors associated with the static ARD characterization experiments, the using of such tests for the investigation into the rate of change in ARD potentials with time is dependent on the number and duration of the bioleach column experiments. In addition, only discrete data points are collected from such experiments. The necessity of kinetic ARD characterization experiments for the prediction of ARD generation from waste rock samples was noted.

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## **6. Investigation into the use of in-bed sampling for the *in situ* sampling of kinetic ARD bioleach column experiments**

In order to minimise the inter-column variability found when tracking the course of the leaching process by sacrificing individual columns, an in-bed sampling technique was used, whereby a solid sample was removed from one column without termination of the entire experiment. Application of this method in place of many, identical column experiments could potentially reduce experimental error by eliminating the inter-column error ascribed to the inherent differences between the column experiments operated under equivalent operating conditions.

To consider the suitability in replacing five bioleach column experiments with fewer experiments in which in-bed sampling was performed, two regular column experiments were performed over a 50 day period in conjunction with two column experiments with in-bed sampling under identical conditions. Both water-fed and acid-fed conditions were investigated with approximately 300 g (wet mass) of solid removed from the mid to lower portion of the column during in-bed sampling. The water- and acid-fed conditions used for this study were identical to those described in Sections 3.2 and 3.3 respectively; however, the ore mineralogy differed to that used in the previous experiments. Although the copper, iron and sulphur grades were within a similar range to previous samples, the waste rock sample used in these experiments was constructed from four different waste rock samples to achieve this. A more detailed mineralogical description is provided as waste rock C in Appendix 11.1. The experiments were run with inoculation so as to exclude the variations in leaching performance due to any differences in microbial populations.

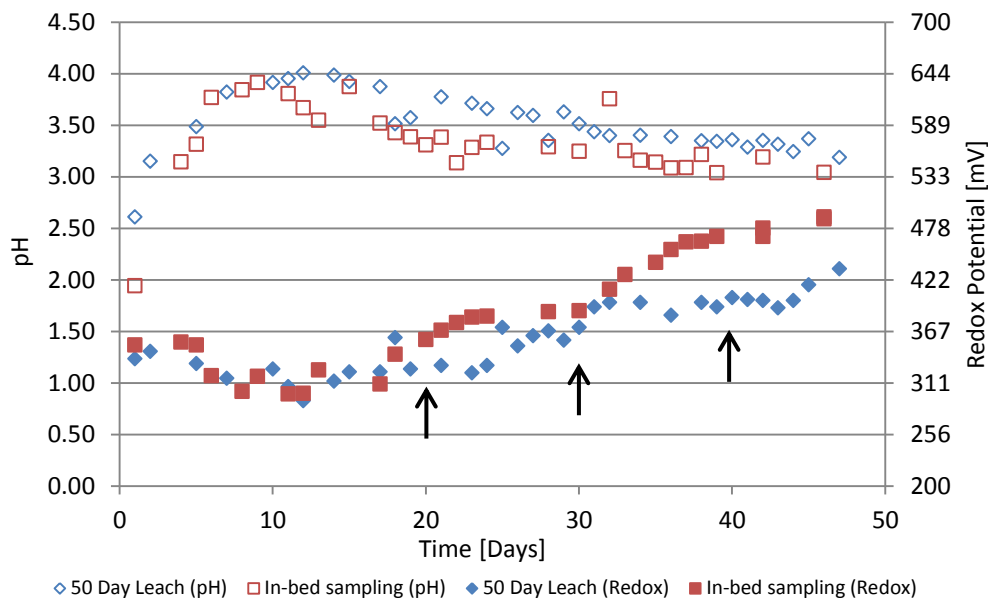
### **6.1. Comparison of column experiments under water-fed conditions**

The pH of the leachate from both experiments (Figure 6-1) rose initially due reaction of the acid added during agglomeration with acid consuming minerals within the waste rock samples. The pH of the leachate solutions rose to a maximum of approximately pH 4.0 after 10 days before decreasing to a pH of 3.0 by the end of the experiment. Given that the pH of the water feed was approximately pH 5.5, this decrease in pH with time suggested the occurrence of acid-forming, mineral oxidation within both column reactors.

The redox potential profiles for the in-bed and 50-day column experiments showed similar trends for the initial 10 days of leaching (Figure 6-1). After 18 days, the potentials deviated, with the column experiment run using the in-bed sampling technique showing a greater relative increase. This increase in redox potential correlated with the decrease in pH and may have been due to the “inoculation” of the waste rock sample due to the presence of a native microbial population in the ore samples. Removal of a solid sample may also have affected the hydrodynamics of the leach columns, thus allowing an increase in the exposure of the minerals to the feed solution, as well as enhancing penetration of air into the rock bed.

The redox potential for both column reactors, however, remained below 550 mV, indicating the absence of an extensive oxidative environment and suggesting a limited ferric iron supply through chemical oxidation or microbial action over the duration of the experiment. At experiment termination however, the rising potentials indicated that given a longer experimental duration, ferric

iron dominated leaching may have become significant in the oxidation of the minerals under the water-fed conditions. This is in agreement with the water-fed experiment results presented in Section 3.2.

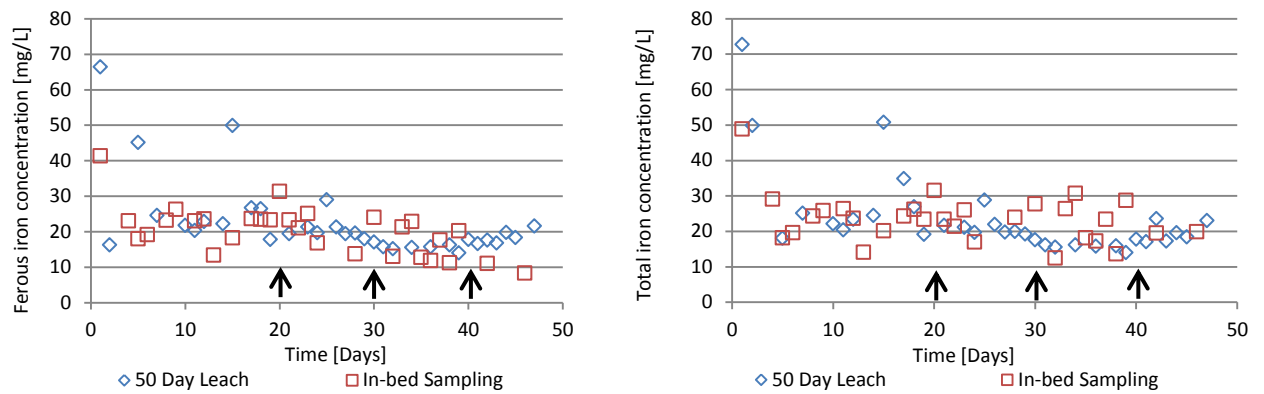


**Figure 6-1: pH and redox potential profiles for continuous irrigation of agglomerated waste rock with water feed for the comparison of in-bed sampled and 50-day columns. Arrows indicate in-bed sampling points**

The ferrous and total iron concentrations profiles are presented in Figure 5-2. With exception of high initial concentrations) over the first two sample days due to acid-leaching during ore agglomeration (data not shown), the low concentrations and small differences between the ferrous and total iron values observed suggested quicker mineral leaching as compared to microbial ferrous iron oxidation. The rising redox potentials near the end of the experiment however suggested the increase in the relative rate of microbial iron oxidation over the rate of mineral leaching.

The pH range of 3.0 to 4.0 found in these column suggested iron precipitation in the bioleach columns. As this precipitation is often mediated through a net acid forming set of reactions, the generation of acidity from this process would have contributed to the decreasing trend in pH. Precipitation of the ferric iron would also have removed this leaching agent from solution, resulting in a slower leaching rate as compare to an acidic system. No significant differences were observed between the in-bed and 50-day column experiment, suggesting similar mineral leaching environments in both reactors.

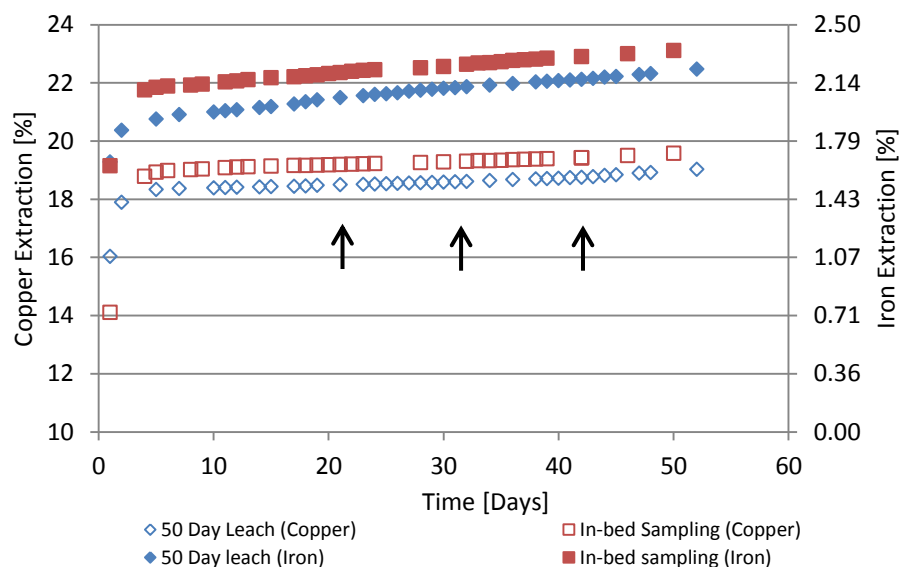
The iron extraction profiles (Figure 6-3) indicated a slight elevation in the amount of iron extracted in the in-bed sampled column experiment. This slight increase could be a consequence of elevated redox potentials as observed in Figure 6-1. Examination of the rate of extraction indicated that differences in the extraction profiles may have been due to increased iron leaching over the initial 4 days, suggesting some possible variations in initial iron-mineral content or packing. Thereafter, the rate of extraction for both column experiments was similar.



**Figure 6-2: Ferrous and Total iron concentration profiles for continuous irrigation of agglomerated waste rock with water feed for the comparison of in-bed sampled and 50-day columns. Arrows indicate in-bed sampling points.**

A similar result was observed in the copper extraction profile with a slight elevation in the amount extracted when using the in-bed sampling technique. As with the iron extraction profiles, this difference was most probably due to initial differences in easily-soluble copper mineral content of the two waste rock samples or their packing. This difference did not arise due to the in-bed sampling method.

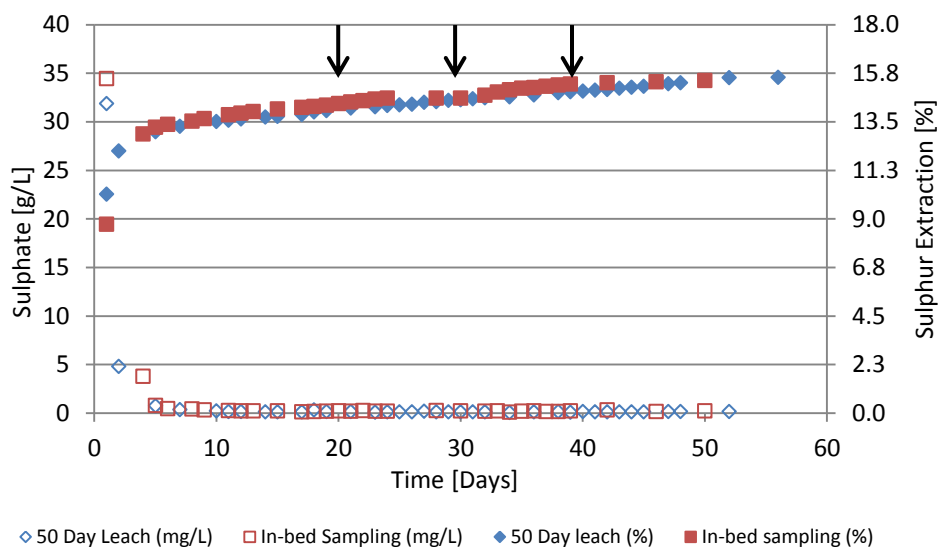
The trends in the iron and copper leaching were similar to those reported in Section 3.3. The initial leaching period ( days 1-4) corresponded to the rapid reaction of the acid-soluble minerals with the acid added during agglomeration and the associated washout of these leached products. A much slower leaching period followed (days 4-50), corresponding to the decreasing trend observed in the pH of leachate; the low redox potentials suggested limited, but positive, microbial activity. This phase of leaching was likely indicative of slow leaching of the mineral sulphides at these conditions.



**Figure 6-3: Copper and iron concentration and extraction profiles for continuous irrigation of agglomerated waste rock with water feed for the comparison of in-bed sampled and 50-day columns. Arrows indicate points at which solids were sampled**

Due to the importance of the sulphide component to the generation of ARD, sulphate measurements were conducted on the leachate solution over the course of the experiment. It was thus assumed that all sulphur removed from the waste rock sample was present as sulphate in the leachate solution. The trends observed in the sulphate concentration and sulphur extraction profiles (Figure 5-4) are similar to those observed for the iron and copper data presented. The initial high sulphate concentrations recorded in the leachate of both column experiments were due to the reaction of acid-soluble, sulphide minerals with the acid added during agglomeration. The rapid drop in concentrations thereafter indicated the unfavourable sulphide oxidation environment within the bioleach columns as a result of the water feed solution.

Although the initial values were slightly different between the two bioleach columns, with the in-bed column showing the higher sulphate concentration, there was no significant difference observed between the concentrations thereafter and the difference was not a result of in-bed sampling. The sulphur extraction profiles show similar trends and values for both bioleach column experiments, with no statistical difference between the amounts of sulphur extracted from each experiment. Again, two distinct phases of sulphur extraction were observed, with the initial phase a consequence of waste rock agglomeration and the second, slower phase, corresponding to the decreasing pH levels and low redox potentials, a result of slower, acid leaching of sulphide minerals within the waste rock samples.



**Figure 6-4: Sulphate concentration and sulphur extraction profiles for continuous irrigation of agglomerated waste rock with water feed for the comparison of in-bed sampled and 50-day columns. Arrows indicate in-bed, solid sampling points.**

The  $TD_{Cu}$  estimates for the bioleach columns operated with and without in-bed sampling were estimated across varying terminal leaching durations, corresponding to the number of days before termination of the experiment (Table 6-1). The  $TD_{Cu}$  for the column experiments operated with and without in-bed sampling were estimated at  $12 \pm 3$  and  $18 \pm 2$  years respectively. These averages were estimated over the final 40 days of leaching (terminal leaching data points taken over of 10, 20, 30 and 40 days) as the estimate obtained at a terminal leaching duration of 50 days included the

copper extraction associated with the agglomeration process. The rate of extraction over the initial four days of leaching, shown in Figure 6-3, was significantly different to that experienced over the remainder of the experiment and was thus excluded from the  $TD_{Cu}$  estimation.

The long time periods necessary for completion of ARD generation were due to the unfavourable leaching conditions under the water-fed conditions. The similarities in the copper extraction profiles led to similar  $TD_{Cu}$  estimates, with the difference between the two data sets likely due to the initial difference in copper extraction over the first four days of leaching, resulting from differences in waste rock samples or column packing.

Terminal duration calculations from the iron extraction profiles were not performed due to the poor iron solubility at the pH values of the leachate. This is especially true given the suggested iron precipitation. Terminal durations estimated from the sulphur extraction curves (Table 6-2) however were 2-3 times smaller than the  $TD_{Cu}$  estimates. The  $TD_{Sulphur}$  values were  $4.5 \pm 0.2$  and  $5.0 \pm 0.5$  years for the in-bed sampled and 50-day bioleach columns respectively. In addition, the  $TD_{Sulphur}$  values showed no significant difference between the two bioleach experiments. The differences experienced between the  $TD_{Cu}$  and  $TD_{Sulphur}$  estimates reflected the recalcitrant nature of the chalcopyrite mineral within the waste rock samples. Whereas the  $TD_{Sulphur}$  estimates considers all the removal of all sulphide minerals, the  $TD_{Cu}$  estimate accentuated the behaviour of the chalcopyrite mineral.

**Table 6-1:  $TD_{Cu}$  estimations using variable terminal leaching data points for the in-bed sampled and 50-day bioleach column experiments under continuous irrigation with water.**

<b>Terminal</b> leaching duration [days]	50-day $TD_{Cu}$ [years]	In-bed Sampling $TD_{Cu}$ [years]
10	20	8
20	16	11
30	18	14
40	19	16
50	6	10

**Table 6-2:  $TD_{Sulphur}$  estimations using variable terminal leaching data points for the in-bed sampled and 50-day bioleach columns under continuous irrigation with water**

<b>Terminal</b> leaching duration [days]	50-day $TD_{Sulphur}$ [years]	In-bed Sampling $TD_{Sulphur}$ [years]
10	4.2	4.4
20	4.6	5.1
30	4.6	5.4
40	4.6	5.2
50	3.2	3.8

The leachate profiles observed for water-fed experimentation on this particular waste rock composition are similar to those presented in Section 3.2, thus highlighting the importance of the feed solution, or liquid phase in the ore bed, on the oxidative environment present in the bioleach columns and, ultimately, the composition of the leachate.

Here, however, the decreasing trend in leachate pH indicated the differences in mineralogy of waste rock A and C. The low redox potential values also indicated the faster relative mineral dissolution rate as compared to microbial ferrous iron oxidation for this particular mineralogy over the course of the experiment. Precipitation of ferric iron, although removing an oxidizing agent from the reaction system, may have also contributed to the decreasing trend in pH.

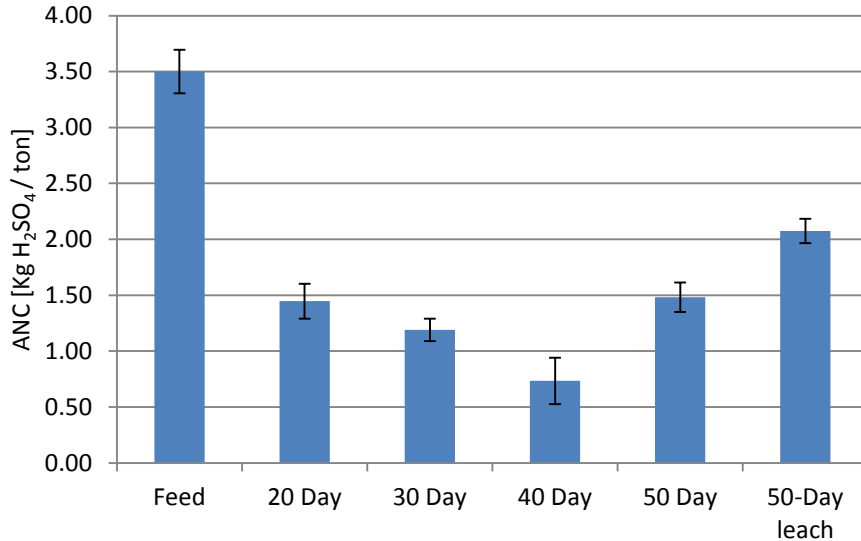
Overall, little significant difference was observed between the leachate profiles of the in-bed and 50-day bioleach columns. The small differences in leachate profiles are particularly insightful given that solid samples were removed from the in-bed sampled column at regular intervals.

The main advantage to the in-bed column technique, however, was the ability for solid sampling without termination of the experiment. In contrast to the 50-day leach column, the in-bed sampling technique allowed for solids analysis over time. The solids sampled were subjected to static ARD prediction tests, with an additional comparison between the 50-day solid sample and the results from the 50-day leach column that was not subjected to in-bed sampling.

The ANC results for the solid samples taken from the bioleach columns under water-fed conditions with and without in-bed sampling are presented in Figure 6-5. The solid samples extracted via the in-bed sampling technique show a decreasing trend in the ANC with time. This trend, however, was not followed by the 50-day column sample. In addition, there is a statistical difference between the 50 day sample collected following in-bed sampling and that taken from the 50-day bioleach column experiment without in-bed sampling.

These observed differences may have been as a result of the in-bed sampling method, which targeted the same section of the column for every sample. Previous studies (Mosby & Enstad, 1996; Silva et al., 1996 as cited in McGlinchey, 2004; Boss, 1986) have recognized the occurrence of particle segregation based on size in heterogeneous solid mixtures. Given the targeting of a particular section of the bioleach column by the in-bed sampling technique, the size of the extracted particles may not have been representative of the entire bulk sample. In addition, the in-bed sampling method did not allow for a representative solid sample to be taken. Overall therefore, the lack of homogeneity within the individual bioleach columns, and between the column experiments, may have been responsible for the differences in trend between the 20-, 30- and 40-day ANC values and that of the 50-day value.

The removal of solid material without representative sampling of the entire waste rock sample may also have resulted in the discrepancy in the ANC value obtained for the 50-day sampled obtained by in-bed sampling and that of the 50-day column operated without in-bed sampling. The lower ANC values may have been directly linked to the changes in solid-liquid contact as a result of the in-bed sampling procedure.



**Figure 6-5: ANC results for the in-bed column samples and the 50-day leach under water-fed conditions**

A similar trend was observed for the MPA, NAPP and NAG profiles (Figure 6-6) where differences in the rates of sulphur removal were observed between samples. Here, however, given the error associated with the LECO analysis and the NAG experiments, no statistical difference between these values were observed. In addition, Figure 6-6 compares the MPA values calculated from LECO analysis (LECO MPA) were compared to those calculated using the sulphur extraction data from the leachate analysis (Extraction MPA)). For the feed sample, the total sulphur percentage resulting from LECO analysis was used, with this representing 0 % extraction. Extraction MPA values were then calculated by subtracting the percentage sulphur recovered into the leachate solution from this initial value. These calculations are detailed in Appendix 11.4.

With the exception of the 50-day sample taken by in-bed sampling, the Extraction MPA corresponded, within the error range, with the values as calculated from LECO analysis. This data showed no significant difference in residual sulphur content, and therefore MPA, for samples after 20 days of bioleaching.

The presented leachate and solid analysis data therefore showed different results in the comparison between the in-bed sampling technique and the once off, 50-day bioleach column experiment. With the exception of the redox potential profiles, no significant differences were observed in the leachate results. This is particularly true in the iron, copper and sulphur extraction curves presented. Differences were, however, observed from the analysis of the ARD potentials of the solid samples. The decreasing trend in ANC value observed from the in-bed samples over the first 40 days of column leaching was not followed by the 50 day sample (Figure 6-5). In addition, the ANC values of the solid samples collected from the 50-day column leach did not agree with those of the 50 day in-bed sample.

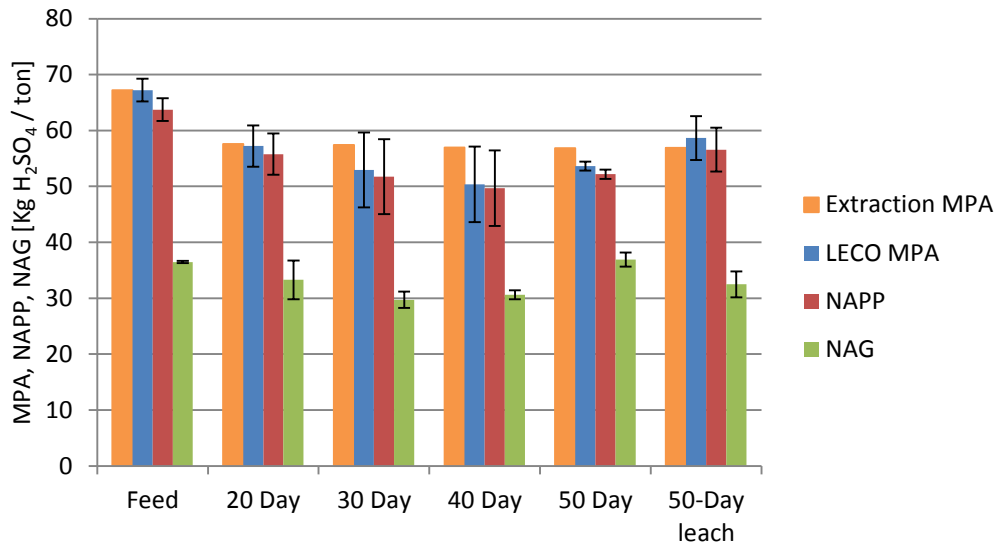


Figure 6-6: MPA, NAPP and NAG profiles for the in-bed and 50-day bioleach column experiments under water-fed conditions

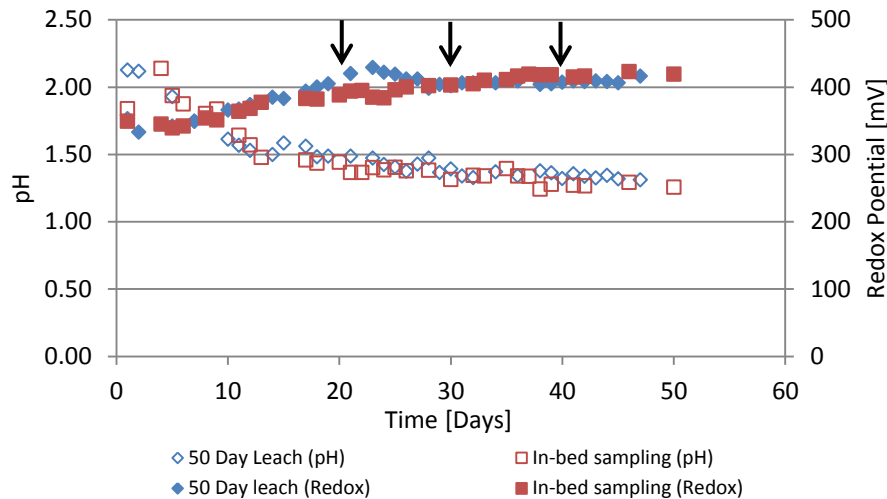
In contrast with the ANC values, no significant differences were observed between the NAPP and MPA values for the leached sample. In addition, comparison of the percentage sulphur removed from the leachate data and the LECO analysis from the solid data showed good agreement. Overall however, especially given the ANC values and the unsubstantiated possible explanations behind these differences, the leachate and solids data provided conflicting conclusion on the reproducibility of the bioleach column experiments conducted with or without in-bed sampling under water fed conditions.

## 6.2. Investigation of the in-bed sampling technique under acidic feed conditions

Although an investigation using water as the feed solution provides possibly the best simulation of a typical waste rock dump environment, the excessive experimental duration required for ARD investigations under these conditions provided a motivation for the inclusion of experiments using an acid feed solution to provide a better representation of an active ARD generating waste rock dump. Investigation into the suitability of the in-bed sampling technique for use under acid feed conditions was performed by replicating the column experiments described in Section 5.1. under the acid feed conditions used in Section 3.3. These experiments were not inoculated. This provided a comparison of the two column operating techniques under predominantly acid-leaching conditions, conditions more closely representing an ARD generating waste rock dump than the water-fed experiments.

