UNIVERSITY OF CAPE TOWN

An Experimental Investigation of Leachate Generation Predictions of Waste from Copper Sulphide Ore Processing

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Thanks to GOD the Father, Son Jesus Christ and Holy Spirit for giving me strength,

This thesis is dedicated to my Mom for showing me endless love, there's no way I can pay you back, but I will always love you

Synopsis

The greatest environmental liability in the mineral processing industry is the prolonged environmental pollution and degradation of groundwater and land, resulting from Acid Mine Drainage (AMD) formation from mine wastes due to oxidation of sulphide minerals. AMD enhances the mobilisation of trace and minor metals contained in the wastes, thereby generating contaminated leachate, which may pollute the ground and surface water. It is imperative to minimise post-closure environmental impacts and liability associated with the long-term generation and dispersion of contaminated leachate from solid mine deposits. Therefore, prediction of the environmental impacts associated with solid mineral waste is essential to their effective management during all phases of a project life cycle including post-closure.

Solid mineral wastes are generally not well characterised and the ultimate fate of contaminants following waste disposal is poorly understood. It is necessary to investigate and understand the transport mechanisms of trace and minor metals and their complexes to understand their chemical cycles in nature. Mobility, transport, and partitioning of metals are strongly dependent on the specific chemical forms of metals, which in turn can change as the waste in a deposit ages, becoming different from that subjected to testing. Therefore; measurement of total metal concentration in the waste and use of standardised leachate extraction batch tests provide limited information required to evaluate the environmental impacts of solid mineral wastes.

The thesis investigates the design and application of a systematic empirical waste characterisation protocol so as to generate reliable data which can be interpreted in such a way that the potential release of contaminated leachate, and ultimate related environmental impacts, can be adequately and effectively forecast. A particular aim is to show how suitable laboratory protocols for AMD prediction procedures and metal chemical speciation can be used to augment mineralogical and composition knowledge prior to the selection of appropriate leaching tests to feed into leachate prediction modelling. Most of the laboratory work was carried out on tailings from a porphyry copper sulphide ore sample from the Kennecott deposit in Utah.

The XRD analysis carried out on the tailings sample, and total metal analysis carried out on ore, concentrate and tailings confirmed that the mineralogical make-up of the sample, as well as major, minor and trace metal content agreed with recently published generalised predictions for the character of main process streams in copper sulphide concentrators.

The AMD prediction test methods investigated were acid neutralisation capacity (ANC) test (Standard Sobek 1978, Skousen H_2O_2 and Additional/Incremental H_2O_2 ANC test) and Net Acid Generation (NAG) tests (Single addition, sequential and kinetic NAG test). The mineralogy of the sample indicated that the sample has a significant acid forming potential, as evident from the maximum production acidity (MPA) of 89 kg H_2SO_4/t. As expected from the mineralogical data, Skousen H_2O_2 and Additional/Incremental H_2O_2 ANC tests were found to be suitable for Cu-tailings sample studied since they corrected for siderite effects, and also produced comparable results. The single addition NAG test did not reliably reflect the acid forming potential of the sample because of a relatively high S content of 2.9 wt%, resulting in catalytic decomposition of H_2O_2, which in turn underestimate the net acid generation of the sample. The results demonstrated that detailed tests such as sequential and kinetic NAG tests can be used to overcome these limitations. The sequential NAG test indicated that over 98 % of the total S was oxidised after 3 stages. A considerable amount of acidity was produced in stage 2, showing a significant lag in acid production. Kinetic NAG test confirmed the above findings by showing a long lag in acid production, and slow reactivity of pyrite and carbonate minerals, through pH and temperature profiles.

Two types of 7-step sequential extraction procedures were conducted with metals extracted from the following operationally-defined phases, in the given order:

> **Sequential extraction scheme A**: *Water soluble; Exchangeable; Amorphous Fe-oxide; Crystalline Fe-oxide; Organic matter and secondary Cu-sulphide; Primary sulphides; Residual (silicates).*
> **Sequential extraction scheme B**: Water soluble; Exchangeable; Carbonate; Amorphous Fe-oxide; Crystalline Fe-oxide; Primary sulphides; Residual (silicates).

The results indicated that when applying sequential extraction procedures to Cu tailings samples it is i) possible to distinguish between the exchangeable fraction and carbonate fraction (if required), and ii) necessary and important to separate the organic matter and secondary Cu-sulphide fraction from the primary sulphide fraction, and iii) necessary and important to apply a kinetic dissolution study to help obtain the contact time required for complete dissolution of a particular fraction and enhance the selectivity of reagents.

The mobilisation, under natural conditions, of major metals, Ca>Mn>Mg>Cu and minor metals, Cd>Co>Zn>Ni>Pb associated with the ion exchangeable and carbonate phases was found to be feasible. This indicated a release of metals that are readily available for uptake and potentially mobile into the environment. Although the extractions were conducted on relatively unoxidised tailings, the results indicated that some secondary precipitates of Fe (III) oxyhydroxide were present, probably due to oxidation of sulphides in the mill process water and during storage. The metal content in the amorphous Fe oxide fraction is expected to increase during weathering processes, since Fe (III) oxyhydroxide exhibits a strong affinity for metals. Primary sulphides accounted for significant amounts of Fe, Cu, Cr, Zn,

Cd, As, Mo, Ag, Pb and Ni, which are probably present as sulphides. These metals are expected to be released by oxidation process.

The AMD prediction tests and the sequential extraction results indicated that a prior knowledge of the mineralogy of a waste sample is required in order to i) avoid choosing a method that would yield unreliable results, and ii) enhance the interpretation of the results obtained by these prediction methods. The information derived from the AMD prediction tests and sequential extraction procedures provided an understanding of the mechanisms and parameters controlling AMD production and metal release. A generic structure of a solid mineral waste characterisation protocol was developed by combining the application of mineralogical analysis, AMD prediction procedures, sequential extraction procedures and kinetic dissolution studies aimed to generate geochemical information that can be used to study factors and mechanisms influencing AMD production and metal release.

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PART A

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Glossary

The major terms used in this thesis are listed below:

ABA	Acid base accounting for acid generation prediction.
Additional/Incremental H_2O_2 ANC method	ANC test method used to account for siderite effects. This procedure involved addition H_2O_2 and NaOH to the ANC digest solution until the pH stabilises.
After-boil NAG_{pH}	NAG_{pH} after applying the boiling step in the NAG test
AMD	Acid mine drainage caused by sulphide oxidation.
ANC	Acid neutralisation capacity of a sample in kg H_2SO_4/t determined by acid digestion and back titration with NaOH. ANC is equivalent to neutralisation potential (NP) although kg $CaCO_3$/t
ARD	Acid Rock Drainage caused by sulphide oxidation.
Fizz rating	Involves reaction of sample with 25% HCl to determine the strength of HCl and NaOH, and the volume of HCl required for ANC tests.
HOAc	Acetic acid (CH_3OOH).
ICP-MS	Inductively Coupled Plasma, coupled with Mass Spectroscopy used for metal analysis in solutions.
KNAG	Kinetic Net Acid Generation. Same as single addition but pH and temperature are monitored with time.
Lag period	Time to reach the temperature maximum in NAG test due to catalytic decomposition of H_2O_2.
LECO analysis	High temperature combustion-infrared spectrophotometric used to determine total S.
Metal chemical speciation	Refers to metal occurrence in or distribution among different species, also referred to as metal partitioning.
MPA	Maximum potential acidity, determined from total S content, kg H_2SO_4/t.
NAG tests	Net acid generation test, involving reaction of a sample with 15 % H_2O_2 and back titrates to pH 4.5 and 7.0. NAG test variations employed in this study were single addition NAG test, the sequential NAG test, and the kinetic NAG test.

NAG at pH 4.5	Measures the acidity of the solution titrated to pH 4.5 kg H_2SO_4/t.
NAG at pH 7.0	Measures the acidity of the solution titrated to pH 7.0 kg H_2SO_4/t.
NAG_{pH} or After-boiling NAG_{pH}	pH of the NAG test solution after heating the solution.
NAPP	Net Acid Producing Potential, determined from MAP – ANC (kg H_2SO_4/t).
NH_4OAc	Ammonium acetate.
Post-boiling NAG_{pH}	pH of the NAG test solution before the application of the heating step.
Sequential extraction procedures/schemes	Test method used to separate metals into different chemical forms/phases.
Sequential NAG test	This is a multi-stage procedure involving a series of single addition NAG tests on one sample (*i.e.* 2.5 g of sample is reacted two or more times with 250 ml aliquots of 15% H_2O_2). At the end of each stage, the sample is filtered and the solution is used for measurement of NAG_{pH} and NAG capacity.
Single addition NAG test	Involves a single addition of 15 % H_2O_2, the sample is filtered after the test; solution is used for measurement of NAG_{pH} and NAG capacity.
Skousen H_2O_2 siderite correction ANC test	Modification of the standard Skousen ANC test used to improve the efficiency of this test by accounting for siderite effects. Digestion includes a boiling step.
Standard Skousen ANC test	This test involved digestion and titration to pH 7.0, without H_2O_2 addition.
XRD	X-ray diffraction for mineralogical analysis.

Chapter 1

INTRODUCTION

1.1 Overview of mineral processing and environmental impacts

The safe management of large-volume wastes has been identified as a key performance element for environmental sustainability in the mining industry, and this includes the possible release and migration of metals into surrounding water bodies. Prolonged environmental pollution and degradation of groundwater and land is known to be the greatest environmental liability in the mineral processing industry. Extensive mining activities have produced high volumes of waste in the past. South Africa's total waste generated in 2001 was estimated to be 566 million tonnes with the majority of 464 million tons (82%) being generated by the mining sector (CMSA, 2001).

Acidic sulphur-rich wastewaters are the by-products of a variety of industrial operations such as galvanic processing; however the major producer of such effluents is the mining industry (Johnson & Hallberg, 2005), with long-term and potentially devastating consequences for the environment and the health of humans and animals. Acid mine drainage (AMD) has been described as the largest single environmental problem facing the mining industry, particularly because it is persistent and costly, and tends to be a liability for mines long after they cease to operate. The impacts associated with AMD are primarily caused by dissolved metals released either directly from sulphide minerals or by acid attack on associated minerals within the rock. A key parameter that determines the environmental risk associated with mine sites is the drainage pH, as low pH normally is associated with high metal concentrations and mobility.

In brief, the major cause of AMD is the accelerated oxidation of iron pyrite (FeS_2), which is the most abundant sulphide mineral in the earth's crust, and other sulphidic minerals, resulting from the exposure of these minerals to both oxygen and water. AMD issues may be associated with mining and processing of a wide range of ores including: Coal, Copper, Gold, Lead, Zinc, and Iron ore and heavy minerals. Overburden and waste rocks, floatation tailings, open pit voids and spent ore are the potential sources of AMD on a mine site. Mining activities are temporary and after closure all areas including the tailings deposit must be left in a physically and chemically stable condition. The potentially acid-forming material

needs to be managed so that environmental impacts do not occur due to AMD where acidic water, with associated high metal content, is released to the environment, which may impact groundwater and land, both from surface and underground mines, for decades or even hundreds of years after mine closure.

Acid mine drainage (AMD) may form in underground workings of deep mines, although this is generally insignificant when a mine is in active production as water tables are kept artificially low by pumping. However, after closure and the pumps turned off, the rebound of the water table can lead to contaminated groundwater being discharged. Sometimes it may lead to tragic events like the one that took place at old mines near Krugersdorp on the West Rand in 2002 when polluted water entered the environment through a borehole upstream and an old vent shaft pushed open by the force of the water (Mines & Communities, 2005). Oxidising iron pyrites tinged the water bright red with low pH and also had toxic metal levels.

While AMD generation is a natural process, its potential magnitude can be greatly increased by mining due to greater accessibility of air through mine workings, wastes and tailings; greater surface areas for sulphides in mine workings, wastes especially tailings and; different composition of tailings as a results of mineral processing (Nordstrom & Alpers, 1999). Johnson & Hallberg, 2005 reported that the AMD that flows from tailings may be more aggressive than that which discharges from the mine itself, due to the more disaggregated and more concentrated nature of the acid generating minerals in these wastes materials.

There is a great need to minimise post-closure environmental impacts and liability associated with the long-term generation and dispersion of contaminated leachate from solid mine deposits. Therefore, prediction of the environmental impacts associated with solid mineral waste is essential to their effective management during all phases of a project life cycle including post-closure.

1.2 Problem statement

The increasingly strict environmental regulations require the development of new analytical methods and meaningful tools that can generate data that can be interpreted in such a way that the leachate generation and ultimate environmental impact of the solid mineral wastes can be adequately forecast. The determination of total metal concentration is insufficient if the ultimate goal is to estimate mobility and bioavailability of metals. Concerning natural systems, the mobility, transport, and partitioning of metals are strongly dependent on the specific chemical forms of metals, which in turn can change as the waste in a deposit ages. In addition, it is the speciation of a metal, rather that its total concentration, that influences its effect on an organism. Standardised leachate extraction batch tests such as the Toxicity

Characteristic Leaching Procedure (TCLP), which are used to determine whether the solid waste exhibits hazardous characteristics, also provide only limited information on the mobility and bioavailability of metals on the waste in its state as subjected to testing.

Solid mineral wastes are generally complex and the validity and interpretation of the results derived from such extraction and analytical procedures are deficient, due to the fact that empirical waste characterisation, such as the ones mentioned above, are applied to wastes indiscriminately with little consideration of their complex nature in terms of their physical and chemical interactions, which hinder an understanding of leachate generation behaviour. Thus solid mineral wastes are not well characterised and the ultimate fate of contaminants following waste disposal is poorly understood. It is necessary to investigate and understand the transport mechanisms of trace and minor metals and their complexes to understand their chemical cycles in nature.

This problem is being addressed by the Water Research Commission (WRC) project entitled "Solid Mineral Waste Impact Predictions" (WRC K5/1550), with the aim to enhance capabilities for the reliable, quantitative prediction of water-related impacts associated with solid waste and to provide means of effectively integrating such information into decision-making process.

The project aims to overcome the above shortcomings through developing a conceptual methodology for solid mineral waste characterisation and leach behaviour of various wastes to the mining and mineral processing industries to predict impacts (Task 2 of the WRC-project by Petrie *et al.*, 2004). This methodology entails the predictions of key waste characteristics on the basis of their sources (ore and composition) and origin (waste generating process). Broadhurst *et al.*, 2005b (Task 6 of the WRC-report) developed a methodology for doing so, and illustrated it by predicting the key characteristics of waste streams from the beneficiation of copper sulphide ores. However, her methodology still needs to be demonstrated in a case study. Copper sulphide tailings from the Kennecott Utah Copper Corporation's Bingham Canyon mine were selected as a case study to help focus the research. Equally, the advanced leachate generation assessment protocols suggested in other tasks of the WRC project need to be put to the test and assessed within this case study.

1.3 Study objectives

Based on the problem statement, the work presented in this study aims to achieve the following primary objectives:

1. To design, confirm, and fine-tune a systematic empirical waste characterisation protocol so as to generate data which can be interpreted in such a way that the potential release of contaminated leachate, and ultimately related environmental impacts, can be adequately and effectively forecast. In particular, the aim is to investigate suitable laboratory protocols for:

Acid Mine Drainage Evaluation:

- Use the knowledge of the mineralogy of the waste to provide a framework to choosing the most appropriate method for AMD prediction test and assess the reliability of AMD interpretation.
- Investigate a variety of Acid Mine Drainage (AMD) testing protocols, so as to identify opportunities for AMD test modification and improvement.

Metal chemical speciation:

- Evaluate a set of sequential extraction procedures and determine their limitations and applicability to copper tailings.
- Obtain a relationship between the mineralogy of the waste and the sequential extraction data.
- Show how this knowledge can be used to understand the mode of occurrence of metals in copper sulphide tailings essential for environmental assessment.
- Identify and quantify contaminants that will be potentially released and/or influence contaminant release to the environment.

2. To validate the first-order predictions for metals deportment into tailings from copper sulphide ore processing as predicted on the basis of source (ore type and composition) and origin (generation process).

To achieve both objectives 1 and 2, laboratory testwork was undertaken on a Cu-tailings sample, generated from an ore sample of the well known porphyry Cu-deposit at Kennecott Copper Utah.

1.4 Research approach and thesis structure

In summary, the research approach comprised:

1. A literature review of the generic proposed systematic approach to waste characterisation and leachate generation prediction, acid mine drainage (AMD) generation mechanisms including the factors affecting AMD generation and chemical extraction for metal speciation.
2. An experimental work programme aimed at obtaining relevant data for waste characterisation and to achieve the objectives of the study.
3. Evaluation of the findings including a discussion of advantages and limitations of individual tests.
4. Optimisation of some of the test methods employed based on the findings.
5. Summary and conclusion of the thesis.

The thesis is structured as follows:

Chapter 2: ***Literature Review***	Existing literature is critically assessed to outline: • The major AMD processes and methods for AMD prediction. • The available sequential extraction methodologies and their application to mine wastes.
Chapter 3: ***Methodology***	Sample acquisition, test approach and methodologies are outlined.
Chapter 4: ***Mineralogical Characterisation*** ***Evaluation of First-order Metal Deportment Modelling***	The results of the mineralogical characterisation of the Kennecott copper tailings are presented, which provide background information for the selection of test methods and enhance the interpretation of the tests in Chapter 5 and 6. Validation of the first order predictions for metal deportment is also presented in this chapter.

Chapter 5: ***Acid Base Accounting (ABA) & net Acid Generation (NAG) Tests Results***	ABA (three variations) and NAG (three variations) are presented and discussed based on the mineralogical findings in Chapter 4.
Chapter 6: ***Sequential Extraction Procedure results***	This chapter focuses on the comparison of the results obtained by the two types of sequential extraction schemes employed in this study. It highlights the limitations of these sequential extractions and provides background information for modification. A modification process of the sequential extraction schemes to obtain optimum extraction in selected phases/fractions. An empirical waste characterisation protocol for the evaluation of solid mineral wastes is presented. This protocol is based on the outcomes of the test procedures conducted in this research.
Chapter 7: ***Summary and Conclusions***	Major outcomes are summarised, and recommendations listed.

The thesis includes an appendix in PART B of the thesis that contains details of experimental procedures that were used during the study. The appendix also contains tables of results and diagrams that were used to evaluate the findings.

Chapter 2

LITERATURE REVIEW

As discussed in Chapter 1, the interpretation of results derived from current available waste characterisation methodologies is deficient and applied to waste indiscriminately, thus there is a need to improve waste characterisation in terms of both general approach, and the design and interpretation of empirical methodologies. This chapter begins with a brief outline of the proposed approach to waste characterisation and leachate generation prediction (Section.2.1 and 2.2).

Section 2.3 provides an overview of the AMD to obtain an understanding of AMD generation and subsequent metal release. Section 2.4 indicates the waste characterisation methods that are critically reviewed in this chapter. The methods of predicting AMD are presented in Section 2.5. Sequential extraction procedures and their applications are described in Section 2.6, followed by a summary of the literature review in Section 2.7.

2.1 A conceptual waste characterisation approach

Laboratory scale determination of waste characteristics is a necessary and integral part of the reliable and accurate quantification of contaminant release, and ultimately related environmental impacts. A conceptual methodology for solid waste characterisation and leachate generation prediction has been developed in Task 6 of the WRC-project K5/1550 (Broadhurst *et al.*, 2005b). This conceptual methodology is illustrated in Figure 2.1. Prediction of waste characteristics on the bases of source and origin is a fundamental component in this conceptual methodology, and is used to inform the test procedures in Levels 2 and 3.

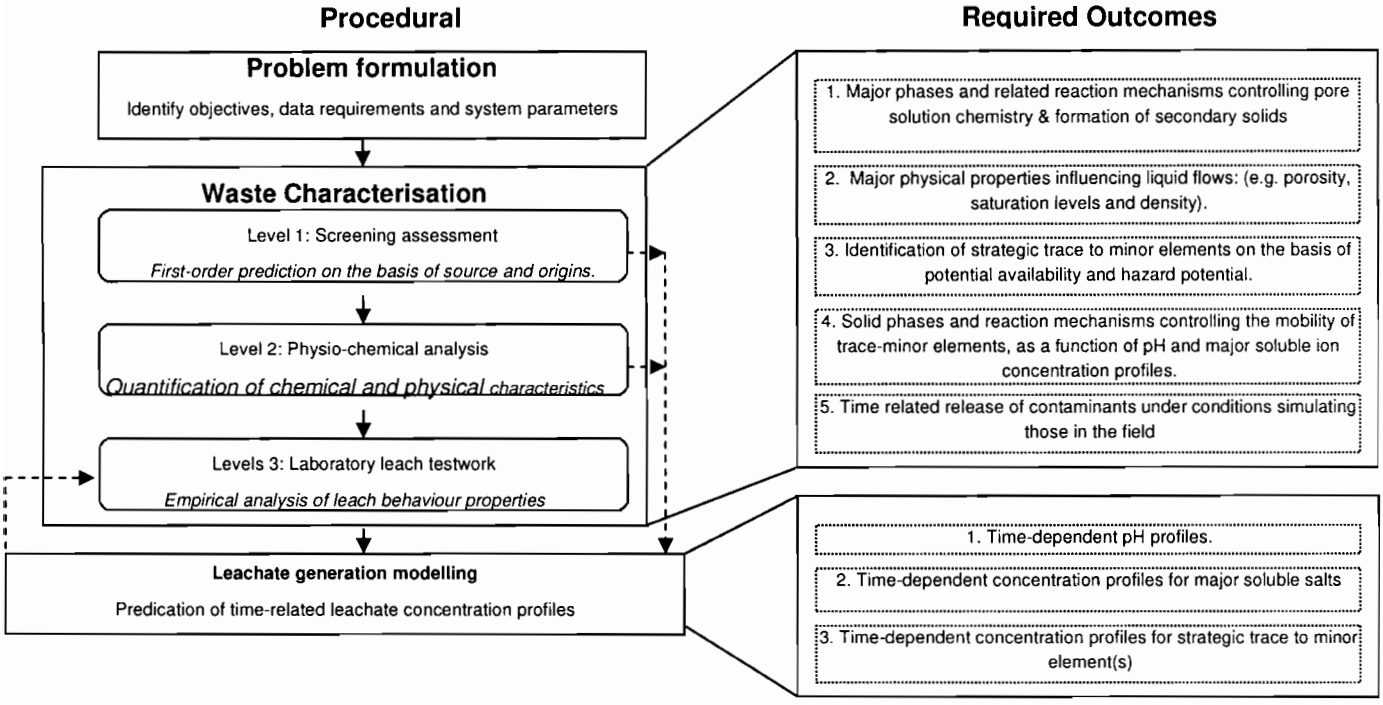


Figure 2.1: Procedural Framework for Systematic Solid Mineral Waste Characterisation and Leachate Generation Predictions, and Related Outcomes (Broadhurst *et al.*, 2005)

This procedure can be summarised as follows:

***Level 1**: Screening Assessment*

The purpose of this level it to predicts potential concentration, form, and leach behaviour of elements on the basis of sources (ore type and composition) and origins (generating process), with respect to the mechanisms and parameters influencing element deportment through the ore →beneficiation→ waste→ leachate→ environmental impact chain. This step provides an indication of what needs to be analysed for, instead of applying test methods formulaically and blindly. A good understanding of the geological characteristics of mineral deposits is crucial to the development of effective mining-environmental prediction practices.

***Level 2**: Physio-Chemical Analysis*

Chemical waste characterisation involves chemical analysis to determine total element concentration, sulphur and carbon speciation, mineralogy and acid generation or neutralising capacity of the waste. The sequential extraction test will provide information on the mode of occurrence and availability of the contaminants. Analytical techniques used for chemical analysis are discussed in Section 2.4 through 2.6. The physical properties of the waste can include: particle size distribution,

porosity, density, moisture content and surface area. The knowledge of the physio-chemical properties will then support the Level 1 predictions and provide properties influencing leach behaviour.

Level 3: Laboratory Leach Test Work

Empirical laboratory leach tests are conducted to obtain information and data pertaining to the general leach behaviour. Level 1 and 2 predictions can be supported through manipulation of the leach parameters such as pH and liquid/solid ratio. Leach conditions should correspond with expected ranges in a typical disposal scenario.

A comprehensive first order data set pertaining to the metal concentration in porphyry copper sulphide ore, tailings and concentrate was predicted and presented by Broadhurst *et al.*, 2005a in Task 4 of the WRC-project.

2.2 Leachate generation

Leachate generation occurs when water percolates through the solid waste deposit. Highly acidic conditions due to oxidation of sulphide minerals increase the dissolution, mobilisation and transportation of toxic metals, causing them to leach from the solid phase to the liquid phase. The contaminated leachate flows to the base of the waste deposit and if a suitable liner and leachate collection system are not in place, the liquid (which generally contains acid, salts and dissolved metals released during exposure) contaminates the surrounding soil and groundwater. Surface wash-off of soluble metals on the outside of the waste deposit may also play a major role in the release and impact on soil and ground water due to further distribution of contaminants (van der Sloot & Dijkstra, 2004).

An understanding of the parameters and mechanisms governing the leachate generation is required in order to predict the long-term behaviour of solid mineral wastes. There are two key processes that control the release of contaminants from the solid waste to the liquid phase: physical transport mechanism (surface wash-off, percolation, diffusion) and chemical mechanism (solubility controlled release or availability in the waste) (van der Sloot & Dijkstra, 2004).

Solid mineral wastes usually show percolation dominated release (i.e. release due to percolation of water through the solid waste deposits). The percolating water forms an aqueous environment which fills the pore voids between solid waste particles. Most solid waste particles are porous and the aqueous phase may diffuse into the particle pores, exposing the outside and inside surfaces of the particles to the aqueous environment. Under these conditions, soluble species such as metal ions and salts can be removed from the solid

phase. Figure 2.2 presents mechanisms governing the release of contaminants from the solid to the liquid phase. The main reaction mechanisms controlling the mobility of solid waste metals include: dissolution/precipitation, oxidation/reduction and adsorption/desorption.

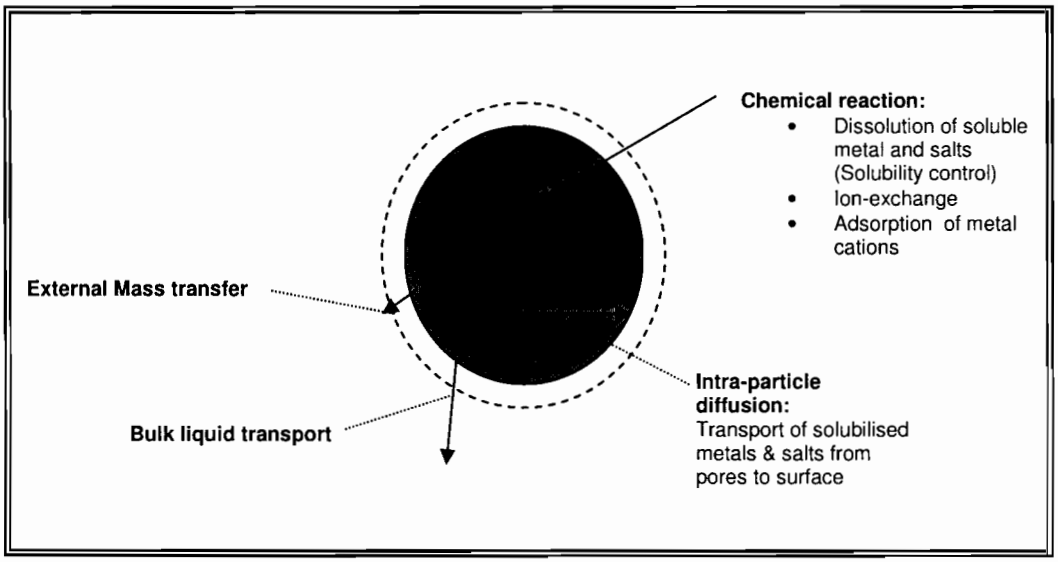


Figure 2.2: Mechanisms governing leachate generation

Chemical factors influencing leachate generation include: pH, chemical form and distribution of contaminants; metal availability or total composition/concentration; acid-base buffering capacity, redox and time. The physical transportation factors include the ones mentioned in Section 2.1, with an addition of percolation and surface wash-off and diffusion. pH is probably the most important factor governing metal solubility from mineral surfaces, transport, and eventually bioavailability of metals in aqueous solutions (John and Leventhal, 1995; van der Sloot & Dijkstra, 2004). Particulate size and resulting total surface area are both important factors in adsorption processes and can affect metal bioavailability (Salomons, 1995).

Despite the deficiencies mentioned in Chapter 1, test procedures such as batch leach procedure (TCLP, water leach and acid rainfall tests), column leach test, serial batch test, sequential chemical extraction and acid generation/neutralisation test, can be used to provide a better understanding of complex and leach behaviour within the solid waste deposits, provided they are systematic and informed by the characteristics of the solid wastes being tested and, mechanisms and parameters involved in leachate generation.

2.3 Overview of Acid Mine Generation (AMD)

The process of acid generation and metal release leading to formation of acid mine drainage has been extensively reported (Nordstrom & Alpers, 1999; Jambor, 2003). Many metals occur mainly as sulphide ores (e.g. zinc in sphalerite), which tend to be associated with pyrite (FeS_2), which is the most abundant mineral. Sulphide minerals that are exposed by mining are unstable in the presence of atmospheric oxygen or oxygenated ground waters, and oxidation of the pyrite and other sulphide minerals generate acidic metal-rich mine drainage.

2.3.1 AMD generation mechanisms

The relative resistance of different sulphide minerals to weathering varies and depends on factors such as, crystallinity, trace element content, and mineral assemblage (Hammarstrom & Smith, 2002). The amount of acid generated is a complex function of whether oxygen or aqueous ferric iron is the oxidant, and whether hydrous metal oxides or other minerals precipitate as a result of the oxidation process (Plumlee & Logsdon, 1999).

Table 2.1 lists some of the important weathering and oxidation reactions that controls the formation and hydrochemical composition of AMD. The oxidation of pyrite and the formation of acid mine drainage may be considered to take place in three major steps:

- Oxidation of pyrite by oxygen (Eq. a). This reaction release ferrous iron (Fe^{2+}) and sulphuric acid.
- The ferrous ions released in Eq. a are subsequently oxidised by oxygen to produce ferric iron (Fe^{3+}) and consuming acidity in the process (Eq. b). Oxidation reaction equation b proceeds rapidly if the environment is oxidising and near neutral conditions, but is inhibited in reducing or acidic. In this mechanism Fe^{2+} and Fe^{3+} ions are cycled between the pyrite oxidation reaction and Fe^{2+} ion oxidation reaction.

  In general, the rate of oxidation of pyrite increases with the concentration of ferric iron thus controlled by the rate of oxidation of ferrous iron, and decreases with the concentration of Fe^{2+} and H^+ ions (Holmes & Crundwell, 2000; Dold, 2005). Aqueous ferric iron is a very aggressive oxidant. When it reacts with sulphides (Eq. d), it generates significantly greater quantities of acid than are generated by oxygen-driven oxidation. Sulphide oxidation by ferric iron is also considerably faster than the reaction with oxygen as an oxidant (Nordstrom & Alpers, 1999) and the regeneration of ferric iron (which is reduced to ferrous on reaction with pyrite) is the key reaction in promoting the ongoing oxidation of the sulphide minerals (Johnson & Hallberg, 2005). Oxidation of pyrite by ferric ions occurs at low pH conditions.

- Acid mine water, rich in ferric iron, will completely oxidise, hydrolyse and may precipitate to form ferric hydroxides depending on pH-Eh conditions, generating a much greater net production of acidity (Eq. c). Reaction equation c produces acidity in the form of H^+. Dold, 2005 reported that, if pH is less than about 3.5, the solid ferric Fe^{3+} oxyhydroxides/oxyhydroxysulphates is unstable and Fe^{3+} remains in solution, hence solids form if the pH is above about 3.5.

Table 2.1: Stoichiometry of some of the weathering and oxidation reactions (Banwart & Malmström, 2001)

	Process	Reaction stoichiometry	Tracer
a	Pyrite oxidation (oxygen path)	$FeS_2(s) + H_2O + 7/2O_2(aq) \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$	Fe, SO_4^{2-}
b	Ferrous iron oxidation	$2Fe^{2+} + 1/2O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O$	Fe
c	Ferric iron precipitation	$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H^+$	Fe
d	Pyrite oxidation by (ferric iron path)	$14Fe^{3+} + FeS_2(s) + 8H_2O \rightarrow 2SO_4^{2-} + 15Fe^{2+} + 16H^+$	Fe, SO_4^{2-}
e	Sphalerite oxidation	$ZnS(s) + 2O_2(aq) \rightarrow Zn^{2+} + SO_4^{2-}$	Zn^{2+}, SO_4^{2-}
f	Chalcopyrite oxidation	$CuFeS_2(s) + 4O_2(aq) \rightarrow Fe^{2+} + Cu^{2+} + 2SO_4^{2-}$	Fe, Cu^{2+} SO_4^{2-}
g	Calcite weathering $6 \leq pH \leq 9$	$CaCO_3(s) + H^+ \rightarrow Ca^{2+} + HCO_3^-$	Ca^{2+}
h	Calcite weathering $pH \leq 6$	$CaCO_3(s) + 2H^+ \rightarrow Ca^{2+} + CO_2(g) + H_2O$	Ca^{2+} ($CO_2(g)$)
i	Dolomite weathering $6 \leq pH \leq 9$	$MgCa(CO_3)_2(s) + 2H^+ \rightarrow Mg^{2+} + Ca^{2+} + 2HCO_3^-$	Mg^{2+}, Ca^{2+}
j	Dolomite weathering $pH \leq 6$	$MgCa(CO_3)_2(s) + 4H^+ \rightarrow Mg^{2+} + Ca^{2+} + 2CO_2(g) + 2H_2O$	Mg^{2+}, Ca^{2+} ($CO_2(g)$)
k	Biotite weathering	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2(s) + 7H^+ \rightarrow K^+ + 3(Mg^{2+}, Fe^{2+}) + Al(OH)_3(s) + 3SiO_2(s) + 3H_2O$	K^+, Fe, Mg^{2+}
l	Plagioclase weathering (oligoclase)	$Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_8(s) + 1.3H^+ + 1.3H_2O \rightarrow 0.3Ca^{2+} + 0.7Na^+ + 1.3Al(OH)_3(s) + 2.7SiO_2(s)$	Ca^{2+}, Na^+

The overall reaction for the breakdown of pyrite to Fe^{3+} oxyhydroxides or oxyhydroxysulfates and generation of acid is given by:

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \qquad \text{Eq. 1}$$

The ferric hydroxide oxidation product shown in reaction equation 1 can include a variety of secondary Fe^{3+} oxide, oxyhydroxide or oxyhydroxide-sulphate minerals such as goethite, ferrihydrite, schwertmannite and jarosite. Oxidation of other sulphide minerals such as sphalerite (Eq. e) and chalcopyrite (Eq. f) can occur, which may not necessarily produce acidity. Reaction equations e and f can release significant amounts of soluble metal ions such as Zn^{2+} and Cu^{2+}, respectively to the solution (Banwart & Malmström, 2001). The solubility and therefore the mobility and bioavailability of metal ions are strongly dependent on the pH. Solubility of metal increases with decreasing pH, and more dissolved metals become potentially available for incorporation in biological processes as pH decreases (John & Leventhal, 1995). Therefore attenuation of acidity and pH buffering are key controls on the environmental behaviour of metals ions that are released in minewater discharge.

The most effective minerals for neutralising acidity generated by oxidation of pyrite minerals and for buffering the pH are those containing calcium carbonate and magnesium carbonate, including calcite, magnesite, dolomite, and ankerite ($CaCO_3$, $MgCO_3$, $CaMg(CO_3)_2$, and $CaFe(CO_3)_2$, respectively) (Plumlee & Logsdon, 1999; Lapakko, 2002). Dissolution of carbonates release alkaline earth and metal cations, including Ca, Mg, Fe, Mg and Mn, which may participate in the formation of secondary solid minerals, including simple hydroxide solids. In some cases the secondary solid minerals formed through dissolution of carbonates can later dissolve and contribute to acid neutralisation (Dold, 2005). Reaction equations g through j in Table 2.1 illustrate the dissolution of some of the common carbonate minerals mentioned above. The carbonate minerals reactivity decrease in the following sequence: calcite ($CaCO_3$); rhodochrosite ($MnCO_3$); siderite ($FeCO_3$); dolomite ($CaMg(CO_3)_2$ and magnesite ($MgCO_3$) (Lapakko, 2002). Siderite may act under certain conditions as a neutraliser and under other conditions as acid producer. However, it was suggested that Fe, Al and some Mn bearing carbonates do not provide net acid neutralisation under oxidising conditions. This is due to oxidation of the released Fe, Al or Mn, the subsequent hydrolysis and precipitation of these metals, and the consequent acid production. These mechanisms are described in Section 2.5.3.

When reactive carbonates are absent or depleted aluminosilicate minerals such as chlorite, biotite, K-feldspar, muscovite and albite in the tailings play a role in long-term acid neutralisation (Weber *et al.*, 2004b). However, in practice, most silicates provide much less neutralising capacity than carbonates because of their slow reaction kinetics. In most cases silicates weathering will only provide a significant source of neutralisation potential under strongly acidic conditions and in the very long term (Plumlee & Logsdon, 1999). As indicated by Table 2.2, dissolution of aluminosilicates consumes acid but contributes base cations (Ca, Mg, and Fe (II)), alkali metals (Na, K) and dissolved Si and Al to the tailings pore water (Blowes *et al.*, 2003). They reported that metals are released by dissolution of aluminosilicate minerals under the low pH conditions that prevail in the unsaturated zone of many tailings impoundments, where amounts of Al dissolved decline as the pH rises above 3.5. The reaction rates of aluminosilicates decrease in the order: biotite, chlorite> albite, K-feldspars> muscovite > quartz.

Table 2.2: Dissolution reactions of aluminosilicates that may neutralise the acidity and release additional dissolved metals (Nordstrom & Alpers, 1999; Plumlee & Logsdon, 1999).

Al-silicate mineral	Dissolution reaction	Tracer	
Biotite	$K(MgFe)_{1.5}AlSi_3O_{10}(OH)_2 + 10H^+ \leftrightarrow K^+ + 1.5\ Mg^{2+} + 1.5Fe^{2+} + Al^{3+} + 3H_4SiO_4$	K, Mg, Al, Fe(II)	Eq. 2
K-feldspar	$KAlSi_3O_8 + 4H^+ + 4H_2O \leftrightarrow K^+ + Al^{3+} + 3H_4SiO_4$	K, Al	Eq. 3
Albite	$NaAl\ Si_3O_8 + 4H^+ + H_2O \leftrightarrow Na^+ + Al^{3+} + 3H_4SiO_4$	Na, Al	Eq. 4
Muscovite	$KAl_3Si_3O_{10}(OH)_2 + 10H^+ \leftrightarrow K^+ + 3Al^{3+} + 3H_4SiO_4$	K, Al	Eq. 5
Ca-plagioclase	$CaAl_2Si_2O_8 + 2H^+ + H_2O \leftrightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4$	Ca^{2+}	Eq. 6

Smart *et al.*, 2004 described an AMD evolution trend (Figure 2.3) as a useful aid for the discussion of methods to manage AMD and determine where a waste rock dump sits on this trend. A primary evaluation of sulphide mine waste is not only to classify the waste material into acid forming or non-acid forming, but also to estimate the peak acid (and metal) release rates, and expected AMD duration. This AMD evolution trend provides a summary of the AMD generation mechanisms described in the previous paragraphs i.e. generation of acidity by sulphide oxidation, and weathering of carbonates and silicates to consume the generated acid. It also illustrates that pH is the key parameter for assessing mine water contamination.

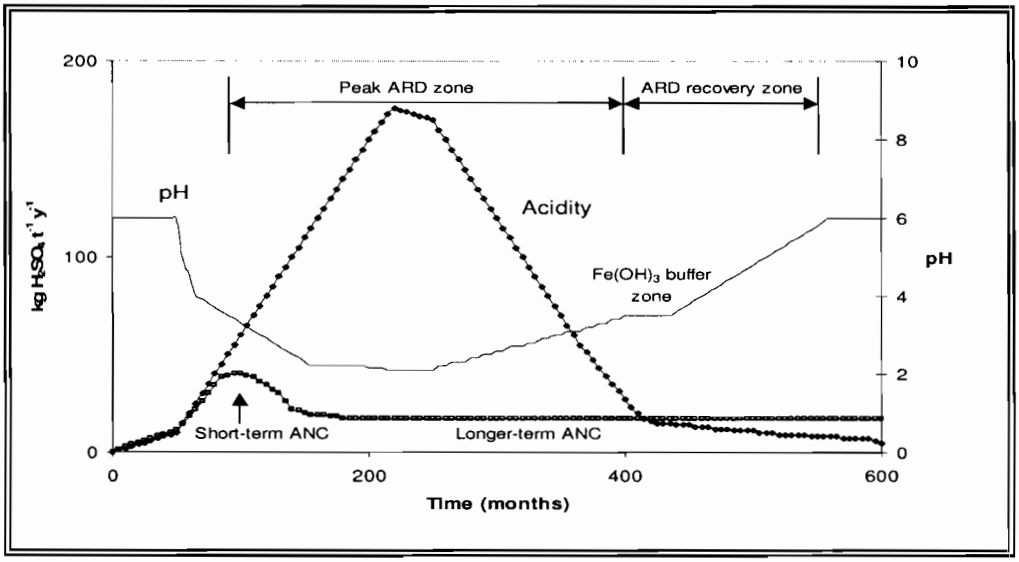


Figure 2.3: Schematic Acid Mine Drainage Evolution Trend (after Smart *et al.*, 2004)

The following were derived to provide an understanding of the AMD evolution trend (*Note that they referred acid mine drainage (AMD) as acid rock drainage (ARD)*):

- AMD peak zone is associated with sulphide mineral oxidation in excess of acid neutralisation by high sulphide oxidation and acid generation in excess of acid neutralisation capacity (ANC) release rates.
- Short-term ANC is derived from carbonates and cation exchange on silicate minerals.
- Long-term ANC may be determined by silicate dissolution kinetics after carbonate exhaustion. Decreasing sulphate and metal load, with increasing pH values would suggest that eventually sulphide acidity generation rates will match the longer-term inherent acid neutralisation rates of the sample, usually derived from silicates.
- AMD recovery zone occurs when the longer-term aluminosilicate ANC is in excess of acid generation (i.e. near sulphide exhaustion).
- AMD recovery zone is characterised by decreasing sulphate and metal content, however this can be prolonged by dissolution of minerals like jarosite and subsequent Fe $(OH)_3$ precipitation and acid release.

2.3.2 Formation of Fe (III) secondary minerals

Formation of secondary Fe(III) oxyhydroxide, oxide, hydroxide and hydroxyl(oxy)sulphate minerals results in the attenuation of metals through primary oxidation and hydrolysis/dissolution reaction products (see Section 2.3.1, Table 2.1). The formation of these secondary minerals plays an important role in the transport and attenuation of trace metals, controlling trace metal concentration through adsorption and co-precipitation. Figure 2.4 summarises the key reaction mechanisms controlling the release of metals in the oxidised and non-oxidised zones of the tailings deposit in an impoundment. Table 2.3 shows some of the most common Fe (III) secondary precipitates identified in sulphide tailings and the classification of these minerals in terms of their kinetic factors such as pH and concentration.

Adsorption onto primary minerals, the formation of secondary minerals such as covellite and iron oxyhydroxides and hydroxides, and co-precipitation with the minerals below the oxidation front, have been shown to be important scavenger mechanisms retaining the oxidation products before the percolating water reaches the groundwater (Carlsson *et al.*, 2002). In particular, adsorption onto mineral surfaces and desorption of heavy metals were found to be the key processes in the unoxidised zone.

The extent of formation of the secondary precipitates in sulphide tailings depends on the pH-Eh conditions, temperature, and availability of primary oxidation and hydrolysis/dissolution reaction products such as Fe (III), SO_4, Cl, Al, Ca, Na, H_3O^+ and K. Precipitation of these minerals can occur in near neutral or even alkaline environments if the acid generated by the oxidation of pyrite is significantly neutralised (Murad & Rojik, 2003).

Highly water-soluble sulphates, such as gypsum ($CaSO_4.5H_2O$) are formed under oxidising conditions and high evaporation rates. They can store acid and metals which can be released by dissolution of these soluble secondary minerals during rainfall or laboratory leach tests (Plumlee & Logsdon, 1999). This mineral group is an important factor leading to seasonal fluctuations in contamination levels of ground and surface waters, especially in semi-arid and arid climates (Dold, 2005). Though reported to have relatively low dissolution kinetics (Nordstrom & Alpers, 1999), jarosite (K, Na, H_3O, Fe (III)-hydroxysulphate) can readily release acid and metals during rainfall and laboratory leach tests (Plumlee & Logsdon, 1999). Dold, 2005 reported that jarosite may liberate acidity and metals by transformation to goethite. These secondary sulphates can release significant amounts of dissolved Fe^{3+} which can encourage further pyrite oxidation.