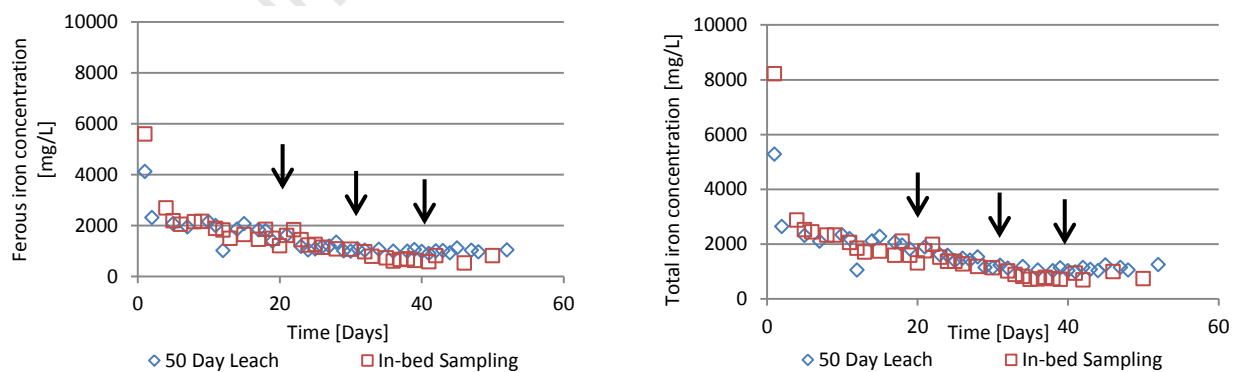
As seen in Figure 6-7, the pH of the leachate solution rose initially due to the neutralization of the acid added on agglomeration by the ANC of the waste rock samples. Thereafter, due to continuous acid feed, the pH of the leachate fell steadily, reaching values of approximately pH 1.2; close to the pH of the feed solution, pH 1.15. The similar pH profiles for both experimental columns suggested that the pH of the leachate was not affected by the in-bed sampling technique and was dominated by that of the feed solution which was identical for these two experimental columns.

The redox potential curves also displayed similarities between the two experiments. In contrast to the water-fed experiments, there was less variation between the redox potential profiles of the two experiments. In addition, the potentials for the experiment remained at approximately 400 mV for the last month of the experiments, suggesting a low activity of any native iron-oxidizing microbial species within the waste rock samples. Due to the relatively low ferric iron concentrations, metal extraction was dominated by acid leaching.



**Figure 6-7: pH and redox potential profiles for continuous irrigation of agglomerated waste rock with acidic feed for the comparison of in-bed sampled and 50-day columns. Arrows indicate in-bed sample days**

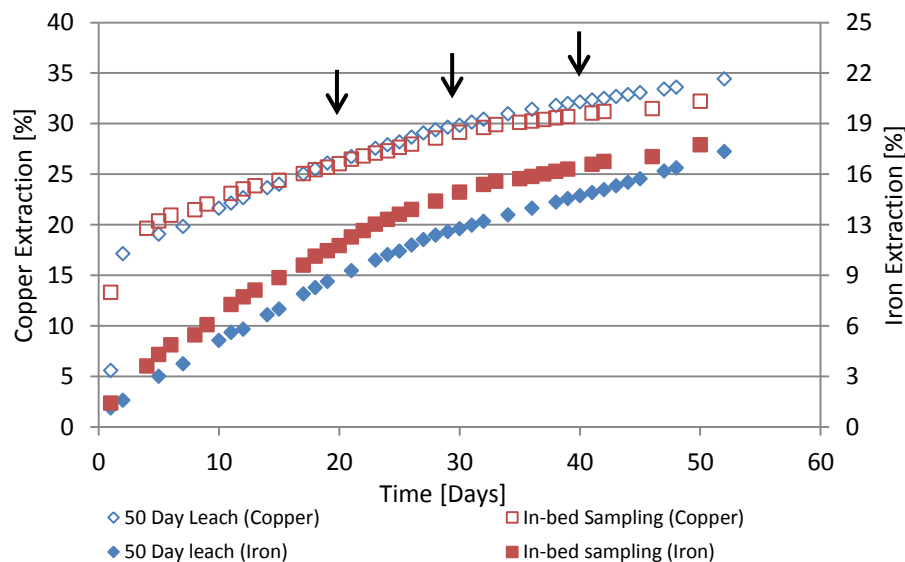
The low microbial activity in acidic bioleach column experiments was also suggested by the dominance of ferrous iron over ferric iron. The high initial iron concentrations were due to the reaction between the acid soluble, iron-bearing minerals and the acid added during agglomeration. The gradual decrease in iron concentration resulted from the slower, mainly acid-mediated oxidation of iron containing components. Once again, under these predominately acid leaching conditions, there was little observed difference between the experimental bioleach columns run with and without in-bed sampling.



**Figure 6-8: Ferrous and total iron concentration profiles for continuous irrigation of agglomerated waste rock with acidic feed for the comparison of in-bed sampled and 50-day columns. Arrows indicate in-bed sampling points**

Similar to the water-fed experiments, no real difference in percentage copper extraction was observed between the acidic bioleach column experiments with and without in-bed sampling (Figure 6-9). Initially, approximately 20 % of the copper was extracted during the first 4 days of the experiment due mainly to the agglomeration process. By the end of the experiment, 32 – 34 % of the total copper was extracted.

The iron extraction profiles showed some difference in percentage extraction, with the in-bed sampled column displaying a higher degree of extraction throughout the course of the experiment. With the exception of that observed over the first 5 days, the rate of iron extraction was similar in both experiments. This suggested that there was little difference between the functionality of the bioleach column experiments in the presence and absence of in-bed sampling. Although the final extraction percentages are similar, the differences in the initial rate of iron extraction may be due to differences in the mineralogy or the ore packing. This was also suggested by the differences in copper extractions over the initial 2 days of leaching.

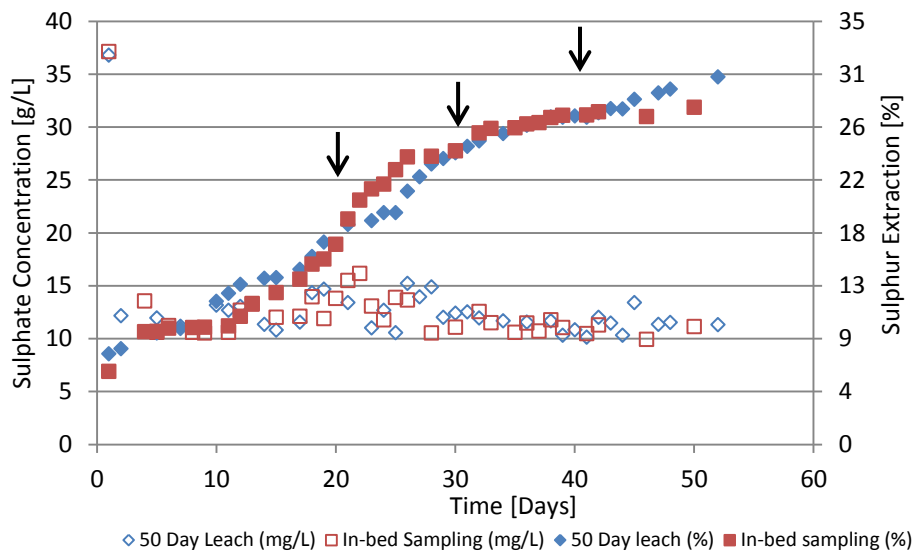


**Figure 6-9: Copper and iron extraction profiles for continuous irrigation of agglomerated waste rock with acidic feed for the comparison of in-bed sampled and 50-day columns. Arrows indicate the points of in-bed sampling**

The similar sulphate concentration and associated sulphur extraction profiles shown in Figure 5-10 further suggested little difference between the two columns. The high initial concentrations over the first 2-3 days were due to the acid added during agglomeration and fluid flow through the column.

The sulphur extraction profiles (Figure 6-10) between the acid-fed columns were similar in the presence and absence of in-bed sampling. Sulphur extraction was calculated from the sulphate concentration removed in the leachate and the initial head grade in the solid sample. The errors associated with the method for sulphate determination in the liquid phase was expected to dominate the errors associated with sulphur extraction, with a lesser contribution from volume measurement and the LECO analysis. The error in the barium chloride assay for the turbidimetric determination of sulphate has been previously estimated as 12 % (Moosa, 2000). In addition, given

that the experiments were not inoculated and the low redox potential values, the assumption that all sulphur within the leachate presented as sulphate may be incorrect.



**Figure 6-10: Sulphate concentration (primary y-axis) and sulphur extraction (secondary y-axis) profiles for continuous irrigation of agglomerated waste rock with acidic feed for the comparison of in-bed sampled and 50-day columns. Arrows indicate days of in-bed sampling**

The Terminal Duration estimations from the copper extraction curves for each experiment are presented in Table 6-3 with averages over the first four values (the final 40 days of leaching) giving estimates of  $1.0 \pm 0.2$  and  $1.2 \pm 0.3$  years for the columns operated with and without in-bed sampling respectively. These values are in agreement with the copper extraction curves presented in Figure 6-9 where little difference was observed between the two profiles over the duration of the experiment.

**Table 6-3: TDCu estimations using variable terminal leaching data points for the in-bed sampled and 50-day bioleach column experiments under continuous irrigation with acid feed media.**

<b>Terminal</b> leaching data points [days]	50-day column TD <sub>Cu</sub> [years]	In-bed sampling TD <sub>Cu</sub> [years]
10	1.6	1.1
20	1.4	1.1
30	1.0	0.9
40	0.9	0.8
50	0.7	0.6

Terminal durations estimated from the sulphur extraction data are presented in Table 6-4. In contrast to the TD<sub>Cu</sub> estimates, the TD<sub>Sulphur</sub> values show significant variability between the in-bed and 50-day bioleach column experiments. The large variations in TD<sub>Sulphur</sub> estimates observed for the in-bed sampled column could possibly be due to the errors associated with the barium chloride assay. As the number of data points increased, however, the estimates more closely resembled those of the continuously run, 50-day column. Here, the TD<sub>Sulphur</sub> value of  $0.7 \pm 0.2$  years,

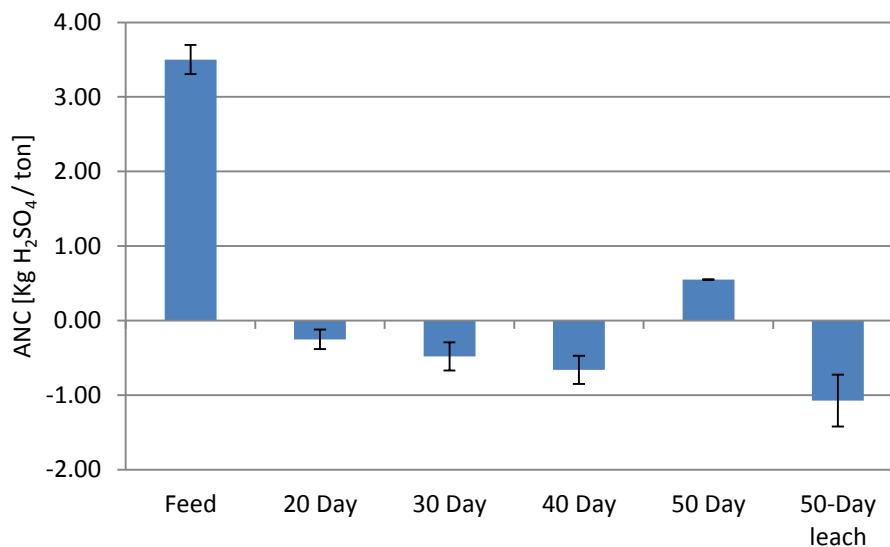
approximately half that of the in-bed sampled column at  $1.5 \pm 1.2$  years. The large variability in the in-bed sampled estimate however serves to negate any comparison between these two values.

**Table 6-4: TD<sub>Sulphur</sub> estimations using variable leaching data points for the in-bed and 50-day bioleach columns under continuous irrigation with acidic feed**

<b>Terminal</b> leaching duration [days]	50-day column TD <sub>Sulphur</sub> [years]	In-bed Sampling TD <sub>Sulphur</sub> [years]
10	0.8	3.3
20	0.9	1.4
30	0.6	0.9
40	0.5	0.5
50	0.5	0.5

As before, ARD characterization tests were performed on the solid samples collected using the in-bed sampling technique, together with the 50 day sample taken from both columns with and without in-bed sampling. As observed under previous acidic feed conditions (Section 3.7 & Section 4.2), there was a total reduction in the ANC of the in-bed sampled column after 20 days of leaching; with no statistical difference observed between the 20, 30 and 40 day samples collected by in-bed sampling.

Similar to the water-fed column experiments, differences were observed between the 50 day samples from columns with and without in-bed sampling. These differences may be due to the sampling technique itself which targets a specific region within the bioleach column and may cause separation of samples according to size fraction, as discussed previously. Alternatively, it may be attributed to the taking of a grab sample of approximately 300 g compared with a representative sample prepared from the 4 kg of material



**Figure 6-11: Static ANC results for the column experiments with and without in-bed samples under acidic feed conditions**

The decrease in sulphur content of the solid samples followed a predictable trend as suggested by the sulphur extraction curve in Figure 6-10. As before, comparison of the MPA values as calculated

from the LECO data of the recovered solids and as calculated from the extraction data was performed. The two MPA calculations showed good agreement, with the extraction MPA values lying within the error of those calculated from total sulphur analysis using LECO. Although a similar trend was observed however, the errors involved in the LECO analysis resulted in no overall statistical difference between the leached samples.

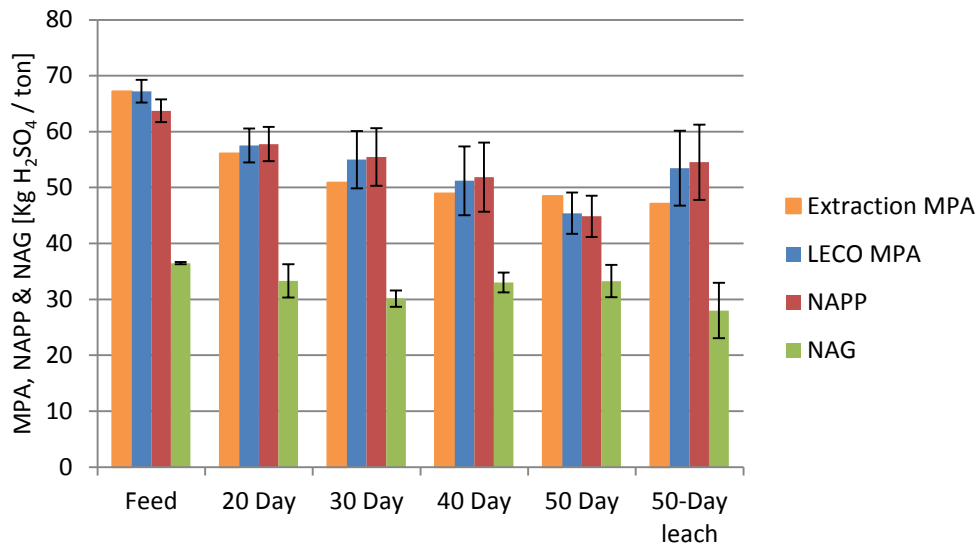


Figure 6-12: MPA, NAPP and NAG static prediction results for the column comparison under acid-fed conditions

Contrary to the results obtained under water-fed conditions, the leachate and solids data for the experiments conducted using an acidic feed were consistent, with the main difference being the total decrease in the ANC values. The errors involved with the LECO analysis, and hence the NAPP values, masked any difference between the leached samples, following the initial removal of ANC, as suggested by the sulphur extraction measured in the leachate.

### 6.3. Chapter Summary

The investigation into the use of the in-bed sampling technique in the replacement of the many, identical bioleach column reactors was performed under un-inoculated conditions with both water and acid feeds used. Both the leachate and solids data from these experiments were analysed and compared.

The leachate results for the water-fed column experiments displayed, with the exception of the redox potential profiles, no significant differences between the any of the measured properties. The differences in redox potential were attributed to the reduced iron solubility under the water-fed conditions, and the role of iron precipitation in changing the ferrous: ferric ratio within the leachate solution. Similarly, no significant variations were experienced in the leachate results for the acid-fed experiments. Although small differences were observed in the iron extraction profiles, there was no supporting variation in the other profiles to suggest this difference was as a consequence of the column operation, rather than small differences in the charge of ore used for each experiment.

Contrasting results were obtained in the analysis of the leachate and the solid samples for the water-fed experiment. While the leachate results showed little difference, large variations were observed in the ANC values for these experiments. Rather than suggesting differences in column operation however, the variations in solids data were explained by the errors incurred through particulate sampling using grab samples rather than a representative sampling technique.

Indeed, the sampling methodology used in the in-bed sampling technique can be defined as “non-probabilistic” sampling (Gy, 2004). This is due to the sampling technique targeting a specific region within the bioleach column experiment. The probability therefore of a solid sample of being selected which does not lie within this region is negligible. Thus, this method can never produce a representative sample (Gy, 2004) of the entire waste rock sample within the bioleach column. In contrast, the solids sampled for the 50-day sample constituted the remaining waste rock within the bioleach column.

In-bed sampling technique for column operation therefore, although appropriate for studies involving analysis of mineral surfaces associated with bioleaching and microbial population dynamics within bioleach columns (Chiume *et al.*, 2012 ), is not appropriate when sampling of the solid phases for mineral analysis is required.

In addition to the errors associated with the sampling of the solid phase, the errors in total sulphur analysis by LECO, as observed from the error bars presented in Figure 6-12, did not allow for differences between solid samples to be observed. Accurate conclusions therefore, in the face of the trends observed from the average values and aside from the errors associated with the lack of representative solids sampling, cannot be made concerning the reduction in sulphur grade due to leaching over these durations.

## 7. Experimental Review of ARD Characterization Methods

The discrepancies observed between the NAPP and NAG results in Sections 3.7. and Section 4.2. necessitated a further review of these ARD characterization methods. This included a review of the literature on ARD characterization tests together with experimental work performed to determine the validity of the findings of previous authors on the waste rock samples utilized in this study. Those experiments were used to determine the errors involved with sample preparation and the validity and reproducibility in the ANC, MPA and NAG experiments. Further, the use of the biokinetic test (Hesketh *et al.*, 2010) was investigated with discussion on its applicability and interpretation. For the experimental comparison presented in this chapter, waste rock from the bioleach experiment run under water-fed conditions at 32 °C (Section 3.3) was used. For the biokinetic tests, the waste rock samples leached with a continuous acidic feed at 32 °C (Section 4.1.) were used.

### 7.1. Sample preparation

Variables which influence the ARD characterization tests include the sampling regime and the particle size of the test samples (Lapakko, 2002). Due to this, and the small quantities required in each method, representative sampling is particularly important (Jambor *et al.*, 1997). Since the four kilograms of waste rock used in the bioleach column experiments had a maximum particle size of approximately 2 cm, representative sampling of the leached ore was required prior to ARD test-work.

To minimize sampling error, the complete 4 kg charge of waste rock from the bioleach columns experiments was milled at the end of the experiment and passed through a 200 µm sieve. A 10-pot, rotary riffler and an 8-way rotary sample divider were then utilized to separate between seven and ten grams representatively. A minimum of three repeats were used per ARD test.

To investigate whether these separate milled samples were representative, ANC tests were conducted on four separate samples of 7-10 g; with each sample having been separated representatively from the entire milled bioleach column sample. ANC tests were chosen due to their ease and low reported error. These results are compared in Figure 7-1.

To confirm whether the repeats of the ANC tests in Figure 7-1 were statistically identical, an ANOVA analysis was performed (Schaeffer & McClave, 1995). The analysis quantified the differences in the sample means and compared these to the experimental error associated with the method. An F-test (Schaeffer & McClave, 1995) was used to determine whether the differences between the means were significant. A 95 % confidence interval was used in the ANOVA analysis for the determination of significant deviation of the presented results. ANOVA analysis was performed on all results presented unless otherwise explicitly stated. Detailed ANOVA analysis is presented in Appendix 11.3.

The results of the ANC tests showed no significant difference between the waste rock samples, indicating the suitability of the method used in sample preparation from the 4 kg waste rock leach experiments.

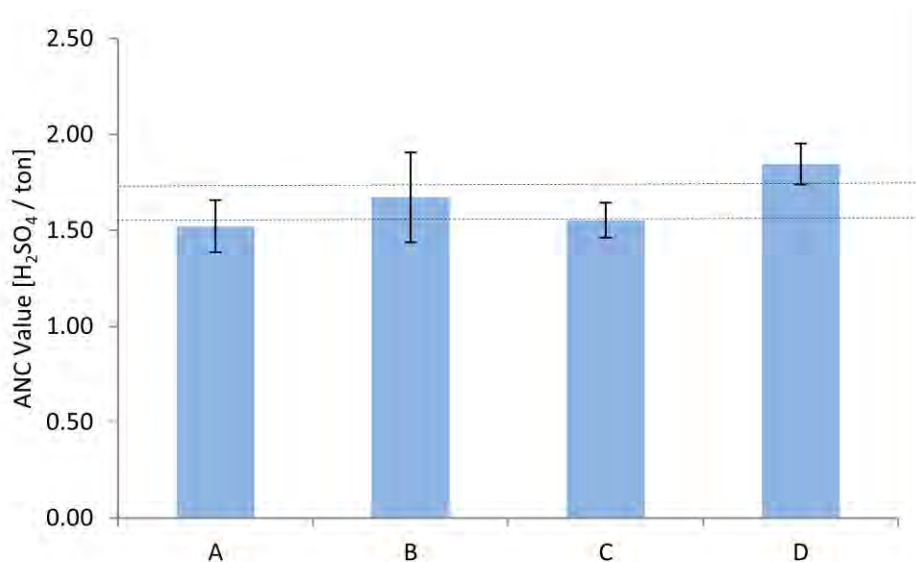


Figure 7-1: ANC repeats conducted on leached waste rock samples with water using the incremental Skousen method to show reproducibility in the separated samples. Dashed lines indicate the 95 % confidence interval on the mean value

## 7.2. Acid base accounting

Acid base accounting is widely used in the characterization of acid drainage potential of rock samples; incorporating both the neutralizing and acid producing potentials of the ore. ABA provides simple, rapid and cost effective screening for large sample quantities (Lawrence & Scheske, 1996) and, although not always sufficient for a quantitative ore analysis, is a useful method for preliminary ore classification (Paktunc, 1998).

The acid neutralizing potential (ANC) is calculated through reaction of an ore sample with a dilute acid, followed by a titration to quantify the amount of acid consumed. The maximum acid production (MPA) potential is calculated theoretically from the total sulphur content and the assumption that all sulphur is fully oxidized to sulphate according to stoichiometry. This difference is reported as a net acid producing potential value (NAPP) with units of kg H<sub>2</sub>SO<sub>4</sub> / ton of ore (Jambor and Blowes, 1998):

$$NAPP = MPA - ANC$$

Major criticism of the acid base accounting method is that it provides no information about the rates of acid production and neutralization (Jambor *et al.*, 2002; Stewart *et al.*, 2006). The calculation suppresses the magnitudes of the neutralizing capacity, leading to potential errors in classification. Further, the test does not account for the relative rates of acid generation and neutralization, thus limiting its predictive value. Many authors have also questioned whether the conditions under which the ANC and MPA values are measured provide an accurate representation of the net acid generating potential of sample in real world waste and tailings dumps (Jennings & Dollhopf, 1995; Lawrence & Scheske, 1996; Skousen *et al.*, 1997). The assumptions and shortcomings of the specific methods for ARD neutralization and acid production potentials are discussed below.

## 7.2.1. Acid Neutralizing Capacity

### 7.2.1.1. Introduction

Three different experimental methods for the determination of the ARD neutralization potential were presented in Section 2.6.1 and are outlined in Table 6-1. To further understand the differences in methodology and the effect these have on the neutralizing potential and the acid base accounting calculation, the literature regarding these methods was reviewed. Thereafter, each method was performed on an individual waste rock sample and the results compared..

**Table 7-1: Outline of the Sobek, Skousen and Incremental Skousen ANC prediction methods highlighting differences in volumes, boiling durations and H<sub>2</sub>O<sub>2</sub> addition procedures.**

ANC method	HCl addition	H <sub>2</sub> O addition	Boiling duration [min]	H <sub>2</sub> O <sub>2</sub> addition		H <sub>2</sub> O <sub>2</sub> procedure	Notes
				Volume [mL]	Molarity [M]		
Sobek	As per Fizz rating	20 mL	2 hours at 80 °C	N/A	N/A	N/A	Additional H <sub>2</sub> O added after boiling to a volume of 120 mL
Skousen		Up to 100 mL	5 min at 100 °C	5 mL	30 % (v/v)	Added at pH 4.5 & pH 7.0	15 min rest period & 5 min boil after H <sub>2</sub> O <sub>2</sub> addition
Incremental Skousen				10 drops		Added after each NaOH addition	15 min rest period after each H <sub>2</sub> O <sub>2</sub> addition

### 7.2.1.2. Review of ANC tests

Paktunc *et al.* (2001) showed that ANC reproducibility amongst different ANC methods was poor with the variation often a result of the outcome of the Fizz rating performed before each method (Lapakko, 2002). The fizz rating is a qualitative test which is subjective and open to personal bias (Evans & Skousen, 1995; Skousen *et al.*, 1997; Paktunc *et al.*, 2001).

Differences in magnitude of the ANC values were as a direct result of the differences in method. Weber *et al.* (2004) showed that the ANC value is highly dependent on the iron and aluminum carbonate and silicate components. Of particular importance is the extent of oxidation of the ferrous to ferric iron and the subsequent hydrolysis of this product. White *et al.* (1999), in experiments comparing the Sobek and Standard Skousen methods in the presence of siderite, found that there was insufficient time in the Sobek method for the complete hydrolysis of the ferric iron; resulting in a significant difference between the values from each method. Similar conclusions were drawn by Weber *et al.* (2004) when modifying the Sobek method through the addition of H<sub>2</sub>O<sub>2</sub>.

During modification of the Sobek method with the addition of H<sub>2</sub>O<sub>2</sub>, Weber *et al.* (2004a) found that the H<sub>2</sub>O<sub>2</sub> addition resulted in the oxidation of sulphide minerals within the ore sample leading to an under-estimation of the ANC. The authors suggested a drop-wise addition might limit this oxidation. Stewart *et al.* (2006) outlined a methodology which included the filtering of the ore sample, as per the Skousen method, and the drop-wise addition of the H<sub>2</sub>O<sub>2</sub> after each titration step to ensure ferrous oxidation.

### 7.2.1.3. Experimental investigation of ANC methods

The results for the Sobek, Skousen and Incremental Skousen methods for ANC quantification are presented in Figure 7-2, with each method presenting a statistically different ANC value for the same ore sample. For the purpose of this investigation, and since the waste rock sample was identical, the Fizz rating was the same for all methods employed; thus eliminating this major source of error. The presence of siderite in the qualitative mineralogy supplied by the mining house, suggested that differences between the Sobek and Skousen methods may have been a result of the presence of this mineral. The difference between the results of the two Skousen methods was due to the differences in H<sub>2</sub>O<sub>2</sub> addition. Incomplete digestion of the 5 ml H<sub>2</sub>O<sub>2</sub> aliquot could have affected the pH of the ANC liquor and ultimately the ANC value.