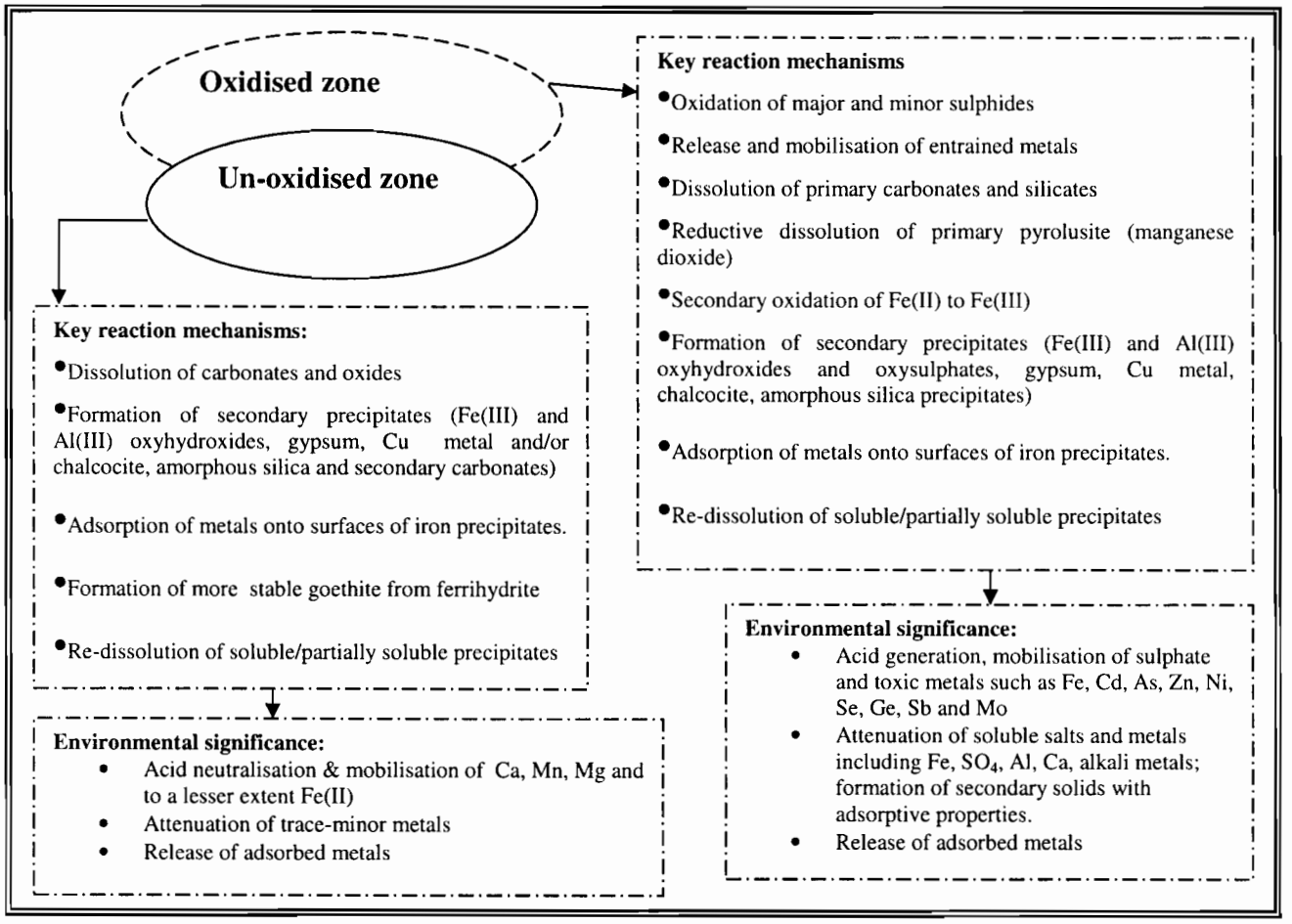


Figure 2.4: Key reactions controlling metal release in the oxidised and non-oxidised zones.

Table 2.3: The most common Fe (III) secondary precipitates in sulphide tailings and classification on the bases of kinetic factors such as ion concentration and pH (Nordstrom & Alpers, 1999; Plumlee & Logsdon, 1999; Dold, 2005).

Mineral	Oxidation product/s required	pH	Concentration	Reaction equation
Ferrihydrite [$Fe_5(OH)_8.4H_2O$] $5Fe^{3+}+12H_2O \leftrightarrow Fe_5HO_8.4H_2O + 15H^+$	Fe (III)	Favoured by pH greater than 5.0 (or near neutral)	Elevated Fe concentration, lower SO_4^{2-} activity conditions	Eq. 7
Goethite ([α-FeO(OH)]) $Fe^{3+}+ 2\ H_2O \leftrightarrow$ α-FeO(OH) + $3H^+$	Fe(III)	Acidic condition pH<4.0	Low SO_4^{2-} concentration	Eq. 8
Schwertmannite[$Fe_8O_8(OH)_6SO_4$] $8Fe^{3+}+SO_4^{2-}+14H_2O \leftrightarrow Fe_8O_8(OH)_6(SO_4)+ 22H^+$	Fe (III), SO_4^{2-}	Acidic conditions with pH = 3.0 to 4.0	SO_4^{2-} concentrations ranging form 1000 - 3000 mg/l	Eq. 9
Jarosite([(K,Na,H_3O)$Fe_3(OH)_6(SO_4)_2$] $3Fe^{3+}+ K^+ + 2SO_4^{2-} + 6H_2O \leftrightarrow KFe_3(OH)_6(SO_4)_2 + 6H^+$ $3Fe^{3+}+ Na^+ + 2SO_4^{2-} + 6H_2O \leftrightarrow NaFe_3(OH)_6(SO_4)_2 + 6H^+$ $3Fe^{3+}+ H_3O^+ + 2SO_4^{2-} + 6H_2O \leftrightarrow H_3OFe_3(OH)_6(SO_4)_2 + 6H^+$	K, Na, H_3O, Fe(III), SO_4^{2-}	Low pH values (1.5 -3.0)	Elevated SO_4^{2-} concentration (>3000 mg/l)	Eq. 10
Gypsum $Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4.2H_2O$	Ca, SO_4^{2-}			Eq. 11
Hematite $2Fe^{3+}+ 3H_2O \leftrightarrow Fe_2O_3 + 6H^+$	Fe^{3+}			Eq. 12

Ferrihydrite [$5Fe_2O_3.9H_2O$] and schwertmannite [$Fe_8O_8(OH)_6SO_4$] are poorly crystalline forms of hydrous ferric oxide/hydroxide phases (considered to be amorphous Fe(III) oxide) that seems to be the first phases to form upon weathering. In zones of water table fluctuation, direct precipitation of goethite and indirect precipitation of hematite via ferrihydrite or by dehydration of goethite may occur (Xie & Dunlop, 1998), and this may cause a partial release of metals. Nordstrom & Alpers, 1999 reported that ferrihydrite is known to convert to hematite if conditions are maintained between pH 5.0 and 9.0, and outside of this range most of the ferrihydrite dissolves and reprecipitates as goethite. Maghemite may, however, be formed by the oxidation of magnetite, dehydration of lepidocrocite and transformation of other Fe oxides. Hematite (Fe_2O_3) and goethite (α-FeO(OH)) are the most common and stable forms of ferric oxide and oxyhydroxide respectively (Nordstrom & Alpers, 1999).

2.3.3 Formation of solid aluminum oxide minerals

The attenuation of Al (III) and K released by the dissolution of aluminosilicates can also occur through further reactions to form secondary minerals such as aluminum oxide, hydroxide and hydroxysulphate, as describes according to reaction equations in Table 2.4.

Table 2.4: Formation of some of the common aluminum oxide, hydroxide and hydroxysulphate.

Precipitation reaction	
Kaolinite: $2Al^{3+} + 2H_4SiO_4 + H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 6H^+$	Eq. 13
Gibbsite: $Al_2Si_2O_5(OH)_4 + 5H_2O \leftrightarrow 2Al(OH)_3 + 2H_4SiO_4$	Eq. 14
Alunite: $3Al^{3+} + K^+ + 2SO_4^{2-} + 6H_2O \leftrightarrow KAl_3(OH)_6(SO_4)_2 + 6H^+$	Eq. 15

Kaolinite is the most stable and common secondary product formed during dissolution of aluminosilicates in natural environments. Ca-silicate minerals can also react, consuming acid, to form kaolinite (Eq. 6, Table 2.2). According to reaction equation 14, secondary kaolinite may dissolve to form gibbsite, a reaction that does not neutralise acid (Dold, 2005). Other secondary minerals that may be formed during the dissolution of alumino-silicates include, hydroxide such as diapsore (α-AlOOH), boehmite (γ-AlOOH) and bayerite (α-$Al(OH)_3$), and hydroxysulphate such as natroalunite ($NaAl_3(OH)_6(SO_4)_2$) and ammoniumalunite ($(NH_4)Al_3(OH)_6(SO_4)_2$). In acid mine water, Al-hydroxysulphate minerals such as alunite become more stable than kaolinite and gibbsite, however at pH<5.5 (depending on SO_4^{2+} and K activities) gibbsite becomes unstable relative to alunite (Nordstrom & Alpers, 1999).

2.4 Empirical waste characterisation methodologies

Leaching characteristics of a waste are affected by the physical properties (particle size distribution in particular) and mineralogy of the waste. These factors need to be considered in the interpretation of the test results. The commonly used standard techniques for the determination of the physical properties, mineralogy and total metal content have been described in Crock *et al.*, 1999. These methods include Malvern mastersiser, Atomic Adsorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP) techniques for total metal analysis and, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectrometry (SEM-EDS) and Optical Microscopy for mineralogical analysis. These methods require no further development; therefore they will not be discussed in this dissertation.

Chemical characterisation methods such as acid generating prediction tests and sequential extraction procedures are likely to require some development/optimisation, since there is a great deal of controversy regarding the interpretation of results derived from these methods. Hence in the next sections, literature has been critically reviewed on these methods to see how they can be improved and used in this study.

2.5 Methods for predicting Acid Mine Drainage

If acid mine drainage is to be prevented, then its accurate prediction is necessary. A comprehensive set of methods has been developed for predicting acid forming and non-acid forming behaviour in different waste samples. Analytical methods used to predict acid generation of solid wastes are classified as either static or kinetic tests. Static tests are simple and inexpensive tests that provide qualitative information on the balance between acid-generating and acid-neutralising processes in a waste sample (U.S EPA, 1994b), they do not account for rate of reactions. The most commonly used static tests are:

- Paste pH
- Acid-base accounting (ABA)
- Single Addition and Sequential Net Acid Generation (NAG)

The kinetic methods are used to:

a. provide a qualitative assessment of the likely lag periods for acid generation and neutralising reactions under laboratory controlled conditions.
b. provide an indication of the reactivity of sulphides and buffering minerals within the sample.

The most common kinetic tests are:

- Kinetic Net Acid Generation (KNAG)
- Leach columns
- Humidity cells

The leach columns and humidity cells test procedures were not reviewed or conducted in this study.

2.5.1 Paste pH

Paste pH can provide an indication of the amount of sulphide oxidation in a sample and accumulation of contaminants in the form of secondary mineral phases e.g. jarosite ($KFe_3(SO_4)_2(OH)_6$) and melenterite ($FeSO_3.7H_2O$) (Weber *et al.*, 2004b). However, it provides little indication of the potential of a sample to produce AMD, and this is due to the fact that pyrite oxidation reactions are time dependent.

2.5.2 Acid Base Account (ABA)

The acid-base account involves estimation of both the acid forming and acid neutralising capacities of a sample. The results are expressed as Net Acid Producing Potential (NAPP)

which represents the balance between the acid forming capacity (which is based on the sulphide-sulphur content) and the Acid Neutralisation Capacity (ANC). NAPP gives the theoretically determined amount of acid that a sample can produce and it is determined as follows: NAPP (kgH_2SO_4/ton of sample) = Maximum Potential Acidity (MPA) – ANC. MPA is the amount of acid that could be generated by the sulphur contained within a sample.

Based on the stoichiometry of the pyrite oxidation reaction (Eq. a in Table 2.1) and assuming all sulphur is available as reactive pyrite, MPA is determined as follows: MPA (kg H_2SO_4/ton of sample) = wt% total S × 30.6. The ANC (kg H_2SO_4/ton of sample) of a sample quantifies the inherent acid buffering and it is commonly assessed by acid digestion followed by back titration with base to determine the amount of acid consumed by the sample. ANC is equivalent to neutralisation potential (NP) although NP is expressed in kg $CaCO_3$/ton of sample. Table 2.5 summarises various ABA test methods used to evaluate the acid-producing capability of mine wastes. The summaries include information from Miller *et al.*, 1991; Mills, 1998; Crock *et al.*, 1999 and EPA & Hardrock Mining, 2003.

Table 2.5: The most commonly reported and used Acid Bases Accounting test methods

Static Test & Reference	MPA Determination	ANC/NP determination
Sobek ABA (Sobek *et al.*, 1978)	MPA uses sulphur speciation and LECO analyser. Based on sulphide-sulphur content	60 mesh (0.24mm) sample. ANC/NP uses fizz test and heated HCl (usually 80-to-90 °C) that dissolves carbonates and most silicate minerals. NaOH titration endpoint of 7.0.
Modified Sobek ABA (Lawrence & Wang, 1996)	Requires sulphur speciation and LECO analyse. Based on sulphide-sulphur content.	60 mesh (0.24mm) sample. ANC/NP uses fizz test and HCl at ambient temperature that dissolves carbonates and reactive silicate minerals. Agitate for 24 hr, pH 1.4-2.0 required after 6 hr agitation. NaOH titration endpoint of 8.3, rather than unstable pH 7.0.
Peroxide Siderite correction for Sobek Method (Skousen *et al.*, 1997)	Requires sulphur speciation and LECO analyser. Based on sulphide-sulphur content.	ANC/NP uses fizz tests and heated HCl. 30% H_2O_2 added prior to titration to oxidize ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) from dissolved siderite.
BCRI initial (Duncan & Bruynesteyn, 1979)	Based on total sulphur content	ANC/NP is determined by titrating with 1N H_2SO_4, a stirred mixture of 10g sample (-100 to -400 mesh) and 100 ml distilled H_2O. The mixture is titrated until pH 3.5 is reached and less than 0.1 ml of H_2SO_4 is added over 24 hr at ambient temperature.
Lapakko ANC/NP Modification of BCRI Test	Based on total sulphur content	10g solid (-150 to -325 mesh) and 100 ml deionised H_2O is titrated with (0.1-1.0N) H_2SO_4 until pH 6.0 is reached and less than 0.1 ml of acid is added over 4 hrs. In this test, digestion occurs at pH 6.0 rather than in more acidic environment like in BCRI test.

Lawrence & Wang, 1997 and Skousen *et al.*, 1997 studied the effect of fizz test on the measurements of ANC and found that greater amounts of acid used during sample digestion yielded higher ANC values. Weber *at el.*, 2004a related the ANC variation to the highly

subjective fizz test, affected by personal bias and liable to misinterpretation. Lapakko, 1992 concluded that the potential range of the acid addition is mainly limited by the objective criterion of the target digestion pH range rather than the subjective interpretation of the fizz test. For example, in the modified ABA (see Table 2.5) the amount of acid is based on the "fizz test", but is also limited by requiring a pH range of 1.4 to 2.0 at the end of digestion. BCRI and Lapakko ANC test shows that amount of acid is limited by requiring pH of 3.5 and 6.0 respectively. AMIRA, 2002 suggested that the ANC solution pH after digestion be in the range of 0.8 to 1.5. If the pH > 1.5 then additional acid is required, if ANC digest solution pH is below the range, then less acid is required.

Different static test methods can lead to significant variations in the ANC values for the same sample (Mills, 1998). White *at el.*, 1999 and Lapakko, 2002 reported that the ANC variability for a given sample is most influenced by i) differences in sample particle size ii) amount and concentration of acid addition iii) the back titration endpoint and iv) sample mineralogy. According to the study by White *at el.*, 1999 using Sobek ABA, reducing particle size of three samples from -0.25 in (6.35mm) to -325 mesh (1.4 mm) increased NP from 8 to 43 kg $CaCO_3$/ton. This reflects dissolution of acid-neutralising minerals due to an increase in mineral surface area which, in turn can overestimate the NP of large particles. They concluded that overestimation would be greater for the BCRI and Lapakko methods, which use finer particles.

2.5.3 Effects of Fe, Al and Mn bearing carbonates

The presence of Fe bearing carbonates in a sample can lead to variations in ANC values. As indicated in Section 2.3.1 siderite, along with calcite and dolomite, are the common carbonate minerals. When present in the sample, siderite reacts quickly with acid and contributes to the alkaline-producing potential of the sample. Continued weathering of siderite provides no acid neutralising potential. This is because the acid consumed during dissolution is re-released upon oxidation of Fe^{2+} to Fe^{3+} and subsequent precipitation to ferric oxyhydroxides. Reaction equations 16 through 18 show the weathering reactions of $FeCO_3$ that represent field conditions (Skousen *et al.*, 1997):

$$FeCO_3 + 2H^+ \rightarrow Fe^{2+} + CO_2 + H_2O \qquad \text{Eq. 16}$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad \text{Eq. 17}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad \text{Eq. 18}$$

Siderite dissolution releases Fe^{2+} (Eq. 19) during ANC test conditions. The Fe^{2+} produced by reaction 19 is unstable and will slowly oxidise to Fe^{3+} (Eq. 20) and consume additional HCl. The Fe^{3+} will consume base ions upon titration with NaOH and precipitate as ferric hydroxide (Eq. 21).

$$FeCO_3 + 2HCl \Rightarrow Fe^{2+} + 2Cl^- + H_2O + CO_2 \qquad \text{Eq. 19}$$

$$4Fe^{2+} + O_2 + 4HCl \Rightarrow 4Fe^{3+} + 4Cl^- + 2H_2O \quad \text{Eq. 20}$$

$$Fe^{3+} + 3NaOH + 3Cl^- \Rightarrow Fe(OH)_3 + 3NaCl \quad \text{Eq. 21}$$

The same process can affect Al and Mn containing carbonate minerals (Weber *et al.*, 2004a):

$$Al^{3+} + 3H_2O \Rightarrow Al(OH)_3 + 3H^+ \quad \text{Eq. 22}$$

$$Mn^{2+} + 1/2O_2 + H_2O \Rightarrow MnO_2 + 2H^+ \quad \text{Eq. 23}$$

Incomplete oxidation of Fe^{2+} and incomplete hydrolysis of Fe^{3+} prior to titration or at the end of ANC test can overestimate the ANC values. The standard procedure as outlined by Sobek *et al.*, 1978 does not allow sufficient time for Fe^{2+} oxidation and subsequent precipitation of Fe^{3+} hydroxide. Therefore high ANC values can be generated with samples containing high amounts of iron bearing carbonates (e.g. siderite). Incomplete oxidation of Fe^{2+} in standard neutralisation tests is therefore an important consideration in evaluating the neutralising potential of siderite bearing tailings. Skousen *et al.*, 1997 and Weber *et al.*, 2004a suggest hydrogen peroxide (H_2O_2) addition to precipitate Fe^{3+} to $Fe(OH)_3$ prior to titration. This is because hydrolysis of Fe^{3+} consumes base (NaOH) upon titrating, resulting in overestimation of ANC. They termed this test the Modified Sobek ANC test. Several variations to the Modified Sobek ANC test were described and employed by Weber *et al.*, 2004a, b to accelerate the oxidation and hydrolysis of Fe in the ANC test solutions.

2.5.4 Net Acid Generation (NAG) test methods

The NAG test is based on the procedure developed by Finkelman & Giffin, 1986. This test is usually used in conjunction with other static methods such as net acid producing potential (NAPP) determination, to give an indication of the acid forming potential (Gerson *et al.*, 2004). NAG measures the acid forming potential of a sample by allowing both the acid forming and acid neutralising reactions to occur simultaneously during the NAG test. Hence the final solution after complete reaction is a direct measure of the net acid generated by the sample.

Essentially, it involves the addition of hydrogen peroxide (H_2O_2) to a pulverised sample of a waste material or process residue to accelerate oxidation of reactive sulphide minerals. This is followed by measurement of the pH (termed NAG_{pH}) of the reaction solution and titration of any net acidity produced. H_2O_2 is chosen as a strong oxidant for rapid emulation of the relatively slow oxidation in a field environment by H_2O and O_2 (Jennings *et al.*, 2000) and the reaction describing the H_2O_2 oxidation of sulphide minerals is expressed as follows:

$$FeS_2 + 15/2H_2O_2 \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ + 4H_2O \quad \text{Eq. 24}$$

The actual acidity is provided by initially titrating the NAG solution to pH 4.5, then continuing the titration up to pH 7.0. Titration to a pH 4.5 accounts for acidity due to

oxidation and free acid such as SO_4^{2-} and acidity generated due to hydroxylation of dissolved Al and Fe, whereas titration of the solution to a pH of 7.0 accounts for metallic ions that precipitate out as hydroxides (particularly Zn^{+2} and Cu^{+2}) between pH 4.5 and 7.0 (Tran *et al.*, 2003).

Several variations of the NAG test methods have been used to accommodate a wide geochemical variability of mine waste material and provide different types of information (Finkelman & Giffin, 1986; Miller *et al.*, 1991; Mills, 1998; Trans *et al.*, 2003; Weber *et al.*, 2004b). Three main NAG test procedures are the single addition NAG test, the sequential NAG test and the kinetic NAG test. These test procedures are summarised in Table 2.6.

Table 2.6: Variation of NAG test procedures (Finkelman & Giffin, 1986; Miller *et al.*, 1991; Weber *et al.*, 2004b)

Test	MPA Determination	Test Procedure
Single addition NAG	Based on total sulphur (or pyritic sulphur) content	Involves addition of 250 ml of 15% H_2O_2 to 2.5 g of pulverised sample. Sample is allowed to react for 24 hr, after 24 hr NAG_{pH} is measured heating the sample on a hot plate for 1.5 to 2 hr and allowed to cool. NAG_{pH} is measured, and then the sample is filtered. NAG capacity of the solution is measured. Retain the solids for residual sulphur analysis and filtrate for titration.
Sequential NAG	Based on total sulphur (or pyritic sulphur) content	This test involves sequential stages (250 ml of 15 % H_2O_2 solution) on one sample. At the end of each NAG stage, the sample is filtered and the NAG_{pH} and NAG capacity of the solution are measured. The NAG is repeated on the solid residue until the NAG_{pH} is $\geq$ 4.5. The overall capacity of the sample is determined by summing the individual acid capacities from each stage.
Kinetic NAG	Based on total sulphur (or pyritic sulphur) content	Same as single addition NAG except that the rate of pH and temperature change is monitored during the reaction.

An investigation conducted by AMIRA, 2002 indicated that samples with pyritic-S contents of <1% were completely oxidised in the single addition NAG test, but above 1% were not. This may lead to underestimation of acid forming potential in high S samples. Thus, the single addition NAG test may not account for the total acid potential of a given sample. Complete catalytic decomposition of H_2O_2 may occur before all the reactive sulphides have oxidised (Gerson *et al.*, 2004). A temperature rise is commonly observed in the NAG test due to catalytic decomposition of H_2O_2 by metal ions during sulphide oxidation (discussed in the next section). The sequential NAG test is used to overcome the limitations associated with the single addition NAG test.

2.5.5 Kinetic NAG test

The kinetic NAG test (KNAG) involves monitoring the rate of pH change and solution temperature during the single addition NAG test. The final pH of the reacted solution is the net result of reactions involving several different components in the sample. It therefore does not provide kinetic information regarding the reactivity of the sample (Finkelman & Giffin, 1986). Variation in these parameters during the test provides an indication of the kinetics of sulphide oxidation and acid generation during the test. Rapid pH decrease and final NAG_{pH} < 4.5 indicates reactive sulphide minerals in excess of neutralising reactions, whereas a slow pH decrease and high final NAG_{pH} >6.5 indicates the presence of neutralising minerals in excess of acid produced by sulphide oxidation (Weber *et al.*, 2004b).

Finkelman & Giffin, 1986 found that the rate of the pH change and temperature rise is proportional to the pyrite content of the sample. However, according to their findings, temperature is not as sensitive an indicator as the pH change. An investigation by Miller *et al.*, 1991, working with waste rock samples, indicated that the time to reach the temperature peaks and pH minima are functions of sulphur reactivity. Figure 2.5 shows some experiments carried out by Steward, 2005 in order to evaluate the kinetic NAG test for predicting the kinetics of sulphide oxidation and acid generation. Their results indicated that samples with S content >2% can reach temperature peaks > 100 °C and pH minima of <2. They also indicated that complete catalytic decomposition of H_2O_2 can occur, resulting in incomplete S oxidation. The pH and temperature profiles for the potentially acid forming samples were similar but with different lag periods prior to the pH minima and temperature maximum. Results by Miller *et al.*, 1991 and Weber *et al.*, 2004b indicated that samples with higher NAPP values generally exhibited a shorter lag period.

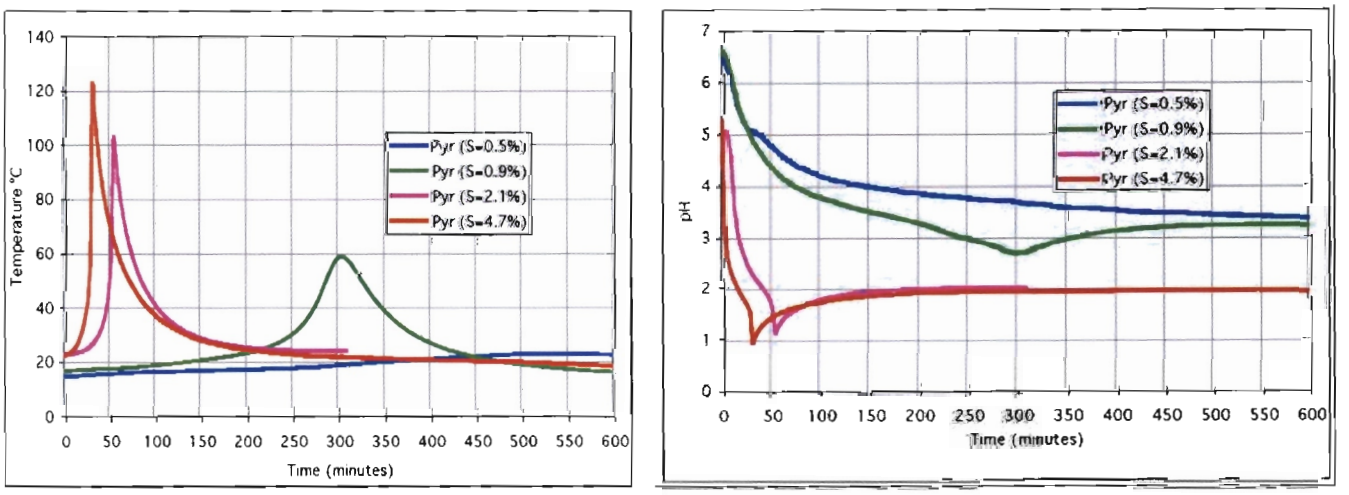


Figure 2.5: Kinetic NAG temperature and pH profile for prepared pyrite/quartz mixes containing 0.5, 0.9, 2.1 and 4.7 wt %S as pyrite (Steward, 2005).

2.6 CHEMICAL SPECIATION ANALYSIS OF METALS

2.6.1 Metal speciation

Measurement of the total metal concentration in the waste provides inadequate information pertaining to their mobility and bioavailability, since not all forms of a given metal are equally soluble (Tessier *et al.*, 1979; Usero *et al.*, 1998; Li & Thornton, 2001). However, the total metal concentrations do place an upper limit on metal bioavailability. In order to estimate the real bioavailability of metals and their potential toxicity, it is necessary not only to determine the total concentrations, but also the different chemical forms or ways of binding between trace and minor metals and the solid phases of the sample (Nurmesniemi *et al.*, 2005). Metals are found in several different forms like sulphides, sulphates, carbonates, silicates, oxides and also as the native metals in minerals (Jeong, 2003). Their mobility depends strongly on their specific chemical form, which in turn can change as the waste in a deposit ages. Therefore, understanding of the mode of occurrence of metals in a solid waste is useful to characterise the leaching behaviour by dividing the total concentration of metals into fractions (van Herck & Vandecasteele, 2001).

Sequential extraction procedures provide an important approach to separate metals into different chemical forms. Several sequential extraction procedures/schemes have been developed to predict the distribution of metals between different fractions/phases, and to estimate mobility and bioavailability of metals in a solid waste material. In a sequential extraction procedure a solid sample is subjected to reagents/extractants, with progressively increasing extraction capacity in series, to selectively dissolve a particular mineralogical constituent, which is a potential carrier of trace and minor metals in a sample. The basic assumption of sequential extraction is that the reagents used are able to dissolve one phase selectively without solubilisation of the others (Fonseca and da Silva, 1998). The extractants more commonly used in sequential extraction schemes fall generally within the following groups: unbuffered salts, weak acids, reducing agents, oxidising agents and strong acids (Filgueiras *et al.*, 2002). Section 2.6.2 provides a detailed review of the sequential extraction procedures.

The chemical composition of major and minor metals in a mine waste is evident in their environmental signatures, with some variability due to weathering processes such as oxidation, secondary mineral precipitation and sorption. The common primary mineralogic sources for some environmental major and minor metals are shown in Table 2.7. For each metal the minerals are listed in general order of reactivity in the environment. Under natural weathering conditions, the stability of these minerals is one of the important factors controlling the geochemical cycle of metals (Dang *et al.*, 2001). Some of these metals

released due to the weathering process are shown in Tables 2.1 and 2.2. This information is useful for predicting and estimating metal mobility.

Table 2.7: Common primary mineralogic sources for some environmentally major and minor metals (Modified after Plumlee& Logsdon, 1999).

Metal	Common mineral source
Si	Aluminosilicates: K-feldspar ($KAlSiO_3$), albite ($NaAlSi_3O_8$), biotite ($K(FeMg)_2Al_3Si_2O_{10}(OH)_2$); muscovite ($KAl_3Si_3O_{10}(OH)_2$), chlorite ($(MgFe)_5Al(Si_3Al)O_{10}(OH)_8$). Quartz ($SiO_2$).
Ca	Sulphates: gypsum, anhydrite ($CaSO_4$); Carbonates: calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), ankerite ($(Ca,Fe)CO_3$; fluorite (CaF_2); calcium-silicates.
Mg	Dolomite, amphiboles, chlorite and biotite.
Na	Albite and micas.
K	Alumino-silicates: K-feldspar, biotite, muscovite and micas.
Al	Alumino-silicates
Fe	Pyrite (FeS_2) >>marcasite (FeS_2) > pyrrhotite (FeS) ; siderite ($FeCO_3$), ankerite; Hematite (Fe_2O_3); amphiboles, biotite, chlorite, muscovite; magnetite (Fe_3O_4).
Mn	Rhodochrosite ($MnCO_3$); alumino-silicate, Mn-silicates.
S	Sulphides, sulphosalts, sulphates minerals.
F	Fluorite (CaF_2), silicates
Ba	Feldspar and other alumino-silicates; barite ($BaSO_4$).
Zn	Sphalerite (ZnS), other sulphides, sulphosalts, Zn –silicates.
Cd	Sphalerite (ZnS), greenocktite (CdS)
Cu	Copper sulphide minerals: chalcopyrite ($CuFeS_2$) > bornite (Cu_5FeS_4), > chalcocite (Cu_2S).
Pb	Galena (PbS), sulphosalts, feldspars.
As	Enargite (Cu_3AsS_4), arsenopyrite (FeAsS) and other sulphides; sulphosalts.
Sb	Stibnite (Sb_2S_3), terahedrite ($(CuFe)_{12}Sb_4S_{13}$), sulphosalts.
Ni	Ni-sulphide, pyrite and other sulphides.
Co	Cobaltite (CoAsS), alumino-silicates.
Cr	Chromite ($FeMgCr_2O_4$) (relatively nonreactive).
Hg	Native Hg; cinnabar (HgS); galena; sulphosalts.
Mo	Sulphides, molybdenite (MoS_2) (relatively nonreactive)
Se	Sulphides; selenides; selenates.
U	Uraninite (UO_2), feldspars.
Ag	Acanthite/Argentite (Ag_2S).

2.6.2 Overview of sequential chemical procedure: Historical background

Different sequential extraction procedures have widely been used to study the binding forms of metals and metal speciation in soil and sediments (Tessier *et al.*, 1979; Usero *et al.*, 1998; van Ryssen *et al.*, 1999; Li & Thornton, 2001; Ngiam & Lim, 2001; Galán e*t al.*, 2002; Sahuquillo *et al.*, 2003; Hlavay *et al.,* 2004). Most of them mimic the basic procedure initially developed for sediments by Tessier *et al.*, 1979 for the fractionation of metals into the following fractions: i) exchangeable fraction, representing the most easily available metals, ii) carbonate fraction, iii) Fe, Mn and Al oxide fraction, iv) organic matter and sulphide fraction, and (v) residual fraction.

The application of sequential extraction procedures is still subject to much controversy (Li *et al.*, 2001). Although some methods have widely been used, none has been unreservedly accepted by the scientific community (Fuentes *et al.*, 2004). Given the wide range of extraction procedures used, the results obtained are seldom comparable since they present important variations that depend on the extraction method used (Marguí *et al.*, 2004). The solubility of certain minerals of interest may also differ significantly, due to the conditions of formation (Dold, 2003b). For example the results may be too high in the iron and manganese oxide fractions if the carbonates have not been completely dissolved or too low if part of the iron and manganese oxide fraction have been extracted already (Usero *et al.*, 1998). Therefore, lack of selectivity of chemical reagents may lead to attack of other metal bearing phases (Gómez Ariza *et al.*, 2000).

Sequential extractions are operationally defined i.e. the selectivity of the extraction procedure itself depends on factors such as (Fonseca & da Silva, 1998; Han *et al.*, 2001; Li *et al.*, 2001; Hlavay *et al.,* 2004):

- *Chemicals/reagents employed*: Efficiency of an extractant to dissolve or desorb metals will usually be increased with increasing concentration.
- *Extraction time and nature of contact*: Effects of extraction time are related to the kinetics of the reactions between solid sample and extractant.
- *Solution/solid ratio*: The relative amounts of extractant added to solid sample have various implications on the results.
- *Extraction steps:* Selectivity, redistribution and re-adsorption.

Other factors influencing metal speciation include pH and redox conditions, the solubility of solid compounds, the oxidation state of metals, sorption-desorption reactions and biochemical processes (Smith & Huyck, 1999).

Particularly important, besides the type of extracting solution used, is the pH of the extractant, the temperature and the time of extraction. Han *et al.*, 2001 and Li *et al.*, 2001 described re-distribution of metals as follows:

> *"The metals released from certain components/fractions would have an opportunity to re-associate with remaining undissolved solid components/fractions, or freshly exposed surfaces before recovery of extract.'*

Metals contained in various fractions/phases may be redistributed by geochemical or biological processes or by changing geochemical conditions. Re-distribution of metals during sequential extractions leads to difficulties associated with achieving selective dissolution and incomplete recovery of trace metals from geochemical phases (Gómez Ariza *et al.*, 2000; Li & Thornton, 2001; Hlavay *et al.*, 2004). Incomplete knowledge of the complex solid waste, coupled with the lack of selectivity of some reagents, can also make interpretation difficult. Despite these limitations, sequential extraction procedures have for some time been proposed as useful tools that can provide the following information (Gatehouse *et al.*, 1977; Tessier *et al.*, 1979; Filgueiras *et al.*, 2002):

- Characterisation of pollution sources.
- Evaluation of metal mobility and bioavailability.
- Identification of binding forms of metals for assessing metal accumulation, pollution and transport mechanisms.

Commonly, metals are extracted from several or, all of the operationally defined phases/fractions presented in Table 2.8, in the given order (modified from John & Leventhal, 1995 and Salomons, 1995). In the same table, qualitative interpretation of the mobility and biological availability for the various fractions is given. The relationship between metal mobility in the different operationally defined phases and leachant strength is also illustrated. As shown by Table 2.8, the mobility and bioavailability of metals decrease in the order of the extraction sequence. These kinds of speciation schemes, thus give a first impression of the reactivity of the metals in the waste, as well as qualitative information on their reactivity under changing conditions.

Some published sequential extraction schemes are listed in Table 2.9. Some of these schemes may be modifications of one another with minor variations in the chemical extractant and operating conditions (Tessier *et al.*, 1979[1]; Dold, 2003a[2]; Hall *et al.*, 1996[3]; Keersten & Forstner, 1991[4]; Cardoso & Martin, 1986[5] and Sondag, 1981[6]).

Leachant strength

Table 2.8: Mobility and biological availability for various fractions in the sequential extraction procedures (modified from John & Leventhal, 1995 and Salomons, 1995)

Fraction	Metal Species	Mobility & Mechanism
Water soluble	Consists of metals that are easily soluble, e.g. chlorides.	Highly liberated and reactive salts
Ion exchangeable	Exchangeable (dissolved) cations and easily soluble.	High mobility. Amount of each metal that will be released under acidic conditions, dependent on the pH. The ion exchangeable fraction includes weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes and metals that can be coprecipitated with carbonates present in the solid waste. Readily available for up take.
Carbonates	Metal in solution cation and anion complexes and hydrated ions.	High mobility. Metal solubilities are affected strongly by pH and tend to increase with decreasing pH.
Amorphous and poorly crystalline Fe-oxides; Mn-oxides	Metals adsorbed to iron-manganese oxide particles.	Medium mobility. Amount of each metal bound to Fe/Mn oxide that will be released under more reductive conditions. Change in redox (Eh) conditions (reducing conditions) may cause a release, but some metals precipitate if sulphide minerals present is insoluble. This fraction is controlled by the rate and extent of Fe/Mn dissolution/precipitation.
Crystalline Fe-Oxide	Metals bound to crystalline structures of Fe oxides.	Medium mobility. Depend upon conditions such as pH values, degree of oxide crystallinity.
Sulphide/organic bound (Oxidisable fractions)	Metal bound to various forms of sulphide minerals and organic matter.	Medium/High. Metals released when decomposition/oxidation of organic matter occurs. Strongly dependent on environmental conditions. Under oxygen-rich conditions, oxidation of sulphide minerals causes the release of metals.
Residual Crystalline	Metals with the strongest association to the crystalline structure of the minerals.	Low mobility. Metals are not expected to be released over a reasonable time span. Only available after weathering or decomposition.

Metal mobility

Table 2.9: Some published sequential extraction procedures used for speciation of metals and to estimate the mobility and bioavailability of metal.

Fraction and leach solution										Ref
Water soluble	**Water soluble/adsorbed/exchangeable/carbonates**	**Exchangeable fraction**	**Adsorbed carbonates**	**Mn oxides**	**Fe(III)-oxyhydroxide**	**Fe- oxides**	**Sulphides and organics**	**Metals in sulphide phase**	**Residual**	
		1 M $MgCl_2$, pH 7.0, 1 hr	1M NaOAc, pH 5.0 adjusted with HOAc, 5 hr	0.04M NH_2OHCl in 25% (v/v) HOAc, pH 2.0, 6 hr, 96 °C			30%H_2O_2, pH 2.0 adjusted with HNO_3, 5 hr at 85 °C, extracted with 3.2 M NH_4 – acetate in 20% HNO_3 (v/v), 0.5 hr		Hot HF – $HClO_4$ conc.	1
50 ml de-ionised H_2O, shake for 1 hr		1M NH_4 – acetate, pH 4.5 adjusted with 1M Acetic Acid, shaking 2 hr			0.2 M NH_4 – oxalate, pH 3.0 adjusted with 0.2 M oxalic acid, 1 hr in darkness	0.2 M NH_4 – oxalate, pH 3.0 adjusted with 0.2 M oxalic acid, at 80 °C, 2hr	35% H_2O_2, in water bath, 1 hr	750 mg $KClO_3$ and 5ml 12 M HCl, followed by 4 M HNO_3 at 90°C	HNO_3, HF, $HClO_4$, HCl	2
	20 ml 1M NaOAc, pH 5.0 adjusted with HOAc, 6 hr				20 ml 0.25M NH_2OHCl in 0.25M HCl, 2 hr, at 60 °C	30 ml 1.0 M NH_2OHCl in 25% (v/v) HOAc, 3 hr, 90 °C	750 mg $KClO_3$ and 5ml 12 M HCl, followed by 4 M HNO_3 at 90°C			3
		1M NH_4 – acetate, pH 7.0 adjusted with 1M Acetic Acid, shaking 2 hr	1M NaOAc, pH 5.0 adjusted with HOAc, 5 hr	0.1M NH_2OHCl in 0.01M HNO_3, pH 2.0 , 12hr	0.1 oxalate buffer pH 3.0, 24 hr in the dark		30% H_2O_2, pH 2.0 (HNO_3), 2 hr at 85 °C, extracted with 1M NH_4 – acetate in 6% HNO_3 (v/v), 12 hr		Hot HNO_3 conc.	4
	1M NH_4Ac, pH 4.5 adjusted with 1M Acetic Acid, shaking 2 hr			0.1M NH_2OHCl in 0.01M HNO_3, at pH 2.0	0.175M $(NH_4)_2C_2O_4$ – 0.1M $H_2C_2O_4$, pH 3.3, in darkness	0.175M $(NH_4)_2C_2O_4$ – 0.1M $H_2C_2O_4$, pH 3.3, under UV irradiation	35% H_2O_2		Hot HCl-HNO_3-HF attach	5
		1M NH_4 – acetate, pH 4.5 adjusted with 1M Acetic Acid, shaking 2 hr	1M NaOAc, pH 5.0 adjusted with HOAc, 5 hr	0.1M NH_2OHCl in 0.01M HNO_3, at pH 2.0		0.1 M NH_4 – oxalate, pH 3.3 adjusted with 0.1M oxalic acid, 60 °C, 2 hr in darkness	35% H_2O_2, in water bath, 1 hr		HNO_3, HF, $HClO_4$, HCl	6

2.6.3 Application of the most common reagents in sequential extraction

The following paragraphs describe the application of the most widely used reagents for leaching each fraction and their limitations. Some of these reagents are listed in Table 2.9. The targeted operationally defined fractions, qualitative interpretation of the mobility and bioavailability, and the conditions in which metals in each fraction can be released are given in Table 2.8.

Ion exchangeable fraction

The exchangeable fraction includes metals that are bound via electrostatic forces to the negative sites on the solid surface. For the extraction of the exchangeable fraction, a combination of major cations with either Cl^-, NO_3^- or acetate has been used, with concentrations ranging between 0.05 - 1 M and pH in neutral range (Hlavay *et al.*, 2004). The most widely used reagents to liberate exchangeable metals via electrostatic forces to the negative sites on the solid surface are presented in Table 2.10 (Tessier *et al.*, 1979; McLean & Bledsoe, 1992; Filgueiras *et al.*, 2002).

Table 2.10: The reagents that are usually employed for leaching the metals bound to exchangeable fraction (Tessier *et al.*, 1979; McLean & Bledsoe, 1992; Filgueiras *et al.*, 2002).

Reagent		Remarks
Acetate salts	NH_4 – acetate (NH_4OAc)	Acetate and chloride salts, apart from leaching the exchangeable fraction, they enhance the extraction of transition metals as a result of their complexing action.
Chloride salt	$MgCl_2$, $CaCl_2$, $BaCl_2$, LiCl/CsCl	
Ammonium salts	NH_4Cl, NH_4NO_3	Can lower the pH and encourage the hydrolysis of clays.
Nitrate salts	$NaNO_3$, $Mg(NO)_3$, $Sr(NO_3)$, KNO_3	Advantageous over chloride and acetate salts, since no metal complexing takes place due to the nitrate anion, and as a result, cation exchange is the only operating mechanism.

$MgCl_2$ and NH_4OAc at 1 M concentration have been the most extensively used reagents for leaching the exchangeable fraction. Many sequential extraction schemes use 1M NH_4OAc and pH adjusted to 4.5 with CH_3OOH (HOAc) (Gatehouse *et al.*, 1977; Sondag, 1981; Cardoso & Martin, 1986; Fonseca & da Silva, 1998). Tessier *et al.*, 1979 considered $MgCl_2$ (pH 7.0) because NH_4OAc is known to have the ability to attack both exchangeable and carbonate fractions.

Carbonate fraction

Chao, 1984 and Span & Gaillard, 1986 reported that the 1M Na-acetate/acetic-acid (pH 5.0) extractant may partially attack the Fe-Mn oxide minerals and leaves the lattice structure of silicate minerals intact. These studies were confirmed by Hanahan, 2004 who studied the selectivity of 1M Na-acetate/acetic-acid (pH 5.0) for metal release in carbonates. His results demonstrated that 1M Na-acetate/acetic-acid (pH 5.0) also release metals associated with hydroxides. This was indicated by the solubilised Al, Ca and Mg-hydroxides by this extractant. However, mineralogy of the material studied will govern the selectivity of 1M Na-acetate/acetic-acid (pH 5.0) on hydroxides.

Despite the short-comings of this extractant solution, by first removing the adsorbed, exchangeable and carbonate (Na-acetate/acetic-acid extractable) fractions, the efficiency of selective extraction reagents may be improved and provide more informative results (Hanahan, 2004). In some sequential extraction schemes the exchangeable and adsorbed metals with those coprecipitated with carbonates are grouped and extracted with either Na-acetate/HOAc (Hall *et al.*, 1996; Carlsson *et al.*, 2002) or 1M NH_4OAc /HOAc (Sondag, 1981; Cardoso & Martin, 1986; Fonseca & da Silva, 1998; Galán *et al.*, 2002; Dold, 2003a).

Reducible fraction

Iron and Manganese oxides are of principal importance in the fractionation of trace metals in soil, sediments and solid mineral waste material, due to their occurrence and strong scavenging of toxic metals (Chao, 1984). This scavenging is present as coatings on mineral surfaces, which can occur by any or a combination of the following mechanisms: coprecipitation; adsorption; surface complex formation and ion exchange (Filgueiras *et al.*, 2002). These mineral phases should be considered explicitly when estimating the bioavailability of metals (Tessier *et al.*, 1979). Generally, Fe and Mn oxides are more important than Al and Si oxides because of their greater adsorption capacity. They dissolve as the redox potential decreases and reprecipitate as the environment becomes oxygenated (Chao, 1984).

In principle, the reducible fraction could be split into three fractions: easily reducible fraction (Mn oxides); moderately reducible fraction (amorphous Fe oxides); and poorly-reducible fraction (crystalline Fe oxides). So far, this classification is addressed in a few schemes. Amorphous Fe oxides are generally believed to be more chemically reactive on a per weight basis than crystalline oxides (Hall *et al.*, 1996). They are also known to retain anions and metals more readily than crystalline Fe oxides (Knapp *et al.*, 2002), with the capacity for sorption decreasing with increasing age and degree of crystallinity. Dissolution of the crystalline phases will depend on the degree of crystallinity (Hall *et al.*, 1996). It is on this basis that the amorphous and crystalline Fe phases are separated in the sequential

extraction procedures. Therefore, in order for selective dissolutions for the Fe-oxides to be useful in partitioning of metals, the sequential extraction/s should be able to differentiate between amorphous, poorly crystalline and crystalline Fe-oxides (Chao, 1984).

Several extraction solutions have been employed to dissolve the amorphous Fe oxide and Mn oxide, and crystalline Fe oxide phases. Chao & Zhou, 1983 compared the efficiency and specificity of several extraction solutions to dissolve amorphous and poorly crystalline iron oxides:

- 0.175 M Ammonium oxalate ($NH_4C_4O_4$) – 0.1M Oxalic acid ($H_2C_2O_4$) pH 3.3, in the dark.
- 0.25 M Hydroxylamine Hydrochloride ($NH_2OH.HCl$) in 0.25M HCl.
- 0.25 M Hydroxylamine Hydrochloride ($NH_2OH.HCl$) in 25% (v/v) Acetic acid.
- Hydrochloric acid.
- 3% oxalic acid in a boiling water bath.

Their results indicated that hematite and goethite dissolved sparingly in acid ammonium oxalate solution, to the extant of <1% after 4 hr of reaction. The acid ammonium oxalate solution dissolved significant amounts of Fe in magnetite and organic complexes. The extent of dissolution by HCl depends on acid concentration and the temperature of the reaction. At elevated temperatures, HCl can attack primary and secondary silicate minerals, as well as clay (Chao & Zhou, 1983; Chao, 1984; Ribet *et al.*, 1995). At room temperature, HCl seemed to be specific and dissolve 1 to 2% of the magnetite, hematite and goethite minerals tested. HCl dissolved up to 60% of the magnetite, hematite and goethite minerals at elevated temperature. Leinz *et al.*, 2000 used 4M HCl for 30 minutes at 94 ° in their sequential extraction procedure to extract the crystalline Fe-oxide phases in the mine wastes. The Fe, K and Pb extracted by this leach indicated high extraction of K and Pb jarosite. They recommended the use of HCl for extraction of mine wastes, because of its effectiveness for extracting jarosite with the crystalline Fe oxide phases.

Oxalic acid is effective in dissolving both amorphous and crystalline Fe oxides, especially at the boiling water temperature (Chao & Zhou, 1983). The lack of specificity in differentiating between amorphous and crystalline Fe-oxide, on the basis of difference in dissolution rates, makes oxalic acid an inappropriate extractant for amorphous Fe-oxides (Chao, 1984).

Hydroxylamine hydrochloride ($NH_2OH.HCl$) and acidity can be used to selectively dissolve Mn-oxides, amorphous Fe-oxides and crystalline Fe-oxides (Tessier *et al.*, 1979; Ribet *et al.*, 1995; Hall *et al.*, 1996; Fonseca & da Silva, 1998; Han *et al.*, 2001, McGregor & Blowes, 2002). Chao & Zhou, 1983 demonstrated that 0.25 M $NH_2OH.HCl$ in 25% CH_3OOH at 70 °C dissolved 1 to 4% of the crystalline Fe-oxides, depending on the reaction time. They also

indicated that a longer reaction time can overestimate the amorphous Fe-oxide fraction. A better reaction time for $NH_2OH.HCl$-CH_3OOH was 90 min with <2% of the crystalline Fe-oxides dissolved. Fonseca & da Silva, 1998 employed a method developed by Chao, 1972, 0.1 M $NH_2OH.HCl$ in 0.01M HNO_3, pH 2.0. The action of the $NH_2OH.HCl$ under these conditions is specific to Mn-oxides. Crystalline Fe-oxides such as goethite, hematite and magnetite do not dissolve in this leach. However, $NH_2OH.HCl$ in HNO_3 medium appears to release substantial amounts of trace metals bound to organic matter, consequently, the recovery of trace metals in the oxide fraction may be overestimated at the expense of the oxidisable fraction (Filgueiras *et al.*, 2002).

Ribet *et al.*, 1995 studied the potential for metal release by reductive dissolution of weathered mine tailings and they reported that the rate of Fe release was strongly dependent on the temperature and concentration of $NH_2OH.HCl$. The experiments were conducted to determine the concentration of $NH_2OH.HCl$ and type of acid (HCl or CH_3OOH (HOAc)). Their results showed that 2 M $NH_2OH.HCl$ was required for complete extraction, because tailings are rich in iron. This concentration is 50 times that suggested by Tessier et al., 1979. The use of HCl seemed to be more efficient, although it was suspected that HCl would increase dissolution potential of the silicate fraction, hence HOAc was used. This agreed with the study by Chao & Zhou, 1983, where they found that HCl-acidified $NH_2OH.HCl$ solution extracted the amorphous Fe-oxide 2 to 3 times faster than the HOAc-acidified solution at the same temperature.

$NH_2OH.HCl$/HOAc medium is capable of breaking the bonds between metals, and amorphous and poorly crystalline Fe oxides without attacking either the silicate or the organic matter fraction (Filgueiras *et al.*, 2002). $NH_2OH.HCl$ /HOAc leach may overestimate the amorphous Fe oxides because of some attack on crystalline Fe oxides. Chao & Zhou, 1983 showed that after 30 min, 0.25 M $NH_2OH.HCl$ in 0.25 M HCl at 70 °C dissolved <1 % of the crystalline Fe-oxides except for magnetite. They lowered the temperature of 0.25 M $NH_2OH.HCl$/0.25 M HCl extraction from 70 to 50 °C in order to reduce the dissolution of all crystalline Fe-oxide tested (hematite, goethite and magnetite) to <1 %, while maintaining the desirable feature of specificity for the amorphous Fe-oxide minerals. Hall *et al.*, 1996 employed 0.25 M $NH_2OH.HCl$/0.25 M HCl extraction to amorphous Fe oxyhydroxide phases in various sulphidic-rich samples but at an intermediate temperature of 60 °C as there seemed to be continued dissolution of amorphous Fe oxide minerals at lower temperature. They found that i) 20 – 25% of Zn, Cu, Pb, Ni and Co were extracted, ii) 0.25M HCl lead to significant dissolution of sphalerite and galena and, iii) this leach dissolved a considerable amount of soluble organic components.

Moreover, the acid ammonium oxalate solution has been used to extract metals incorporated in amorphous and poorly crystalline iron oxides in sequential extraction procedures (Sondag, 1981; Cardoso & Martin, 1986; Dold, 2003a, b; Hanahan, 2004). The acid ammonium oxalate solution (0.175M Ammonium oxalate– 0.1M Oxalic acid, pH 3.3, in the dark) commonly known as Tamm's reagent has been extensively used as a selective extractant to remove metals bound to amorphous and poorly crystalline iron oxides. Tamm's reagent has been claimed to release significant amounts of iron from amorphous iron oxide and magnetite (17 to 20 % after 4 hr), but only little crystalline hematite and goethite (to an extent of < 1 % after 4 hr of reaction) (Chao & Zhou, 1983).

The effects of variation in other extraction parameters e.g. pH (3-3.5), concentrations of reagents (0.113 – 0.2 M for $NH_4C_4O_4$; 0.087 – 0.2 M for $H_2C_2O_4$) and solution/soil ratio (5:1-100:1) on the extractability of trace metals can hardly be evaluated, particularly, variation in solution/soil ratios which leaves uncertainty on the comparability of these procedures (Hlavay *et al.*, 2004). A buffered solution which consists of 0.2 M ammonium oxalate brought to pH 3.0 with 0.2 M oxalic acid in darkness, dissolved the amorphous and poorly crystalline Fe-oxides within 2 hr, while leaving the crystalline phases essentially (<2 %, depending on crystallinity) undissolved (Chao, 1984). Dold, 2003a used this leach in the sequential extraction procedure to extract metals in the amorphous and poorly crystalline Fe phases in copper sulphide mine waste. He showed that the application of 1 hr of 0.2 M NH_4-oxalate (pH 3.0, in darkness) leach ensures that only secondary ferric phases such as schwertmannite, ferrihydrite and jarosite go into solution.

To extract either total amount of iron oxides or the crystalline iron phases subsequent to removal of the amorphous and poorly crystalline iron oxide, hydroxylamine hydrochloride and acid oxalate solutions can be employed under strong reducing conditions: extraction solutions at boiling water temperatures (between 80-95 °C) and acid oxalate solutions under UV radiation (20 – 100 °C) or under illumination. As suggested by Chao & Zhou, 1983 and Hall *et al.*, 1996 that increasing the temperature maximises the degree of dissolution of the crystalline phases, and this permit differentiation between the amorphous and crystalline Fe-oxides (Dold, 2003b).

As proposed by Tessier *et al.*, 1979; 0.04M $NH_2OH.HCl$/25%(v/v) HOAc (pH 2.0 at 85 °C) can extract metals bound to reducible oxides, such as Mn-oxides, and amorphous and crystalline iron oxides. However, 0.04M $NH_2OH.HCl$/25%(v/v) HOAc (pH 2.0 at 85 °C) leach does not distinguish between the Mn and Fe oxides (i.e. amorphous and crystalline Fe oxides). Based on their conclusions, only the amorphous and poorly crystalline Fe oxides were attacked by this leach. They studied the effects of leaching time on Fe concentration in

0.04M $NH_2OH.HCl$/25%(v/v) HOAc (pH 2.0 at 85 °C) in the reducible fraction. They found that increasing the leaching time from 6 to 24 hr did not result in higher Fe concentrations, indicating complete dissolution of reducible Mn-Fe oxide phases. Ribet *et al.*, 1995 found that for the Nickel Rim tailings, extraction of reducible iron was complete after 24 hr of leaching in a 2 M $NH_2OH.HCl$ – (v/v) 25% HOAc (pH 2.0 at 95 °C). Over 80 % of Fe, Ni, Cu, Cr and Co was found to be potentially available for release by reductive dissolution reactions. However too long contact time of extracting solution with the solid sample may:

- increase the possibilities of attacking other phases (Tessier *et al.*, 1979).
- cause the formation of secondary phases in the system because of readsorption of the cations already separated in a given extraction step or co-precipitation, which may decrease the concentration of metals in the fractions.

Fanfani *et al.*, 1997 applied the sequential extraction procedure derived from Tessier *et al.*, 1979 to abandoned mine tailings. They had six repeated extractions in the reducible fraction using 0.04 M $NH_2OH.HCl$/25% HOAc, because complete dissolution of the reducible fraction was not achieved in one extraction due to high Fe content. After six repeated extractions the distribution of metals showed relative high proportions in the reducible fraction, indicating strong scavenging efficiency of Fe-Mn oxides for metals (Salomons, 1995). Increasing the concentration of the reducing agent ($NH_2OH.HCl$) from 0.5 M to 1 M was reported to increase the extractability of metals (Sahuquillo *et al.*, 1999). This may be due to more effective attack on the more refractory amorphous and crystalline Fe-oxide phases.

Organic matter and sulphide fraction

Metals may be bound to or present as sulphide minerals and/or organic compounds. In this fraction the type of extraction changes from reducing to oxidising. Several reagents have been used for the dissolution of sulphide minerals: H_2O_2-asorbic acid; oxalic acid; mixture of $KClO_3$/HCl; mixture of $KClO_3$/HCl followed by 4 M HNO_3. Chao & Sanzalone, 1977 found that $KClO_3$/HCl followed by 4 M HNO_3 leach was most efficient in dissolving chalcopyrite, pyrite, galena, molybdemite, sphalenite and cinnabar. It will probably cause partial destruction of silicates along the edges and surfaces, however they emphasised that there is little danger of confounding a metal in the sulphide with that from the silicate, if the metal of interest is not a major constituent in the silicate structure. The $KClO_3$, HCl and 4 M HNO_3 leach is described fully by Chao & Sanzalone, 1977 and Hall *et al.*, 1996. Chao, 1984 reported that the H_2O_2 – asorbic acid leach will not attack other mineral phases such as silicates; however Mn-oxides and organic compounds may be dissolved if they are not removed first. Chao & Sanzalone, 1997 reported that the oxalic acid dissolution was not

effective in dissolving sulphides and this was supported by constant sulphur content after the dissolution.

Residue fraction

The residue fraction consists of silicates and some other resistant mineral phases. This fraction is commonly dissolved with highly concentrated acids such as HNO_3, HF, $HClO_4$, HCl and species digestion procedures. Dissolution after fusion with alkaline fluxes such as sodium carbonate, dithium metaborate and lithium tetraborate is also possible. A detailed comparison of the digestion methods is provided in Andersen *et al.*, 2004 and Pruseth *et al.*, 2005.

2.6.4 Kinetic dissolutions

As indicated, sequential extraction procedures are operationally defined. An important parameter in partial and sequential extractions is the time of contact with each reagent. The correct choice of contact time is obtained from the kinetic dissolution curves, where the extraction for a given sample and reagent is considered to be complete when the amount of the extracted metals reaches an extraction plateau. The knowledge of the kinetic dissolutions is important:

- for mineral separation (Chao & Sanzalone, 1977)
- for determination of secondary phases (especially Fe, Al, and Mn hydroxides), and to study their role in metal retention (e.g. sorption, co-precipitation, and solid solution) by sequential extractions in the (Dold & Fontbote, 2002; Dold, 2003b).
- to evaluate the optimum time for reducing and dissolving the Fe and Mn oxides (Tessier *et al.*, 1979; Chao & Zhou, 1983; Fonseca & da Silva, 1998).

A literature survey on this subject indicates that data on kinetics of the dissolution process are rather scarce. Hence in order to know what time of extraction is suitable for the most precise determination of metals fraction kinetic studies should be undertaken.

2.6.5 Application of sequential extraction procedures to mine wastes

Recently, sequential extraction procedures have been increasingly applied in the mine waste environment to i) evaluate mobility of metals in mine wastes and their availability to the environment, ii) to study processes of sulphide oxidation and the retention of metals by primary and secondary phases (via precipitation and sorption process) (Kontopoulos *et al.*, 1995; Ribet *et al.*, 1995; Fanfani *et al.*, 1997; Leinz *et al.*, 2000; Marguí *et al.*, 2004). The sequential extraction may provide information useful for evaluating the near and long term effects of wastes on the environment (Leinz *et al.*, 2000).

Fanfani *et al.*, 1997 concluded that the interpretation of weathering processes through sequential extraction procedures has the following two advantages: a) to avoid the use of typical mineralogical laboratory equipment b) to study the behaviour of some trace metals that have an environmental impact but are difficult to detect with a mineralogical study since they do not form specific minerals. Leinz *et al.*, 2000 reported that differences in mineralogical compositions influence the selection of procedures commonly used for extraction of metals from soil and sediments when they are applied to mine wastes.

Applications of sequential extraction schemes for metal partitioning in mine wastes are shown in Tables 2.11 and 2.12. In each table, the type of scheme, metals and remarks are included. In some studies the application of dissolution kinetic tests and the monitoring of dissolved phases in sequential extraction by XRD and DXRD were used to indicate which minerals are dissolved in each leach fraction (Ribet *et al.*, 1995; Dold, 2003). For example, a Differential X-ray powder diffraction (DXRD) analysis of acid mine drainage precipitate containing schwertmannite and ferrihydrite showed that only 15 min contact time with 0.2 M NH_4-oxalate/Oxalic acid (pH 3.0) was sufficient for the dissolution of schwertmannite (Dold, 2003a, b).

Ribet *et al.*, 1995; Dold & Fontbote, 2001 and Carlsson *et al.*, 2002 used the sequential extraction procedures to provide an understanding of how various metals occur at different depths, which is important for the understanding of the present state of the tailings impoundment. This could be a useful tool for predicting future conditions in a tailings impoundment. For example, a mineralogical study by Ribet *et al.*, 1995 indicated that sulphide minerals originally present in the vadose zone at the time of tailings deposition, have been replaced by a series of secondary precipitates, the most abundant secondary minerals being goethite, gypsum and jarosite. Sequential extraction can provide information about the potential release of metals contained in these minerals and conditions at which they can be released under natural conditions.

As indicated in Tables 2.11 and 2.12, when applied to mine waste, the sequential extraction procedures can indicate the zones where sulphide minerals have been depleted through oxidation processes and where carbonate minerals were consumed by pH-buffering reactions. Sequential extraction procedures can also provide information on the dissolution of aluminosilicates. According to Carlsson *et al.*, 2002 metals such as Ca, Fe, Al, As, Cr, Cu, Zn and Mn exhibited increased amounts in the amorphous iron oxyhydroxide and/or crystalline iron oxide fractions in the unoxidised zone of the tailings. This indicated transport of mobilised metals from oxidised zone with percolating water into unoxidised zone where they are retained by processes such as adsorption and/or by the formation of secondary minerals. Phases with strong adsorptive or retentive power will hold the metals to their

surface through physio-chemical bonding and incorporate them into their structure (Chao, 1984).

Literature, therefore, shows that sequential extractions can be chosen as the best approach to assess weathering processes. Sequential extractions allow single metals to be associated with certain phases and indicate immediate information on the mobility of metals. A detailed mineralogical study should accompany the study of mine wastes using sequential extractions to improve the accuracy of the interpretations of data.

Table 2.11: Application of sequential extraction procedures to partition metals in mine wastes.

Author	Extraction scheme	Sample	Metals	Remarks
Kontopoulos *et al.*, 1995	5-fractions (Tessier *et al.*, 1979): • *exchangeables* • *carbonates* • *reducible,* • *oxidisable* • *residue*	Sulphidic tailings in Lavrion	Pb, Zn, Cd, Cu, As, Cr, Ni, Hg	High Pb, Cd and As in the soluble or readily available fractions (exchangeable & carbonate fractions).
Ribet *et al.*, 1995	3-fractions: • *water soluble* • *reducible (Fe oxide and (oxy)hydroxides)* • *residual*	Weathered Tailings - Nickel Rim mine tailings	Fe, Al, Mg, Ni, Cr, Cu, Mn, Zn, K, Pb, Co, Ca	The greatest accumulation of metals was in the reducible fraction, indicating that the high amounts of metals were potentially available for release by reductive dissolution of Fe(III)-bearing secondary minerals. High Al, Mg and K due to aluminosilicate dissolution to form Al- hydroxide or basic Al-sulphate solids, or coprecipitation of Al with Fe(III)-(oxy)hydroxide solids. The Fe concentrations decreased from the upper part of the tailings, where concentrations were as high as 200 mg/g, to the partly-oxidised and then non-oxidised zones. High Fe near the tailings surface resulted from the more intensive sulphide oxidation processes occurring in the upper part of the tailings, indicating that the tailings near the surface were cemented by secondary precipitates, dominated by jarosite, goethite and gypsum.
Fanfani *et al.*, 1997	5-fractions: • *waster soluble, exchangeable fraction,* • *easily soluble carbonates, reducible oxides* • *fraction bound to organic matter* • *sulphides*	Abandoned mine tailings -a neutralised drainage highly contaminated by heavy metals.	Fe, Mn, Zn, Pb, Cd, Cu, Ni, Co	Fe and Mn appeared to be strongly immobilised mainly in an oxide form. Ni and Cu were incorporated in the Fe-oxide, but mostly in the organic matter and sulphide fraction. Zn, Cd and Co were much more mobile, temporally hosted in the oxide phases from which they are easily removed in the early steps. Zn in the water soluble ascribed to high solubility of $ZnSO_4$. Ca and Mg easily mobilised as Ca, Mg-SO_4 in the water soluble. Pb weakly adsorbed on Fe-oxide and silicates, therefore extracted in the exchangeable and carbonate fractions. They recommended an extraction scheme that can distinguish siderite and iron oxyhydroxides.
Leinz *et al.*, 2000	7-fractions: • *water soluble, exchangeable* • *carbonates* • *amorphous Fe and Mn oxide, crystalline Fe oxide, sulphides* • *residual.*	Acid generating mine wastes	Fe, K, Pb, Zn, Cu	Zn and Cu were more favourably partitioned in crystalline Fe oxide and sulphide phases, while Pb was more partitioned in the amorphous and crystalline Fe oxide phases. K was almost exclusively in the silicates, most likely in muscovite. Zn, Pb and Cu in the water soluble, exchangeable and carbonate fractions indicated potential mobility of these metals. The amounts of metals extracted from each phase varied with particle size and the presence of jarosite influenced the selection of the procedure for extracting the crystalline Fe oxide phases. High metals in the reducible fraction, indicated strong scavenging efficiency of Fe-Mn oxides for metals.

Table 2.12: Application of sequential extraction procedures to partition metals in mine wastes *(continue)*

Author	Extraction scheme	Sample	Metals	Remarks
Dold & Fontebote, 2001	7-fractions: • *water soluble, exchangeable, amorphous Fe and Mn oxide, crystalline Fe oxide* • *organic matter and secondary Cu-sulphides* • *primary sulphides* • *residual*	Tailings from La Andina, El Teniente & El Salvator porphyry Cu deposit	SO_4, Al, Mg, Na, Cu, Zn, Mn	High concentration of SO_4, Al, Mg, Na, Cu, Zn and Mn in the water soluble fraction at the top of the tailings was consistent with abundance water soluble sulphates. Cu and Zn in sulphide fraction were low through out the whole tailings, indicating that nearly all mobile metals were mobilised upward and that primary zone is significantly affected by oxidation and low pH conditions. Significant dissolution of secondary jarosite was indicated by increased K concentration in the leach.
McGregor & Blowes, 2002	2-fractions: • *water soluble* • *reducible*	Sulphide-bearing mine tailings (Fault lake, Nickel Rim and East mime cemented tailings)	Fe, As, Cd, Co, Cu, Ni, Zn	Fe extracted from reducible fraction within Fault lake, Nickel Rim and East mime cemented tailings was 84.1%, 54.1% and 49.8% respectively, indicating that Fe-bearing phases within the cemented vary between sites. Gypsum and jarosite in Nickel Rim and East mine tailings indicated by soluble sulphates and Ca in the water soluble fraction.
Carlsson *et al.*, 2002	5-fractions: • *adsorbed/exchangeable/carbonate;* • *labile organics; amorphous Fe oxyhydroxides* • *and Mn oxides* • *crystalline Fe oxides* • *organics and sulphides*	Sulphide-rich mine tailings	Al, Ca, Mg, Mn, Si, Ba, Cr, Fe, As, Cd, Co, Cu, Hg, Mo, Ni, Zn	For Ca, Al, Mg, Mn and Si in the oxidised and unoxidised zone, the major source was the residual. In unoxidised zone 80.4 wt.% of Fe in the sulphide fraction, 9.9 wt.% from the residual, 4.9 wt.% in Fe in the amorphous iron oxyhydroxides, 2.1 wt.% in the adsorbed/exchangeable/carbonate and crystalline iron oxide fractions.
Dold, 2003a	7-fractions: • *water soluble, exchangeable, amorphous Fe and Mn oxide, crystalline Fe oxide,* • *organic matter and secondary Cu-sulphides* • *primary sulphides* • *residual*	Cu-sulphide tailings from porphyry copper and from Fe-oxide Cu–Au deposits.	Cu, Al, Mg, Ca, Fe, Mn, Zn, K	Dold, 2003 used the extraction scheme employed by Dold & Fontebote, 2001 to obtain a detailed knowledge of the dissolved phases in each step of the sequential extraction and to develop a new sequence for the specific purpose of studying Cu-sulphide mine waste. The application of kinetic dissolution tests and the monitoring of dissolved phases in sequential extraction by XRD and DXRD indicated which minerals are dissolved in each leach step. Use of the water soluble fraction as the first step in sequential extractions for mine tailings was strongly recommended.
Jeong, 2003	5-fractions ((Tessier *et al*, 1979): • *exchangeables* • *carbonates* • *Cu-oxides* • *Cu organic matter and sulphides, residue (Cu-silicates)*	Copper in Mine Wastes	Cu, Fe	Carbonate and oxide fractions were the largest pools of Cu (50-80%), whereas the organic matter fraction was the largest reservoir (32%). The concentrations of Fe and Cu were inversely correlated in the oxide fraction suggesting that Cu may occur as a surface coating on iron oxides. Environmental parameters including particle size, water content and hydrologic setting, were found to be factors controlling speciation of Cu in the solid phase.

2.7 Summary of the literature review

The preceding review of literature showed that an understanding of the parameters and mechanisms governing acid mine drainage (AMD), hence the leachate generation is required for adequate prediction of the long-term behaviour of solid mineral wastes. Meaningful analytical tools are required to adequately predict the complex formation of AMD in the environment. The most widely used static test methods for AMD characterisations are: acid-base accounting (acid neutralisation capacity (ANC) tests) and net acid generation (NAG) test (single addition and sequential NAG tests). These tests involve single measurements in time. Kinetic tests such as the kinetic NAG can provide information on the sulphide reactivity, oxidation kinetics and leaching behaviour of metals.

However, it has been shown that each method has its limitations and the use of ABA and NAG procedures in isolation leads to uncertainties and limitations. Hence an integrative approach is required when applying these tests to overcome their limitations. The mineralogical analysis of the solid waste can provide information required for the selection of these tests and enhance the interpretation of the result. The following issues need to be considered when using the AMD prediction tests:

- The presence of siderite ($FeCO_3$) in the sample which can affect the ANC test results.
- Incomplete oxidation and hydrolysis of Fe which can overestimate the ANC results.
- During static the NAG test catalytic decomposition of H_2O_2 may occur before all pyrite is oxidised.
- Validation of the heating step in NAG test in terms of the dissolution of acid forming and neutralising minerals.

Application of several sequential extraction schemes to mine waste can provide:

- information pertaining to the mobility of metals and their availability to the environment.
- information required to study processes of sulphide oxidation and the retention of metals by primary and secondary phases.
- an understanding of how various metals occur at different depths, which is important for the understanding of the present state of the tailings impoundment and to predict the future behaviour of the mine wastes.

Sequential extractions have also been used to study the behaviour of some trace metals that have an environmental impact, but are difficult to detect with a mineralogical study since they do not form specific minerals. Limitations in sequential extraction are due primarily to a lack of specificity of sequential extraction procedures, time of contact of solid and extractants and redistribution of metals among solid phases, coupled to insufficient mineralogical information of a particular mine waste.

Chapter 3

METHODOLOGY

Based on the study objectives and literature review presented in Chapters 1 and 2, the following hypotheses have been formulated:

1) In order for the AMD prediction tests and sequential extraction procedures to be selected and interpreted, one needs to have a good knowledge of the sample mineralogy.

2) First-order deportment modelling on the basis of sources (ore *type and composition*) and origins (*generation process*), of the environmentally significant trace and minor components from copper sulphide ores into tailings will result in reliable predictions, and can be confirmed by total element analysis in ores and tailings.

This chapter begins by presenting an overview of the schematic chart of the experimental test work programme for chemical characterisation (Section 3.1) of the copper mine tailings sample employed to test the above hypotheses, followed by a description of the Kennecott copper deposits (Section 3.2).

This is followed by a detailed description of the laboratory flotation technique used to generate the copper tailings and sample preparation in Sections 3.3 and 3.4 respectively. Section 3.5 provides a brief description of the chemical reagents. The main empirical waste characterisation methodologies used to confirm the formulated hypotheses are presented in Sections 3.6 through 3.9, followed by conclusions in Section 3.10.

3.1 Experimental testwork programme

The objective of the experimental testwork programme presented schematically in Figure 3.1 was to generate comprehensive and relevant chemical properties of a copper sulphide ore and tailings samples so as to validate the hypotheses. This experimental testwork programme is based on Levels 1 and 2 of the conceptual methodology for solid waste characterisation and leachate generation prediction presented in Chapter 2.

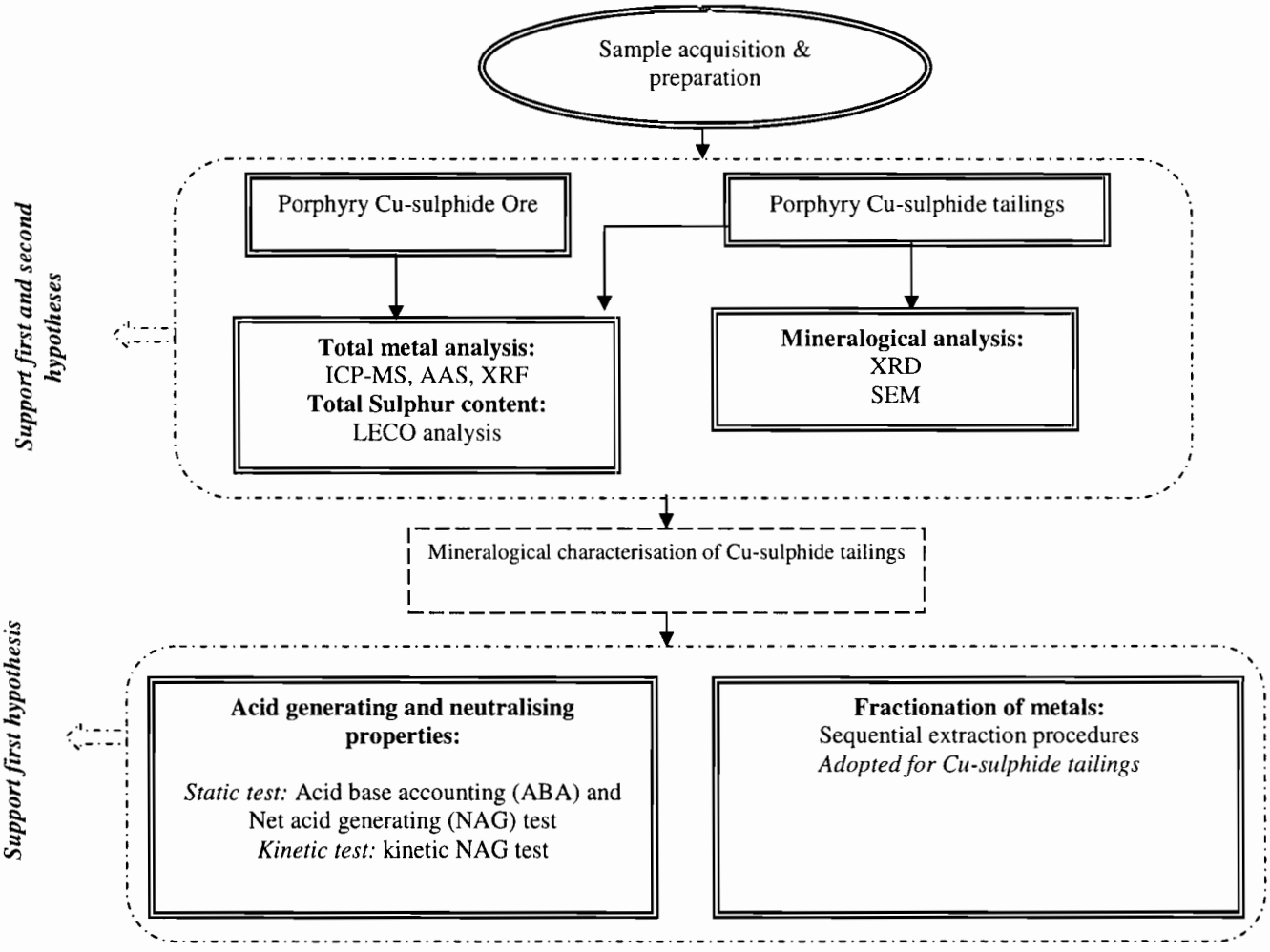


Figure 3.1: Schematic outline of the empirical testwork programme for chemical characterisation of the porphyry copper sulphide tailings from the Kennecott copper mine.

A bulk sample of run-of-mine ore was obtained from the Kennecott Utah Copper Corporation's Bingham Canyon mine, located near Salt Lake City, in early 2002. The geology of the Bingham Canyon porphyry copper ore deposit and the beneficiation process has been well documented (US EPA, 1994a; Maughan *et al.*, 2002; Borden, 2003). However, the data pertaining to the geochemical chemical characteristics (i.e. compositions and metal speciation) of the Kennecott Cu-sulphide tailings is unavailable.

3.2 Kennecott Copper Utah: Geology of the Bingham Copper Ore Body

Porphyry copper deposits account for more than 40% of world copper production and more than a third of world copper reserves (Borden, 2003). The Bingham Canyon Cu–Au–Mo porphyry body is one of the largest porphyry copper deposits in the world, containing 27.5 Mt of copper, 0.78 Mt of molybdenum, 1600 t of gold and 17,700 t of silver (Landtwing *et*

al., 2005). Large-scale open-pit mining was first implemented at Bingham Canyon in 1906, and net production from the ore body totals more than 15 million tonnes of copper. The metal by-products of copper mining at Bingham Canyon include silver, uranium, selenium, platinum, and palladium (US EPA, 1994a).

At the Bingham Canyon porphyry copper deposit, sulphide mineralisation progresses outward from a low-grade core through the following general zones: chalcopyrite–pyrite (being the most abundant sulphide ore minerals); pyrite; chalcopyrite–bornite; molybdenite and sphalerite– galena (Maughan *et al.*, 2002). The central portion of the ore body, exposed in the bottom of the pit, consists of a low grade core, characterised by a relatively low pyrite (generally less than 0.5% total sulphides). Pyrite is usually concentrated in a zone that is generally at the outer edge of the chalcopyrite/copper zone of the ore body and this zone is characterised by over 5% pyrite (Borden, 2003), which is several times higher than the average pyrite content of the rest of the ore body (US EPA, 1994a).

Chalcopyrite is the principal copper mineral in the primary portion of the copper zone with lesser molybdenite and pyrite, although bornite is common in ore from the central portion of the ore body (US EPA, 1994a). Generally, pyrite and to a lesser extent chalcopyrite, bornite and molybdenite are the primary minerals contributing to acid production in Bingham Canyon porphyry copper deposit. The main copper zone of the ore body and the surrounding pyrite halo are generally net acid-generating and the rock will tend to acidify when exposed to the atmosphere.

The main ferrous iron mineral is siderite and the deposits also have an alteration assemblage that contains abundant white mica, clay, and carbonate minerals (Cox *et al.*, 1996). Porphyry deposits exhibit a characteristic pattern of hydrothermal alteration, which includes potassic (quartz; K-feldspar; biotite and anhydrite) assemblages in the center and grades outward to chlorite, albite, and epidote assemblages (Cox *et al.*, 1996).

3.3 Experimental details of the laboratory flotation test on Kennecott ore samples

The copper tailings sample used in this study was fresh, unoxidised tailings collected by floating 1.13 kg of milled Kennecott copper ore. The flotation cell used for the laboratory-scale batch flotation test is a modified 3 *l* Leeds batch flotation cell, as illustrated in Figure 3.2. Milling of the ore was performed by wet milling, using 600 ml of water for 7 minutes at 90 rev/min. The milled ore was transferred into the flotation cell, while stirring at approximately between 800 and 900 rev/min. Calcium oxide (CaO) was used to adjust the pH of the milled ore in the cell to between 10.5 and 11. About 12 and 30 g/ton of the

collector and frother respectively were used, while stirring at 1200rev/min. Concentrate collections were made at 30s intervals for 15 min.

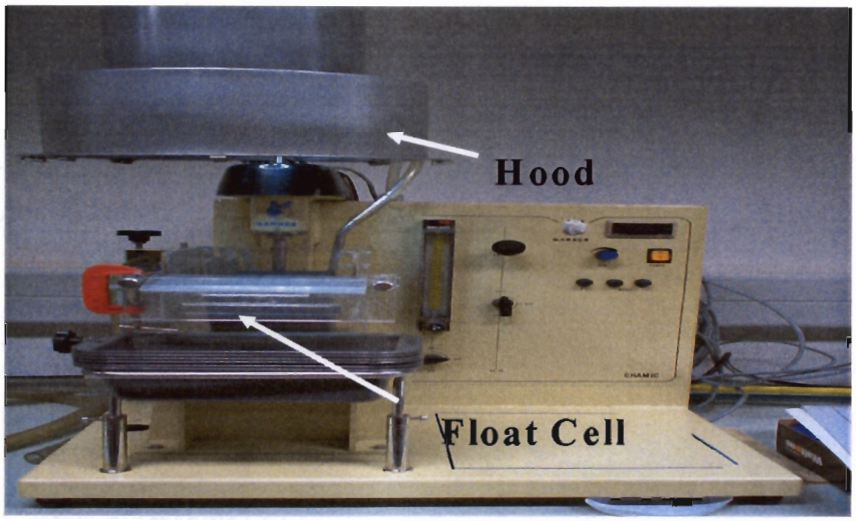


Figure 3.2: Laboratory-scale flotation apparatus used for the flotation of the Kennecott ore.

3.4 Sample preparation

Sample preparation forms a very important first step to all subsequent analysis. The milled ore and tailings were oven dried at < 40°C to prevent decomposition of minerals contained in the samples and then rotary split to obtain approximately 200 g representative subsamples using a rotary sample divider. The 200 g subsamples were rotary split to obtain 100 g subsamples, which were then split to obtain approximately 20g subsamples and placed in polyethylene plastic bags. The 20 g subsamples were pulverised to an average of 42 μm prior to chemical analysis by the selected tests. The particle size distribution of the sample was determined using Malvern analysis (see Appendix B).

3.5 Chemical reagents

All chemicals used in this study were reagent grade. Deionised water used in preparing the stock solutions and for making the reagents for each sequential extraction procedure was obtained from Milli-Q® UV PLUS system (Millipore Co.). Cleaning of all plastics and glassware used for the experiments was carried out by soaking in 20% HNO_3 (v/v) for 24 hr and rinsed with sufficient distilled water and deionised water in order to avoid contamination. Deionised and distilled water was used for all dilutions. Redox and pH were measured with a Metrohm Pt electrode and the pH electrode was calibrated using two Titrisol pH 4.0 and 7.0 buffers.

3.6 Mineralogical characterisation methods

This section presents the mineralogical methods that were selected to characterise the copper tailings sample as the basis for test selection and to assist interpretation of the results.

3.6.1 X-ray Diffraction (XRD) and Scanning electron microscope (SEM) analysis

X-ray Diffraction (XRD) analysis was performed on the copper tailings sample. The XRD patterns were recorded using PANalytical X'pert Pro with X'celerator detector, using CoK_{α} radiation over a 2Θ range from 5° to 90°. Scanning was set at a step size of 0.008 ° and accumulation time 4.63 sec per step, measuring 2 degrees at a time. Power was set at 45 kV 40 mA. Autoquan software was used to quantify the mineral phases.

Analysis by scanning electron microscope coupled with Energy Dispersive Spectrometry (SEM-EDS) of the sample was conducted to provide an understanding of the distribution of major minerals.

3.6.2 Total sulphur content analysis

The total sulphur content of each sample was determined by combustion-infrared spectrophotometer LECO analysis. The solid residuals from the test employed were air dried at ambient temperature in the ThermoChem dryer and analysed for total S using LECO analysis.

3.7 Outline of the test methods used for predicting AMD

A summary of the acid generation prediction methods are provided in this section as background to the acid potential prediction test results presented in Chapter 5.

3.7.1 Acid Neutralisation Capacity (ANC) test procedures

The acid neutralisation capacity (ANC) was determined on the sample by three different ANC methods:

- Standard Sobek (1978)
- Skousen H_2O_2 siderite correction
- Additional/Incremental H_2O_2 ANC method

The H_2O_2 siderite correction and Additional/Incremental H_2O_2 ANC methods were modified from standard Skousen *et al.*, 1997 and Weber *et al.*, 2004a to improve the efficiency of these tests, by preventing or minimising incomplete Fe hydrolysis on samples containing significant Fe content or siderite. The Incremental H_2O_2 ANC test used in this study is

similar to the one described by Weber *et al.*, 2004a. The samples were monitored every 24 hr over 72 hr for any pH drop and corrected back to pH 7.0 with NaOH. Detailed description of the modified procedure for each method may be found in Appendix E.

Note that the paste pH test was not conducted because the sequential extraction procedures (described in Section 3.9) include the water soluble as the first fraction to be leached. In the water soluble fraction the pH of a sample is determined by equilibrating the sample in deionised water. This gives an indication of the inherent acidity.

3.7.1.1 Fizz rating

Each ANC test method was dependent on the fizz test to estimate the amount and strength of HCl required to dissolve the reactive carbonates present in the sample. A fizz rating was assigned according to Sobek *et al.*, 1978 guidelines (Table 3.1), by placing approximately 0.5 g of sample on a watch glass adding one or two drops of 25% HCl and noting the reaction. The presence of carbonates is indicated by a bubbling or audible fizz. The modifications of the ANC test methods are also based on the methodology of Sobek *et al.*, 1978. Fizz rating is highly subjective, therefore the amount and strength of acid is also limited by measuring the ANC solution pH, which is required to be in the range 0.8 to 1.5 (AMIRA, 2002). All ANC test methods were conducted in duplicate samples and blanks (no sample added) were prepared.

Table 3.1: Fizz rating and acid-base tabulations for the determination of ANC by titration.

Reaction	Fizz Rating	HCl molarity (M)	HCl volume (ml)	NaOH molarity (M)
No reaction	0	0.5	4	0.1
Slight reaction	1	0.5	8	0.1
Moderate reaction	2	0.5	20	0.5
Strong reaction	3	0.5	40	0.5
Very strong reaction	4	1.0	40	0.5
Carbonate reaction	5	1.0	60	0.5

3.7.1.2 Standard Sobek ANC test

2 g dry pulverised sample was digested in HCl. The concentration and volume of HCl was based on the fizz rating. 20 ml of deionised water were used to flush the sample to the bottom. The combined solid samples and HCl solution were heated at 90 °C for 1-2 hr, and then cooled at room temperature for 1 hr. The reaction was complete when no gas evolution was visible and particles settled evenly over the bottom of the flask. Deionised water was added to give a total of 125 ml and pH of mixture was measured. The sample was filtered and back titrated using standardised NaOH (depending on the concentration of HCl used as listed in Table 3.1) to pH 7.0 and recorded the NaOH volume added to determine the final ANC of the samples.

3.7.1.3 H_2O_2 siderite correction (Skousen *et al.*, 1997) ANC test

This procedure involved the addition of HCl (according to fizz rating) to 2 g samples. Solution was topped up to 100 ml with deionised water prior to boiling for 5 min. After cooling the pH was measured then sample was filtered and treated with 5 ml 30% H_2O_2 to promote oxidation of dissolved Fe(II) and precipitation of Fe(III) oxyhydroxide, and then boiled for a further 5 min. After second cooling, the sample was filtered to remove the secondary Fe minerals formed during oxidation and hydrolysis of Fe. The solution was then back titrated with NaOH to pH 7.0 to determine the final ANC of the samples. The solutions were left to sit for a further 24 hr, the pH adjusted if required and a further 5ml of H_2O_2 added. This last step was repeated over 72 hr.