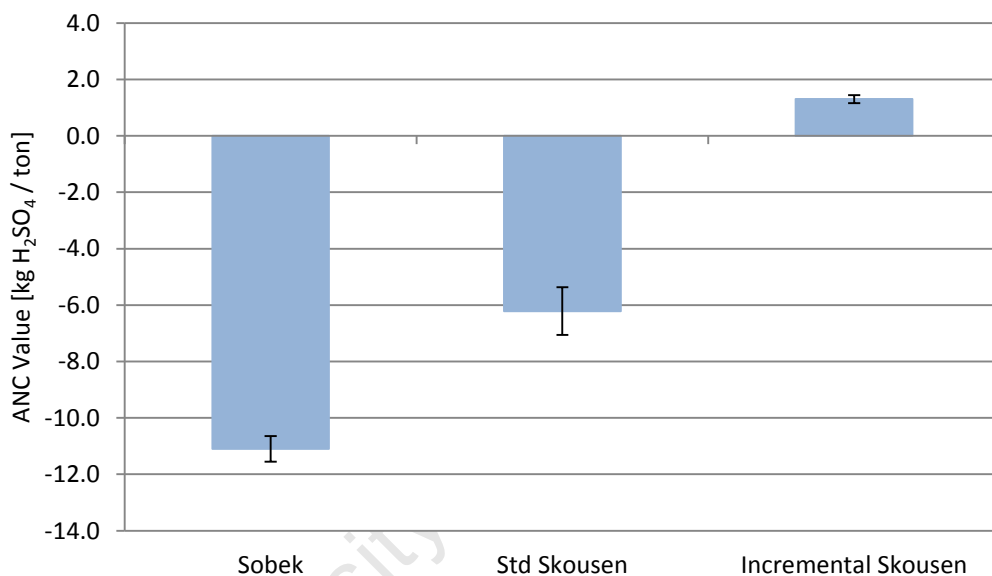


Figure 7-2: Comparison of the Sobek, Standard Skousen & Incremental Skousen ANC methods conducted on leached waste rock samples with water

Although the ANC methodology in this study was used for comparison between leaching of the same waste rock sample under different conditions, some limitations of the ANC static tests were relevant. For a quantitative analysis, especially for samples with ANC values less than 20 kg H<sub>2</sub>SO<sub>4</sub> / ton, the knowledge of a detailed mineralogy is prescribed since even small amounts of ferrous-containing minerals have been shown to have significant effects on ANC values (Jambor *et al.*, 2003).

The level of detection of the tests is not sufficient to provide an accurate, quantitative analysis but can provide a useful method for waste classification (Lawrence & Scheske, 1996). In particular, the ANC test does not account for the relative reactivity of the acid consuming minerals. The high temperatures experienced during the tests, improbable in a waste heap situation, also enhanced the rate of acid consumption for many minerals; especially true for the silicates in the ore sample (Lawrence & Scheske, 1996; Jambor *et al.*, 2002). These tests thus provide a maximum acid neutralizing capacity, provided ferrous iron oxidation is avoided.

The negative ANC values reported can be attributed to the reactivity of pyrite and other sulphides at high temperatures and may occur even if significant neutralizing potential was present within the sample (Weber *et al.*, 2003). These negative values cannot be ignored by assuming “0” for all negative values since this would mask the effect of this value in the NAPP (Weber *et al.*, 2004).

In conclusion, for the purpose of this study, the Incremental Skousen methodology was performed for the qualitative ANC analysis. This was selected due to the possible presence of siderite in the waste ore samples and the fact that the Incremental Skousen method showed good reproducibility between different samples and different laboratories (Kania, 1998). The addition of H<sub>2</sub>O<sub>2</sub> also had little effect on the ANC value in the absence of siderite (Skousen *et al.*, 1997).

### 7.2.2. Maximum potential acidity

The maximum potential acidity is the theoretical maximum amount of acid that can be produced from an ore sample should all the sulphur be oxidized. This calculated value is based on the assumption that all sulphur within the sample is present as pyrite and can potentially undergo complete oxidation to sulphate (Weber *et al.*, 2005). The MPA value is calculated using the following equation:

$$MPA = 30.6 * S_{Total}$$

The total sulphur is in the form of a percentage value; giving the MPA value units of kg H<sub>2</sub>SO<sub>4</sub> / ton of ore.

The accuracy of the MPA value is thus dependent on the measurement of the total sulphur content. Problems associated with the use of total sulphur and the assumptions involved have been discussed extensively (Jennings & Dollhopf, 1995; Paktunc, 1999; White *et al.*, 1999; IWRI & EG, 2002). Hedin and Erickson (1988) found that leachate results were more strongly related to the total sulphur content of a sample than the pyritic sulphur. Brady & Smith (1990) found that total sulphur quantification is more precise with less interference than quantification methods for different forms of sulphur. As an indication of the obtainable range of total sulphur percentages, four different quantification methods were applied to the same sample: ICP-MS, LECO, XRF and XRD. The total sulphur percentages determined are compared in Figure 7-3.

For ICP analysis, digestion of the samples was performed through sequential reaction with concentrated hydrochloric, hydrofluoric and nitric acids in the Analytical Laboratory at the Department of Chemical Engineering, University of Cape Town. Although ICP analysis has been reported as the most accurate method for sulphur determination in liquor, it is very sensitive to the calibration of the machines used (Czerewko *et al.*, 2003). In addition, inaccuracies may occur as a result of the resistance of some minerals to digestion (Crock *et al.*, 1999).

High temperature combustion (LECO) analysis was conducted as described in Section 2.5.2. Although chlorine and fluorine gas interferes with the SO<sub>2</sub> measurements (Lapakko, 2002), the waste rock samples lacked significant quantities of either element. Partial combustion of galena and chalcopyrite in the waste rock samples may have led to an underestimation of the total sulphur

(Lapakko, 2002). On comparison with other sulphur determining techniques, Czerewko *et al.* (2003) reported good agreement and suggested LECO as a method of choice when dealing with many samples.

Mineral analysis provides a semi-quantitative technique for the determination of total sulphur content which is less accurate than the chemical techniques (Czerewko *et al.* 2003). These techniques are also more time and effort consuming and should only be conducted when small sample numbers are involved (Lapakko, 2002). For comparison, XRF and XRD analysis were performed.

XRF analysis involves irradiation of samples with the resultant radio-activities measured by gamma-ray spectroscopy, leading to quantification of elements within the sample. This form of analysis is qualitative since not all elements are identified and is highly dependent on the calibration standards used (Lapakko, 2002; Czerewko *et al.* 2003).

XRD analysis involves quantification of minerals via x-ray diffraction. Total sulphur content was calculated directly from the mineralogy obtained using this technique. The large discrepancy between the XRD calculation and the other methods is explained by the limit of detection of approximately 1.5% (Lapakko, 2002) which forms the major limitation to this method of mineral quantification. Since the samples used are of a low grade, the copper sulphides, in which form the majority of sulphur lies, are present in low concentrations with the majority below this detection limit. Poor crystallinity of the minerals in samples also provides a source of error (Czerewko *et al.*, 2003).

The quantification of the total sulphur of the waste rock sample after leaching with water obtained using the tests presented above is compared in Figure 7-3. For comparison, the total sulphur calculated from the bulk mineralogy was 2.6%. Digestion with ICP-MS and XRD resulted in substantial underestimation of the sulphur content. LECO analysis and normalized XRF resulted in sulphur contents consistent with the bulk mineralogy. For the experiments completed in this project, LECO analysis was used for the determination of the total sulphur content, due to its accuracy, good reproducibility and the ease of handling the high numbers of samples analyzed (Czerewko *et al.* 2003).

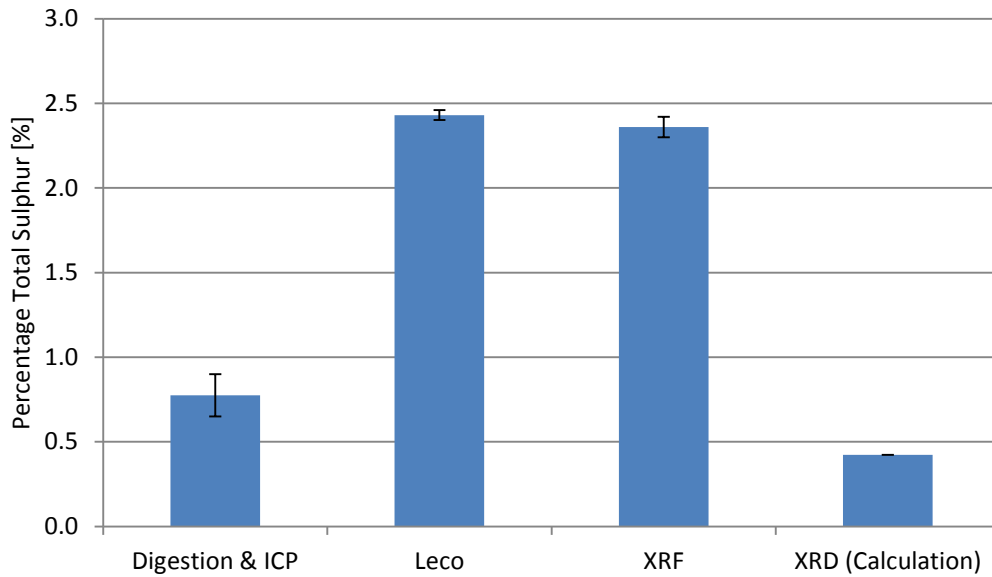


Figure 7-3: Comparison of LECO, ICP-MS, XRF and XRD methods for total sulphur quantification of a leached waste rock sample with water

### 7.3. Net acid generation experiments

The Net Acid Generation (NAG) test was developed in response to a need for a rapid field test for ARD characterization (Coastech Research Inc., 1989). In particular, the need for analytical sulphur analysis necessary in the determination of the NAPP value was overcome (Lappako & Lawrence, 1993). Experiments conducted by Miller *et al.* (1991) however, found that NAG results often yielded much lower values than the corresponding NAPP tests. These authors reported NAG values at approximately two-thirds of the corresponding NAPP (Lappako & Lawrence, 1993). Figure 7-4 shows the NAPP and NAG values obtained from tests conducted on waste rock leached with water, and shows a similar NAG-NAPP ratio ( $0.64 \pm 0.05$ ) to that reported by Miller *et al.* (1991).

An explanation of the reported inconsistencies was the incomplete oxidation of the sulphide minerals (Lappako & Lawrence, 1993). In fact, Mizra *et al.* (1992) tested the use of hydrogen peroxide to oxidize sulphide minerals in coal, coal-pyrite and ore-pyrite samples. These authors reported incomplete oxidation of the sulphide minerals. Modification of the NAG tests for use on coal wastes (O'Shay *et al.*, 1990) demonstrated good sulphide oxidation (97-102 %). However results from a similarly modified method used on mine waste samples (Lappako & Lawrence, 1993) showed some discrepancies between the NAPP and NAG results. These authors suggested that the accuracy was linked to the elevated neutralizing potential values due to the incomplete oxidation of ferrous iron released from certain minerals during hydrogen peroxide oxidation. This discrepancy was elevated in samples with a high ANC: MPA ratio (Lappako & Lawrence, 1993).

The qualitative assessment of waste samples provided by the NAG tests is still useful in waste characterisation, especially in field conditions where quantitative, analytical assessment of the total sulphur content of the samples is difficult (Lappako & Lawrence, 1993). Miller *et al.* (1991) suggested that measurement of the pH of the solution after hydrogen peroxide decomposition was sufficient to provide sample classification as potentially acid forming or not. This idea was used in the

formation of the waste characterisation using the ARD Classification Plot (Miller *et al.*, 1997), where samples are classified by the NAPP value and the solution pH from the NAG test. Further ARD classification in this project was conducted using Characterisation Plots to track changes in ARD potential; pertaining directly to the removal of sulphur from the waste rock samples.

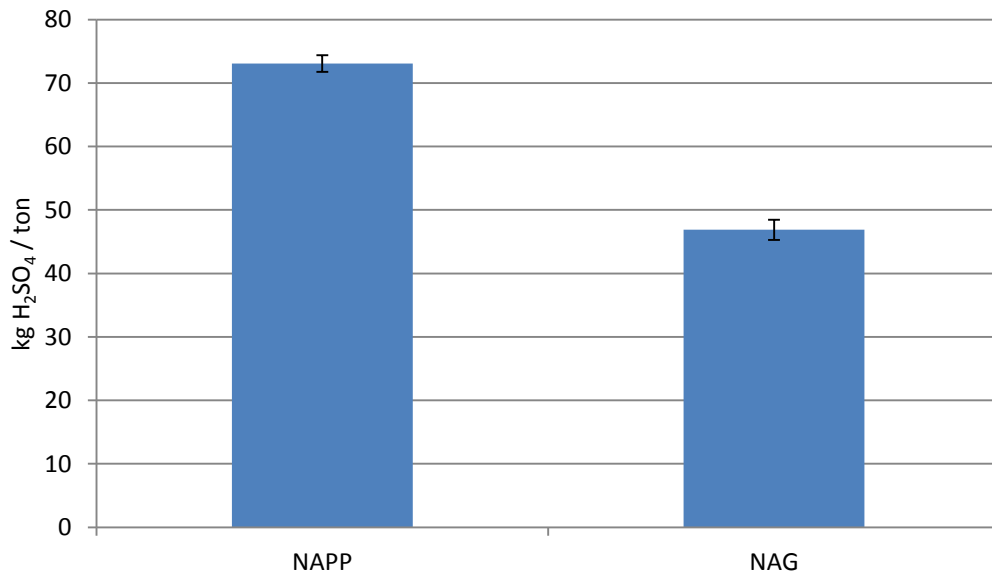


Figure 7-4: Comparison of the NAPP and NAG methods for net acid production quantification of a leached waste rock sample with water

For further work in this study, no quantitative comparison between the NAG and NAPP values was performed. Characterisation plots, however, were utilized to track changes in ARD potential; pertaining to the removal of sulphur from the waste rock.

## 7.4. Biokinetic accelerated weathering flask tests

### 7.4.1. Introduction

Static ARD characterization tests give “worse case scenarios” for the generation of ARD. Further, they provide no information on the of ARD generation (Hesketh *et al.*, 2010; Villeneuve *et al.*, 2009). To counter this, kinetic tests can be performed which attempt to mimic the natural ARD generation environments. The most common kinetic test experiments are humidity cells and column leach tests (Sapsford *et al.*, 2009). Whereas static tests only allow for the oxidation of samples using chemicals, kinetic and column leach experiments allow for the investigation of mitigating materials, for example limestone, varying conditions such as temperature or microbial inoculation on ARD generation (US EPA, 1994). The necessary experimental duration for ARD characterization, especially with investigation including micro-organisms, remains a major disadvantage of these kinetic tests (Hesketh *et al.*, 2010).

To address this major limitation, Hesketh *et al.* (2010) developed the biokinetic accelerated weathering tests to gain an understanding of the potential rate of ARD generation on a reduced time frame. Milled waste rock samples underwent microbial bioleaching in suspended culture shake flasks for 90 days with the pH, redox potential and iron measured to illustrate the relative rates of

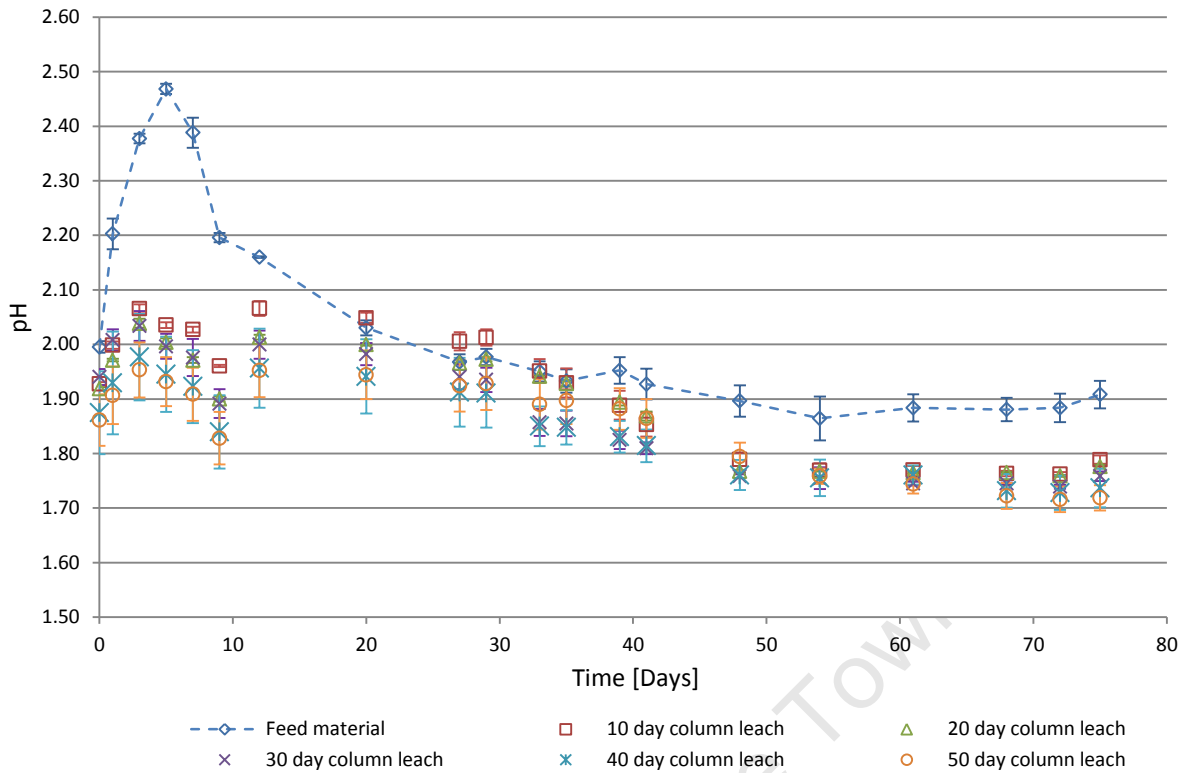
acidification in order to provide additional information for enhanced ARD prediction. Of primary interest for ARD characterization are the rates of acidification and release of soluble ions from the sulphide fraction.

To assess the potential of the biokinetic test for this application, it was conducted using two different methodologies. These are described in detail in Section 2.6.2. In one set of experiments, the pH of each flask was downward-controlled to a pH of 2.0 daily by the addition of  $H_2SO_4$ , while the pH was not controlled in the other experimental setup. To interrogate the information gained from the biokinetic tests, the post-leach waste rock samples described in Section 2.1.1 (Waste rock sample B, Appendix 11.1) were used in conjunction with the feed sample. The biokinetic flask tests were run in triplicate over 90 days and the pH, redox potential and soluble iron species were monitored.

#### 7.4.2. Non-pH Controlled biokinetic tests

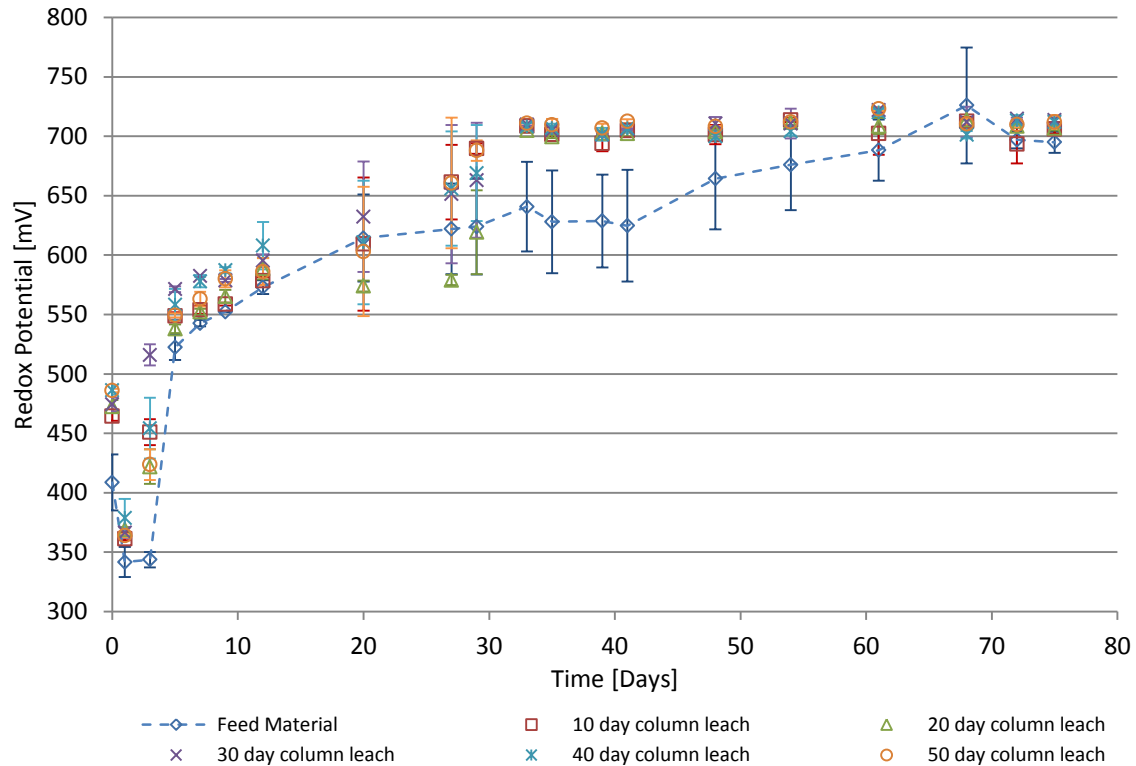
Biokinetic flask experiments were conducted over an 90 day period with the changes in pH, redox potential and iron concentration recorded daily for the initial ten days. Thereafter test samples were collected twice a week until day 40, and once a week until the end of the tests. The pH profiles for the different flask experiments are presented in Figure 7-5.

The initial increase in pH for the feed sample was indicative of the acid reaction with the acid neutralizing fraction of the waste rock; an indication of ANC. Flask experiments containing leached samples lacked this increase, highlighting the removal of the neutralizing capacity from the samples during bioleaching. This was in agreement with the changes in ANC observed in Section 4.2. The subsequent rapid decrease in pH for the feed sample illustrated acid generation within this flask and was in contrast to the other flask experiments. Here however, the small decrease in pH over the 30-50 day period was balanced by the initial increase. This difference showed the removal of the acid soluble and acid forming minerals during the column bioleaching stage. For leached samples, the decrease in pH, and thus acid generation, occurred after approximately 20 days, possibly due to the microbially-mediated, ferric oxidation of the mineral sulphides. The pHs stabilized after approximately 60 days, with the feed and leached samples at pH 1.9 and pH 1.7 respectively.



**Figure 7-5: pH profiles for the non-pH controlled Biokinetic flask experiments for waste rock samples leached with acidic feed for differing durations.**

The redox potential of the leachate solution (Figure 6-6) was used as an indicator of microbial activity, with the rapidly increasing profiles to a value of approximately 550 mV indicating an oxidative environment created by the active microbial culture, resulting in the dominance of ferric iron after approximately 10 days. A further increase in redox potential to approximately 700 mV was observed after approximately 30 days, coinciding with decrease in pH to a value below pH 1.9. The profile for the feed sample showed a significant difference from the leached samples after 30 days, with a final redox potential reached after 50 days, the duration necessary for the feed sample to reach pH 1.9.



**Figure 7-6: Redox potential profiles for non-controlled pH Biokinetic flasks for waste rock samples leached with acidic solutions for differing durations**

For the biokinetic assay, the ferrous and total iron concentrations are presented as cumulative concentrations; possible since the volume of each flask experiment was kept approximately constant through the addition of distilled water on every sample day to replace evaporative losses. The cumulative ferrous and total iron concentration profiles are given in Figure 6-7 and Figure 6-8 respectively.

The cumulative total iron profiles for the leached samples were similar over the course of the biokinetic tests. The ferrous iron concentration remained below 25 mg/L throughout the test, hence similar soluble ferric iron concentrations resulted in each of the leached waste rock samples. The feed sample however deviated significantly from the leached samples, with low total iron concentration (< 200 mg/L) observed between days 10 and 40. The ferrous iron concentration profiles remained in the range 5 – 10 mg/L, indicating a decreased amount of soluble ferric iron in the feed sample as compared to the leached samples. Similar concentrations (250 – 350 mg/L total iron and ferric iron), however, were observed in all biokinetic flasks by the end of the experiment. This suggests that the presence of the neutralizing components within the feed sample significantly affected the solubilisation of iron until such time as the pH of the solution fell below pH 2.0 (day 25 for the feed sample). This is expected to result from precipitation of the ferric iron above this pH value (Deveci *et al.*, 2004).

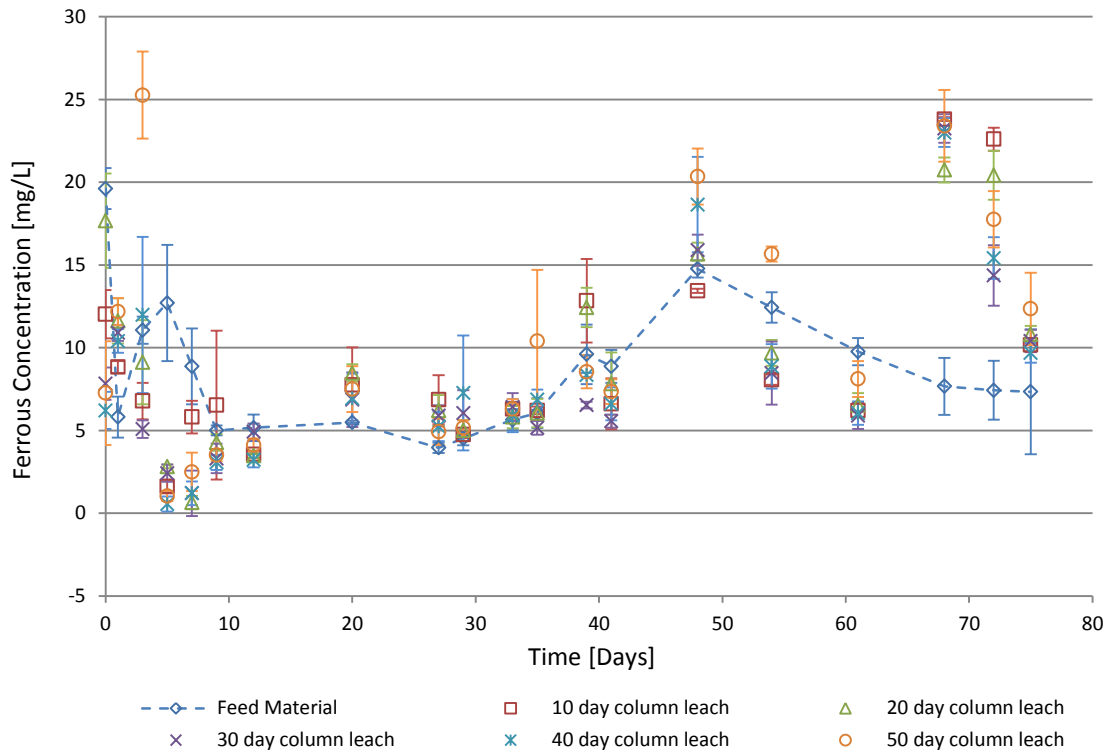


Figure 7-7: Cumulative ferrous concentration profiles for the pH non-controlled Biokinetic flask experiments for waste rock samples leached with acidic solutions for differing durations

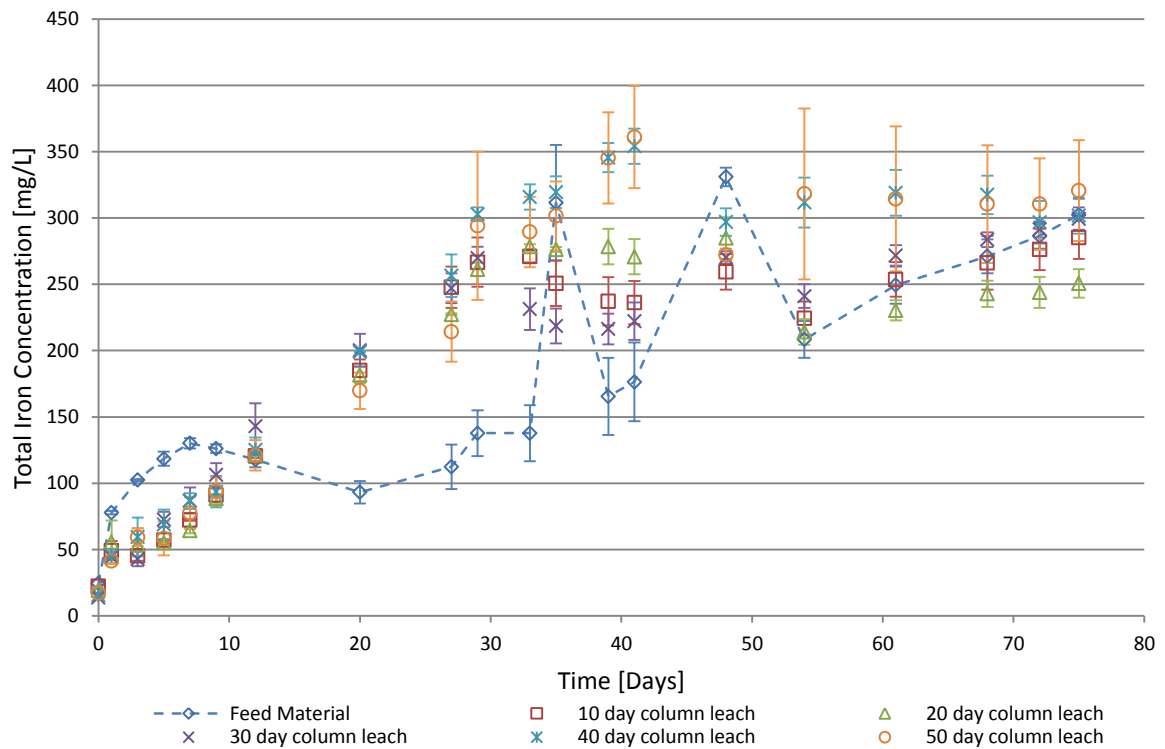


Figure 7-8: Cumulative total iron concentrations for the pH non-controlled Biokinetic experiments using waste rock samples leached with acidic solutions for differing durations

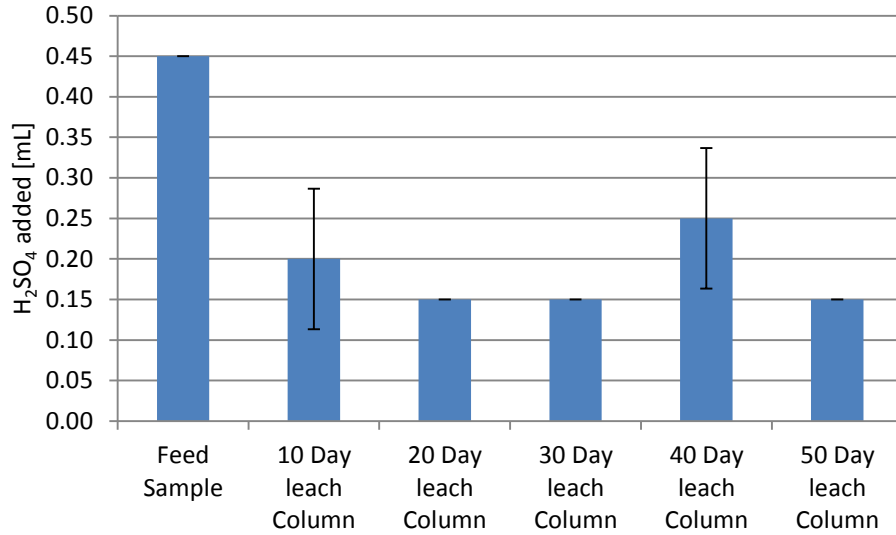
The differences observed between the feed and leached waste rock biokinetic tests were due to the initial increase in pH governed by the ANC of the waste rock sample. This is consistent with the differences observed in static ANC values in Section 4.4 where a significant decrease in ANC occurred after 10 days of leaching. No significant difference was observed between the leached samples. From the biokinetic tests, the ANC of the waste rock is governed by acid-soluble minerals which were rapidly leached in the initial stages of experimentation.

Due to the reaction of the acidity with this ANC, the pH of the feed increased, resulting in a longer lag period necessary for similar redox potentials. The iron concentration profile however, although lagging initially, reached a similar final concentration as the other flask experiments. This was due to a greater availability of iron minerals in the feed as this sample had not undergone previous column leaching.

#### **7.4.3. pH Controlled biokinetic tests**

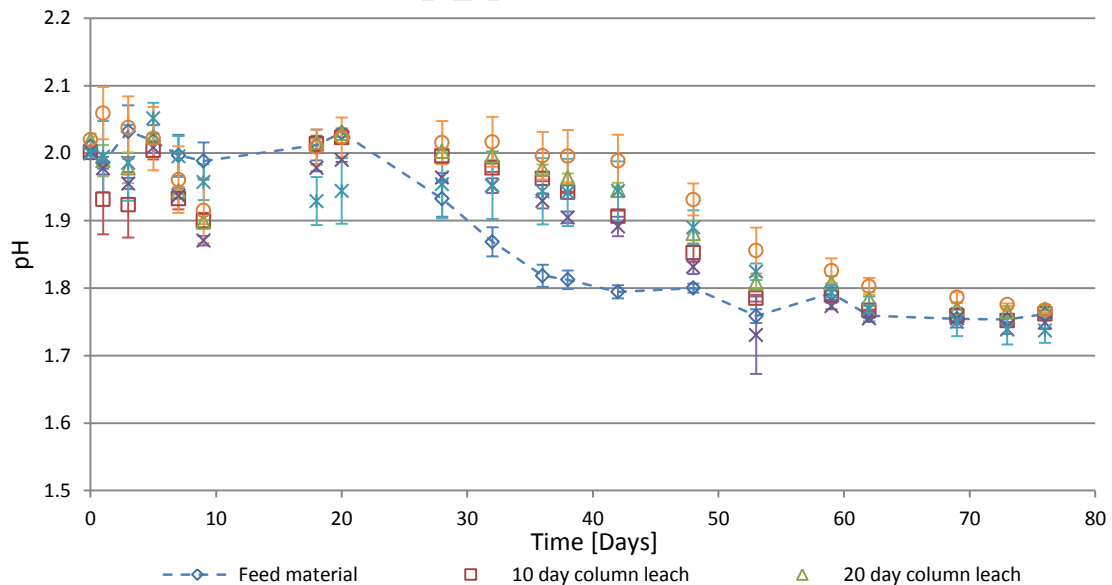
As the ANC of the sample was found to have a large effect on the bioleaching progression in the biokinetic tests, triplicate repeat flasks were run in which the pH was adjusted downwards to pH 2.0 at daily intervals. This pH control countered the rise in pH due to the reaction of the ANC and thus allowed the leaching to proceed under acidic conditions. Tests were performed identically to the tests without pH control with the exception of the drop-wise addition of 96-98 %  $\text{H}_2\text{SO}_4$  using a burette. The pH controlled tests were conducted on both the feed and leached waste rock samples to enable comparison of the changes observed between these flask sets and the data collected under non-controlled pH conditions.

The volumes of 96-98 %  $\text{H}_2\text{SO}_4$  necessary for the control of the pH are presented in Figure 7-9. The effect of column leaching on the ANC of the waste rock sample is clear, with an approximate 45 % reduction in the 10-day leached sample. No significant difference was observed between the amounts of acid added to the biokinetic tests performed on the leached samples taken after 10 to 50 days of bioleaching. This corresponds with the static ANC values in Section 4.4 which shows a decrease in ANC with leaching, but no significant difference between the duration of exposure to leaching.



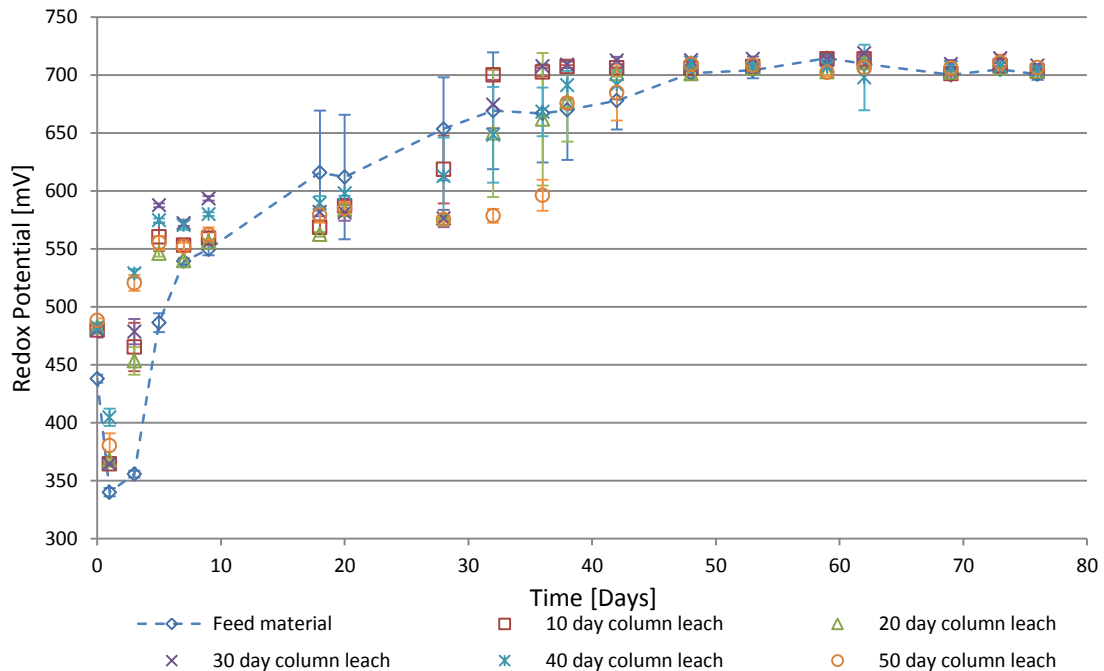
**Figure 7-9: Volumes of 96-98 % H<sub>2</sub>SO<sub>4</sub> necessary for the adjustment of the pH to pH 2.0 for the pH controlled biokinetic tests**

Figure 7-10 shows the pH profiles of the pH controlled tests, with the earlier observed rise in pH of the feed experiment now suppressed by the acid addition. No acid addition was required after day 5 for the leached samples and day 10 for the feed sample. After day 30, the pH in all the flasks decreased due to acid generation. The rate of pH decrease was faster for the biokinetic test on the feed sample than the leached samples. This faster decrease was due to the larger quantity of easy accessible sulphide minerals present in the feed sample and thus larger acid formation over the same time period. These minerals were removed from the leached samples during the bioleach column experiments.



**Figure 7-10: pH profile for the pH controlled, Biokinetic experiments using waste rock samples leached with acidic solutions for differing durations**

The suppression of the ANC through the addition of the H<sub>2</sub>SO<sub>4</sub> resulted in no lag in microbial activity in contrast to the high pH flasks shown in Figure 7-6. This comparatively enhanced microbial activity and produced a similar oxidative environment in the feed test and tests on the leached waste rock samples, resulting in similar redox potential profiles shown in Figure 7-11, with the exception of a small delay in the initial increase in the redox potential of the feed sample (± 3 days).



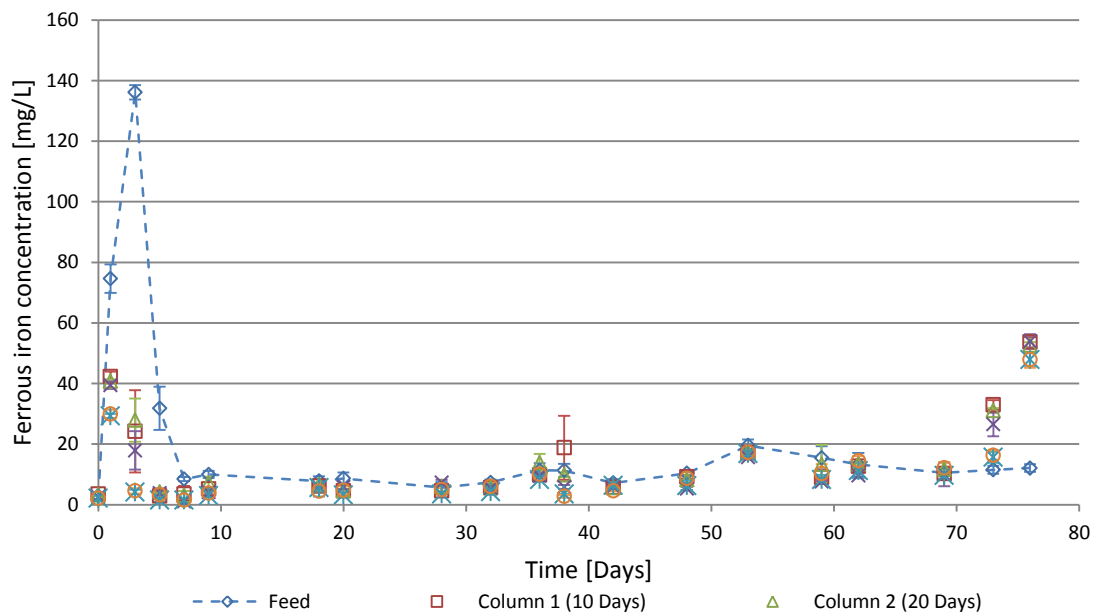
**Figure 7-11: Redox potential profiles under pH-controlled conditions using waste rock samples leached with acidic solutions for differing durations**

In contrast to the ferrous iron profiles for the biokinetic tests of the leached samples, tests on the feed sample showed an initial rapid increase in ferrous concentration due to the rapid leaching of iron-bearing minerals within the sample. The absence of these minerals in the leached samples was a result of their prior bioleaching.

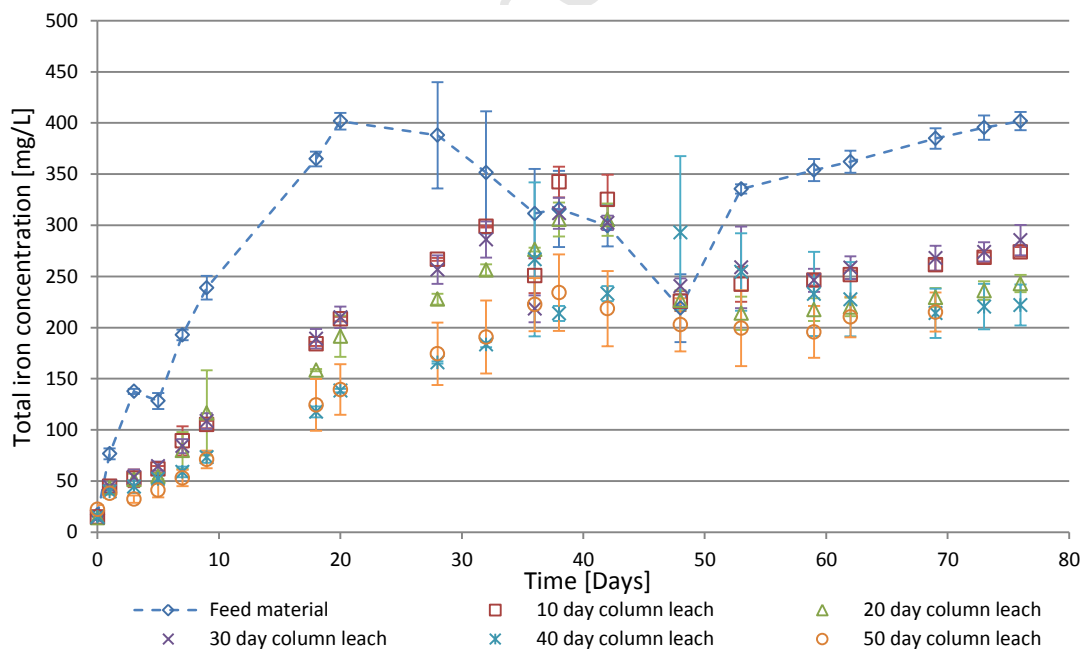
The total iron profile of the feed material showed a rapid increase, with the difference in magnitudes between the ferrous and total iron concentration due to the activity of the bioleaching microorganisms present in the test flasks. The resultant higher ferric concentrations were responsible for the increased iron leaching rate observed under pH-controlled conditions. The noticeable change in total iron concentration after approximately 30 days suggested iron precipitation within the biokinetic flasks. The rapid decrease in pH observed at the same time supports ferric iron precipitation as protons are produced during ferric iron precipitation. The large error bars recorded from the triplicate feed flask tests however indicated the differing extent of iron precipitation within the flask replicates.

Biokinetic tests performed on leached samples for longer durations (40-50 days) exhibited a slower increase in total iron concentrations as compared to those leached for 10-20 day period. In addition, the rapid initial increases in total iron of the feed sample and the noticeable difference in

concentrations between feed and leached samples, suggested that iron-bearing minerals were a major constituent of the ANC components present in the waste ore samples.



**Figure 7-12: Cumulative ferrous concentration profiles for Biokinetic experiments under pH-controlled conditions using waste rock samples leached with acidic solutions for differing durations**



**Figure 7-13: Cumulative total iron concentrations under pH-controlled conditions using waste rock samples leached with acidic solution for differing durations**

#### 7.4.4. Findings from biokinetic tests

The differences observed between the feed and leached samples for both the pH controlled and non-controlled biokinetic tests were governed by the changes in mineralogy as a result of prior bioleaching. These changes linked to those observed in the static ANC data presented in Section 4.4. The differences in iron concentrations between the feed and leached tests highlighted the removal of iron during column bioleaching. No significant difference was observed between the total iron concentrations of the leached sample tests. This was in agreement with the sulphur data (Section 4.4) due to the majority of iron-bearing minerals present in the waste rock being mineral sulphides

The differences observed in the feed biokinetic tests under pH controlled and non-controlled conditions serves to highlight the role of the ANC in the initial establishment of a microbially mediated ARD generating waste rock dump.

Upon comparison of the static and biokinetic tests, Hesketh *et al.* (2010) observed that the biokinetic tests resulted in similar final pH values as the static NAG tests and that the ANC calculated from the necessary amounts of  $H_2SO_4$  added to the biokinetic tests corresponded to the static ANC values. In addition, the biokinetic tests supported the characterisation of the samples as either acid-forming or non-acid forming. In the investigation using waste rock samples presented, only the classification of the feed and leached samples from the static and biokinetic tests were in agreement.

#### 7.5. Summary of ARD characterization methods

The differences in the NAPP and NAG results presented in Sections 3.7, 4.2 and 5.2 necessitated a re-examination of the ARD characterization methodology. This was completed through the use of experimental examples. Although large errors have been attributed to and reported as a result of incorrect sample preparation techniques, the waste rock splitting methodology utilized in this study was adequate to ensure statistically significant ANC repeats, as demonstrated by use of ANOVA analysis.

Inaccuracies in acid-base accounting include errors associated with both the ANC experiments and sulphur quantification for MPA calculation. Three methods for the experimental determination of the ANC of the waste rock samples were tested (Sobek, Skousen and Incremental Skousen) and compared. Explanations suggested for the observed differences included interference of siderite and the potential for over-estimation by  $H_2O_2$ . Given the short-comings of the methods presented and the uncertainties associated with the mineralogy, especially concerning the presence of siderite, it was decided to continue using the incremental Skousen as the preferred method for ANC determination due to the possible presence of siderite in the waste rock and the good reproducibility shown between samples.

Errors associated with the NAPP calculation centre around the inaccuracy associated with total sulphur determination. Different methods for this were investigated and the limitations and advantages with each method discussed. Due to the large number of samples and the good reproducibility of the LECO analysis technique, it was decided to continue to use this method for the determination of the total sulphur content of the waste rock samples.

The results of the NAG - NAPP comparison were consistent with previous findings by Miller *et al.* (1991), with the NAG value approximately two-thirds that of the NAPP. These authors suggested that incomplete sulphide oxidation was responsible for this difference. It was thus decided that, due to these two values not being numerically comparable, a combination of the NAPP and NAG<sub>pH</sub> data would be used to graphically characterize the ARD potentials, using the approach by Stewart *et al.* (2006).

The use of biokinetic flask tests to gain information concerning the rates of ARD generation was investigated according to Hesketh *et al.* (2010). Test work included pH-controlled and non-controlled flasks with the recording of the pH, redox potential and iron concentration curves over the time.

The trends in ANC could be determined from the biokinetic tests as an increase in the pH of the flask solution. This increase and its effect on the optimum environment for the microbial populations utilized in the experiments resulted in a retardation of the microbial activity. This was most accentuated in the feed sample over the leached samples containing lower ANC values. The control of the test flask below pH 2.0 influenced the rate of iron leaching from the samples. From the volumes of H<sub>2</sub>SO<sub>4</sub> necessary for pH correction, no significant difference between the ANC levels for different leaching durations was observed, consistent with the trends in ANC values as reported by the static tests.

In contrast to Hesketh *et al.*, (2010), there was no correlation between the static ANC values and the amount of H<sub>2</sub>SO<sub>4</sub> needed to suppress the rise in initial pH. Also, no similarity was observed between the NAG pH values and the final biokinetic pHs. Classification of the samples as acid forming from the biokinetic tests did however correlate with the static results.

## **8. The addition of pyrite concentrate for enhanced ARD generation rate**

Following the refinement of the terminal duration estimation method in Section 4.3., the assessment of reproducibility or column leaching experiments in Section 5.2 and 5.3 and the review of the ARD prediction methods in Chapter 6, the effect of pyrite addition as a source of easily accessible iron and sulphur lixiviate, was investigated using a different waste rock sample (Waste rock sample C, Appendix 11.1).

Bioleach column experiments were conducted over different durations with solid sampling occurring as outlined in Section 4.1. Multiple column experiments were conducted in a similar manner to those presented in Sections 4.1 and 4.2 to ascertain the level of reproducibility between column experiments. Copper and sulphur extraction were measured as a proxy for ARD generation due to all the copper within the ore being present as copper-sulphide minerals. In addition to the pH, redox potential and iron concentration measurements, sulphur extraction was determined through the measurement of the sulphate concentration of the leachate solution and is also presented.

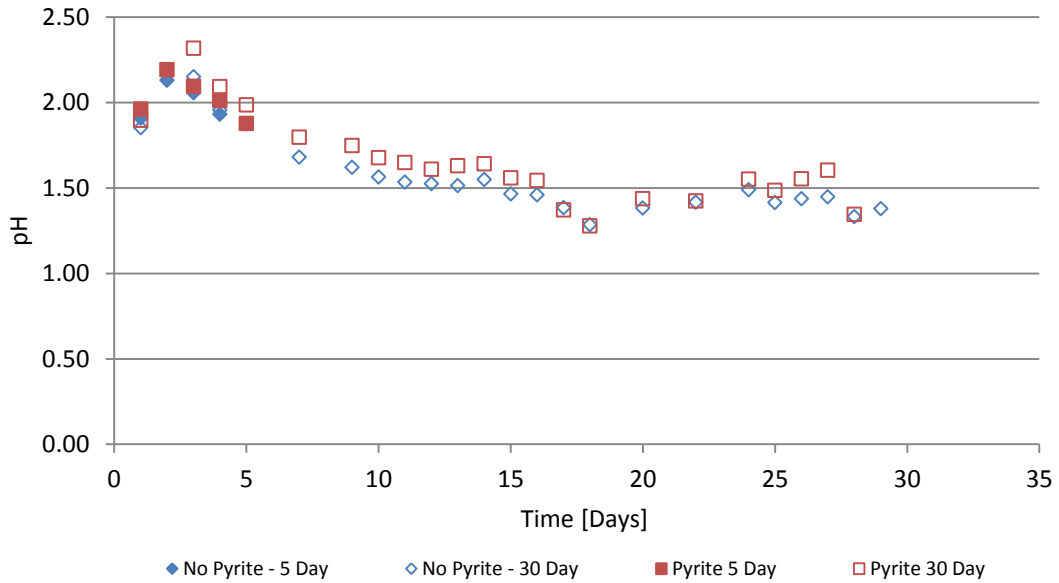
ARD characterization tests were conducted using the methodologies outlined in Section 2.7. and reviewed in Section 6.2. In addition to the static ABA tests, biokinetic tests were performed to investigate the effect of the pyrite addition on the sulphide content and potential for ARD generation from post leached samples. Changes in ARD potential were also tracked using characterisation plots.

### **8.1. Comparison between bioleach column experiments with and without pyrite addition**

Using column bioleaching, the effect of the addition of a 1% (w/w) pyrite concentrate to the low grade waste rock on the rate of ARD generation was investigated. To illustrate the effect on Ore type C, experiments with added pyrite were compared with columns with no pyrite supplementation over different time durations. As the most rapid change in ARD static tests, especially ANC, had been previously experienced over a short time period, column experiments were run over 5 days, with solids analysis thereafter. In addition, since an established oxidizing environment for mineral sulphide bioleaching had been established previously after approximately one month, further column experiments were conducted for a period of 30 days. The leachate results of these experiments are presented on a single set of axis to enable comparison between similar experimental duration and to give an indication of continuity over time of the bioleach experiments under similar conditions.

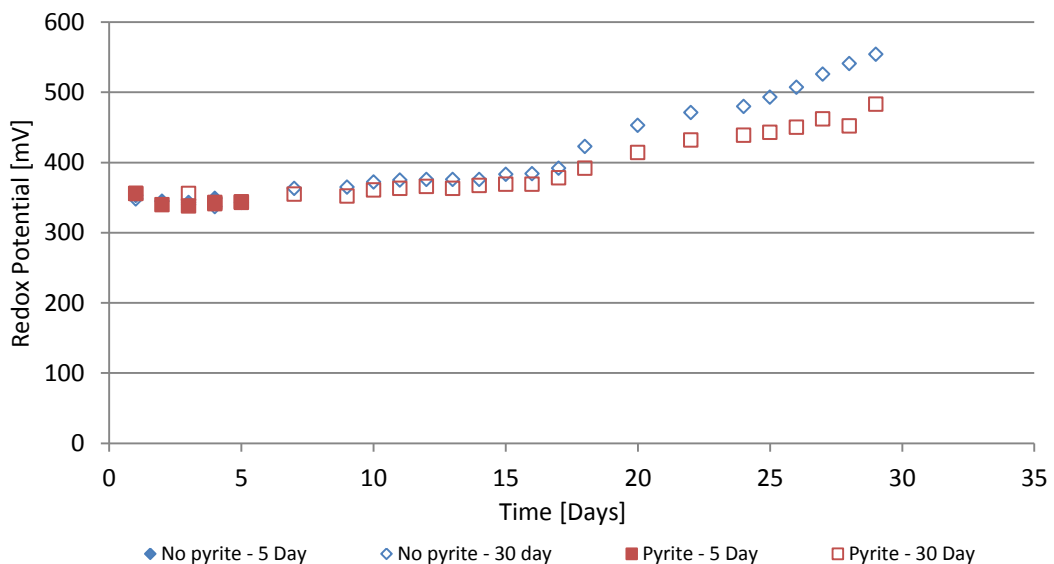
#### **8.1.1. Liquid phase analysis**

The pH profiles for the experiments are presented in Figure 8-1, with both columns with and without pyrite showing similar trends. This suggested that the pH of the leach liquor was dependent more on the pH of the feed solution than on the ARD generation from the bioleach column experiments over the 30-day period investigated. This was in agreement with the findings from Section 3.3.