3.7.1.4 Additional/Incremental H_2O_2 ANC test

The sample was digested as described for Standard Sobek ANC test, except that the procedure involved adding 10 drops of 30% H_2O_2 at pH 4.5 noting the pH drop due to hydrolysis reactions. If a pH drop occurred the solution was back titrated again to pH 4.5 and further 10 drops of H_2O_2 were added. This step was repeated until no significant pH drop was observed and then back titration continued to pH 7.0 to determine the final ANC of the samples. The solutions were left to sit for 24 hr, the pH adjusted if required and further 10 drops H_2O_2 added. This last step was repeated over 72 hr.

3.7.2 Net Acid Generation (NAG) test methods

As part of this project, single addition NAG, sequential NAG and kinetic NAG testing were carried out on the copper tailings sample. Detailed description of the NAG test procedures may be found in Appendix F.

The NAG test methods used in this study were as follows:

- Static NAG – single addition and sequential NAG test.
- Kinetic NAG test (KNAG).

3.7.2.1 Single addition NAG test

2.5 g of pulverised sample was placed into a 500 ml conical beaker and 250 ml of a solution of 15% H_2O_2 was carefully added to the conical flask to encourage the rapid oxidation of reactive sulphides. The pH of the 15% H_2O_2 solution was adjusted to 4.5 using dilute NaOH. NaOH solution was made up by adding 1 g NaOH to 100 ml of deionised water as suggested by AMIRA, 2002. A watchglass was placed on top of the beaker and then placed in a fume hood to react for 24 hr. After the reaction, the beaker was placed on a hot plate and gently heated for a minimum of 1.5-2 hr. This was to ensure that effervescence stops, indicating a complete catalytic decomposition of H_2O_2. Deionised water was added as required to maintain the volume approximately constant of 250 ml. The final NAG_{pH} was measured, and then the sample was filtered. The NAG solution was titrated to pH 4.5 and 7.0, while

swirling with appropriate NaOH solution based on the measured NAG_{pH} as shown in Table 3.2.

Table 3.2: Concentration of NaOH required for titrating NAG solutions based on NAG_{pH}.

NAG_{pH}	Concentration of NaOH required
NAG_{pH} is > 2	0.1 M NaOH
NAG_{pH} is ≤ 2	0.5 M NaOH

Final NAG_{pH}< 4.5 indicates reactive sulphide minerals in excess of neutralising reactions, whereas a high final NAG_{pH} (>4.5) indicates the presence of carbonates (ANC) with acid neutralising capacities in excess of acid produced by sulphide oxidation.

3.7.2.2 Sequential NAG test

The sequential NAG test was conducted in the same manner as the single addition NAG test, except that after measuring the NAG_{pH} the liquor was separated from the solids, and then titrated to pH 4.5 and 7.0. The remaining solids were air dried then subjected to LECO analysis for total S content and then reacted further with 15% H_2O_2. The procedure was repeated until the NAG_{pH} reaches a value of 4.5 or greater. Overall NAG capacities (kg H_2SO_4/ t) of the sample at NAG_{pH} 4.5 and 7.0 were determined by summing the individual NAG capacities from each stage.

3.7.2.3 Kinetic NAG test

The kinetic NAG test was used to provide an indication of the reactivity of sulphide and buffering minerals within the sample and to provide a quick lag time for acidification. Essentially, the kinetic NAG test is the single addition NAG test; refinements include the monitoring of pH and solution temperature during the test to obtain kinetic information regarding the reactivity of the sample.

The kinetic NAG test was carried out with pH and temperature probes immersed in the solution during the reaction and values recorded continuously at 2 min intervals for the first 30 min. This was done to provide the information on the dissolution rate of soluble salts in the early stages of the reaction. The measurements were taken at 10 min intervals after the first 30 min. The lag period is defined as the time to reach the temperature maximum due to catalytic decomposition of H_2O_2. Rapid pH decrease indicates reactive sulphide minerals in excess of neutralising reactions.

3.8 Sample classification

Figure 3.3 shows how the acid forming potential of a sample is classified on the basis of the S, ANC, NAPP, NAG (both single addition and sequential NAG) and kinetic NAG test

results into the following categories: non acid forming (NAF) and potential acid forming (PAF). This flowchart can be used to classify samples that appear to have conflicting NAG and NAPP results because kinetic and sequential NAG tests provide more information to obtain a better understanding of the oxidative behaviour of the sample. An uncertain classification is used when there is an apparent conflict between the NAPP and NAG results (i.e. when the NAPP is positive and $NAG_{pH} > 4.5$ or when the NAPP is negative and $NAG_{pH} \geq 4.5$).

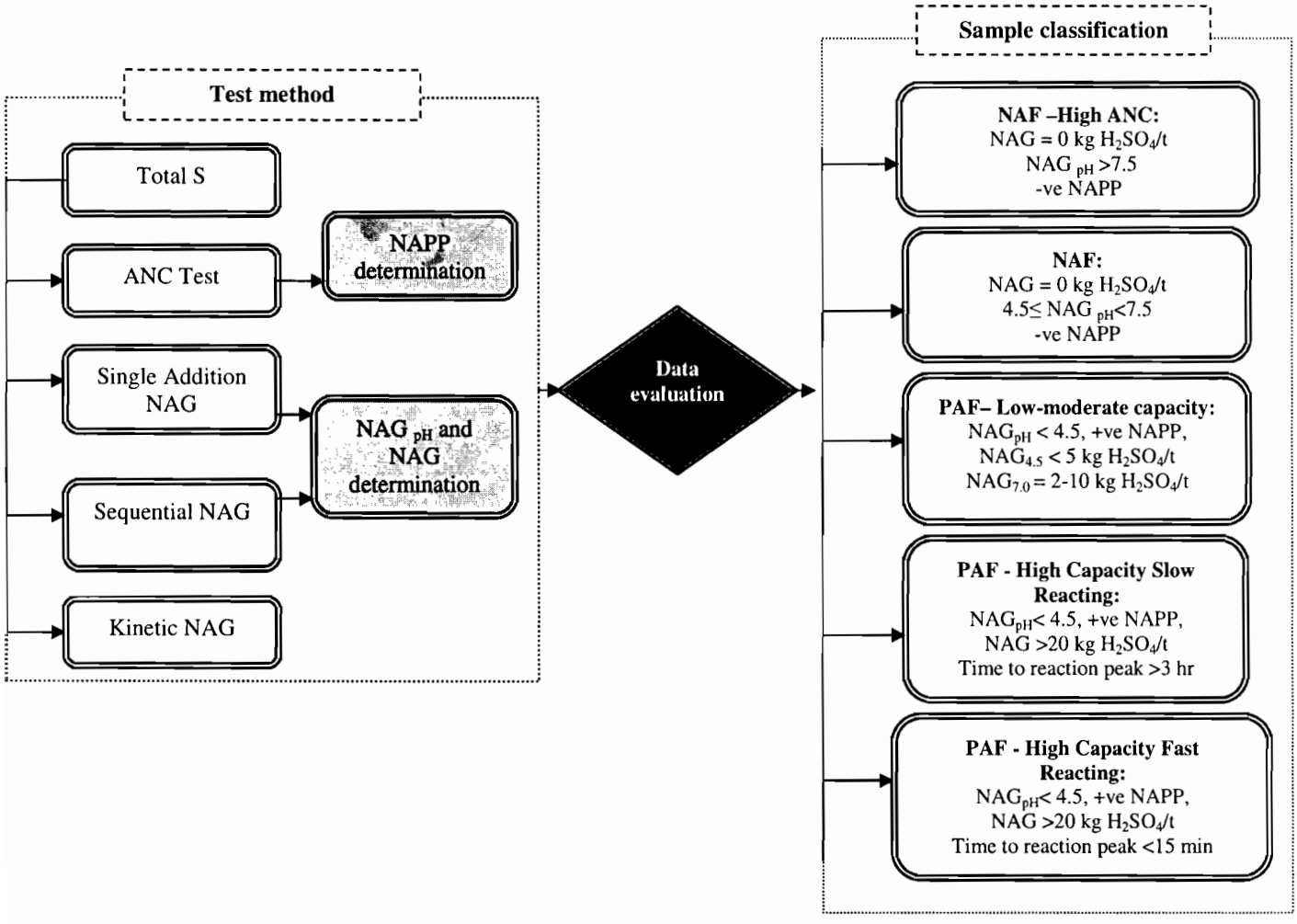


Figure 3.3: Flowchart showing the classification criteria of samples on the basis of ANC, NAPP, NAG (both single addition and sequential) and kinetic NAG results.

The AMD prediction tests were also conducted on the tailings samples from some well known Cu-processing operations for comparison purposes. Two samples were collected at different depths (25 and 40 m) from the tailings impoundment of Piuquenes/La Andina in Chile and one was collected from the Konkola Copper Mines Limited-Nchanga concentrator in Zambia. The porphyry Cu-tailings samples from La Andina in Chile consist of pyrite,

chalcopyrite, chalcocite, covellite, molybdenite, sphalerite, galena, tennanite and a gangue of ankerite, siderite, gypsum, quartz and very minor calcite. Copper tailings from Konkola Copper Mines Limited consist of chalcopyrite, bornite, chalcocite, pyrite, calcite, ankerite, dolomite, native copper, mica and silicate.

3.9 Sequential extraction procedures/schemes

Tables 3.3 and 3.4 outline the two sequential extraction procedures selected to determine the binding forms of metals in the studied Cu –tailings sample. The first sequential extraction scheme (A) was the modified seven step procedure which was adopted for the study of sulphide-rich copper mine tailings (Dold & Fontboté, 2002; Dold, 2003a). The second sequential extraction scheme (B) used in this study was slightly modified from Ribet *et al.*, 1995; Hall *at el.*, 1999 and Carlosson *et al.*, 2002.

Table 3.3: Sequential extraction scheme A adopted for sulphidic mine tailings (Scheme A: adopted after Dold & Fontboté, 2002 and Dold, 2003a).

Fraction	Leach	Preferentially dissolved minerals	References
F1: Water soluble	40 ml de-ionized H_2O, shaking for 1 hr, 25 °C	Soluble salts: Gypsum, and possibly jarosite	Fanfani *et al.*, 1997; Ribet *et al.*, 1995
F2: Exchangeable	20 ml 1M NH_4 – acetate, pH 4.5 adjusted with 1M CH_3OOH, shaking 2 hr	Ion exchangeable and carbonate	Gatehouse *et al.*, 1977; Sondag, 1981; Cardoso & Martin, 1986; Fonseca & da Silva, 1998
F3: Amorphous and poorly crystalline Fe-oxides	20 ml 0.2 M NH_4 –oxalate, pH 3.0 adjusted with 0.2 M oxalic acid, 1 hr in darkness	MnO_2, secondary jarosite, ferrihydrite, schwertmannite	Han *et al.*, 2001; McGregor & Blowes, 2002; Dold,2003a
F4: Crystalline Fe-Oxide	20 ml 0.2 M NH_4 –oxalate, pH 3.0 adjusted with 0.2 M oxalic acid, at 90 °C, 2 hr in a water bath	Goethite, hematite, magnetite	Ribet *et al.*, 1995; Han *et al.*, 2001; McGregor & Blowes, 2002; Dold, 2003a
F5: Secondary sulphides and organics	5 ml 35% H_2O_2, in a water bath, 1 hr	Covellite, chalcocite, digenite	Sondag, 1981
F6: Primary sulphide	750 mg $KClO_3$ and 5ml 12 M HCl, followed by 4 M HNO_3 at 90°C in a water bath	Pyrite, chalcopyrite, galena, covellite	Chao & Sanzolone, 1977; Hall *et al.*, 1996
F7: Residue	Aqua Regia (HCl, HNO_3), HF, $HClO_4$	Silicate minerals	Tessier *et al.*, 1979

Table 3.4: Sequential extraction scheme B: modified after Ribet *et al.*, 1995; Hall *at el.*, 1999 and Carlosson *et al.*, 2002).

Fraction	Leach	Preferentially dissolved minerals	References
F1: Water soluble	40 ml de-ionized H_2O, shaking for 1 hr, 25 °C	Soluble salts: Gypsum, and possibly jarosite	Fanfani *et al.*, 1997; Ribet *et al.*, 1995
F2: Exchangeable	20 ml 1M NH_4 – acetate, pH 4.5 adjusted with 1M CH_3OOH, shaking 2 hr	Ion exchangeable	Gatehouse *et al.*, 1977; Sondag, 1981; Cardoso & Martin, 1986; Fonseca & da Silva, 1998
F3B: Adsorbed carbonates	20 ml 1 M NaOAc adjusted to pH 5.0 with HOAc, 25 °C, 2 hr	Carbonates minerals e.g. calcite, dolomite	Tessier *et al.*, 1979; Fanfani *et al.*, 1997; Carlosson *et al.*, 2002; Hanahan, 2003
F4B: Amorphous and poorly crystalline Fe-oxides	20 ml 0.25 M $NH_2OH.HCl$ in 0.25 M HCl, pH 2.0, 50 °C, shaking for 2hr in a water bath	MnO_2, secondary jarosite, ferrihydrite, schwertmannite	Chao & Zhou, 1983; Hall *et al.*, 1996
F5B: Crystalline Fe-Oxide	30 ml 2 M $NH_2OH.HCl$ in 25% CH_3OOH, pH 2.0, shaking for 3 hr, 90 °C in a water bath	Goethite, hematite, magnetite	Ribet *et al.*, 1995; Han *et al.*, 2001; McGregor & Blowes, 2002
F6: Sulphides and organics	750 mg $KClO_3$ and 5ml 12 M HCl, followed by 4 M HNO_3 at 90°C in a water bath	Pyrite, chalcopyrite, galena, covellite	Chao & Sanzolone, 1977; Hall *et al.*, 1996
F7: Residue	Aqua Regia (HCl, HNO_3), HF, $HClO_4$,	Silicate minerals	Tessier *et al.*, 1979

Sequential extractions A and B were carried out progressively on an initial weight of 1 g of the tailings sample measured (with the actual mass recorded) into high density polyethylene (50 ml) centrifuge tubes to minimise losses of solid materials. All extractions were performed in duplicates and blanks were prepared for each fraction to assess contamination during analysis. For the fractions requiring temperature maintenance, the extractions were conducted in a shaking water bath maintained at a given temperature as indicated in Tables 3.3 and 3.4. Whenever NH_4-oxalate extraction was performed to dissolve the amorphous Fe oxide, the centrifuge tubes were wrapped with aluminum foil to exclude light and prevent attack on more crystalline Fe oxides (Chao & Zhou, 1983; Dold & Fontboté, 2002; Dold, 2003a).

The NH_4-oxalate solution was exposed to light by removing the aluminum foil to increase the dissolution of more crystalline Fe oxide phases. The amorphous Fe oxide fraction in Scheme B was extracted at 50 °C to minimise the degree of the dissolution of crystalline Fe oxide phases.

Following each extraction or washing, the supernatant was separated from the residue by centrifuging at high speed, 12500 rpm and temperature controlled at 20 -25 °C for 20 min. The supernatant was removed using a pipette and placed in acid-cleaned polyethylene

bottles. The residues were rinsed with 5 ml of deionised water and centrifuged again and this was done twice. The supernatant rinses were combined with the original solution in the labeled polyethylene bottles for analysis. The detailed experimental procedures of the sequential extraction schemes A and B are presented in Appendix H. Major metals: Fe, Cu, Al, K, Ca, Mg, Mn, Si; and trace metals: Co, C, Zn, Cd, As, Mo, Ag, Pb, V, Be and Ni in the sequential extraction solutions were determined by ICP-MS. The sum of all dissolution steps gives the total concentration of each metal recovered.

3.9.1 Total metal analysis

The aims of conducting total metal concentration on the ore, tailings and concentrate samples were to:

1. *Validate the sequential extraction data*

   Total metals analysis was conducted on the tailings in order to assess the accuracy of the sequential extraction procedure data. This was done by comparing the total recovery (sum of fractions) of metals with the total metal concentration and then determines the recovery values (%).

2. *Validate the first order predictions for metal deportment*

   Total metals analysis was conducted on the ore, tailings and concentrate samples in order to validate the first order predictions for metal deportment into tailings from porphyry copper sulphide ore.

Samples of approximately 1 g were measured into 50 ml high density polyethylene centrifuge tubes (the actual mass was recorded). In this digestion 2 ml of HF was added to the samples and heated for 20 min at 90 °C in a water bath. After cooling, samples were digested with Aqua Regia Leach, 10 ml of (1: 1 (v/v)) mixture of HNO_3 and HCl for 6 hr at 90 °C. After that, 5 ml of HF and 2 ml $HClO_4$ were added and then samples were heated for 6 hr at 90°C. Solutions were transferred into 50 ml volumetric flasks and volumes made up to approximately 50 ml with deionised water and then were filtered into 100 ml polyethylene plastic bottles.

All the analyses (for ore, tailings and concentrate samples) were run in triplicate and blank analyses by using three portions of 1 g sub samples. The solutions were analysed by ICP-MS for major metals: Fe, Cu, Al, K, Ca, Mg, Mn and Si; and trace metals: Co, C, Zn, Cd, As, Mo, Ag, Pb, V, Be and Ni. The residual fraction in the sequential extraction procedures were dissolved using this method.

3.10 Conclusions

This chapter presented the schematic chart of the experimental testwork and the test procedures used to characterise the Kennecott copper tailings to provide data that can be interpreted in such a way that the:

- Hypotheses stated in the beginning of the chapter are tested.
- Main objectives of the study (see Chapter 1) are achieved.

The detailed description of the waste characterisation tests employed in this study, such as ABA, NAG and sequential extraction procedures are provided in the Appendices E, F and H respectively. The data is presented and discussed in Chapter 4: mineralogical characterisation; Chapter 5: ABA and NAG; and Chapter 6: Sequential extraction.

Chapter 4

MINERALOGICAL CHARACTERISATION AND EVALUATION OF FIRST ORDER METAL DEPORTMENT MODELLING

The aims of this chapter were to:

- Provide the mineralogical characterisation of the Cu-sulphide tailings that forms a background for the selection of tests, and interpretation of the results in the subsequent chapters.
- Discuss the first order deportment modelling of metals from copper ore into tailings.

Section 4.1 presents the mineralogical analysis obtained by XRD, SEM-EDS and LECO analysis. This is followed by the evaluation of the first order metal deportment modelling in Section 4.2, where the total metal analysis obtained by ICP-MS is used to validate the first order predictions for metal deportment into tailings from copper sulphide ore processing made by Broadhurst *et al.*, 2005a in Task 4 of the WRC report. The mineralogical results are used to confirm the predicted concentration of major phases in porphyry type Cu sulphide tailings.

4.1 Mineralogical characterisation

Mineralogical analysis can provide details on:

- Sulphide minerals in the sample. Not all sulphide minerals produce acid, and determining the relative proportion of sulphide minerals can provide information on the acid generating potential of the sample.
- Neutralising minerals that would assist to assess the acid neutralisation capacity of the sample.

Therefore, knowledge of the mineralogy of the waste provides a framework in choosing the most appropriate method for acid-base accounting and interpreting the results. Also to ensure appropriate geochemical interpretation, it is crucial to combine the application of sequential extraction with detailed mineralogical studies of the copper mine tailings.

4.1.1 X-ray Diffraction analysis

The XRD results showed that the most common sulphide minerals in the studied porphyry copper tailings are, in decreasing order, pyrite and chalcopyrite, and comprises 2.92 and 0.5 wt% of the sample respectively, giving a total sulphide content of 3.4 wt%. The two most common carbonate minerals present in the sample were found to be calcite ($CaCO_3$, 2.43 wt %) and siderite ($FeCO_3$, 2.55 wt %). XRD also showed traces of ankerite [$Ca(Mg,Fe)(CO_3)_2$], dolomite [$CaMg(CO_3)_2$] and magnesite [$CaMg(CO_3)_2$].

The gangue minerals are by far the most abundant minerals. Quartz (SiO_2) is the most abundant in the gangue minerals 53 wt %, followed by the aluminosilicate minerals such as chlorite ($(MgFe)_5Al(Si_3Al)O_{10}(OH)_8$), 16 wt %); sanidine ($KAlSi_3O_8$, 9.8 wt %) which is in the K-feldspar group and muscovite ($(K,NH_4,Na)Al_2$ (Al, $Si)_4O_{10}(OH)_2$), 9.3 wt %).

The only iron oxide mineral quantified by XRD is hematite (Fe_2O_3, 4.2 wt %). Other oxides such manganese oxides (MnO_2) and goethite (α-FeO(OH) were also detected by XRD, but they are present in relatively minor quantities. Table 4.1 shows the mineralogical composition of the Cu sulphide tailings sample determined using XRD analysis. The XRD patterns are shown in Appendix C. The LECO analysis indicated that the average total sulphur in the sample is 2.9 wt %.

Table 4.1: Mineralogical characterisation of the Kennecott copper tailings

Mineral	Molecular formula	Concentration (wt %)
Pyrite	FeS_2	2.9 ± 0.21
Chalcopyrite	$CuFeS_2$	0.5 ± 0.13
Calcite	$CaCO_3$	2.4 ± 0.51
Siderite	$FeCO_3$	2.6 ± 0.48
Quartz	SiO_2	53 ± 1.2
Muscovite	$(K,NH_4,Na)Al_2$ (Al, $Si)4O_{10}(OH)_2$)	9.3 ± 0.81
Sanidine	$KAlSi3O_8$ (K-feldspars group)	9.8 ± 0.75
Chlorite	$(MgFe)_5Al(Si_3Al)O_{10}(OH)_8$)	15.6 ±1.5
Hematite	Fe_2O_3	4.2± 0.30

4.1.2 Scanning-electron microscopy (SEM) analysis

SEM-EDS examination of the sample was conducted to provide i) an understanding of the distribution of major minerals within the sample, ii) qualitative metal composition in the minerals and iii) to confirm the analytical results from XRD. Figure 4.1 shows the SEM image of the sample. The results show bright white crystals which were identified as pyrite

minerals. The element composition of these crystals is 49 wt % S, 34 wt % Fe and 1.5 wt % Cu suggesting that pyrite is abundant compared to chalcopyrite. The remainder of the sample contains mainly the quartz and Al-silicate minerals as shown by the dark minerals.

The major element composition of these dark minerals is 37.6 wt % O, 61.3 wt % Si and 4.5 wt % Al with traces of 0.63 wt % Fe, 0.13 wt % Cu, 0.38 wt % Ca and 0.37 wt % Mn. The distribution of minerals in the sample indicates that gangue minerals such as quartz and aluminosilicates are relatively abundant in the tailings sample as indicated by the XRD results. The element compositions also indicate that the gangue minerals are associated with the carbonate and iron oxide minerals.

Figure 4.1: SEM image of the porphyry Cu-tailings from Kennecott copper sulphide ore.

4.2 Evaluation of first order metal deportment modelling

A better understanding of the distribution of minor and trace ore metals during beneficiation can play a role in the evaluation of environmental metals. This section follows Level 1 of the 3 level waste characterisation hierarchy (see Chapter 2, Section 2.1) which aims to predict first order metal deportment and their forms on the basis of sources (ore type and composition) and origins (generating processes). Predicted concentration ranges for metals and main mineral groups in generic flotation tailings from porphyry copper sulphide ores have been presented in Task 4 of the WRC report by Broadhurst *et al.*, 2005a. These predictions are also presented in Appendix A.

Major metals: Cu, Fe, Si, Al, Mg, K, Ca, Na and Mn, and minor metals: Co, Cr, Zn, Cd, As, Mo, Ag, Pb, V, Be, Ni and Re were selected to validate the first order predictions for metal

deportment into tailings from copper sulphide ore. These metals were determined by ICP-MS after conducting total metal analysis on the porphyry Cu ore, tailings and concentrate samples according to the method described in Section 3.9.1. The major minerals in the tailings sample were determined by XRD analysis as discussed in Sections 3.6 and 4.1.

A comparison of the predicted concentration ranges and the experimental values of metals in the ore, tailings and concentrate are presented in Table 4.2. Generally, the results indicate that the experimentally determined concentrations of the major metals such as Fe, Si, Mg, K, Ca and Na, and the moderately abundant and minor metals such as Mn, Co, Cr, As, Ag and Be agree with the predicted ranges, although the experimental values of Al are below the predicted ranges in the ore, tailings and concentrate. Cu is below the predicted range in the ore and concentrate.

Table 4.2: Predicted concentration ranges and experimental measurements for porphyry-type copper sulphide ores, tailings and concentrates

	Predicted typical concentration ranges			Experimental concentrations		
	Ore	**Tailings**	**Concentrate**	**Ore**	**Tailings**	**Concentrate**
Major ore metals (%)						
Cu	0.5-1.0	0.08-0.15	25-30	0.21	0.12	0.9
Fe	1-10	0.8-9.5	15-30	11.6	7.2	29
Major rock-forming ore metals (%)						
Si	21-34	21-35	2.5-8	20.1	23	0.2
Al	4.0-10	4.0-10	0.5-2.2	0.44	0.49	0.1
Mg	0.2-3	0.2-2.6	0.02-0.6	0.2	0.32	0.12
K	0.3-3.4	0.3-3.5	0.03-0.8	1.66	1.3	0.77
Ca	0.4-4	0.4-4.5	0.05-1.0	0.33	0.91	0.38
Na	0.3-3	0.3-3.2	0.03-0.7	0.042	0.045	0.01
Moderately abundant and minor ore metals (ppm)						
Mn	100-2000	100-2000	11-450	958	1244	144
Co	2.5-50	0.3-15	70-1700	18.3	18.5	63
Cr	10-200	10-200	1-50	232	269.7	247
Zn	150-1600	15-500	4000-55000	129	117.7	389
Cd	2-200	0.2-60	50-6840	0.8	1.35	1.1
As	5-1800	2-550	100-62000	56	27.9	389
Mo	15-1500	1-500	400-50000	23.7	25.5	64
Ag	1.0-70	0.2-10	20-2500	2.2	1.47	19.6
Pb	30-300	5-100	800-11000	46	36.0	136
V	15-300	15-300	2-70	22.8	37.1	61
Be	0.5-30	1-30	0.2-5	0.9	1.07	1.03
Ni	8-150	1-50	200-5000	54	109.2	23.1

Deportment of metals to the tailings and concentrate is largely dependent on their mineralogy, speciation and mode of occurrence in the sulphide ore body (Broadhurst *et al.*, 2005a, Task 4 of the WRC report) (see Figure 4.2):

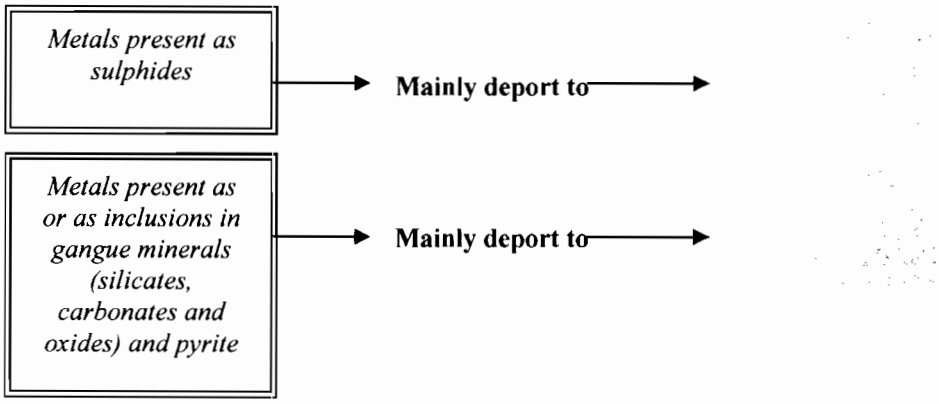


Figure 4.2: Deportment of metals to the tailings and concentrate as a function mineralogy, speciation and mode of occurrence in the sulphide ore body.

The experimental results indicate that the concentration levels of gangue metals such as Si, Al, K, Mg and Na in the tailings are similar to the ones in the ore (but mostly a bit higher) which agrees with the predictions. The predictions suggest that metals such as Co, Zn, Cd, As, Mo, Ag, Pb, Ni and Re report mainly to the concentrate. This was confirmed by the experimentally determined values of Co, Zn, As, Mo, Ag, Pb and Re, although Zn, Cd, Mo and Pd are below the predicted ranges in the concentrate. Both experimental and predicted values of Mn, Cr, V and Be indicate that these metals deport mainly to the tailings, although Cr is above the predicted ranges in the ore, tailings and concentrate.

The major rock forming metals such as Si, Al, K, Na, Mg and Ca (i.e. metals present as/in oxide, carbonate, silicate and pyrite minerals) reported mainly in the tailings. The experimental Fe value in the concentrate is consistent with the predicted concentration ranges. Fe reported mainly in the concentrate because it is associated with copper (mainly chalcopyrite) and iron (mainly pyrite) sulphide minerals. The concentration of Cu was very low in the concentrate, indicating a poor recovery of Cu during the laboratory flotation test on the Cu-sulphide ore.

Some of these metals are highly toxic e.g. Mo>As>Cd>Ag>Ni>Pb>Co, and subsequent deportment of these metals to tailings can have significant implications in terms of environmental impact.

The predicted concentrations of the main groups and their major components in porphyry type Cu sulphide tailings are shown in Table 4.3. Generally, the results obtained by XRD analysis, for major minerals are consistent with the predicted typical concentrations of the main mineral groups.

Table 4.3: Predicted concentrations of the main mineral groups and their major components in porphyry-type Cu sulphide tailings.

	Predicted ranges		Analytical values
Mineral group	**Predicted typical concentration (%)**	**Major minerals comprising each group**	**Concentration (%)**
		Sulphide minerals	
Copper sulphide minerals	0.08-0.2	▪ Chalcopyrite: 43-97% of total ▪ Bornite: up to 39% of total ▪ Chalcocite: up to 17%	Chalcopyrite: 0.5
Iron sulphide minerals	2-18	Mainly pyrite	FeS_2: 2.9
		Gangue minerals	
Silicate gangue minerals	82-96	▪ Quartz: 35-45% ▪ K-Feldspar: 20- 25% ▪ Muscovite and/or chlorite: ≤10%	▪ Quartz: 53 ▪ K-Feldspar: 9.8 ▪ Muscovite: 9.3 ▪ Chlorite: 15.6 Total silicate gangue minerals: 88
Carbonate gangue minerals	0.5-4	Mainly calcite with lesser amounts of dolomite, ankerite and/or siderite	Calcite: 2.4 Siderite: 2.6
Trace to minor gangue minerals	1-7	▪ Iron oxides (haematite, magnetite)	Hematite: 4.2

4.3 Conclusions

4.3.1 Mineralogical characterisation

Mineralogical characterisation was carried out on the copper tailings to provide information on sources and identity of potential metals, and sources of acid generation or neutralisation, to assist interpretation of the data generated in this study. XRD showed that pyrite and chalcopyrite were the most common sulphide minerals. Gangue minerals such as quartz and aluminosilicates (chlorite, K-feldspar and muscovite) form the bulk of the sample. Calcite ($CaCO_3$) and siderite ($FeCO_3$) were the only carbonates that were quantified by XRD with Autoquan.

The most abundant iron oxide was hematite (FeO_3). Other minerals that were detected by XRD but not quantified due to high detection limits were carbonates such as ankerite [$Ca(Mg,Fe)(CO_3)_2$], dolomite [$CaMg(CO_3)_2$], magnesite [$CaMg(CO_3)_2$]; and Fe and Mn oxide such as geothite (α-FeO(OH)) and MnO_2. The sample was relatively unoxidised, and the sequential extraction data is expected to indicate whether secondary minerals were formed due to the reaction of some of the sulphide minerals in the mill process water.

4.3.2 Validation of the first order predictions for metal deportment

The results presented in Section 4.2 demonstrated that the predictions made by Broadhurst *et al.*, 2005a can provide a fundamental understanding of the deportment of metals on the basis of sources and origins. The knowledge of metal deportment is useful for evaluation of the environmental impacts of a mine waste and these predictions can be useful as guidelines. By conducing total metal analysis and mineralogical characterisation on ore, tailings and concentrate, metal deportment can be evaluated with these predictions used as guidelines.

The experimentally determined concentrations of the major metals were consistent with the predicted concentration ranges, except for Al and Cu. A low recovery of copper in the concentrate showed a poor recovery during the flotation test. The major mineral phases obtained by XRD were also consistent with the predicted concentrations of the main minerals. However, the concentration levels of the moderately abundant and minor metal were lower than the predicted ranges. These results indicated that the Cu-tailings sample used in this study was representative of a typical porphyry copper sulphide tailings.

Chapter 5

ACID BASE ACCOUNTING AND NET ACID GENERATION TEST RESULTS

The results of the static acid generation prediction tests and kinetic NAG test carried out on the copper tailings samples are presented in this chapter. The main objectives of this chapter were to:

- Evaluate and compare different acid generation prediction tests and determine their reliability on the studied porphyry Kennecott copper tailings sample.
- Evaluate to what extent prior knowledge of the mineralogy of the sample is required in order to:
  - ❖ Avoid choosing a method that would yield unreliable result.
  - ❖ Enhance the interpretation of the results obtained by AMD prediction methods.

The chapter begins by comparing the acid neutralisation capacity (ANC) tests results (Section 5.1). The static and kinetic net acid generation (NAG) tests results are presented in Sections 5.2 and 5.3. The acid forming characteristics such as ANC, NAPP and NAG were determined in order to evaluate the tests and study the behaviour of the samples. The calculation methods used to determine these parameters are shown in Appendix G.

A priori, the studied sample is believed to have a significant acid forming potential, as evident from the maximum potential acidity (MPA) determination:

$$MPA = wt\%\ S \times 30.6 = 89\ kg\ H_2SO_4/t \qquad \text{Eq. 25}$$

5.1 Acid Neutralisation Capacity (ANC) test results

The fizz test was performed to determine the concentration of HCl and NaOH, and the volume of HCl required during ANC digestion procedures and to maintain the final pH of the ANC solution between 0.8 and 1.5 as suggested by AMIRA, 2002. No attempt was made to study the effects of fizz rating on the ANC tests. However it is known that high fizz ratings yield high ANC values. Table 5.1 shows the assigned fizz ratings after reaction of a sample with 25% HCl.

Table 5.1: Fizz ratings after observing the reaction of the Kennecott Cu tailings sample with 25% HCl. A fizz rating was assigned according to Sobek *et al.*, 1978 guidelines (Table 3.1).

Reaction	Fizz Rating	HCl molarity (M)	HCl volume (ml)	pH of ANC solution after digestion	Targeted pH range
Slight reaction	1	0.5	8	1.81	0.8 – 1.5
Moderate reaction	2	0.5	20	1.12	

The reaction between the carbonates and HCl did not appear to be a strong one. It was, therefore, concluded that double the HCl volume for moderate reaction (i.e. 20 ml for strong reaction fizz rating) might shift the pH below the targeted range. Only the slight and moderate reaction ratings were assessed. The moderate reaction fizz rating shifted the ANC solution pH within the targeted range as shown in Table 5.1. This rating was used for the ANC test methods on the studied Kennecott copper tailings sample.

5.1.1 Standard Sobek ANC test

The previous investigations (Skousen *et al.*, 1997; Weber *et al.*, 2004a) have shown that the standard Sobek test can produce enormous values of ANC due to incomplete oxidation of Fe in the solution. In this study the standard Sobek test method was employed to investigate the extent to which the Fe release from siderite ($FeCO_3$) and other Fe bearing minerals (as indicated by the XRD analysis) can influence the ANC test results. Upon titration of the standard Sobek test ANC solution, a thick green precipitate was formed at around pH 6, which changed to dark green/black upon further titration to pH 7.0. This indicated unoxidised Fe^{2+} released due to the dissolution of $FeCO_3$ and FeS_2, and lack of hydrolysis of Fe^{3+} which consumes the NaOH upon titration (see Section 2.5.3, Eqs. 19 -21). The test indicated an ANC of 66 kg H_2SO_4 /t.

5.1.2 Additional/Incremental and Skousen H_2O_2 ANC test

The ANC and NAPP values obtained by Skousen H_2O_2 (siderite correction) and additional/incremental H_2O_2 ANC tests are shown in Figure 5.1. The initial values were obtained immediately after initial back-titration and adjusted values were determined by pH adjustment of the ANC digest solutions at 24, 48 and 72 hr. The results indicate that for all the tests pH adjustments were not necessary after 24 hr. The observations made on these two tests are discussed in the following sections. Samples were filtered prior to titration and H_2O_2 addition to prevent the generation of additional acidity (beyond that already generated during the ANC digestion) due to H_2O_2 enhanced oxidation of sulphides (Skousen *et al.*, 1997).

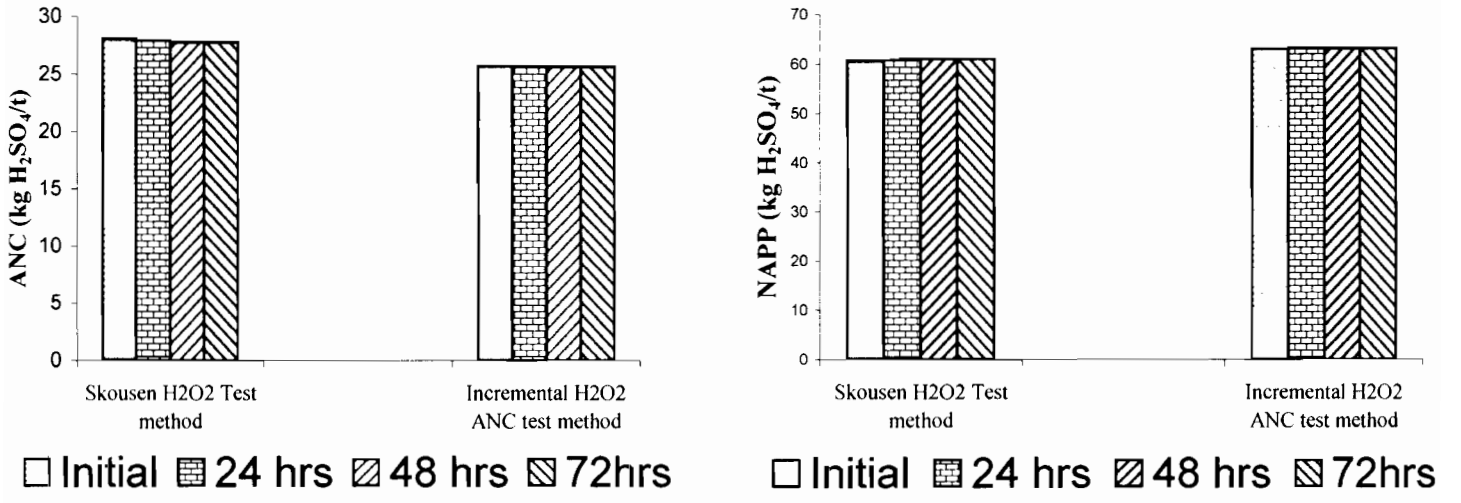


Figure 5.1 : Results for Skousen and Incramental/additional H_2O_2 ANC test immidiately after back titration and after adjusting ANC values by pH adjustment of the digest ANC solutions at 24, 48 and 72 hr.

5.1.2.1 Additional/Incremental H_2O_2 ANC test

The incremental ANC test was found to be time consuming, involving several additions of H_2O_2 and NaOH especially when stabilising the pH solution at 4.5. However, it provided a better control in terms of stabilising the pH. 10 drops of H_2O_2 were added at pH 4.5 resulting in a pH drop to 2.82 and a brown precipitate formed in the solution which is associated with the oxidation of Fe^{2+} to Fe^{3+}, which was then hydrolysed to form Fe (III) oxyhydroxides solids. As indicated in Chapter 2 precipitation of these solids generates acid.

Weber *et al.*, 2004a suggested that the size of pH drop can provide an indication of Fe in solution that was predominately derived either from $FeCO_3$ or reactive sulphides. A further 10 drops of H_2O_2 were added after adjusting the pH back to pH 4.5. The pH dropped to 4.4 after leaving for 15 min, indicating that a significant amount of Fe was oxidised by the first 10 drops of H_2O_2. A further adjustment of pH to 4.5 and addition of 10 drops of H_2O_2 showed no change in pH, which indicated little continued oxidation and thus hydrolysis. Continuance of the back titration to pH 7.0 showed a stabilised pH. Addition of 10 drops of H_2O_2 at pH 7.0 dropped the pH slightly to 6.96 after leaving for 15 min. Based on these observations; the incremental H_2O_2 ANC test provides a better control on the behaviour of the solution without addition of large excess of H_2O_2. A total of 30 drops (~1.1 ml) of H_2O_2 was required to solve the problem of incomplete Fe hydrolysis during ANC determination. The maximum potential acidity (MPA) of the sample was found to be 89 kg H_2SO_4 /t, giving the average ANC and NAPP values 26 and 63 kg H_2SO_4 /t respectively, after monitoring the solutions for 72 hr.

5.1.2.2 Skousen H_2O_2 ANC test

The Skousen H_2O_2 ANC test involved digestion in the boiling procedure and addition of H_2O_2 after digestion, then boiling of solution. The solutions changed to pale/yellow after H_2O_2 addition indicating the oxidation of Fe in the solution. A brown precipitate was formed upon boiling the solutions indicating the oxidation of Fe^{2+} to Fe^{3+} which was then hydrolysed to form Fe (III) oxyhydroxide solids. The pH of the solution before H_2O_2 addition and boiling was 1.12 (which is within the targeted range, see Table 5.1), which dropped to 1.09 after boiling. This indicates the acidity generated by the oxidation of Fe^{2+} and subsequent hydrolysis of Fe^{3+} (see Chapter 2 for reaction equations).

The Skousen H_2O_2 ANC test was less operator intensive, but an excess of 10 ml H_2O_2 was required to oxidise Fe^{2+} in solution to Fe^{3+}. Excess of H_2O_2 may require longer reaction time or a boiling step for the pH of the digest solution to stabilise. Continuance of this test for 72 hr indicated an ANC and NAPP of 28 and 61 kg H_2SO_4 /t respectively, which is comparable to the incremental H_2O_2 ANC test results.

5.2 Single Addition and sequential NAG tests

A variety of NAG tests including single addition, sequential and kinetic NAG tests were carried out on the copper tailings sample as outlined in Section 3.7.2. The NAG tests were conducted in this assessment since they rely on the direct oxidation of sulphide minerals, rather than the theoretical estimation of acidity in the determination of NAPP and MPA. NAG test results are presented in the following subsections. A number of single addition NAG tests were carried out in detail to study the sensitivity of NAG test on the heating stage and to justify the inclusion of this step during the NAG test, which is presented in Section 5.2.3.

5.2.1 Single addition NAG test

Mineralogy derived from XRD showed two sulphide minerals in the sample, FeS_2 (2.9 wt %) and $CuFeS_2$ (0.5 wt %). This indicates that the presence of significant concentration of metallic ion such as Cu^{2+} derived from the oxidation of Cu sulphide is likely. The acid generation during the NAG test was due to the oxidation of these two common sulphide minerals in the sample as demonstrated by Eqs. 26, 27 and 28 (Gerson *et al.*, 2004):

$$FeS_2 + 15/2H_2O_2 \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ + 4H_2O \quad \text{Eq. 26}$$

$$\text{pH} < 5.5 \quad CuFeS_2 + 15/2H_2O_2 \rightarrow Cu^{2+} + Fe(OH)_{3(s)} + 2SO_4^{2-} + 2H^+ + 4H_2O \quad \text{Eq. 27}$$

$$\text{pH} > 5.5 \quad CuFeS_2 + 17/2H_2O_2 \rightarrow Cu(OH)_{(s)} + Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ + 4H_2O \quad \text{Eq. 28}$$

Table 5.2 shows the single addition NAG results. The after-boil NAG_{pH} of the solution was determined to be 2.6, indicating that the sample is potential acid forming. The NAG to pH 4.5 for this tailings sample was 11 kg H_2SO_4/ t. This indicates that a significant amount of the acidity generated was due to the H_2SO_4 released in oxidation reaction equation 26 and presence of metallic ion especially Cu^{2+} due to oxidation equation 27. The difference in the NAG values to pH 4.5 and 7.0 (10.8 kg H_2SO_4/ t and 15.1 kg H_2SO_4/ t respectively) confirms that the acidity released from Eq. 28, where Cu^{2+} precipitate as hydroxides at pH between 4.5 and 7.0 is small compared to the acidity associated with the generation of H_2SO_4 in Eqs 26 and 27.

Analysis of NAG solution at NAG_{pH} = 2.6 (i.e. prior to titration) showed that 12 mg/g of Cu were released into the solution due to the oxidation of $CuFeS_2$ (Eq. 27). The concentration of Zn was found to be 0.7 mg/g indicating that oxidation of Zn sulphides is likely to have occurred. Low concentration of Zn shows that Zn sulphide minerals occur at very small quantities. The results also show that only 63 % of the total sulphur was oxidised in the single addition NAG test, indicating that complete decomposition of H_2O_2 occurred before all the reactive sulphides have oxidised. Thus the single addition NAG test conducted on the tailings sample did not account for the total potential acidity of the copper tailings sample. The sample contains 2.9 wt % of total S and full accounting of the total acid potential in samples with S content >2 wt% require additional NAG stages.

Table 5.2: Single addition NAG test results for the Kennecott copper tailings. The sample contains 2.9 wt% of FeS_2 and 0.5 wt% $CuFeS_2$ as determined by the mineralogical analysis.

Test	After-boil NAG_{pH}	$NAG_{4.5}$ kg H_2SO_4/ t	$NAG_{7.0}$ kg H_2SO_4/ t	% S before NAG test	S content after NAG test	% of S oxidised
Single addition NAG test	2.6	10.8	15.1	2.4	1.1	63

5.2.2 Sequential NAG test

The sequential NAG test is a multi-stage procedure involving a series of single addition NAG tests on one sample until no further acidity to NAG_{pH} of 4.5 is formed. This test was carried out to overcome the incomplete oxidation of sulphide minerals in the sample due to catalytic decomposition of H_2O_2 as indicated by the single addition NAG test results in Section 5.2.1. This test is recommended in situations where the single addition NAG/NAPP ratio is low (<0.5) (AMIRA, 2000). The single addition NAG/NAPP ratio in this case was found to be 0.24 and that only 63% of S was oxidised during the single addition NAG (see Table 5.2) indicating the need for further testing. This was done by introducing fresh H_2O_2 to

the solids until there was no further reaction with the sulphide minerals. The sequential NAG test results are presented in Table 5.3 and they are discussed in the subsequent paragraph.

Table 5.3: Sequential NAG test results for the Kennecott copper tailings. The % S content was obtained by summing %S of FeS_2 and $CuFeS_2$ as determined by the mineralogical analysis.

Seq. NAG stage	Pre –boil NAG_{pH}	After-boil NAG_{pH}	$NAG_{4.5}$ kg H_2SO_4/ t	$NAG_{7.0}$ kg H_2SO_4/ t	% of S oxidised
1	2.42	2.6	10.8	15.1	63
2	2.29	2.71	9.8	12.2	35
3	4.1	4.5	2.2	12	2
Total	-	-	22.7	39.6	100

The results indicate a significant amount of acidity at NAG_{pH} of 4.5 (10 kg H_2SO_4/ t) in stage 2 and as mentioned in Section 5.2.1. The acidity generated at this pH is due to pyrite oxidation and presence of metallic ion such as Cu^{2+} due to oxidation of chalcopyrite. This shows significant lag in acid production, however this is to be confirmed by the kinetic NAG test results in the Section 5.3. After stage 3, ~100 % of total S was oxidised, indicating that all S measured was mainly present as pyritic form. Total NAG of 22.7 and 39.6 kg H_2SO_4/ t at pH 4.5 and 7.0 respectively, were produced by the sequential NAG test compared to an average of about 62 kg H_2SO_4/ t produced by the Skousen H_2O_2 and additional/incremental H_2O_2 ANC tests.

5.2.3 Effects of the heating step on NAG test: NAG sensitivity

The application of a heating step in the NAG test was investigated using the Kennecott copper mine tailings by preparing a duplicate NAG test. Both sets of samples (A and B) were allowed to react for 24 hr as per normal NAG procedure, and then pre-boil NAG_{pH} was measured in both samples. Sample A was filtered and 10 ml subsample was retained for pre-boil metal analysis. Both sets of samples were then boiled for 2 hr as per normal procedure, allowed to cool, and topped to their original volumes. Filtered and unfiltered after-boil NAG_{pH} were measured. Sample B was filtered and 10 ml subsamples were retained from both samples for filtered and unfiltered after-boil metal analysis. Metal analysis was performed by ICP-MS.

The heating step in NAG test is applied to:

- remove residual H_2O_2 by further oxidation of pyrite in the undigested portion of the sample, which encourages reactions that may not take place in normal duration of NAG test.
- enhance interaction between acid producing and acid neutralising minerals.

The results for this investigation are presented in Figure 5.2 and Table 5.4. The results in Figure 5.2 show that the unfiltered-boil NAG_{pH} is higher than the filtered-boil NAG_{pH}. This indicates that the increase in NAG_{pH} is directly related to interaction of the NAG solution

and the solids. Both samples contained residual H_2O_2 (indicated by effervescence) which further reacted with the pyrite during the heating step. The filtered solution was pale prior to boiling indicating the presence of Fe ions in the solution. A yellow/brown precipitate was formed during boiling of the filtered solution indicating oxidation and hydrolysis of these Fe ions into Fe^{3+} oxyhydroxides or oxyhydroxysulphates. This precipitate was filtered after boiling for solution analysis. As discussed in Section 2.3, formation of these precipitates can produce significant amounts of acidity into the solution; consequently filtered after-boil NAG_{pH} is lower than the pre-boil NAG_{pH}.

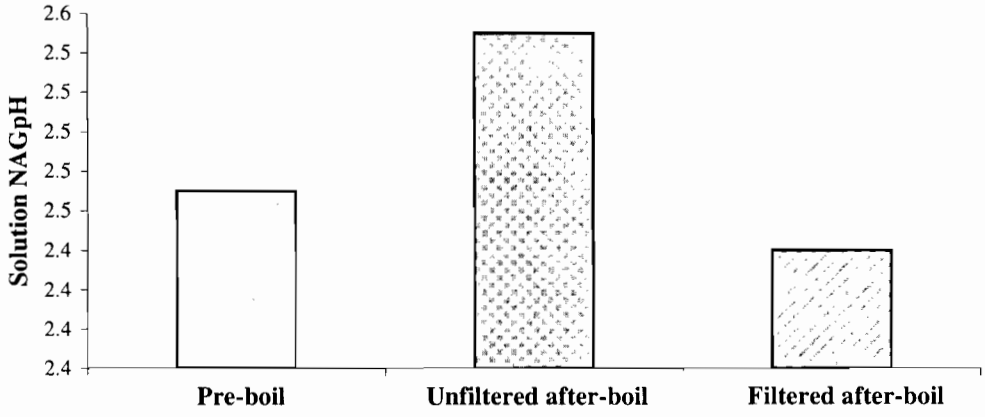


Figure 5.2: Pre-boil NAG_{pH}, unfiltered after-boil NAG_{pH} and filtered after-boil NAG_{pH} measuments.

Table 5.4: Metal analysis of pre-boil, filtered after-boil and unfiltered after-boil NAG solutions.

	Solution NAG_{pH}		
	Pre-boil	*Unfiltered after-boil*	*Filtered After-boil*
NAG_{pH}	2.42	2.6	2.37
	Metal concentrations (mg/g)		
Metal	*Pre-boil*	*Unfiltered after-boil*	*Filtered After-boil*
Fe	4	6	3
Mg	0.8	0.9	0.8
Mn	0.4	0.7	0.4
Ca	2.7	3.2	2.7
Cu	12	12	12
Zn	0.1	0.1	0.1
Si	0.6	0.9	0.6

The concentrations of Mg, Mn, Ca and Si remained constant between pre-boil and filtered after-boil NAG solutions. The concentrations of these metals in the filtered after-boil NAG solution were not expected to increase since there was no further contact between the solid and solution to encourage further dissolution of minerals. The concentration of Cu remains consistent in all three solutions. This may indicate that the major Cu-sulphide minerals (e.g. 0.5 wt % $CuFeS_2$) were completely oxidised by reaction equation 27 after reacting the

sample for 24 hr. There is a significant increase in the concentration of Fe, Mg, Mn, Ca and Si in the unfiltered after-boil solution, as compared to the cations in the pre-boil and filtered after-boil solutions. Increase in the concentration of Mg, Mn and Ca suggests that, a further interaction between the solid and solution upon boiling results in further reactions of the neutralising minerals such as $CaCO_3$, $MgCO_3$, $MnCO_3$ and $CaMg(CO_3)_2$.

A decrease in the NAG_{pH} in the filtered after-boil solution is confirmed by the decrease in Fe concentration in the filtered after-boil solution. This indicates that some of the Fe cations have gone through oxidation and hydrolysis reactions to form the Fe^{3+} oxyhydroxide or oxyhydroxysulphate precipitates which releases acid. An increase in the Fe concentration in the unfiltered after-boil solution is due to a further reaction of the pyrite oxidation that is encouraged during the heating step. It must also be taken into account that the presence of siderite ($FeCO_3$) may increase the concentration of Fe in the unfiltered after-boil solution. As discussed in Section 2.5.3 dissolution of the siderite minerals produce acidity due to the re-release of acid upon oxidation of Fe^{2+} to Fe^{3+} and subsequent formation of Fe (III) oxyhydroxides. The consistent concentrations of Cu in all three solutions suggest that there was no Fe released from $CuFeS_2$ during the boiling step of the unfiltered solution.

This investigation suggests that the exclusion of the heating step in the NAG test can give incorrect characteristics of the sample, as it may indicate that the sample has a high acid forming potential, whereas the sample is acid neutralising. Therefore the results showed that the heating step is essential for further release of alkalinity from the neutralising minerals and for further reaction of the pyrite in the sample.

To further illustrate this, the heating step was conducted on the copper tailings samples from Konkola Copper Mines Limited – Nchanga concentrator, which are acid neutralising with the following characteristics: %S = 0.6 %; ANC = 121 kg H_2SO_4/ t and NAPP = -107 kg H_2SO_4/ t (all characteristics determined by the author). The results showed a pre-boil NAG_{pH} of 4 which is slightly acidic and after heating the sample the results showed an after-boil NAG_{pH} of 6.5 indicating that the heating step enhanced the reaction of the neutralising minerals.

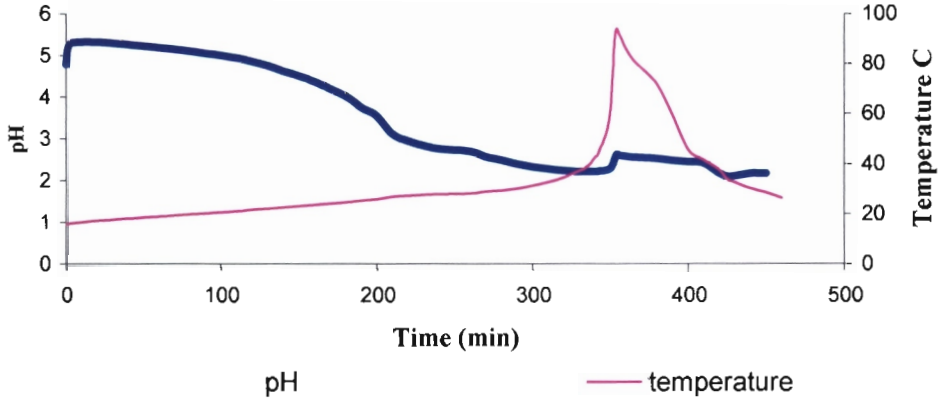
These results also provided an indication of the extent of the chemical reactions prior to the heating step. For example the Cu concentration in the solutions indicated that the Cu sulphide minerals were competently oxidised prior to the heating step.

5.3 Kinetic NAG test (KNAG)

The objectives of the kinetic NAG study were to:

- Provide an indication of the reactivity of sulphide and buffering minerals within the sample to enhance the interpretation and evaluation of the AMD prediction test methods.
- Provide a quick estimate lag time for acidification.

The kinetic NAG temperature and pH profile for the Kennecott Cu tailings sample is shown in Figure 5.3.



Static geochemistry data:
Total S = 2.9 %
MPA = 89 kg H_2SO_4/ t
ANC = 27 kg H_2SO_4/ t
NAPP= 62 kg H_2SO_4/ t
After-boil NAG_{pH} = 2.6
Total NAG to pH 4.5 = 22.7 kg

Figure 5.3: Kinetic NAG profile for the Kennecott Cu-tailings sample. Catalytic decomposition of H_2O_2 occurred at approximately 354 min as indicated by solution temperature peak of 94 °C.

The initial pH of the H_2O_2 was 4.7 and the results indicated a pH of 5.26 after 2 min, which reached a maximum of 5.33 after 10 min. This rise in pH is a function of rapid dissolution of highly reactive carbonates such as calcite ($CaCO_3$) contained in the sample. The pH begins to drop after approximately 20 min; however it only drops below 4.5 after 150 min. This indicates that the rate of acid neutralisation offered by the ANC was greater than the rate of acid generation from the sulphides in the first 20 min. As the reaction proceeds the ANC provided by the reactive buffering minerals is insufficient to neutralise the acidity generated by increasing pyrite oxidation. According to Table 2.1 the consumption of acidity by $CaCO_3$ can be described as follows:

$$\text{pH} \leq 6 \quad CaCO_3 + 2H^+ \Rightarrow Ca^{2+} + H_2O + CO_2 \qquad \text{Eq. 29}$$

The pyrite oxidation dropped the pH to 2.22 by 300 minutes and the reaction showed a temperature peak of 94 °C at 354 min. The kinetic NAG profile provides the following information regarding the pyrite minerals contained in the sample:

- The slow decrease in the pH profile of this sample is characteristic of low pyrite reactivity and also depletion of acid neutralising minerals.
- The presence of the high temperature peak of the sample with total NAG capacities at pH 4.5 and 7.0 of 22.7 and 39.6 kg H_2SO_4/t respectively, indicates that the acidity formed is mainly due to pyrite oxidation. This is consistent with the mineralogy derived from XRD analysis (see Table 4.1, Chapter 4) which showed that the major sulphide mineral is present as pyrite.
- The sample exhibits a longer lag period (354 min) before H_2O_2 catalytic decomposition confirming that the sample contains slow reactive pyritic S. As shown in Section 5.2.2, the sequential NAG test was required to oxidise the remaining sulphides and obtain a better indication of NAG capacity of the sample.

The temperature rise was accompanied by a slight rise in pH (from 2.22 to a maximum of 2.62 at 94 °C), indicating that there were remaining buffering minerals that required elevated temperatures to dissolve. This was also confirmed by the investigation of the heating step on NAG test (Section 5.2.3). Figure 5.3 shows that the buffering minerals released were insufficient to neutralise the acid released, as a results the pH began to drop after reaching the peak. As indicated in Chapter 2, Figure 2.3, the AMD peak zone is associated with sulphide mineral oxidation in excess of the acid neutralisation capacity (ANC) release rates. The precipitation of Fe (III) oxyhydroxides occurred as the sample reached the peak and this was indicated by yellow precipitates in the sample. The single addition NAG test indicated that very little buffering minerals remained in the solids after catalytic decomposition of H_2O_2, since the NAG_{pH} increased slightly from 2.42 to 2.6 after boiling the unfiltered sample.

The kinetic NAG test was conducted on the porphyry Cu-tailings samples from La Andina in Chile and Cu-tailings from Konkola Copper Mines Limited (coded KonCuM) to further illustrate the reliability of this test. The samples from Andina were collected at different depths 25 and 40 m, and were coded as AND25m and AND40m respectively. Figures 5.4 and 5.5 show the kinetic NAG results for La Andina, Konkola and Kennecott Cu tailings samples. Note that Kennecott Cu-tailings sample is coded as KenCu for comparison purposes. All the static geochemistry data of AND25m, AND40m and KonCuM samples were determined by the author.

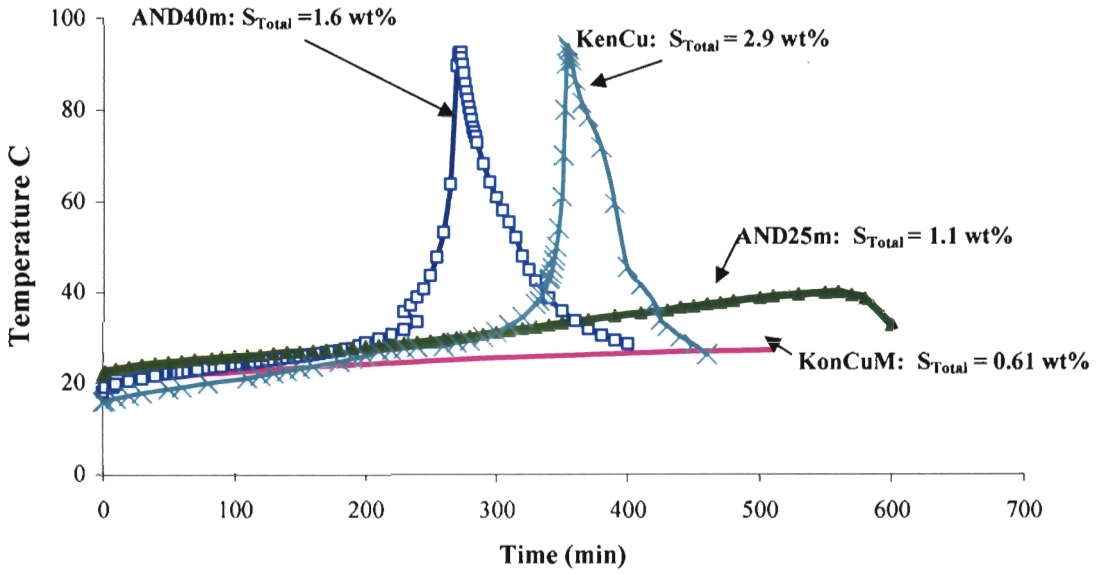


Figure 5.4: Kinetic NAG temperature profiles for La Andina Cu tailings samples (AND40m:Total S= 1.6%; ANC = 5.7 kg H_2SO_4/t; NAPP = 42 kg H_2SO_4/t; NAG_{pH}= 2.4 and AND25m: Total S=1.1%; ANC= 7 kg H_2SO_4/t; NAPP= 24.82 kg H_2SO_4/t; NAG_{pH}=2.61), Konkola Cu tailings (KonCuM: Total S = 0.61%; ANC = 127.1 kg H_2SO_4/t; NAPP = -107.1 kg H_2SO_4/t; NAG_{pH} =6.5) and Kennecott Cu tailings sample (KenCu: see Figure 5.3 for static geochemistry data).

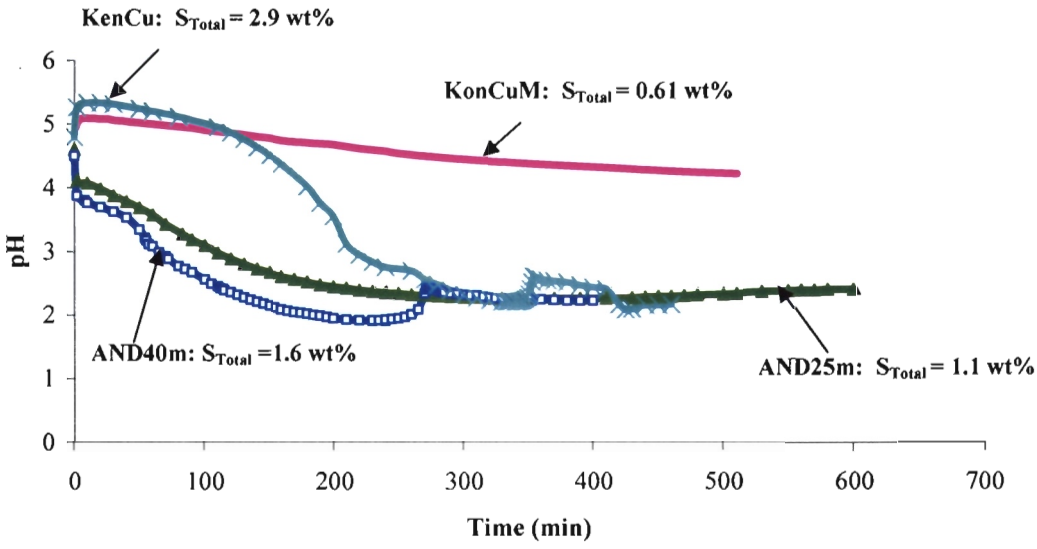


Figure 5.5: Kinetic NAG_{pH} profiles for La Andina Cu tailings samples (AND40m and AND25m), Konkola Cu tailings (KonCuM) and Kennecott Cu tailings sample (KenCu).

The results show that the lag time to reach the temperature peak is mainly dependent on the pyrite content or the forms of sulphur in the total S content and the reactivity of S in the form of reactive pyrite. The following observations were summarised:

- The AND25m sample showed a temperature peak of 40 °C despite containing total S content of 1.1 wt%. This shows that the total S measured was mainly present as non-pyritic forms. This is indicative of the presence of soluble sulphate minerals in the sample due to oxidation processes that increased the S content in sulphate forms. This was also indicated by a rapid pH drop from 4.6 to 4 after the first 2 min (see Figure 5.5).
- The temperature profile of AND40m depicted a significant temperature peak (91.3 °C) at 273 min. This shows that the sulphur in the total S measured was mainly present as pyrite with faster reactivity as compared the KenCu sample. Sample AND 40m indicated the presence of soluble sulphates as depicted by rapid pH drop from 4.5 to 3.87 after the first 2 min (note that pyrite oxidation may also contribute to this rapid pH drop) (see Figure 5.5). However, a relatively fast pyrite reactivity is confirmed by a pH drop to <2 after 195 min as indicated by Figure 5.5, which was mainly due to the continued oxidation of sulphide minerals after the initial pH drop.
- The lack of a significant temperature peak for KonCuM is due to the high ANC (as indicated in Section 5.2.3) in excess of the acidity generated by oxidation reactions and also due to low total S content. This is indicated by pH>4.3 throughout the kinetic NAG test as shown by Figure 5.5, and an after-boil NAG_{pH} of 6.5.

The above findings demonstrate that the temperature peak and the pH profile during kinetic NAG test can be used to indicate the presence of significant pyrite and the presence of non-pyritic S forms, such as sulphates that may contribute to the total S content of the sample. This confirms that the kinetic NAG test and other NAG test variations discussed in this chapter can remove bias towards acid generation potential estimation of a sample by MPA, since the NAG results represent a direct measure of the net acid generated by the sulphur in pyritic forms.

5.3.1 Implications of the AMD prediction results

These results suggest that, under natural conditions, the rapid dissolution of buffering minerals to neutralise the acidity formed by the initial oxidation reaction of pyrite, may occur during the early stages of weathering processes, providing a short term ANC. Slow reactivity of the pyrite minerals allows for the ANC donated by the carbonates to dominate the initial oxidation processes of pyrite, thereby increasing the pH in the oxidation zone. However; the rate of oxidation is a function of time, as the pyrite oxidation increases, more ferrous iron is formed which is then oxidised to form ferric ions. Oxidation of pyrite by ferric ions generates more acidity (see Chapter 2, Table 2.1 for the reactions). Therefore; the ANC test results of the Kennecott Cu tailings show that the ANC becomes insufficient when the tailings dump is exposed to the atmosphere for long periods, without any form of

rehabilitation. Slow sulphide reactivity implies a significant lag in acid production under atmospheric oxidative conditions before the ANC is consumed and acidic conditions develop.

5.4 Conclusions

The results presented in Sections 5.1 and 5.2 do not show conflicting NAPP and NAG results. The sample has a positive NAPP and a NAG_{pH} of 2.6 indicating the capacity to form acid. According to Figure 3.3 in Section 3.8, the sample can be classified as potential acid forming (PAF) of high capacity, but slow reacting. Table 5.5 summarises the acid forming characteristics used to classify the Kennecott Cu tailings sample.

Table 5.5: Summary of the acid forming characteristics of the Kennecott Copper tailings

Total %S	MPA kg H_2SO_4/ t	ANC kg H_2SO_4/ t Skousen H_2O_2	ANC kg H_2SO_4/ t Incremental H_2O_2 ANC tests	NAPP kg H_2SO_4/ t Skousen H_2O_2	NAPP kg H_2SO_4/ t Incremental H_2O_2 ANC tests	After-boil NAG $_{pH}$	NAG_7 kg H_2SO_4/t	AMD status
2.9	89	28	26	61	63	2.6	39.6	PAF of high capacity, slow reacting

ANC test reliability/limitations

- The presence of siderite ($FeCO_3$) in the sample can significantly affect the ANC test results. The reaction mechanism of $FeCO_3$ during the ANC test unstabilises the pH due to the consumption of base NaOH by Fe^{3+} generated from the siderite and other Fe-bearing minerals such as reactive pyrite. It has been shown that $FeCO_3$ provide no acid neutralising potential. Therefore standard Sobek ANC test was not suitable for estimating the acid forming potential of the tailings.
- Skousen H_2O_2 (siderite correction) and additional/incremental H_2O_2 ANC tests successfully overcome this limitation. These two tests accelerated the Fe oxidation and hydrolysis processes and prevented the overestimation of ANC values.
- The additional/incremental H_2O_2 ANC test was found to be time consuming, however it provided a better control on the behaviour of the sample. As these two tests produced comparable results, the additional effort was not necessary in this case.

NAG test reliability/limitations

- The NAG tests remove bias towards acid generation capacity estimated by MPA and NAPP determination for samples containing reactive sulphides or acidic soluble

sulphates. This is because the NAG tests represent a direct measurement of the net amount of acid generated by the sample.

- The investigation of the application of heating step during NAG test has shown that the exclusion of the heating step can lead to incorrect characteristics of a sample.
- The single addition NAG test has been shown to lead to incorrect results or conflicting NAG and NAPP due to catalytic decomposition of H_2O_2 before complete oxidation of sulphides. Only 63 % of S was oxidised in a single addition NAG test indicating the need for sequential and kinetic NAG tests.
- It was demonstrated that there was remarkable improvement in carrying out the sequential NAG test since over 99 % of total S was oxidised in three stages. Significant amount of acidity was formed in stage 2 showing significant lag in acid production. This was confirmed by the kinetic NAG test which indicated long lag period before reaching the temperature peak. Sequential NAG test provides a better estimate of total acid potential than the single addition NAG test.
- The total sequential NAG acidity of 39.6 kg H_2SO_4/t suggests that the NAPP value of between 61 and 63 kg H_2SO_4/t from the Skousen H_2O_2 and additional/incremental H_2O_2 ANC test may overestimate the acid generating capacity of this sample.
- It was demonstrated that the kinetic NAG test provides information regarding the reactivity of sulphide and carbonate minerals, and also an indication of the forms of sulphur in the total S content. The studied sample contains reactive carbonate minerals that are most likely to be effective in the early stages of oxidation processes.

These results indicate that the use of ABA and NAG procedures without prior knowledge of the sample mineralogy can lead to uncertainties. Therefore, an integrated approach of these procedures together with the mineralogical studies is required to improve the interpretation of the results.

Chapter 6

SEQUENTIAL EXTRACTION PROCEDURE RESULTS

The results of sequential extraction schemes carried out on sulphide Cu-tailings samples are presented in this chapter. The main objectives of this chapter were to:

- Evaluate a set of sequential extraction procedures and determine their limitations and applicability to copper mine tailings.
- Show how such procedures can be used to provide the mode of occurrence of metals, and estimate the mobility and bioavailability.

In this chapter, the fractionation of metals associated with the fractions/phases evaluated in the sequential extraction schemes are presented in graphical form. Selected results are presented in tabular form and more sequential extraction results used to assess the data are presented in Appendix I.

This chapter begins by discussing the reliability of the adopted sequential extraction schemes in terms of metal recovery in Section 6.1. Comparison of the sequential extraction schemes is discussed in Section 6.2 and the environmental implications of the sequential extraction data is given is Section 6.3. Based on the sequential extraction results, a kinetic study of the dissolution of selected fractions is presented in Section 6.4, followed by a summary of the sequential extraction investigations in Section 6.5. Finally, a systematic empirical waste characterisation protocol for mine wastes is presented in Section 6.6.

It should be stated that the main interpretation is centered on the:

- Solubility;
- Possible chemical associations ;
- Potential mobility and bioavailability;
- Relationship between the mineralogical and the chemical forms.

Metal mobility and bioavailability is interpreted according to the results from the two sequential extraction schemes employed in this study. The mineralogical results from XRD (Table 4.1) and information provided in Tables 2.7 and 2.8 were used to enhance the interpretation of the results.

6.1 Element recovery: Validation of the sequential extraction data

The percent recovery relative to a single digestion using a mixture of strong acids (used for total metal analysis) is an important consideration in the reliability of a sequential extraction data. Recovery is defined as follows:

$$\%\ Metal\ recovery = \left[\frac{\sum SequentialExtractionProcedure}{SingleAcidDigestion} \right] \times 100 \qquad \text{Eq. 30}$$

The single digestion with strong acids used for reference was a mixture of strong acids used in the residual fraction digestion for each sequential extraction procedure as described in Section 3.9.1. The average percentage recoveries were obtained by comparing the total concentration of each metal (sum of fractions) with the total metal concentration, according to Eq. 30. The average recoveries attained with sequential extraction schemes A and B are presented in Table 6.1.

Generally, the results agreed with each other although discrepancies between the sequential extractions and single acid digestion values occurred for some metals, especially the trace metals. The average Fe recoveries were 98 and 97 % for Scheme A and B respectively, indicating comparable Fe values by both schemes. Larger amounts of Cu (118 wt %) and Mn (116 wt %) were recovered with Scheme A than were released by single acid digestion. Low recovery of 80 wt% was obtained for Ca with Scheme A, and Scheme B recovered only 85 wt% of Cu. The recoveries of most trace metals varied between 97 and 115 wt%.

Table 6.1: The percentage recoveries obtained from the two different sequential extraction schemes applied to the Kennecott copper sulphide tailings in duplicate analysis of 1 g of sample for each sample.

Metal	Total metal analysis	Total Scheme A	Total Scheme B	% Recovery Scheme A	% Recovery Scheme B
	Major metals (mg/kg)			wt %	
Fe	71536	70247	69510	98	97
Cu	1169	1378	991	118	85
Al	4986	5280	5719	106	115
K	13128	12693	13881	97	106
Ca	9099	7247	8918	80	98
Mg	3202	3427	3497	107	109
Mn	1244	1440	1261	116	101
Si	232882	218459	220243	94	95
	Trace metals (mg/kg)			wt%	
Co	18.5	19.3	19.5	104	105
Cr	269.7	309	309	115	115
Zn	117.7	133.5	131.1	113	111
Cd	1.35	1.46	1.31	108	97
As	27.9	28.9	32.8	103	118
Mo	25.5	28.2	28.5	111	112
Ag	1.47	1.6	1.41	109	96
Pb	36.0	40.1	34.8	111	97
V	37.1	37.8	40.4	102	109
Be	1.07	0.6	0.98	56	91
Ni	109.2	122.4	120.4	110	108

6.2 Comparison of the sequential extraction procedures/schemes: Metal speciation patterns

The tailings sample was submitted to the two 7-step sequential extraction schemes with an assumption that each extractant/reagent was able to dissolve in a selective way the selected phases. Note that the first two extraction steps (water soluble and ion exchangeable fractions) are the same in both schemes; therefore the results are very similar since the two schemes were conducted on the same tailings sample. In order to estimate the mobility and bioavailability, metals among fractions were grouped into the readily mobilised, potentially mobilised and low mobile fractions.

Figures 6.1 and 6.2 depict the partitioning of major metals: Fe, Cu, Al, K, Ca, Mg, Mn and Si; and trace metals: Co, Cu, Zn, Cd, As, Mo, Ag, Pb, V, Be and Ni obtained by the sequential extraction schemes A and B. The general picture of the metal partitioning is drawn by giving average metal wt% amounts in each fraction with respect to the total amounts in the tailings, providing a better way of comparison between the metal occurrence and potential for mobilisation and release. The sequential extraction schemes indicate that each metal exhibits a distinctive partitioning pattern.

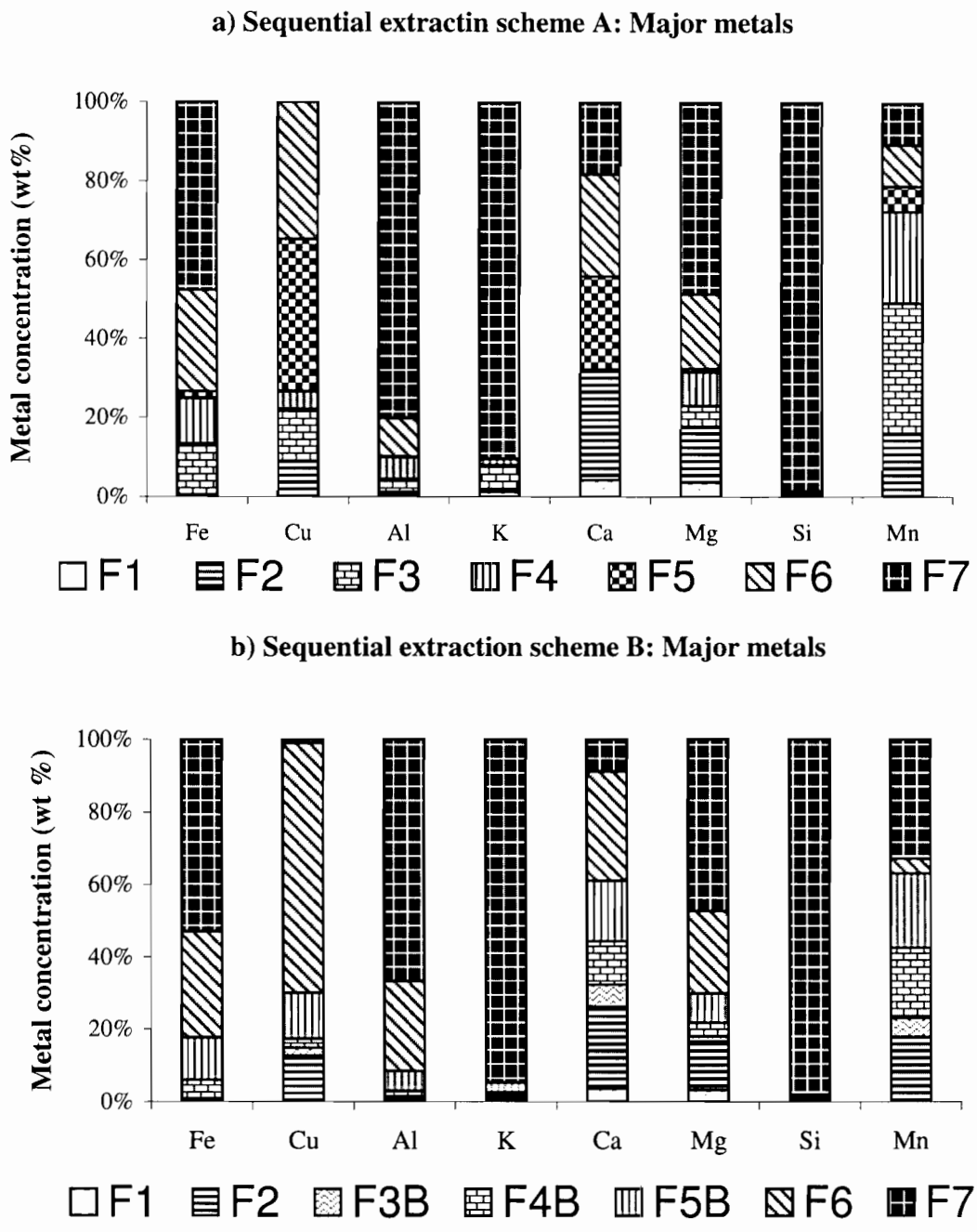


Figure 6.1a, b: Fractionation patterns of the major metals: Fe, Cu, Al, K, Ca, Mg, Si and Mn based on all the fractions in the copper tailings sample for the sequential extraction schemes A and B.

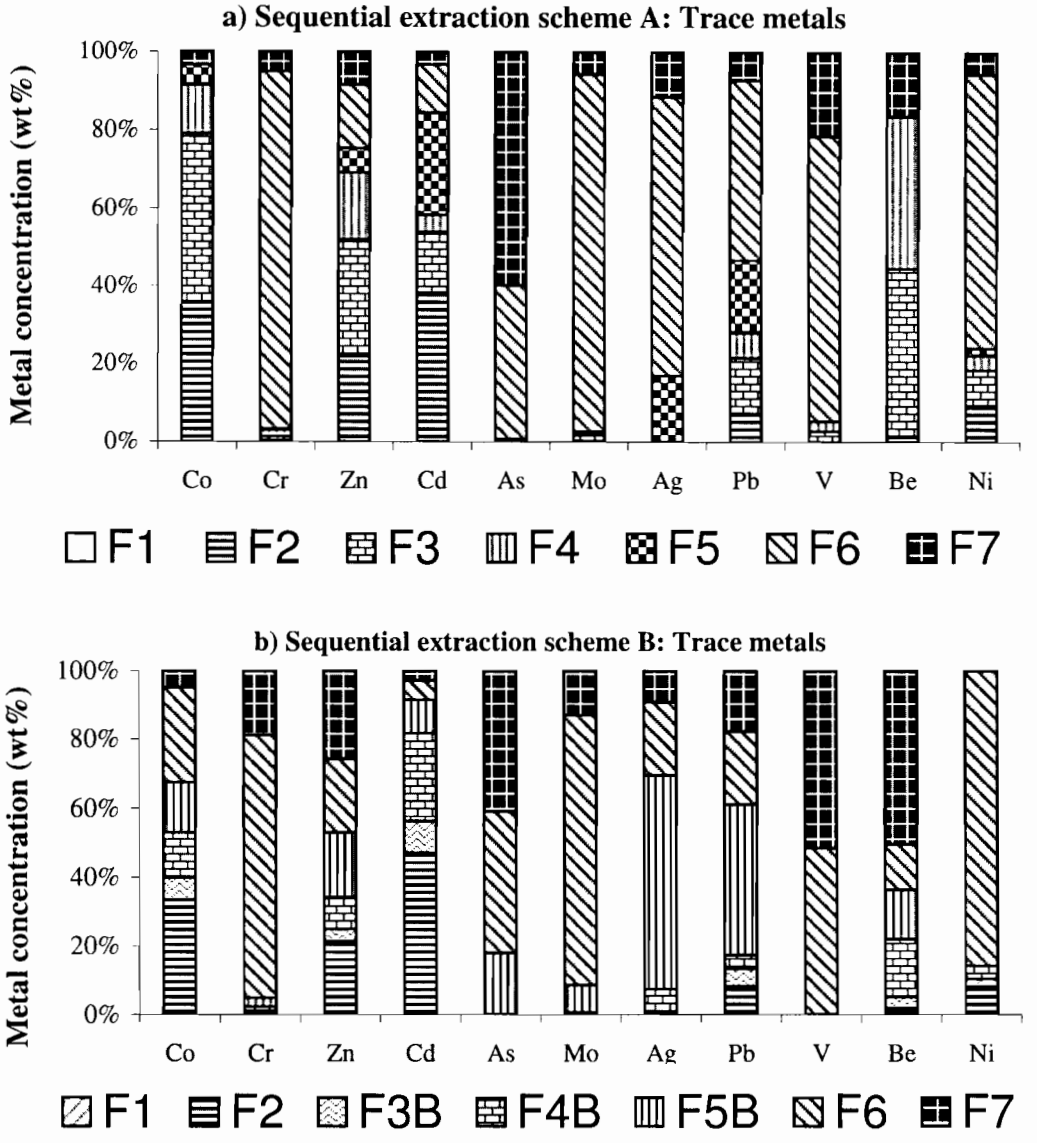


Figure 6.2a, b: Fractionation patterns of the trace metals: Co, Cr, Zn, Cd, As, Mo, Ag, Pb, V, Be and Ni based on all the fractions in the copper tailings sample for the sequential extraction scheme A and B.

Scheme A: *F1: Water soluble; F2: Exchangeable; F3: Amorphous Fe-oxide; F4: Crystalline Fe-oxide; F5: Organic matter and secondary Cu-sulphide; F6: Primary sulphides; F7: Residual (silicates).*

Scheme B: *F1: Water soluble; F2: Exchangeable; F3B: Carbonate; F4B: Amorphous Fe-oxide; F5B: Crystalline Fe-oxide; F6: Primary sulphides; F7: Residual (silicates).*

6.2.1 Water-soluble fraction

This fraction is the first to be brought into solution in any sequential extraction scheme. It contains metals derived from i) re-dissolution of tertiary phases accumulated during drying and evaporation of the pore water, ii) re-dissolution of water soluble primary and secondary phase such as gypsum ($CaSO_4.2H_2O$) (Ribet *et al.*, 1995; McGregor & Blowes, 2002). For the selectivity of the exchangeable fraction, it is important to release the water-soluble fraction first.

The sequential extraction results showed that K (1 wt %), Ca (4 wt %) and Mg (4 wt %) were available as water soluble and adsorbed cations. This suggests that Ca was released by the dissolution of primary and secondary gypsum ($CaSO_4.2H_2O$) (gypsum was not quantified by XRD due to high detection limits). The concentration of sulphates (SO_4^{2+}) was 280 mg/l in the tailings discharge liquor, indicating that gypsum precipitation is likely to have occurred after floating and drying of samples.

The Ca within the gypsum is derived from pH-buffering reactions between the pore water and Ca-bearing carbonate minerals such as calcite ($CaCO_3$) and dolomite (Ca, Mg $(CO_3)_2$) (McGregor & Blowes, 2002). SO_4 may be derived from the oxidation of sulphide minerals in the mill process water. Mg in the water soluble fraction may be due to dissolution of ($MgSO_4.6H_2O$). Most of the trace metals were not detected in the water soluble fraction. The only trace metals extracted from this fraction were Co (0.02 wt %), Mo (0.2 wt %), Ag (0.5 wt %) and Pb (0.5 wt %). This can be explained in terms of the mode of occurrence of these trace metals and this is discussed in the subsequent sections.

It is worth noting that the pH of the mixture (water and sample) dropped from 10 to 9.1 after extraction of metals from the water soluble fraction. This is consistent with the above findings that a relative proportion of metals released in this fraction were due to the dissolution of water soluble sulphate minerals. The strongly alkaline pH after extraction is due to the fact that the sample was relatively unoxidised. These results indicate that the water soluble fraction provides an indication of the inherent acidity due to sulphide oxidation, which makes it an important fraction when studying the behaviour of mine wastes using sequential extraction procedures.

6.2.2 Ion exchangeable fraction

The 1 M NH_4-acetate/ 1 M CH_3OOH leach at pH 4.5 was used to extract metals bound to ion exchangeable fraction. The acidic NH_4-acetate leach extracted major metals such as Fe (0.7 wt %); Cu (11 wt %); Al (1.4 wt %); Ca (22 wt %); Mg (14 wt %) and Mn (18 wt %). The release of Fe and Mn in the exchangeable fraction can be attributed to solubilisation of $FeCO_3$ and $MnCO_3$ or $(Ca,Mn)CO_3$ in acidic solutions of NH_4-acetate rather than to the

attack of Fe and Mn oxides (Chao, 1984). The exchangeable Cd, Co, Zn, Ni and Pb in the tailings accounts for 44 wt, 35 wt %, 24 wt %, 10 wt % and 7.5 wt % of the total Cd, Co, Zn, Ni and Pb concentrations in the tailings respectively. Other trace metals extracted in the exchangeable fraction are Be (1.7 wt %) and Cr (0.7 wt %). SEM analysis of mine tailings by Ribet *et al.*, 1995 indicated that Fe oxides such as goethite are Ni- bearing. It is likely; therefore; that adsorption or coprecipitation with goethite is probably one of the dominant solid phase controls on dissolved Ni in the exchangeable fraction.

The Ca and Mg extracted are due to a partial dissolution of the carbonate minerals such as calcite and dolomite in the NH_4-acetate leach. Mn in the exchangeable may be from the dissolution of $MnCO_3$ or $(Ca,Mn)CO_3$. It is known that some of the carbonate can go into solution in the NH_4-acetate leach (Tessier *et al.*, 1979; Cardoso & Martin, 1986; Dold, 2003a). Acidification that occurs when a solid waste is exposed to the atmosphere mainly affects the carbonates because they are dissolved when mine wastes and sediments are acidified. Therefore, release can be expected for metals bound to carbonates, such as Zn, Cd, Ni, Mn and Ca (Filgueiras *et al.*, 2002). The acidic NH_4-acetate leach is also selective for smithsomite and willemite (galena and sphalerite), as a result some trace metals such as Zn and Pb in these minerals may be extracted (Fonseca & da Silva, 1998), also sphalerite may contain amounts of Cd (Dold, 2005).