**Figure 8-1: pH profile for the 5- and 30-day column experiments comparing the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions**

The redox potential profiles are presented in Figure 7-2. Differences were observed in the presence and absence of pyrite after 17 days. The redox potential in the absence of pyrite exceeded that in its presence between days 17 and 30. This may result for two reasons; either the microbial population in the absence of additional pyrite was more active over the same period, or the presence of pyrite resulted in the solubilisation of more iron, giving a higher total soluble iron concentrations while the ferrous oxidation rate remained similar. Through this, the ratio of ferrous to ferric iron will increase. This difference was in contrast to the redox potential profiles presented in Section 3.5 which showed no difference upon pyrite supplementation.



**Figure 8-2: Redox potential profiles for bioleach columns investigating the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions**

The pyrite-supplemented columns experienced elevated ferrous and total iron concentrations after 10 days of column leaching. Since iron release due to acid leaching occurred in both systems over the initial 10 days, no significant difference was observed over this period. Thereafter however, the elevated ferrous iron concentrations suggested pyrite dissolution, which in turn, since pyrite is an acid insoluble mineral, suggests elevated levels of ferric iron within the bioleach column. The elevated iron concentration in the pyrite supplemented, 30-day column experiments occurred in the absence of a rise in the redox potential, suggested that the microbial population present within the bioleach columns was unable to oxidize all the ferrous released from pyrite oxidation. The release of the iron indicated an increase in the microbial activity, due to the increased levels of ferric iron necessary for the pyrite oxidation.

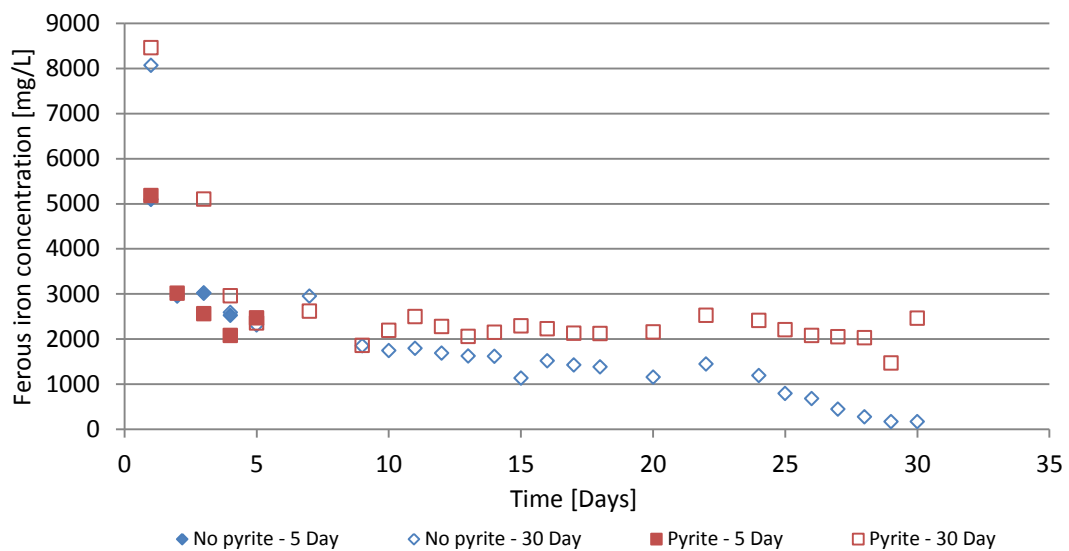


Figure 8-3: Ferrous iron concentration profiles for bioleach column experiments investigating the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions

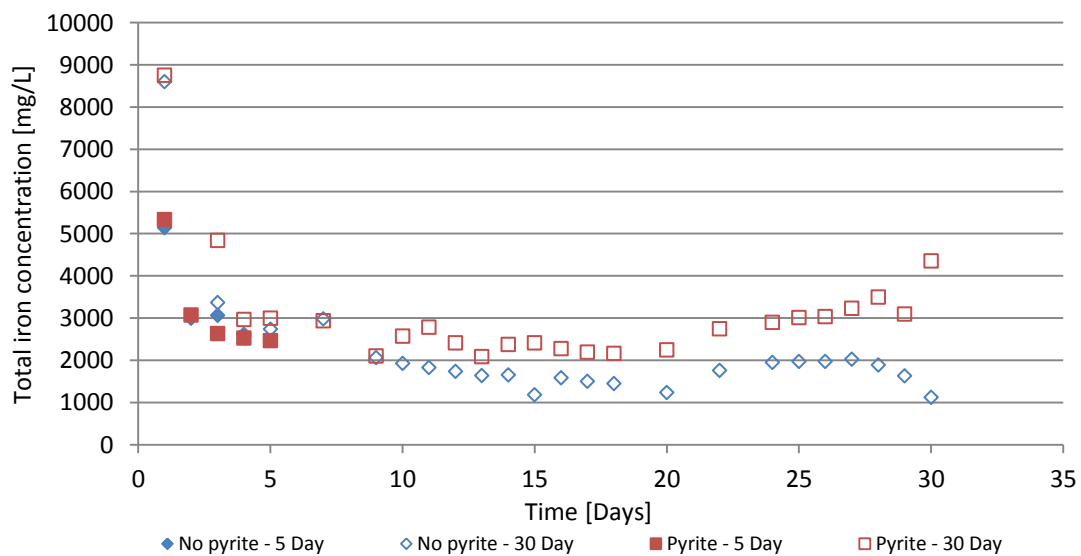
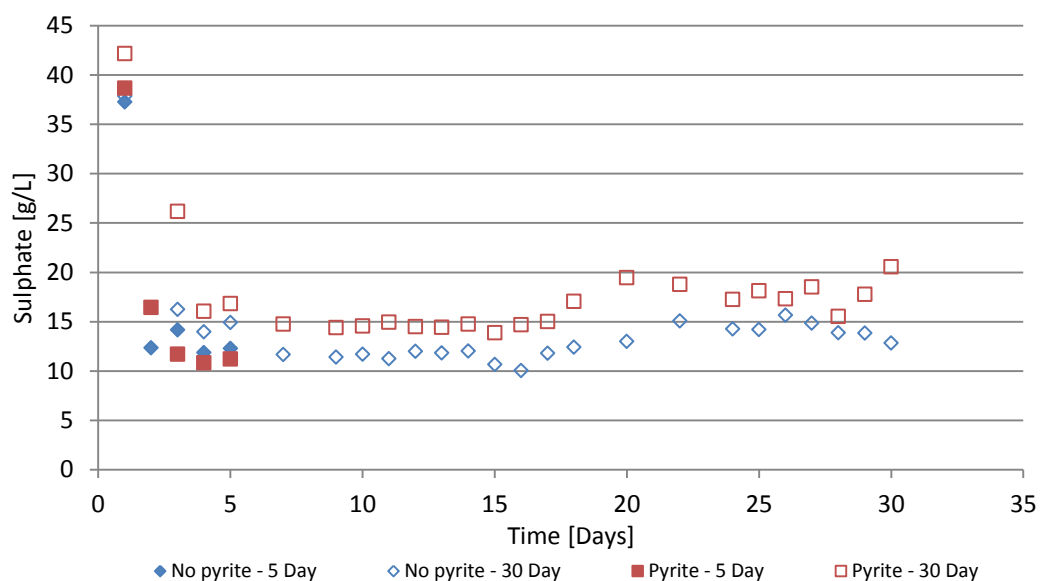


Figure 8-4: Total iron concentration profiles for columns investigating the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions

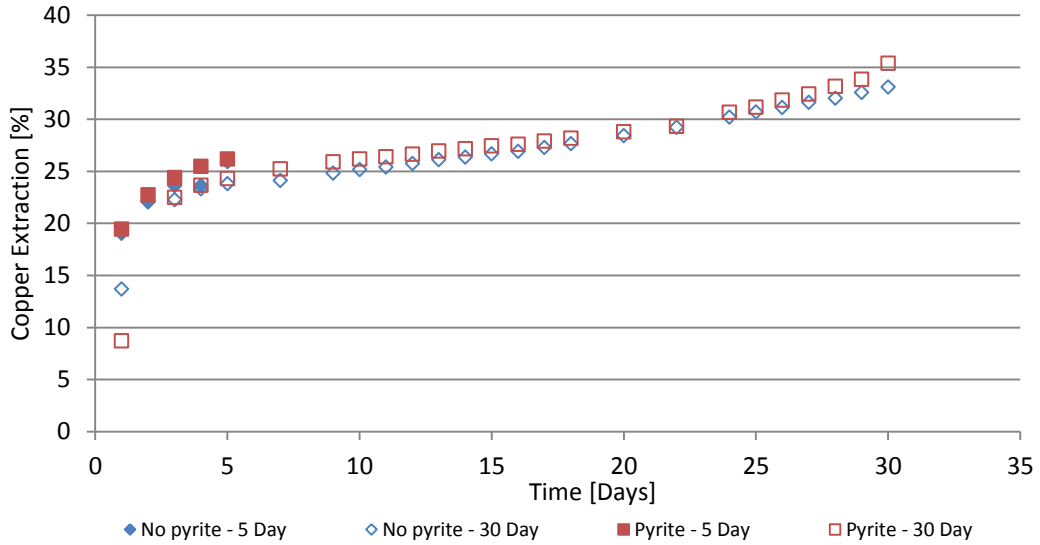
In conjunction with the elevated iron concentrations, elevated sulphate concentrations were observed in the 30-day pyrite column experiment. The sulphate concentrations of the 5-day columns decreased rapidly from approximately 38 g/L after day one, to 11.5 g/L after 5 days, slightly above the sulphate concentration of the feed medium of approximately 10 g/L.

In the 30 day columns, the fractional increase in sulphate released from the pyrite-supplemented column relative to that without pyrite was similar to that for the total iron concentrations. Calculated on a mass basis, the observed increase in the sulphate concentration from the pyrite-supplemented column resulted in a release of an additional 10 g of sulphur over the course of the 30 day experiments, equivalent to approximately half of the additional sulphur added to the column as pyrite. However, variations in the sulphate concentration were also observed for similar columns, hence the detection limit of the method used may be in question.



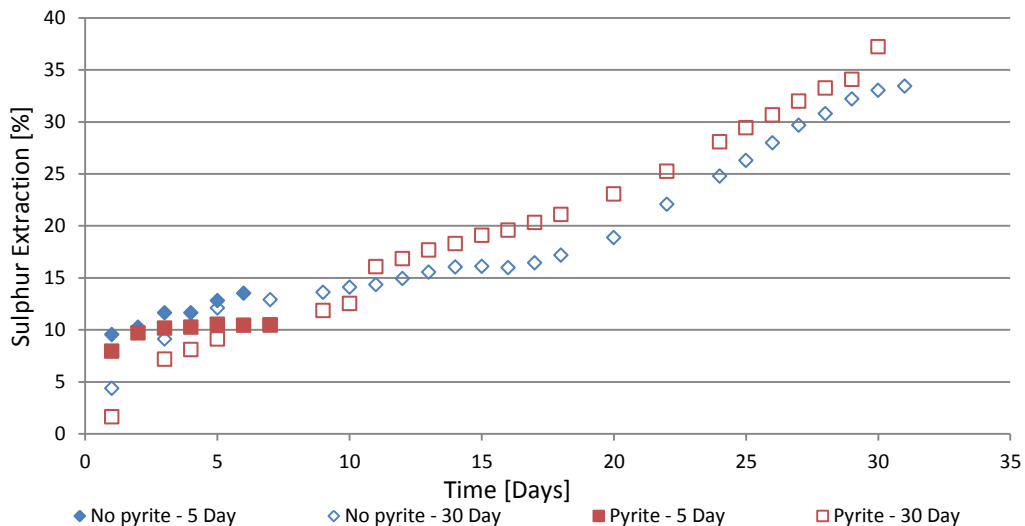
**Figure 8-5: Sulphate concentration profiles for column experiments comparing the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions**

The elevated iron and sulphur concentrations experienced with the pyrite addition did not result in an increase in copper extraction in these columns, consistent with the sulphur calculation which suggested that the elevated iron and sulphur extraction were as a result of pyrite leaching and not copper sulphide minerals. Once again, the observed differences between the 5- and 30-day bioleach columns highlighted the inherent error in the bioleach column experiments, owing to differences in packing and mineralogy at the 4 kg scale, despite representative sampling.



**Figure 8-6: Copper extraction profiles for bioleach column experiments comparing the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions**

Sulphur extraction was calculated using the mass of sulphur leached calculated from the sulphate concentrations and leachate column as a percentage of the total sulphur within the waste rock sample. Where the bioleach experiments were supplemented with pyrite concentrate, the sulphur removed was taken as a percentage of the sum of sulphur in the waste rock and that in the added pyrite material. Leading from the elevated sulphate concentrations in Figure 8-5, an increase in the sulphur extraction was observed in the pyrite-supplemented, 30-day bioleach column in Figure 7-7. This elevated extraction suggested that the presence of pyrite concentrate within the bioleach column stimulated sulphide oxidation. A lack of corresponding elevated copper extraction data (Figure 7-6) however suggested the enhanced removal of non-copper bearing sulphide minerals from the waste rock.



**Figure 8-7: Sulphur extraction profiles for bioleach column experiments comparing the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions**

For the  $TD_{Cu}$  estimations (Table 8-1), only extraction data from the 30-day column experiments was used, as the extraction over the initial 5 day period was governed by acid addition from the agglomeration process. The  $TD_{Cu}$  values were estimated using a linear extrapolation of the copper extraction data (Figure 8-6) with the terminal leaching duration varied. This variation was completed to obtain a clear picture of the change in  $TD_{Cu}$  as the leaching experiments progressed.

The terminal durations were estimated at  $0.55 \pm 0.08$  and  $0.53 \pm 0.04$  years for the pyrite supplemented and non-pyrite supplemented experiments respectively. The identical values is consistent with the copper extraction profiles in Figure 8-6 and suggested that pyrite supplementation did not have a significant effect on the rate of copper sulphide leaching over the 30 day period where no temperature increase was mediated.

**Table 8-1:  $TD_{Cu}$  estimations for the 30-day column experiments comparing the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions**

<b>Terminal</b> Leaching Duration [Days]	$TD_{Cu}$ : No additional pyrite [Years]	$TD_{Cu}$ : Pyrite supplementation [Years]
10	0.46	0.49
20	0.59	0.54
25	0.61	0.57

The  $TD_{Sulphur}$  estimates were calculated in a similar manner, via linear extrapolation of the sulphur extraction data. Once again, the initial 5 days of leaching was discarded due to the dominance of the acid leaching from agglomeration. The  $TD_{Sulphur}$  estimates were  $0.26 \pm 0.03$  and  $0.26 \pm 0.04$  years for the pyrite supplemented and non-pyrite supplemented bioleach columns respectively. Therefore, although a difference in extraction values was observed (Figure 8-7), the rates of sulphur extraction were sufficiently close so as to result in identical  $TD_{Sulphur}$  values. Similar to the  $TD_{Cu}$  estimates therefore, pyrite supplementation had no significant effect on the terminal duration of the waste rock where no temperature increase was mediated.

**Table 8-2:  $TD_{Sulphur}$  estimations for the 30-day column experiments comparing the effect of a 1% (w/w) pyrite concentrate addition to the bioleaching of inoculated waste rock under acid feed conditions**

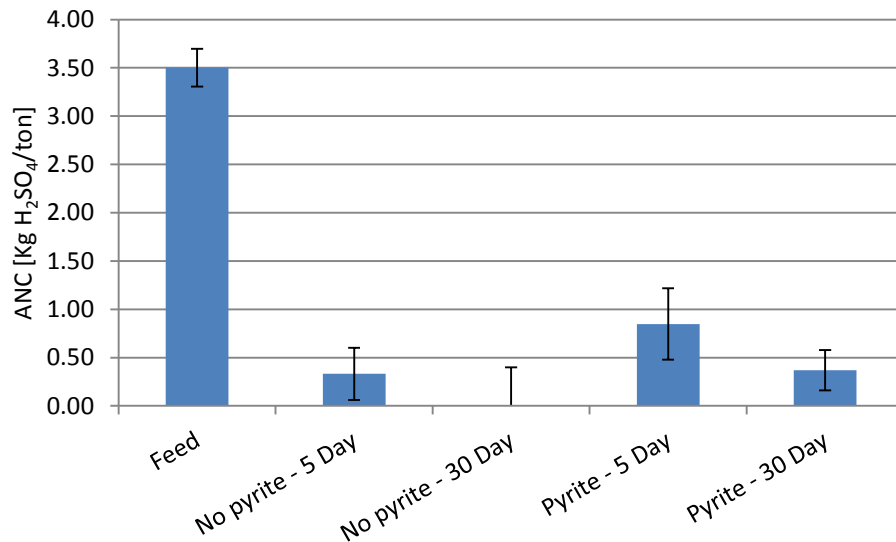
<b>Terminal</b> Leaching Duration [Days]	$TD_{Sulphur}$ : No additional pyrite [Years]	$TD_{Sulphur}$ : Pyrite supplementation [Years]
10	0.23	0.21
20	0.27	0.27
25	0.28	0.29

### 8.1.2. Analysis of the solid phase

After leaching for the specified duration, solids samples were prepared for ARD characterization tests. ANC and MPA static tests were conducted on the solid samples. In addition, an ARD characterization plot was used to track changes in the post-leaching ARD potential of the samples.

The ANC results, as presented in Figure 8-8, showed no significant difference between the ANC values with and without the addition of the pyrite concentrate after either 5 or 30 days of bioleaching. This was consistent with the previous ANC results of waste rock samples after irrigation

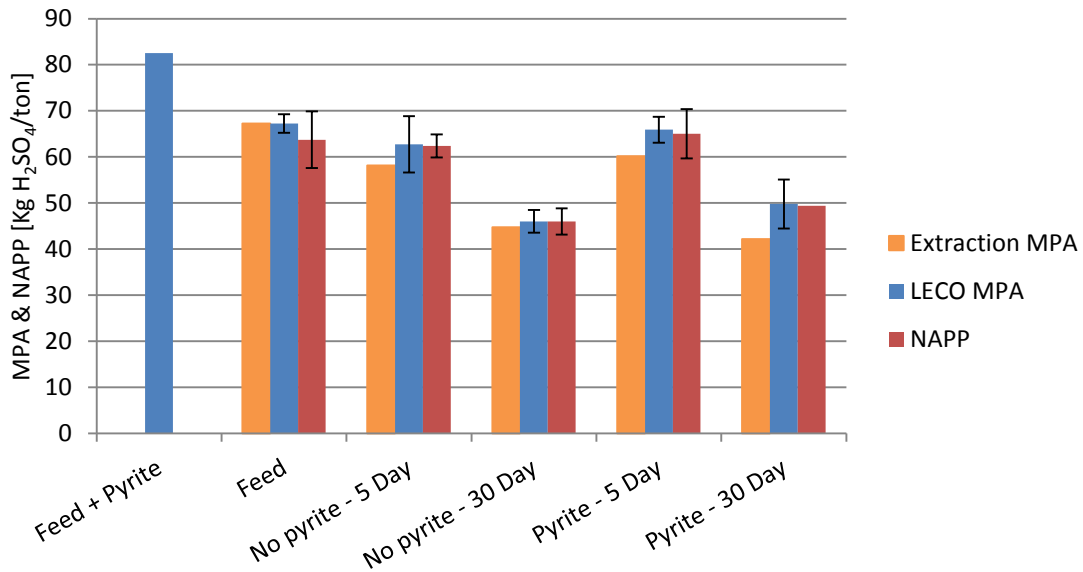
with acidic feed solution. These results also highlighted a difference between ore mineralogies A and B, with Ore type A experiencing an 80% decrease in the ANC after 50 days of column bioleaching as compared to the effective 100% decrease experienced over the shorter experimental duration using waste rock type C.



**Figure 8-8: ANC results showing the changes in neutralizing capacity of the waste rock samples with and without additional pyrite concentrate leached under acidic feed conditions**

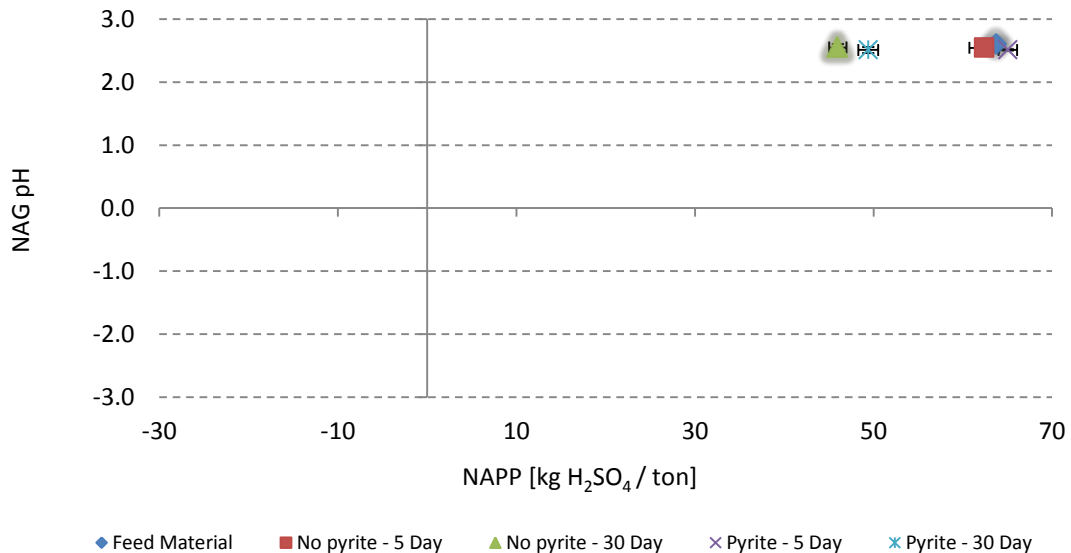
The MPA and NAPP static test results are presented in Figure 7-9. Although a decrease in the total sulphur content of the pyrite-supplemented column from the theoretical MPA of the feed (Feed + Pyrite) was observed, no significant differences were observed in the sulphur percentage of the pyrite and non-pyrite sample. As expected from the sulphur extraction values, a decrease in the MPA and NAPP values was experienced with an increase in experimental duration. No significant difference as a consequence of pyrite supplementation however was observed for either the 5- or 30-day experiments.

MPA values, as calculated from the change in sulphur content of the waste rock using the sulphur extraction data (as in Section 5.1) were also compared against those obtained using LECO analysis. Good agreement was obtained between the two different calculation methods, with the values for the experiments conducted without pyrite supplementation lying within the error ranges of the LECO MPA values.



**Figure 8-9: MPA and NAPP results showing the changes in ARD prediction comparing the 5- and 30-day experiments in the presence and absence of additional pyrite concentrate under acid feed conditions**

Using the NAPP and NAG<sub>pH</sub> data, a characterization plot was constructed to track the changes in ARD potential visually. Although no differences were observed in the NAPP values for the 30-day column experiments, Figure 8-10 gives a good indication of the effect of leaching duration on the ARD potential. In agreement with the terminal duration estimates, the characterisation plot also suggested that pyrite supplementation had little significant effect on the ARD potentials of samples leached for identical durations where no increase in temperature was mediated by the pyrite addition.



**Figure 8-10: Characterization plot to determine the effect of an addition of 1% pyrite concentrate to the ARD potential of waste rock leached under acidic feed conditions**

### **8.1.3. Summary of comparison between column experiments with and without pyrite addition**

The leachate profiles showed a lag in the redox potential for bioleach columns with added pyrite concentrate. This lag was also suggested by the increased ferrous concentration as observed in Figure 8-3. The higher total iron concentrations showed however that leaching of the additional pyrite material was taking place and, due to the acid insolubility of pyrite, this dissolution was a direct result of ferric oxidation of the mineral. Although similar elevations in sulphate concentrations were observed for the pyrite supplemented experiment, the copper extraction profiles for the 30-day experiments showed not significant differences. Given the dominance of chalcopyrite in the waste rock samples, and the limited temperature increase observed within the column experiments as a result of pyrite-supplementation, the lack of a significant in the copper extracted was in agreement with literature concerning chalcopyrite leaching at 32 °C (Rawlings *et al.*, 2003). In addition, on a mass basis, the observed elevations in sulphate concentration resulted in an extra 10 g of sulphur removed from the column experiment, the equivalent of half of the addition sulphur added as pyrite mineral, suggesting the elevated iron and sulphur concentrations a result of the oxidation of the additional pyrite mineral. Variations in the sulphate concentration between the similar columns of 5- and 30-day durations, however, highlighted the possible limitations of the detection limit of the quantification method.

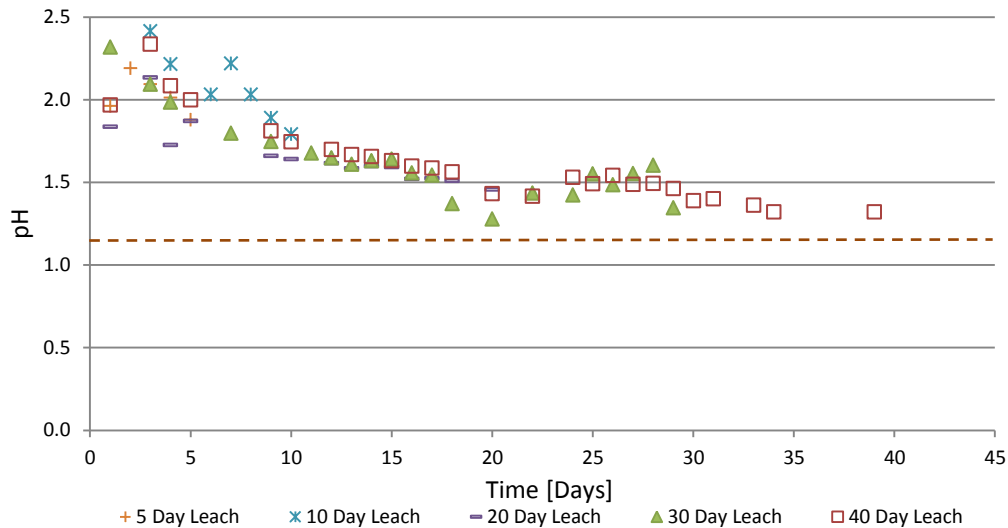
In agreement with this is the lack of a significant difference in the terminal duration estimates from both the copper and sulphur extraction profiles. Here, the estimates showed no significant difference in the duration necessary for complete copper and sulphur removal, and hence ARD generation, as a result of pyrite supplementation. In addition, no significant differences were observed as a result of pyrite supplementation in the ARD prediction results from the solids analysis.

## **8.2. The use of multiple bioleach columns to investigate the experimental errors associated column leaching of waste rock type C**

Five replicate column experiments were conducted with an aim of gaining an understanding of the inherent errors of the bioleach column experiments. For these repeats, the pyrite-augmented bioleach column experiment described in 8.1 was repeated over a 40 day period, with solids analysis occurring at 10 day intervals. From this, clearer insight into the significance of the differences observed in Section 7.1 could be obtained. The 4 kg solid samples were statistically split from the same bulk sample as those reported in Section 7.1. The experimental duration was chosen to allow comparison of the results with those obtained for waste rock type B from Section 4.1.

### **8.2.1. Analysis of the liquid phase**

The pH profiles presented in Figure 8-11 show the similarity in the leachate pHs between the pyrite-augmented column experiments. The immediate initial rise in pH to a maximum of pH 2.4, due to the reaction of the ANC with the acidic feed solution, was followed by a gradual decrease following partial depletion of the ANC, with the stabilization of the pH at a value slightly above that of the feed solution, pH 1.15.