6.2.3 Acid soluble fraction: Adsorbed carbonate fraction (Adopted in sequential extraction scheme B)

The acid soluble fraction contains the metals which are precipitated or coprecipitated with carbonates. The carbonate fraction essentially includes metals associated with Ca, Mg and Mn carbonates. Scheme B used the 1M Na-acetate/1 M CH_3OOH leach at pH 5.0 to extract carbonate bound metals. These metals were extracted by first removing the water soluble and exchangeable fractions. Scheme B showed that the average Ca, Mg and Mn extracted from carbonate fraction were 6, 2 and 5 wt% respectively. The low extracted amounts of these metals from this fraction indicate that most of the Ca, Mg, Mn-carbonate minerals were dissolved in the exchangeable fraction in the NH_4-acetate leach.

Dold, 2003a found the Na-acetate leach for the adsorbed carbonate metals to be unnecessary because of the ability of 1 M NH_4-acetate/ 1 M CH_3OOH (pH 4.5) leach to dissolve carbonates. Thus 1 M NH_4-acetate/ 1 M CH_3OOH (pH 4.5) leach was not suitable to distinguish between exchangeable and bound-to-carbonate metals. Therefore, exchangeable and bound-to-carbonate metals can be evaluated together using NH_4-acetate at pH 4.5. However, this also depends on the objectives of the application of the sequential extraction on the mine wastes.

An average of 0.12 wt% of Fe was extracted from the carbonate fraction. This low percentage of Fe can be attributed to solubilisation of $FeCO_3$ in acidic solutions of sodium acetate rather than to the attack of Fe oxides/hydroxide. Leinz *et al.*, 2000 used the 1M Na-acetate/1 M CH_3OOH leach at pH 5.0 leach in their sequential extraction to study the speciation of metals in mine wastes, and they found that Fe was not extracted in the carbonate fraction. This reagent is capable of dissolving carbonates and dolomite without significant attack on organic matter and Fe oxides/hydroxide (Filgueiras *et al.*, 2002).

An average of 0.4 wt%, 0.25 wt% and 0.21 wt% of K, Al and Si were extracted in this fraction. This may indicate the attack on the edges of aluminosilicates by this leach. Trace metals such as Cd, Co, Pb, Zn, Be and Ni were extracted in this fraction, at the following corresponding concentrations, 9 wt%, 7 wt%, 5 wt%, 4 wt%, 3 wt% and 2 wt%. As illustrated in Section 6.2.2 the acidic conditions results the release of Zn, Cd, and Ni in the carbonate fraction.

A distinction between the exchangeable and carbonate fractions can be achieved by leaching the exchangeable fraction with the most widely used reagents such as $MgCl_2$, $BaCl_2$ and NH_4-acetate (NH_4OAc) at 1 M concentration and pH 7.0. This prevents dissolution of carbonate phases which can occur under acidic conditions. The metals associated with the carbonate fraction can be released with 1M Na-acetate/1 M CH_3OOH leach and pH between 4.5 and 5.0. This increases the dissolution of carbonate minerals with minimal attach on organic matter, Fe/Mn oxide and aluminosilicates.

6.2.4 Reducible fraction

The reducible fraction usually consists of oxides and hydroxides of Mn and Fe. This fraction was split into three fractions: easily reducible fraction (Mn oxides); moderately reducible fraction (amorphous Fe oxides); and poorly-reducible fraction (crystalline Fe oxides). However the Mn oxides were extracted together with the amorphous iron oxides in both sequential extraction schemes.

6.2.4.1 Amorphous Fe oxide or Fe (III) oxyhydroxides fraction

This fraction is made up of iron oxyhydroxides such as secondary jarosite and ferrihydrite from which trace metals are removed in a reducing environment. The 0.2 M NH_4-oxalate/0.2 M oxalic-acid solution (pH 3.0), in the dark, was used to extract amorphous Fe oxides in an operationally defined sequential extraction scheme A. This leach was replaced with 0.25 M hydroxylamine hydrochloride/0.25 M HCl (pH 2.0) in extraction Scheme B. Table 6.2 shows the major and trace metals extracted from the amorphous Fe oxide fraction in Scheme A and B.

The acidic $NH_2OH.HCl/HCl$ leach in Scheme B showed a relatively low extraction of Fe (5 wt %) in the amorphous Fe oxide phase. The NH_4-oxalate leach used in Scheme A extracted 13 wt % of Fe. This may indicate that the $NH_2OH.HCl$ leach dissolved relatively low amounts of amorphous Fe oxide phases even with longer dissolution time of 2 hr as compared to 1 hr adopted for NH_4-oxalate leach in Scheme A. The concentration of $NH_2OH.HCl$ and HCl may not be adequate to dissolve amorphous Fe oxide. Alternatively, at the adopted reagent concentrations (0.25 M $NH_2OH.HCl$/0.25M HCl), longer extraction time may be required.

Table 6.2: Major and trace metals extracted from the amorphous Fe oxide fraction in Scheme A and B with 0.2 M NH_4-oxalate/0.2 M oxalic-acid leach (in darkness) and 0.25 M $NH_2OH.HCl$/0.25M HCl leach respectively.

Metal	Scheme A: NH_4-oxalate/Oxalic acid (in darkness) (wt %)	Scheme B: $NH_2OH.HCl$/HCl leach (wt %)
Fe	13	5
Cu	13	2
Al	3.3	1.8
K	6	0.5
Mg	5.4	4
Mn	32	20
Co	45	14
Zn	30	10
Mo	2	0.5
Pb	14	4
Be	43	16
Ni	9	4
Ag	-	7

Ribet *et al.*, 1995 found that the concentration of $NH_2OH.HCl$ required for complete conversion of amorphous phases in mine tailings was 2 M. They determined in their experiments that > 80 wt% of Fe and Co, and between 21 -62 wt% of Ni, Cu, Cr, K and Al in the oxidised tailings were associated with the Fe (III) oxyhydroxides. Given that these extraction procedures were performed with relatively unoxidised copper tailings with a very small amorphous Fe oxides content, most of the metals such as Fe, Cu, As, Zn and Pb that remained after this leach were expected to be in sulphide form.

However, both sequential extractions provide an indication that amorphous Fe oxide may be the source of the metals leached in this fraction. Figure 2.4 (Section 2.3.2) shows that formation of secondary precipitates of Fe (III) oxyhydroxide may occur in the unoxidised zones, probably due to the oxidation of sulphides in the mill process water. Indeed, most of the siderite ($FeCO_3$) and part of the anglesite ($PbSO_4$) were also leached in this fraction

owing to the relatively acidic solutions (pH 3.0 and 2.0 for Scheme A and B respectively) (Fanfani *et al.*, 1997). Most of the Fe extracted in the amorphous Fe oxide in both schemes may be due to insufficient dissolution of $FeCO_3$ in the exchangeable and carbonate fractions. Only between 0.12 and 0.7 wt% of Fe was leached in the exchangeable and carbonate fractions respectively.

This indicates that not only Fe in the amorphous Fe oxide phase was underestimated by the $NH_2OH.HCl$ leach, but also other major metals bound to or in amorphous phases. The K extracted in the amorphous Fe oxide in both schemes may indicate the dissolution of the jarosite minerals.

6.2.4.2 Crystalline Fe-oxide fraction

All primary iron oxides such as hematite, magnetite, goethite and maghemite, as well as secondary ferric minerals, such as primary and secondary jarosite, and natrojarosite are extracted in this fraction. The NH_4-oxalate (Scheme A) and $NH_2OH.HCl$ (Scheme B) were used under strong reducing conductions to extract metals bound to crystalline Fe oxide phases. Table 6.3 presents the major and trace metals extracted from the crystalline Fe oxides in Scheme A and B.

Table 6.3: Major and trace metals extracted from the crystalline Fe oxide fraction in Scheme A and B with 0.2 M NH_4-oxalate/0.2 M oxalic-acid leach (exposed to light) and 2 M $NH_2OH.HCl$/25% HOAc leach respectively.

Metal	Scheme A: NH_4-oxalate (exposed to light) (wt %)	Scheme B: $NH_2OH.HCl$ leach (wt %)
Fe	12	11
Cu	5	11
Al	6	6
K	1.4	3
Ca	0.18	16
Mg	9	9
Mn	27	21
Co	13	15
Zn	20	21
Mo	1	9
Pb	7	42
As	0	21
Be	22	13
Ni	4.1	4.2

The NH_4-oxalate leach under illumination extracted 12 wt % of Fe from the crystalline Fe oxide phases, while 2 M $NH_2OH.HCl$/25% HOAc extracted 11 wt% of Fe from the crystalline Fe oxide phases. The acidic NH_4-oxalate solution extracted more Fe with a

reaction time of 2 hr at 90 °C, as compared to the reaction time of 3 hr for the $NH_2OH.HCl/HOAc$ leach at the same temperature. An average of 8.7 mg/g and 8.1 mg/g of Fe was extracted from the crystalline Fe oxide fraction with Scheme A and B respectively. This indicates that, to some extent 2 M $NH_2OH.HCl$/25% HOAc was effective in dissolving the crystalline Fe oxide phases, but requiring longer reaction time. Ribet *et al.*, 1995 suggested that for mine tailings, a high concentration of $NH_2OH.HCl$ and longer reaction period may be required because they are rich in Fe. However, these results can also raise a question as to whether the increase in Fe concentration in the crystalline Fe oxide fraction was due to inadequate dissolution of the earlier amorphous Fe oxide phases (Hall *et al.*, 1996). Especially for Scheme B, because 13 wt% of Fe was extracted in the amorphous Fe oxide with NH_4-oxalate leach (Scheme A) as compared to 5 wt% extracted with $NH_2OH.HCl$ leach.

The 2 M $NH_2OH.HCl$/25% HOAc leach showed a significant increase in the major metals extracted from the crystalline Fe oxide phases. These results do not seem to contradict the question posed earlier about inadequate dissolution of amorphous Fe oxide phases leading to a significant increase in the metals extracted from the crystalline Fe oxide fraction. A significant amount of Mn extracted from amorphous and crystalline Fe oxide fraction indicates the ability of $NH_2OH.HCl$ to dissolve Mn oxide (Chao, 1984). The results also showed an increase in some of the trace metals in the crystalline Fe oxide fraction with $NH_2OH.HCl/HOAc$.

Covellite is a secondary Cu-sulphide that may be susceptible to reductive dissolution; consequently it may have contributed to the Cu concentration extracted from amorphous and crystalline Fe oxide in both schemes.

6.2.5 Organic matter, secondary Cu-sulphides and primary sulphides fraction

As metals bound to organic matter and sulphides can be easily released under oxidising conditions, an oxidation process is usually applied to leach metals associated with the organic matter and sulphide phases. The sulphide fraction includes metals that can be transferred to the environment only during a complex weathering process.

Scheme A separated the organic matter and secondary Cu-sulphide fraction from the primary sulphide fraction, while Scheme B combined the two fractions to form organic matter and primary sulphide fraction. Metals from the organic matter and secondary Cu-sulphide fraction in Scheme A were extracted with hot 35% H_2O_2 oxidising leach. The H_2O_2 reagent can attack the amorphous Fe/Mn oxides, which requires a prior dissolution of the reducible phase (Filgueiras *et al.*, 2002). The metals released from these fractions are shown in Table 6.4.

The results indicate that the hot 35% H_2O_2 oxidising leach was selective to organic matter and secondary Cu-sulphides such as covellite (CuS), chalcocite (Cu_2S) and bornite Cu_5FeS_4). On average, 46 wt% of Cu went into solution in the hot 35% H_2O_2 leach. Significant amounts of Cd, Ag and Pb were extracted, 28 wt %, 18 wt% and 21 wt% respectively. This suggests that other sulphide minerals such as greenocktite (CdS), argentite (Ag_2S) and galena (PbS) may have been oxidised in the hot 35% H_2O_2 leach. Plumlee & Logsdon, 1999 reported that Cd also disperses as sphalerite (ZnS) (see Table 2.7), however only 7 wt% of Zn was extracted in this leach, meaning that most of the Cd comes from the oxidation of Cd-sulphide such as greenocktite (CdS) by 35% H_2O_2. An average of 2 wt% of Ni was extracted in this leach.

Table 6.4: Major and trace metals extracted from the: organic matter and secondary Cu-sulphide fraction (hot 35% H_2O_2 oxidising leach) and primary sulphide fraction (KCl_3/HCl/HNO_3 leach) in Scheme A; and organic matter and primary sulphide fraction (KCl_3/HCl/HNO_3 leach) in Scheme B.

Metal	Organic matter and secondary Cu-sulphides fraction (hot 35% H_2O_2 oxidising leach)	Primary sulphide fraction (KCl_3/HCl/HNO_3 leach)	Organic matter and primary sulphides (KCl_3/HCl/HNO_3 leach)
	Scheme A	Scheme A	Scheme B
Fe	1.6	25	29
Cu	46	41	58
Al	0	10	28
Ca	19	21	29
Mg	1.02	20	25
Si	0.09	0.4	0.5
Mn	7	12	4
Co	5	0.1	29
Cr	0.3	92	87
Zn	7	18	24
Cd	28	13	5
As	0	41	48
Mo	0.17	92	88
Ag	18	78	20
Pb	21	51	21
V	0	75	53
Ni	2	79	95

Chao & Sanzolone, 1977 found the combination of KCl_3, HCl and HNO_3 to be an effective treatment in dissolving the primary sulphide minerals such as pyrite, chalcopyrite, galena, molybdenite, sphalerite and tetrahedrite. Both Scheme A and B used this leach to dissolve primary sulphide minerals. The Fe and Cu extracted for Scheme A are 25 wt% and 41 wt% respectively. This indicates that pyrite and chalcopyrite were greatly dissolved in KCl_3/HCl/HNO_3 leach. Scheme B also showed increased amounts of Fe and Cu in this fraction, 29 wt% and 58 wt% respectively. There is more Fe and Cu in the primary sulphide

fraction in Scheme B than in Scheme A, because both primary and secondary sulphides were extracted with one leach, while Scheme A removed the secondary Cu-sulphides first.

The $KCl_3/HCl/HNO_3$ leach may cause partial destruction of silicates along edges, corners, and surfaces (Chao & Sanzolone, 1977). Thus some of the Al, Ca, Mg, Si and Mn extracted with the sulphide minerals may be due to partial dissolution of Al-Ca-Mg-Mn silicates. On average 10 wt%, 21 wt%, 20 wt%, 0.4 wt% and 12 wt% of Al, Ca, Mg, Si and Mn respectively were extracted for Scheme A, and 28 wt%, 29 wt%, 25 wt%, 0.5 wt% and 4 wt% of Al, Ca, Mg, Si and Mn respectively were extracted for Scheme B.

Scheme A indicates that i) no As and V were extracted by the hot 35% H_2O_2 leach, ii) between 0.17 and 0.3 wt% of Mo and Cr, were extracted by the hot 35% H_2O_2 leach, and iii) between 75 and 92 wt% of V, Cr and Mo were extracted in the primary sulphide fraction by the $KCl_3/HCl/HNO_3$ leach. This indicates that most of these metals occur as or in primary sulphides, with Mo primarily as molybdenite (MoS_2). Scheme B also showed high extraction of Cr and Mo in the primary sulphide fraction, between 87 and 88 wt %. Relatively high concentrations of Ni in the primary sulphide occur in the form of pentlandite and nickeliferous pyrite in the tailings. On average, both schemes extracted between 79 – 95 wt % of Ni in the primary sulphide fraction.

A considerable proportion of Zn was extracted from the primary sulphide fraction, where 18 wt% and 24 wt% of Zn was recovered for Scheme A and B respectively. Pb is dominant in the primary sulphide fraction, 51 wt%, as depicted by Scheme A results. However, Scheme B indicates that Pb is dominant in crystalline Fe oxides (42 wt %), hence high extraction of Pb in the crystalline Fe oxide phases of Scheme B resulted in relatively low recovery in the sulphide fraction. Nevertheless, Pb and Zn in this fraction probably arise from primary galena and sphalerite associated with the Kennecott ore. A relatively low recovery of Co in the amorphous Fe crystalline fraction for Scheme B leads to a considerable proportion, 29 wt % of Co accumulated in the primary sulphide fraction. Scheme A indicates that up to 45 wt% of Co was extracted in the amorphous Fe oxide fraction, which may have resulted in very low Co (between 0.1 and 5 wt %) in the organic matter and secondary Cu-sulphides, and primary sulphide fraction.

These results suggest that application of the hot 35% H_2O_2 leach to dissolve the organics and secondary Cu-sulphides prior to the dissolution of primary sulphide can help to distinguish between the secondary and primary sulphide, which is important to study their role in metal retention and mobilisation.

6.2.6 Residual (silicate) fraction

The residual fraction consists mainly of metals that occur as and/or in silicate minerals. This fraction was digested with aqua regia (HCl/HNO_3), HF, $HClO_4$ and $HClO_4$. Sequential extraction scheme A and B indicate that major metals such as Al, K, Fe and Mg are the major sources of the residual fraction. The proportion of Al, K and Fe in this fraction accounts for approximately 47–95 wt% of the total Al, K, Fe and Mg in the tailings. It must be noted that the distribution of metals in the residual fraction depends on the metal content released in the previous fractions (Marguí *et al.*, 2004).

A relatively large proportion is in the form of SiO_2, the remainder of the silicate gangue being the aluminosilicate minerals commonly in the form of muscovite, K-feldspars and chlorite as indicated by the XRD results. Si accounts for 98 wt % in the residual fraction of the total Si content in the tailings, for Scheme A and B, and both sequential extraction schemes show that the Si extracted in the other fractions is < 1 wt %. Al was mainly extracted in the residual fraction, 85 wt % and 67 wt % for Scheme A and B respectively. It is also clear that K occurs almost exclusively in the residual/silicate phase, 85 wt% and 95 wt% for Scheme A and B respectively. This indicates the dissolution of aluminosilicate (muscovite, K-feldspars and chlorite) present in the sample. Dissolution of aluminosilicate contributes base cations (Ca, Mg, and Fe (II)), alkaline metals (K) and dissolves Si and Al into the solution.

Mn extracted in the residue fraction accounts for 12 wt% and 33 wt% for Scheme A and B respectively. An increase in Mn concentration in residue fraction of Scheme B, as compared to Scheme A, may be due to low extraction of Mn in the preceding extraction steps, especially in the amorphous and crystalline Fe oxide fractions. This is also manifested by higher extraction of Fe in the residue fraction of Scheme B, accounting for 51 wt%, as compared to 47 wt % of Fe extracted in the residue fraction of Scheme A. The Cu extracted was < 1 wt% for both schemes, indicating that all Cu was extracted in the previous fractions and that Cu is not associated with the silicates or any mineral that may be resistant.

6.3 Environmental implications of the metal speciation pattern

Despite the shortcomings of some of the reagents employed in this study in terms of selectivity, the speciation patterns from the sequential extraction schemes are useful for assessing the environmental impact of the Cu-mine tailings in terms of potential mobilisation and bioavailability of the major and minor metals. Metals may be transported in the environment by different chemical mechanisms: i) in solution or adsorbed on solids, where they are readily available, ii) hydroxides and oxides, organics and sulphides, where there are changes required before they are released, iii) crystalline structures of minerals such as silicates, where they are not easily available in nature.

From the environmental point of view, the water soluble fraction is the most readily available fraction. The sequential extraction procedures showed that this fraction contained very small amounts of K, Ca and Mg and traces of toxic metals such as Co, Mo, Ag and Pb. Weathering of these tailings may form water soluble sulphates thereby increasing the concentration of these metals and other minor metals that may be released when water percolate through the tailings. Occurrence of these metals in this fraction can have a significant implication in terms of environmental impacts.

The metals in the exchangeable fraction give an indication of the amount of metals that are weakly adsorbed on major phases such as Fe/Mn hydroxides and oxides, and silicates/clays (Fanfani *et al.*, 1997; Fuentes *at el.,* 2004). The exchangeable fraction includes i) weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction, ii) metals that can be released by ion-exchange processes, and iii) metals that can be coprecipitated with carbonates (Filgueiras *et al.*, 2002). Changes in the ionic composition, influencing adsorption–desorption reactions, or lowering of pH could cause remobilisation of metals from this fraction (Fuentes *at el.,* 2004). Generally, metals in the exchangeable and carbonate fractions are considered readily available for uptake and potentially mobile into the environment. All metals in these fractions are transferred to the environment at a slightly acidic or mild pH.

A significant proportion of major metals, Ca>Mn>Mg>Cu and minor metals, Cd>Co>Zn>Ni>Pb in the tailings, are associated with the exchangeable fraction. Although it was shown by both schemes that most of the carbonate minerals were extracted in the exchangeable fraction. This indicates that desorption and ion-exchange may lead to the release of these easily mobile metals. In tailings dumps, high pH conditions regulate the behaviour of metals by keeping them as hydroxyl, aqueous metal complexes and carbonate bound forms. Therefore, high pH conditions in tailings dumps can reduce the mobility of these metals and other associated metals, thereby decreasing the exchangeable form, which is highly mobile (Song *et al.*, 1999). Proportions of the exchangeable fraction in the oxidised samples are higher than that in relatively fresh samples (Dang *et al.*, 2001). This implies that mobilisation capabilities of metals get enhanced as more metals are transformed into the exchangeable phase with time, thereby increasing the metals that may be easily mobilised.

The primary sulphide fraction accounts for considerable amounts of Fe, Cu, Cr, Zn, Cd, As, Mo, Ag, Pb and Ni (see Section 6.2.5). Metal sulphide minerals can break down easily because they are vulnerable to oxidation when exposed to air and water. Under environmental conditions the oxidation of sulphide minerals can cause a release of these metals, and metals from decomposition of sulphides are adsorbed or complexed by the Fe

(III) oxyhydroxide minerals. As indicated in Section 2.3.1, when ferrous ion is oxidised by the dissolved oxygen in solution, the product is strongly dependent on pH. When pH is greater than 3.5, oxidation reaction c (Table 2.1) follows and forms Fe (III) oxyhydroxide minerals. Since Fe (III) oxyhydroxide phases exhibit a strong affinity for metals, it is likely that part of the metals dissolved from sulphides could be adsorbed or coprecipitated with these secondary minerals (Dang *et al.*, 2001). Therefore, the sequential extraction results suggest that the release and mobilisation due to oxidation, under natural conditions, of Fe, Cu, Cr, Zn, Cd, As, Mo, Ag, Pb and Ni associated with the primary sulphide phases is feasible, which can lead to the increase of metal concentrations in the reducible fraction (particularly Fe (III) oxyhydroxide).

Under reducing and acidic conditions, the dissolution of Fe(III)-(oxy)hydroxides and crystalline Fe oxides contained in the tailings may occur. This releases the potentially toxic metals previously adsorbed onto or coprecipitated with the Fe(III)-(oxy)hydroxides as described above. From the environmental point of view, this means that metals in this fraction are potentially bioavailable. The sequential extraction results indicated that major metals such as Cu, Al, K, Ca, Mg and Mn, and minor metals such as Co, Zn, Mo, Pb, As, Be and Ni may be release from the reducible fraction.

The residual fraction is the non mobile fraction and is potentially the least harmful. From the environmental point of view, this fraction can only be mobilised after weathering or decomposition, and therefore have only very long-term effects. Thus, this fraction is an assessment of the 'worst case environmental scenario in which the components of the solid waste are soluble and mobile. As confirmed by XRD and sequential extraction results Al, K, Fe, Mn and Mg are associated with the silicate minerals. Both schemes showed the minor metals such as Co, Cr, Zn, As, Mo, Ag and Pb may be released by the dissolution of silicates. Table 2.2 shows the dissolution of aluminosilicates that can play a role in long-term acid neutralisation after depletion of reactive carbonates. This process is also illustrated in Figure 2.3, where the metals bound to silicates are released near sulphide exhaustion.

6.4 Kinetic dissolution study: Modification of the amorphous and crystalline Fe oxide fraction

Schemes A and B showed that Fe is mostly present in the residual fraction, between 47 and 51 wt % of the total Fe concentration in the tailings. A considerable proportion, between 25 and 29 wt%, appeared to be in the primary sulphide fraction. The Fe extracted in the crystalline Fe oxide fraction was between 11 and 12 wt%, where the Fe oxides predominately occur as hematite, goethite, magnetite and maghetite. Between 5 and 13 wt% was extracted in the amorphous Fe oxide fraction for Scheme A and B respectively. The low recovery of Fe in the reducible fraction may be attributed to inadequate dissolution of Fe

hydroxide and oxide in the amorphous and crystalline Fe oxide fractions. Although the sample was relatively unoxidised, higher amounts of Fe and other metals were extracted in the amorphous Fe oxide in Scheme A, as compared to the ones extracted in Scheme B. This provides some indication of inadequate extraction of metals in this phase.

As mentioned in Chapter 2, an important parameter in sequential extraction is the time of contact between the solid waste and the reagent. It was suspected that low recovery of Fe in the reducible fraction especially the crystalline Fe oxide where most of the highly crystalline Fe phases are found, was due to short time of contact.

The reducible fractions (amorphous and crystalline Fe oxides) for Schemes A and B were optimised for extractant efficiency for amorphous and crystalline Fe oxide phases in the Cu-tailings studied. The sample was subjected to a kinetic dissolution study in order to understand the specific dissolution kinetics i.e. particularly time of contact of the complex amorphous, poorly crystalline and crystalline Fe oxides. The extraction was considered to be complete when the amount of the extracted Fe in the solution reached an asymptotic value (extraction plateau), or when there was insignificant change in Fe concentration with time. The dissolution-time curves for this study were developed by reacting the sample with freshly prepared extraction solutions as follows:

Sequential extraction A:
2.5 g of samples were shaken in 250 ml Erlenmeyer flasks containing 0.2 M NH_4 –oxalate brought to pH 3.0 by 0.2 M oxalic acid at 25 °C and taking 10-ml subsamples with syringes at 30, 60, 90, 120, 180, 240, 300, 360, 420, 480, 540, 600, 660, 720 min. This test was conducted in duplicate. During the first 360 min, the flasks were wrapped with aluminium foil to exclude light and prevent attack on more crystalline Fe oxyhydroxide/oxide phases. The samples were exposed to light after 6 hours, followed by heating the sample to 85 – 90 °C in a water bath, for selective dissolution of crystalline Fe oxides.

Sequential extraction B:

- *Amorphous and poorly crystalline Fe oxide fraction*: 2.5 g of samples were shaken in 250 ml Erlenmeyer flasks containing 0.25 M $NH_2OH.HCl$ brought to pH 2.0 using 0.25 M HCl at 50 °C.
- *Crystalline Fe oxide fraction:* 2.5 g of samples were shaken in 250 ml Erlenmeyer flasks containing 2 M $NH_2OH.HCl$ brought to pH 2.0 by 25% CH_3OOH, pH 2.0 at 90 °C.

In both fractions, 10-ml subsamples were taken with syringes at 30 min intervals for the first 90 min, then at 1 hr intervals for 13 hr and again 1 hr intervals after 23 hr. All subsamples collected during the kinetic dissolution study of sequential extraction schemes A and B were

filtered immediately with 0.45µm Teflon inline membrane filters for syringes, into high density polyethylene (50 ml) centrifuge tubes. The dissolved Fe were analysed in duplicate using Atomic Adsorption Spectroscopy (AAS). The concentration of Mn was determined for the same extractions to provide an indication of the efficiency of the extraction method.

6.4.1 Sequential extraction scheme A

Figure 6.3 presents the dissolution-time curve of iron oxides by 0.2 M NH_4 –oxalate/0.2 M oxalic acid at 25 °C in darkness for the amorphous and poorly crystalline Fe oxide phases and 0.2 M NH_4 –oxalate/0.2 M oxalic at 90 °C for crystalline Fe oxide phases.

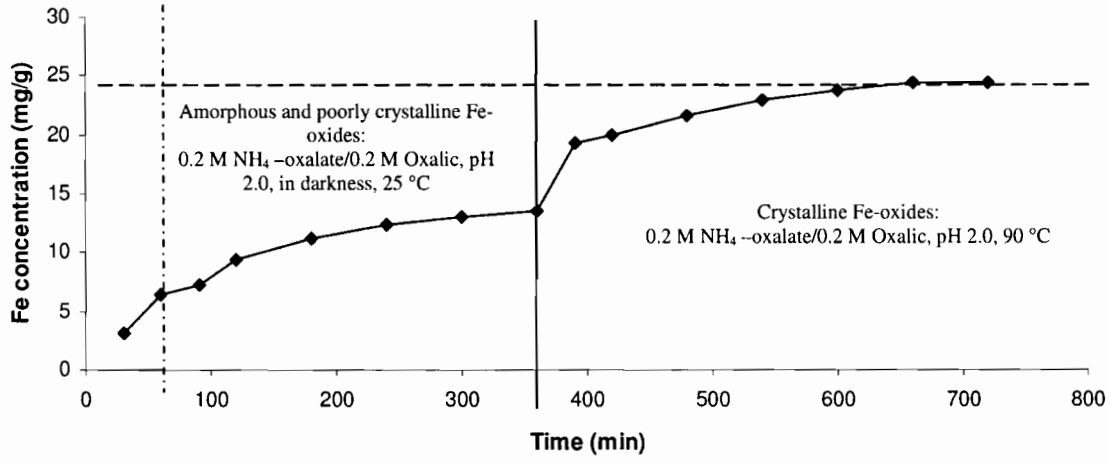


Figure 6.3: Dissolution kinetic curve of Fe in the amorphous and crystalline Fe oxide fractions:2.5 g of samples were leached with 0.2 M NH_4 –oxalate/0.2 M Oxalic, pH 2.0, in darkness, at 25 °C and 0.2 M NH_4 –oxalate/0.2 M Oxalic, pH 2.0, at 90 °C. The vertical dashed line shows where the green/gray colour appeared, horizontal dashed line shows the extraction plateau and solid line shows where the samples were exposed to light and heated at 90 °C.

The dissolution of amorphous Fe-oxide fraction increased significantly with time during the first 180 min. The difference in cumulated Fe concentration was insignificant when the time of extraction was longer than 240 min (4 hr). This means that extraction time needed for the extraction of metals in the amorphous Fe oxide in the Cu-tailings studied is 4 hr. An increase in the Fe concentration in the solution was confirmed by a change in colour from brown (being the original colour of the copper tailings) to green/gray colour after 1hr of extraction (colour change point is shown by the dotted lines in Figure 6.3). This colour change indicates a significant increase in the dissolution of the secondary Fe (III) hydroxide (Dold, 2003).

The solid line indicates where the sample was exposed to light and heated at 90 °C. A significant rise in the cumulated Fe concentration (from around 13 to 19 mg/g) shows that

increasing the operating temperature and exposing the samples to light increased the degree of dissolution of crystalline iron oxyhydroxides or oxides. It must also be taken into account that in the presence of Fe (II) containing minerals (e.g., siderite, magnetite), the dissolution rate of other Fe oxides (goethite, hematite, etc.) may be enhanced.

Table 6.5 shows a comparison of the amounts of Fe extracted from amorphous and crystalline Fe oxide by the NH_4 –oxalate/ oxalic acid leach procedures described in Scheme A and kinetic dissolution study. The concentration of Fe in the crystalline Fe oxide obtained by the kinetic dissolution test was determined by subtracting the total Fe extracted in the amorphous Fe oxide fraction after 6 hr (before exposing the sample to light, see Figure 6.3) from the total Fe extracted after 11 hr.

Table 6.5: Shows the amount of Fe extracted in the amorphous and crystalline Fe oxide fractions by Scheme A and kinetic dissolution study.

	Fraction and leaching time	
	Amorphous Fe oxide: Obtained by NH_4 –oxalate/ oxalic acid leach from scheme A	**Amorphous Fe oxide: Obtained by kinetic dissolution test**
	0.2 M NH_4 –oxalate/0.2 M oxalic, pH 3.0, at 25 °C for 1 hr, in darkness	0.2 M NH_4 –oxalate/0.2 M oxalic, pH 3.0, at 25 °C for 4 hr, in darkness
Fe (mg/g)	9.1	13
Fraction and leaching time		
	Crystalline Fe oxide: Obtained by NH_4 –oxalate/ oxalic acid leach from scheme A	**Crystalline Fe oxide: Obtained by kinetic dissolution test**
	0.2 M NH_4 –oxalate/0.2 M oxalic, pH 3.0, at 90 °C for 2 hr	0.2 M NH_4 –oxalate/0.2 M oxalic, pH 3.0, at 90 °C for 5 hr,
Fe (mg/g)	8.1	12

The amount of Fe extracted increased up to 5 hr (measured from 360 to 660 min), and then remained constant for longer shaking periods. It therefore, appeared that extraction time beyond 5 hr did not have a pronounced effect on the release of Fe in the tailings sample, and that the 5 hr extraction was adequate for the extraction in the crystalline Fe oxide fraction.

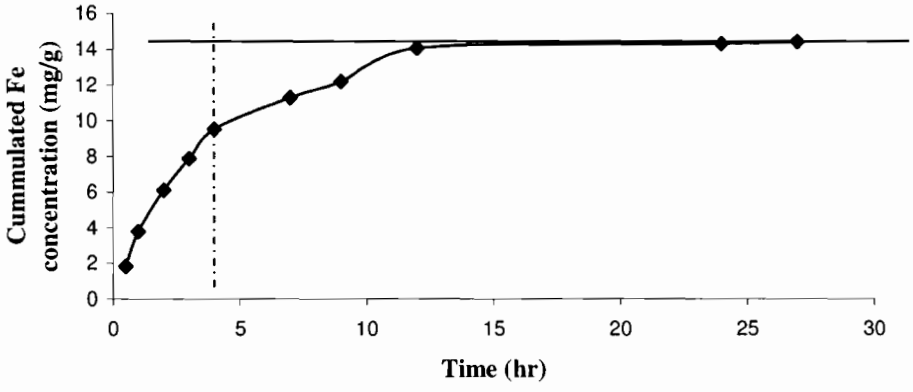
6.4.2 Sequential extraction scheme B

6.4.2.1 Amorphous Fe oxide

Figure 6.4 shows the dissolution kinetic curve of Fe and Mn with 0.25 M $NH_2OH.HCl$/0.25 M HCl, pH 2.0 at 50 °C. The results indicate that the extraction of Fe in the amorphous Fe oxide was complete after approximately 13 hr. The concentration of Fe extracted in the

amorphous Fe oxide in Scheme A started showing an insignificant increase after about 5 hr at around 13 mg/g, compared to the Fe in Scheme B which shows an extraction plateau at around 14.1 mg/g after 13 hr. This indicates that the 0.2 M NH_4 –oxalate/ 0.2 M oxalic acid leach provides a greater dissolution of the amorphous Fe oxide with shorter extraction period, compared to the 0.25 M $NH_2OH.HCl$/0.25 M HCl leach. The concentration of Mn started to level off after approximately 10 hr leaching time.

a) Fe in the amorphous Fe oxide fraction



b) Mn in the amorphous Mn oxide fraction

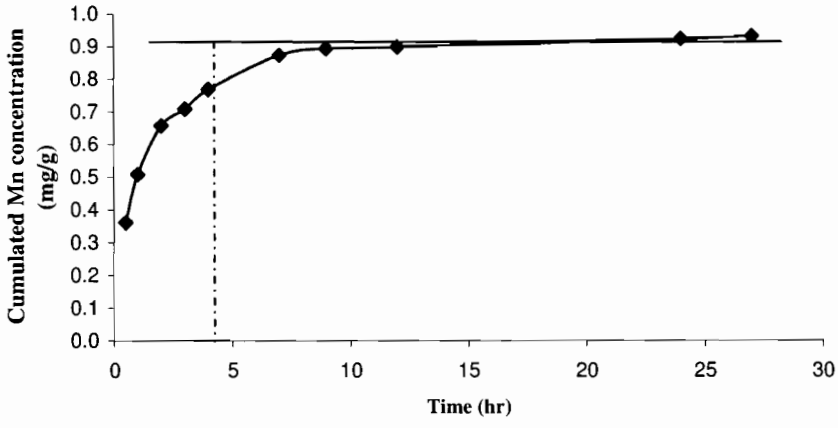


Figure 6.4 a, b: Dissolution kinetic curves of Fe and Mn in the amorphous Fe oxide. 2.5 g of samples were leached with 0.25 M $NH_2OH.HCl$ brought to pH 2.0 using 0.25 M HCl at 50 °C. The vertical dashed line shows where the green/gray colour appeared and solid horizontal line shows the extraction plateau.

6.4.2.2 Crystalline Fe oxide

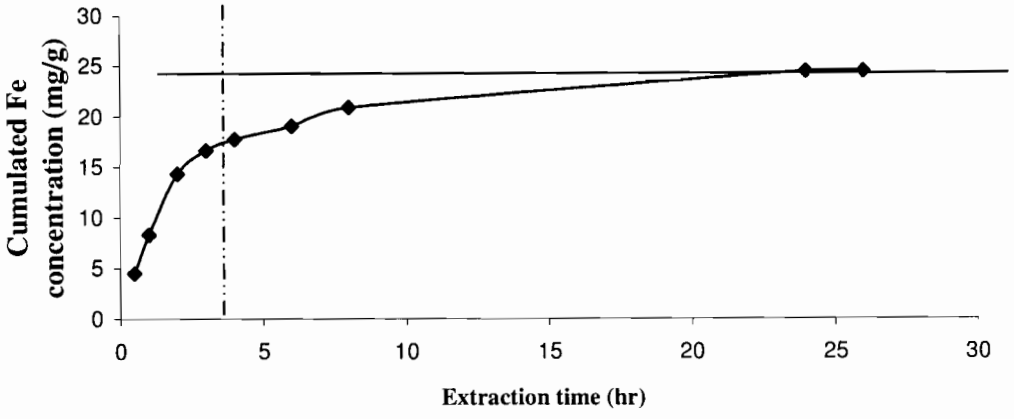
Results for the cumulative kinetic dissolution study of Fe and Mn with 2 M $NH_2OH.HCl$/25% CH_3OOH are shown in Figure 6.5. Visual monitoring of the dissolution kinetics showed a change in sample colour from brown to gray after 1hr, indicating an increase in the dissolution of Fe oxides.

The study indicates that the extraction plateau by 2 M $NH_2OH.HCl$/25% CH_3OOH was reached in 24 hr for Fe (Figure 6.5a). These findings are in agreement with the results obtained from the kinetic dissolution test on mine tailings by Ribet *et al.*, 1995. They suggested that for Fe rich soils or mine tailings, a high concentration of the reducing agent and longer reaction period may be required (Ribet *et al.*, 1995). The Fe concentration in the crystalline Fe oxide in Scheme A started levelling off at around 5 hr, once again indicating the efficiency of acid ammonium oxalate in dissolving crystalline Fe phases.

Determination of Mn showed that (Figure 6.5b):

- The extraction of Mn was complete about the same time as Fe. It is assumed, therefore, that some of the Mn metals are associated with the crystalline Fe oxide, probably in the form of MnO_2. The dissolution of Mn oxide in this leach was confirmed by the 7-step sequential extraction procedure B in Section 6.2.

a) Fe in the crystalline Fe oxide fraction



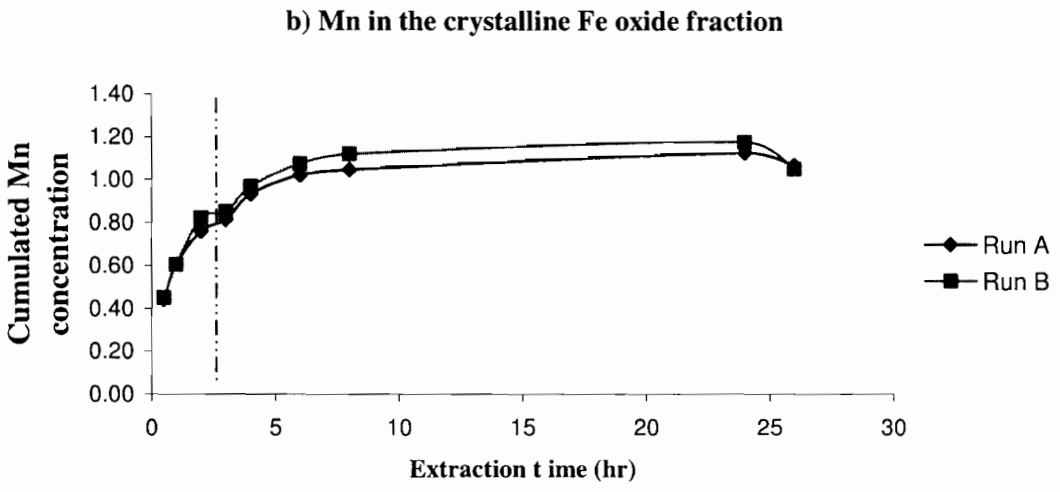


Figure 6.5 a,b: Dissolution kinetic curves of Fe and Mn in the crystalline Fe oxide. 2.5 g of samples were leached with 2 M $NH_2OH.HCl$ brought to pH 2.0 by 25% CH_3OOH, at 90 °C. The vertical dashed line shows where the green/gray colour appeared and solid horizontal line shows the extraction plateau.

Table 6.6 presents the Fe extracted from the amorphous and crystalline Fe oxide fractions by the $NH_2OH.HCl/HCl$ leach procedures in Scheme B and the kinetic dissolution study.

Table 6.6: Shows the amount of Fe extracted in the amorphous and crystalline Fe oxide fractions by Scheme B and kinetic dissolution study.

Fraction and leaching time		
	Amorphous Fe oxide: Obtained by $NH_2OH.HCl/HCl$ leach from scheme B	**Amorphous Fe oxide: Obtained by kinetic dissolution test**
	0.25 M $NH_2OH.HCl$/0.25 M HCl, pH 2.0, at 50 °C, for 2 hr	0.25 M $NH_2OH.HCl$/0.25 M HCl, pH 2.0, at 50 °C, for 12 hr
Fe (mg/g)	3.6	14.1
Fraction and leaching time		
	Crystalline Fe oxide: $NH_2OH.HCl/HCl$ leach from scheme B	**Crystalline Fe oxide: Obtained by kinetic dissolution test**
	2 M $NH_2OH.HCl$/25% CH_3OOH, pH 2.0, at 90 °C, for 3 hr	2 M $NH_2OH.HCl$/25% CH_3OOH, pH 2.0, at 90 °C, for 24 hr
Fe (mg/g)	8.1	11

The results suggest that, for the Cu- tailings studied, the time needed to extract the crystalline Fe oxide phases must not be longer than 24 hr. Longer extraction time may lead

to readsorption of metals, which results in a decrease in the concentration of metals already extracted in the crystalline Fe oxide phase.

6.5 Summary of the sequential extraction procedure investigations

This chapter has focused on the application and comparison of two types of 7-step sequential extraction procedures to Kennecott Cu-tailings sample, known to be potentially acid forming (see Chapter 5). The sequential extraction procedures were employed in order to understand the mode of occurrence of metals, and use the data to estimate metal mobility and bioavailability. Metals were extracted from the following operationally defined fractions:

- ***Scheme A:*** *F1: Water soluble; F2: Exchangeable; F3: Amorphous Fe-oxide; F4: Crystalline Fe-oxide; F5: Organic matter and secondary Cu-sulphide; F6: Primary sulphides; F7: Residual (silicates).*
- ***Scheme B:*** *F1: Water soluble; F2: Exchangeable; F3B: Carbonate; F4B: Amorphous Fe-oxide; F5B: Crystalline Fe-oxide; F6: Primary sulphides; F7: Residual (silicates).*

Examination of results leads to the following conclusions:

6.5.1 Comparison of the sequential extraction schemes

- Results from Scheme B confirmed that 1 M NH_4-acetate/ 1 M CH_3OOH leach at pH 4.5 is able to extract exchangeable and bound-to-carbonate metals. The use of these reagents depends on the aims of the sequential extraction schemes i.e. whether both fractions are required.
- The acid NH_4 –oxalate leach provides greater dissolution of the amorphous and crystalline Fe oxide fractions at shorter reaction time as compared to the acid $NH_2OH.HCl$ leach.
- Inadequate dissolution of the amorphous Fe oxide in Scheme B leads to an increase in metal concentrations in the subsequent steps.
- As indicated in Scheme A, the application of the hot 35% H_2O_2 leach to dissolve the organics and secondary Cu-sulphides prior to the dissolution of primary sulphide was necessary to distinguish between the secondary and primary sulphide, which is important to study their role in metal retention and mobilisation.

6.5.2 Modification of the amorphous and crystalline Fe oxide fractions: a kinetic dissolution study

The kinetic dissolution test results have shown that it is necessary to modify the sequential extraction schemes and adapt them to a specific mineralogy of mine tailings. Based on the results of the kinetic experiments, the following modifications of sequential extraction schemes A and B are recommended to optimise the leaching times for chemical sequential

extractions used to extract metals in the amorphous and crystalline Fe oxide fraction in the studied copper tailings (old extraction times are shown in brackets):

Sequential A:

- ***Amorphous Fe oxide fraction***: 0.2 M NH_4 –oxalate/0.2 M oxalic acid, pH 2.0, at 25 °C in darkness, allowing the mixture to react for 4 hr (changed from 1 hr).
- ***Crystalline Fe oxide fraction***: 0.2 M NH_4 –oxalate/0.2 M oxalic, pH 2.0 at 90 °C, allowing the mixture to react for 5 hr (changed from 3 hr).