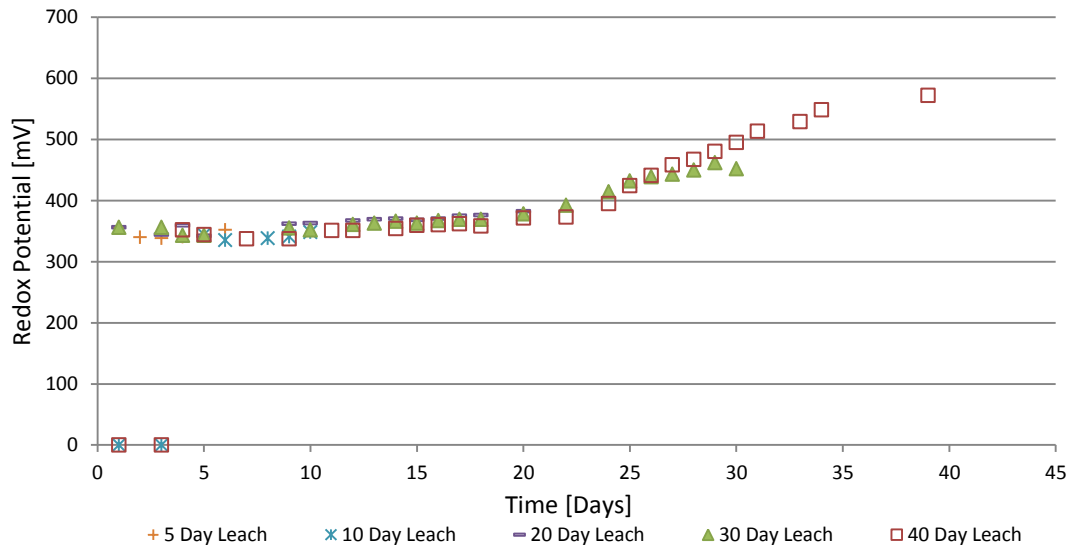
**Figure 8-11: pH profiles for multiple 1% pyrite-supplemented bioleach column experiments under acidic feed conditions to investigate errors associated with column bioleaching. The dashed line represents the pH of the feed solution**

Similarly, little difference was observed in the redox potential profiles of the five replicate bioleach columns. The bioleach columns exhibited a gradual increase in the redox potential to a value of approximately 580 mV over a forty day period, indicating the increasing dominance of the rate of mineral leaching over microbial ferrous iron oxidation in the early stages of the experiment and its reversal by day 40.

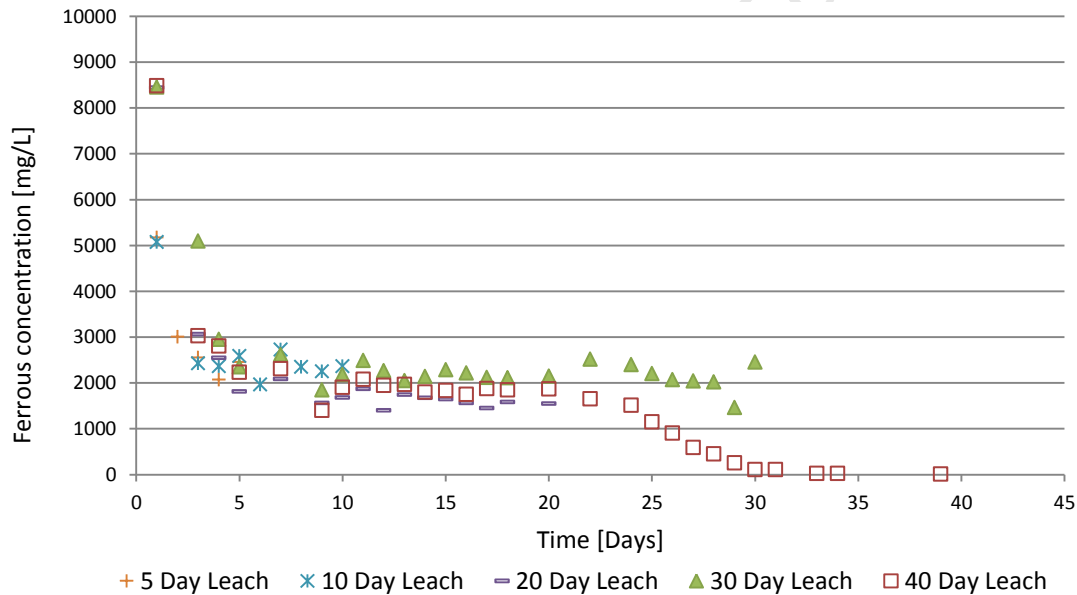
The experimental error of the bioleach experiments was demonstrated by the spread of the redox potential curves in Figure 8-12. This suggested that differences between the pyrite-supplemented and the non-pyrite supplemented experiments were due to tangible differences in the ratio of ferrous to ferric iron within the leachate solutions of the two column experiments and was as a direct result of the addition of the pyrite concentrate.

The redox potential curves are supported by the decreasing trends of the ferrous iron concentrations as presented in Figure 8-13. The initial high ferrous concentrations were indicative of the acid solubilised iron associated with the neutralizing minerals within the waste rock samples.

The differences in the 20-, 30- and 40-day bioleach columns indicated that prior to the rise in redox potential (day 20), the combined experimental error in the bioleach columns and the error in ferrous iron measurements was approximately 16 % of the mean value. This increased during the period of increasing redox potential and was possibly due to differences in activity of the microbial populations. In particular, it was evident that microbial leaching in the 30-day column was delayed. A clear onset of active ferrous iron oxidation between day 20 and 25 was seen in the 40-day column, as supported by the redox potential data. This suggested that the difference between the ferrous concentrations as observed within the pyrite-supplemented and non-supplemented columns (Figure 8-3) was within the experimental error of the experiment and ferrous iron measurement as observed from the replicate columns.



**Figure 8-12: Redox potential profiles for multiple 1% pyrite-supplemented bioleach column experiments using waste rock C under acidic feed conditions to investigate the experimental errors associated with column bioleaching**



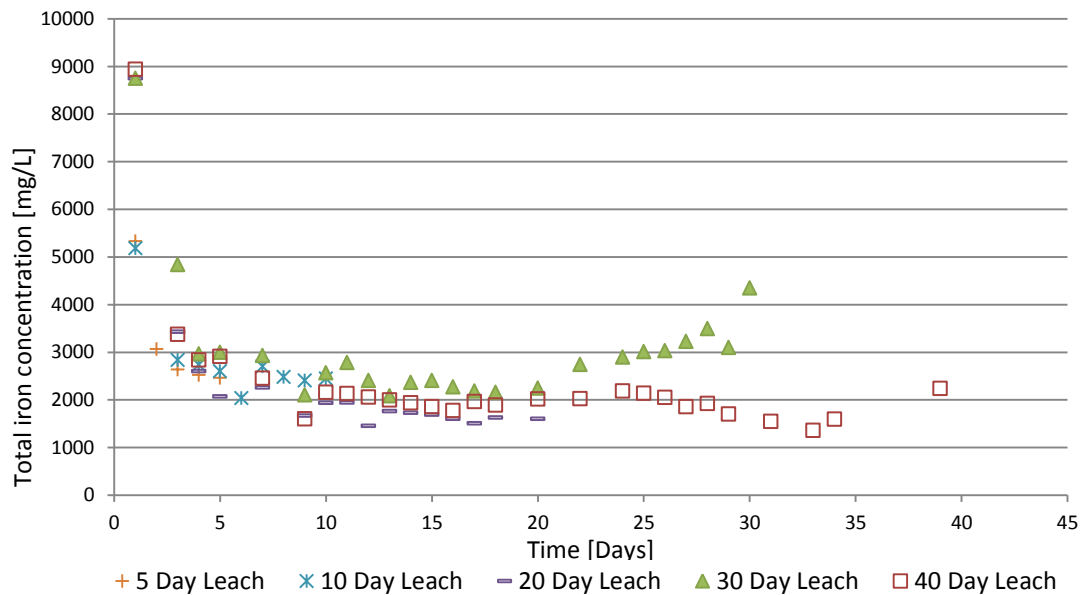
**Figure 8-13: Ferrous iron concentration profiles for pyrite-supplemented bioleach column experiments under acidic feed conditions**

The total iron concentration profiles are presented in Figure 7-14, with the difference between these and the ferrous iron profiles, indicating the concentrations of ferric iron. The ferric iron concentrations increase from approximately 0 at the start of the experiment to between 2000-2500 mg/L after day 40. The decrease in both ferrous and total iron concentrations between days 27 and 30 may be indicative of iron precipitation within the bioleach column.

A large discrepancy in the total iron profiles was only observed with the rise in redox potential with the total experimental error in column leaching experiments and the total iron quantification between the 20-, 30- and 40-day total iron profiles approximately 17 % of the mean after 20 days of leaching. The differences between the leach columns increased thereafter with the increasing total

iron concentrations exiting the bioleach column. Upon termination of the 30-day column, the error between these two columns was approximately 25 %, exacerbated by the possible iron precipitation in the 40-day leach column.

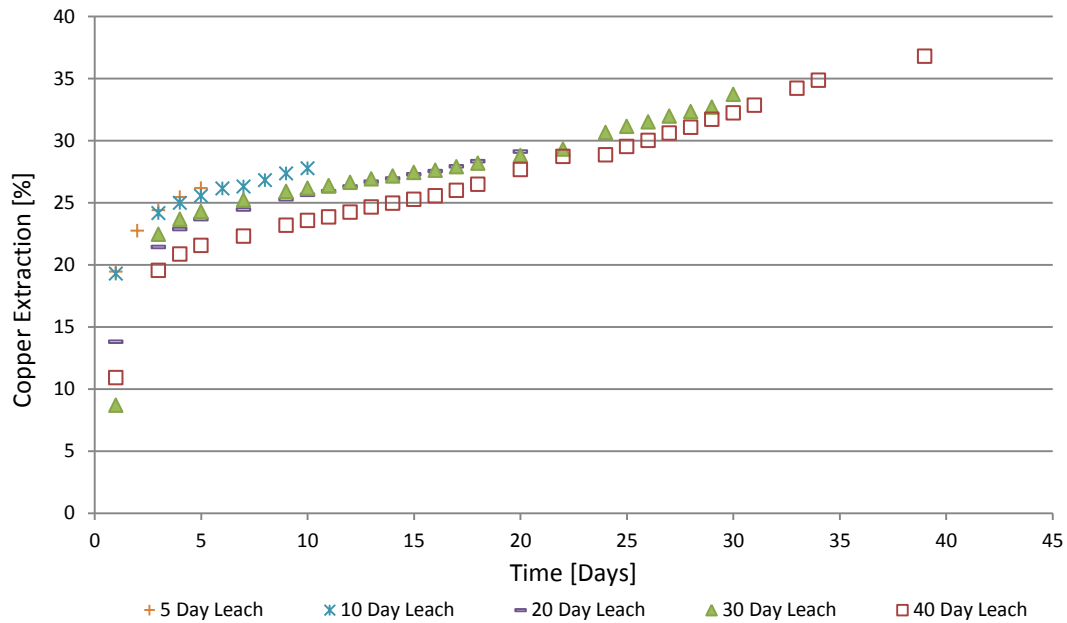
The observed difference between the multiple pyrite-supplement column under identical conditions, suggested that the differences between the bioleach columns with and without additional pyrite were not significant, with a difference of approximately 18 % of the mean (Figure 7-4) as compared to the 17 % of the mean reported from Figure 7-14.



**Figure 8-14: Total iron concentration profiles for reproduced pyrite-supplemented bioleach experiments with waste rock B under acidic feed conditions**

The copper extraction profiles are given in Figure 8-15. The largest differences in the copper concentration in the leach solution were found in the initial leaching phases. The experimental error in the extraction values was 25% at the first sample day. This can be attributed to differences in contacting on agglomeration and initial packing. This difference narrowed over leaching duration, with the experimental error between the 30- and 40-day leaching columns approximately 2% after 30 days. This result was in agreement with the differences observed between the 5- and 30-day bioleach experiments conducted under the pyrite investigation in Section 7.1, indicating that the addition of a pyrite concentrate did not enhance the dissolution of copper.

Given that the dominant copper mineral in the waste rock samples was chalcopyrite, the lack of significant difference in copper extraction was not unexpected. That the rate of copper extraction was constant between 20 and 40 days of leaching, when the ferric iron concentration increased from approximately zero to 2500 mg/L, is consistent with the literature concerning the leaching of chalcopyrite at different ferric iron concentrations at 32 °C (van Hille *et al.*, 2010).



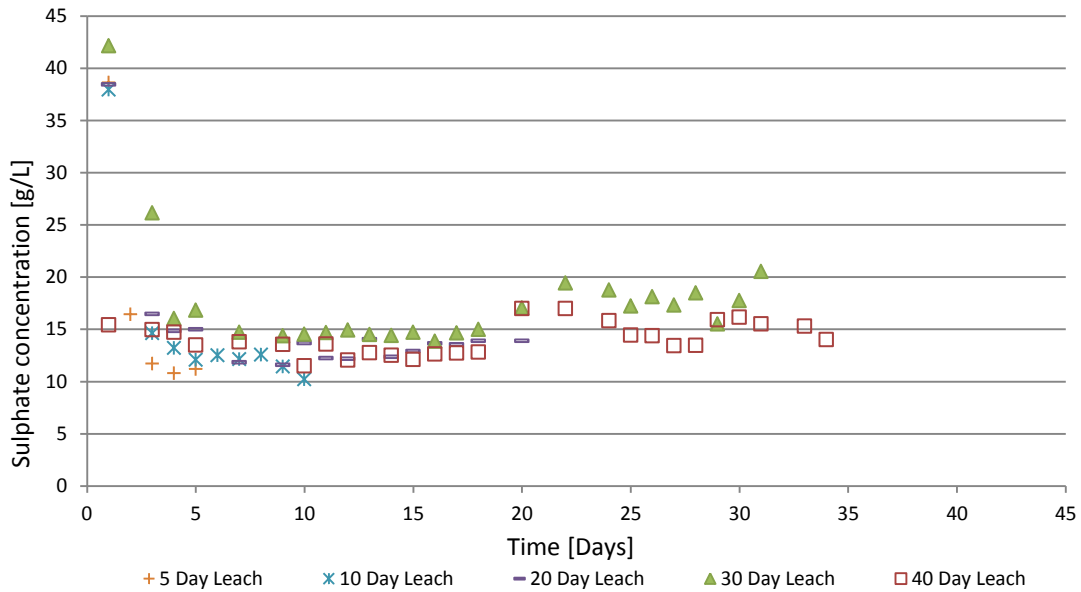
**Figure 8-15: Copper extraction profiles for bioleach experiments supplemented with pyrite concentrate under acidic feed conditions**

The sulphate concentration profiles given in Figure 8-16, showed similar trends between the five columns. The high initial sulphate concentrations, due to the acid soluble, sulphur-containing minerals, decreased rapidly over the first four days before plateauing just above the feed sulphate concentration of 10 g/L. The increases in sulphate concentration, corresponding to an increase in the redox potential after approximately 20 days of leaching, suggested an increase in the leaching of sulphur-containing minerals within the bioleach columns, owing to the activity of iron and sulphur oxidizing micro-organisms.

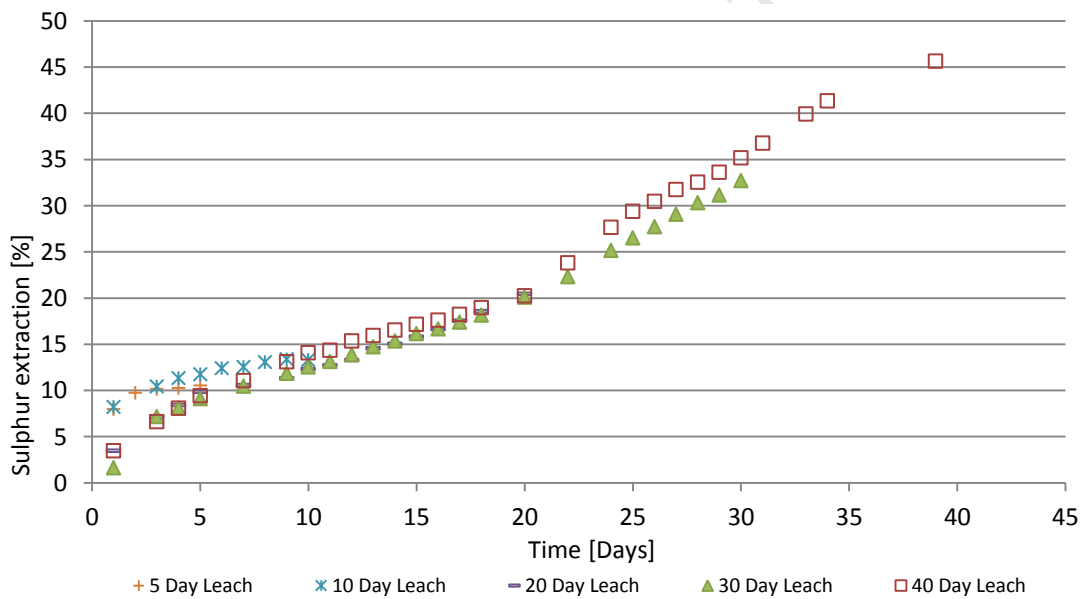
The coefficient of variance in sulphate concentration across the replicate columns was approximately 16 % after 5 days of leaching. This decreased to 10 % after 20 days owing to the removal of the acid soluble sulphur-containing minerals, but increased, with a subsequent increase in the redox potential, to an experimental error of approximately 14% after 30 days of bioleaching.

Due to the similar trends observed in the sulphate concentration profiles for each bioleach column, the sulphur extraction from each experimental column was similar. The noticeably low experimental errors, observed in Figure 8-17, indicated the convergence of the amounts of sulphur released in each experiment as the duration proceeded, confirming reproducibility.

The range of the sulphur extraction profiles indicated that the differences observed between the pyrite-supplemented and non-supplemented experiments, shown in Figure 7-7, were likely due to experimental error between the column experiments. At a redox potential of approximately 350mV, the error observed in Figure 8-17 was approximately 3%. Similarly, between the pyrite-supplemented and non-supplemented columns, a 5% difference was observed. By the end of the 30-day experiments, differences of 6 and 8% were observed in Figure 8-17 and Figure 8-7 respectively.



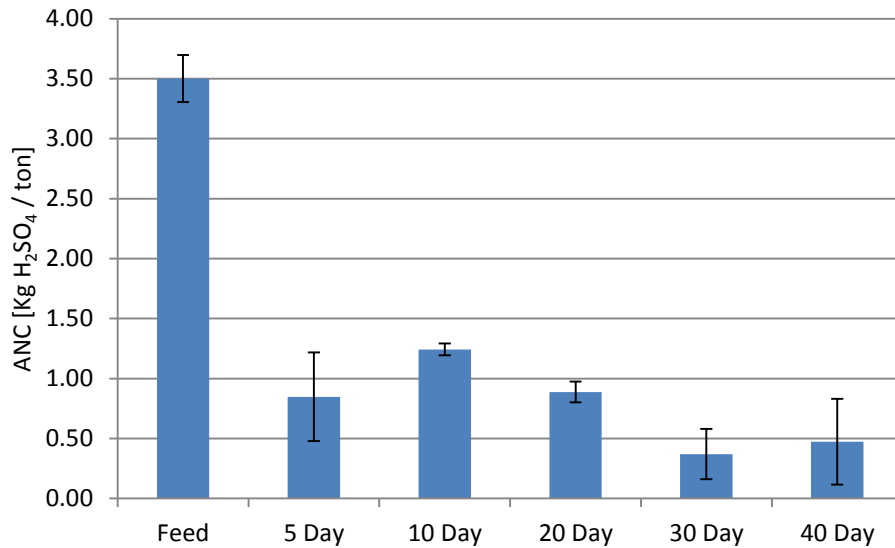
**Figure 8-16: Sulphate concentration profiles for pyrite-supplemented bioleach column experiments over different experimental durations**



**Figure 8-17: Sulphur extraction profiles for pyrite-supplemented column experiments detailing the similarities between profiles over time**

### 8.2.2. Solid phase analysis

A rapid decrease in ANC, due to the reaction of the neutralizing minerals with the acidic feed, was observed. Although there was an overall decreasing trend in the ANC with time, there was no significant difference between ANC values on solids leached for 5 to 40 days. Further, no significance was observed between these and the non-pyrite supplemented experiments in Figure 8-8. This was not unexpected since the decrease in ANC was due to the acidic feed solution and gangue mineralogy, common to all experiments under investigation.



**Figure 8-18: Changes in ANC for pyrite-supplemented column experiments with time**

Figure 8-19 details the MPA and the NAPP trends with time. Here, it is evident that two distinct groups of MPA and NAPP values exist, separated after 20-days of leaching. Before this, when the redox potentials were below approximately 350mV and thus acid leaching dominated, there was no statistical difference in the observed sulphur percentages of the waste rock samples.

A significant difference between the sulphur content of the feed waste rock sample and the post-leaching samples after 20- and 30-days of leaching was observed. This result indicated a clear separation between the sulphur removed during the acid leaching dominant phase and that amount removed as a consequence of the activity of the bioleaching micro-organisms. This is identical to the result obtained for the pyrite-augmentation investigation, with no significant difference observed between the sulphur percentages of the pyrite- and non-pyrite-supplemented bioleach columns. The NAPP value for the 40-day leach sample however, does not follow this trend. This is in contrast to the similar leachate profiles of this column experiment with the 30-day column, and may be as a result of errors incurred during sample preparation.

the MPA values from LECO analysis (LECO MPA) were compared to those calculated using the sulphur extraction data from the leachate analysis (Extraction MPA, Figure 7-17). For the feed sample, the total sulphur percentage resulting from LECO analysis was used, with this representing 0 % extraction. Extraction MPA values were then calculated by subtracting the percentage sulphur recovered into the leachate solution from this initial value. With the exception of the 10- and 40-day samples, a similar decreasing trend with time was observed between the two MPA values. Significant differences however were observed in the 10- and 40-day samples, with the LECO MPA value significantly higher than that estimated from the sulphur extraction profile.

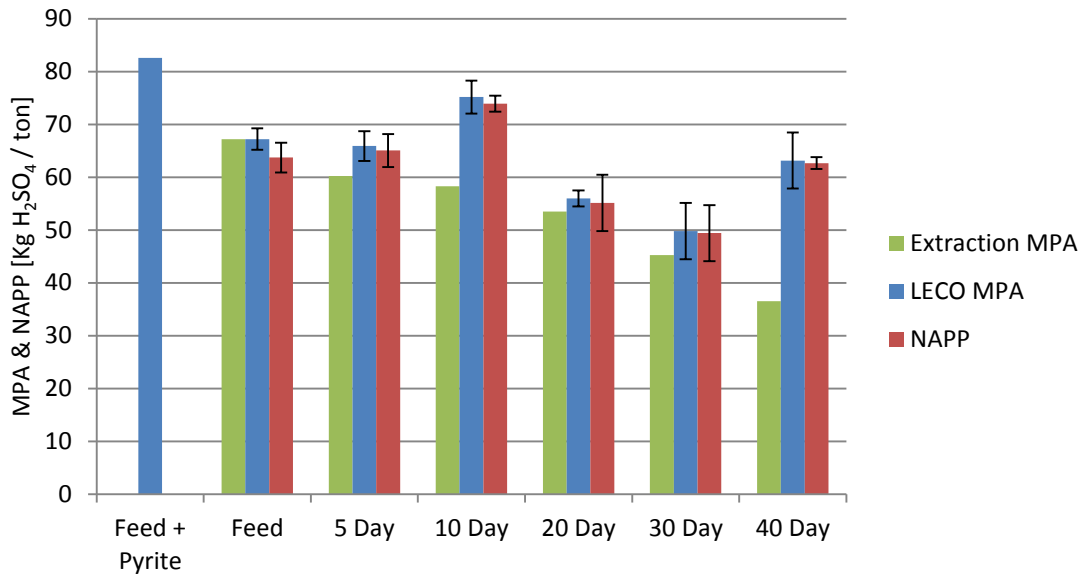


Figure 8-19: MPA and NAPP results for reproducible, pyrite-supplemented column experiments

The Characterization plot (Figure 8-20) presents a graphical representation of the change in NAPP with experimental duration. In addition, this plot also included the resultant NAG pH from reacting the solid residue with a 15 % hydrogen peroxide solution. Although a decrease in the NAPP was observed, there was not enough sulphur removed to affect the resulting NAG pH. The experimental duration of the leach period therefore was insufficient to change the classification of this waste rock sample. This was expected given the dominance of chalcopyrite within the waste rock sample and the difficulty of leaching this mineral at 32 °C over the 40 day experimental duration.

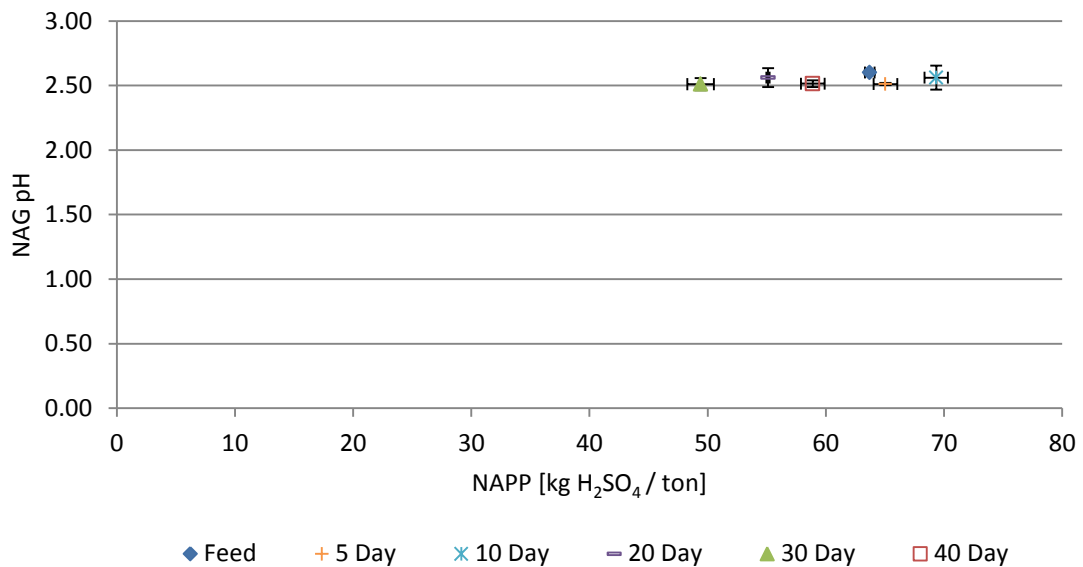


Figure 8-20: Characterization plot for pyrite-augmented bioleach columns with time

### 8.2.3. Biokinetic accelerated weathering tests

Biokinetic flask tests were run in accordance with the method outlined in Section 2.6.2. Liquid analysis was conducted detailing the changes in pH, redox potential and the ferrous and total iron concentrations.

The pH profiles are presented in Figure 8-21. The magnitude in the initial rise in pH provides an indication of the ANC potential due to reaction with the acidic liquid medium. In the case of the leached samples, this was a measure of the residual ANC after bioleaching as observed in Figure 8-18. The pH of the feed sample rose initially to approximately pH 2.5 before decreasing to a final pH of 2.0, slightly higher than that of the bioleached samples after 60 days. The lower ANC of the 10-day sample resulted an initial rise in pH to pH 2.25. A higher pH was sustained as compared to the other leached samples, suggesting ongoing release of ANC. After 60 days, however, the pH was similar to the others at pH 2.0. The 40-day sample showed a lower initial rise in pH to pH 2.2 than the other leached samples. Thereafter, the pH decreased to pH 2.0 by day 20, and further to pH 1.88 after 60 days. By the end of the tests, the pH values of the 30- and 40-day samples were similar at  $\text{pH } 1.85 \pm 0.03$ , while the pH of the feed and 10-day samples were  $\text{pH } 2.0 \pm 0.01$ . This suggested the importance of the relative amounts of sulphur removed (Figure 8-19) during leaching on the acidification during microbial leaching and hence the final pH values of these biokinetic tests.