Sequential B:

- ***Amorphous Fe oxide fraction***: 0.25 M $NH_2OH.HCl$/0.25 HCl, pH 2.0, at 50 °C, allowing mixture to react for 12 hr (changed from 2 hr).
- ***Crystalline Fe oxide fraction***: 2 M $NH_2OH.HCl$/25% CH_3OOH, pH 2.0, at 90 °C, allowing the mixture to react for 24 hr (changed from 3 hr).

The above study indicates that in order to improve the operational selectivity of the sequential scheme on a particular sample, a kinetic study is necessary.

6.5.3 Reliability/limitations

- In general, sequential extraction procedures have allowed the determination of the distribution of metals into the geochemical fractions or phases, which account for relative proportion of each metal transported by different chemical mechanisms.
- Sequential extractions provided an indication of the behaviour of some trace metals that have an environmental impact but are difficult to detect with a mineralogical study since they do not form specific minerals. For example, they showed traces of toxic heavy metals such as Mo, Cd, Ag and Pb in the exchangeable fraction.
- It was demonstrated that some reagents used to extract particular phases may attack other phases, but this is limited and it does not seriously limit the usefulness of the sequential extraction procedures.
- It has been demonstrated in Section 6.3 that the sequential extraction data can provide the following information:
  - ❖ Mobility and bioavailability of metals (i.e. metals that are readily/potentially available for up take, and that are not easily released).
  - ❖ The chemical mechanisms that may lead to the release of metals associated with various phases.
  - ❖ The oxidation state of the sample.

6.5.4 Relationship between mineralogical investigations and sequential extraction procedures: selection of a suitable scheme

In this chapter, the chemical partitioning of Fe, Cu, Al, K, Ca, Mg, Mn, Si Co, C, Zn, Cd, As, Mo, Ag, Pb, V, Be and Ni forms in the different fractions/phases was determined in

parallel with the mineralogical forms. The mineralogical analysis of the sample in Chapter 4, and the primary mineralogic sources for some environmental metals provided in Section 2.6.1, provided useful information for the selection of sequential extraction scheme suitable for the Cu-tailings sample studied and also for interpretation of the data.

The XRD analysis showed the presence of silicates and Fe oxide in the sample, which retains exchangeable metals on their surfaces by relatively weak electrostatic interactions that can be released by ion-exchange processes. The ion exchangeable metals can be coprecipitated with carbonate minerals which were also shown by the XRD. The traces of toxic metals in the exchangeable fraction get enhanced as more metals are weakly adsorbed on the surfaces of the secondary Fe hydroxide/oxide that are formed during weathering of a waste.

In Scheme B, the carbonate fraction is extracted after the exchangeable fraction while Scheme A extracts these two fractions with one leach. It was demonstrated that the carbonates bound metals already came out in the exchangeable fraction. The proportion of the silicates and Fe oxide in the sample is greater as compared to the carbonate minerals. This indicates that they may have contributed a considerable amount of the metals in the exchangeable fraction. However, some traces of toxic metals may be present as carbonate forms; for example, traces of Pb extracted may be present as cerussite ($PbCO_3$). This suggests that the knowledge of mineralogy and separation of the exchangeable and carbonate fractions can provide reliable information on the metals associated with the exchangeable and carbonate fractions.

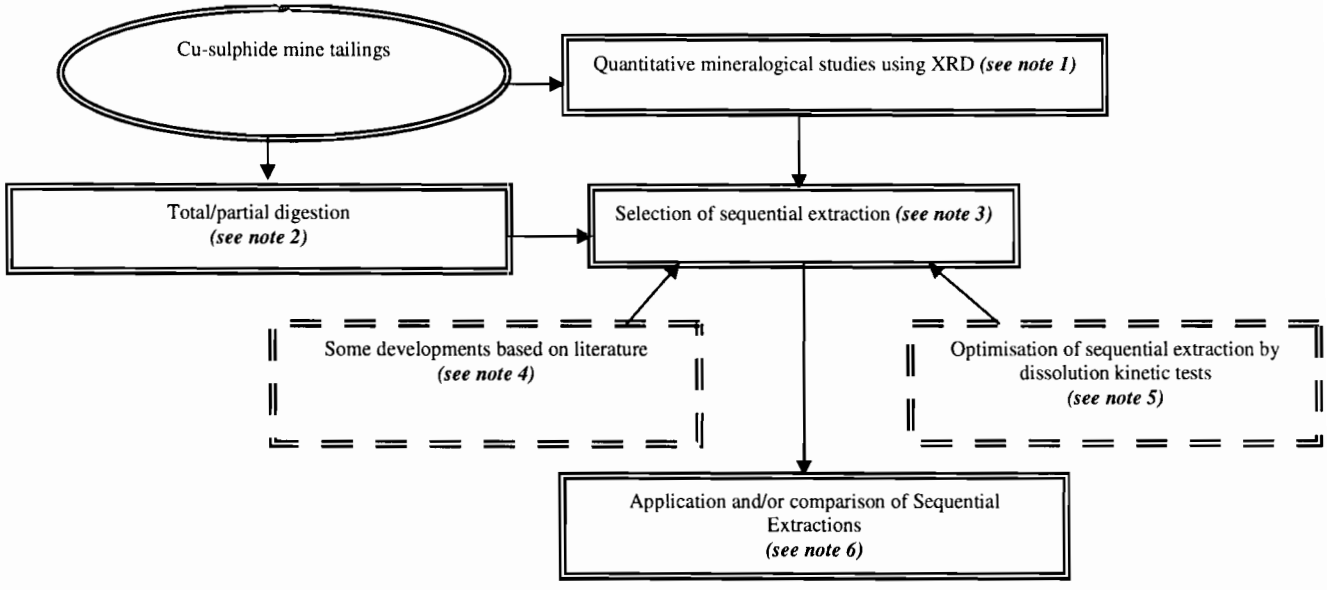
Scheme A separates the organics and secondary Cu-sulphide and primary sulphide fractions. It is important and useful to distinguish between the secondary sulphide minerals such as covellite and chalcocite, and primary sulphides such as pyrite, chalcopyrite, molybdenite, galena, sphalerite, tetrahedrite, and cinnabar. Also this is important because the primary and secondary Cu enrichment processes are important in Cu-sulphide mine tailings. Scheme A showed that sulphides such as greenocktite (CdS), Argentite (Ag_2S) and Galena (PbS) were present as secondary sulphide minerals. According to Table 2.7 metals such as Cd, Co and Ni can also disperse in sphalerite and pyrite.

Based on the outcomes of this chapter and conclusions drawn, the sequential extraction procedure suitable for the Cu-tailings sample studied and that can be suitable for a variety of Cu-tailings mine wastes is the sequential extraction scheme A. It is suggested that the exchangeable and carbonate fractions be separated when applying sequential extraction scheme A. The XRD analysis identified three types of minerals that can carry metals in the exchangeable form, carbonates, Fe/Mn oxide and silicates. Therefore, it is necessary to

distinguish and quantify the metals coprecipitated or adsorbed on the surfaces of these minerals in the exchangeable fraction, and the metals present as carbonates. Furthermore, a kinetic study of the dissolution of organic matter and secondary Cu- sulfides in 35% H_2O_2 could enhance the selectivity of this leach procedure.

6.5.5 Modification of the sequential extraction procedure/s

Based on the results obtained and conclusions drawn in this chapter, the sequential extraction procedures can be modified according to the optimisation process summarised in Figure 6.6. This is a generic modification process and can be used to optimise extraction times for various extraction procedures applied to mine wastes.



- **Note 1:** Knowledge waste's mineralogy should inform selection of phases and enhance the interpretation of results.
- **Note 2:** Metal analysis by total/partial digestion method on the tailings is required to evaluate metals recovery and assess the reliability of sequential extraction procedure/s.
- **Note 3:** Sequential extraction procedure/s adapted for a particular mine waste should be based on other studies.
- **Note 4:** Development of sequential extraction procedures based on several sequential procedures adopted for mine tailings.
- **Note 5:** The correct choice of the time of contact or extraction is obtained from cumulative kinetic dissolution curves. The kinetics dissolution study can be conducted on phases that are known to be metal scavengers e.g. Mn-oxide, reducible phases such as F (III) oxyhydroxides or amorphous Fe oxides and crystalline Fe oxides.
- **Note 6:** Application of sequential extraction procedure/s on the mine waste and evaluate the reliability of sequential extraction/s data as the percent recovery relative to a single total/partial digestion.

Figure 6.6: Flowchart for the modifications of the sequential extraction procedures for the Kennecott Cu tailings studied.

6.5.6 Summary of mechanisms controlling AMD formation and metal release

The data from the test procedures employed in this study was used to provide an understanding of the mechanisms and parameters influencing AMD production and metal release. Based on the AMD and sequential extraction results, the chemical mechanisms controlling AMD and the transport of metals in the environment can be summarised as follows:

- Dissolution of carbonate minerals may occur in the early staged of AMD formation, providing a short-term ANC, releasing Ca, Mg and Mn. The sequential extraction showed that dissolution of carbonate can release metals such as Cu, Cd, Co, Zn, Ni, Pb (coprecipitated with carbonates, Fe/Mn oxides and silicate minerals) by ion exchange process.
- The kinetic NAG test indicated depletion of carbonate minerals and slow reactivity of sulphide by a slow decrease in pH. As primary and secondary sulphides oxidise, acid and formation of Fe (III) oxyhydroxide/hydroxysulphates is enhanced. Although some sulphide minerals do not form acid, they contribute to the increase in metals released.
- As pH decreases significant amounts of Fe, Cu, Cr, Zn, Cd, As, Mo, Ag, Pb and Ni can be released though sulphide oxidation, as indicated by the sequential extraction results. The kinetic NAG results showed yellow precipitates of Fe (III) oxyhydroxide/hydroxysulphates at the peak zone where pH was less than 3. These secondary minerals have strong affinity for metals and adsorption is the key process.
- After sulphide exhaustion, the metals bound to silicate minerals (residual fraction in sequential extraction) may be released as the dissolution of silicates occur to provide the long term ANC. As indicated in Chapter 2, this can be prolonged by dissolution of water – soluble sulphates (see Chapter 6) and Fe(III) oxyhydroxide (termed amorphous Fe oxide in sequential extraction procedures), which releases acidity and metals during rain fall and change in redox conditions (reducing conditions).

6.6 Systematic empirical waste characterisation protocol for mine wastes

An empirical waste characterisation protocol for the evaluation of solid mineral wastes is presented in this section, based on the outcomes of the test procedures conducted in this research. The suggested protocol is presented in Figure 6.7. It follows Levels 1 and 2 of the 3-level characterisation hierarchy suggested in the WRC report (see Chapter 2, Figure 2.1). This waste characterisation protocol combines the application of i) mineralogical analysis, ii) AMD prediction procedures, iii) sequential extraction procedures and iv) kinetic dissolution studies, aimed to generate geochemical information that can be used to study factors and

mechanisms influencing AMD production and metal release, thereby predicting the environmental impacts of a mine waste.

The approach undertaken in this study and the comparison of test methods in Chapter 5 and 6 has been used to form this protocol. This protocol incorporates the optimisation process of the sequential extraction procedure presented in Section 6.5.5. The structure of the protocol is described as follows:

- As demonstrated in Chapter 4, predictions of waste characterisation on the basis of sources and origin can provide a better understanding of the distribution of major and minor ore metals during beneficiation, which plays a role in the evaluation of environmental metals.
- As demonstrated in the preceding chapters, the selection and interpretation of the solid waste characterisation protocol results is mainly facilitated by the mineralogical analysis.
- Total metal analysis on the samples aims to:
  - ❖ Identify the strategic metals on the basis of their environmental significance.
  - ❖ Evaluate the deportment of metals on the basis of sources and origins.
  - ❖ Provide a comparison of the total recovery (sum of fractions) of metals with the total metal concentration, which is necessary to assess the recovery of the sequential extraction procedure.
- Level 1 in the AMD prediction procedures consists of AMD screening tests that identify uncertainties in classification that may require further investigation. The test procedures involve static laboratory procedures that evaluate the balance between acid generation processes (oxidation of sulphide minerals) and acid neutralising processes (dissolution of alkaline carbonates). This enables the determination of the i) MPA and ANC, and the difference between the MPA and ANC to give NAPP, ii) NAG_{pH} which indicates the reactive ANC and net acid generation (NAG). As indicated in Chapter 5, the standard Sobek ANC test can be used to investigate the potential effects of the siderite in the sample, before using the Modified H_2O_2 ANC test methods. Although paste pH test is not reliable for AMD classification of samples, it can reflect the presence of oxidation products (see Section 6.2.1).
- Level 2 of the AMD prediction methods provides a better understanding of AMD characteristics of the waste and correct uncertainties (e.g. when $NAG_{pH} \geq 4.5$ and NAPP>0; $NAG_{pH}<4.5$ and NAPP$\leq$0; NAG/NAPP<0.5) that may be identified in the AMD screening procedures. These tests depend on the nature of the sample and the information required.

  The sequential NAG test provides information on the total acid potential and should be conducted on samples with high total S (mostly S>1wt%), in which catalytic

decomposition of H_2O_2 in single addition NAG test may result in incomplete oxidation of sulphide as it was demonstrated in Chapter 5. It can also be used on samples containing secondary sulphate minerals or other non acid forming sulphide minerals which can result in single addition NAG acidity << NAPP. Kinetic NAG test provide more information regarding sulphide and carbonate reactivity and estimate lag time for acid generation.

The modified criteria for classification of samples based on the information provided by the AMD prediction procedures is provided in Chapter 3, Figure 3.3.

- Metal partitioning using sequential extraction procedures will provide additional information regarding the:
  - ❖ Processes controlling AMD production and metals release.
  - ❖ Mode of occurrence of metals.
  - ❖ Metals which are readily or potentially available for up take and mobile in the environment and metals that can not be easily released to the environment.

Thus, combining the AMD characteristics of the mine waste, and the detailed partitioning of metals, provide reliable information useful to predict the potential release of metals in mine waste and the related environmental impacts. This confirms that the determination of total metal concentration and the use of standardised leachate extraction batch tests such as TCLP provide limited information required to evaluate the environmental impacts of solid mineral wastes. Also, an integrative test approach can resolve many limitations of the individual test methods.

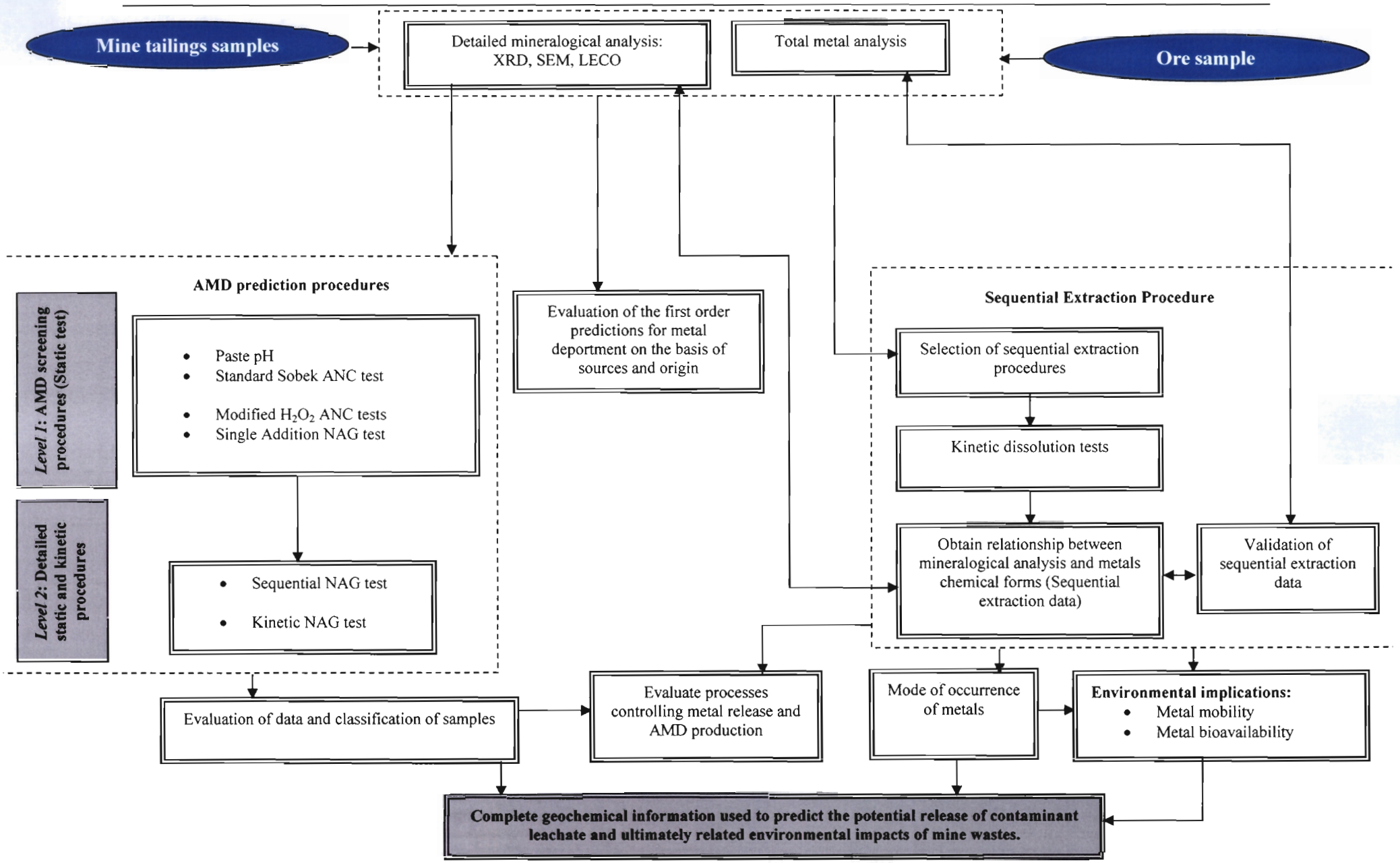


Figure 6.7: Flowchart showing a generic systematic empirical waste characterisation protocol.

Chapter 7

SUMMARY AND CONCLUSIONS

This chapter reviews the key objectives of the research, which were presented in Chapter 1 and provides a summary of the major findings of this research. The two hypotheses formulated in Chapter 3 are revisited to indicate how the experimental evidence supports them. This chapter begins by describing the motivation for conducting this research in Section 7.1. The key objectives and a summary of the major outcomes of this research are presented in Section 7.2. Section 7.3 provides the validation of the hypotheses, followed by the recommendations in Section 7.4.

7.1 Motivations for conducting the research

Solid mineral wastes are not well characterised by standardised leachate extraction batch tests such as TCLP. The determination of total metal also provides insufficient information required to predict the environmental impacts of solid mineral wastes. Forms of a given metal are not equally soluble and the mobility, transport and partitioning of metals are strongly dependent on their specific binding forms. The current available prediction methods such as AMD prediction methods lead to discrepancies because they are often used in isolation and also without the knowledge of the mineralogy of a sample.

Thus, an integrative approach of the methodologies that provide, i) information on the binding forms of metals to mineral phases, ii) predict the acid mine drainage (AMD), being the major source of leachate generation, can provide adequate data that can be used to predict the environmental impacts of a particular mine wastes. The characterisation of waste was based on Level 1 (first order prediction on the basis of sources and origins) and Level 2 (determination of physio-chemical properties) in the procedural framework for systematic waste characterisation presented in Chapter 2, Figure 2.1, using a case study.

7.2 The key objectives of the research

As indicated in Chapter 1, the work presented in this study aimed to address the following primary objectives:

1. To design, confirm, and fine-tune a systematic empirical waste characterisation protocol so as to generate data which can be interpreted in such a way that the

potential release of contaminated leachate, and ultimately related environmental impacts, can be adequately and effectively forecast. In particular, the aim is to investigate suitable laboratory protocols for:

Acid Mine Drainage Evaluation:

- Use the knowledge of the mineralogy of the waste to provide a framework to choosing the most appropriate method for AMD prediction test and assess the reliability of AMD interpretation.
- Investigate a variety of Acid Mine Drainage (AMD) testing protocols, so as to identify opportunities for AMD test modification and improvement.

Metal chemical speciation:

- Evaluate a set of sequential extraction procedures and determine their limitations and applicability to copper tailings.
- Obtain a relationship between the mineralogy of the waste and the sequential extraction data.
- Show how this knowledge can be used to understand the mode of occurrence of metals in copper sulphide tailings essential for environmental assessment.
- Identify and quantify contaminants that will be potentially released and/or influence contaminant release to the environment.

2. To validate the first-order predictions for metals deportment into tailings from copper sulphide ore processing as predicted on the basis of source (ore type and composition) and origin (generation process).

These objectives were achieved by conducting laboratory test work on the Cu-tailings sample, generated from an ore sample of the well known porphyry Cu-deposited at Kennecott Copper Utah.

Sections 7.2.1 through 7.2.7 provide a summary of the outcomes of Chapters 4, 5 and 6. If the reader is familiar with the summaries provided at the end of these chapters, he/she may skip Sections 7.2.1 and 7.2.7 to Sections 7.3 and 7.4. Section 7.3 provides a conclusive illustration of how the work presented in this study was used to validate the hypotheses formulated in Chapter 3. This is followed by Section 7.4 which, provides the recommendations based on the conclusions provided in this study.

7.2.1 Mineralogical characterisation

The XRD analysis of the sample indicated pyrite (2.92 wt %) and chalcopyrite (0.5 wt %) as the major sulphide minerals in the sample. LECO indicated a total S content of 2.9 wt%, giving the sample a significant maximum production acidity of 89 kg H_2SO_4/t. Gangue minerals such as quartz and aluminosilicates (chlorite, K-feldspar and muscovite) form the

bulk of the tailings sample. XRD detected the following carbonate mineral siderites ($FeCO_3$)> calcite ($CaCO_3$) >(ankerite [$Ca(Mg,Fe)(CO_3)_2$], dolomite [$CaMg(CO_3)_2$], magnesite [$CaMg(CO_3)_2$]). The most abundant iron oxide was hematite (FeO_3), and other Fe and Mn oxide detected were goethite (α-FeO(OH)) and (MnO_2).

7.2.2 Evaluation of the first-order predictions for metals deportment

Validation of waste composition on the basis of sources and origin has shown that:

- The major rock forming metals such as Si, Al, K, Na, Mg and Ca (i.e. metals present as/in oxide, carbonate, silicate and pyrite minerals) reported mainly in the tailings, with their concentration levels similar to the one in the ore. This agrees with the predictions made by Broadhurst *et al.*, 2005a in Task 4 of the WRC report.
- Fe reported mainly in the concentrate because it is associated with copper (mainly chalcopyrite) and iron (mainly pyrite) sulphide minerals.
- The experimentally determined values of Co, Zn, As, Mo, Ag, Pb and Re confirmed that these metals report mainly to the concentrate as suggested by the predictions. Both experimental and predicted values of Mn, Cr, V and Be indicated that these metals deport mainly to the tailings.
- Low concentration of Cu in the concentrate indicated a poor recovery of Cu during the laboratory flotation tests on the Cu-sulphide ore.
- The results obtained by XRD analysis, for major minerals are consistent with the predicted typical concentrations of main mineral groups.

7.2.3 Investigation of variety of AMD prediction methodologies

As indicated in Chapter 5, four static acid generation prediction tests; standard Sobek ANC test, Additional/Incremental and Skousen H_2O_2 ANC test, and single NAG test, were evaluated as AMD screening tools and two detailed AMD tests sequential NAG test, kinetic NAG test. The outcomes of these tests were:

- The major factor influencing the determination of acid neutralisation capacity (ANC) results is the presence of siderite in the Cu-tailings sample studied. The potential effects of the siderite were investigated using standard Sobek ANC test. This test showed that siderites had a significant influence on the ANC values because of incomplete oxidation of Fe^{2+} and Fe^{3+} and incomplete hydrolysis of Fe^{3+} during back titration leading to an ANC value of 66 kg H_2SO_4/t.
- Incremental and Skousen H_2O_2 ANC test were employed to correct for the siderite effects and the results showed a decrease in ANC values to 27 and 28 kg H_2SO_4/t respectively. These two tests were modified to provide enough time for complete oxidation and hydrolysis of Fe with H_2O_2.

- Incremental H_2O_2 ANC test was found to be time consuming, however it ensured complete hydrolysis at pH 4.5 and stable pH when titrated to pH 7.0.
- Only 63% of the total S was oxidised during the single addition NAG test, indicating that catalyst decomposition of H_2O_2 can lead to uncertainties due to incomplete oxidation of sulphide on the S content and sulphide reactivity. This indicated the need for detailed static test such as sequential NAG test.
- Experimental evidence showed that sequential NAG was able to oxidise over 98% of total S after 3 stages, thereby providing a better estimate of the acid producing potential. It was concluded that the amount of acidity produced in the stages of sequential NAG test provide some indication of the reactivity of pyrite and lag in acid production.
- These findings were supported by the kinetic NAG test which provided the following information (see Figure 5.3):
  - ❖ Acidity formed during oxidation was due to pyrite oxidation.
  - ❖ Sample contains slow reactive pyrite.
  - ❖ Significant lag in acid production based on the total S and kinetic NAG profiles.
  - ❖ Proportion of pyritic S in a sample based on kinetic NAG temperature profiles.
- Evaluation of AMD prediction tests demonstrated that use of ABA and NAG test results together can resolve many uncertainties that may lead to misclassification of samples.

Thus, evaluation of AMD prediction tests demonstrated that knowledge of the mineralogy would help select the appropriate test/s to predict the acid generation potential of a sample. Based on the evaluation of the AMD prediction results and the classification criteria in Figure 3.3, the sample was classified as potential acid forming of high capacity but slow reacting.

7.2.4 Sequential extraction procedure investigations

As indicated in Chapter 3, two types of sequential extraction schemes were employed in order to demonstrate the applicability of sequential extractions to mine tailings. Metals were extracted from the following operationally-defined phases:

- Sequential extraction scheme A: *Water soluble; Exchangeable; Amorphous Fe-oxide; Crystalline Fe-oxide; Organic matter and secondary Cu-sulphide; Primary sulphides; Residual (silicates).*

- Sequential extraction scheme B: *Water soluble; Exchangeable; Carbonate; Amorphous Fe-oxide; Crystalline Fe-oxide; Primary sulphides; Residual (silicates).*

The main factors that affect sequential extractions were reviewed in Chapter 2 and no attempt was made in this research to study all factors. Only the effects of extraction time were studied. However, the evaluation of the two sequential extraction schemes demonstrated that other factors such as the selectivity/efficiency of the reagents employed, pH and redistribution/re-adsorption had an influence on the extraction results. A comparison of the two extraction schemes demonstrated that the amount of metals extracted at each fraction depends on the type of reagents used and the sequence in which they were applied. Some reagents used were capable of dissolving targeted phases, with a significant attack on the others. For example:

- NH_4-acetate/CH_3OOH leach was capable of dissolving both exchangeable and carbonates fractions.
- KCl_3/HCl/HNO_3 leach used to extract primary sulphide bound metals can cause partial destruction of the silicate, and this was indicated by a release of Al, Ca, Mg, Si and Mn in this fraction.

Comparison of the two sequential extraction schemes demonstrated the following:

- The Na-acetate/CH_3OOH leach for carbonate bound metals is not necessary for sequential schemes that employ NH_4-acetate/CH_3OOH leach to extract the exchangeable bound metals, for the reason mention above.
- When applying sequential extraction to copper tailings, it is necessary and important to separate the organic matter and secondary Cu-sulphide fraction from the primary sulphide fraction.
- Scheme A showed that by separating these two fractions, it is possible to distinguish the secondary Cu sulphide minerals and other metals that are present as secondary sulphides, from the primary sulphide minerals responsible for AMD formation.

The experimental study of the dissolution kinetics has indicated the importance of the dissolution techniques to reduce some of the operational problems. These results have shown that it is necessary to modify the sequence and adapt it to the specific mineralogy of mine tailings.

- The correct choice of the contact time of the solid and reagent required for optimum extraction can be obtained from the cumulative kinetic dissolution curves. Too long extraction time can lead to a decrease in the concentration of metals and a possible formation of secondary phases because of readsorption of the cations already extracted in a given extraction step.
- Determination of Mn in the dissolution kinetics of the reducible iron fraction showed that constant concentrations were reached during the extraction by NH_2OH.HCl at

about the same time as Fe, indicating that Mn was associated with the reducible iron fraction.

Despite the limitations of sequential extraction schemes, the experimental evidence showed that sequential extractions can be used to:

- Determine the mode of occurrence of metals in mine wastes by partitioning them into operationally defined phases.
- Study the behaviour of some trace metals that have environmental impacts but are difficult to detect with a mineralogical study because they do not form specific minerals. Some metals are weakly adsorbed or coprecipitated on other major phases, e.g. metals bound exchangeably to mineral phases or carbonates.
- Confirm the mineralogical studies of a given tailings sample.

7.2.5 Metal partitioning and environmental implications

As indicated in Chapter 6, the speciation patterns from the sequential extraction schemes are useful for assessing the environmental impact of the Cu-mine tailings in terms of potential mobilisation and bioavailability of the major and minor metals.

- According to the sequential extraction results, the mobilisation, under natural conditions, of major metals, Ca>Mn>Mg>Cu and minor metals, Cd>Co>Zn>Ni>Pb associated with the ion exchangeable and carbonate phases is feasible. Metals in these fractions are considered readily available for uptake and potentially mobile into the environment.
- Although the extractions were conducted on relatively unoxidised tailings, the results indicated that some secondary precipitates of Fe (III) oxyhydroxide were present, probably due to oxidation of sulphides in the mill process water and during storage. Fe (III) oxyhydroxide exhibits a strong affinity for metals, and a change in conditions leading to oxidation and subsequent formation of these secondary minerals can cause readsorption of metals to the amorphous Fe oxide.
- Primary sulphides account for significant amounts of Fe, Cu, Cr, Zn, Cd, As, Mo, Ag, Pb and Ni, which are probably present as sulphides. The review of the geology of the Kennecott copper ore body in Chapter 3, showed the presence of the following primary sulphides: pyrite, chalcopyrite, bornite, molybdenite and sphalerite. Therefore, the mobilisation of these minerals, due to oxidation is feasible. From the environmental point of view the metals in the reducible and sulphide fractions are potentially mobile, and available for up take.

7.2.6 Mechanisms controlling AMD formation and metal release

The mechanisms controlling AMD production and metal release are presented in Section 6.5.5. These mechanisms were derived from the AMD prediction test and sequential extraction results. A summary of these mechanisms is presented in Table 7.1.

Table 7.1: Summary of mechanisms and parameters affecting AMD production and metal release based on AMD prediction tests and sequential extraction procedures (see Chapter 6)

AMD prediction procedures	Sequential extraction procedures
Dissolution of carbonate minerals, providing a short-term ANC.	Release metals such as Ca, Mg, Mn, Cu, Cd, Co, Zn, Ni, Pb (coprecipitated with carbonate, Fe/Mn oxide and silicate minerals) by ion exchange process.
Depletion of carbonate minerals and slow reactivity of sulphide decreases pH.	Formation of Fe (III) oxyhydroxide/hydroxysulphates and adsorption of metals is enhanced.
Precipitation of Fe (III) oxyhydroxide/hydroxysulphates at the peak zone where pH was less than 3.0.	Significant amounts of Fe, Cu, Cr, Zn, Cd, As, Mo, Ag, Pb and Ni by sulphide oxidation under low pH. Adsorption of these metals to Fe (III) oxyhydroxide/hydroxysulphates
Dissolution of silicates occur to provide the long term ANC.	Release of metals bound to the silicates (residual fraction). Possible dissolution of the water soluble secondary sulphates, releasing acidity.

7.2.7 Systematic empirical waste characterisation protocol

A major outcome of this research was the design/development of an empirical waste characterisation protocol for quantification of geochemical characteristics of mine wastes. The suggested protocol follows Levels 1 and 2 of the 3-level characterisation hierarchy suggested in the WRC report (see Chapter 2, Figure 2.1) and is presented in Chapter 6, Figure 6.7. The tests employed in this research were critical to developing the final waste characterisation protocol. The structure of the protocol can be summarised as follows:

- Predictions of waste characterisation on the basis of sources and origin can provide a better understanding of the distribution of major and minor ore metals during beneficiation, which plays a role in the evaluation of environmental metals.
- Mineralogical and total metal analysis, used for selecting a suitable test variation and to enhance the interpretation of the results derived from the tests methods.
- Level 1 in the AMD prediction procedures involves screening tests that identifies uncertainties in classification requiring further investigation.
- Level 2 of AMD prediction procedures provide a better understanding of AMD characteristics of the waste and correct uncertainties (e.g. when $NAG_{pH} \geq 4.5$ and $NAPP > 0$; $NAG_{pH} < 4.5$ and $NAPP \leq 0$; $NAG/NAPP < 0.5$) that may be identified in the

AMD screening procedures. These tests depend on the nature of the sample and the information required.

- Sequential extraction procedures provide detailed information on processes controlling AMD production and metals release; mode of occurrence of metals; and metals which are readily or potentially available for up take and mobile in the environment, and metals that can not be easily released to the environment.
- Combination of the results from these test procedures provides relevant information useful to predict the potential release of metals in mine waste and the related environmental impacts. This eliminates discrepancies arising from the inappropriate use of the available prediction methods, determination of total metal concentration and the use of methodologies such as TCLP to assess the environmental impacts of the solid mineral wastes.

7.3 Validation of hypotheses

As indicated in Chapter 3, the thesis aimed to validate the following hypotheses:

1. Prior knowledge of the mineralogy is required for selection of the AMD prediction test and sequential extraction procedures and to enhance interpretation of data.

   The results in Chapters 5 and 6 have indicated that a detailed mineralogical analysis is required to select suitable AMD prediction tests and sequential extraction procedures for waste characterisation. The ANC tests results in Chapter 5 showed that the use of standard Sobek ANC test overestimated the ANC values, due to the presence of siderites and other iron containing minerals, and this made this test unsuitable for the Cu-tailings sample studied. As expected from the mineralogical data, Skousen H_2O_2 and Additional/Incremental H_2O_2 ANC tests were found to be suitable for this sample since they corrected for siderite effects.

   The sample contained carbonate, silicate and Fe/Mn oxide minerals, which indicated that it was necessary to evaluate metals in the exchangeable, carbonate and reducible fractions. Carbonates, silicates and Fe/Mn oxides retain exchangeable metals on their surfaces by relatively weak electrostatic interactions.

2. First-order deportment modelling on the basis of sources (*ore type and composition*) and origins (*generation process*), of the environmentally significant trace and minor components from copper sulphide ores into tailings will result in reliable predictions, and can be confirmed by total metal analysis in ores and tailings.

A discussion in Chapter 4, Section 4.2, demonstrated that the predictions made by Broadhurst *et al.*, 2005, can provide a fundamental understanding of the deportment of metals on the basis of sources and origins. The knowledge of metal deportment is useful for evaluation of the environmental impacts of a mine waste and by conducing total metal analysis and mineralogical characterisation on ore, tailings and concentrate, metal deportment can be evaluated with these predictions used as guidelines.

Although, 1) the experimental concentration levels of the minor metals were below the predicted range, 2) concentration of Cu in the tailings and concentrate show poor recovery, the concentration of other major metals such as Fe, Si, Mg, K, Ca and Na were in agreement with the predictions. The concentrations levels of the major minerals analysed were also consistent with the predicted concentrations of main mineral phases. These results also showed that the ore used in this study was representative porphyry copper sulphide ores.

These results have served as experimental evidence in support of the first and the second hypotheses presented in Chapter 3.

7.4 Recommendations

Based on the conclusions, the following recommendations are made:

7.4.1 AMD prediction tests

For routine analysis, where the mine samples have not had a quantitative mineralogy done, the Skousen H_2O_2 ANC test should be used to correct for the effects of siderites that may be present in the sample, since the additional/incremental H_2O_2 ANC test has been found to be time consuming. If the mineralogy of the sample has been quantified, the standard Sobek ANC test should be used only if the amount of siderite does not significantly affect the ANC results, otherwise Skousen H_2O_2 ANC test should be used. If the presence of siderites has no major influence on the results, then the acid production potential of a sample can be estimated based on the standard Sobek ANC test, which consumes less time.

The NAG test procedures can provide reliable information for predicting the AMD potential of a waste. It is recommended that the heating step be conducted during the NAG test and also that the samples should be filtered only after the heating step. This avoids making decisions based on incorrect characteristics of a sample.

7.4.2 Sequential extraction procedures

The sequential extraction scheme A did not distinguish the exchangeable fraction from the carbonate fraction i.e. it dissolved both fractions in a single step. A leach solution that will minimise the dissolution of carbonate minerals in the exchangeable fraction is required. This will enable the extraction of Ca, Mn and Mg in the carbonate fraction which will provide a good estimation of the buffering capacity. A list of reagents used for extraction of carbonate bound metals is presented in Chapter 2, and a further investigation of these reagents may provide useful information in terms of their selectivity and their limitations.

It is recommended that the exchangeable fraction be leached with the most widely used reagents such as $MgCl_2$, $BaCl_2$ and NH_4-acetate (NH_4OAc) at 1 M concentration and pH 7.0, to prevent dissolution of carbonates phases, which can occur under acidic conditions. Metals in the carbonate fraction can be leached with 1 M Na-acetate/1 M CH_3OOH leach and pH between 4.5 and 5.0. This increases the dissolution of carbonate minerals with minimal attach on organic matter, Fe/Mn oxide and aluminosilicates.

It is also recommended that a kinetic dissolution study be conducted on the organic matter and secondary Cu sulphide fraction to enhance the selectivity of this leach prior to extraction of primary sulphide minerals.

The arbitrary choice of the time of contact in the amorphous and crystalline Fe oxide can yield data of doubtful validity. These fractions are known to contain large amount of metals. It is recommended that a kinetic dissolution study be conducted to optimise for extractant selectivity and efficiency for secondary Fe-oxyhydroxides and crystalline Fe oxide.

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An Experimental Investigation of Leachate Generation Predictions of Waste from Copper Sulphide Ore Processing

PART B

Appendices

Appendices- Table of Contents

Appendices- List of Table

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Appendix A: First order predictions for metal deportment

The first order data set pertaining to the metal concentrations in porphyry copper sulphide ore, tailings and concentrate as predicted by Broadhurst *et al.*, 2005a in Task 4 of the WRC-project. These predictions were used in Chapter 4.

Table A-A: Predicted element concentration ranges of major and moderately abundant metals for porphyry-type copper sulphide ores, tailings and concentrates.

Sulphide ore-forming elements				Lithophilic gangue-forming elements			
Element	**Ore**	**Tailings**	**Concentrate**	**Element**	**Ore**	**Tailings**	**Concentrate**
Major ore elements (%)							
Cu	0.5-1.0	0.08-0.13	25-30	Si	21-34	21-35	2.5-8
Fe	1-10	0.8-9.5	15-30	Al	4-10	4-10	0.5-2.2
S	2-11	1.0-11	20-30	Mg	0.2-3	0.2-2.6	0.02-0.6
				K	0.3-3.4	0.3-3.5	0.03-0.8
				Ca	0.4-4	0.4-4.5	0.05-1.0
				Na	0.3-3	0.3-3.2	0.03-0.7
Moderately abundant ore elements (ppm)							
Zn	150-1600	15-500	4000-55000	Ti	450-9000	400-9000	50-2000
Pb	30-300	5-100	800-11000	P	100-6000	100-6100	15-1400
As	5-1800	2-550	100-62000	F	60-3000	60-3000	7-680
Mo	15-1500	2-450	400-50000	Mn	100-2000	100-2000	11-450
Bi	2-200	0.2-60	50-7000	B	50-1000	50-1000	5-230
Sb	2-200	0.2-60	50-6840	Ba	40-860	45-880	5-200
Cd	2-200	0.2-60	50-6840	REE	10-850	10-870	1-190
Ni	8-150	1-50	200-5000	Sr	30-600	30-600	3-130
Se	10-100	1-30	300-3000	Rb	10-600	10-600	1-140
				Zr	10-500	50-500	1-110
				Cl	10-500	50-500	1-110
				V	15-300	15-300	2-70
				Li	5-300	15-300	0.5-70
				Sn	15-300	15-300	2-70
				Cr	10-200	10-200	1-50
				Nb	2-200	10-200	0.1-40
				W	5-100	5-100	0.5-20

Appendix A continues...

Table A-B: Predicted element concentration ranges of minor, trace and scares metals for porphyry-type copper sulphide ores, tailings and concentrates.

Minor ore elements (ppm)							
Element	**Ore**	**Tailings**	**Concentrate**	**Element**	**Ore**	**Tailings**	**Concentrate**
Minor ore elements (ppm)							
Ag	1.0-70	0.1-20	20-2500	Ga	2-80	2-80	0.1-15
Co	2.5-50	0.3-15	70-1700	Sc	1-70	1-70	0.1-15
Ge	2-20	0.5-10	80-1000	Be	0.5-30	1-30	0.2-5
				Hf	0.5-25	0.5-30	<0.1-5
				Br	0.5-25	0.5-30	<0.1-5
Trace ore elements (ppm)							
Tl	0.6-6	0.06-2	15-200	U	<1-10	1-10	0.1-2
Pt	0.05-5	0.01-2	1-170	Ta	<1-10	0.1-10	0.01-2
Au	0.04-4	0.002-1	1-140	I	<1-5	0.05-5	<0.01-1
Pd	0.1-2	0.01-3	3-350				
Hg	0.2-1.5	0.02-0.5	5-70				
Scarce ore elements (ppm)							
Te	0.1-1.0	0.01-0.5	3-30				
In	0.1-1	0.01-0.5	3-50				
Re	0.01-1	<0.01-0.5	0.5-30				

Appendix A continues...

Table A-C: Predicted typical concentration ranges for the main mineral groups in generic flotation tailings from porphyry copper sulphide ores.

Mineral Group	Typical Concentration (%)	Major minerals comprising each group
Sulphides	2-18	o Iron sulphides: 91-99% o Copper sulphide : 1-8% o Trace-minor sulphides: ≤ 2%
Copper sulphide minerals	0.08-0.2	o Chalcopyrite: 43-97% of total o Bornite: up to 39% of total o Chalcocite: up to 17%
Iron sulphide minerals	2-18	Mainly pyrite
Trace/minor sulphide minerals	0.02-0.09	o Arsenopyrite: up to 10% of totoal o Sphalerites: up to 66% of total o Galena: typically 10% of total o Molybdenite: typically 8% of total
Lithophilic gangue minerals	84-98	o Major Silicate minerals: 90-98% of total o Major Carbonates: 0.5-4% of total o Other: 1-8 %
Silicate gangue minerals	82-96	o Quartz: 35-45% o K-Feldspar:20- 25% o Albite:≤10% o Biotite: ≤10% o Muscovite and/or chlorite: ≤10%
Carbonate gangue minerals	0.5-4	Mainly calcite with lesser amounts of dolomite, ankerite and/or siderite
Trace to minor gangue minerals	1-7	o Cassiterite (SnO_2) o Iron oxides (magnetite and haematitie) o Ti minerlas (sphene,Ilmentite and rutile) o Apatite ($Ca_5(PO_4)_3(F, Cl. OH)$) o Barite ($BaSO_4$) o Anhydrite ($CaSO_4$) o Fluorite (CaF_2) o Tourmaline ($NaFe_3Al_6(BO_3)Si_6O_{18}(OH)_4$ o Rhodocrosite ($MnCO_3$) o Zircon ($ZrSiO_4$) o REE minerals (monazite)

Appendix B: Physical characterisation

Table B-A: Particle size distribution of the pulverised Kennecott Cu tailings sample obtained by Malvern mastersizer

Result: Analysis Table

ID: Wisani PC 2 Run No: 9 Measured: 4/11/06 3:25PM
File: HELEN Rec No: 429 Analysed: 4/11/06 3:25PM
Path: C:\SIZERS\DATA\ Source: Analysed

Range: 300RF mm Beam: 2.40 mmSampler: MS17 Obs': 28.7 %
Presentation: 3QHD Analysis: Polydisperse Residual: 1.565 %
Modifications: None

Conc. = 0.0212 %Vol Density = 2.900 g/cm^3 S.S.A. = 0.4041 m^2/g
Distribution: Volume D[4, 3] = 42.14 um D[3, 2] = 5.12 um
D(v, 0.1) = 1.96 um D(v, 0.5) = 18.66 um D(v, 0.9) = 119.82 um
Span = 6.317E+00 Uniformity = 1.897E+00

Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
0.05	0.00	0.58	0.67	6.63	3.12	76.32	3.43
0.06	0.00	0.67	0.82	7.72	3.15	88.91	3.40
0.07	0.00	0.78	0.93	9.00	3.16	103.58	3.25
0.08	0.00	0.91	1.04	10.48	3.16	120.67	2.94
0.09	0.00	1.06	1.14	12.21	3.16	140.58	2.48
0.11	0.00	1.24	1.21	14.22	3.18	163.77	1.93
0.13	0.00	1.44	1.28	16.57	3.19	190.80	1.38
0.15	0.00	1.68	1.37	19.31	3.20	222.28	0.84
0.17	0.00	1.95	1.52	22.49	3.21	258.95	0.29
0.20	0.00	2.28	1.71	26.20	3.21	301.68	0.00
0.23	0.04	2.65	1.94	30.53	3.21	351.46	0.00
0.27	0.10	3.09	2.22	35.56	3.22	409.45	0.00
0.31	0.18	3.60	2.50	41.43	3.25	477.01	0.00
0.36	0.28	4.19	2.74	48.27	3.29	555.71	0.00
0.42	0.39	4.88	2.93	56.23	3.35	647.41	0.00
0.49	0.53	5.69	3.05	65.51	3.39	754.23	0.00
0.58		6.63		76.32		878.67	

Appendix B continues...