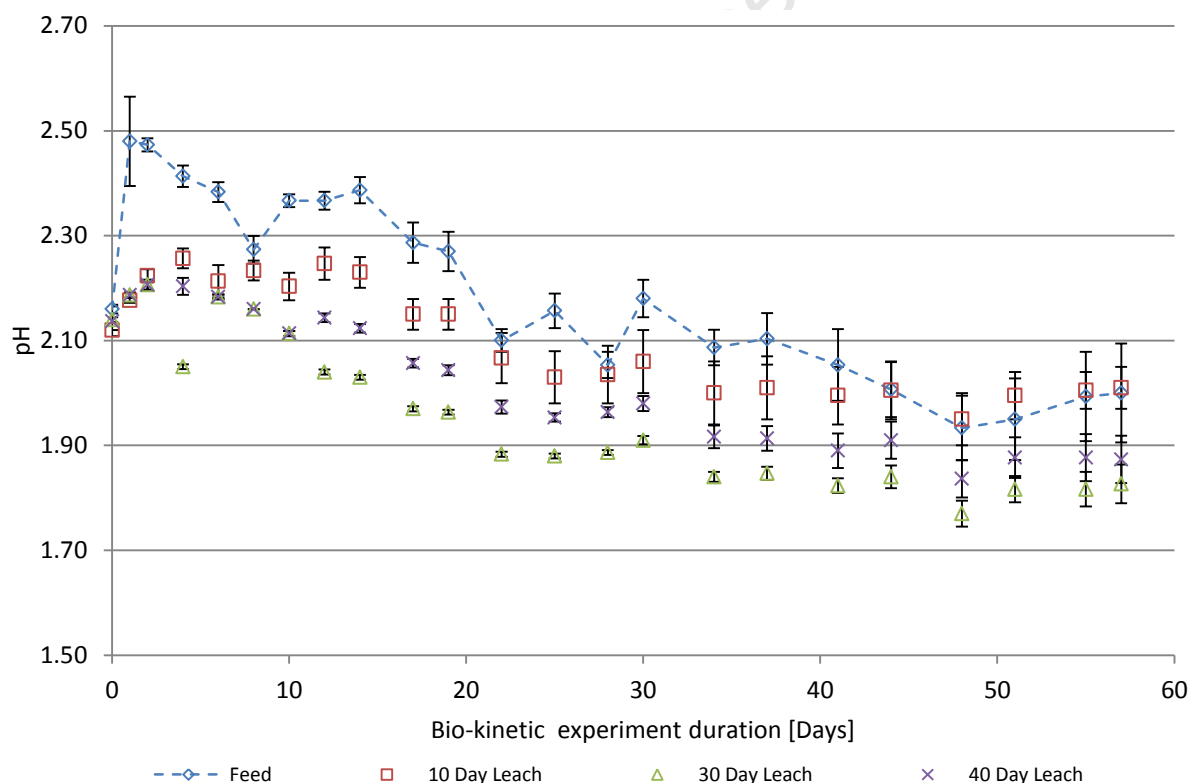
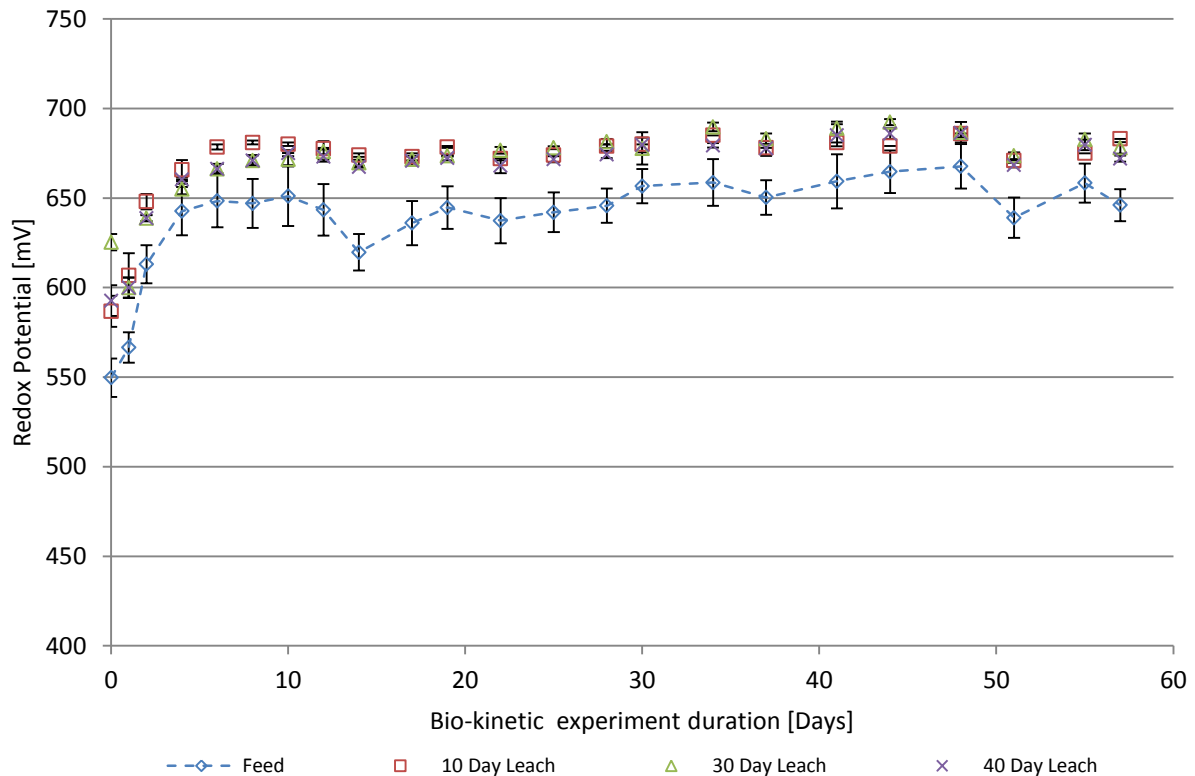


Figure 8-21: Biokinetic pH profile for leached, pyrite-augmented samples.

Figure 8-22 details the redox potential profiles, showing no significant difference between the leached samples. A difference however was observed in the feed sample, which showed a lower redox potential with time. The higher pH in the feed sample, resulted in lower relative ferric iron regeneration as compared to the leached samples. The increased available leachable iron in the feed

sample, however, resulted in more soluble ferrous iron and a lower relative ferric to ferrous iron ratio. The higher iron concentrations and flask pH may also have led to iron precipitation.

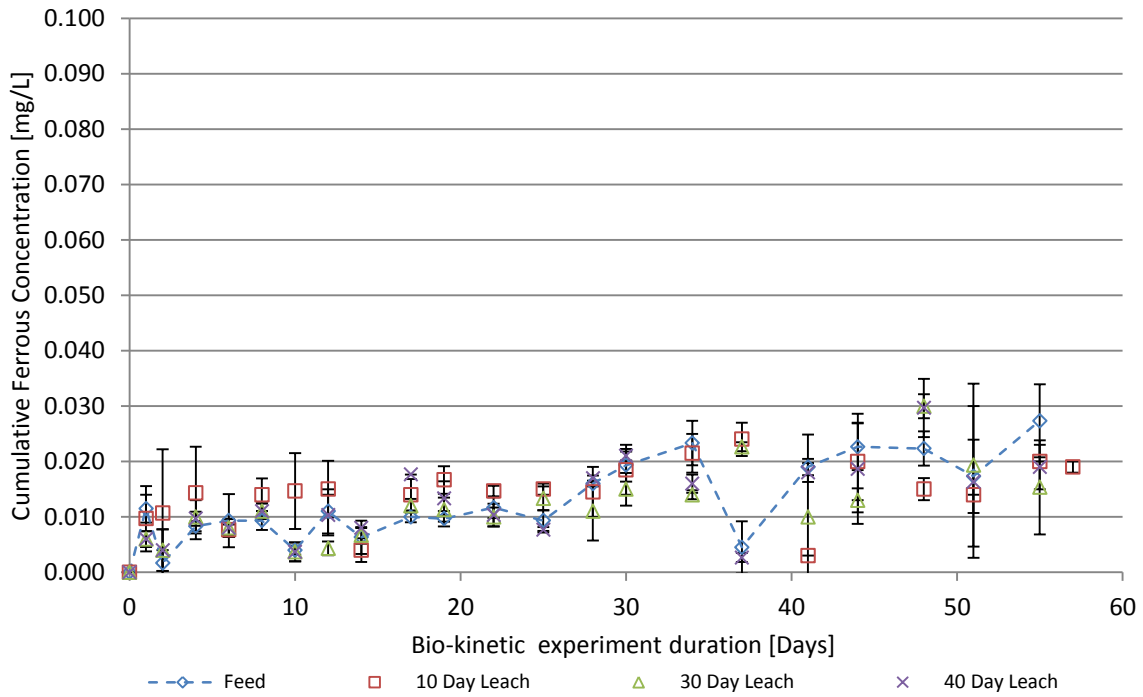


**Figure 8-22: Redox potential profiles for the Biokinetic experiments conducted on post-leached, pyrite-augmented samples**

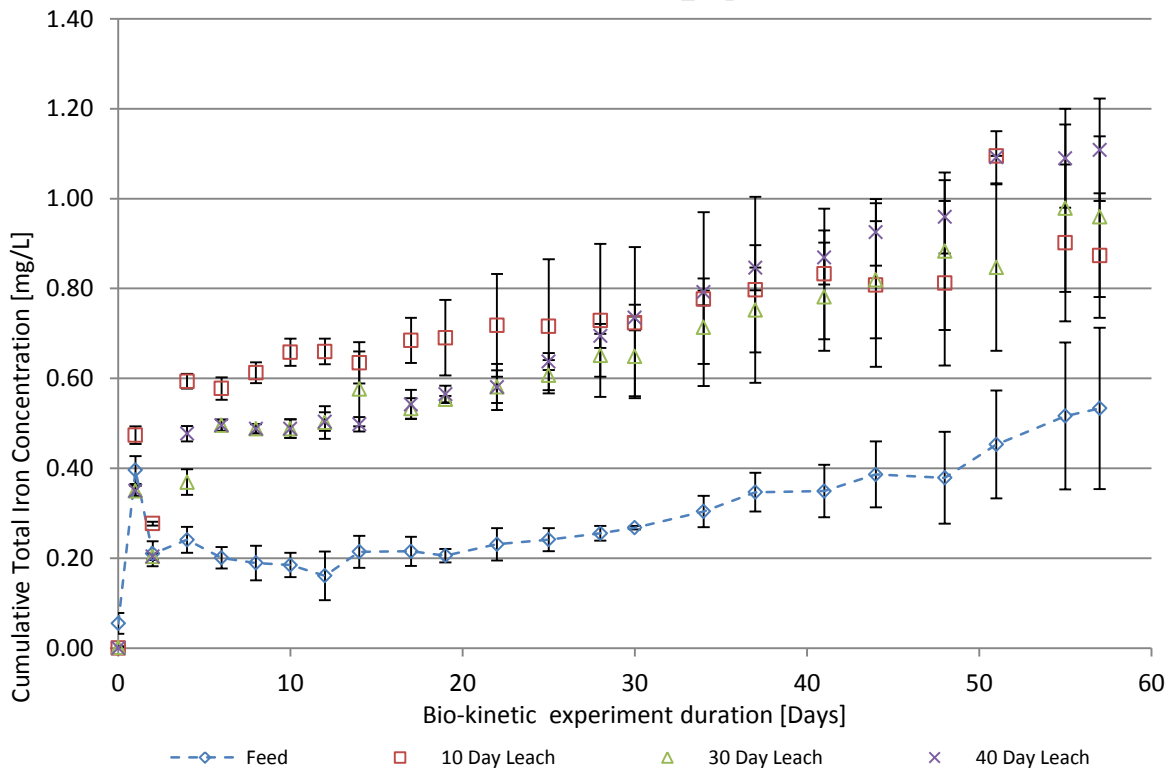
The low iron concentrations present in the biokinetic tests are observed in Figure 8-23 and Figure 8-24, with the difference between the two values indicating the high level of activity of the iron-oxidizing micro-organisms within each flask. The low ferrous iron levels present in the flask triplicates together with the 0.01 mg/L detection limit of the phenanthroline ferrous iron quantification method (APHA, 1998) resulted in relatively large percentage errors, with consequence that no significant difference was observed between these profiles.

Significant differences however were observed in the total iron profiles. Initially the 10-day leached sample exhibited a faster rate of iron extraction, due to the higher concentration of easily soluble iron-containing mineral species within the 10-day solid sample. This difference however ceased after an experimental duration of approximately 20 days. No significant difference was observed between the 30- and 40-day leached samples.

A large difference was observed between the feed and the leached samples, with much lower total iron concentrations observed in the feed samples. This was possibly due to the effects of the higher ANC of the feed samples, which resulted in the initial rise in pH and subsequent precipitation of iron within these biokinetic flasks.



**Figure 8-23: Cumulative ferrous concentration profiles for the Biokinetic experiments conducted on post-leached, pyrite-augmented samples**



**Figure 8-24: Cumulative total iron concentration profiles for the pyrite-augmented, Biokinetic experiments**

The differences between the pre- and post-20 day column leached sample, as represented by the 10- and the 30- and 40-day biokinetic flasks, were indicative of leaching governed by acid attack and

ferric iron solubilisation respectively. This resulted in the more rapid initial release of iron in the 10-day leach.

Larger differences were observed between the feed and the leached samples as a result of the increased ANC. The subsequent rise in pH of the feed samples may be expected to lead to ferric iron precipitation and thus a decreased iron concentration within the biokinetic flasks. This interferes with the interpretation of the biokinetic data in the absence of experimentation to determine the extent of precipitation.

### 8.3. Chapter Summary

The addition of a 1% (w/w) pyrite concentrate to a simulated waste rock dump was used to investigate the increase in iron and sulphur lixiviate source on the rate of ARD generation. While in the dump, this addition will also increase the temperature of the leach. The effect of temperature on the rate of bioleaching was investigated separately in Section 3.5. The leachate results from bioleach column experiments showed differences for the redox potential, iron concentration and sulphur extraction profiles due to leaching of the pyrite. In contrast, no significant difference was observed in the terminal rate estimations or the static ARD characterisation tests conducted on the solid samples. The latter however, was due to the relatively large errors associated with these characterization tests.

Although the differences in redox potentials was explained through analysis of the ferrous and total iron concentration curves, the questions surrounding the other leachate differences, while present in sulphur extraction but absent in copper extraction data, together with the dissociation between the leachate and corresponding solids analysis, necessitated the investigation into the inherent errors associated with bioleach column test-work.

The leachate profiles for the replicate bioleach columns run over different experimental durations showed good general agreement; especially under conditions of mainly acid leaching at redox potentials below approximately 400mV, corresponding to an experimental duration of 20 days. Experimental errors in the iron concentration profiles increased with increasing duration and a rise in the redox potential whereas the copper and sulphur extraction converged as time progressed. This convergence is most likely due to the scarcity of the easily leachable minerals with time and the natural progression towards chalcopyrite leaching, with relatively slow kinetics at this temperature (Rawlings *et al.*, 2003) where as possible iron precipitation exacerbated errors in bioleach column experiments and iron quantification.

From the investigation into the inherent errors involved during bioleach column operation, it was observed that the differences between the pyrite-supplemented and non-pyrite supplemented, 30-day leach experiments lay within the bounds of experimental column error. These observations were limited to the leachate solution analysis with the experimental error of the solids analysis greater than any observed differences due to pyrite addition.

This result was not unexpected given the dominance of chalcopyrite mineral on the copper sulphide within the waste rock and the aims of the pyrite mineral addition. At 32 °C, the aim of a pyrite addition would be to increase the acidity, the ferric iron concentration, and the operating

temperature of the waste rock dump. In the laboratory scale experiment, the effect of a pyrite addition was to increase the acidity and ferric concentration within the bioleach columns, with an increase in temperature not possible due to the lack of insulation and large surface area-volume ratio of the bioleach columns.

While the effect of an increase in temperature was shown to increase the rate of sulphide removal for chalcopyrite-dominated waste rock (Section 3.5), an increase in ferric concentration and acidity, in the absence of a rise in temperature, was not able to accelerate the leaching of the chalcopyrite mineral. This was in agreement with previous studies by van Hille *et al.* (2010) and Rawlings *et al.* (2003).

Analysis of the post-leached solids showed an approximate 75% decrease in the ANC over the first 5-days of leaching, governed by the removal of the ANC through reaction with the acidic feed solution. Thereafter, no further statistical difference was found in the ANC values between 5- and 40-days of leaching. No similar decrease was observed in the percentage sulphur of the waste samples until 20 days of leaching had elapsed, when an approximate 18 % decrease in the NAPP between days 20 and 30 was observed. The leached samples could be divided into two groups with respect to the MPA of the solid sample, distinguished by a rise in the redox potential. This suggested that the difference in the sulphur removed occurred with an increase in the microbial activity.

To further investigate the ARD potentials of the leached solids before and after the rise in redox potential, biokinetic tests were performed on the 10-, 30- and 40-day samples. Comparison with the feed sample was used to gain an insight into the leaching behaviour of each of these samples under accelerated microbial leaching conditions. The significance of the ANC was highlighted by the comparison of the feed and leached samples. In addition, the lower redox potentials observed in the feed over the leached samples suggested a faster rate of mineral leaching relative to microbial activity. Overall, clearer results were expected for a larger experimental duration (90 days).

## 9. Conclusions

### 9.1. Summary of Findings

#### 9.1.1. Effect of operating conditions on ARD generation

The objective of this study was to investigate the designed acceleration of ARD generation from waste rock through the establishment of favourable conditions for the growth and colonization of ARD forming micro-organisms. In this study, the effect of an acidic feed solution, forced aeration, elevated temperature, and an additional iron and sulphur lixivate source on the rate of ARD generated from a low grade, copper bearing waste rock sample was examined within laboratory scale column reactors.

Bioleach column experiments at the 4 kg scale were used to investigate the generation of ARD at these conditions over a 144 day period, with measurement of the leachate pH, redox potential and soluble metal concentrations used to assess the ARD generation. Of particular interest was the effect of changing the leaching conditions on the rate of ARD generation and the remaining ARD potential of the waste rock after bioleaching.

The soluble metal concentrations were used as an indicator for the generation of ARD. Of particular significance was the time estimated for total ARD generation from the waste rock sample under leaching conditions imposed. The terminal duration (TD) was defined to provide a measure of this by linear extrapolation of the extraction curves from each of the bioleach column experiments. While terminal duration was considered in the context of copper, iron and sulphur leaching, in this section of the thesis the terminal duration based on copper ( $TD_{Cu}$ ) was used due to interferences by iron precipitation., especially in the water-fed column where the pH of the leachate remained above pH 3.5 for the duration of the experiment, and the large experimental errors previously reported for sulphate determination by the barium sulphate method.

The most significant variable for the acceleration of ARD generation was the pH of the feed solution. In comparison between the water- and acid-fed experiments, the acidic feed allowed for significantly greater metal mobilization with time, with the acidic conditions favouring the growth and colonization of the acidophilic micro-organisms inoculated into each experiment. The terminal duration for complete ARD generation from the copper extraction data decreased from  $30 \pm 1.0$  years to  $1.6 \pm 0.1$  years upon the replacement of the intermittent water feed with a continuous acidic feed. Based on the study of Vries (2013) on the impact of intermittent irrigation, this effect can be attributed mainly to the acidity of the feed.

The effects of aeration and an increase in reaction temperature were consistent with the theory of ARD generation as outlined by the reaction equations. The lack of aeration to the bioleaching system slowed the rate of ARD generation due to the lack of both oxygen and carbon dioxide. Oxygen acts an electron donor in sulphide oxidation while carbon dioxide is a carbon source for autotrophic bioleaching micro-organisms. In the absence of forced aeration, ARD generation was not totally prevented due to air infiltration into the reactor system. The terminal duration for the bioleach

experiment under non-aerated conditions was  $2.3 \pm 0.1$  years, as compared to the  $1.6 \pm 0.1$  years necessary for total ARD generation in the aerated system.

Consistent with thermodynamic theory, an increase in reactor temperature from 32 °C to 42 °C increased the rate of ARD generation. Bioleaching at the elevated temperature led to the highest overall copper extraction within the 144 day period. This resulted in a terminal duration of  $1.3 \pm 0.1$  years as compared to the  $1.6 \pm 0.1$  years necessary for total ARD generation at 32 °C. Increase in bioleaching temperatures can be achieved by ensuring availability of liberated metal sulphides such as pyrite for exothermic reaction.

Although an increase in the easily accessible iron and sulphur sources led to a decrease in the time necessary for the leachate to reach a redox potential of 550 mV, this did not result in an increase in the rate of ARD generation. This was in agreement with van Hille *et al.* (2010), who showed a disconnect between an increase in the ferric iron concentrations and the extent of copper leaching from a low grade, chalcopyrite ore, similar in mineralogy to the waste rock used in this study, at similar experimental conditions. The terminal duration necessary for this experiment,  $2.8 \pm 0.3$  years, was longer than that experienced without the additional pyrite concentrate,  $1.6 \pm 0.1$  years.

Static ARD prediction tests were performed on the post leached, solid waste rock samples to quantify the inherent acid neutralizing and generating potentials of the samples. These were compared to the tests performed on the feed, with the difference an indication of the reduction in ARD potential as a result of bioleaching. This change in ARD potential was extrapolated to give an estimate of the terminal duration from the solids analysis.

Regardless of feed solution acidity, the ANC decreased to less 50 % of the starting waste rock sample. The loss in ANC was greater than that expected from the acid addition during the agglomeration stage, indicating the loss of inherent neutralizing potential as a result of water flow through the column. For the experiments conducted with an acidic feed, there was a total reduction in the ANC of the leached samples.

A smaller decrease in the ARD generating potential, as calculated from the percentage total sulphur in the solid material, was observed. In the case of the water fed column in particular, there was an insignificant decrease in the percentage total sulphur relative to the starting waste rock. The trend in sulphur removal mirrored that of the copper extraction in that the highest decrease in ARD generating potential was observed in waste rock from the elevated temperature experiment. The difference in the relative removal of the ANC and sulphur suggested the possibility for an increase in the ARD generating potential with time.

Extrapolation of the differences between the ARD generating potentials was used to estimate the terminal durations from both the NAPP and NAG test results. Estimations from the NAPP results showed a decrease in the time necessary for ARD generation from 10.7 years for the water-fed experiments to between 1.2 – 3.0 years for the experiments performed with an acidic feed solution. The experiment run at the elevated temperature resulted in the lowest terminal duration.

Terminal duration estimations using the NAG static test results were not possible as no statistical difference was observed between the feed and leached values. This was in contrast with the decrease in percentage total sulphur observed from LECO analysis of the leached waste rock samples and the subsequent decreases in potential observed from the NAPP tests.

In order to provide a consistent comparison between the TD estimates from the leachate and solids data, terminal durations were estimated using the initial and final copper extraction data points. Comparison of these to the NAPP estimates indicated similar magnitudes and trends, but not a direct match in estimates. The linear average between the initial and final copper extraction percentages was not consistent with the extraction profiles which showed an initial rapid rise in extracted copper, followed by a slower, constant rate of the remainder of the experiment. This illustrated the need for time course data for rigorous comparison of the terminal durations between the leachate and solids data.

#### **9.1.2. Rate of ARD generation from leachate and static ARD prediction tests**

To study the relative rates of ANC removal and onset of acid generation and to provide time-course data, five bioleach column experiments were conducted under identical conditions over shortened time periods. One column was sacrificed every ten days for solids analysis, with the view of building a successive picture of the changes in ARD potentials with time. This also allowed for further investigation into the differences between the rate of decrease of the ANC and sulphur content observed from the 144 day experiments.

Similar to the results from the longer term column experiments, a noticeable difference in the rate of decrease of the ANC and MPA was observed over the 50 days. The ANC of the waste rock samples was rapidly removed over the first 10 days of bioleaching, with an approximate 73 % removed over this period. Thereafter however, no significant difference in the ANC values was observed from the waste rock samples from the remaining 40 days of leaching. That any neutralizing capacity remained after the initial 10 days of leaching, where acid added in the feed solution was enough to completely remove this inherent neutralizing ability, suggested channelling within the bioleach column reactor.

In contrast to the observed rapid decreases in ANC, the removal of the potential for ARD generation, as measured by the percentage total sulphur, occurred at a significantly slower rate. Thus, where approximately 73% of the ANC was removed within the initial 10 days of leaching, only approximately 11 % of the total sulphur was removed within the same period. Over the course of the remaining 40 days of bioleaching however, no significant decrease was observed in the sulphur percentage. This lack of statistically significant difference may have been due to the large errors associated with the static ARD tests rather than a lack of sulphur removal, as inferred from the leaching of the copper sulphide minerals.

For estimation over the shortened experimental time frame, the terminal duration estimates were refined to exclude the rapid leaching that as observed over the initial 10 day period. There was limited correlation between these estimates from the leachate extraction data and those estimated from the change in ARD potentials from the static ARD experiment. In addition, the inherent errors

associated with the static ARD tests called into question the use of terminal duration estimations from these data sets.

Investigation into the ANC removal and ARD generation over the shortened time frame raised questions regarding reproducibility of bioleach column reactors and further confirmed the large errors in reproducibility observed in the static ARD prediction tests. These issues were further investigated.

### **9.1.3. Use of the in-bed sampling technique for the improvement of column reproducibility**

In order to minimise the inter-column variability found when tracking the course of the leaching process by sacrificing individual columns, use of an in-bed sampling technique developed by Chiume *et al.* (2012), whereby a solid sample was removed from one column without termination of the entire experiment, was investigated. Both water and acidic feed irrigation was investigated under un-inoculated conditions.

Analysis of the leachate solutions for the water fed experiments showed difference in the redox potential profiles, while the pH, copper and sulphur extraction profiles were consistent. This was explained due to the reduced iron solubility at the pHs of the water-fed experiments. Inconsistent results were obtained between the leachate and solids data. In particular, the ANC results showed large differences between the in-bed sampled solids, the 50-day in-bed sample and the 50-day sample from the column operated without in-bed sampling. Although similar discrepancies were observed in the mean MPA values, the errors associated with the LECO quantification resulted in statistically insignificant differences between these values.

Leachate profiles under acid-fed conditions for the columns operated with and without in-bed sampling showed good reproducibility. Similarly, the solids data showed no statistical difference between methods, due mainly to the total decrease in the ANC of the waste rock samples. Once again, the relatively large errors in total sulphur quantification resulted in statistically insignificant differences between MPA value of the leached samples.

Overall therefore, use of the in-bed sampling technique provided similar leachate profiles for both water and acid-fed systems. Thus the use of the in-bed sampling technique for the studies of the liquid-phase leachate is appropriate. Analysis of the solid samples, however, in particular the ANC analysis under water fed conditions, highlighted the limitation of this technique for use in investigations requiring sampling of the solid phase. Since the sampling method targets a particular section of the waste rock sample, a negligible probability exists for the inclusion of solids outside this section. Following sampling theory as outline by Gy (2004), such a sampling regime can never result in a representative sample of the solid phase within the bioleach column. It was concluded therefore that use of the in-bed sampling technique for this investigation into the changes in ARD potential of the solid phase was not appropriate.