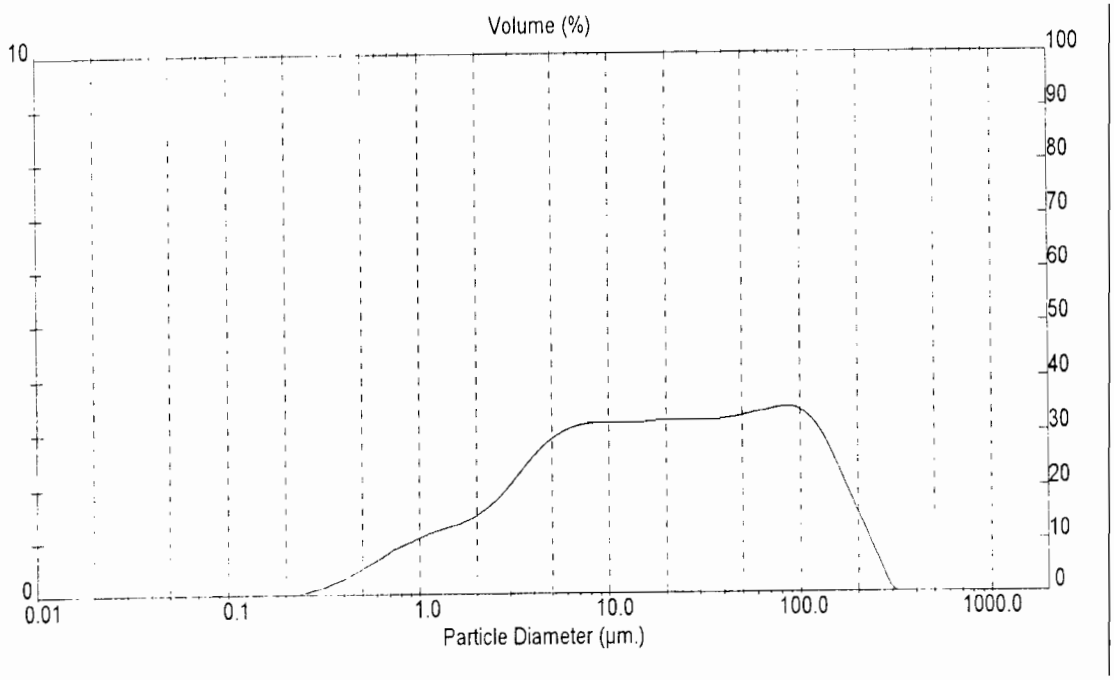

Figure B.1: A graphical representation of the particle size distribution of the pulverised Kennecott Cu tailings sample obtained by Malvern mastersizer

Appendix C: Mineralogical characterisation

Figure C1 shows the XRD patterns for the Kennecott copper sulphide tailings used in this study.

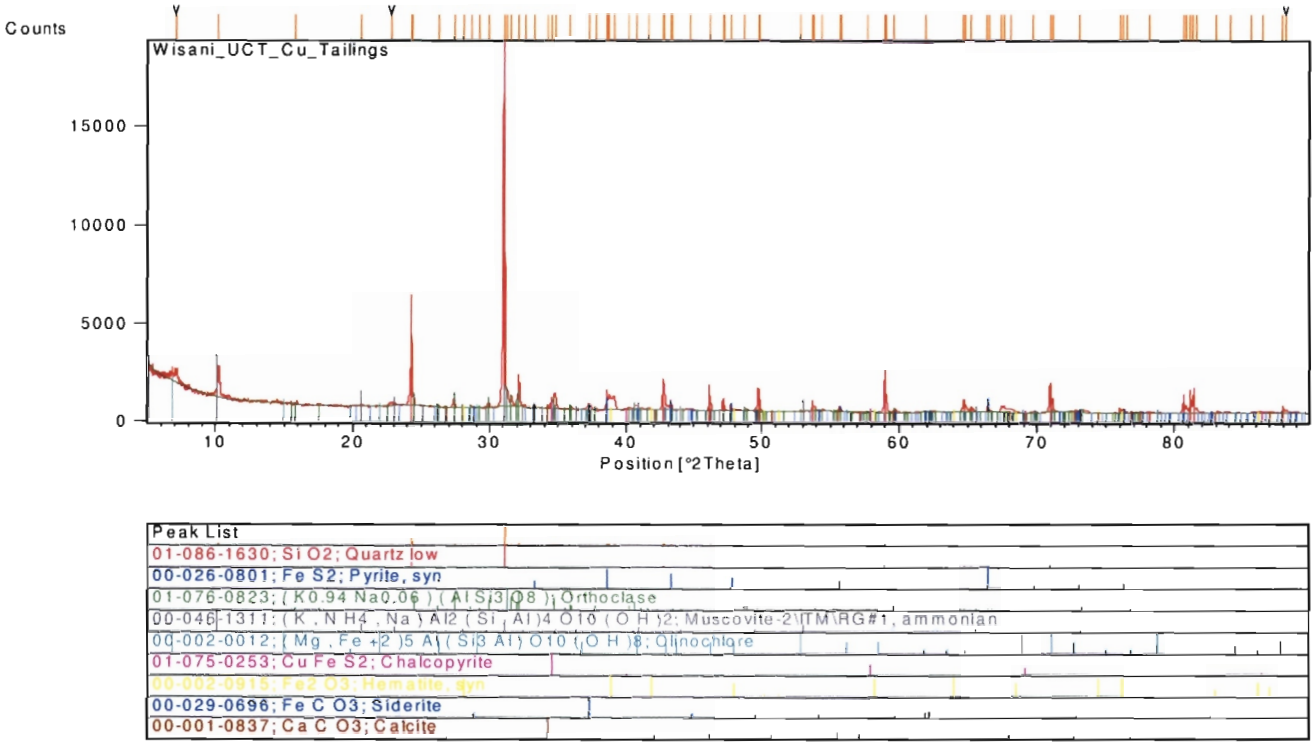

Figure C.1: XRD pattern for the tailings.

Appendix D: Total Metal Analysis

Chapter 4 and 6 data tables

Table D-A: Analytical results (in triplicates) of the Aqua Regia Leach ((HCl, HNO_3), HF, $HClO_4$) as described in Section 3.9.1. Data was obtained by ICP-MS in ppb.

Metal	Ore samples			Tailings samples			Concentrate samples		
	Ore1	Ore2	Ore 3	Tailings 1	Tailings 2	Tailings 3	Concentrate1	Concentrate2	Concentrate3
	Major metals (ppb)								
Fe	2582001	2425973	2278874	1539280	1476465	1489238	559872	638777	680495
Cu	42492	45258	47141	24697	24250	24662	16819	20397	20621
Al	77569	110932	92389	140793	85741	87081	135780	159128	169320
K	234299	249993	238967	301151	274784	250557	15963	16605	16813
Ca	25320	72742	50612	191343	190458	190566	n.d.	7715	8575
Mg	44615	33674	30608	65876	68287	66106	2120	2650	2766
Mn	21074	19977	19226	26647	25406	26192	273	310	337
Si	4319000	4382000	4407000	5180000	5437000	4481000	3516	3100	3416
	Trace metals (ppb)								
Co	372.84	391.57	388.66	384.60	384.41	395.51	109	133	132
Cr	4816	5198	4914	6073	5656	5711	511	634	703
Zn	2889	2756	2697	2700	2499	2527	689	835	956
Cd	16.4	16.4	15.9	28.9	28.8	28.8	1.84	2.24	2.88
As	2222	2330	2207	2238	2179	1993	284	327	350
Mo	481	518	496	555	524	529	96.0	135.4	135.3
Ag	43.8	48.7	46.2	32.8	29.5	31.0	33.2	47.7	43.9
Pb	930	1017	955	777	738	752	290	248	325
V	1528	1758	1666	1615	1769	1510	451	581	623
Be	20.0	20.2	19.8	25.6	21.5	21.3	2.96	2.76	0.93
Ni	1548	1107	1377	2616	2675	2539	50.0	44.26	53.0
n.d: not detected									

Appendix D continues....

Table D-B: Analytical results (in triplicates) of the aqua regia leach ((HCl, HNO_3), HF, $HClO_4$) as described in Section 3.9.1. Data was obtained by ICP-MS in mg/kg.

	Ore samples			Tailings samples			Concentrate samples		
	Ore1	**Ore2**	**Ore 3**	**Tailings 1**	**Tailings 2**	**Tailings 3**	**Concentrate1**	**Concentrate2**	**Concentrate3**
	Major metals (mg/kg)								
Fe	122652.8	116063.7	108480.3	73385.9	70387.9	70835.5	261867.0	292480.3	330017.0
Cu	2018.9	2165.8	2244.7	1177.8	1156.5	1173.4	7866.6	9339.1	10000.4
Al	3640.8	5264.2	4354.7	6719.8	4092.2	4146.7	63507.8	72860.7	82114.3
K	11125.3	11956.6	11372.0	14361.4	13102.9	11919.4	7466.3	7602.9	8153.6
Ca	3104.9	3482.5	2411.0	9132.4	9090.2	9074.6	n.d	3532.4	4158.5
Mg	2113.3	1604.7	1450.7	3144.1	3259.2	3147.9	991.5	1213.2	1341.5
Mn	1001.0	955.6	915.1	1271.8	1212.6	1247.2	127.9	141.9	163.5
Si	198169.9	202609.2	202794.8	240071.6	252337.7	206238.1	1644.7	1419.4	1656.8
	Trace metals (mg/kg)								
Co	17.65	18.67	18.44	18.36	18.35	18.83	50.94	60.93	64.25
Cr	221.40	241.25	226.53	282.28	262.39	264.42	238.81	290.30	340.79
Zn	132.20	126.76	123.32	123.72	114.13	115.19	322.33	382.23	463.76
Cd	0.75	0.76	0.73	1.35	1.35	1.34	0.86	1.03	1.40
As	28.46	33.84	27.78	29.33	26.53	17.57	133.01	149.76	169.50
Mo	22.78	24.69	23.54	26.41	24.92	25.10	44.91	62.00	65.64
Ag	2.07	2.32	2.19	1.55	1.40	1.46	15.55	21.83	21.31
Pb	43.83	48.31	45.10	37.09	35.23	35.81	135.86	113.50	157.67
V	11.70	22.80	18.32	77.06	23.25	10.89	211.07	266.14	302.24
Be	0.94	0.96	0.93	1.21	1.01	1.00	1.38	1.26	0.45
Ni	58.39	37.68	50.37	109.57	112.40	105.64	23.39	20.27	25.70
n.d: not detected									

All data obtained by ICP-MS and AAS were converted from ppb/ppm in the solution to mass basis as follows:

1. From ppb to mg/kg

$$mg/kg = \frac{\left[ppb/1000\right] \times V_{solution}}{W_s}$$

2. From ppm to mg/kg

$$mg/kg = \frac{ppm \times V_{solution}}{W_s}$$

Where $V_{solution}$ is the volume of the solution analysed and W_s is the weight of the digested or dissolved sample. Conversions to mg/g were done by unit conversions.

Appendix E: Acid Neutralising Capacity (ANC) Test Procedures

E.1 Fizz rating

A fizz ratting of the neutralisation potential is made for each sample to insure the addition of sufficient HCl acid required to react with the calcium carbonate present in the sample. The fizz rating was obtained by performing a fizz test as follows:

1. Place approximately 0.5 g of sample on a watch glass or piece of aluminium foil.
2. One or two drops of 25% HCl is added to the sample.
3. The presence of $CaCO_3$ is indicated by a bubbling or audible fizz.
4. The fizz or bubbling is rated as indicated in Table E-A.

Table E-A: Fizz Ratings and associated acid quantities and concentrations to be used in the ANC determination.

Reaction	Fizz Rating	HCl molarity (M)	HCl volume (ml)	NaOH molarity (M)
No reaction	0	0.5	4	0.1
Slight reaction	1	0.5	8	0.1
Moderate reaction	2	0.5	20	0.5
Strong reaction	3	0.5	40	0.5
Very strong reaction	4	1.0	40	0.5
Carbonate reaction	5	1.0	60	0.5

E.2 Standard Sobek ANC test

E.2.1 Digestion method for standard Sobek ANC test

Duplicate samples and a blank (no sample added) were prepared

1. Place approximately 2.00 g of dry pulverised sample into a 250 ml Erlenmeyer flask.
2. Carefully add volume and concentration of HCl to each beaker. N.B: The amount and molarity of HCl is based on the fizz rating.
3. Add 20 ml of deionised water to flush the sample to the bottom.
4. Heat the combined solid samples and HCl solution at 90 °C for 1-2 hr, and then cool at room temperature for 1 h.
5. Top up the solution to 125 ml with deionised water

6. Measure the pH of the mixture. If the pH is in the range 0.8 to 1.5, then proceed with the titration.

N.B: The reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask. Weber et al, 2004a,b, heated the samples to 80 – 90 °C on a hot plate for 2 hrs to ensure complete reaction.

Table E-B: Guidelines for adjusting the pH within the target range prior to back titration (AMIRA, 2002).

pH of mixture	Remarks
pH>1.5	Additional acid needs be added to the sample so that the total amount added is equivalent to the next highest fizz rating or the test needs to be re-started on a new sub-sample using the next highest fizz rating, except when the test is being run at a fizz rating of 0).
pH<0.8	Too much acid may have been added, except when the test is being run at a fizz rating of 5. In such cases it recommended to repeat the test using the next lowest fizz rating.

E.2.2 Back titration for standard Sobek ANC test

1. Filter ANC digest solution before back titration.
2. Titrate the solution to pH 7.0 over 1 hr.
3. Leave the solution to sit for 24 hr
4. Check pH and back-titrate with NaOH to pH 7.0.
5. Repeat steps 3 and 4 over 72 hr

E.3 H_2O_2 siderite correction (Skousen et al, 1997) test

E.3.1 Digestion method for Skousen H_2O_2 ANC test

Duplicate samples and a blank (no sample added) were prepared

1. Place approximately 2.00 g of dry pulverised sample into a 250 ml Erlenmeyer flask.
2. Carefully add volume and concentration of HCl to each beaker. According to fizz rating.
3. Top up the solution to 100 ml with deionised water
4. Boil the solution for 5 min

E.3.2 Back titration for Skousen H_2O_2 ANC test

1. Filter ANC digest solution before back titration.
2. Back titrate the solution with NaOH (using burette) to pH 4.5.
3. Add 5ml of 30% H_2O_2, and boil for further 5 min
4. Continue to back-titrate with NaOH to pH 7.0.
5. Leave the solution for approximately 24 hours.
6. Check pH and back-titrate with NaOH to pH 7.0.
7. Add 5ml of 30% H_2O_2, boil for 5 min.
8. Check pH and back-titrate with NaOH to pH 7.0.
9. Repeat steps 5 to 8 over 72 hours

E.4 Additional/Incremental H_2O_2 ANC test

E.4.1 Digestion method

The sample in this test was digested as per standard Skousen ANC test.

E.4.2 Back titration for Additional/Incremental H_2O_2 ANC test

1. Filter ANC digest solution before back titration.
2. Back titrate the solution with NaOH (using burette) to pH 4.5.
3. Add 10 drops of 30% H_2O_2, leave for 15 minutes.
4. Check pH and back-titrate with NaOH to pH 4.5.
5. Repeat steps 3 and 4 until no significant pH change is observed after step 3.
6. Back-titrate with NaOH to pH 7.0.
7. Add 10 drops of 30% H_2O_2, leave for 15 minutes.
8. Check pH and back-titrate with NaOH to pH 7.0.
9. Repeat steps 6 and 8 until no significant pH change is observed after step 7 (no pH change to two decimal places in 15 minutes).
10. Leave the solution for 24 hours.
11. Check pH and adjust with further back titration to pH 7.0 if required.
12. Add 10 drops of 30% H_2O_2, and leave for approximately 24 hours.
13. Repeat steps 10 to 12 over 72 hours.

Appendix F: Net Acid Generation (NAG) Test Procedures

F.1 Single addition NAG test procedure

A sample is reacted with H_2O_2 solution to rapidly oxidise sulphide minerals contained within a sample, then measurement of the pH of the solution after reaction of a sample with peroxide is complete. The peroxide solution is used to oxidise sulphide minerals to sulphates.

Reagents:

- Sodium Hydroxide (NaOH) – 0.10 M and 0.50 M
- 15 % v/v H_2O_2.

NOTE:

- H_2O_2 should be at room temperature before commencing the test.
- Check pH of the 15% H_2O_2 prior to use to ensure it is greater than or equal to pH 4.5
    - If pH <4.5, add dilute NaOH until the pH > 4.5
    - Use NaOH solution made up by adding 1 g NaOH to 100 ml of de-ionised water.
    - Aim for pH of 4.5, not greater than 6.0

1. Weigh approximately 2.5 g of pulverised sample into a 500 ml conical beaker.
2. Carefully add 15% H_2O_2 to the conical flask.
   Note: *The hydrogen peroxide should be at room temperature before commencing the test.*
3. Cover with a watch glass and place mixture inside fume – hood for 24 hours
   Note: *The NAG reaction can be vigorous and NAG solutions can "boil-over" if the reaction is too rapid.*
4. After the reaction, placed place the beakers on a hot plate and gently heat until effervescence stops or for a minimum of 2 hr.
5. Measure the pre-boil NAG_{pH}
   Note: *The sample must not boil dry. Deionised water was added as required to maintain the volume approximately constant.*
6. Cool the sample to room temperature
7. Rinsed down solid that has adhered to sides of flask into the solution using de-ionised water, to give a final volume of 250 ml.
8. Record the final pH of the solution (After-boil NAG_{pH})
9. Filter the NAG solution and retained both solids and filtrate for further analysis

10. Solution were titrated to pH 4.5 and 7.0, while stirring, with the appropriate NaOH concentration based on NAGpH as follows:

    when $NAGp_H$ is > 2 Titrate with 0.10 M NaOH

    when NAG_{pH} is ≤ 2 Titrate with 0.50 M NaOH

11. The volume of NaOH used during titration was recorded and NAG value was determined according to NAG calculation in Table G-A.

F.2 Sequential NAG test

1. Steps 1 to 11 of the single addition NAG test forms stage 1 of the sequential NAG test procedure.

2. The single addition NAG test were then repeated using the solid residue from the first stage (i.e. repeat steps 2 through to 11). This is called Stage 2. Subsequent repeats will be called stage 3, stage 4 and so on.

3. Repeat Steps 2 to 11 until no further reaction is observed AND the filtered NAG liquor has a pH greater than or equal to 4.5.

F.3 Kinetic NAG test

To obtain information on the acid generation rate of a sample, the pH and temperature of the NAG solution was monitored during the single addition NAG test.

Note: The reaction kinetics are influenced by the starting temperature of reagents. It is therefore recommended that the starting temperature of the H_2O_2 is at room temperature when carrying out a kinetic NAG test.

Appendix G: Acid Base Accounting (ABA) and Net acid generation (NAG) tests

G.1 Calculation methods of the ANC, NAPP and NAG

Table G-A: Methods of calculations of the ANC, NAPP, and NAG

Test method	Equation	Comments
NAPP (Net Acid Production Potential)	NAPP = MPA - ANC	ANC can be determined by a number of ANC test methods
MPA (Maximum Potential Acidity)	MPA = wt% total x 30.6	Total S determined by either LECO or XRF
Standard Sobek ANC test (1978)	$ANC = \frac{[Vol_{HCl} \times M_a] - [Vol_{NaOH} \times M_b] \times C \times 49}{SampleWeight_{(g)}}$ Where M_a is the acid molarity; M_b is the base molarity; B is the standard difference associated with the blank procedure: C =(M_a x Vol_{HCl} in blank)/(M_b x Vol_{NaOH} titrated in blank). ANC in kg H_2SO_4/t.	See Appendix and Section 3.7 in PART A
H_2O_2 siderite correction ANC test (Skousen *et al*, 1997)	As for Standard Sobek ANC test in kg H_2SO_4/t	See Appendix E and Section 3.7 in PART A
Additional/Incremental H_2O_2 ANC method	As for Standard Sobek ANC test in kg H_2SO_4/t	See Appendix E and Section 3.7 in PART A
NAG test	$NAG = \frac{49 \times V \times M}{W}$ in kg H_2SO_4/t Where V =volume of NaOH used in titration (ml); M = molarity of NaOH used in titration (mol/L); W = weight of sample (g).	See Appendix F and Section 3.7 in PART A

G.2 Chapter 5 data tables and graphs

G.2.1 Skousen and Incremental H_2O_2 ANC tests

Determination of ANC, NAPP using equations in Table G-A

Table G-B: Calculations of ANC and NAPP in kg H_2SO_4/t for Skousen H_2O_2 ANC test.

Blank					
	ml acid added	20			
	ml base added	13.9			
	constant C	1.4			
	M acid	0.5			
	M base	0.5			
Sample 1		**Initial**	**24 hrs**	**48 hrs**	**72hrs**
	Mass sample (g)	2.0087			
	M base	0.5	0.5	0.5	0.5
	ml base added after titration	12.3	12.31	12.32	12.32
	ml acid added	20	20	20	20
	ml acid consumed	1.2	1.1	1.1	1.1
	M acid	0.5			
	ANC	28.1	27.9	27.7	27.7
	NAPP	60.7	60.8	61.0	61.0
Sample 2		**Initial**	**24 hrs**	**48 hrs**	**72hrs**
	Mass sample (g)	2.0011			
	M base	0.5	0.5	0.5	0.5
	ml base added after titration	12.3	12.31	12.31	12.31
	ml acid added	20	20	20	20
	ml acid consumed	1.15	1.14	1.14	1.14
	M acid	0.5			
	ANC	28	28.0	28.0	28.0
	NAPP	60.6	60.7	60.7	60.7
	Average (ANC)	28	28	28	28
	Avarege (NAPP)	60.6	60.8	60.9	60.9

Table G-C: Calculations of ANC and NAPP in kg H_2SO_4/t for Additional/Incremental H_2O_2 ANC test.

blank					
	ml acid added	20			
	ml base added	17.9			
	constant C	1.1			
	M acid	0.5			
	M base	0.5			
Sample 1		Initial	24 hrs	48 hrs	72hrs
	Mass sample (g)	2.021			
	M base	0.5	0.5	0.5	0.5
	ml base added after titration	16	16.01	16.01	16.01
	ml acid added	20	20	20	20
	ml acid consumed	1.1	1.1	1.1	1.1
	M acid	0.5			
	ANC	26	26	26	26
	NAPP	63	63	63	63
Sample 2		Initial	24 hrs	48 hrs	72hrs
	Mass sample (g)	2.02			
	M base	0.5	0.5	0.5	0.5
	ml base added after titration	15.9	16.01	16.01	16.01
	ml acid added	20	20	20	20
	ml acid consumed	1.1	1.1	1.1	1.1
	M acid	0.5			
	ANC	27.1	26	26	26
	NAPP	62	63	63	63

G.2.2 Single addition and sequential NAG tests

Table G-D: Determination of NAG in kg H_2SO_4/t for Single addition and sequential NAG tests.

Unfiltered boiled sample		
Stage 1		
	Initial	**pH adjustments after 24 hr**
Mass sample (g)	2.5009	2.5009
Vol NaOH NAG_{pH} 4.5	5.5	5.5
Vol. NaOH NAG_{pH} 7.0	7.6	7.7
M NaOH	0.1	0.1
NAG (kg H_2SO_4)/t pH=4.5	10.8	
NAG (kg H_2SO_4)/t pH=7.0	14.9	15.1
Stage 2		
	Initial	**pH adjustments after 24 hr**
Vol NaOH NAG_{pH} 4.5	5	5
Vol. NaOH NAG_{pH} 7.0	6.2	6.2
M NaOH	0.1	0.1
NAG (kg H_2SO_4)/t pH=4.5	9.8	
NAG (kg H_2SO_4)/t pH=7.0	12.2	12.2
Stage 3		
	Initial	**pH adjustments after 24 hr**
Vol NaOH NAG_{pH} 4.5	1.1	1.1
Vol. NaOH NAG_{pH} 7.0	5	6.3
M NaOH	0.1	0.1
NAG (kg H_2SO_4)/t pH=4.5	2.2	
NAG (kg H_2SO_4)/t pH=7.0	10	12

G.2.3 NAG sensitivity: Effects of heating step

Table G-E: Metal analysis of pre-boil, filtered after-boil and unfiltered after-boil NAG solutions obtained by ICP-MS

Solution NAGpH			
	Pre-boiling	*Unfiltered post-boiling*	*Filtered post-boiling*
NAG_{pH}	2.47	2.6	2.4
Element concentrations (ppb)			
	Pre-boiling	*Unfiltered post-boiling*	*Filtered post-boiling*
Fe	39683	57294	28484
Mg	7663	9412	7577
Mn	4158	6580	4182
Cu	11247	12158	11753
Ca	26617	31545	28108
Na	34302	61954	39333
K	2669	3210	3050
Si	5958	8602	5917
Zn	642	716	668
Al	1356	1520	1505

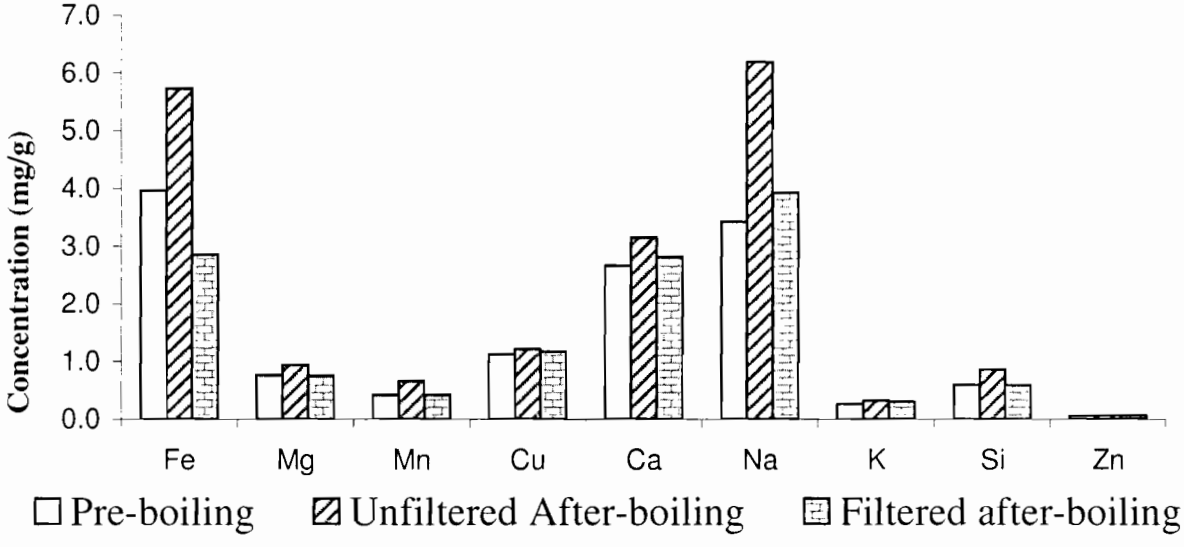

Figure G.1: Graphical presentation of the NAG sensitivity results.

Appendix H: Sequential Extraction Procedures

H.1 Sequential Extraction Scheme A

All leach are performed in polypropylene centrifuge tubes. The following sequential extraction procedure is proposed after Dold, 2003; Hall *et al*, 1996 and Ribet *et al*, 1995.

N.B: Use deionised water to prepare stock solutions and for making the reagents for extraction steps.

Step 1: Water soluble fraction

1. Weigh 1 g of tailing sample into 50 ml screw-cap centrifuge tube
2. Add 40 ml of deionised water
3. Continuously shake the mixture for 1 hr at room temperature.
4. Centrifuge and decant supernatant liquid into a labelled test tube
5. Wash the residue with 5 ml deionised H_2O, vortex and centrifuge again twice. Add supernatant rinse to the test-tube. ***N.B: do this twice***

Step 2: Exchangeable fraction (Ammonium Acetate Leach)

1. To the residue from step 1, add 20 ml of 1M NH_4 – acetate solution, brought to pH 4.5 by 1M Acetic Acid
2. Vortex contents for 5-10 s
3. Cap and place in an orbital shaker for 2 hr
4. Centrifuge and decant the supernatant liquid into a labelled test tube.
5. Rinse the residue with 5 ml of distilled H_2O, vortex and centrifuge again. Add supernatant rinse to the test-tube ***N.B: Do this twice***
6. Make up to the 30 ml mark and analyse
7.

Step 3: Amorphous Fe oxide fraction

1. To the residue from step 2, add 20 ml of 0.2 M NH_4 –oxalate brought with 0.2 M oxalic acid to pH 3.0.
2. Cover the centrifuge tube with aluminium paper to protect the content from light
3. Cap and shake for 1 hr in darkness
4. Centrifuge and decant the supernatant liquid into a labelled test tube.
5. Rinse the residue with 5 ml of distilled H_2O, vortex and centrifuge again. Add supernatant rinse to the test-tube ***N.B: Do this twice***
6. Make up to the 30 ml mark and analyse

Step 4: Crystalline Fe oxide

1. To the residue from step 3, add 20 ml of 0.2 M NH_4 –oxalate brought with 0.2 M oxalic acid to pH 3.0.
2. Mix and heat in a water bath at 85 - 90° C for 2 hr with cap on tightly
3. Vortex every 10 min
4. Centrifuge and decant the supernatant liquid into a labelled test tube.
5. Rinse the residue with 5 ml of distilled H_2O, vortex and centrifuge again. Add supernatant rinse to the test-tube ***N.B: Do this twice***
6. Make up to the 30 ml mark and analyse

Step 5: Organics and secondary Cu-sulphides: H_2O_2 Leach

1. Add 5 ml 35% H_2O_2 to the residue from step 4, heat in water bath for 1 hour
2. Vortex contents every 10 mins.
3. Centrifuge and decant the supernatant liquid into a labelled test tube.
4. Rinse the residue with 5 ml of distilled H_2O, vortex and centrifuge again. Add supernatant rinse to the test-tube ***N.B: Do this twice***
5. Make up to the 30 ml mark and analyse

Step 6: Metals in primary sulphide fraction($KClO_3$, HCl, and HNO_3)

1. Add to residue from step 5, add 750 mg of $KClO_3$ and 5 ml of 12 M HCl
2. Cap and vortex (care, content may froth)
3. Add a further 10 ml of HCl
4. Cap and vortex
5. After 30 min add 15 ml of distilled H_2O
6. Cap, vortex and centrifuge for 10 min
7. Decant supernatant liquid into a labelled test tube
8. To the residue add 10 ml of 4 M HNO_3
9. Cap and vortex
10. Place in a water bath at 90°C for 20 min
11. Vortex and centrifuge for 10 min.
12. Decant supernatant liquid into the previous labelled test tube (i.e. mixing the $KClO_3$/HCl extractant with this HNO_3 leachate)
13. Rinse the residue with 5 ml of water, vortex and centrifuge again; do this twice and add supernatant rinses to the test-tube. Make up to 50.0 ml and analyse.

Step 7: Residual fraction: Aqua Regia (HCl, HNO_3), HF, $HClO_4$

Samples of approximately 1 g were measured into 50 ml polystyrene centrifuge tubes (the actual mass was recorded). In this digestion 2 ml of HF was added to the samples and heated for 20 min at 90 °C in a water bath. After cooling samples were digested with Aqua Regia Leach, 10 ml of (1: 1 (v/v)) mixture of HNO_3 and HCl for 6 h at 90 °C. After that, 5 ml of HF and 2 ml $HClO_4$ for 6 h at 90°C. Solutions were transferred into 50 ml

volumetric flasks and volumes made up to 50 ml with deionised water and then were filtered into 100 ml polyethylene plastic bottles.

H.2 Sequential Extraction Scheme B

Step 1: Water soluble fraction

As for sequential extraction scheme A

Step 2: Exchangeable fraction (Ammonium Acetate Leach)

As for sequential extraction scheme A

Step3: Carbonate fraction

1. To the residue add 20 ml of 1.0 M CH_3COONa solution, brought to pH 4.5 with 1.0 M acetic acid
2. Vortex contents for 5-10 s
3. Cap and place in an orbital shaker for 2 hr
4. Centrifuge and decant the supernatant liquid into a labelled test tube.
5. Rinse the residue with 5 ml of distilled H_2O, vortex and centrifuge again. Add supernatant rinse to the test-tube ***N.B: Do this twice***
6. Make up to the 30 ml mark and analyse

Step 4: Amorphous Fe oxide fraction

1. To the residue from step 2, add 20 ml 0.25 M $NH_2OH.HCl$ adjusted to pH 2.0 with 0.25 M HCl at 50 °C
2. Cap and shake for 2 hr in darkness
3. Centrifuge and decant the supernatant liquid into a labelled test tube.
4. Rinse the residue with 5 ml of distilled H_2O, vortex and centrifuge again. Add supernatant rinse to the test-tube ***N.B: Do this twice***
5. Make up to the 30 ml mark and analyse

Step 5: Crystalline Fe oxide fraction

1. To the residue from step 4, add 30 ml of 2 M $NH_2OH.HCl$ brought to pH 2.0 by 25% CH_3OOH at 90 °C.
2. Cap and shake for 3 hr in darkness
3. Centrifuge and decant the supernatant liquid into a labelled test tube.
4. Rinse the residue with 5 ml of distilled H_2O, vortex and centrifuge again. Add supernatant rinse to the test-tube ***N.B: Do this twice***
5. Make up to the 40 ml mark and analyse

Step 6: Metals in sulphides phases 4 M $KClO_3$, HCl, and HNO_3

As for the primary sulphide fraction in sequential extraction scheme A

Step 7: Aqua Regia (HCl, HNO_3), HF, $HClO_4$

As for sequential extraction scheme A and total metal analysis.

Appendix I: Chapter 6 data tables

I.1 Metal distribution at each extraction step for sequential extraction schemes A and B

Table I-A: Distribution of metals in the leached fractions of the tailings obtained by sequential extraction scheme A (mg/kg).

Major metals								
	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	Total
Fe	0	295	9092	8145	1167	18081	33467	70247
Cu	0	122	184	59	536	477	0	1378
Al	2.5	59	177	290	10	515	4226.5	5280
K	168	54	804	186	6	0	11475	12693
Ca	307	2000	20	17	1718	1881	1306	7247
Mg	125	474	193	291	33	649	1662	3427
Si	0	193	566	1204	211	978	215308	218459
Mn	0	228	482	334	92	151	152	1440
Minor metals								
	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**Total**
Co	0	6.9	8.4	2.4	0.98	0.014	0.6	19
Cr	0	0.9	3.2	5.2	0.9	283	16	309
Zn	0	29	40	23	8	22	11	133
Cd	0	0.6	0.23	0.06	0.4	0.2	0.05	1.5
As	0	0.2	0	0	0	11	17	29
Mo	0.1	0.006	0.46	0.18	0.04	26	1.6	28
Ag	0	0	0	0	0.3	1.1	0.18	1.6
Pb	0	2.9	5.7	2.6	7.5	18	2.9	40
V	0	0	1.0	0.97	0	28	8	38
Be	0	0.01	0.3	0.2	0	0	0.1	0.6
Ni	0.013	12	11	4.7	2.3	86	6.8	122

Scheme A: *F1: Water soluble; F2: Exchangeable; F3: Amorphous Fe-oxide; F4: Crystalline Fe-oxide; F5: Organic matter and secondary Cu-sulphide; F6: Primary sulphides; F7: Residual (silicates).*

Table I-B: Distribution of metals in the leached fractions of the tailings obtained by sequential extraction scheme B (mg/kg).

Major metals								
	F1	**F2**	**F3B**	**F4B**	**F5B**	**F6**	**F7**	**Total**
Fe	0	503	86	3599	8068	20494	36760	69510
Cu	0.00	126	22	24	125	684	10	991
Al	2.0	67	13	89	312	1421	3815	5719
K	122	124	54	67	366	0	13148	13881
Ca	327	2016	543	1071	1499	2675	788	8918
Mg	116	461	51	132	284	798	1656	3497
Mn	0	225	66	247	258	51	414	1261
Si	0	147	479	193	1928	1244	216253	220243
Minor metals								
	F1	**F2**	**F3B**	**F4B**	**F5B**	**F6**	**F7**	**Total**
Co	0.004	6.5	1.3	2.5	2.8	5.4	0.96	19
Cr	0	2	1	4	8	236	58	309
Zn	0	28	5	12	25	28	34	131
Cd	0	0.6	0	0	0	0	0	1.3
As	0	0	0	0	6	14	13	33
Mo	0.05	0	0	0.1	2.3	22	4	29
Ag	0.01	0	0	0.1	0.9	0.3	0.13	1.4
Pb	0.2	2.7	1.8	1.4	15	7.4	6.2	35
V	0	0	0	0	0	20	21	40
Be	0	0.02	0.03	0.17	0.14	0.13	0.5	0.98
Ni	0	10	3	4.6	0.0	103	0	120

Scheme B: *F1: Water soluble; F2: Exchangeable; F3B: Carbonate; F4B: Amorphous Fe-oxide; F5B: Crystalline Fe-oxide; F6: Primary sulphides; F7: Residual (silicates).*

I.2 Kinetic dissolution study

Table I-C: A kinetic dissolution study of the amorphous and crystalline Fe oxide fractions for sequential extraction scheme A.

Sample1	**2.5045**	**g**					
Sample 2	**2.5047**	**g**					
Volume	**250**	**ml**					
	0.25	**L**					
		Sample1	**Sample 2**	**Sample1**	**Sample 2**	**Average**	**Average**
Time (hr)	Time (min)	mg/l	mg/l	mg/g	mg/g	mg/l	mg/g
Amorphous Fe oxide *0.2 M NH_4 –oxalate brought to pH 3.0 by 0.2 M oxalic acid at 25 °C and taking 10-ml subsamples with syringes. Flasks were wrapped with aluminium foil to exclude light and prevent attack on more crystalline iron oxyhydroxide/oxide.*							
0.5	30	30.95	32.6	3.1	3.3	31.8	3.2
1	60	64.41	60.72	6.4	6.1	62.6	6.2
1.5	90	72.44	65.92	7.2	6.6	69.2	6.9
2	120	94	94.6	9.4	9.4	94.3	9.4
3	180	112.3	108.4	11.2	10.8	110.4	11.0
4	240	118.6	124.4	12.4	12.4	121.5	12.4
5	300	130.3	125.5	13.0	12.5	127.9	12.8
6	360	134.8	135.9	13.5	13.6	135.4	13.5
Crystalline Fe oxide *0.2 M NH_4 –oxalate brought to pH 3.0 by 0.2 M oxalic acid at 85 – 90 °C and taking 10-ml subsamples with syringes. Samples were exposed to light after 6 hours, followed by heating the sample to 85 – 90 °C for selective dissolution of crystalline Fe oxides.*							
0.5	390	192.9	175.4	19.3	17.5	184.2	18.4
1	420	199.1	211.5	19.9	21.1	205.3	20.5
2	480	216.2	241.0	21.6	24.1	228.6	22.8
3	540	230	249.1	23.0	24.9	239.6	23.9
4	600	238.2	233.8	23.8	23.3	236.0	23.6
5	660	243.9	278.3	24.3	27.8	261.1	26.1
6	720	245	287.4	24.5	28.7	266.2	26.6

Table I-D: A kinetic dissolution study of the amorphous Fe oxide fraction for sequential extraction scheme B.

Sample 1	**2.5035**	**g**
Sample 2	**2.5021**	**g**
Volume	**0.25**	**L**

2.5 g of samples were shaken in 250 ml Erlenmeyer flasks containing 0.25 M $NH_2OH.HCl$ brought to pH 2.0 using 0.25 M HCl at 50 ℃

Fe analysis

Time (hr)	Sample1 mg/l	Sample 2 mg/l	Sample1 mg/g	Sample 2 mg/g	Average mg/l	Average mg/g
0.5	19.01	17.64	1.9	1.8	18.3	1.8
1	43.15	32.55	4.3	3.3	37.9	3.8
2	62.78	59.45	6.3	5.9	61.1	6.1
3	79.12	78.58	7.9	7.9	78.9	7.9
4	96.62	94.39	9.6	9.4	95.5	9.5
7	109	117	10.9	11.7	113.0	11.3
9	116	128	11.6	12.8	122.0	12.2
12	142	140	14.2	14.0	141.0	14.1
24	144	143	14.4	14.3	143.5	14.3
27	145	144	14.5	14.4	144.5	14.4
29	149	148	14.9	14.8	148.5	14.4
32	150	149	15.0	14.9	149.5	14.5

Mn analysis

Time (hr)	Sample1 mg/l	Sample 2 mg/l	Sample1 mg/g	Sample 2 mg/g	Average mg/l	Average mg/g
0.5	3.76	3.47	0.38	0.35	3.62	0.36
1	5.27	4.90	0.53	0.49	5.09	0.51
2	6.5	6.65	0.65	0.66	6.58	0.66
3	7.12	7.06	0.71	0.71	7.09	0.71
4	7.61	7.77	0.76	0.78	7.69	0.77
7	8.51	8.99	0.85	0.90	8.75	0.87
9	8.6	9.31	0.86	0.93	8.96	0.89
12	8.72	9.28	0.87	0.93	9.00	0.90
24	9.31	9.20	0.93	0.92	9.26	0.92
27	9.4	9.30	0.94	0.93	9.34	0.93
29	9.39	9.33	0.94	0.93	9.36	0.93
32	9.4	9.20	0.94	0.92	9.30	0.93

Table I-E: A kinetic dissolution study of the crystalline Fe oxide fraction for sequential extraction scheme B.

Crystalline phases						
Sample 1	**2.5035**	**g**				
Sample 2	**2.5021**	**g**				
Volume	**0.25**	**l**				
2.5 g of samples were shaken in 250 ml Erlenmeyer flasks containing 2 M $NH_2OH.HCl$ brought to pH 2.0 by 25% CH_3OOH, pH 2.0 at 90 ℃						
Fe analysis						
Time (hr)	**Sample1 mg/l**	**Sample 2 mg/l**	**Sample1 mg/g**	**Sample 2 mg/g**	**Average mg/l**	**Average mg/g**
0.5	48.2	41.7	4.8	4.2	45.0	4.5
1	85.6	81.2	8.5	8.1	83.4	8.3
2	137	150.0	13.7	15.0	143.5	14.3
3	158	175.0	15.8	17.5	166.5	16.6
4	169	186.0	16.9	18.6	177.5	17.7
6	184	197.0	18.4	19.7	190.5	19.0
8	201	217.0	20.1	21.7	209.0	20.9
24	245	240.0	24.5	24.0	242.5	24.5
26	245	229.0	24.5	22.9	237.0	24.5
Mn analysis						
Time (hr)	**Sample1 mg/l**	**Sample 2 mg/l**	**Sample1 mg/g**	**Sample 2 mg/g**	**Average mg/l**	**Average mg/g**
0.5	4.44	4.51	0.44	0.45	4.48	0.45
1	6.06	6.05	0.61	0.60	6.06	0.60
2	7.61	8.21	0.76	0.82	7.91	0.79
3	8.14	8.52	0.81	0.85	8.33	0.83
4	9.33	9.69	0.93	0.97	9.51	0.95
6	10.24	10.75	1.02	1.07	10.50	1.05
8	10.49	11.20	1.05	1.12	10.85	1.08
24	11.29	11.79	1.13	1.18	11.54	1.15
26	10.7	10.53	1.07	1.05	10.62	1.06