#### 9.1.4. Review of static ARD prediction methods

The discrepancies observed between the NAPP and NAG static tests necessitated an investigation into the relevance of these methods for use in the characterisation of ARD from waste rock. This was completed using different static methodologies on waste rock samples to investigate the sources of error noted by previous authors. Although large errors in the reproducibility of the static test results have been reported previously due to representative sampling issues, the methodology used in this study to sample the 4 kg columns was adequate to ensure statistically representative samples, within a 95 % confidence interval, as observed from ANC test repeats.

Errors in the acid base accounting method for ARD characterisation has been associated with the incorrect use of ANC test methodologies and the selection of methods for the determination of the sulphur species used in the calculation of the maximum potential acidity of samples. Three different ANC methodologies were compared using one waste rock sample, with the difference and shortcomings of each discussed in light on the mineralogy of the samples used in this study. It was concluded that for the purpose of this investigation, the incremental Skousen method (Stewart *et al.*, 2006) provided the best estimation for the determination of the ANC.

Further errors associated with quantification of the NAPP value are associated with the method used to quantify the total sulphur of the sample. Four different methods were employed, with the differences and limitations of each discussed. Due to the high number of samples and the good reproducibility of LECO analysis reported, this method was selected for total sulphur quantification in this study.

The discrepancies observed between the NAPP and NAG results were consistent with the findings of Miller *et al.* (1991). Here the authors stated that the NAG values obtained were approximately two-thirds of the NAPP. This was attributed to incomplete sulphide oxidation in the NAG experiments. As a result, and for the purposes of this investigation, only the NAG pH was used in the characterization of the ARD potentials of waste rock samples, rather than the acid requirement. This characterization was done using a combination of NAG pH and NAPP, according to the characterization plots of Miller *et al.* (1997).

To gain information concerning the rates of ARD generation from the bioleach samples, biokinetic accelerated weathering tests were performed as outlined by Hesketh *et al.* (2010). Here, the finely ground, leached waste rock samples were bioleached using shake flask tests in which the pH, redox potential and iron concentrations were recorded with time. The effect of the ANC of the feed sample was observed from the initial rise in pH of the non-pH controlled flask tests. This rise resulted in a slower rate of bioleaching of the waste rock feed sample. In contrast, the leached waste rock samples showed a limited rise in pH due to the absence of the majority of the starting ANC, allowing for an increased rate of ARD generation as compared to the feed sample. No difference, however, was observed in the biokinetic test results from samples leached for differing durations. This correlated to the statistically insignificant changes in percentage total sulphur from the static ARD tests.

The role of the ANC was supported by the pH controlled flask tests where suppression of the initial rise in pH was countered through correction of the pH to a value of approximately 2.0. Hesketh *et al.* (2010) reported good agreement with the amount of acid added and the static ANC value. Here however, no correlation between these values was observed. Similarly, the previous authors reported good agreement of the final pH of the biokinetic tests with that of the pH of the static NAG experiment. Biokinetic tests performed on the waste rock samples, however, did not show this correlation. The classification of the samples as ARD generating was achieved through use of both the static and biokinetic tests.

#### 9.1.5. The effect of a 1% pyrite addition on the rate of ARD generation

Addition of liberated pyrite to the waste rock has potential to both increase the temperature of the dump, due to the exothermic oxidation reactions, and to provide a source for the generation of ferric iron and acid as leach agents. The effect of an easily accessible iron and sulphur lixiviate source was investigated through the addition of 1% (w/w) to a waste rock sample during the agglomeration process, in the absence of the temperature increase owing to the small scale experimental set-up. These experiments were compared to non-pyrite supplemented bioleach columns over 5 and 30 day periods. Comparison of the leachate profiles from these experiments showed differences in the redox potentials, iron concentrations and sulphur extraction. These were contrasted by the similar terminal durations estimated from both the copper and sulphur extraction profiles. The static ARD characterisation tests also showed no significant difference between the waste rock samples. These discrepancies necessitated further column experiments to investigate the limits in column reproducibility.

To this end, five, identically operated bioleach columns experiments were conducted with a view to quantifying the limitations with respect to reproducibility associated with the bioleach columns and further investigating whether the differences observed with and without pyrite-supplementation were significant. The differences observed between the replicate bioleach columns and those between the pyrite supplemented and non-supplemented experiments were similar, suggesting little effect of a 1 % pyrite addition on the rate of ARD generation.

Changes in the progression of ANC removal with increasing redox potential were also observed. Here, two distinct groups of ANC removal was observed, with a significant drop in ANC upon establishment of active bioleaching populations. Similarly, a relationship between the removal of sulphur and a rise in redox potential was observed. These samples were further analysed using biokinetic tests. The initial increase in pH of the biokinetic test was correlated with the residual ANC in the solid sample. The establishment of the “active” bioleaching population within the bioleach columns was mirrored by a decrease in solution pH. The pH of the feed and 10-day leached samples reaching a value of approximately 2.0, while tests of samples leached for the longer duration of 30 and 40 days reached a pH of approximately 1.87 over the two month test. The biokinetic flask redox potential and iron concentration profiles showed a large difference between the feed and leached samples. This was indicative of the effect of leaching on further iron liberation from the waste rock within the biokinetic tests.

## 9.2. Concluding Remarks

The aim of this study was to investigate the designed acceleration of ARD generation through establishing conditions favourable for growth and colonization of bioleaching micro-organisms to ensure the continuous supply of the leaching agents,  $\text{Fe}^{3+}$  and  $\text{H}^+$ . In this, the effects of acidity, aeration, increased temperature and pyrite addition were investigated using bioleach column experiments. The effects on the removal of ARD potential were assessed using Terminal Durations, estimated by linear extrapolation of the extraction data. The addition of acidity, aeration and an increased temperature resulted in a decrease in the time necessary for complete removal of the ARD potentials as estimated from the leachate data, whereas an addition of pyrite concentrate in the absence of its associated increase of temperature increased the time necessary. On a second waste rock sample of differing mineralogy, no significant effect of a 1% (w/w) pyrite addition on the rate of ARD generation was observed. Static characterization tests performed on the solid phases from both these experiments, however, did not support these findings.

These differences necessitated investigations into the inherent experimental errors using bioleach column reactors and the applicability of the static ARD characterization tests to waste rock samples. While the use of an in-bed sampling technique was suitable for investigations of the leachate from and microbial communities associated with the mineral ore surface in bioleach column experiments, the technique was not suitable for investigations requiring the analysis of samples of the solid phase due to the non-representative nature of the grab samples.

Furthermore, an investigation into the commonly used static ARD characterization tests revealed the common sources of error in the methods. It was demonstrated that, with milling of the entire 4 kg charge and its representative sampling, suitably representative solid phase samples could be attained. Further, the incremental Skousen test was selected for ANC determination and the LECO test confirmed as most appropriate for the determination of the sulphur content of solids routinely. The use of the biokinetic test on waste rock samples was investigated. While this method showed correlation with the ANC and NAG values for a tailings sample (Hesketh *et al.*, 2010), similar direct correlation was not obtained for the waste rock sample used in this study. The biokinetic tests however did provide information concerning the rate of ARD generation in the microbial and, in particular, a measure of the ANC and ARD generation potential.

## 9.3. Recommendations for further work

In conducting investigations into the accelerated removal of ARD generating potential, no attempt was made to optimize sulphide removal through the application of these conditions. The findings from this investigation, however, may be used to highlight areas for further investigation.

### 9.3.1. Application of ARD acceleration conditions from waste rock with different mineralogies

The application of added acidity, aeration and an increase in temperature significantly reduced the estimated time necessary for total ARD generation. Application of one or more of these conditions to a specifically constructed waste rock dump could further inform the feasibility of accelerated

sulphide removal of the larger particle sizes often constituting waste rock dumps. In addition, the application of such methods to waste rock samples whose mineralogies are not dominated by recalcitrant minerals such as chalcopyrite may show a greater acceleration in the removal of ARD potential.

### **9.3.2. Investigations into the differing rates of ANC and sulphur removal from waste rock**

This study highlighted differences in rates of removal of acid neutralizing and acid forming components within the waste rock samples. This understanding is important for the effective prediction of ARD from waste rock over time; hence approaches to this prediction should be investigated through the use of appropriate modelling regimes. Further investigation into this phenomenon could inform proposed ARD mitigation techniques which focus on the co-disposal of acid neutralizing and acid forming materials for the *in-situ* neutralization of ARD. In particular, the removal of the ANC component in bioleach column experiments conducted using a water feed solution at pH 5.5 is of particular interest since it has been shown (Section 1.1) that such conditions may exist for commercial waste rock dumps.

### **9.3.3. Investigations into the applicability of the biokinetic tests and its relationship to static ARD characterization tests for waste rock samples**

In the development of the biokinetic test, Hesketh *et al.* (2010) found good agreement between the biokinetic tests results and results from the ANC and NAG static characterization tests. Although the biokinetic results provided valuable information concerning the rates of ARD generation and the effect of the ANC on ARD formation within the batch system, no correlation between the ANC of the waste rock samples and the necessary amounts of H<sub>2</sub>SO<sub>4</sub> was observed. In addition, no correlation between the pH of the post-boil NAG solution and the achieved pH within the biokinetic flask tests was observed with the waste rock samples used in this study. A refinement of this biokinetic ARD test would aid in the characterization of the future rates of ARD generation from waste rock samples.

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## A. Appendices

### A.1. Waste rock mineralogies

Ore samples used in this study were constructed so as to resemble common, copper-bearing waste rock. Samples A & B were constructed using copper-bearing ore from Chile, South America and a run of mine sample from a zinc operation in South Africa. The bulk mineralogies for sample A and B are presented in Table A-1. Waste rock type C was constructed using two different copper bioleaching ores from Chile, South America, and zinc-bearing, run of mine and waste rock samples from South Africa. Obtained ore mineralogies are presented in .Copper, iron and sulphur grades for waste rock types A, Band C were quantified using acid digestion and AAS or ICP analysis for the copper and iron, and sulphur grades respectively. These are presented in **Error! Reference source not found.**

**Table A-1: Bulk mineralogy for waste rock types A & B constructed from a copper bioleaching and run of mine zinc ores**

Mineral	Formula	Weight %
Chalcopyrite	CuFeS <sub>2</sub>	1.27
Pyrrhotite 3T	FeS	0.45
Sphalerite	ZnS	0.44
Pyrite	FeS <sub>2</sub>	2.62
Chalcocite	Cu <sub>2</sub> S	0.13
Covellite	CuS	0.20
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	0.07
Enargite	Cu <sub>3</sub> AsS <sub>4</sub>	0.07
Galena	PbS	1.70
Rutile	TiO <sub>2</sub>	0.13
Goethite	FeO(OH)	0.07
Hematite	Fe <sub>2</sub> O <sub>3</sub>	0.13
Alunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	0.33
Svanbergite	SrAl <sub>3</sub> (PO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>	0.39
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH, F, Cl)	0.00
Hornblende	Ca <sub>2</sub> (Mg, Fe, Al) <sub>5</sub> (Al, Si) <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	1.31
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	16.45
Quartz	SiO <sub>2</sub>	39.80
Mica		21.52
Amphibole	(Mg,Fe) <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (Mg,Fe) <sub>3</sub> (OH) <sub>6</sub>	0.58
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	4.84
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>	3.73
Na orthoclase		1.90
Plagioclase	(Na, Ca)AlSi <sub>3</sub> O <sub>8</sub>	1.11
Biotite	K(Mg, Fe) <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (F, OH) <sub>2</sub>	0.33
Chlorite	(Mg,Fe) <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (Mg,Fe) <sub>3</sub> (OH) <sub>6</sub>	0.46

**Table A-2: Mineralogies for copper-bearing bioleach samples and the zinc run of mine sample used in the construction of waste rock C.**

Mineral	Formula	Bioleach A [wt %]	Bioleach B [wt%]	Zinc ROM [wt%]
Chalcopyrite	CuFeS <sub>2</sub>	0.5	0.5	2.79
Pyrrhotite 3T	FeS			1.33
Sphalerite	ZnS			1.31
Pyrite	FeS <sub>2</sub>	1.7	4	
Chalcocite	Cu <sub>2</sub> S	0.3	0.2	
Covellite	CuS	0.1	0.3	
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	0.1	0.1	
Enargite	Cu <sub>3</sub> AsS <sub>4</sub>		0.1	
Galena	PbS			5.03
Rutile	TiO <sub>2</sub>	0.2	0.2	
Goethite	FeO(OH)	0.3	0.1	
Hematite	Fe <sub>2</sub> O <sub>3</sub>	0.6	0.2	
Alunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	0.1	0.5	
Svanbergite	SrAl <sub>3</sub> (PO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>	0.1	0.6	
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH, F, Cl)	0.3	0	
Hornblende	Ca <sub>2</sub> (Mg, Fe, Al) <sub>5</sub> (Al, Si) <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	0.3	2	
Magnetite	Fe <sub>3</sub> O <sub>4</sub>		0.2	48.37
Quartz	SiO <sub>2</sub>	30.2	44.8	31.11
Mica			28.6	8.33
Amphibole	(Mg,Fe) <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (Mg,Fe) <sub>3</sub> (OH) <sub>6</sub>			1.73
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	4.3	7.4	
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>	18.9	5.7	
Na orthoclase		6.2	2.9	
Plagioclase	(Na, Ca)AlSi <sub>3</sub> O <sub>8</sub>	13.7	1.7	
Biotite	K(Mg, Fe) <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (F, OH) <sub>2</sub>	2	0.5	
Chlorite	(Mg,Fe) <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (Mg,Fe) <sub>3</sub> (OH) <sub>6</sub>	3.9	0.7	
Muscovite		15.5		
Corundum		0.1		

**Table A-3: Copper, iron and sulphur grades for waste rock samples A and B**

Waste rock Sample	Copper [%]	Iron [%]	Sulphur [%]
A	0.49	11.85	2.60
B	0.58	13.50	3.15
C	0.32	8.09	2.20

## A.2. ARD characterization tests

### A.2.1. Acid neutralizing capacity (ANC) tests

#### A.2.1.1. Fizz Rating

The fizz rating was used to determine the concentration and quantity of HCl, as well as the concentration of NaOH, used in the acid digestion and back titration of the waste rock samples during the ANC tests. Approximately 0.5 g of waste rock was reacted with 1-2 drops of 25 % HCl. The audible/visible fizz is noted, with the intensity rated according to Table A-4. The corresponding concentrations and quantities of the HCl and NaOH are then used in the ANC tests.

Table A-4: Fizz rating systems for determination of the HCl and NaOH requirements for the ANC tests

Reaction intensity	Fizz rating	HCl molarity [M]	HCl volume [mL]	NaOH molarity [M]
None	0	0.5	4	0.1
Slight	1	0.5	8	0.1
Moderate	2	0.5	20	0.5
Strong	3	0.5	40	0.5
Very strong	4	1.0	40	0.5
Carbonate	5	1.0	60	0.5

#### A.2.1.2. Sobek ANC test (Sobek, 1978)

##### Acid Digestion

- Weigh 2 g of dry sample into a 250 mL Erlenmeyer flask.
- Add HCl as per fizz rating.
- Add 20 mL deionised water to wash sample to the bottom of the flask.
- Heat the mixture at 80-90 °C for 2 hours, then cool to room temperature for one hour.
- Top up solution with 125 mL deionised water.
- Measure and record the pH of the mixture.

##### NaOH Titration

- Filter ANC solution
- Titrate the solution to pH 7.0 over a one hour period.
- Leave the solution to sit for 24 hours.
- Check the pH and correct to pH 7.0 with NaOH.
- Repeat until a stable pH is reached.

#### A.2.1.3. Skousen ANC test (Skousen *et al.*, 1997)

##### Acid Digestion

- Weigh 2 g of dry sample into a 250 mL Erlenmeyer flask.
- Add HCl as per fizz rating.
- Top up the solution with 100 mL deionised water.
- Boil the solution for 5 minutes.

- Cool to room temperature.

#### NaOH Titration

- Filter ANC solution.
- Back titrate the solution with NaOH (fizz rating) to pH 4.5.
- Add 5 mL, 30 % H<sub>2</sub>O<sub>2</sub> and boil for 5 minutes.
- Cool, and continue to titrate to pH 7.0.
- Leave the solution to stand for 24 hours.
- Check pH and titrate to pH 7.0.
- Add 5 mL, 30 % H<sub>2</sub>O<sub>2</sub> and boil for 5 minutes.
- Check pH and titrate to pH 7.0.
- Repeat over 72 hours.

#### **A.2.1.4. Incremental Skousen ANC test (Skousen *et al.*, 1997)**

##### Acid Digestion

- Follow acid digestion procedure as per Skousen ANC test.

##### NaOH Titration

- Filter ANC solution.
- Back titrate the solution with NaOH (fizz rating) to pH 4.5.
- Add 10 drops, 30 % H<sub>2</sub>O<sub>2</sub> and leave for 15 minutes.
- Check pH and titrate to pH 4.5
- Add 10 drops, 30 % H<sub>2</sub>O<sub>2</sub> and leave for 15 minutes.
- Repeat until no significant change in pH is observed.
- Back titrate the solution with NaOH to pH 7.0.
- Add 10 drops, 30 % H<sub>2</sub>O<sub>2</sub> and leave for 15 minutes.
- Check pH and titrate to pH 7.0
- Repeat until no significant change in pH is observed.
- Leave the solution to rest for 24 hours.
- Check pH and titrate to pH 7.0
- Add 10 drops, 30 % H<sub>2</sub>O<sub>2</sub> and leave for 24 hours.
- Repeat over a 72 hour period.

#### **A.2.1.5. ANC calculation**

The ANC of the sample is calculated using:

$$ANC = \frac{Volume_{HCl} * M_{acid} - Volume_{NaOH} * C * 49}{W_{sample}}$$

Where M<sub>acid</sub> is the molarity of the acid (M), W<sub>sample</sub>, the mass of the sample (g) and “C” taking into account the differing molarities of the NaOH and HCl solutions.

$$C = \frac{Volume_{HCl \text{ in Blank}}}{Volume_{NaOH \text{ titrated in Blank}}}$$

A conversion factor of 49 results in the ANC units of kg H<sub>2</sub>SO<sub>4</sub> / ton.

### **A.2.2. Net acid producing potential (NAPP)**

Quantification of the net acid production potential uses the difference between the maximum potential acidity (MPA) and the acid neutralizing capacity (ANC) of the ore samples.

$$NAPP = MPA - ANC$$

This difference is reported as a net acid producing potential value (NAPP) with units of kg H<sub>2</sub>SO<sub>4</sub> / ton of ore.

The maximum potential acidity of the samples is calculated using the total sulphur content determined via LECO analysis and the assumption that all the sulphur undergoes complete oxidized to form sulphuric acid.

$$MPA = 30.6 * S_{Total}$$

The total sulphur is in the form of a percentage value; giving the MPA value units of kg H<sub>2</sub>SO<sub>4</sub> / ton of ore.

### **A.2.3. Net acid generation (NAG; Miller *et al.*, 1997)**

Net acid generation tests use hydrogen peroxide to oxidize all the sulphur in a sample, with measurement of the resulting pH and necessary volume of NaOH used in the back titration to pH 7.0 allowing for the characterisation of the potentials for ARD generation. NAG tests were conducted as outlined by Miller *et al.* (1997).

#### **A.2.3.1. Single addition NAG test**

- Note: The 15 % H<sub>2</sub>O<sub>2</sub> solution should be at room temperature, with a pH of between pH 4.5 – pH 6.0.
- Weigh approximately 2.5 g of sample in a 500 mL Erlenmeyer flask.
- Add 250 mL, 15 % H<sub>2</sub>O<sub>2</sub> to the flask.
- Weigh the flask and record the mass.
- Cover with a watch glass and allow to stand for 24 hours.
- Measure the pre-boil NAG<sub>pH</sub>
- Gently heat the flask until effervescence stops or for a minimum of 2 hours. Add deionised water as necessary to prevent the sample from boiling dry.
- Allow the sample to cool to room temperature.
- Rinse down any solids that have adhered to the sides of the flasks to give a total mass corresponding to the pre-boil mass recorded.
- Record the final pH of the solution (NAG<sub>pH</sub>)
- Filter the solution, retaining both the solid and liquid phases.
- Titrate the solution to pH 4.5 and pH 7.0 and record the NaOH volumes used.

The NAG of the sample is calculated using:

$$NAG = \frac{49 * V * M}{W}$$

Where V is the total volume of NaOH used (mL), M is the molarity of the NaOH solution and W is the mass (g) of ore sample used in each reaction step. The inclusion of the constant, 49, in the equation allows for units of NAG of kg H<sub>2</sub>SO<sub>4</sub> / ton ore.

#### **A.2.3.2. Sequential NAG test**

- Carry out the single addition NAG test as stage 1 of the sequential test.
- Using the solid filter residue, repeat the single addition NAG procedure.
- Repeat until no further reaction is observed **and** the pH of the filtered NAG solution is above pH 4.5.
- The NAG of the sample is the sum of the NAGs calculated from each of the single addition steps.

#### **A.2.4. Biokinetic tests (Hesketh *et al.*, 2010)**

Biokinetic tests were conducted on the waste rock samples to gain insight in the rate of ARD generation. The tests were conducted as outlined by Hesketh *et al.* (2010).

- Add 150 mL autotrophic basal salts (ABS) solution to a 250 mL Erlenmeyer flask.
- Fit cotton wool bung, cover with foil, and autoclave to sterilise AND solution.
- After cooling, weigh in 7.5 grams of waste rock system into the flask.
- Inoculate with 10<sup>9</sup> cells per species from a mixture culture of iron and sulphur oxidizing micro-organism.
- Measure the redox potential and ensure the solution is at pH 2.0. using H<sub>2</sub>SO<sub>4</sub> if required.
- Record the mass of each flask before placing on a shaking incubator at 150 rpm at 37 °C.
- Before sampling, weigh the flask and top up with deionised water to account for water losses from evaporation.
- Record pH, redox potential, ferrous and total iron concentrations every sample day.

### A.3. ANOVA analysis (Schaeffer & McClave, 1995)

ANOVA analyses was used on the results obtained from the static ARD characterization tests in order to determine the significance of the observed differences between results. A 95 % confidence interval was set as the level of significance between experimental results. An example of the use of an ANOVA analysis in the determination of significance between six ANC experiments (A-F) conducted in triplicate is presented in Table A-5.

**Table A-5: Results from repeated ANC tests for samples A-F showing the use of ANOVA analysis in the determination of significant differences between samples**

Sample	ANC Values			Average ANC	Sum ANCs
	1	2	3		
A	3.70	3.17	3.30	3.39	10.18
B	0.99	0.67	1.10	0.92	2.76
C	1.33	1.23	0.89	1.15	3.45
D	1.33	0.89	1.41	1.21	3.63
E	0.33	0.99	1.10	0.81	2.43
F	0.55	0.77	0.78	0.70	2.11

Table A-6 details the quantification of the  $F_0$  and p-value, both giving an indication of the presence of significant differences in the six different ANC values. The  $F_0$  value is compared to the F-value given for a 95 % confidence interval (0.998, data not shown), which if larger, indicated the presence of significant differences between the six ANC values.

**Table A-6: ANOVA analysis table showing determination of the  $F_0$  and p values for the repeated ANC tests**

Variation	Sum of Squares	Degrees of freedom	Mean Square	$F_0$	p-value
Experiment	15.38	5	3.08	41.06	$3.87 \times 10^{-7}$
Error	0.9	12	0.07		
Total	16.28	17			

In addition, a Least Squared Difference (LSD) table may be constructed so as to determine which values within the data set show a significant difference. The LSD table compares every ANC value against all others to determine an "LSD" number. These are then compared against the LSD number determined using a set (95 %) confidence interval (1.61, data not shown) which, if larger, indicates the pair of values which are significantly different. These results are presented in Table A-7, which indicates that sample A is significantly difference from all other samples. In addition, no significant difference was observed between samples B-F.

**Table A-7: Least square difference table indicating the sources of significant differences between ANC values**

Sample	A	B	C	D	E	F
A		2.47	2.24	2.18	2.58	2.69
B			0.23	0.29	0.11	0.22
C				0.06	0.34	0.45
D					0.40	0.51
E						0.11

#### A.4. Terminal duration calculations

Terminal durations were estimated to predict the time necessary for the total removal of the ARD potential from the waste rock samples. These estimates were calculated from the leachate extraction curves through linear extrapolation.

##### A.4.1. Terminal duration estimations from leachate extraction profiles

Linear extrapolation was performed by fitting a linear trend line to the data of interest. Figure A-1: Terminal duration estimations from the linear extrapolation from copper and iron extraction profiles. shows linear trend lines fitted through the last four data points of copper and iron extraction profiles. Copper extraction as a function of time is given by the formula:

$$\text{Copper extraction \%} = 0.0075 * \text{Time days} + 8.0821$$

While iron extraction as a function of time is given by:

$$\text{Iron extraction \%} = 0.00009 * \text{Time days} + 0.2669$$

To extrapolate the time necessary for complete copper and iron extraction [100%], the equations are re-arranged:

$$\text{Time for 100\% copper extraction [years]} = (100 - 8.0821)/(0.075 * 365.25]$$

And

$$\text{Time for 100\% iron extraction [years]} = (100 - 0.2669)/[0.00009 * 365.25]$$

The times required for total copper and iron extraction therefore, the  $TD_{Cu}$  and  $TD_{Fe}$  estimates, are 3.35 and 3034 years respectively.

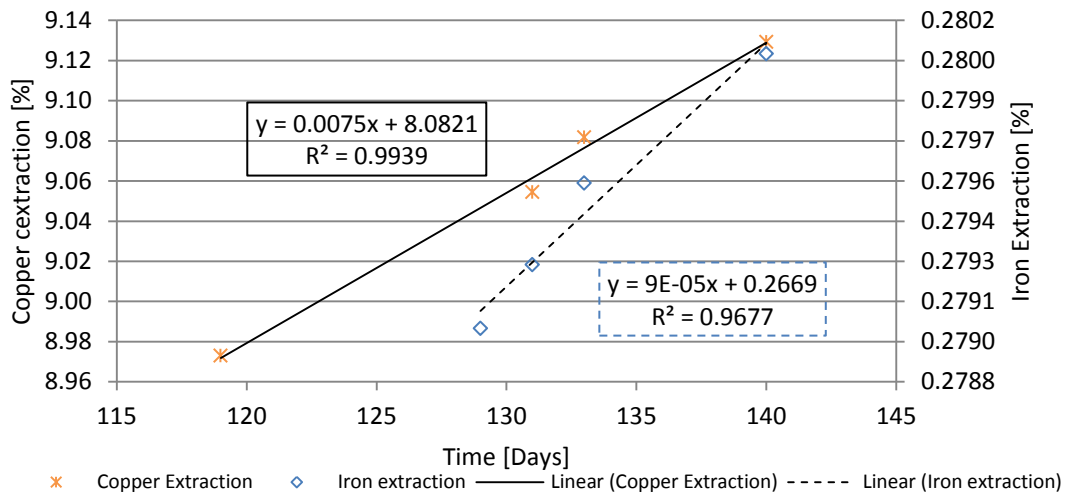


Figure A-1: Terminal duration estimations from the linear extrapolation from copper and iron extraction profiles.

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